

The Effect of Liquid Structure on Contact Angle Hysteresis

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September 29, 1966



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ABSTRACT

Contact angle hysteresis was measured for a variety of liquids on condensed monolayers of 17-(perfluoroheptyl)-heptadecanoic acid adsorbed on polished chromium. The hysteresis was shown to be simply related to the molecular volume of the liquid and to result from the penetration of liquid molecules into the porous monolayer. However, contact angle hysteresis was negligible when the average diameter of the liquid molecules was larger than the average cross-sectional diameter of the intermolecular pores. It is shown that it is possible to estimate intermolecular pore dimensions of such adsorbed monolayers by contact angle hysteresis measurements on a series of liquids having gradations in molecular volume. The results of this investigation reveal that liquid penetration, even into pores of molecular dimensions, is a cause of significant contact angle hysteresis, and it is also shown how liquids can be selected for contact angle investigations on organic solid surfaces so that there will be freedom from this source of hysteresis.

PROBLEM STATUS

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

AUTHORIZATION

NRL Problem C02-10
Project RR 001-01-43-4751

Manuscript submitted May 16, 1966.

THE EFFECT OF LIQUID STRUCTURE ON CONTACT ANGLE HYSTERESIS

INTRODUCTION

Difficulties in obtaining significant and reproducible contact angles have been reported by many investigators. Frequently, large differences have been observed between the contact angle θ_A obtained in slowly advancing the liquid boundary of a sessile drop over a dry surface and the angle θ_R observed in slowly receding the liquid boundary of that drop over the previously wetted surface. As a result, there has been much discussion about which contact angle is the more significant, and, if both are, what function of the two would be most useful. Early studies of Adam and Jessop (1) led them to suggest that the contact angle hysteresis ($\theta_A - \theta_R$) is caused by a frictional force acting along the surface which operates with equal intensity when both advancing and receding motions are just prevented. Adam (2) later stated that this treatment was "probably nothing but a formal description, however." Wenzel's pioneering investigation of the contact angle in relation to surface roughness (3) led many investigators to propose that surface roughness is the cause of contact angle hysteresis. Cassie (4) later extended Wenzel's treatment of rough surfaces to include heterogeneous surfaces. In a recent series of papers (5), Johnson and Dettre examined the effects of both surface roughness and heterogeneity in detail. They concluded that surface roughness has only a secondary effect on contact angle hysteresis and stated that hysteresis is caused primarily by surface areas "of different intrinsic wettability or surface energy."

Zisman and coworkers (6-8) showed many years ago that penetration by molecules from a water drop can cause appreciable hysteresis in the contact angle on a condensed monolayer of a long-chain fatty acid or amine adsorbed on a smooth solid surface. The explanation given was that whereas the advancing drop usually moved over a hydrophobic surface free of water, the receding drop moved over a composite hydrophobic-hydrophilic surface in which the intermolecular pores were saturated with water. Later, Levine and Zisman (9) pointed out that since n-alkane molecules could adsorb with fatty acid or with primary fatty amine molecules during monolayer preparation, there was the possibility of obtaining contact angle hysteresis with sessile drops of these alkane liquids. They recommended and demonstrated the usefulness of liquids, like methylene iodide, which are unable to penetrate and adsorb in such monolayers. A subsequent investigation by Bewig and Zisman (10) of the contact potentials of these adsorbed films fully confirmed the correctness of the preceding conclusions.

Because we believed that the shape and size of the molecules of any liquid sessile drop could contribute to contact angle hysteresis when they were such that they could penetrate the pores of an adsorbed condensed monolayer, we measured values of θ_A and θ_R for a number of pure liquids on a smooth polished chromium surface covered with an adsorbed monolayer of 17-(perfluoroheptyl)heptadecanoic acid. This monolayer was expected to be more closely packed than one containing branched-chain molecules, but not so closely packed as the normal aliphatic acids and primary amines. Because of its generally low solubility and weak acidity of the particular acid used, and because of its high adsorptivity on chromium surfaces, the selected system was considered ideal for the purpose of this investigation.

EXPERIMENTAL MATERIALS AND PROCEDURES

The 17-(perfluoroheptyl)heptadecanoic acid used in these experiments was prepared by Brace (11). It was a highly purified crystalline solid which melted between 91° and 92°C; as in another recent investigation (12), it was used in the "as-received" condition. The acid was adsorbed as a monolayer on a clean, polished, chromium substrate using the melt-retraction method (6,13) while maintaining the substrate a few degrees above the melting point of the acid. A 3/8-inch chromium disk, 1/16-inch thick, was used as the substrate; the chromium, which was produced by the "Iochrome" process (14), was of 99.9 percent purity or better. It was prepared by polishing the flat surface to a mirror finish on a polishing wheel covered with a Buehler "Selvyt" cloth using levigated alumina having an average particle size of 0.3 micron. The resulting polished surface was wiped on a clean "Selvyt" cloth under flowing distilled water to remove loosely held alumina particles and then was dried in air from which organic contamination had been removed.

Advancing and receding contact angles of the liquid sessile drop under study were measured at 23°C and 50-percent R.H. using a goniometer telescope with independently movable cross hairs. All contact angles reported here were obtained on sessile drops under conditions of thermal and mechanical equilibrium. Each advancing contact angle was obtained during a slow stepwise increase in the volume of the sessile drop arising from the addition of successive small increments of the liquid; results were always reproducible within $\pm 1^\circ$. The receding contact angle was obtained by two independent methods designed to show that the observed values were not a result of monolayer dissolution by the liquid drop. These two methods were: (a) decreasing the volume of the sessile drop through the stepwise removal of small increments of the liquid, and (b) first immersing the monolayer-coated substrate in the liquid in question for periods of between 5 seconds and 10 minutes, then removing this liquid, and finally measuring the contact angle of a new sessile drop of the same liquid on this pretreated surface. No differences in the contact angle were observed with varying immersion times within these limits, and no differences were observed between the two methods of measurement. Receding contact angles were reproducible within $\pm 2^\circ$. Each contact angle reported here represents the average of at least four independent measurements, each of which was performed on an independently adsorbed monolayer to guarantee reproducibility of the results reported and to eliminate the possibility of anomalous results caused by surface capillarity and diffusion.

Every liquid used for contact angle measurement was a high-purity preparation from the source indicated in the footnotes to Table 1. Each liquid was percolated through a long column of activated alumina and silica gel just before use in order to remove polar impurities and to minimize chemical deterioration or contamination during storage.

RESULTS

The results of our measurements of the advancing contact angle θ_A and receding contact angle θ_R for each of a variety of liquids on polished chromium coated with a retracted monolayer of 17-(perfluoroheptyl)heptadecanoic acid are given in Table 1. Good agreement was found between values of θ_A for the liquids investigated here and for those same liquids reported earlier by Shafrin and Zisman (12). As expected, there was a good rectilinear correlation between $\cos \theta_A$ and γ_{LV} , the liquid surface tension, and a much poorer correlation between $\cos \theta_R$ and γ_{LV} . No obvious relationship was found between the contact angle hysteresis ($\theta_A - \theta_R$) and γ_{LV} . Drops of hexadecane, dicyclohexyl, Aroclor 1242 (principally trichlorodiphenyl), sym-tetrabromoethane, and glycerol did not exhibit hysteresis. (We considered the contact angle hysteresis to be zero when $\theta_A - \theta_R$ was 2 degrees or less because of the precision of our measurements.) The other liquids investigated showed varying amounts of hysteresis even though their surface tensions also covered the surface tension range of 27.6 to 63.4 dynes/cm.

Table 1
Contact Angles of Various Liquids on Monolayers of
17-(Perfluoroheptyl)Heptadecanoic Acid Adsorbed on Chromium

Liquid	Liquid Surface Tension, γ_{LV} at 20°C (dynes/cm)	Advancing Contact Angle, θ_A (degrees)	Receding Contact Angle, θ_R (degrees)	Contact Angle Hysteresis, $\theta_A - \theta_R$ (degrees)	Calculated Molecular Volume at 20°C (cc/gram-mole)
n-Alkanes					
Hexadecane ^a	27.6	73	72	1	292.6
Tetradecane ^a	26.7	68	65	3	253.3
Decane ^a	23.9	61	57	4	194.8
Octane ^a	21.8	57	53	4	163.0
Miscellaneous					
Water	72.8	114	105	9	18.0
Glycerol ^b	63.4	110	109	1	73.0
Methylene iodide ^b	50.8	98	75	23	80.5
sym-Tetrabromoethane ^b	49.7	90	89	1	116.6
Ethylene glycol ^b	47.7	98	91	7	55.8
Aroclor 1242 (trichlorobiphenyl) ^c	45.3	88	86	2	186.5
Nitrobenzene ^b	43.9	80	74	6	102.3
Iodobenzene ^b	39.7	83	78	5	111.9
Bromobenzene ^b	36.5	76	70	6	105.0
Chlorobenzene ^b	33.2	71	61	10	101.8
Dicyclohexyl ^c	32.8	76	75	1	187.5
Benzene ^d	29.0	66	54	12	88.8
m-Xylene ^b	28.9	66	58	8	122.9
Mesitylene ^b	28.5	66	62	4	139.0

Liquid source:

a. Lachat Chemicals Co., Inc.

c. Monsanto Chemical Co.

b. Eastman Organic Chemicals (White label grade).

d. Phillips Petroleum Co. (Research grade).

Table 1 shows that the liquids whose contact angle hysteresis was small were composed of larger molecules than those whose hysteresis was large. If the observed contact angle hysteresis was caused by liquid penetration of the monolayer coating the solid surface, as hypothesized, the cross-sectional dimensions of pores in the monolayer should be as large or larger than the cross-sectional dimensions of the molecules in the liquid sessile drop. We do not know precisely the molecular arrangement of the molecules in this retracted monolayer on chromium. However, we can estimate the molecular dimensions of each liquid from its molecular volume. Therefore, $\theta_A - \theta_R$ is plotted in Fig. 1 for each liquid as a function of the gram-molecular volume at 20°C (the quotient obtained by dividing the gram-molecular weight of the liquid by its density in grams per cubic centimeter at 20°C). All of the data points, with the exception of those for water, ethylene glycol, and glycerol, fit within a zone or band which extends to a minimum value, as molecular volume increases, at about 125 cc/gram-mole. The points for the associated liquids, water, ethylene glycol, and glycerol, form a separate but well-defined band which is displaced toward much smaller molecular volumes.

Members of three homologous series of liquids are included in Fig. 1: the methyl-substituted benzenes, the monohalogenated benzenes, and the n-alkanes. Among the methyl-substituted benzenes, contact angle hysteresis progressively decreases in the order benzene > m-xylene > mesitylene as the number of methyl groups per molecule and the molecular volume increase. Similarly, the contact angle hysteresis for the halogenated benzenes decreases in the order chlorobenzene > bromobenzene > iodobenzene. The n-alkanes exhibited hysteresis which also decreased with increasing molecular volume (except that $\theta_A - \theta_R$ for octane was equal to that for decane). None of the alkane liquids exhibited the large hysteresis effect one would expect to result from contact by molecules able to assume a rod-like shape. Although molecules of these liquids readily adsorb in a monolayer of a fatty acid or amine during its formation by adsorption from a dilute solution (10), they do not readily penetrate into a previously formed condensed monolayer. We can understand this in terms of the low probability of the alkane assuming the rod-like configuration and the orientation necessary for diffusion into the pores of an oriented monolayer of rod-like acid molecules.

In order to confirm our conclusion that the adsorbed 17-(perfluoroheptyl)heptadecanoic acid monolayer could be penetrated by the molecules of a given liquid, the advancing contact angle of methylene iodide was measured on the monolayer before and after prewetting it with the liquid in question. A freshly prepared metal disk coated with an acid monolayer was immersed in each of the liquids studied for 10 minutes and then removed slowly with the plane of the disk vertical. Because of the large receding contact angle observed with these films, the disk emerged free from adhering drops of liquid. The immersion time used was long enough to allow any monolayer penetration to occur, but not so long, as indicated by the equality of the two methods of measuring θ_R (see section on experimental procedure), as to allow appreciable monolayer dissolution. The advancing methylene iodide contact angle observed on the resulting prewetted surface is given in Table 2 for each liquid studied. At the bottom of Table 2 is given for comparison the value of the advancing contact angle of methylene iodide obtained on the monolayer before prewetting. One would expect liquids having larger molecules to be less able to penetrate and remain in the monolayer than those having smaller molecules; hence preimmersion in the former should cause a smaller change in the methylene iodide contact angle than in the latter. The data in Table 2 indicate that this, in fact, does occur; those liquids causing the smallest change in methylene iodide contact angles were also those exhibiting little or no contact angle hysteresis in Table 1.

DISCUSSION

Considering the series of liquids used here, and the fact that the occurrence of hysteresis on this monolayer coating was virtually eliminated when the molecular volume of

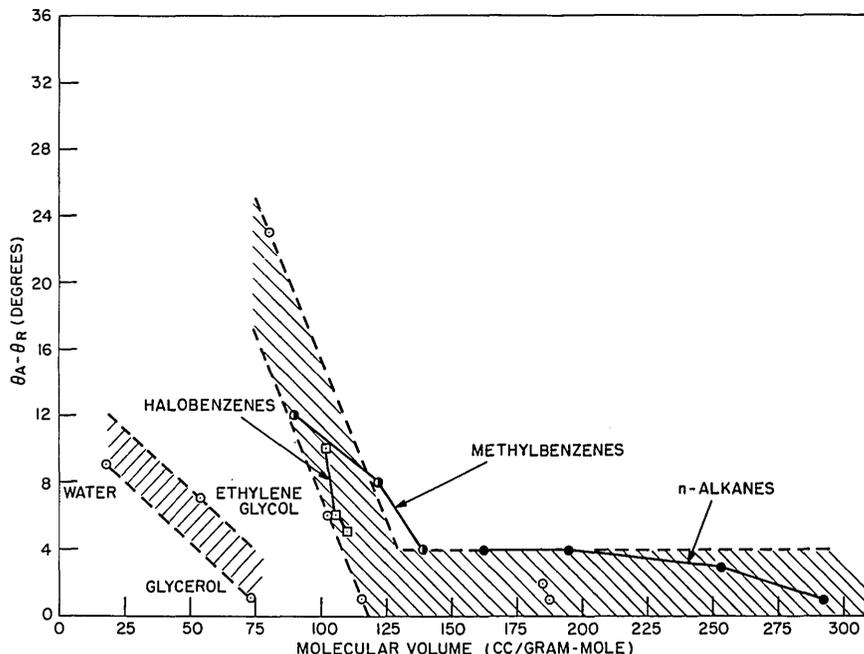


Fig. 1 - Contact angle hysteresis ($\theta_A - \theta_R$) vs molecular volume for various liquids on adsorbed 17-(perfluoroheptyl)heptadecanoic acid monolayers

the liquid exceeded about 125 cc/gram-mole, one can estimate that the average cross-sectional area of the intermolecular pores in the adsorbed monolayer is approximately 40\AA^2 . (This calculation is based on the assumption that the molecules of a liquid having a molecular volume of 125 cc/gram-mole would just penetrate the monolayer, and that they are of spherical shape.)

Measurements on a Stuart-Briegleb molecular model of 17-(perfluoroheptyl)heptadecanoic acid indicate that the maximum cross-sectional area occupied by this molecule in its fully extended configuration is 29\AA^2 . This area requirement arises entirely from the cross-sectional area of the perfluorinated chain. It is not difficult to visualize a monolayer composed of molecules of these dimensions having intermolecular pore areas averaging 40\AA^2 , if one considers that the perfluorinated chain segment of the molecule is sterically hindered from free rotation about the C-C bonds. Rotation of the fluorocarbon chain around a C-C bond from 0 to 180 degrees changes the angle between the adjacent linear segments of the molecule about that bond from 0 degree continuously to 42 degrees, respectively. It is thus possible for such molecules to depart radically from a linear configuration. It would be impossible for molecules of a random, nonlinear configuration to orient in a close-packed, well-ordered manner. This model of molecular packing does not agree with any of the three suggested earlier (12) in which the perfluoro groups were considered to be close packed. However, there is some recent evidence which indicates that the perfluoro groups may not adlineate well: the difficulty in obtaining electron diffraction patterns of this monolayer suggests that there is a lack of repetitive organization in the monolayer (15), and the relatively large area per molecule (about 37\AA^2) obtained for this acid when adsorbed as a monolayer on water (16) indicates that the molecules do not close pack readily even under an externally applied film compression.

An observation should be made at this point concerning the associated liquids, water, ethylene glycol, and glycerol. The contact angle hysteresis for each of these liquids has been plotted in Fig. 1 as if each existed in an unassociated state. However, the associated

Table 2
 Advancing Contact Angles of Methylene Iodide on
 17-(Perfluoroheptyl)Heptadecanoic Acid Monolayers
 Pre-Treated with Various Liquids

(23°C; 50% R.H.)

Pre-treatment Liquid	Advancing CH ₂ I ₂ Contact Angle (degrees)
sym-Tetrabromoethane	97
Glycerol	97
Aroclor 1242	96
Dicyclohexyl	95
Hexadecane	95
Tetradecane	95
Mesitylene	95
m-Xylene	93
Glycol	93
Iodobenzene	93
Nitrobenzene	92
Chlorobenzene	92
Bromobenzene	91
Octane	91
Decane	91
Water	91
Benzene	90
Monolayer before pre-treatment	98

nature of these liquids is well known. Stevenson (17) has recently concluded from infrared absorption data that fewer than 1 percent of the molecules in liquid water at ordinary temperatures exist in a nonhydrogen-bonded state. If water were an unassociated liquid, the observed contact angle hysteresis of 9 degrees would correspond to a molecular volume of between 95 cc/gram-mole and 115 cc/gram-mole instead of the calculated 18 cc/gram-mole (see Fig. 1). This suggests that under these experimental conditions, liquid water, on the average, behaves as if it were associated in clusters of about six water molecules. Similar reasoning suggests that both ethylene glycol and glycerol behave as associated clusters of about two molecules.

In the earlier work of Baker, Shafrin, and Zisman (6) on the hydrophobic properties of condensed retracted monolayers of n-octadecyl amine adsorbed on platinum foil, it was reported that water exhibited a reproducible contact angle hysteresis of 12 degrees. Although monolayers of n-octadecylamine are more closely packed than those of the segmentally fluorinated acid studied here, when adsorbed on the same metal, Timmons and Zisman (18) have shown that monolayers of stearic acid are more widely spaced when adsorbed on platinum than when adsorbed on chromium. The contact angle hysteresis of 9 degrees for water, reported here on monolayers of the segmentally fluorinated acid adsorbed on chromium, and the 12-degree water hysteresis reported earlier on monolayers of n-octadecylamine adsorbed on platinum suggest that the intermolecular pore dimensions are comparable in each of these systems.

The data presented here are not intended to suggest that liquid penetration of a monolayer is the sole cause of contact angle hysteresis. However, we have demonstrated that considerable hysteresis on monolayer-coated surfaces does result from such penetration. It has also been shown that such hysteresis is virtually eliminated when the molecules of the liquid are large compared to the intermolecular pores of the solid surface. We also have found that observations of the contact angle hysteresis with a suitable series of liquids in contact with the given solid will yield a smaller molecular volume at which $\theta_A = \theta_R$ and so will yield information on the average cross-sectional dimensions of intermolecular pores. Similar experiments are needed on solids coated with other types of adsorbed monolayers so chosen as to have widely differing packing densities and pore dimensions; such contact angle measurements could be augmented by radiotracer techniques using C-14 labeled liquids.

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1. ORIGINATING ACTIVITY <i>(Corporate author)</i> Naval Research Laboratory Washington, D. C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE THE EFFECT OF LIQUID STRUCTURE ON CONTACT ANGLE HYSTERESIS			
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> An interim report on one phase of the problem.			
5. AUTHOR(S) <i>(Last name, first name, initial)</i> Timmons, C. O., and Zisman, W. A.			
6. REPORT DATE September 29, 1966		7a. TOTAL NO. OF PAGES 11	7b. NO. OF REFS 18
8a. CONTRACT OR GRANT NO. NRL Problem C02-10		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6436	
b. PROJECT NO. RR 001-01-43-4751		9b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i> None	
c.			
d.			
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11. SUPPLEMENTARY NOTES None		12. SPONSORING MILITARY ACTIVITY Dept. of the Navy (Office of Naval Research)	
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Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
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