

The Adsorption of Carbon-14-Labeled Stearic Acid on Soda-Lime Glass

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL DATA	1
Preparation of Glass Surfaces	1
Preparation and Purification of Solutions	2
Preparation of Stearic Acid Monolayers	3
STUDIES OF ADSORBED FILMS	4
Thermal Desorption	4
Solvent Desorption and Exchange	4
Other Removal Processes	8
Relationship Between Contact Angle and Surface Coverage	9
Limitations of the Method	10
CONCLUSIONS	12
REFERENCES	12

ABSTRACT

Procedures have been devised for producing highly compacted monomolecular layers of carbon-14-tagged stearic acid on fire-polished soft (soda-lime) glass through retraction from a nitrobenzene solution. While thermal desorption studies indicated a small quantity of weakly bonded stearic acid on the surface, its rate of removal by other mechanisms (dissolution and isotopic exchange) suggests that only a single type of bonding exists. The rate of loss of stearic acid-1-C¹⁴ increased with increasing temperature, but the scatter in the data prevented the calculation of the activation energy for desorption.

Difficulties in defining the surfaces under investigation rather than weaknesses in the radiochemical technique are the major handicaps in applying radiotracers to the study of surface chemical phenomena.

PROBLEM STATUS

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

AUTHORIZATION

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THE ADSORPTION OF CARBON-14-LABELED STEARIC ACID ON SODA-LIME GLASS

INTRODUCTION

The investigation of the surface chemistry of the metallic state through the study of the adsorption of various radioactive molecules on metallic substrates required the development of a reproducible reference surface of known roughness. In the preliminary report of these studies (1), fire-polished glass was used as the reference surface; it was shown to accommodate a monolayer of stearic acid (octadecanoic acid) having the close-packing characteristic of stearic acid on water at film collapse pressures. The present report covers further studies on the preparation of adsorbed monolayers of radioactive stearic acid on fire-polished soft (soda-lime) glass and some observations of the properties of these adsorbed films.

EXPERIMENTAL DATA

Condensed monolayers of stearic acid containing stearic acid-1-C¹⁴ tracer were prepared on soft glass by retraction from a nitrobenzene solution of the radioactive material. As indicated in the previous report (1), extreme care was required in sample preparation and in assuring the purity and integrity of the retracting solution.

Preparation of Glass Surfaces

None of the procedures normally employed for the preparation of physically clean glass surfaces (washing with water, detergent, acid, or base; polishing with alumina; treatment with a sequestering agent (EDTA); flaming over a gas burner; and heating in an oven up to 500°C) led to the production of close-packed monolayers on either soda-lime glass or Pyrex glass on retraction from a 0.1% stearic acid solution in nitrobenzene. Though on occasion the stearic acid films on soft glass exhibited contact angles θ of 65 to 68 degrees toward the standard methylene iodide (CH₂I₂) test liquid, they did not give readings of 70 degrees or higher as expected for surfaces containing an array of close-packed methyl groups. On Pyrex glass, retraction was poor, and $\theta_{\text{CH}_2\text{I}_2}$ rarely exceeded 50 degrees.

While pretreatment of the soda-lime glass at temperatures below its softening point appeared to cause little improvement in the contact angle of the retracted films, a dramatic change was produced when that glass was heated at a sufficiently high temperature to cause flow. A few minutes of heating at 750 to 800°C sufficiently modified the surface so that subsequently a highly compacted stearic acid monolayer could be deposited within 1 to 2 minutes; contact angles in excess of 70 degrees were readily obtainable. Heating to higher temperatures or for longer periods of time or permitting the samples to cool excessively long (>10 min) in the laboratory atmosphere reduced the adsorptive capacity of the glass surface. The proper heat treatment permitted the preparation of highly compacted stearic acid films by the retraction technique and assured, as well, that the surface scratches and flaws were smoothed out so that the surface roughness factor could be regarded as unity (i.e., the ratio of the true surface area to the apparent area was unity).

In this study, glass blanks were cut to the approximate dimensions 5.4 cm by 3.8 cm by 0.32 cm from a sheet of double-strength window glass (Pittsburgh Plate Glass Company). The samples were washed with Tide detergent, rinsed with water, air dried, and then placed in a 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 sample and supporting stainless-steel sheet (Type 316) on which it rested were removed from the furnace. (A thin layer of alumina prevented sticking of the glass to the stainless steel.) As soon as the sample had cooled to near 200°C (about 2 to 3 min), it was quenched in clean nitrobenzene; then it was removed, drained, and immersed in the retracting solution. This procedure protected the freshly prepared surface from exposure to the laboratory atmosphere and assured a clean, dehydrated surface.

Preparation and Purification of Solutions

The working solution for the preparation of adsorbed films of radioactive stearic acid was made by dissolving 6.6 mg of stearic acid-1-C¹⁴ (5.0 mCi/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 1.12 mg/ml. Radioactivity measurements of four aliquots of this solution showed it to have a specific activity of 1082 ± 8 counts/min per μg of stearic acid when spread uniformly over a 2.54-cm-diameter area of glass and counted under standard, reproducible conditions on a Tracerlab Model CE 14 low level β counter, which had been modified to handle higher count rates and to permit automatic recording.

When it was found that a duplicate preparation of this standard solution made at a later date gave retracted films having high, variable activity and unsatisfactory contact angles, a cleanup procedure, using activated alumina as an adsorbent, was devised. This procedure was applied to the original solution, with a resulting slight increase in contact angles and a small reduction in the activity of retracted films (1).

Repeated treatments of the solution with 50-mg portions of oven-dried adsorptive alumina caused a progressive decrease in the radioactivity of the nitrobenzene solution through loss of adsorbable radioactive impurity but, primarily, through loss of the tagged stearic acid. Retracted films prepared from this solution at various stages of purification indicated that the adsorbed radioactivity per unit area (i.e., the specific activity of the stearic acid) had changed relatively little ($< 4\%$). This purified solution consistently produced stearic acid-1-C¹⁴ monolayers having methylene iodide contact angles in the range of 70 to 73 degrees and an average radioactivity of 1377 counts/min. The standard deviation of a single radioactivity measurement from a series of 15 samples having contact angles of 70 to 73 degrees was ± 33 counts/min or $\pm 2.3\%$.

The duplicate of this solution, after being cleaned up with adsorptive alumina, produced retracted films of equivalent quality. Comparison of the radioactivity of retracted films made prior to and following addition of a known amount of inert stearic acid to this solution (i.e., "isotope dilution") showed that the specific activity of the stearic acid (i.e., the ratio of active to inactive stearic acid) had not changed measurably during the cleanup. Thus, the radioactive impurity, while having a higher affinity for glass than the stearic acid, was a very minor contributor to the total radioactivity of the solution. This solution of lower specific activity (600 to 610 counts/min for a close-packed stearic acid monolayer) was used in some of the subsequent studies.

Frequent filtration through a particulate filter (Millipore Type NR, 1- μ pore size) kept the solution free of extraneous dust and reduced the occurrence of retracted films with higher-than-normal radioactivity.

Preparation of Stearic Acid Monolayers

In the preliminary study of the adsorption of stearic acid- $1-C^{14}$ on iron (1), soda-lime (soft) glass was used as the reference surface. In this initial study, the nitrobenzene solution of stearic acid had a concentration of 1.12 mg/ml, somewhat less than half the estimated saturation value. Since some anomalous results had been observed with sample immersion times in the interval of 4 to 8 min, a study was conducted on the interrelation of concentration and time in the production of compacted monolayers of stearic acid on soft glass.

Methylene iodide contact angles and radioactivity measurements were made on several series of the carefully cleaned, fire-polished glass plates, which had been immersed for various times in nitrobenzene solutions having stearic acid concentrations of 0.8, 0.08, 0.04, and 0.008 mg/ml. These solutions were prepared from the carefully purified solution to which additional inactive stearic acid had been added (described in the previous section). Nitrobenzene-repellent films were obtained on glass immersed in the three more concentrated solutions; however, at a concentration of 0.008 mg/ml, retraction was generally not obtained over the entire surface, and the measurements were meaningless. As indicated in Table 1, highly compacted monolayers of stearic acid were readily obtained over a concentration range of 0.8 to 0.04 mg/ml (2.8×10^{-3} M to 1.4×10^{-4} M), but the immersion time required to accomplish this increased with dilution. The previously observed region of high activity and low contact angle was again observed but only for the most concentrated solution. At the lower concentrations and for short immersion times there was considerable variability in the extent of stearic acid adsorption.

Table 1
Effect of Solution Concentration and Immersion Time on the Formation of Adsorbed Films of Stearic Acid on Soda-Lime Glass at Room Temperature (ca. 24°C)

Concentration of Stearic Acid* in Nitrobenzene								
0.8 mg/ml			0.08 mg/ml			0.04 mg/ml		
Immersion Time (min)	Radioactivity (counts/min)	Contact Angle toward CH_2I_2 (degrees)	Immersion Time (min)	Radioactivity (counts/min)	Contact Angle toward CH_2I_2 (degrees)	Immersion Time (min)	Radioactivity (counts/min)	Contact Angle toward CH_2I_2 (degrees)
0.5	603	72,73,71	2	439	65,67,69	0.5	442	63,63,64
1	594	72,73,72	4	428	64,62,63	1	442	65,65,66
2	610	72,73,72	8	451	62,63,65	2	426	60,61,63
	601	70,72,71	15	586	71,72,72		391	61,63,62
	604	72,72,72	22	599	71,72,72	5	585	70,71,71
4	608	72,72,72	30	606	72,73,73	10	482	65,65,67
6	603	73,74,73	40	605	71,71,72	20	491	65,65,64
8	717	69,69,69	80	596	71,72,72	30	585	71,71,72
	799	69,70,69	120	601	71,73,72	40	591	71,72,71
10	670	69,70,70				80	605	72,71,72
12	663	72,72,71				120	607	72,71,73
15	601	69,71,72						
20	610	72,71,72						
40	602	71,72,73						
16 hours	1425	52,51,51						
	710†	61,60,60†						

*Specific radioactivity of the tagged stearic acid in this carefully purified solution was only 44% of that employed in the previous study (i.e., 605 counts/min corresponds to a highly compacted monolayer).

†After wiping with dry tissue paper.

The formation of adsorbed films of C^{14} -tagged stearic acid having identical properties (radioactivity and contact angle) when produced on fire-polished soft glass by retraction from solutions differing over 20-fold in concentration is adequate indication that some special, limiting degree of surface packing is being obtained. From the known specific activity of the stearic acid, it may be readily determined that this special condition corresponds to that of a close-packed monolayer of vertically oriented stearic acid molecules (1).

STUDIES OF ADSORBED FILMS

To learn more about the stearic acid-glass system, some of the glass plates having close-packed monomolecular layers of the tagged stearic acid were treated by several procedures designed to leave depleted, or partially removed, films of stearic acid on the glass surface.

Thermal Desorption

Studies were made of the changes in the radioactivity and surface packing of stearic acid- $1-C^{14}$ monolayers on soda-lime glass during thermal depletion of the adsorbed material. Data on the decrease in surface coverage with time, as deduced from the measured radioactivity of the surface, for desorption at 85° , 90° , 95° , 100° , and $105^\circ C$ and the corresponding contact angle data are listed in Table 2. In practice, pairs of nearly identical samples were desorbed simultaneously. No reason for the disagreement in the data obtained under supposedly identical conditions could be found; it could not be related either to variations in atmospheric moisture or to differences in the thermal environment within the oven. This disagreement is apparently the result of real differences in the composition of the glass surfaces.

As was found for stearic acid films on iron (1), more than one mode of bonding is indicated. Differences between the iron and glass surfaces did show up in the relative amounts of the tightly and loosely held components and in their tenacity of bonding. While at $100^\circ C$ the loosely held, "physically" adsorbed stearic acid on iron was evaporated with a half-life of about 10 min, on soda-lime glass the removal half-time of the more volatile component was about 2 hr. On glass the loosely held stearic acid represents less than 40% of the total adsorbed monolayer, while on iron it represented about 60% of the total. The rate of loss of the more strongly bonded stearic acid from the glass surface increased with increasing temperature, but unfortunately the scatter in the data was such that no meaningful information on the heat of desorption could be derived from an Arrhenius plot of $\log k$ against $1/T$.

Solvent Desorption and Exchange

The rate of removal of adsorbed stearic acid monolayers by clean nitrobenzene at room temperature varied from sample to sample, but the constant slope of the desorption curve (\log of surface coverage vs time) was suggestive of the presence of only a single type of bonding between the stearic acid molecules and the glass surface. Similar studies of the exchange of stearic acid- $1-C^{14}$ monolayers with a solution of inactive stearic acid in nitrobenzene (1 mg/ml) gave essentially the same results, as indicated in Figs. 1 and 2. The data from which these curves have been constructed are contained in Tables 3 and 4. The dissolution studies were of necessity discontinued when the contact angle was reduced to a value where retraction of the nitrobenzene no longer occurred and drops remained on the surface; in the exchange studies, no significant decrease in contact angle resulted, since there was a simple replacement of radioactive stearic acid molecules by normal, inactive molecules.

Table 2
Thermal Desorption of Stearic Acid Monolayers on Soda-Lime Glass

Temperature (°C)	Desorption Time* (min)	Surface Coverage (%)	Contact Angle† (degrees)						
		Sample S-25		S-26		S-27		S-29	
85	0	100.0	72,73,72	100.0	72,73,72	100.0	72,72,72	100.0	72,73,72
	60	93.0	68,68,68	86.5	68,68,69	90.2	69,69,69	90.4	69,69,69
	120	92.0	68,68,68	84.6	68,68,69	89.3	69,67,69	86.6	69,68,69
	180	89.6	69,68,68	83.3	68,68,68	88.5	69,68,69	85.3	69,68,68
	330	85.7	66,68,68	82.5	68,68,68	83.0	67,68,68	80.8	68,68,68
	1290	84.9	66,67,66	76.8	65,66,66	-	-	-	-
	1320	-	-	-	-	77.1	67,67,68	74.4	68,67,67
		S-2		S-4		S-5		S-8	
90	0	100.0	71,71,72	100.0	71,72,72	100.0	72,72,73	100.0	72,71,72
	60	93.0	69,70,69	93.2	68,68,68	92.8	68,68,69	93.7	68,69,70
	120	90.2	68,67,67	89.2	67,67,67	87.7	68,67,68	90.0	67,67,67
	180	87.2	66,66,66	86.0	65,66,66	83.9	65,66,67	87.1	66,66,65
	240	84.3	66,66,66	83.7	66,66,67	80.7	66,66,67	84.5	66,66,66
	1200	72.0	59,60,60	-	-	-	-	70.8	60,60,61
	1230	-	-	70.6	60,61,60	72.4	61,60,61	-	-
		S-32		S-33		S-39		S-40	
95	0	100.0	72,73,72	100.0	72,72,72	100.0	72,73,72	100.0	72,73,73
	60	97.0	69,70,70	98.2	70,71,70	91.4	69,70,71	92.5	70,69,69
	120	96.0	68,68,68	95.0	68,69,70	84.8	67,69,68	87.2	67,68,68
	180	94.2	68,68,67	91.9	67,67,67	81.1	65,66,65	81.7	65,66,67
	240	93.0	66,66,67	90.9	65,66,66	78.0	64,65,65	79.4	66,65,66
	1200	83.0	66,66,65	80.8	63,63,64	46.0	59,59,60	71.6	63,61,61
		S-10		S-11		S-15		S-16	
100	0	100.0	72,71,71	100.0	72,72,72	100.0	72,73,72	100.0	72,72,72
	60	76.4	67,66,67	80.6	67,66,68	85.5	67,65,67	75.1	65,67,67
	120	66.1	64,63,64	76.6	64,65,64	80.1	64,65,65	67.4	66,65,64
	180	59.0	60,63,61	71.4	64,65,64	73.2	65,64,64	61.2	63,64,63
	240	-	-	-	-	68.6	65,65,64	53.0	63,63,64
	1140	20.7	49,50,52	44.3	54,54,55	-	-	-	-
	1200	-	-	-	-	30.8	55,56,55	33.3	54,56,54
		S-70		S-71		T-1		T-3	
105	0	100.0	72,72,72	100.0	73,72,72	100.0	72,73,73	100.0	72,73,72
	60	84.4	65,67,66	88.8	67,67,64	-	-	-	-
	120	78.9	63,62,63	83.1	64,64,65	-	-	-	-
	180	70.9	62,62,64	75.9	63,62,64	-	-	-	-
	240	58.3	63,64,62	69.2	64,62,62	62.3	65,65,65	72.0	65,64,65
	480	-	-	-	-	57.1	61,62,63	61.8	62,63,62
	1200	32.4	56,58,54	43.8	54,53,55	-	-	-	-
	1680	-	-	-	-	30.9	54,55,55	43.1	53,55,55
	5280	-	-	-	-	5.4	48,47,49	8.2	48,47,46

*Samples desorbed in pairs in separate compartments of oven.

†Toward methylene iodide.

The tenacity of the stearic acid bonding is indicated by the great disparity in the time required to produce a compacted monolayer on a clean glass surface (~ 2 min) and that required for exchange with a similar inactive solution or removal by clean nitrobenzene. The observed half-times for exchange and dissolution of the stearic acid were approximately 5 min and 2 min, respectively, at room temperature.

An interesting experiment was conducted with samples which had undergone exchange to replace approximately one-half of the tagged stearic acid with inactive stearic acid molecules. This involved a comparison of the loss in radioactivity during thermal desorption at 100°C of partially exchanged films with that of reference films of adsorbed radiostearic acid. It was anticipated that the rate of loss of radioactivity would be slower in the exchanged films than in the standard films, since in the former the remaining radioactivity would be held at the more strongly bonding sites. The results proved otherwise, as indicated in Table 5, where, within the scatter of the data, both types of samples appeared to lose radioactivity at the same relative rate. This suggests that, if there is more than one form of bonding present, there must be lateral exchange between molecules adsorbed at the different types of sites on the glass surface.

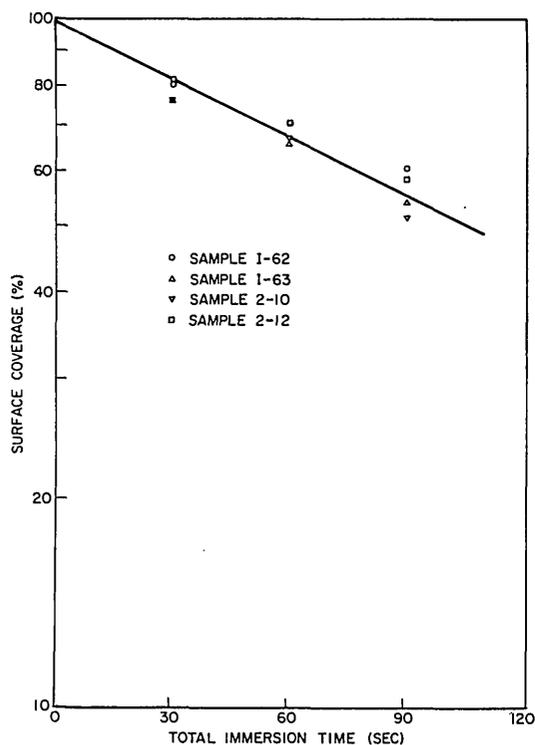


Fig. 1 - Removal of adsorbed stearic acid from soda-lime glass by nitrobenzene

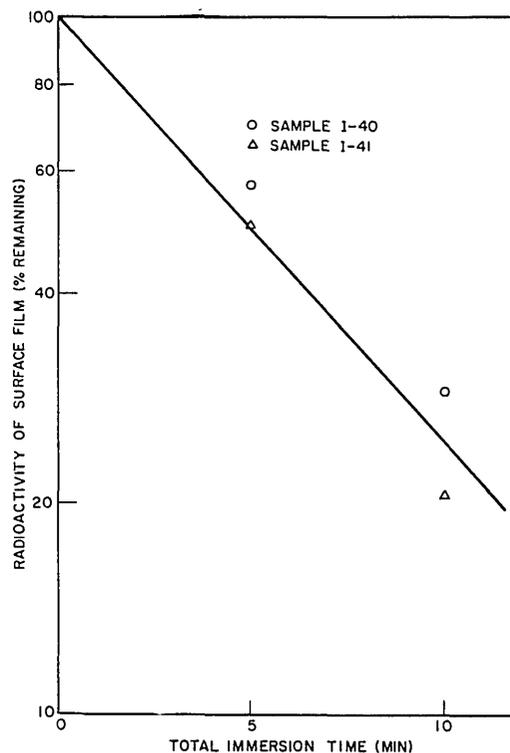


Fig. 2 - Exchange of adsorbed C¹⁴-tagged stearic acid with a nitrobenzene solution of inactive stearic acid

Table 3
Nitrobenzene Desorption of Stearic Acid Monolayers
on Soft Glass at Room Temperature (ca. 23°C)

Sample	Total Desorption Time* (sec)	Radioactivity (counts/min)	Surface Coverage (%)	Contact Angle † (degrees)
I-62	0	1252	100.0	73,73,73
	30	1020	81.5	66,65,68
	60	884	70.6	64,64,64
	90	760	60.7	62,61,62
I-63	0	1280	100.0	73,73,73
	30	972	75.9	65,66,66
	60	840	65.6	65,64,65
	90	692	54.1	62,61,60
Z-10	0	1280	100.0	73,71,73
	30	976	76.2	65,68,65
	60	860	67.2	65,65,65
	90	656	51.3	60,60,61
Z-12	0	1330	100.0	73,73,73
	30	1064	80.0	65,65,65
	60	940	70.6	65,65,64
	90	780	58.6	61,59,60

*Thirty-sec immersions in fresh portions of nitrobenzene.

†Methylene iodide contacting liquid.

Table 4
Exchange of Adsorbed C¹⁴-Tagged Stearic Acid
With Inactive Stearic Acid in Nitrobenzene Solution*

Total Exposure Time (min)	Radioactivity		Contact Angle (degrees)†
	Counts/min	Percent	
Sample I-40			
0	1273	100.0	73,73,73
5	729	57.3	73,73,73
10	369	29.0	73,73,72
Sample I-41			
0	1249	100.0	72,73,74
5	629	50.4	72,73,73
10	263	21.1	73,72,72

*One-mg/ml concentration.

†Methylene iodide contacting liquid.

Table 5
Thermal Desorption (100°C) of Isotopically Exchanged and Solution-Depleted
Monolayers of Stearic Acid on Soda-Lime Glass

Desorption Time (hr)	Radioactivity (counts/min)	Surface Coverage (%)	Contact Angle Toward CH ₂ I ₂ (degrees)	Radioactivity (counts/min)	Surface Coverage (%)	Contact Angle Toward CH ₂ I ₂ (degrees)
Monomolecular Films of C ¹⁴ -Tagged Stearic Acid Exchanged With Inactive Stearic Acid in Nitrobenzene						
Sample I-40				Standard I-42*		
0	369	100.0	73,73,72	1297	100.0	73,73,73
1.5	310	84.0	68,68,69	1133	87.4	67,68,66
3.5	282	76.4	69,69,67	1097	84.6	68,68,67
8.5	-	-	-	-	-	-
19.5	261	70.7	67,67,67	957	73.8	66,66,67
36.0	243	65.9	63,64,63	779	60.1	61,63,61
54.0	209	56.6	57,58,59	649	50.0	60,57,60
Sample I-41				Standard I-43*		
0	263	100.0	73,72,72	1281	100.0	72,73,73
1.5	218	82.9	68,68,68	1197	93.4	68,68,67
3.5	205	77.9	68,68,68	1131	88.3	-
8.5	190	72.9	67,68,68	1101	85.9	68,68,68
19.5	171	65.0	66,66,65	1001	78.1	66,67,66
36.0	-	-	-	-	-	-
54.0	-	-	-	-	-	-
Monomolecular Films of C ¹⁴ -Tagged Stearic Acid Depleted by Immersion in Nitrobenzene						
Sample I-62				Standard I-60*		
0	760	100.0	62,61,62	1272	100.0	73,72,72
0.5	740	97.4	64,63,64	1224	96.2	72,73,72
5	684	90.0	65,64,64	1176	92.4	71,72,70
25	636	83.7	60,62,60	996	78.3	66,66,67
48	552	72.6	58,59,58	816	64.2	61,63,64
Sample I-63				Standard I-61*		
0	692	100.0	62,61,60	1292	100.0	73,73,72
0.5	680	98.3	65,64,64	1232	95.4	72,72,72
5	652	94.2	66,65,64	1152	89.2	70,71,70
25	604	87.3	62,61,61	860	66.6	66,66,66
48	473	68.4	58,58,60	564	43.7	62,61,63

*The standard samples were prepared at the same time and desorbed alongside their counterparts which had undergone depletion or exchange.

Table 6
Depletion of Stearic Acid Monolayers on Soda-Lime Glass by Wiping

No. of Wipes*	Radioactivity (counts/min)	Contact Angle Toward CH ₂ I ₂ (degrees)
Sample 1 (Dry† Tissue Condition)		
0	1420	72,72,73
3	1295	70,72,71
6	1240	71,69,70
9	795	63,65,60
12	695	59,59,58
15	648	60,59,60
18	629	59,59,57
Sample 2 (Dry† Tissue Condition)		
0	1322	73,73,74
3	1159	72,72
6	1094	71,71,72
Sample 3 (Moist‡ Tissue Condition)		
0	1349	72,72,73
3	279	49,50,48

*A pad of ChemWipes was drawn across the surface at constant speed and pressure.

†Dried in a desiccator over Drierite for 16 hr.

‡Stored in a desiccator over distilled water for 16 hr.

Other Removal Processes

During the course of these studies, several other observations on the stability of adsorbed monomolecular films of stearic acid were made, which, though incomplete, deserve mentioning. One of these involved the stability of stearic acid monolayers on glass toward rubbing; this subject was of interest because such techniques have reportedly been used to prepare monomolecular layers of stearic acid on various substrates by mechanically wiping off excess material. As indicated in Table 6, a compacted monolayer of stearic acid on soda-lime glass was readily depleted by wiping with a pad of dry tissue paper (ChemWipes), which suggests that it might be difficult to control such a technique so as to leave a complete monolayer on the substrate. Also, as shown in Table 6, this removal process is extremely sensitive to moisture; the rate of activity removal by wiping with tissue that had been conditioned in an atmosphere of high humidity was nearly 10 times that observed for wiping with dry tissue.

The sensitivity toward moisture of close-packed stearic acid monolayers on glass was confirmed by the observation of anomalous contact angles (30 to 40 degrees) toward water droplets; under the same conditions stearic acid films on iron gave water contact angles in the 90- to 100-degree range, which is characteristic of a surface consisting of methyl groups. The stearic acid film was also found to be more readily displaced by distilled water than were films adsorbed on iron. There is evidently sufficient space between the close-packed hydrocarbon chains for water molecules to penetrate to the substrate and disrupt the glass-to-stearic-acid bond.

Relationship Between Contact Angle and Surface Coverage

A series of glass surfaces having different degrees of surface coverage was obtained by varying the cooling time of the glass after removal from the furnace and the immersion time in the nitrobenzene retracting solution. Nine samples, each having the average of three measured contact angles in the range 72 to 73 degrees and radioactivity consistent within $\pm 1.5\%$ of the group average (standard deviation), were assumed to have a highly compacted stearic acid monolayer and were used for reference purposes. Those with surfaces poisoned by atmospheric moisture or other adsorbable impurities had lower contact angles and lower radioactivity as indicated in Fig. 3. There is essentially a straight-line relationship between the degree of surface coverage and the methylene iodide contact angles between the 72- to 73-degree contact angle of a surface consisting of close-packed methyl groups and the 43- to 45-degree contact angle of a fired glass surface conditioned with nitrobenzene vapor.

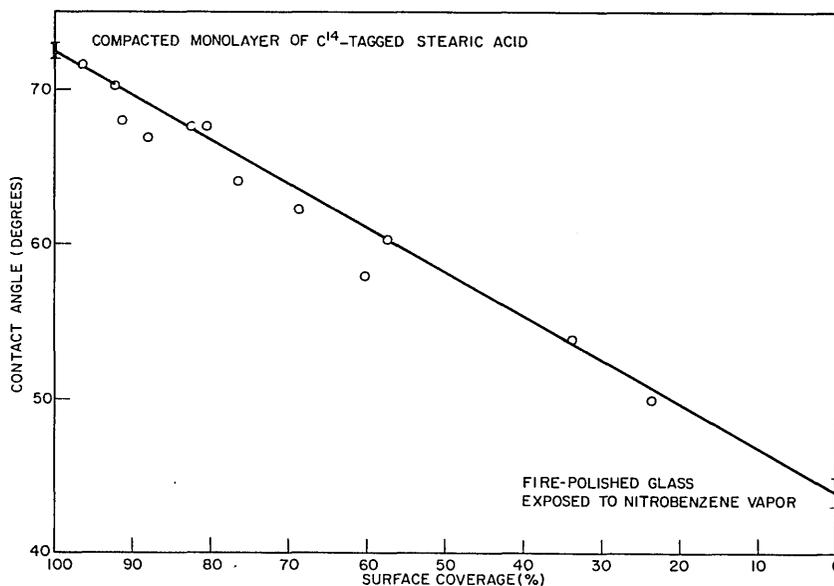


Fig. 3 - Relationship between methylene iodide contact angle and extent of surface coverage of soda-lime glass by stearic acid. Samples were prepared by retraction from a solution of C¹⁴-tagged stearic acid in nitrobenzene.

Thermally depleted films of stearic acid did not show as satisfactory linearity between surface coverage and contact angle. Typical results are shown in Fig. 4. There was greater scatter to the individual points, the loss in radioactivity on heating did not consistently result in a measurable decrease in contact angle, and the slope of the line depended to some extent on the temperature and length of heating. A possible explanation is that the thermal removal of stearic acid left sites free to adsorb material from the atmosphere on cooling, whereas the retraction procedure supplied a more consistent background of adsorbed nitrobenzene to sites not occupied by stearic acid. The extrapolated end point corresponding to the complete evaporation of stearic acid fell between the contact angle (31 to 33 degrees) for clean fire-polished glass cooled for a minimum length of time and that (50 to 53 degrees) obtained after the sample had been exposed for an hour to the same room atmosphere (ca. 50% RH). Shafrin and Zisman (2) have reported clean glass after equilibration in an atmosphere of 1% RH to exhibit a methylene iodide contact angle of ca. 13 degrees, while at 95% RH the contact angle was 36 degrees.

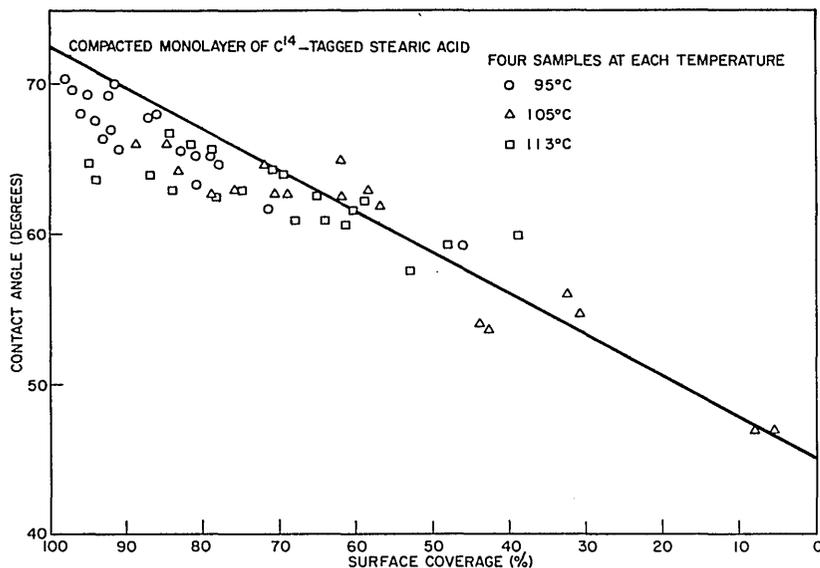


Fig. 4 - Methylene iodide contact angles of thermally depleted films of stearic acid on glass

To determine if other liquids behaved as did methylene iodide, a series of samples having different degrees of surface coverage was prepared by retraction from the radioactive stearic acid solution, and their contact angles toward methylene iodide, isopropylbiphenyl,* nitrobenzene, and nitrobenzene containing inactive stearic acid (1 mg/ml) measured (Table 7). As is indicated in Fig. 5, the behavior of the three pure liquids was more or less parallel. Contact angles of the nitrobenzene containing stearic acid, however, were generally higher than those of the pure nitrobenzene and diverged more with decreasing surface coverage. On clean glass (and on clean iron) the liquid droplets were observed to run around the surface wildly as a result of the imbalance of interfacial tension around the periphery of the drop. Eventually the droplets became hemmed in by the trail of stearic acid they had left behind in their travels and drew in their borders to produce hemispherical surfaces with a high contact angle. This same effect of not being able to wet self-deposited films accounts for the divergence of these contact angles from those observed for pure nitrobenzene on partially covered surfaces; it also accounts for the success of the retraction technique for producing adsorbed monolayers (3).

Limitations of the Method

It has been demonstrated in this and the previous study (1) that radioactive tracers are extremely valuable tools for the study of surface chemical phenomena. The availability of isotopically labeled compounds of high specific activity means that quantitative measurements of extremely small amounts of adsorbed material can be made by relatively simple procedures.

The technique is not limited by problems in radiochemical analysis or standardization but rather by difficulties inherent in the art of preparing, handling, and characterizing the surface under investigation. Extreme precautions are required to prevent adsorption of adventitious molecules on the cleaned, and perhaps activated, surfaces; competitive adsorption between weakly adsorbed organics and strongly adsorbed or chemically combined water is a particular problem at the glass/air interface.

*Approximately 62% meta and 38% para isomers.

Table 7
Comparison of Contact Angles of Stearic Acid Films on
Soft Glass Toward Various Test Liquids

Sample	Radioactivity (counts/min)	Surface Coverage* (%)	Measured Contact Angle θ in Degrees			
			Methylene Iodide	Isopropyl Biphenyl	Nitrobenzene	Nitrobenzene/ Stearic Acid†
I-30	1253	100.0	72,72,73	62,62,63	-	67,68,67
I-31	1268	100.0	72,73,72	63,63,63	-	67,68,68
I-32	1248	100.0	73,73,73	63,62,63	-	67,69,68
I-33	1251	100.0	72,73,72	62,62,62	-	68,68,67
I-82	1263	100.0	73,72,72	62,61,63	65,66,66	66,67,67
I-34	1188	94.7	70,70,71	60,60,60	-	64,65,64
I-50	1153	91.9	70,71,70	60,60,61	65,66,66	66,67,66
I-37	943	75.1	64,65,64	50,51,53	-	58,59,58
I-54	924	73.6	64,65,65	51,53,51	52,53,54	59,58,58
I-38	873	69.6	62,62,63	50,51,50	-	57,57,57
I-84	783	62.4	62,63,62	49,52,52	53,51,52	59,58,59
I-36	694	55.3	60,60,60	50,49,49	-	55,57,56
I-81	651	51.9	60,60,60	48,51,50	55,55,53	62,61,59
I-53	303	24.1	50,51,48	35,35,34	35,38,37	42,42,42
I-80	301	24.0	53,54,53	36,37,37	40,41,43	50,48,49‡
Blank §	0	0.0	22,23,22	6,6,7,6	5,4,6	65,64,65

* Methylene iodide contact angle of 72 to 73 degrees and radioactivity of 1255 counts/min were assumed to be representative of a highly compacted monolayer.

† Nitrobenzene containing 0.1 wt-% stearic acid.

‡ In 10-min this had increased to 52, 51, and 52, where it stabilized.

§ Freshly fire-polished soda-lime glass.

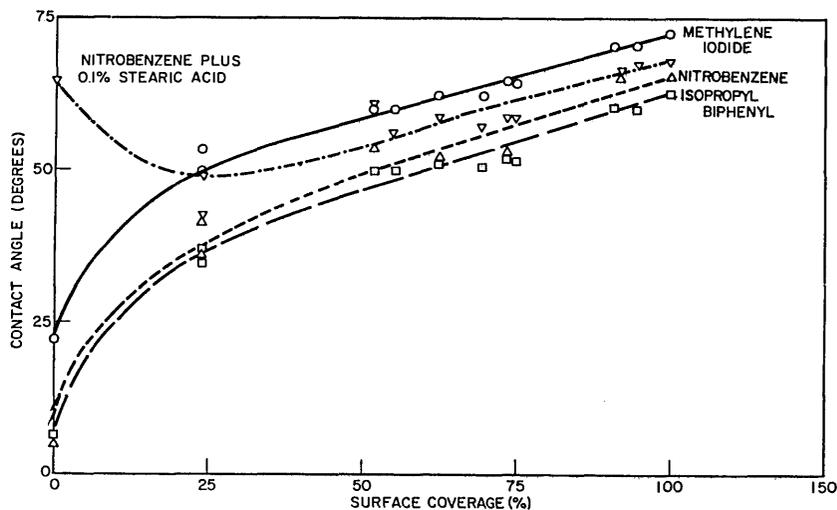


Fig. 5 - Contact angles of selected liquids toward retracted films of stearic acid on glass

The reason for the lack of reproducibility in studies of the rate of loss of radioactivity from identically made and processed monomolecular films of stearic acid-1-C¹⁴ on glass is not known. It must be due to real differences in the number and nature of active adsorption sites on the glass surface. While these differences may involve distinct changes in the composition of the surface layer of atoms, they are too subtle to be detected by other than surface chemical methods such as have been employed in this study. Further refinement of methods for preparing and handling glass surfaces is needed before the full potential of the radiochemical technique can be realized.

CONCLUSIONS

Procedures have been devised for producing highly compacted monomolecular layers of C¹⁴-tagged stearic acid on fire-polished soft (soda-lime) glass through retraction from a stearic acid-1-C¹⁴ solution in nitrobenzene. Solution concentrations in the range of 0.04 to 0.8 mg/ml have been successfully employed to produce condensed films of stearic acid with the time for monolayer formation being roughly inversely proportional to the concentration.

While thermal desorption studies of the radioactive stearic acid monolayers on glass suggest the presence of a weakly bonded component, the rate of loss of radioactivity through stepwise dissolution of the C¹⁴-tagged stearic acid in nitrobenzene or through its exchange with inactive stearic acid in nitrobenzene gives no indication of more than a single type of bonding. Studies of the loss of radioactivity on heating following depletion of the surface C¹⁴ content by exchange or dissolution were not sufficiently reproducible to shed any further light on this question. The rate of loss of stearic acid from the glass surface increased with increasing temperature, but the scatter in the data precluded the obtaining of meaningful information on the activation energy for desorption.

The roughly linear relationship between the surface coverage of glass by stearic acid and the methylene iodide contact angle has been found to hold for other test liquids also (nitrobenzene and isopropylbiphenyl); however, the use of contacting liquids containing surface active materials in solution can lead to anomalously high values, especially at low surface coverages.

Limitations in the application of radiotracer techniques to the study of surface phenomena are imposed by the present state of the art of surface chemistry and surface preparation rather than by the sensitivity or reproducibility of radiochemical procedures. It is recommended that the easily learned radiotracer technology be incorporated in the expanding array of diagnostic methods available to the trained surface chemist.

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13. ABSTRACT

Procedures have been devised for producing highly compacted monomolecular layers of carbon-14-tagged stearic acid on fire-polished soft (soda-lime) glass through retraction from a nitrobenzene solution. While thermal desorption studies indicated a small quantity of weakly bonded stearic acid on the surface, its rate of removal by other mechanisms (dissolution and isotopic exchange) suggests that only a single type of bonding exists. The rate of loss of stearic acid-1-C¹⁴ increased with increasing temperature, but the scatter in the data prevented the calculation of the activation energy for desorption.

Difficulties in defining the surfaces under investigation rather than weaknesses in the radiochemical technique are the major handicaps in applying radiotracers to the study of surface chemical phenomena.

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