NRL Report 6511

Surface Properties of Perfluoroacids as Affected by Terminal Branching and Chlorine Substitution

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February 24, 1967

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ABSTRACT

When an otherwise fully fluorinated carboxylic acid molecule was altered by terminal branching and terminal chlorine atom substitution, significant increases resulted in the wettability of its adsorbed monolayer. Two new homologous series of acids $(CF_3)_2CF(CF_2)_nCOOH$ and $CF_2Cl(CF_3)CF(CF_2)_nCOOH$, where n ranged from 11 to 1 and 9 to 1, respectively, were adsorbed as condensed monolayers on highly polished clean disks of chromium and platinum. The critical surface tension of wetting (γ_c) of each resulting surface was determined by contact angle measurements on homologous series of n-alkanes, open-chain polydimethylsiloxanes, and miscellaneous other liquids. In every case the wettability, expressed as γ_c, was increased by branching or by terminal chlorine substitution. Thus, in the series $(CF_3)_2CF(CF_2)_n$ COOH, γ_c on chromium ranged from 13.3 dynes/cm (when n = 11) to a maximum of 15.2 (when n = 1), whereas in the series CF_2Cl $(CF_3)CF(CF_2)_nCOOH$, γ_c ranged from 17.2 (when n = 9) to around 20 (when n = 1). These results are excellent examples of the effect on γ_c on substituting one terminal chlorine atom in the surface for a fluorine atom. For a given acid monolayer, almost the same γ_c values were obtained on each of the two metals except that γ_c became larger on platinum than on chromium when the acid was a lower homolog in each series. The causes of this divergence relate to a smaller adsorption site spacing and the consequent tighter molecular packing and better chain adlineation of the adsorbed compound on chromium.

PROBLEM STATUS

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

AUTHORIZATION

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

Manuscript submitted November 9, 1966.

SURFACE PROPERTIES OF PERFLUOROACIDS AS AFFECTED BY TERMINAL BRANCHING AND CHLORINE SUBSTITUTION

INTRODUCTION

The influence of chemical constitution on the wetting properties of solid surfaces has been investigated extensively by our Laboratory (1). A surface rich in covalent fluorine atoms had a critical surface tension of wetting (γ_c) which was lower than that of a surface containing any other chemical substituent. The lowest critical surface tensions ever reported were smooth solid surfaces coated with a condensed monolayer of fully fluorinated fatty acids (or derivatives), oriented so as to present an outermost array of close-packed trifluoromethyl groups. As the molecular weight of the adsorbed compound increased, closer packing resulted through increased lateral cohesion and adlineation between neighboring fluorocarbon chains. The high members of the family of fully fluorinated n-alkanoic acids (2) were the compounds best fulfilling the requirements for vertical orientation, close packing, and molecular adlineation; the lowest value of γ_c yet reported (6 dynes/cm at 20°C) was obtained with a condensed monolayer of perfluorododecanoic acid. Partially fluorinated long-chain fatty acids, where the completely fluorinated portion is attached to an unfluorinated alkyl chain terminated by the carboxylic acid group (3), adsorbed as monolayers whose values of γ_c were slightly higher (4). Complete adlineation of adjacent adsorbed molecules of these partially fluorinated acids was not possible because of the smaller cross-sectional diameter of the hydrocarbon segment compared to the fluorocarbon segment.

Since such small departures from complete adlineation of the adsorbed aliphatic molecules caused observable changes in the critical surface tension of the coated solid, any other change in molecular structure affecting molecular packing in the monolayer would also be expected to measurably alter γ_c. This report is concerned with the effect on γ_c of: (a) introducing terminal branching in the fully fluorinated acid molecule and (b) replacing with chlorine a fluorine atom attached to the omega (or terminal) carbon atom. The influence of the metal substrate on the packing density and consequently on the value of γ_c as a measure of the wettability of the adsorbed monolayer was also investigated.

EXPERIMENTAL MATERIALS AND METHODS USED

Compounds investigated were members of two new homologous series of acids with the general formulas $(CF_3)_2CF(CF_2)_nCOOH$ and $CF_2Cl(CF_3)CF(CF_2)_nCOOH$, where n ranged from 1 to 11 and 1 to 9, respectively. Table 1 gives the boiling points and melting points of these compounds as prepared by Hauptschein and coworkers (5). These carefully distilled compounds were used without further purification.

Each compound was adsorbed on plane polished disks of chromium and platinum whose purity was reported as 99.99 wt-% or better for each specimen. A mirror finish was imparted to each metal by standard metallographic procedures which included rubbing on 3M 600-grit silicon carbide paper under water, followed by 4/0 emery paper and then polishing on a metallographic cloth impregnated with an aqueous dispersion of 0.3-micron Al_2O_3 (Linde "Fine Abrasive" A-5175). The last step consisted of gentle rubbing on a grease-free wet cloth followed by copious rinsing with freshly distilled grease-free water to remove any adhering abrasive. The completely water-wetted metal specimen was dried

Table 1
Melting Points and Boiling Points of Branched Fluorinated Acids
$CF_2X(CF_3)CF(CF_2)_nCOOH$*

n	X = F		X = Cl	
	MP (°C)	BP (°C/mm Hg)	MP (°C)	BP (°C/mm Hg)
1	—	141/760	—	100/50
3	—	130/150	—	115/28
5	33-36	115/20	—	134/24
7	61-64	125/10	44-50	141/8
9	88-89	117/0.5	71-74.5	117/0.3
11	100-107	—		

*Reference 5.

in a clean, grease-free oven for 10 minutes at 120°C, cooled in an acid-cleaned covered glass container, and used as soon as possible in the adsorption experiments.

A condensed monolayer of each acid was adsorbed on the clean, dry metal specimen by the melt retraction method (6), which depends on the autophobic property of the molten acid. (When a nonspreading drop of pure acid is rolled over the solid surface, it leaves an adsorbed monolayer behind.) If the acid was solid at room temperature, the metal specimen was first heated to a few degrees above the melting point of the compound. After a 10-minute contact of liquid acid and metal surface, the residual sessile drop of surplus liquid was carefully rolled off and removed with the help of a loop of clean platinum wire. The monolayer-coated specimen was stored briefly at 25°C in a clean covered container until used for the measurements of contact angles.

After each set of measurements, the adsorbed acid monolayer was completely removed from the metal surface to allow adsorption of another acid. A platinum disk could be readily freed of the adsorbed monolayer by brief flaming to a dull red heat; hence the polishing procedure had to be repeated only for the last few steps. A chromium disk, however, held the monolayers of the adsorbed carboxylic acids so tenaciously that even immersion in a 50/50 hot nitric acid-sulfuric acid bath for 3 hours, or ultrasonic agitation in Freon 113 solvent for 15 minutes, could not remove them. Therefore, prior to each adsorption experiment on chromium, the complete procedure, starting with the polishing on 3M 600-grit silicon carbide paper, had to be repeated.

The wettability of each adsorbed monolayer was determined by measuring, with a previously described goniometer telescope (7), the slowly advancing contact angle of each of the various pure liquids listed in Tables 2 and 3. Any traces of polar impurities in each liquid were removed just prior to use by slowly percolating the liquid through an adsorbent column packed with Florisil and activated alumina. Each contact angle reported in Tables 2 and 3 was the average of at least three measurements on different sessile drops using several independently prepared surfaces. Unless stated otherwise, all observations reported were made in room air at 25°C and 50% R.H.

WETTABILITY OF $(CF_3)_2CF(CF_2)_nCOOH$ MONOLAYERS

Table 2 lists the contact angle θ and surface tension γ_{LV} of most of the liquids used for wettability measurements on monolayers of any one of the series of $(CF_3)_2CF(CF_2)_nCOOH$ acids adsorbed on chromium and platinum. In Fig. 1 are plots of $\cos\theta$ vs γ_{LV} for the n-alkane liquids and dimethylsiloxanes on chromium. For the

Table 2
Contact Angles of Liquids on Monolayers of $(CF_3)_2CF(CF_2)_nCOOH$ Series
Adsorbed on Chromium and Platinum (25°C)

Liquids	γ_{LV} (dynes/cm)	Contact Angle θ (degrees)											
		n = 11		n = 9		n = 7		n = 5		n = 3		n = 1	
		Cr	Pt	Cr	Pt	Cr	Pt	Cr	Pt	Cr	Pt	Cr	Pt
n-Alkanes													
Hexadecane	27.6	73	72	72	71	70	69	69	69	68	68	65	57
Tetradecane	26.7	69	69	68	69	66	66	65	65	65	65	63	52
Tridecane	25.9	68	65	66	66	64	65	63	63	62	63	61	49
Dodecane	25.4	66	64	65	65	63	62	60	61	60	59	59	47
Undecane	24.7	64	60	62	63	60	60	59	59	58	52	55	41
Decane	23.9	62	58	60	60	57	58	58	55	56	50	54	40
Octane	21.8	53	52	51	52	49	49	51	52	48	44	47	30
Heptane	20.3	49	48	48	44	42	44	46	45	42	35	41	22
	—	13.3*	13.3*	14.0*	13.9*	14.5*	14.5*	14.8*	14.8*	15.0*	17.2*	15.2*	19.0*
Miscellaneous Liquids													
Water	72.8	116	111	116	106	110	90	110	90	103	70	103	85
Formamide	58.2	104	—	104	—	—	—	—	—	80	—	—	—
Methylene iodide	50.8	98	98	98	97	97	98	97	98	96	95	94	85
Ethylene glycol	47.7	97	unstable	92	unstable	—	—	—	—	75	unstable	—	—
Trichlorobiphenyl	45.3	94	91	—	—	—	—	—	—	—	—	—	—
α-Bromonaphthalene	44.6	87	84	85	84	—	—	—	—	82	55	—	—
Tricresyl phosphate	40.9	84	81	—	81	—	—	—	—	—	—	—	—
α-Methylnaphthalene	38.7	83	80	—	—	—	—	—	—	—	—	—	—
Hexachloropropylene	38.1	79	79	—	—	—	—	—	—	—	—	—	—
Dicyclohexyl	33.0	78	74	—	73	—	—	—	—	—	—	—	—

*Critical surface tension (dynes/cm) of the adsorbed monolayer obtained by extrapolation to cos θ = 1 of the data points for the n-alkanes.

Table 3
Contact Angles of Liquids on Monolayers of $CF_2Cl(CF_3)CF(CF_2)_nCOOH$ Series
Adsorbed on Chromium and Platinum (25 °C)

Liquids	γ_{LV} (dynes/cm)	Contact Angle θ (degrees)									
		n = 9		n = 7		n = 5		n = 3		n = 1	
		Cr	Pt	Cr	Pt	Cr	Pt	Cr	Pt	Cr	Pt
n-Alkanes											
Hexadecane	27.6	56	54	56	55	54	51	52	48	50	26
Tetradecane	26.7	53	51	54	51	52	48	51	46	48	15
Tridecane	25.9	51	49	52	49	48	46	49	43	45	<10
Dodecane	25.4	49	47	50	48	47	43	47	38	40	†
Decane	23.9	43	40	43	41	42	39	42	34	36	†
Octane	21.8	35	31	35	32	36	29	34	22	≈20	†
Heptane	20.3	29	27	29	24	30	22	27	†	†	—
		17.2*	17.8*	17.5*	18.3*	18.0*	18.7*	18.4*	20.2*	19.6*	26.6*
Miscellaneous Liquids											
Water	72.8	108	96	110	84	103	74	94	75	93	58
Formamide	58.2	102	unstable	91	—	—	spread	75	—	—	—
Methylene iodide	50.8	91	92	92	87	90	87	91	unstable	84	74
Ethylene glycol	47.7	95	unstable					65			
Trichlorobiphenyl	45.3	—	—	79	—	—	72	—	—	—	—
α-Bromonaphthalene	44.6	75	68	75	—	—	64	72	—	—	—
Tricresyl phosphate	40.9	—	—	73	—	—	72	—	—	—	—
α-Methylnaphthalene	38.7	—	—	72	—	—	69	—	—	—	—
Hexachloropropylene	38.1	—	—	61	—	—	≈48	—	—	—	—
Dicyclohexyl	33.0	—	—	63	—	—	60	—	56	—	—

*Critical surface tension (dynes/cm) of the adsorbed monolayer obtained by extrapolation to cos θ = 1 of the data points for the n-alkalines.
†Not reproducible.

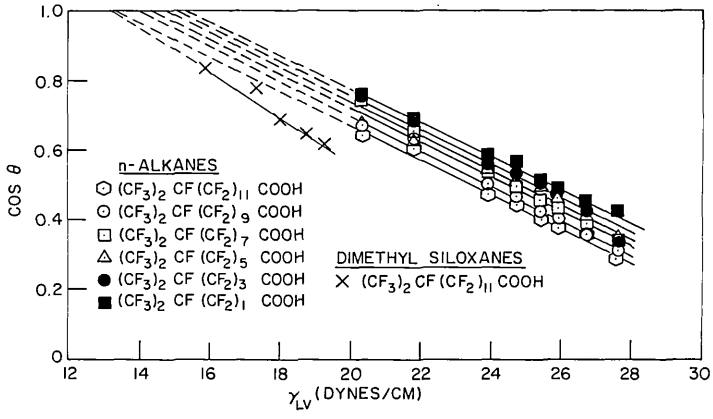

Fig. 1 - Wettability of $(CF_3)_2CF(CF_2)_nCOOH$ monolayers adsorbed on chromium (25°C)

n-alkanes a family of parallel straight lines resulted having a negative slope of 0.050 and intercepts with the line cos θ = 1 ranging from 13.3 dynes/cm for the adsorbed monolayer of the highest homolog, $(CF_3)_2CF(CF_2)_{11}COOH$, to 15.2 dynes/cm for that of the lowest homolog, $(CF_3)_2CF(CF_2)_1COOH$ (Table 2). Similarly, a series of parallel lines with a negative slope of 0.047 resulted when the same fluorinated acids were adsorbed on platinum. Here γ_c varied from 13.3 dynes/cm for $(CF_3)_2CF(CF_2)_{11}COOH$ to 19.0 dynes/cm for the lowest homolog (Table 2). Although γ_c for the monolayer having n = 1 or n = 3 was larger for platinum than for chromium, values for n > 3 were nearly equal for the two metals.

A comparison of the contact angles of various liquids on the $(CF_3)_2CF(CF_2)_{11}COOH$ monolayer adsorbed on chromium with those on platinum reveals that they were nearly the same when the liquids were the n-alkanes (Table 2) or polydimethylsiloxanes (not shown); however, other hydrocarbons or halogen-containing liquids generally exhibited somewhat higher contact angles on the chromium substrate. The possibility that solvent action of the liquid drop had removed the monolayer resting beneath was eliminated when saturation of any of these liquids, such as ethylene glycol, with $(CF_3)_2CF(CF_2)_{11}COOH$ resulted in sessile drops with unaltered contact angles. Apparently the packing of the adsorbed acid molecules was not the same on each metal, and an appreciable difference in the penetration of such small molecules as water, ethylene glycol, and formamide resulted. This difference in packing was even more clearly demonstrated by the considerable difference in the advancing and receding contact angles of the latter group of liquids quite like the results of Timmons and Zisman (8), whereas no such hysteresis was observed with the n-alkanes or other liquids having larger molecular volumes.

EFFECT ON γ_c OF REPLACING A TERMINAL FLUORINE ATOM BY CHLORINE

The critical surface tension of each adsorbed monolayer on chromium and platinum of the $CF_2Cl(CF_3)CF(CF_2)_nCOOH$ series of acids was measured as before using the homologous series of n-alkane liquids; the resulting contact angles and critical surface tension values are given in Table 3. The wetting curves of the alkanes on monolayers of this chlorine-containing group of acids, just as those on the fully fluorinated acids, were rectilinear cos θ vs γ_{LV} plots (negative slope of 0.043); they were nearly the same on each metal substrate for the high homologs, but became noticeably different for those acids having n < 3. When n = 9, γ_c was 17.2 dynes/cm on the chromium substrate and

17.8 dynes/cm on the platinum substrate; however, γ_c changed from 18.4 dynes/cm on chromium to 20.2 dynes/cm on platinum when n = 3 and from 19.6 to 26.6 dynes/cm when n = 1. Only when n = 1 was there poor reproducibility of the n-alkane contact angles.

Previous investigations (7,9-11) had demonstrated that γ_c was lowered when a hydrogen atom in the surface of a solid was replaced with a fluorine atom, whereas γ_c was raised on replacing the hydrogen atom with a chlorine atom. Present data here confirm this conclusion. For example, γ_c of an adsorbed $(CF_3)_2CF(CF_2)_9COOH$ monolayer on chromium was 14.0 dynes/cm (Table 2); the substitution of one chlorine atom on the terminal carbon to form $CF_2Cl(CF_3)CF(CF_2)_9COOH$ raised γ_c of this monolayer to 17.2 dynes/cm (Table 3). The same difference in γ_c of 3.2 ± 0.2 dynes/cm was obtained for all other comparable pairs of adsorbed monolayers investigated as n varied from 9 to 3. With platinum as the substrate, the difference in γ_c was 3.9 ± 0.1 dynes/cm for all values of n from 9 to 5, but increased when n was lower. The rise in γ_c by 3.2 and 3.9 dynes/cm, depending on the metal substrate, is comparable to the reported rise in γ_c of from 2.5 to 4 dynes/cm when the fluorine atoms were replaced progressively by chlorine atoms in the series of halogenated polyethylene surfaces (11). The rise in γ_c following substitution of a chlorine for a fluorine atom was thus of the same magnitude, whether the surface was a closely packed adsorbed monolayer of carboxylic acid or was a polymer whose covalent chlorine and fluorine atoms are distributed statistically in the surface.

Figure 2 compares γ_c for adsorbed condensed monolayers of the two series of terminally branched fluorinated acids on the two metal substrates with that of the straight-chain fluorinated acid series $F(CF_2)_NCOOH$ on the basis of equal values of N, where N is the number of fluorinated carbon atoms in the principal n-alkyl chain. Nearly parallel graphs were obtained for the two branched acid series adsorbed on chromium from the melt (curves B and D) and the straight-chain acid series adsorbed on platinum from solution (curve A). Comparison of curves A and C shows the displacement toward higher values of γ_c as the molecular structure changed from the straight-chain to the terminally branched acid, and comparison of curves C with E (or curves B with D) shows an increase in γ_c on replacing a terminal fluorine by a chlorine atom. The curves C and E for the branched acids adsorbed from the melt on platinum turned upward when N < 7, whereas

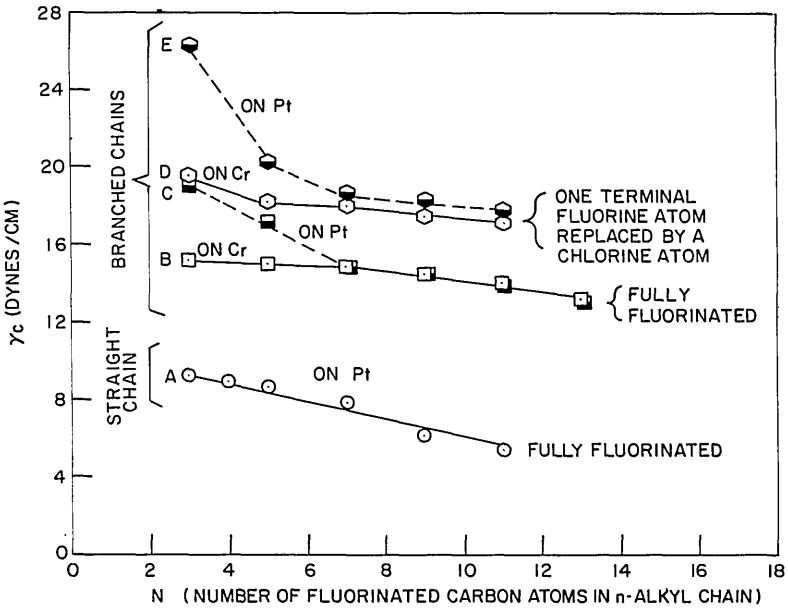

Fig. 2 - Effect of molecular structure on γ_c

curves B and D for these acids adsorbed on chromium remained rectilinear (except for N = 3 in curve D).

INFLUENCE OF METAL SUBSTRATE ON PACKING OF ADSORBED MOLECULES

The difference in γ_c between monolayers of the same low homolog adsorbed on chromium and platinum reveals a difference in the surface density of adsorption sites on these metals. In a recent investigation of stearic acid monolayers adsorbed on various metals Timmons and Zisman (12) observed similar variations in γ_c and explained them in terms of the differences in metal lattice parameters and atomic radii. The carboxylic acids, because of their large cross-sectional areas, could not adsorb over each adsorption site when the cross-sectional radius of the acid was less than twice the atomic radius of the substrate metal. This misfit in packing was shown to become more pronounced as the acids decreased in chain length, because the decreased lateral attraction between the principal chains of the adsorbed molecules promoted looser molecular packing and also increased tilting and vibration away from the vertical. Similar conclusions resulted from the present study of the fully fluorinated branched acids. When cos θ of each n-alkane liquid was plotted against N (the number of fluorinated carbon atoms in the principal n-alkyl chain of the adsorbed fluorinated acid), values of cos θ for chromium (Fig. 3a) and platinum (Fig. 3b) were nearly identical when N ranged from 13 to 7. However, when N = 5, cos θ values for the platinum substrate increased somewhat over those for chromium (i.e., θ became smaller); when N = 3 this difference became markedly larger.

Analogous behavior was observed with films of the terminally monochloro-substituted acids adsorbed on these two metals. When N ranged from 11 to 7, the contact angles of a given n-alkane on the monolayers adsorbed on chromium (Fig. 4a) were nearly the same as on those adsorbed on platinum (Fig. 4b). When N < 7, the contact angles varied widely between metal substrates; for instance, when N = 3 sessile drops of alkanes lower than tetradecane had very small and irreproducible contact angles on the coated platinum, whereas they were larger and reproducible on coated chromium. The comparative behavior of these coated metals followed the same pattern as those coated with the fully fluorinated acids except that detectable variations began with higher members of acids and became even more noticeable with lower ones. In fact, when N of the adsorbed monolayer was 3, no stable contact angles could be obtained on platinum substrate with n-alkanes of lower molecular weight than tetradecane.

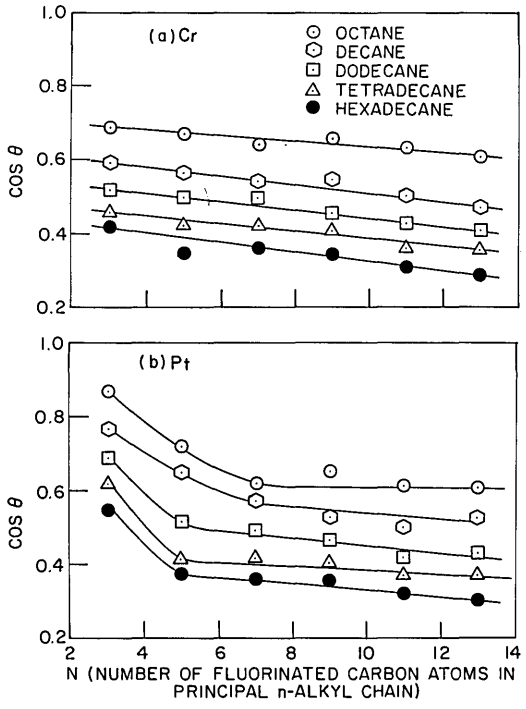

Fig. 3 - Influence of the metal substrate on the packing of adsorbed monolayers of $(CF_3)_2CF(CF_2)_{N-2}COOH$ determined by n-alkanes on (a) chromium and (b) platinum

The smaller contact angles exhibited by the lower n-alkanes might be attributed to the ability of a drop of such a liquid to dissolve the adsorbed monolayer beneath. However, drops of each n-alkane saturated with the appropriate fluorinated acid exhibited

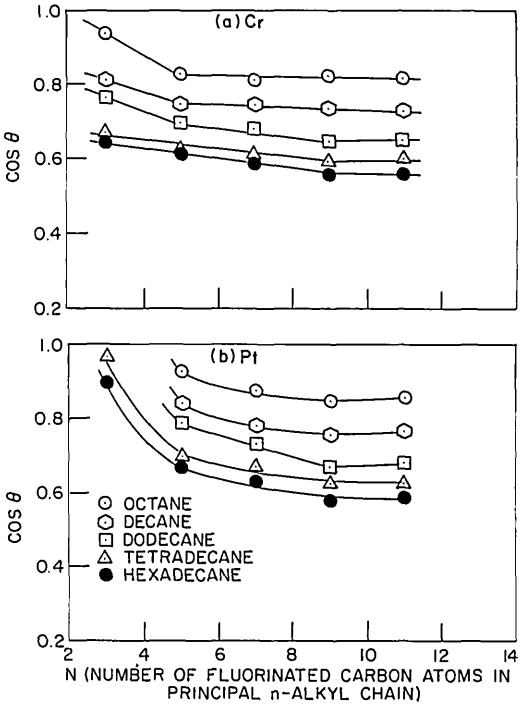

Fig. 4 - Influence of the metal substrate on the packing of adsorbed monolayers of $CF_2Cl(CF_3)CF(CF_2)_{N-2}COOH$ determined by n-alkanes on (a) chromium and (b) platinum

the same contact angles as those observed with the pure n-alkane. The possibility of such solvent action was also investigated in another way by allowing a large drop of the n-alkane liquid to remain on the adsorbed acid monolayer for increasingly longer times. The drop was then removed with a filter paper and a fresh drop of the n-alkane placed on the identical spot. Since in each case the contact angle values were the same, no significant fraction of the adsorbed monolayer could have been removed by the solvent action of the n-alkane. The sharp decrease in contact angles exhibited on monolayer coatings of the short-chain acids (N = 3 and 5) could have resulted from evaporation of the adsorbed monolayers. Therefore, contact angles of freshly deposited drops of an alkane were measured immediately after coating the metal with the monolayer and again 20 hours later to detect any decrease with time. As no difference was observed in the contact angles, the possibility of monolayer evaporation was ruled out.

Since smaller contact angles exhibited by the lower n-alkanes were not artifacts produced by either solution or evaporation of the adsorbed acid monolayer, the cause must lie in a difference in packing of the adsorbed film of the lower acids. The high-molecular homologs of each series pack in a manner which results in the same value of γ_c regardless of the difference in the lattice parameters of the two metals. This does not appear possible unless there is a difference in axial tilting of the molecules adsorbed on these metals. Curves B and C in Fig. 2 show clearly that γ_c is the same when N = 7. Decreased intermolecular cohesion between the adsorbed molecules when $N < 7$ results in increased axial vibration and tilting. This would explain the smaller contact angles and the divergence in curves B and C (and D and E) from that point on. Possibly, if curves D and E were extrapolated to high values of N, they also might eventually merge to indicate again that with adequate molecular chain length the intermolecular attraction becomes sufficient to make the nature of the substrate surface inconsequential.

The cross-sectional radius of the normal (or stretched-out) configuration of a $(CF_3)_2CF(CF_2)_nCOOH$ molecule is 3.9 Å (as measured by Stuart-Briegleb molecular models) which corresponds to a cross-sectional area of 48.2 $Å^2$. This large area was obtained when each branched perfluoroisopropyl group $(CF_3)_2CF-$ located at the terminal of the acid molecule was oriented identically, as shown in Fig. 5a. When alternate adsorbed molecules in each horizontal row were given a 90° rotation around the principal axis, and those in the next row were shifted by one molecule, the resulting planar arrangement, shown in Fig. 5b, was more closely packed. The resulting average area per molecule of this arrangement was only 28.1 $Å^2$ and the corresponding cross-sectional radius was 2.9 Å. Assuming that the acid molecules will adsorb directly over one of the metal atoms which are arranged in a hexagonal close-packed array, they will be able to pack closer on substrates of smaller radius. The atomic radius of chromium atoms in the surface of the metal is smaller than that of platinum (13); hence there will be closer packing of the adsorbed acid molecules on chromium, and γ_c should be lower on chromium

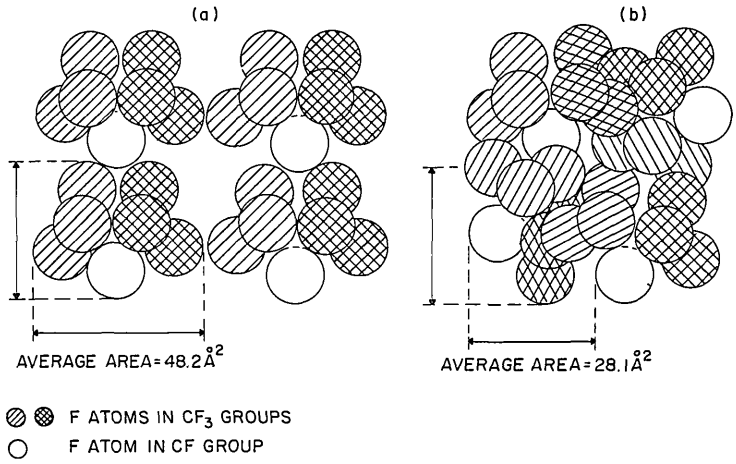

Fig. 5 - End view of $(CF_3)_2CF(CF_2)_nCOOH$ molecules in different packing arrangements

than on platinum. Evidence of higher values of γ_c is found in the adsorbed short-chain acids, where, as discussed earlier, the decreased lateral attraction between the adsorbed molecules of short chain length permits looser molecular packing. This difference in packing becomes more obvious when the cross-sectional radius of the acid is less than twice the atomic radius of the substrate metal.

The much lower melting point of each terminally branched acid than that of the straight-chain acid having the same number of carbon atoms in the n-alkyl chain suggests a somewhat disoriented crystal structure of the branched compound. Figure 6 compares the melting points of the perfluoro-n-alkanoic acids (curve A) with those of the terminally branched acids (curves B and C) on the basis of the same principal chain length. Melting points of these fluorinated acids are also compared with those of the analogous unfluorinated acids, as shown in curves D and E (14). The melting point difference between curves A and B for equal chain length is about 20°C in each case, whereas for the unfluorinated acids the difference between curves D and E is only about 2 or 3°C. Thus, branching on the carbon atom next to the terminal carbon has a much larger disrupting influence on the crystalline structure of the fluorinated than of the hydrocarbon fatty acids, since the bulky

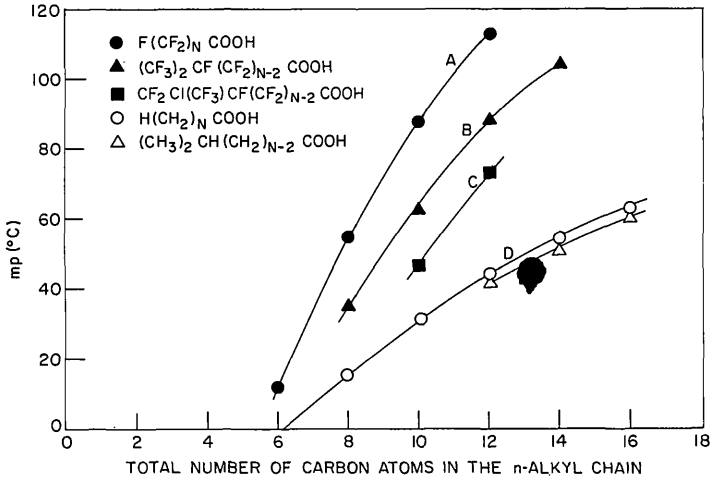

Fig. 6 - Melting points of aliphatic and fluorinated aliphatic acids

perfluoroisopropyl group presents a larger steric hindrance than the much smaller isopropyl group. Hence, close packing as illustrated in Fig. 5b may occur only for the long-chain acids.

As expected, molecules of $CF_2Cl(CF_3)CF(CF_2)_nCOOH$ cause greater disruption and disorientation in the crystal structure because of the presence of the large chlorine atom; this effect is evidenced by the even lower melting points (Fig. 6) and the higher values of γ_c of their adsorbed monolayers.

MAXIMUM PORE SIZE IN ADSORBED MONOLAYER

Timmons and Zisman (8) have recently shown that penetration of adsorbed monolayers by the molecules of liquid occurs when the cross-sectional dimensions of the pores in the monolayer are as large (or larger) than the cross-sectional dimensions of the molecules in the sessile drop. Drops of the n-alkanes showed no significant contact angle hysteresis (difference between the advancing and receding contact angles) on any of the monolayers adsorbed on either metal. However, hysteresis was observed with liquids of such small molecular volumes as water, methylene iodide, ethylene glycol, glycerol, and formamide. Of these liquids, only glycerol was completely free of contact angle hysteresis on monolayers of any of the high homologs of the $(CF_3)_2CF(CF_2)_nCOOH$ series adsorbed on chromium. The molar volumes of these liquids at 25°C expressed in cc/gram-mole are: 18.0 for water, 39.8 for formamide, 55.8 for ethylene glycol, 73.0 for glycerol, 80.5 for methylene iodide, 139.0 for α-bromonaphthalene, and 163.0 for n-octane.

From these data and the contact angle hysteresis observed, we can postulate that the pores between the molecules of a $(CF_3)_2CF(CF_2)_9COOH$ monolayer adsorbed on chromium must be small enough to prevent penetration of an α-bromonaphthalene molecule but large enough to permit penetration of a methylene iodide molecule. Drops of glycerol showed no significant hysteresis, and ethylene glycol with a hysteresis of 4 degrees was a borderline case; however, these compounds can readily associate to form a dimer, corresponding to molar volumes of at least 146.0 and 112.0 cc/gram-mole in the liquid state, respectively. Since liquids of larger molar volume than ethylene glycol did not exhibit hysteresis, its molar volume can be indicative of the limiting size capable of penetrating the monolayer. If the molecules are assumed to be of spherical shape, the average cross-sectional area of the intermolecular pores can be calculated to be approximately 39 $Å^2$.

By using the same reasoning the approximate maximum pore sizes of the other adsorbed monolayers were calculated for all members of the two acid series on both metals. On chromium the pore sizes varied from 39 $Å^2$ to 48 $Å^2$ for adsorbed monolayers of the fully fluorinated acids ranging from $n = 9$ to $n = 3$, and from 45 $Å^2$ to 50 $Å^2$ for the chlorine-substituted acids in the same range of values of n. Comparable pore sizes of the monolayers on platinum ranged from 45 $Å^2$ to 50 $Å^2$ for the branched perfluoroacids. No maximum pore size could be obtained with the chlorinated acids when $n < 5$; however, when $n > 5$, the pore size was about 48 $Å^2$.

Since liquids of small molar volumes can penetrate monolayers of the short-chain homologs, the molecular packing of these acid molecules must be less tight than that of the higher homologs. In addition, the more ready penetration by such liquids through monolayers adsorbed on platinum than on chromium is an indication of the more condensed molecular packing of each monolayer adsorbed on chromium.

CALCULATION OF γ_c FROM SURFACE COMPOSITION

Since the large chlorine atom prevents free rotation of the CF_2Cl- group around the C–C bond, there exist three possible surface chemical positions of the chlorine atom in

molecule, as shown in Fig. 7 as both top view and schematic. Assuming that all three arrangements are equally probable, the actual surface composition of an adsorbed monolayer of $CF_2Cl(CF_3)CF(CF_2)_nCOOH$ molecules will consist of equal proportions of acid as indicated in (a), (b), and (c) of Fig. 7. The lowest value of γ_c obtained for any of the adsorbed monolayers of $CF_2Cl(CF_3)CF(CF_2)_nCOOH$ molecules was 17.2 dynes/cm. Molecular ball models show that of the three types of molecules with CF_3-CF_2Cl, CF_3-CF_2-, and CF_3-CF_2- terminals, the chlorine atom is present in the surface in one molecule (Fig. 7a), is partially present in the surface in another (Fig. 7b), and is completely below the surface in the third (Fig. 7c).

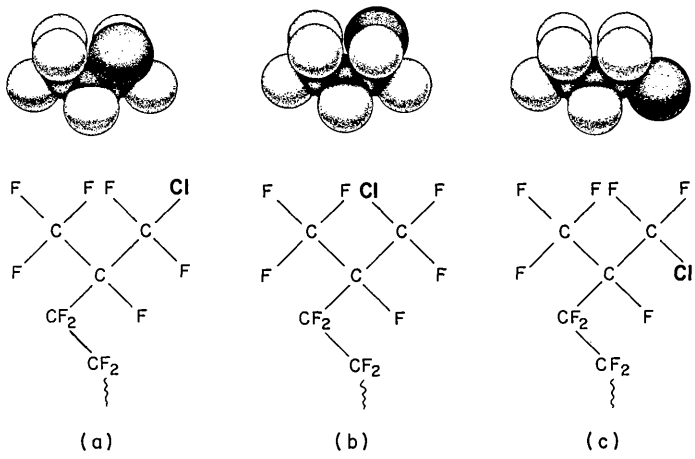

Fig. 7 - Three possible positions of the chlorine atom in the surface

Surfaces whose constitution is comprised solely of a single molecular species in close packing have the following γ_c values: 6 dynes/cm for a CF_3- surface (2), 18 dynes/cm for a $-CF_2-$ surface (7), and 31 dynes/cm for a $-CF_2Cl$ surface (11). If the appropriate contributions determining the value of γ_c of the mixed system are assigned according to their frequency of occurrence in the surface, γ_c can be computed for the surface as follows:

$$\gamma_c = \frac{3\gamma_c(CF_3-) + 2\gamma_c(-CF_2-) + \gamma_c(-CF_2Cl)}{6} .$$

The resulting calculated value of γ_c = 14 dynes/cm is valid only if the acid molecules are packed as closely as the well-adlineated, close-packed, perfluoro-n-alkanoic acids for which γ_c is 6 dynes/cm. However, if to a first approximation the packing of the branched acids terminated by CF_2Cl- groups is of the same surface density as that of the analogous terminally branched perfluoroacids, the value of γ_c for such a spacing should be 13.3 dynes/cm, which is the lowest value of γ_c obtained for these close-packed acids (see Table 2). If γ_c is now computed in the same manner as above, but the value of 13.3 dynes/cm is substituted for that of 6 dynes/cm as the contribution from the CF_3- groups, a value of γ_c of 17.6 dynes/cm is calculated. This is in excellent agreement with the experimental value of 17.2 dynes/cm.

The above computation suggests the possibility of predicting γ_c for any surface whose molecular constitution, atomic arrangement, and surface density (packing) are known.

GENERAL DISCUSSION

The terminally branched perfluoroacids investigated readily formed reproducible, condensed, adsorbed monolayers on smooth metal surfaces. The most closely packed films had critical surface tensions of wetting as low as 13.3 dynes/cm; although these are somewhat larger than the values of γ_c exhibited by condensed adsorbed monolayers of the perfluoro-n-alkanoic acids of the same chain length, they are still much lower than the values of γ_c of polytetrafluoroethylene and polyperfluoropropylene.

Water contact angles on monolayers of all homologs of the branched perfluoroacids are as high as on those of the straight-chain acids (2), especially on substrates so chosen that the intermolecular pore sizes of the adsorbed monolayers are not too large, as for instance on a chromium substrate. However, the contact angles exhibited on the monolayers by organic liquids are somewhat greater with branched than with unbranched perfluoroacids. Condensed monolayers of the fully fluorinated acids were more water repellent for equal chain lengths than the chlorine-substituted acids, but the higher homologs of the latter class of acids also show substantial water repellency.

ACKNOWLEDGMENT

Through the cooperation of Dr. Murray Hauptschein and the Pennsalt Chemicals Corp., the two new homologous series of branched halogenated carboxylic acids investigated here were generously donated to this Laboratory for research in surface chemistry.

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Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*

Naval Research Laboratory
Washington, D.C. 20390

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

SURFACE PROPERTIES OF PERFLUOROACIDS AS AFFECTED BY TERMINAL BRANCHING AND CHLORINE SUBSTITUTION

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

An interim report on a continuing problem.

5. AUTHOR(S) *(First name, middle initial, last name)*

Marianne K. Bernett and W. A. Zisman

6. REPORT DATE

February 24, 1967

7a. TOTAL NO. OF PAGES

16

7b. NO. OF REFS

14

8a. CONTRACT OR GRANT NO.

NRL Problem C02-10

b. PROJECT NO.

RR 001-01-43-4751

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

NRL Report 6511

9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*

10. DISTRIBUTION STATEMENT

Distribution of this document is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Department of the Navy (Office of Naval Research), Washington, D.C. 20360

13. ABSTRACT

When an otherwise fully fluorinated carboxylic acid molecule was altered by terminal branching and terminal chlorine atom substitution, significant increases resulted in the wettability of its adsorbed monolayer. Two new homologous series of acids $(CF_3)_2CF(CF_2)_nCOOH$ and $CF_2Cl(CF_3)CF(CF_2)_nCOOH$, where n ranged from 11 to 1 and 9 to 1, respectively, were adsorbed as condensed monolayers on highly polished clean disks of chromium and platinum. The critical surface tension of wetting (γ_c) of each resulting surface was determined by contact angle measurements on homologous series of n-alkanes, open-chain polydimethylsiloxanes, and miscellaneous other liquids. In every case the wettability, expressed as γ_c, was increased by branching or by terminal chlorine substitution. Thus, in the series $(CF_3)_2CF(CF_2)_nCOOH$, γ_c on chromium ranged from 13.3 dynes/cm (when n = 11) to a maximum of 15.2 (when n = 1), whereas in the series $CF_2Cl(CF_3)CF(CF_2)_nCOOH$, γ_c ranged from 17.2 (when n = 9) to around 20 (when n = 1). These results are excellent examples of the effect on γ_c on substituting one terminal chlorine atom in the surface for a fluorine atom. For a given acid monolayer, almost the same γ_c values were obtained on each of the two metals except that γ_c became larger on platinum than on chromium when the acid was a lower homolog in each series. The causes of this divergence relate to a smaller adsorption site spacing and the consequent tighter molecular packing and better chain adlineation of the adsorbed compound on chromium.

DD FORM 1 NOV 65 1473 (PAGE 1)

S/N 0101-807-6801

Security Classification

Security Classification

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Surface properties						
Adsorption on metals						
Monomolecular films						
Organic compounds						
Fluorine compounds						
Chlorine-fluorine compounds						
Perfluoroacids						
Wettability						
Critical surface tension						
Terminal branching						

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(PAGE 2)

Security Classification