

A Study of the Adsorption of Carbon-14 Labeled Stearic Acid on Iron

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ABSTRACT

Stearic-1-C¹⁴ acid was adsorbed as a close-packed monomolecular layer on mechanically polished iron and fire-polished glass by the method of solution retraction. Measurements of the adsorbed radioactivity were made which allowed the determination of the number of adsorbed molecules per apparent unit area. Measurements of the methylene iodide contact angle on the two monolayer-covered surfaces showed that the surface packing density of stearic acid molecules was essentially the same in both cases. This conclusion, together with the assumption that the fire-polished glass surface had a roughness factor of unity, allowed the calculation of the area occupied per stearic acid molecule and of the roughness factor of the iron surface. The stearic acid molecule was found to occupy about 18.9 Å² on both iron and glass, and the roughness factor for the polished iron surface was 1.33.

Desorption and exchange experiments indicated that about 60% of the monolayer on iron was rather weakly adsorbed and the remainder was probably chemically adsorbed. A rectilinear relationship was found between the measured contact angle and the extent of surface coverage. Additional studies of the temperature coefficients of the removal processes should permit determination of their activation energies and further clarification of the nature of the adsorption bond.

PROBLEM STATUS

This is an interim report; work is continuing on the problem.

AUTHORIZATION

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A STUDY OF THE ADSORPTION OF CARBON-14 LABELED STEARIC ACID ON IRON

INTRODUCTION

Numerous studies have led us to conclude that stearic acid (n-octadecanoic acid) is capable of forming close-packed, vertically oriented monolayers on a variety of metals and other solid substrates so as to present an exposed surface consisting essentially of methyl groups. This deduction arises from the attainment of limiting maximum values for the contact angle of the stearic acid surface toward various test liquids; for methylene iodide vs stearic acid (or other strongly adsorbed compounds of similar structure) this value is about 72° . The close packing and essentially vertical orientation have been confirmed by electron diffraction and electron microscopy.

Recent contact potential studies carried out at this Laboratory suggested that there was a specific interaction between stearic acid and the metal substrate, which varied with the nature of the metal (1). The method employed, however, could not differentiate between the degree of surface coverage (area covered per molecule) and the magnitude of the stearic acid-metal interaction. Other studies have left unclear to what extent other co-adsorbed molecules contributed to the surface coverage and the maximum obtainable contact angle.

There appeared to be a number of cases where a direct, unequivocal assignment of the extent of surface coverage or the area of coverage per molecule in a close-packed film was required. These involved the relationship between contact angle and the degree of surface coverage (or closeness of packing) of monolayers of stearic acid, the roughness factor of the surface (true area/apparent area), the purity of the film (the extent of inclusion of solvent molecules in the film), and the evaluation of various techniques for producing close-packed monolayers.

This report covers the development of techniques for producing and evaluating close-packed monolayers of stearic-1- C^{14} acid adsorbed on iron and soda-lime glass (for reference purposes) and some preliminary studies of the stability of these adsorbed layers.

EXPERIMENTAL PROCEDURES

Preparation of Solutions

The working solution for preparation of adsorbed films of radioactive stearic acid was made by dissolving 6.6 mg of stearic-1- C^{14} acid (5.0 mC/mM, from Volk Radiochemical Company) in 223 g (186 ml) of nitrobenzene (Eastman white label) and adding 202 mg of inactive stearic acid (Eastman white label) to give a final concentration of approximately 1.12 mg/ml. Nitrobenzene was selected as the solvent because its low volatility, high surface tension, different chemical structure, and low solubility for stearic acid were desirable features in the production of monomolecular films by the retraction technique (2). The measured contact angle of close-packed-oriented monolayers of stearic acid toward nitrobenzene and toward the nitrobenzene/stearic acid solution was about 68° .

A later preparation of other radioactive stearic acid solutions in nitrobenzene from the same stearic-1-C¹⁴ acid solid sample gave retracted films of much higher radioactivity and some lowering of the contact angle. This suggested the presence of other surface active materials in the radiostearic acid, which might have resulted from radiation damage during the several months the high-specific-activity sample was kept on the shelf. Treatment with alumina removed the impurity and produced solutions which behaved normally. To verify the purity of the radioactive solution used in the initial phases of this study, a variation of this cleanup procedure was used on the original nitrobenzene solution of tagged stearic acid to remove any products of radiation damage that might have been present. The purification had no significant effect on the methylene iodide contact angles on the retracted films but did result in some decrease in radioactivity. No significant difference in desorption behavior of films prepared before and after cleanup was noted. Radiochemical purity and freedom from extraneous surface active materials, particularly radioactive ones, is necessary in a study of this nature.

Standardization of Counting Techniques

The radioactive films of tagged stearic acid and the required radioactivity standards were counted under a 2-in.-diam, thin-window (0.9 mg/cm²), gas-flow detector tube (Tracerlab Model CE 14L) using conventional Geiger counting techniques. The counting efficiency was approximately 25% for the 0.155-MeV β of C¹⁴. The blanks with the retracted films were masked by brass shields so that only a 2.54-cm-diam radioactive area directly under the center of the counter tube was exposed. Counting times were sufficient to accumulate a minimum of 25,000 counts (i.e., the standard deviation due to counting was about 0.6%), except for some of the severely depleted films.

Standardization was accomplished directly by determining the actual counting rate per μg of C¹⁴-labeled stearic acid deposited in the counting area. A known aliquot of the working solution was diluted with a known volume of benzene in a volumetric flask, and individual aliquots of this solution were removed and evaporated to dryness in a restricted area on a clean blank. A ring of poly-1H,1H-pentadecafluorooctyl methacrylate (3M Company, Polymer A) restricted movement of the evaporating solution and permitted formation of a uniform deposit of stearic acid having an area equivalent to that seen through the mask and centered under the same portion of the counting tube. Addition of a few drops of ethyl alcohol prior to evaporation aided in obtaining uniform films. The volumetric pipettes were flushed several times with the radioactive solutions before being used, to make certain that no depletion of radioactivity took place by adsorption on the walls. The results of standards made on both iron and glass blanks are shown in Table 1. The reproducibility was good and the ratio of the counts obtained on iron and glass is in agreement with the relative backscattering of these two materials (iron/glass ≈ 1.15).

Preparation of Adsorbed Monolayers by the Retraction Technique

The production of close-packed monolayers of adsorbed material requires absolute cleanliness of the substrate so that the effective area per molecule is determined solely by the geometrical size and shape of the adsorbing molecule and the number and arrangement of active sites on the clean surface. Previous studies have indicated that freshly prepared close-packed monolayers of stearic acid and related compounds (hexadecylamine, hexadecyl trimethyl ammonium halides, long chain fatty acids) having a surface of exposed methyl groups exhibit a contact angle of about 70° toward methylene iodide. Consequently, the criterion adopted was that any film having a contact angle less than 70° toward methylene iodide could not be considered to have a close-packed monolayer, though it might contain either more or less molecules than the desired monolayer. As studies progressed it was found that stearic acid films having contact angles as high as

Table 1
Standardization Data for Iron and Glass Substrates

Radioactivity on Iron* (counts/min)	Radioactivity on Glass* (counts/min)
1457	1220
1442	1241
1466	1263
1432	1251
1436	
Av = 1447 [†]	Av = 1244 [†]

*Total count for 1-in. diam circular area; corrected for background count.

[†]Each aliquot mounted contained 1.15 μg of labeled stearic acid.

72° or 73° could be obtained on glass, indicating that the original criterion of 70° was not set sufficiently high. Contact angle measurements were made with a goniometer telescope with independently movable crosshairs, as described in detail elsewhere (3); the absolute error of this technique is about $\pm 1^\circ$.

Absolutely clean retraction of the solution from the surface of interest is required due to the high radioactivity of the solution; a 1 μl droplet in the measured area would contribute a quantity of radiation equivalent to that of a close-packed monolayer. Blotting would not be a reliable means of removing this excess material and, moreover, it may remove stearic acid from other areas of the surface.

Retracted Stearic Acid Films on Iron — The iron samples were flat, rectangular plates of Armco iron (purity >99.9%) measuring approximately 0.6 cm \times 3.8 cm \times 5.4 cm. Initial preparation consisted of abrasion under flowing water using a graded series of carborundum metallurgical papers to a final grit size of 600. This was followed by rough polishing with a 6- μ diamond compound on a nylon cloth, and final polishing to a mirror finish on Buehler "Microcloth" under distilled water using alumina with an average particle size of 0.3 μ . Before the preparation of each monolayer the iron surfaces were given a final cleaning by further polishing under distilled water on a Buehler "Selvyt" cloth using the 0.3- μ alumina. Loosely held alumina particles were removed by rubbing the polished surface with a clean Selvyt cloth under flowing distilled water. The surfaces were then dried by subjecting them to a blast of room air, after which monolayers were prepared immediately.

A series of experiments were run to determine the optimum time required for development of close-packed monolayers of stearic acid on clean iron (Table 2). For each determination a clean iron blank held in a clean (flamed) platinum basket was immersed in the stearic acid/nitrobenzene solution for a given period of time, then withdrawn at the rate of 0.1 cm/sec by use of a 1-rpm motor. The back of the blank was blotted dry and the blank put in a plastic planchet lined with aluminum foil. Contact-angle measurements toward methylene iodide were made at several spots outside the counting area, and then the β activity was counted through a mask as described above. Figure 1 shows the measured contact angle and the radioactivity per unit area as a function of time. With very

Table 2
Effect of Immersion Time on the Formation of Adsorbed Stearic Acid Films
on Iron and Soda-Lime Glass*

Iron			Glass		
Immersion Time [†] (min)	Radioactivity (counts/min)	Contact Angle (degrees)	Immersion Time [†] (min)	Radioactivity (counts/min)	Contact Angle (degrees)
2	1718	56	2	1373	70, 71
2	1958	64	2	1365	71, 71
10	2055	66	2	1360	72, 71
10	2060	67	4	1365	71, 71
20	2145	70	4	1450	70, 71
30	2131	70, 71	6	1625	69, 70
30	2108	70, 70	6	1589	68, 69
60	2122	70	6	1740	69, 69
			8	1485	68, 68
			8	1836	69, 68
			10	1517	69, 70
			15	1416	70, 71
			30	1404	71, 72
			30	1393	70, 71
			60	1460	70, 71

*Samples were prepared from a cleaned up solution of stearic acid-1-C¹⁴ in nitrobenzene.

†Samples were made at random rather than in sequence to eliminate the possible effects of changes in solution composition with time.

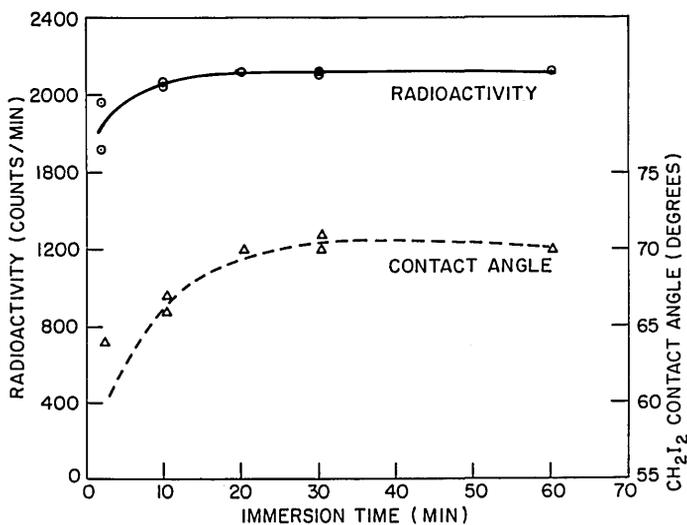


Fig. 1 - Effect of immersion time on some properties of adsorbed stearic acid-1-C¹⁴ films on iron

long immersion (>8 hr) excess radioactivity and a decreased contact angle suggested that some chemical reaction of stearic acid with the iron surface was taking place which resulted in a thicker, less oriented film; with very short immersions (<2 min) the solution did not retract cleanly. From these experiments a standard immersion time of 30 min was selected as the most suitable for production of close-packed monolayers of stearic acid on clean iron; a comprehensive listing of samples made by this procedure is given in Table 3. Only samples having contact angles of $70^\circ \pm 1^\circ$ were used in subsequent experiments. As indicated, samples made from the carefully purified solution appear to have decreased in radioactivity by about 6%.

Table 3
Radioactivity and Contact Angle Data for Stearic Acid Films
Prepared by the Standard Procedures

Iron*			Glass*		
Sample	Radioactivity (counts/min)	Contact Angle (degrees)	Sample	Radioactivity (counts/min)	Contact Angle (degrees)
(a) Samples prepared prior to solution cleanup			(a) Samples prepared prior to solution cleanup		
Fe-19	2170	70	G-1	1400	70
-21	2163	70	-2	1384	70
-22	2650	70, 70	-3 [†]	1353	68, 70
-25	2221	70, 71	-4	1475	70
-26	2191	70	-5	1445	70
-28	2595	70, 70	-6	1410	70
-29	2405	70	-8	1500	70
-30 [†]	2180	68	-9	1440	70, 71
-32	2111	69	-10	1460	70
-34	2418	69	-308	1470	72, 72
-36	2145	70	-309	1480	71, 72
-37	2331	69	-314	1380	70, 71
-38	2025	69	-316	1498	70, 71
-40	2017	69, 70	-321	1413	71, 72
Average: $2265 \pm 202^\ddagger$ (13 samples)			Average: $1436 \pm 47^\ddagger$ (13 samples)		
(b) Samples prepared after solution cleanup			(b) Samples prepared after solution cleanup		
Fe-41	2131	70, 71	Average: $1377 \pm 33^\ddagger$ (15 samples) 70-73		
-42	2108	70, 70			
Average: 2120 (2 samples)					

*Immersion time for iron, 30 min; for glass, 2 min.

[†]Sample omitted from average because of low contact angle.

[‡]Standard deviation of a single measurement.

Retracted Stearic Acid Films on Glass — For reference purposes it was desired to have a surface that had a roughness factor of unity, i.e., one whose apparent area and true area were equal. Glass which had not been ground or polished was considered for this purpose. However, none of the varieties of soft glass or Pyrex glass available, whether polished microscope slides or unpolished window glass, could be cleaned sufficiently by conventional procedures to accept a close-packed monolayer of stearic acid. It was found, however, that soft glass (soda-lime glass) after fire-polishing under controlled conditions could readily be given a highly compacted monolayer of stearic acid from nitrobenzene by the retraction technique. In fact, the methylene iodide contact angles generally fell in the range of 71° to 72° , measurably higher than those produced on the iron. Neither this treatment nor any other tried produced close-packed stearic acid films on Pyrex glass.

The glass samples used in this study were made of double-strength window glass cut to the approximate dimensions of the iron samples. When radioactivity measurements were made, shims were used under the glass samples to maintain the same spacing between the coated surface and the counter window as obtained with the iron samples.

The glass was washed with Tide detergent, rinsed with tap water and then with distilled water, and finally air dried. The individual samples were laid on a cold piece of stainless steel (Type 316) with dimensions of roughly $0.1 \text{ cm} \times 10 \text{ cm} \times 20 \text{ cm}$, whose surface had been lightly dusted with alumina powder to prevent sticking. The stainless steel sheet and glass were added together to a small muffle furnace, which had been preheated to 800°C . After 5 to 10 min, when the edges of the glass showed signs of melting, the stainless steel sheet and glass sample were removed. After a 1-min cooling period, the glass was lifted off the steel with clean forceps, air-cooled for another 2 min, and then immersed in a beaker of clean nitrobenzene. Following this quenching from about 200°C to near room temperature the glass was drained and immersed in the stearic acid/nitrobenzene solution for the appropriate time. It was withdrawn by hand at the rate of roughly 1 cm/sec, carefully wiped dry on the back and sides, and mounted in an aluminum-foil-lined planchet. Radioactivity and contact angle measurements were made as described previously.

A series of experiments in which varied immersion times (Fig. 2) were employed indicated that the optimum time for formation of condensed monolayers of stearic acid on this fire-polished glass surface was about 2 min immersion in the previously described stearic acid solution (1.12 mg/ml). There is no explanation for the anomalous results obtained for immersion periods of 6 to 10 min. Subsequent studies have shown this anomaly to occur only in the more concentrated solutions (i.e., near 1 mg/ml) (4). A listing of samples made by the standard procedure is shown in Table 3; samples prepared from the purified solution had slightly higher contact angles but decreased radioactivity (ca. 4%) relative to those produced with the untreated solution.

RESULTS AND DISCUSSION

Extent of Surface Coverage

The radioactivity of an adsorbed film depends on the following factors: (a) the specific radioactivity of the adsorbed species, (b) the closeness of packing of the molecules, (c) the purity of the film, (d) the true area of the surface, and (e) the efficiency of counting. The contact angles reported here are consistent with those reported by Zisman and coworkers (3,5,6) as being characteristic of monolayers composed of close-packed methyl groups at the monolayer/air interface; film purity is maintained by employing a solvent of low adsorptivity and different molecular structure. From the counter calibration (Table 1) it can be determined that $1 \mu\text{g}$ of the stearic acid- 1-C^{14} deposited in a 1-in.-diam area (5.07 cm^2) gives a counting rate of 1258 counts/min on iron. Thus, an

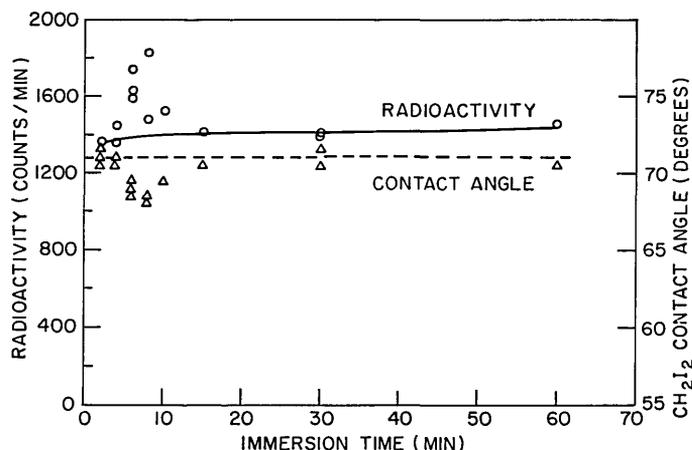


Fig. 2 - Effect of immersion time on some properties of adsorbed stearic acid-1-C¹⁴ films on soda-lime glass

activity of 2120 counts/min and a methylene iodide contact angle of 70° (Table 3) obtained for the retracted films on iron indicate 1.69 μg of stearic acid deposited in a close-packed array over the counting area, or 0.333 μg per cm^2 of apparent surface.

To determine the true area occupied by a stearic acid molecule adsorbed on the iron surface, it is necessary to have some measure of the surface roughness of the iron, i.e., the ratio of the true surface area to the apparent surface area. A reasonable assumption is that a glass sample that has been heated sufficiently for the glass to flow will have a true surface area equal to its measured area (a "roughness factor" of unity); hence, "fire-polished" glass should serve as a good reference material. As shown in Table 3, stearic acid forms highly compacted films (methylene iodide contact angle 70° to 73°) on fire-polished soda-lime glass on retraction from a purified stearic acid-1-C¹⁴/nitrobenzene solution. A comparison of the counting rates of the retracted samples with the radioactivity standard (Table 1) indicates the deposition of 0.250 μg of stearic acid per cm^2 of true surface. The average roughness factor of the surfaces of these iron samples is given by the ratio 0.333/0.250 or 1.33. (If data from Table 3 for samples prepared from the original, unpurified solution are used, the derived roughness factor is 1.35.)

The density of packing of the stearic acid on the glass surface may be determined from the relation

$$\begin{aligned} \text{surface concentration} &= \frac{\text{wt/cm}^2 \times \text{Avogadro's number}}{\text{molecular wt of stearic acid}} \\ &= \frac{0.250 \times 10^{-6} \text{ g/cm}^2 \times 6.025 \times 10^{23} \text{ molecules/mole}}{284.5 \text{ g/mole}} \\ &= 5.29 \times 10^{14} \text{ molecules/cm}^2. \end{aligned}$$

The area per stearic acid molecule is $1.89 \times 10^{-15} \text{ cm}^2$ or 18.9 \AA^2 per molecule. Because of the near equality of methylene iodide contact angles obtained on stearic acid monolayers adsorbed on glass and iron, it is concluded that the monolayers have essentially the same surface packing density on each of these materials.

It is of interest to note that film pressure-vs-area per molecule measurements of stearic acid monolayers adsorbed at the water-air interface give limiting areas per molecule, extrapolated to zero film pressure, of between 20.4 \AA^2 and 23.8 \AA^2 per molecule depending on the substrate pH (7). The actual area per molecule at film collapse is somewhat less; values range between 18.5 \AA^2 and 19.7 \AA^2 , also depending on the substrate pH (7). Measurements of a Stuart-Briegleb ball model of the stearic acid molecule in an extended linear configuration yield cross-sectional areas between 18.5 \AA^2 and 21.3 \AA^2 depending upon the angle of rotation of the carboxyl group. The value of 18.9 \AA^2 found in this study suggests that the molecules of stearic acid adsorbed on iron and glass are arranged in a highly compacted state comparable to that obtained on water at film collapse pressures.

Effect of Surface Roughness

One objective of this study was to determine the effect of surface roughness on the real surface area. This effect can be measured by comparing the quantity of material adsorbed on a surface having a known roughness factor with that adsorbed under equivalent conditions of surface coverage on surfaces of unknown roughness.

Iron surfaces resulting from rough polishing with a $6\text{-}\mu$ diamond compound and abrading with 600-grit (ca. 14μ particle size) and 400-grit (ca. 24μ particle size) carborundum papers were used. Although contact angle measurements were useful in indicating reproducible surface packing on the smoothest surfaces, contact angles showed anisotropy on the rougher surfaces; the 400-grit surface would not allow the formation of a retracted film.

With the assumptions that the fire-polished glass surface had a roughness factor of unity and that the molecular surface-packing density of the monolayers was identical in each case, the radioactivities were measured and the roughness factors were calculated (Table 4).

Table 4
The Effect of Surface Roughness on Real Surface Area

Surface Finish	Observed Radioactivity* (counts/min)	Calculated Roughness Factor
0.3- μ alumina	2120	1.33
6- μ diamond	3030	1.90
600-grit carborundum	5785	3.63

*Total count for 1-in.-diam circular area; corrected for background count.

The observed variation in counting rate ($\pm 10\%$) obtained for monolayers on highly polished iron surfaces when prepared under equivalent conditions may reflect variations in real surface area. However, this series of samples (Table 3) was prepared from a solution that may have contained surface active impurities or particulate matter; hence the effects of these on the variability cannot be discounted.

Depletion of Adsorbed Monolayers

Another objective of this study was the determination of the utility and reliability of contact angle measurements as a method for determining the closeness of packing of an oriented, adsorbed monolayer. Rather than working with incompletely formed monolayers, it seemed desirable to begin with the most highly compact monolayers available and to deplete the surface of adsorbed molecules by appropriate means. The resulting random loss of molecules should be more uniform than the patchiness to be expected by limiting the immersion time in the retracting solution, since in the earlier stages of monolayer formation retraction is only partial or does not occur at all.

Thermal Desorption — Monolayers of stearic acid-1-C¹⁴ adsorbed on iron, on which methylene iodide exhibited contact angles of $70^\circ \pm 1^\circ$, were heated for various increments of time in an oven maintained either at $99^\circ \pm 2^\circ\text{C}$ or $95^\circ \pm 2^\circ\text{C}$. The oven was vented to the atmosphere to minimize re-adsorption and the possibility of reaching a steady-state condition. After each desorption period and subsequent cooling to room temperature the remaining radioactivity was measured together with the resulting methylene iodide contact angle. The results of several independent series of such measurements of radioactivity vs desorption time and of contact angle vs radioactivity are given in Table 5 and shown graphically in Figs. 3 and 4. Complete coverage (100% of a monolayer) was assumed for each sample that met the criterion of a $70^\circ \pm 1^\circ$ contact angle. Samples with low or high initial count rates did not differ noticeably in desorption behavior; hence the initial differences could conceivably represent real differences in surface area.

The rate of loss of radioactivity from monolayers of tagged stearic acid from iron suggests that there are two forms of bonding between the acid and the iron. Desorption of the less strongly bonded component occurred fairly rapidly, with 60% of complete monolayer coverage desorbing in about one hour. The half-time of removal of the weakly adsorbed component was less than 20 min; the removal half-time of the more strongly bonded component was about 10 hr. The iron, or iron oxide, surface used here is probably capable, to some extent, of reacting with the stearic acid and forming the soap. Dubrisay (8) and also Prutton et al. (9) have shown that the fatty acids react with many metals to form the soap only after the metal oxide has been formed. Tingle (10) has also suggested that traces of water must be present for formation of the metal soap. Both oxygen and water are present in our experimental environment. The data presented here indicate that about 60% of the monolayer is adsorbed rather weakly, possibly through a process of physical adsorption, and the remaining more strongly adsorbed 40% is a result of chemical adsorption or soap formation.

The relationship between methylene iodide contact angle and extent of surface coverage on iron shown in Fig. 4 illustrates the sensitivity of the contact angle measurement. The slope of this plot is about 2% per degree. An extension of the plot toward low surface coverage results in an extrapolated contact angle near 20° for zero surface coverage. Methylene iodide is an autophobic liquid which exhibits a contact angle of 16° on a freshly prepared, uncoated iron surface. The scatter of experimental data is due both to difficulties in measuring contact angles, particularly at low coverage, and to uneven removal of stearic acid from the surface.

Solvent Desorption — Several retracted monolayers of tagged stearic acid on iron were immersed in clean portions of freshly distilled diethyl ether for various periods of time at room temperature (ca. 25°C), after which the remaining radioactivity and methylene iodide contact angle were measured, as indicated in Table 6. A plot of the rate of loss of activity is given in Fig. 5; as in thermal desorption, there is evidence of a weakly bonded and of a more strongly held component. At low surface coverages, i.e., after removal of about 50% of the monolayer, the ether could no longer retract cleanly from the surface, and considerable unevenness of surface coverage resulted.

Table 5
Thermal Desorption of Stearic Acid Monolayers from Iron

Desorp- tion Time (min)	Oven Temperature 99 ± 2 °C												Oven Temperature 95 ± 2 °C		
	Sample Fe-28			Sample Fe-29			Sample Fe-32			Sample Fe-42*					
	Radio- activity (counts/ min)	Activity Re- maining (%)	Contact Angle (degrees)												
0	2575	100.0	70, 70	2405	100.0	70	2111	100.0	69	2108	100.0	70, 70			
1	—	—	—	—	—	—	2031	96.2	65	—	—	—			
2	—	—	—	—	—	—	1965	93.1	61, 62	—	—	—			
2.5	—	—	—	1981	82.4	62	—	—	—	—	—	—			
3	—	—	—	—	—	—	1918	90.9	61	—	—	—			
5	1921	74.6	56	1648	68.5	55	—	—	—	1618	76.8	64, 62			
6.5	—	—	—	—	—	—	—	—	—	—	—	—			
10	1748	67.9	56	—	—	—	—	—	—	1485	70.4	58, 58			
13	—	—	—	—	—	—	1108	52.4	47, 49	—	—	—			
15	—	—	—	1371	57.0	51	—	—	—	1361	64.6	55, 55			
20	1378	53.5	51	—	—	—	—	—	—	—	—	—			
30	—	—	—	—	—	—	868	41.1	43, 45	1081	51.3	42, 44			
35	—	—	—	1135	47.2	46	—	—	—	—	—	—			
50	1061	41.2	35	—	—	—	—	—	—	—	—	—			
60	—	—	—	—	—	—	721	34.2	36, 43	865	41.0	37, 38			
65	—	—	—	998	41.5	45	—	—	—	—	—	—			
80	981	38.1	35	—	—	—	—	—	—	—	—	—			
90	—	—	—	—	—	—	658	31.2	35, 37	—	—	—			
140	845	32.8	32	—	—	—	—	—	—	—	—	—			
1020	—	—	—	—	—	—	—	—	—	495	23.5	35, 35			

*Sample prepared by retraction from purified nitrobenzene solution.

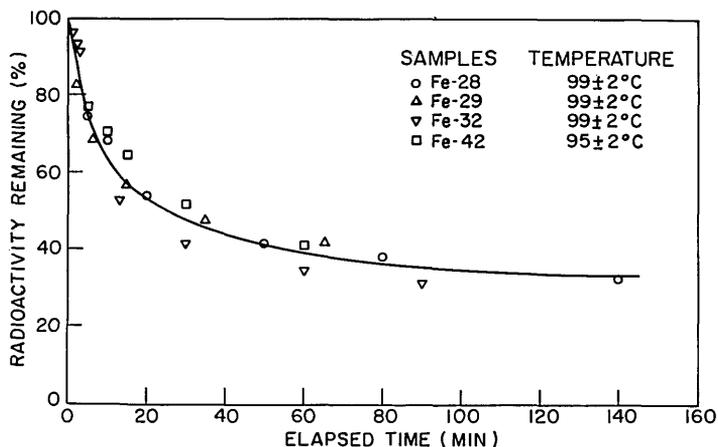
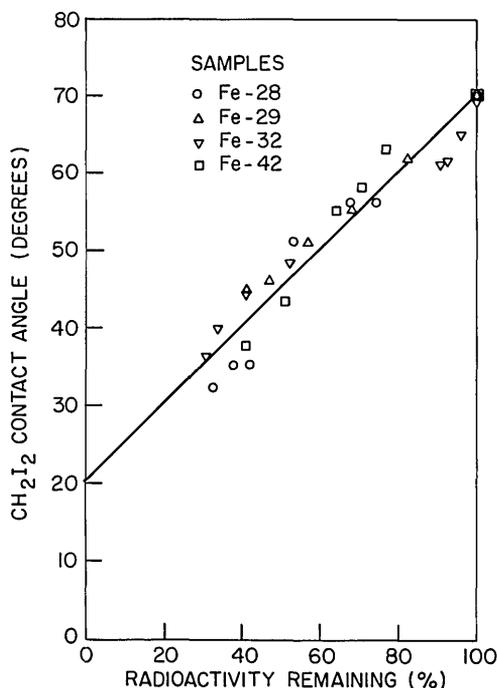


Fig. 3 - Thermal desorption of stearic acid-1-C¹⁴ from iron at 95-99°C

Fig. 4 - Relationship between the methylene iodide contact angle and the extent of surface coverage (radioactivity remaining) of iron by stearic acid



Exchange with Unlabeled Stearic Acid — Monolayers containing radiolabeled stearic acid were allowed to exchange with unlabeled stearic acid in nitrobenzene solution. After each exchange period the radioactivity and the methylene iodide contact angle were measured (Table 7); the contact angle remained at 68 to 71° throughout the experiment, indicating that the monolayer did not become greatly depleted. Figure 6 presents the data as the percentage of a complete monolayer exchanged as a function of time. This curve is very similar to that obtained from desorption experiments. Sixty % of the monolayer is exchanged easily and rapidly, while the remaining 40% is more tenaciously held. This is further evidence for suggesting that about 40% of the stearic acid monolayer on iron is chemically adsorbed.

Table 6
Removal of Adsorbed Stearic Acid by Diethyl Ether at 25°C

Immersion Time (min)	Sample Fe-21		
	Radioactivity (counts/min)	Activity Remaining (%)	Contact Angle (degrees)
0	2163	100.0	70
1	1007	46.5	38
15	779	36.0	28
30	698	32.2	28
31	—	—	—
	Sample Fe-22		
	Radioactivity (counts/min)	Activity Remaining (%)	Contact Angle (degrees)
0	2665	100.0	70, 70
1	1448	54.3	45, 45
15	—	—	—
30	—	—	—
31	984	36.9	28
	Sample Fe-25		
	Radioactivity (counts/min)	Activity Remaining (%)	Contact Angle (degrees)
0	2221	100.0	70, 71
1	905	44.7	36, 37
15	—	—	—
30	—	—	—
31	708	31.9	29

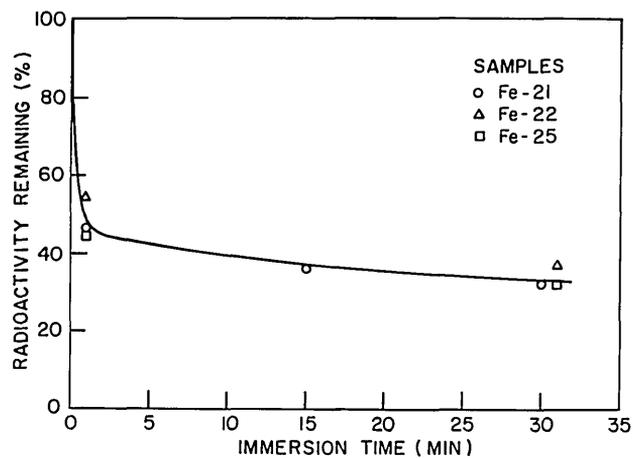


Fig. 5 - Rate of removal of adsorbed stearic acid-1-C¹⁴ by diethyl ether

Table 7
Exchange of Adsorbed Stearic Acid-1-C¹⁴ on Iron
with Inactive Stearic Acid in Nitrobenzene

Immersion Time (min)	Sample Fe-36		
	Radioactivity (counts/min)	Stearic Acid Exchanged (%)	Contact Angle (degrees)
0	2261	0	70
5	1525	32.6	71
10	1325	41.4	71
25	1161	48.7	69
55	—	—	—
60	—	—	—
85	1038	54.1	68
115	—	—	—
120	1001	55.7	69
145	—	—	—
Immersion Time (min)	Sample Fe-37		
	Radioactivity (counts/min)	Stearic Acid Exchanged (%)	Contact Angle (degrees)
0	2331	0	69
5	1663	28.7	69
10	1448	37.9	69
25	1251	46.3	69
55	1135	51.3	68
60	—	—	—
85	995	57.3	69
115	928	60.2	68
120	—	—	—
145	908	61.0	69
Immersion Time (min)	Sample Fe-40		
	Radioactivity (counts/min)	Stearic Acid Exchanged (%)	Contact Angle (degrees)
0	2017	0	69, 70, 69
5	1397	30.7	69, 69
10	1132	43.9	69, 69
25	958	52.5	69, 70
55	—	—	—
60	818	59.4	69, 69
85	—	—	—
115	—	—	—
120	734	63.6	68, 67
145	—	—	—

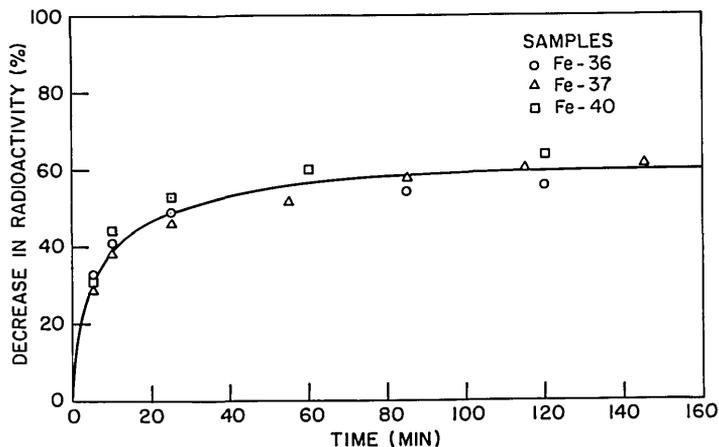


Fig. 6 - Rate of exchange of adsorbed stearic acid-1-C¹⁴ on iron by inactive stearic acid in nitrobenzene solution

SUMMARY

Adsorption studies of radiolabeled stearic acid were made on mechanically polished iron and on fire-polished glass as a reference. For each cm² of apparent area, iron adsorbed 7.06×10^{14} molecules and glass adsorbed 5.29×10^{14} molecules. Contact angle measurements on the two monolayer-covered surfaces showed that the surface packing density of stearic acid molecules was essentially the same in both cases. This fact, together with the assumption that the fire-polished glass had a roughness factor of 1.0, leads to the conclusion that at close packing a stearic acid molecule occupies about 18.9 Å² on both iron and glass, and that the roughness factor for the polished iron surface was 1.33.

Desorption and exchange experiments showed that about 60% of a stearic acid monolayer is rather weakly adsorbed on iron, and the remaining 40% is more tightly bonded, i.e., probably chemically adsorbed. A linear relationship was found between the measured contact angle and the extent of surface coverage of iron. The methylene iodide contact angle had a sensitivity of about 2% of complete monolayer coverage per degree.

Additional studies of the temperature coefficients of these removal processes should permit determinations of their activation energies and further clarify the nature of the adsorption bond.

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13. ABSTRACT Stearic-1-C¹⁴ acid was adsorbed as a close-packed monomolecular layer on mechanically polished iron and fire-polished glass by the method of solution retraction. Measurements of the adsorbed radioactivity were made which allowed the determination of the number of adsorbed molecules per apparent unit area. Measurements of the methylene iodide contact angle on the two monolayer-covered surfaces showed that the surface packing density of stearic acid molecules was essentially the same in both cases. This conclusion, together with the assumption that the fire-polished glass surface had a roughness factor of unity, allowed the calculation of the area occupied per stearic acid molecule and of the roughness factor of the iron surface. The stearic acid molecule was found to occupy about 18.9 Å² on both iron and glass, and the roughness factor for the polished iron surface was 1.33. Desorption and exchange experiments indicated that about 60% of the monolayer on iron was rather weakly adsorbed and the remainder was probably chemically adsorbed. A rectilinear relationship was found between the measured contact angle and the extent of surface coverage. Additional studies of the temperature coefficients of the removal processes should permit determination of their activation energies and further clarification of the nature of the adsorption bond.			

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