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Surface Chemistry of Fluorochemicals

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CONTENTS

ABSTRACT

Research on the surface chemistry of fluorochemicals, including the related development of new fluorine-containing compounds, polymers, and surface treatments, has progressed to the stage where a review of the subject is appropriate. A report has been prepared in the hope that it will serve not only as a record of progress, but will also clarify much of the fundamental information that is available, and will serve as a guide for future investigations and applications.

With the advent of the highly fluorinated organic compounds, it has been possible to prepare surfaces having extremely low free surface energies, much lower than had previously been possible with hydrocarbon derivatives. Because of their low surface energies, fluorinated solids have the most nonwettable and nonadhesive surfaces known. It has been proved that only the outermost molecules of the surface of a solid need be highly fluorinated in order to achieve such low surface energies. In fact the most nonwetting surfaces studied to date were those covered with an adsorbed monolayer of closely packed perfluoro acids, with the perfluoromethyl ($-CF_3$) groups outermost.

It has likewise been found that surface-active agents containing perfluorocarbon terminal groups will lower the surface tension of water far below the values obtainable with hydrocarbon-type wetting agents. Certain fluorinated hydrocarbon derivatives have also been synthesized that show very high surface activity in a wide variety of organic liquids, the extent of surface activity being dependent upon the organophilic-organophobic balance in the fluorine-containing amphipathic molecule.

It is predicted that fluorine-containing monomers and fluorocarbon-substituted surface-active materials will find increasing application in polymers and plastics, as additives for liquids, and as protective coatings on solids.

PROBLEM STATUS

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

AUTHORIZATION

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SURFACE CHEMISTRY OF FLUOROCHEMICALS

INTRODUCTION

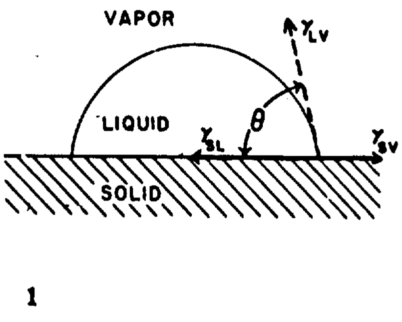
Since the 1940's the advent of fluorinated organic chemicals has had a major impact on science and technology. Certain fluorochemicals prepared just before or during World War II have made it possible to observe greater changes in surface energy, wettability, and surface activity than previously had been possible. Research on surface properties of organic fluorochemicals has since revealed a host of new applications as well as several new areas to be explored. Another important result is that today we have a substantial body of knowledge to teach us much about the relation between the chemical structure and surface properties of liquids and solids.

Why do some fluorochemicals have such extreme surface properties? How does each fluorine atom contribute to the resulting surface activity of the molecule, and what structural rules are there to guide one in designing surface-active fluorochemicals? These questions can be answered in terms of what we have learned about the surface properties of these fluorochemicals. The most important properties are: (a) the equilibrium contact angle of almost any liquid on a solid surface covered with perfluoromethyl or perfluoromethylene groups is much greater than on a solid surface covered with methyl or methylene groups; (b) aliphatic fluorinated polar-nonpolar compounds (such as the carboxylic acids, alcohols, and salts) are much more surface active in water than either their hydrocarbon analogs or <u>any</u> other class of compounds; and (c) fluorocarbon derivatives of the organophobic-organophilic type manifest uniquely high surface activity in nearly all nonaqueous liquids. Each of these topics deserves discussion here.

LIQUID SPREADING AND ADHESION ON LOW-ENERGY SOLID SURFACES

Provided the surface of a solid fluorocarbon polymer is sufficiently smooth and clean, the equilibrium contact angle θ of a sessile drop of any pure liquid on the horizontal surface (Fig. 1) is a reproducible and indicative property (1). A plot of cos θ vs the surface tension γ_{LV} of the liquid is shown in Fig. 2 for the homologous family of n-alkanes on polytetrafluoroethylene. The graphical intercept with the straight line cos $\theta = 1$ is defined as the critical surface tension γ_c of wetting. A similar plot using any other homologous series of liquids results in practically the same value of γ_c. If a similar chart is plotted for a variety of liquids without regard to their structural homology (Fig. 3), the graphical points are nearly all distributed in a narrow rectilinear band rather than a straight line. The lower boundary of this region still defines an intercept at cos $\theta = 1$ which is about the same as that given in Fig. 2 and is taken as γ_c for that system.

Fig. 1 - Schematic diagram of finite contact angle formed by a sessile drop resting on a solid surface



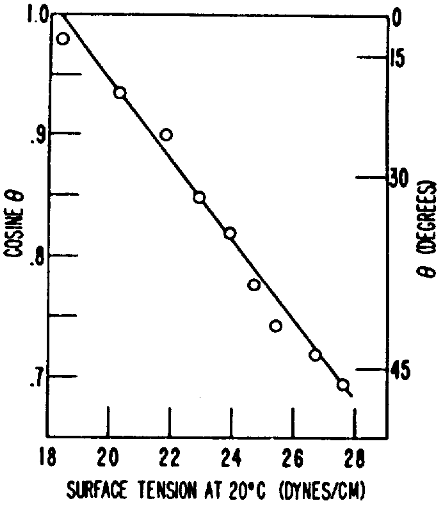


Fig. 2 - Wettability of polytetrafluoroethylene by n-alkanes

Graphical points for the more polar liquids, having surface tensions above 40 dynes/cm, lie on a concave-up curve deviating more from the extended straight line the greater γ_{LV}. The straight-line region is due to the molecules of the low-surface-tension liquids being attracted to the solid surface principally by the London "dispersion" forces. The deviation from linearity occurs because of the additional forces of attraction which are possible with the more polar, higher-surface-tension liquids, such as the formation of weak hydrogen bonds between the fluorine atoms in the surface of polytetrafluoroethylene and the hydrogen atoms of the hydrogen-donating liquids. Figure 3 exemplifies the results of many similar studies of other types of polymeric solids.

A most revealing study was the effect on γ_c of the progressive fluorination (or chlorination) of linear polyethylene. Table 1 compares values of γ_c for the various halogenated polyethylenes and relates them to the polymeric structure and the degree of halogenation of each solid surface. It is assumed that the surface composition of each polymeric solid is statistically the equivalent of that of an individual polymer molecule stretched out in a horizontal configuration at the surface. Thus, the surfaces of linear, unbranched polyethylene and polytetrafluoroethylene are presumed to be comprised essentially of $-CH_2-$ groups and of $-CF_2-$ groups, respectively, poly(vinyl fluoride) to have a surface atomic composition of 25 percent covalent fluorine and 75 percent covalent hydrogen, etc. One can then plot the γ_c data of Table 2 against the estimated atom percent halogenation of polyethylene as shown in Fig. 4. In striking contrast are the descending straight-line

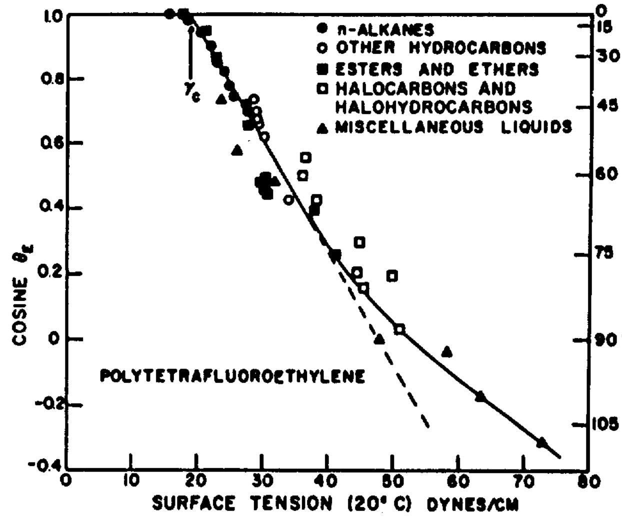
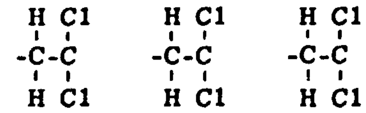
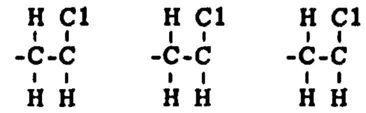
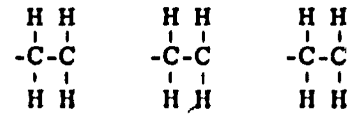
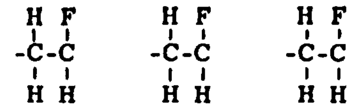
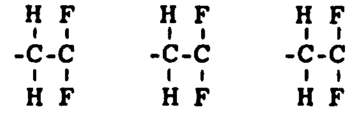
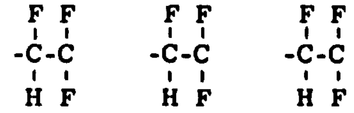
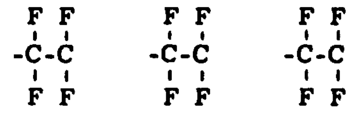


Fig. 3 - Wettability of polytetrafluoroethylene by water and a variety of organic liquids

Table 1
Critical Surface Tension (γ_c) and Constitution of Halogenated Polyethylenes

Polymer	Structural Formula	Critical Surface Tension (dynes/cm)
Poly(vinylidene chloride)	 $-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{Cl}{C}}$	40
Poly(vinyl chloride)	 $-\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{Cl}{\underset{H}{C}}$	39
Polyethylene	 $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}$	31
Poly(vinyl fluoride)	 $-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{F}{\underset{H}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{F}{\underset{H}{C}}$	28
Poly(vinylidene fluoride)	 $-\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{H}{\underset{H}{C}}-\overset{F}{\underset{F}{C}}$	25
Polytrifluoroethylene	 $-\overset{F}{\underset{H}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{F}{\underset{H}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{F}{\underset{H}{C}}-\overset{F}{\underset{F}{C}}$	22
Polytetrafluoroethylene (Teflon)	 $-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}} \quad -\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}$	18

behavior of the fluorohydrocarbons and the ascending asymptotic curve of the chlorohydrocarbons. As will be shown, $\cos \theta$ is a measure of the adhesion of a given liquid to the solid; hence Fig. 4 states that surface fluorination decreases and surface chlorination increases the adhesion of each liquid to the solid. Such a major difference in behavior between covalent fluorine and chlorine is of much surface-chemical importance, but it is not unique to the family of halogens in view of many other anomalies in behavior of the first element of a periodic group.

The extrapolation of the upper graph of Fig. 4 to 100 percent chlorination predicts a value of 40 dynes/cm for a solid surface coated with close-packed covalent chlorine atoms. Fully chlorine-substituted polyethylene is not available, and presumably it cannot be prepared. Since the chlorine atom is much larger than hydrogen, steric hindrance prevents the complete replacement of all the hydrogen atoms. However, perchloropenta-2,4-dienoic acid (Fig. 5) has been adsorbed on polished glass and platinum to form condensed monolayers arranged with each carboxylic acid group in contact with the solid surface and

Table 2
Critical Surface Tension (γ_c) of Low-Energy Surfaces

Surface Constitution	γ_c (dynes/cm at 20°C)
Fluorocarbon Surfaces	
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ and $-CF_2-$	17
$-CF_2-CF_2-$	18
$-CF_2-CFH-$	22
$-CF_2-CH_2-$	25
$-CFH-CH_2-$	28
Hydrocarbon Surfaces	
$-CH_3$ (crystal)	20-22
$-CH_3$ (monolayer)	22-24
$-CH_2-CH_2-$	31
-CH- (phenyl ring edge)	35
Chlorocarbon Surfaces	
$-CClH-CH_2-$	39
$-CCl_2-CH_2-$	40
$=CCl_2$	43
Nitrated Hydrocarbon Surfaces	
$-CH_2ONO_2$ (crystal) [110]	40
$-C(NO_2)_3$ (monolayer)	42
$-CH_2ONO_2$ (crystal) [101]	45

with the two covalent chlorine atoms of the ω-carbon directed outermost. The γ_c for this coated solid was 41 dynes/cm, in good agreement with the extrapolated value. This remarkable result exemplifies the general rule that the wettability of an organic surface is determined solely by the composition and orientation of the outermost atoms in the surface of the solid and is independent of the nature of the underlying material (1). This rule appears correct so long as materials are avoided which contain trapped ionic charges or large unbalanced electrostatic dipoles in the organic surface.

Numerous other polar-nonpolar compounds besides perchloropentadienoic acid have been adsorbed as close-packed monolayers on metals, glass, and other smooth high-energy solid surfaces, and the cos θ vs γ_{LV} graphs of the resulting coated materials have been obtained. Such compounds have included homologous series of fatty acids, amines, amides, and alcohols, as well as a variety of halogenated derivatives. Wetting properties of single crystals of the paraffin hexatriacontane ($C_{36}H_{74}$) also have been investigated. In this crystal the outermost composition of the freshly cleaved surface is comprised of oriented methyl groups in close packing. It is instructive to compare the value of $\gamma_c = 22$ dynes/cm of such a surface with that of 24 dynes/cm of a close-packed monolayer of stearic acid adsorbed on platinum, chromium, iron, aluminum, zinc, nickel, beryllium, or soda-lime glass. The decrease in γ_c of 2 dynes/cm in going from the adsorbed monolayers to hexatriacontane is reasonable, since it results from the slightly closer packing of the methyl groups in the latter material.

In 1947 the value of γ_c for polyethylene was compared by Zisman with that for polytetrafluoroethylene, and the value of γ_c for a surface of close-packed methyl groups with that for a surface of close-packed perfluoromethyl groups. The fact that γ_c of close-packed $-CH_2-$ groups is 31 dynes/cm and that of $-CH_3$ groups in hexatriacontane was only 22 dynes/cm led him to estimate that γ_c for condensed $-CF_3$ groups must be much less than the value of 18.5 dynes/cm for a surface of close-packed $-CF_2-$ groups. Hence, just as the surface of close-packed methyl groups in a condensed monolayer of a fatty acid or fatty primary amine has the lowest surface energy of any aliphatic hydrocarbon film, so should the surface of close-packed perfluoromethyl groups have the lowest surface energy of any fluorochemical film. This argument led Zisman and co-workers (2-5) to investigate the wettability properties of a condensed monolayer of each of the perfluoro fatty acids as soon as it became available by the Simons electrochemical process (6). Acids prepared by the telomerization method (7,8) were also studied; these have a terminal $-CF_2H$ group. Some of the results of these and related studies are compared in Fig. 6. As predicted, a condensed monolayer of any adsorbed perfluoroalkanoic acid had a much lower γ_c than that of any hydrocarbon surface or of polytetrafluoroethylene; indeed, for the most condensed film yet investigated (perfluorolauric acid) γ_c was about 6 dynes/cm, the lowest value of γ_c reported. As will be shown, this result is fundamental in explaining the surface chemistry of fluorocarbons and fluorohydrocarbons, and therefore it is important in surface chemistry.

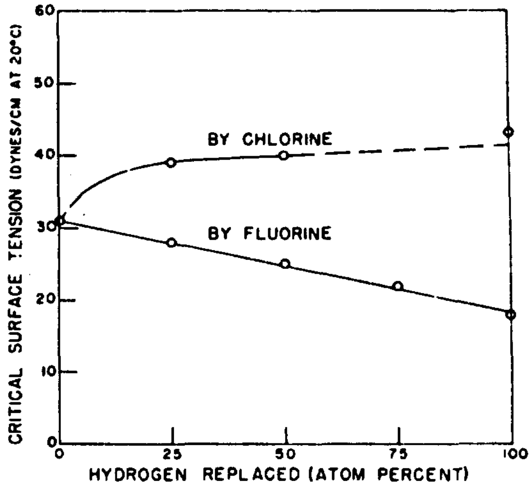


Fig. 4 - The effect of progressive halogen substitution on the wettability of polyethylene-type surfaces

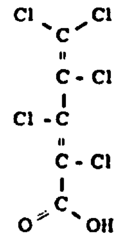


Fig. 5 - Structure of perchloropentadienoic acid

The significance of such low values of γ_c is clearly revealed in Fig. 7. The equilibrium contact angles at 20°C of a selected group of pure liquids were measured on smooth solid surfaces coated with a condensed monolayer of a fluorinated acid. Such large contact angles by organic liquids are spectacular! Here cos θ is plotted against the number of fluorinated carbon atoms per molecule of the adsorbed acid monolayers. These results have suggested a variety of new areas of application; unquestionably, they pointed the way to the now well-known surface treatments for oil, water, and stain-resistant textiles (9-12) and leather (13,14), to new promoters of dropwise condensation for distillation processes, and to new barrier materials to prevent liquid spreading on ball bearings, watches, and other devices (15-18).

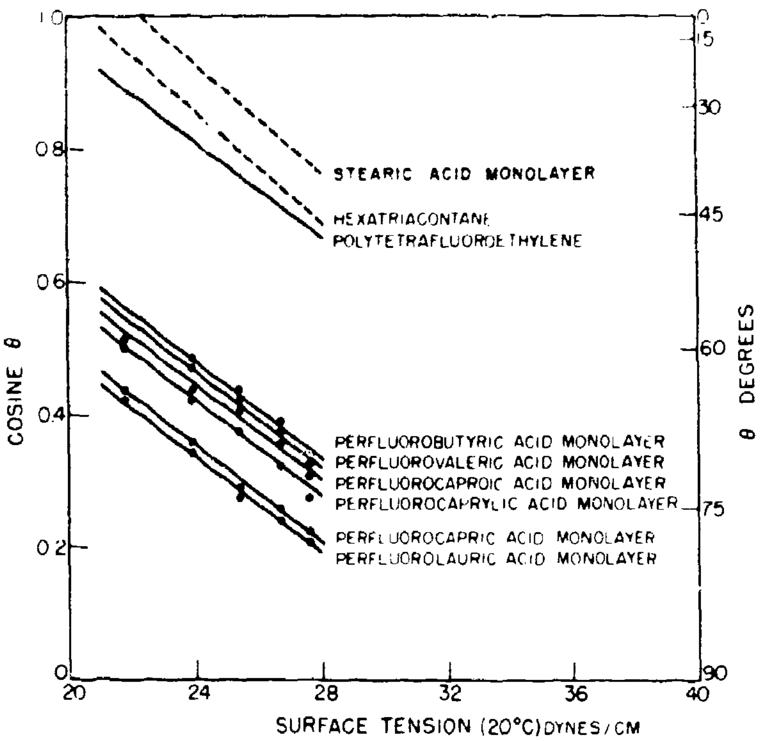


Fig. 6 - Comparison of γ_{LV} vs cos θ relationships for a series of n-alkanes on several different low energy surfaces

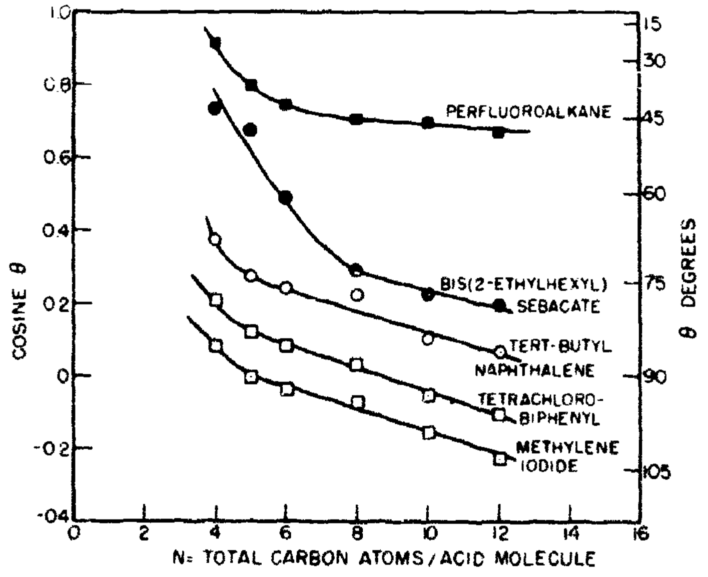


Fig. 7 - The effect of homology in the fluorinated acid monolayers on the contact angles observed for some miscellaneous fluids

Widespread occurrence of the rectilinear relationship between cos θ and γ_{LV} in the large body of experimental data, and the fact that generally these graphs do not cross, make it possible to use γ_c to characterize and compare the wettability of a wide variety of low-energy surfaces (1). Because wettability, and hence γ_c, depends solely upon the nature and packing of the outermost atoms in the solid surface, the results of many investigations of the wettabilities of well-defined, low-energy, solid surfaces can be summarized in the very suggestive form shown in Table 2. In the first column is given the atomic constitution of the organic radicals in the solid surface, and in the second column are the values of γ_c arranged in increasing order. The data have been grouped under subheadings emphasizing the atomic components of primary interest: fluorohydrocarbons and fluorocarbons, hydrocarbons, chlorocarbons and chlorohydrocarbons, and nitrated hydrocarbons. The implications of Table 2 have been discussed more fully elsewhere (1,19), but it is essential to point out here that the first group—the fluorochemicals—have surfaces of lowest γ_c and lowest surface energy. Note that the lowest value of γ_c is that of close-packed perfluoromethyl groups. Replacement of a single fluorine atom by a hydrogen atom in a terminal -CF_3 group has the effect of more than doubling γ_c. For convenience of reference, values of γ_c for smooth, clean surfaces of some important linear organic polymeric solids are arranged in increasing order in Table 3.

Table 3
Critical Surface Tension (γ_c) of Various Polymeric Solids

Polymeric Solid	γ_c (dynes/cm at 20°C)
Polymethacrylic Ester of 1H,1H-pentadecafluoro-1-octanol	10.6
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polychlorotrifluoroethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Poly(vinyl chloride)	40
Poly(vinylidene chloride)	40
Polyhexamethylene adipamide (Nylon 6,6)	46

EXTENT OF FLUORINATION REQUIRED FOR LOW γ_c

What factors determine the minimum number of fluorine atoms needed per organic molecule in order to obtain a very low value of γ_c? This question is important, since fully fluorinated compounds including polymers are difficult to prepare and hence are expensive. The only answers we can give with confidence at present relate to the γ_c values for unbranched aliphatic structures having different extents of fluorination. These answers have resulted from studies of condensed monolayers of ω-trifluorooctadecanoic acid and ω-trifluorooctadecyl amine, both compounds prepared by Gavlin and Maguire (20). Condensed monolayers of a series of progressively fluorinated fatty acids prepared by Brace (21) were also studied.

These organic structures are exemplified by the diagram in Fig. 8 of a carboxylic acid comprising a perfluorinated aliphatic terminal segment attached to an unfluorinated fatty acid segment. The terminal perfluorinated segments varied from one to ten carbon atoms; the unfluorinated segments were the omega-substituted undecanoic and heptadecanoic acids. The total number of carbon atoms per molecule in the acids studied varied from 17 to 23. Each segmented acid was studied as an adsorbed condensed monolayer on polished pure chromium and nickel, and the resulting measurements of γ_c are plotted in Fig. 9 against the number (X) of fluorinated carbon atoms. The dotted curve is a corresponding plot for the homolgous series of perfluoro-n-alkanoic acids adsorbed as condensed films on the same solid (22). It will be seen that complete fluorination of the terminal methyl group caused only a small decrease in γ_c. Not until all the hydrogens on the last seven or eight carbon atoms in the aliphatic chain (Fig. 9) have been replaced by fluorine did γ_c decrease to the value obtained with the perfluoro fatty acid monolayer containing the same amount of fluorine. Therefore, the gains in using these segmented, partially fluorinated fatty acids are: (a) they avoid the high acidity of the perfluoro carboxylic acids, and (b) they allow one to obtain a monolayer coating which has much less volatility than the analogous fatty acid containing the same amount of fluorine.

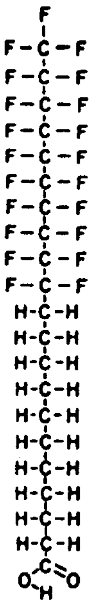


Fig. 8 - Structure of 11-(perfluorodecyl) undecanoic acid

The difficulties in achieving the desired low critical surface tension by merely fluorinating one or a few of the terminal aliphatic carbon atoms appear to contradict the previous statement about the constitutive law of wetting. The difficulty arises from the presence of uncompensated electrostatic dipoles in the adsorbed partially fluorinated fatty acids and their effect in decreasing adlineation of the molecules in the condensed monolayer. It is well known that the electrostatic dipole moment contributions of the various carbon-hydrogen and other bonds can often be added up vectorially to account (within a good approximation) for the total dipole moment of the molecule. In the higher n-alkane derivatives, the total dipole moment of the chain of $-CH_2-$ groups is zero; hence, in the case of the fatty acids the only unbalanced dipoles arise from the contributions of the terminal $-CH_3$ and $-COOH$ groups. Whereas the terminal methyl group makes a dipole contribution estimated to be 0.3 to 0.4 Debye unit (23), the terminal perfluoromethyl dipole is about 1.9 Debyes (24). When the molecules are adsorbed as a condensed oriented monolayer, these terminal dipoles repel each other even though their moments are altered by laterally induced polarization; however, the dipole moment of the $-CF_3$ group remains at least 0.5 Debye in the direction normal to the interface (25). The large

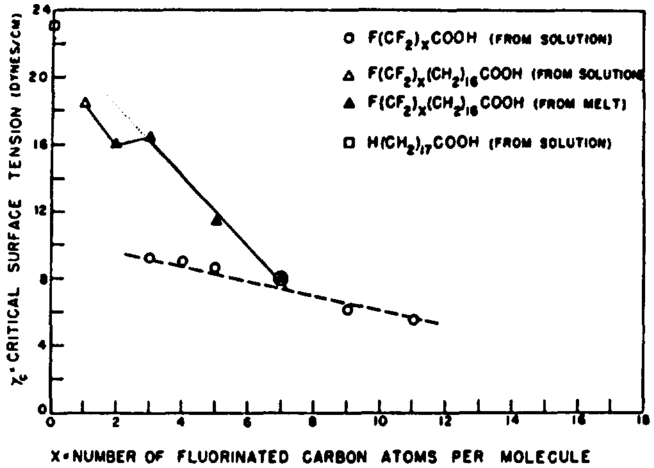


Fig. 9 - The effect of fluorination of the adsorbed acid monolayer on its critical surface tension of wetting by n-alkanes

dipole present in the outermost surface of the partially fluorinated monolayer makes a contribution to the adhesion of the liquid which is in addition to that arising from the London "dispersion" forces. As the molecule is progressively fluorinated, the dipole of the $-CF_3$ terminal may be compensated, in part, by the contributions of the increasing number of $-CF_2-$ groups attached to it; however, there remains an unbalanced dipole at the junction of the fluorinated segments of the aliphatic chain. This junction dipole is further separated from the adhering liquid as progressive fluorination continues; its contribution to liquid adhesion becomes negligible when there are several or more fluorinated atoms in the chain. The repulsion between these uncompensated dipoles, however, will also cause the fluorinated segments of neighboring molecules to separate somewhat. This effect appears significant only when X = 1 or 2. The disruption of chain adlineation becomes minor as the number of CF_2 groups, and the contribution of the attractive "dispersion" force, increases. We conclude that the monolayer is a two-dimensional liquid at low values of X. At higher values it becomes a plastic solid film. Apparently the same packing as a perfluorooctanoic acid monolayer develops when $X > 7$. The need for overcoming the repulsion effect explains the need for a long fluorinated aliphatic segment in the acid molecule.

MONOLAYERS OF HALOGENATED ORGANIC COMPOUNDS ADSORBED ON SOLID SURFACES

Much has been learned in the past 20 years about the adsorption of organic monolayers on solid surfaces and the properties of the resulting coated surfaces. Especially pertinent to this review is the result of the NRL investigations of the adsorbed monolayers of organic halocarbon derivatives – particularly those containing fluorine. Examples of the importance of the properties of such adsorbed monolayers have already been given in discussing surfaces covered with perchloropentadienoic acid (Fig. 5), as well as those covered with oriented close-packed perfluoro-alkanoic acids. In these investigations several methods were used to prepare the monolayers and observe their properties. These were the retraction method, the autophobic liquid technique (a special case of the retraction method), and a modification of the rubbing-down method of Sir William Hardy (26). The first two were developed and investigated fully by Zisman (1), and the third method was recently studied and its limitations discussed, by Levine and Zisman (27,28) and Bewig and Zisman (29).

The retraction method, which is a direct consequence of the constitutive law of wetting, is a process in which a clean, high-energy plane surface is first contacted with a liquid containing adsorbable, polar-nonpolar molecules in solution. Adsorption of the amphipathic molecules occurs at the solid-liquid interface, and the solid is covered by an oriented monolayer which converts it to a low-energy surface. When the plane of the coated solid is held approximately vertically during its withdrawal from the solution, the solution exhibits an appreciable contact angle and then peels back (or retracts), leaving the withdrawn surface of the solid dry but still coated with the adsorbed oriented monolayer. The explanation for this behavior is simple (1,19). The monolayer-coated surface can be removed from the solution unwetted only when withdrawn slowly, and then only when the contact angle of the liquid with the solid is greater than zero. However, $\theta > 0$ only for those liquids having surface tensions γ_{LV} greater than the critical surface tension γ_c of the monolayer-coated solid surface; therefore, the necessary condition for retraction is simply that $\gamma_{LV} > \gamma_c$. Smooth, plane solids covered with adsorbed monolayers can thus be isolated from solutions having surface tensions greater than the values of γ_c of the low-energy surfaces created by the solution-adsorption process.

Monolayers of a wide variety of organic polar-nonpolar compounds have been prepared on solid surfaces by the preceding methods, and many of their physical and chemical properties have been investigated without the experimental difficulties encountered whenever the solution phase is present. Shafrin and Zisman (30) have reviewed the early NRL investigations of a wide variety of polar-nonpolar compounds (aliphatic, cyclic-aliphatic, and aromatic) adsorbed on platinum from aqueous solutions by the retraction method. Monolayers adsorbed from nonaqueous solutions or from the melt have been widely investigated (1,31), especially the families of fatty acids, alcohols, primary amines, and amides. Many classes of halogenated organic compounds were studies, including the perfluoroalkanoic acids (3,27,28,32,33), the telomer acids, $HF_2C(CF_2)_xCOOH$ (4,27,28,32,33), perchloropentadienoic acid (27,28,34), ω-trifluorostearic acid and ω-trifluorostearyl amine (27,28,33,35), the progressively fluorinated alkanoic acids (21,22), the dimer and trimer acids (27,28) of the series $Cl(CF_2CFCl)_xCF_2 \cdot COOH$, and a miscellany of other halogenated acids (27,28) containing F, Cl, or Br.

Properties most thoroughly investigated included contact angles and γ_c, surface potentials, and coefficients of friction. Additional properties are being investigated at NRL and many other laboratories. An interesting radioactive tracer study of perfluorooctanoic acid was made by Shepard and Ryan (36), and a miscellany of friction studies were made by Bowden, Tabor, and co-workers (37).

These investigations of the properties of retracted monolayers adsorbed on solids have been basic contributions to surface chemistry, and they have already thrown much light on a variety of applied problems in wetting, adhesion, friction and wear, electrical properties of surfaces, and corrosion inhibition. For example, Table 4 on abhesive agents is really a byproduct of these studies.

THE REVERSIBLE WORK OF LIQUID ADHESION TO SOLIDS

The reversible work on adhesion W_A of a liquid of surface tension γ_{LV} to a solid can be computed from the equilibrium contact angle θ and the free energy of immersion f_{SV° of the solid in the liquid vapor by the well-known relation of Bangham and Razouk (38,39):

$$W_A = f_{SV^\circ} + \gamma_{LV} (1 + \cos \theta) . \tag{1}$$

Table 4
Critical Surface Tension (γ_c) of Surfaces Coated with Abhesives

Coating Material (All Condensed)	γ_c (dynes/cm at 20°C)
Polymethylsiloxane film	24
Fatty acid monolayer	24
Polytetrafluoroethylene film	18
$HCF_2 \cdot (CF_2)_n \cdot COOH$ monolayer	15
Polymethacrylic ester of 1H,1H pentadecafluoro-1-octanol	10
Perfluorolauric acid monolayer	6

At present there are no data available on f_{SV} for solids of low surface energy. However, if θ is not too close to zero, it can be assumed that f_{SV} will be negligible (1); under such circumstances the reversible work of adhesion is given approximately by W_A, where

$$W_A = \gamma_{LV}(1 + \cos\theta) . \tag{2}$$

This approximation is equivalent to assuming that the amount of adsorbed vapor of the liquid on the low-energy solid surface is much less than a condensed monolayer at ordinary temperatures. Bewig and Zisman (29) have given surface-potential data to support the correctness of this assumption for polytetrafluoroethylene surfaces; Martinet (40) and Graham (41) recently have published adsorption isotherms for the same solid which lead to essentially the same conclusion, so long as extremely low temperatures are not involved.

Assuming that the approximation given by Eq. (2) is correct, and recognizing from Fig. 1 that cos θ is linearly related to γ_{LV} by

$$\cos\theta = 1 + b(\gamma_c - \gamma_{LV}) \tag{3}$$

where b is an experimental constant, it follows that W_A is the second-degree parabolic function of γ_{LV} given in Eq. (4)

$$(W_A)_{max} = \frac{1}{b} + \gamma_c + \frac{b}{4}\gamma_c^2 \tag{4}$$

In Figs. 10 and 11 are plotted some of the data for W_A vs γ_{LV} for various kinds of fluorinated surfaces, and in Table 5 are given the maximum values of W_A read from such charts. Note that the range from highest to lowest γ_c is about 6 to 1 and that the corresponding ratio of $(W_A)_{max}$ is about 3 to 1.

SURFACE ACTIVITY OF FLUOROCHEMICALS IN AQUEOUS SOLUTIONS

Gibbs' classic work (42) proved thermodynamically that any compound in solution which manifests the ability to depress the surface tension (or free surface energy) of the solution must at equilibrium be adsorbed at the gas/solution interface. Until about 1950 the surface-active agents in use were hydrocarbon derivatives consisting of one or more hydrophobic groups (always hydrocarbon or hydrocarbon derivatives) to which were

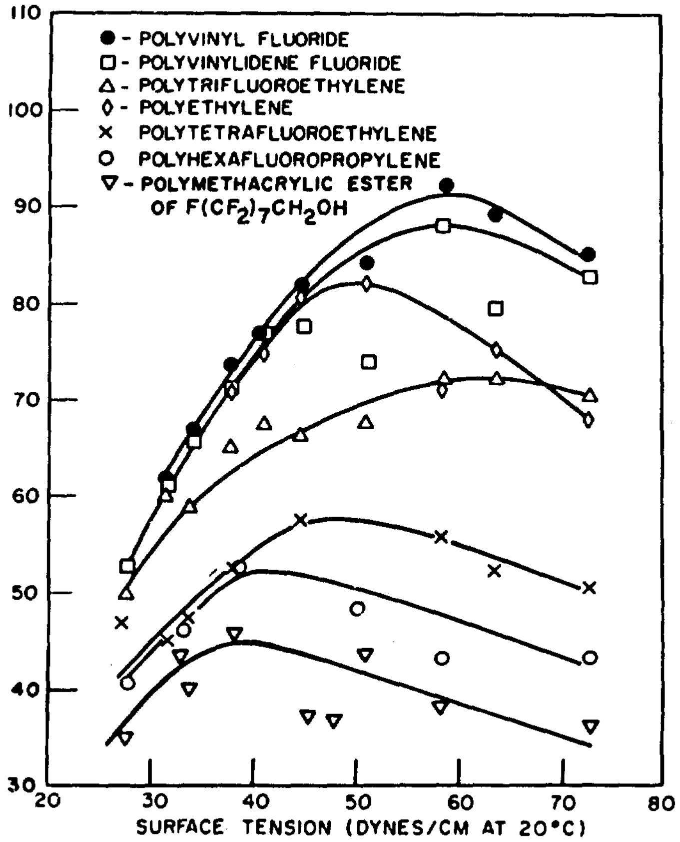


Fig. 10 - Effect of liquid surface tension on W_A, for low surface energy polymeric solids

attached one or more hydrophilic polar groups. A zone chart (Fig. 12) by Fischer and Gans (43) summarizes the surface-tension-depressant behavior of a representative group of such compounds. For convenience, we will refer to such compounds as "conventional" wetting agents. The chart makes it evident that the lowest surface tension of water attainable with any such compound at 20°C is between 25 and 27 dynes/cm.

What determines this minimum surface tension? The answer is most instructive, because the surface tension of the solvent attains its minimum value when the solute molecules are in closest possible packing with the principal hydrophobic chains directed out of the water into the gas phase. If the hydrophobic portion of the solute molecule is an unbranched aliphatic chain, if the molecules are not ionized, and if the polar groups are of smaller cross section than the aliphatic chain, the maximum surface-tension lowering would be expected when adlineated paraffin chains of the solute monolayer reach closest packing. For example, when a lauryl alcohol monolayer is adsorbed on the surface of water as a fully oriented film in closest possible packing, the surface-tension minimum will be attained. It was pointed out earlier by Jarvis and Zisman (44) that when the outermost portion of the oriented monolayer is comprised of n-alkyl chains whose methyl groups approach closest packing, the value of γ_c of that surface should be at least as low as 24 dynes/cm at 20°C. They suggested that the lowest surface tension obtainable with any single, pure conventional surface-active agent in any solvent at 20°C would also approach 24 dynes/cm. The fact that conventional wetting agents do not lower the

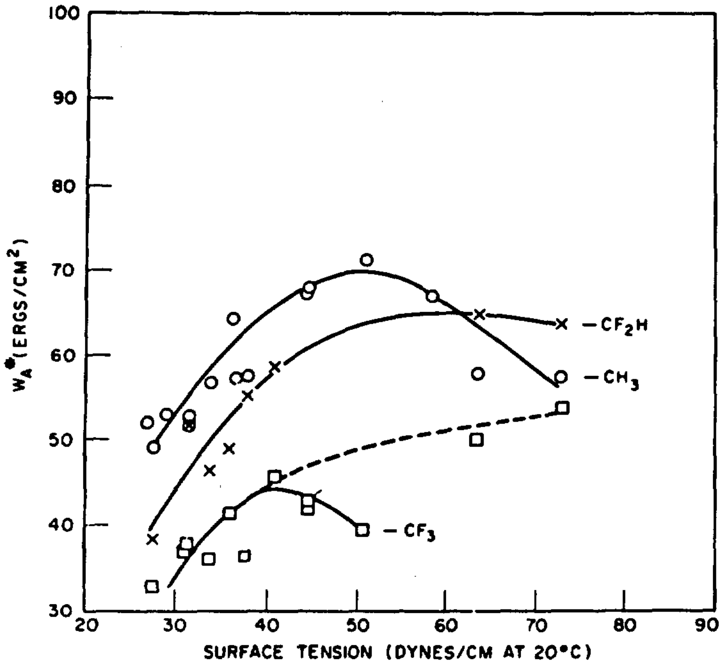


Fig. 11 - Effect of liquid surface tension on W_A, for a solid coated with a condensed monolayer

surface tension of water below 25 to 27 dynes/cm would then be understandable, because these agents must be soluble in water to some extent for the use intended. The problem of attaining closest possible packing of the adsorbed film is, therefore, not easily answered with such a material without creating conditions leading to precipitation of the solute.

One can obtain lower surface tensions, however, by using a slightly insoluble surface-active wetting agent like lauryl alcohol in combination with a material which helps solubilize it in water. Such a solubilizing agent would be a surface-active compound that forms micelles. Such synergistic surface-active systems have been studied for many years by various investigators, even since 1944, when Miles and Shedlovsky (45) first reported the synergistic effect of small concentrations of lauryl alcohol added to sodium lauryl sulphate to lower the minimum surface tension obtainable from about 38 dynes/cm to about 29 dynes/cm at 25°C. Burcik and Newman (46) further investigated this combination of agents and showed that with 7 percent lauryl alcohol present, the surface tension of sodium lauryl sulphate could be lowered to 22.1 dynes/cm at 25°C. Harva (47) showed that the minimum attainable surface tension of 36 dynes/cm of pure sodium laurate could be reduced to about 23 dynes/cm by the addition of 2×10^{-4} molal 1-decanol. A similar minimum value could be obtained by substituting 1-octanol, 1-heptanol, or 1-hexanol for the 1-decanol simply by using a larger amount of alcohol. Shedlovsky, Ross, and Jakob (48) also have shown that a minimum surface tension of 22.6 dynes/cm could be obtained with sodium dodecyl sulphonate by adding 0.5 percent dodecanol.

The presence of a good solubilizing agent such as sodium lauryl sulphate greatly increases the concentration of a slightly soluble alcohol, such as 1-dodecanol, in an aqueous solution. Inasmuch as a dynamic equilibrium exists between the amount of 1-dodecanol adsorbed at the interface and the amount present in solution, the use of the solubilizing agent should lead to more molecules being adsorbed, a closer packing of the hydrocarbon

Table 5
Critical Surface Tension ( ) and Maximum Work of Adhesion (W_A)
of a Series of Related Low-Energy Surfaces

Surface	Atomic Constitution	Atom Percent Replacement of Cl by F	(dynes/cm)	Maximum W_A (ergs cm^{-2})
Perchloropentadienoic acid (monolayer)	$=CCl_2$	0	43	103
Polychlorotrifluoroethylene	$-CF_2-CFCl-$	75	31	73
Polyethylene	$-CH_2-CH_2-$	0	31	82
Poly(vinyl fluoride)	$-CH_2-CHF-$	25	28	92
Poly(vinylidene fluoride)	$-CH_2-CF_2-$	50	25	88.5
Polytrifluoroethylene	$-CHF-CF_2-$	75	22	72.5
Polytetrafluoroethylene	$-CF_2-CF_2-$	100	18.5	58
Polyhexafluoropropylene	$-CF_2-CF(CF_3)-$	50	16.2	52.5
Polymethacrylic ester of 1H,1H-pentadecafluoro-1-octanol	$-CF_3$	100	10.6	45
11-(perfluorodecyl)undecanoic acid (monolayer)	$-CF_3$	100	7.8	41

chains, and thus to a lower surface tension. A surface tension of 22 to 24 dynes/cm appears to be near the minimum surface-tension value that can be obtained when the adsorbed compound is somewhat soluble, i.e., is in equilibrium with molecules present in bulk solvent. With completely insoluble monomolecular films that can be studied on a Langmuir-Adam film balance, where one can apply external pressure to compress the adsorbed molecules into the closest possible area per molecule, it may be possible to reduce the surface tension of water somewhat further. However, the molecules in this configuration would not be in an equilibrium condition.

In order to cause an even greater decrease in the surface tension of water, it is necessary to employ a soluble surface-active agent whose hydrophobic group decreases the surface energy of water below 24 dynes/cm, i.e., below the value of γ_c of close-packed methyl groups. It is apparent that a much greater lowering of the surface tension should be possible if the paraffin chains are replaced by perfluoroalkane chains, for γ_c of a close-packed layer of perfluoromethyl groups is much less than 24 dynes/cm. The same conclusion also follows from the lower intermolecular cohesive energy between close-packed, adlineated perfluoroalkane chains than between adjacent alkane chains. Early hints to this effect were found on comparing the surface tensions of various organic compounds with those of the analogous fully fluorinated derivatives (Table 6).

During the early postwar years many fluorinated aliphatic compounds of higher molecular weight became available for research, and some were later put on the market as surface-active agents. In Fig. 13 are plotted the most reliable surface-tension data at 20 C for aqueous solutions of a variety of compounds as a function of the concentration. Not only is it evident that fluorinated surface-active agents can lower the surface tension of water at 20 C considerably below 24 dynes/cm, but the steep initial slopes reveal how efficient many of them are in accomplishing their tasks. Figure 13 also reveals that none of the agents prepared to date are able to lower the surface tension of water below 14.5 dynes/cm at 20 C. However, it might be possible to lower the surface tension even more by using appropriate synergistic combinations designed to obtain closer packing of the adsorbed perfluoroalkane chains. Where the terminal, or , carbon atom of such compounds has the composition of $-CF_2H$ instead of $-CF_3$, the minimum attainable surface tension is considerably higher, as is clearly shown by Figs. 14 and 15, which are taken from a previous study (49). This result agrees with what would be expected from a consideration of the relative values of , for $-CF_3$ and $-CF_2H$ groups (Table 2).

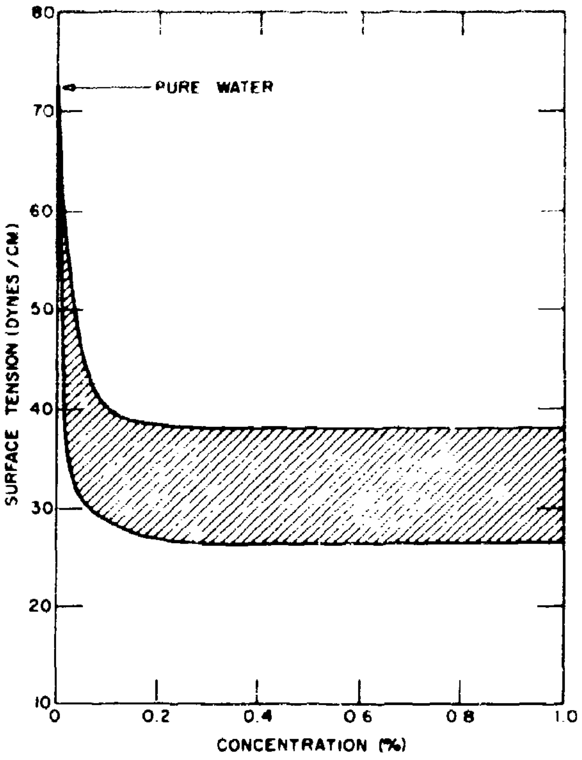


Fig. 12 - Surface-tension values for the majority of the conventional surface-active agents, within shaded area (43)

Surface tension versus log concentration curves for many fluorochemicals in water show discontinuities in slope that are characteristic signs of micelle formation, and the solution concentration associated with the discontinuity is called the critical micelle concentration (CMC). Arrington and

Table 6
Effect of Perfluorination on Surface Tension of Several Organic Liquids at 20°C

Compound	γ_{LV} (dynes/cm)	Perfluorinated Derivative	γ_{LV} (dynes/cm)
n-pentane	13.0	perfluoro-n-pentane	9.9
n-heptane	20.3	perfluoro-n-heptane	13.2
n-octane	21.8	perfluoro-n-octane	13.6
methyl cyclohexane	23.8	perfluoro-methyl cyclohexane	14.7
n-dibutyl ether	22.9	perfluoro-n-dibutyl ether	13.4
n-butanoic acid	26.8	perfluoro-n-butanoic acid	16.3

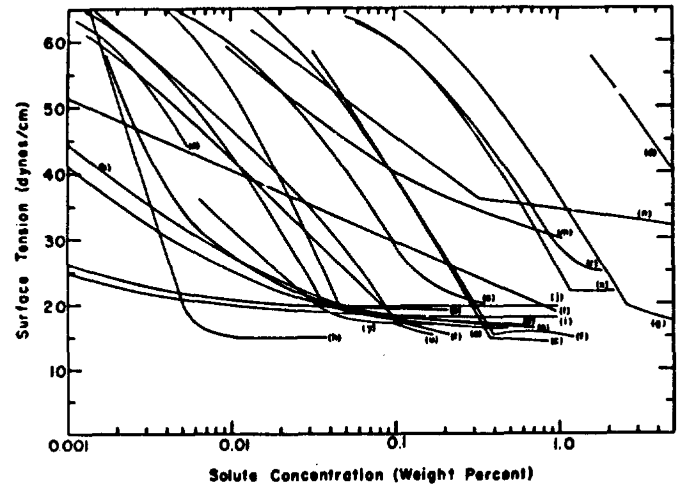


Fig. 13 - Surface tension vs solute concentration curves for a variety of perfluoro derivations in aqueous solution (numbers in parentheses indicate references)

a. Perfluorododecanoic acid (49)
b. Perfluorodecanoic acid (49,54,57)
c. Perfluorooctanoic acid (49)
d. Perfluorobutyric acid (49,54)
e. Perfluorodecanoic acid (86)
f. Perfluorooctanoic acid (54,57,58,86)
g. Perfluorohexanoic acid (54,57,86)
h. $C_7F_{15}CONHC_2H_4N$ · Cl (F-6) (87)
i. $[C_8F_{17}SO_2NHC_3H_6N(CH_3)_3]^+ I^-$ (58)
j. $C_8F_{17}SO_2N(C_2H_5)(C_2H_4O)_{14}H$ (58)
k. $C_8F_{17}SO_2N(C_2H_5)C_2H_4OPO(OH)_2$ (58)
l. $C_8F_{17}SO_3Li$ (58)
m. $C_8F_{17}SO_3K$ (58)
n. $C_8F_{17}SO_3H$ (58)
o. $C_7F_{15}CONHC_3H_6N + (CH_2)_2C_2H_4COO^-$ (58)
p. $[C_7F_{15}CONHC_3H_6N(CH_3)_3]I$ (58)
r. $C_7F_{15}CONH_4$ (58)
s. Perfluorooctanoic Acid in 0.05M KCl (54)
t. Perfluorooctanoic Acid in 0.025M HCl (54)
u. Perfluorooctanoic Acid in 0.05M HCl (54)
x. Potassium Perfluorooctanoate (54)
y. $C_8F_{17}SO_3K$ in 9.4M HNO_3 (88)

Patterson (50) determined the CMC of several perfluoroacids and their ammonium salts. They found that the CMC of the acids was dependent upon chain length and was lower than the CMC of the corresponding hydrocarbon acid. Finally, they reported that the salts of the acids were more soluble than the free acids and had higher CMC values.

Klevens and co-workers (51-55) confirmed the presence in aqueous solution of micelles of perfluoroacids, as well as other fluorochemical derivatives, by utilizing a variety of surface-chemical techniques including electrical conductivity, pH, surface potential, surface tension, and dye-adsorption measurements. Their results are summarized in Table 7. Values of the CMC obtained by the dye-adsorption technique are all somewhat smaller than those determined from surface-tension measurements, but are

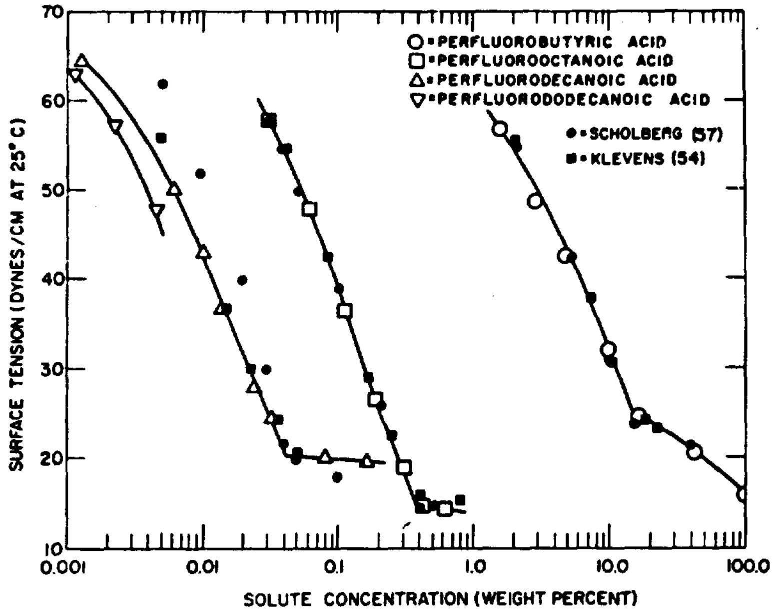


Fig. 14 - Surface tensions of perfluoro acids in aqueous solutions

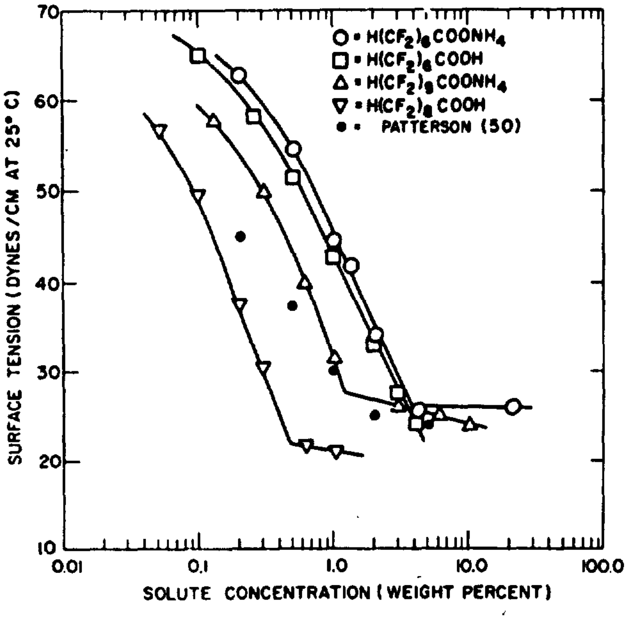


Fig. 15 - Surface tensions of ω-monohydroperfluoro compounds in aqueous solutions

Table 7
A Comparison of the Critical Micelle Concentrations (CMC) of Fluoracids and Potassium Fatty Acid Soaps as Determined by the Spectral-Dye Method*
(T = 25°C)

Number C atoms in chain	Critical Micelle Concentrations (moles per liter)			
	Fatty acid soaps	Perfluoro-acids	Kel-F acids[†]	-Hydro-perfluoro-acids
2		2.06		
3		1.11		
4		0.53	0.70	
5				
6	1.68	0.054	0.062	
7	0.75			0.15
8	0.39	0.0056	0.0091	
9	0.20			0.03
10	0.095	0.00048		
11	0.050			
12	0.025			
13	0.012			
14	0.0058			

*From Ref. 55.
[†] $Cl(CF_2CFCl)_xCF_2COOH$ (X = 1, 2, and 3)

roughly equivalent to the CMC values determined by conductivity studies. The data in Table 7 show that perfluoroacids have much lower CMC values than either the corresponding unfluorinated acids or the -hydroperfluoroacids. It is also worthy of note that there is micelle formation even in perfluoroacetic acid, whereas a four-carbon chain at least is required for micelle formation in salts of the fatty acid (53).

Offsetting their greater surface-tension-lowering ability than conventional surface-active agents, the perfluoroaliphatic compounds have the disadvantage of much higher unit cost. A way to decrease this limitation was revealed when Bernett and Zisman reported (56) the existence of synergistic combinations of a conventional water-soluble agent and a perfluoroalkyl surface-active agent. In these combinations the conventional surface-active agent is believed to serve as the major water-soluble micelle-forming (or solubilizing) ingredient, and the much less soluble perfluoroalkyl compound is the minor ingredient which is solubilized in the hetero (or mixed) micelles. The dynamic exchange of the perfluoroalkyl compound between the hetero micelles and solution keeps the water-air interface covered with an adsorbed monolayer, one essentially comprised of the perfluoroalkyl compounds; hence, the very low surface tensions characteristic of perfluoro surface-active agents can be obtained with much smaller concentration than if a more soluble homologue were used.

Many applications of these new agents have been reported (57,58), and more new uses are being found rapidly. Low-energy solid surfaces such as the polypropylenes, fluorine-containing plastics such as poly(vinyl fluoride), and various solids coated with a monolayer of a fatty acid (or derivative) or with a silicone have become increasingly more common. Whenever such materials must be completely wetted by water (or water emulsions), difficulty is often encountered with solutions of conventional wetting agents. A wetting agent derived from silicones or from fluorinated aliphatic compounds will usually be more effective (49,56). Since many perfluoroalkyl derivatives are able to lower the surface tension of water below the γ_c value of any hydrocarbon surface, such solutions can spread spontaneously on oil or gasoline. This fact is basic to the recent NRL development by Tuve, et al. (59) of a new and impressive water foam fire-fighting technique for fuel fires during aircraft disasters.

INSOLUBLE FLUOROCHEMICAL MONOLAYERS AT THE LIQUID/GAS INTERFACE

In their early investigation of monolayers of fluoroacids and alcohols spread on aqueous substrates, Arrington and Patterson (50) reported that $H(CF_2)_{10}CH_2OH$ could be spread on water to give an insoluble monolayer. From the curve of film pressure (F) vs area per molecule (A), obtained using a conventional Langmuir-Adam hydrophil balance, they determined that the area per adsorbed molecule at closest packing was 25 $Å^2$. (In close agreement is the value of 25.1 $Å^2$ obtained by Bernett and Zisman (25) from measurement on a Stuart-Briegleb ball model.) Fluoroalcohols of lower molecular weight could not be spread successfully by Arrington and Patterson, presumably because of their solubility. Monolayers of the fluorocarboxylic acid $H(CF_2)_{12}COOH$ on 0.01N HCl behaved normally, but on water gave evidence of being unstable. Because their fluorocarboxylic acid monolayer on 0.01N HCl behaved as a perfect two-dimensional gas up to film pressures as high as 5 or 6 dynes/cm, they concluded that intermolecular forces of attraction between adjacent fluorocarbon chains were weaker than those between the hydrocarbon chains.

H. W. Fox (60) studied at NRL the behavior of insoluble monolayers of ω-trifluorostearic acid and ω-trifluorooctadecylamine on aqueous substrates of various pH and found these monolayers were more expanded and less stable than monolayers of the unfluorinated compounds. He attributed the instability to the mutual repulsion of the strong dipoles associated with the ω-trifluoro groups. The large dipole moment of the $-CF_3$ group also greatly reduced the surface potential of the adsorbed monolayer. The maximum surface potential difference of ω-trifluorostearic acid on pH 2.5 was -705 millivolts, which is to be compared with a value of +355 millivolts for stearic acid.

Klevens and Davies (52), from a study of F vs A and surface potential difference (ΔV) vs A for monolayers of $C_9F_{19}COOH$ on aqueous substrates, determined that the energy of adsorption of a $-CF_2-$ group at a water/air interface was at least twice that of a $-CH_2-$ group (1490 cal/mole compared with 725 cal/mole). They also reported that the closely packed acid film caused a remarkably low surface-potential change of $\Delta V = -1000$ millivolts; this value was reported to be independent of substrate pH from pH 2 to pH 12.

Bernett and Zisman (25) determined F vs A and ΔV vs A curves for two homologous series of progressively fluorinated fatty acids spread as insoluble monolayers at the water/air interface. These compounds were the same preparations made by Brace (21) which were described previously in this report as the "segmented" acids. Both series of acids exhibited monolayer stability which increased with increasing length of the fluorocarbon chain. A chain length of at least 18 carbon atoms was necessary in both series of acids for the formation of stable monomolecular films. None of the progressively fluorinated acids produced solid, condensed monolayers. Presumably, that was a result of steric hindrance to chain alignment, since the fluoroalkyl chain has a cross-sectional area roughly 35 percent greater than the unfluorinated alkyl chain to which it is attached. The closest molecular packing observed was 27.5 $Å^2$ per molecule, which is 10 percent greater than the cross-sectional area of the perfluoroalkane chain. Changes in surface potential caused by these adsorbed fluorocarboxylic acid monolayers were also extremely low; for example, 11-(perfluorodecyl)-undecanoic acid caused a ΔV of -815 millivolts at closest packing on 0.01 N H_2SO_7.

Bernett, Jarvis, and Zisman (61) have reported that at high film pressures the F-vs-A curves of 18-fluoro-1-octadecanol were identical with those of 1-octadecanol, but that at low film pressures the 18-fluoro alcohol was somewhat more expanded. The film expansion was again attributed to the large dipole moment of the C-F bond, which leads at close packing to strong repulsion between the similarly oriented dipoles in the terminal $-CH_2F$ groups. Molecular ball model calculations showed that a single fluorine atom in the omega position was too small to sterically hinder packing of the hydrocarbon chain. Only with the larger halogens, iodine and bromine, did the steric factor become significant. The large C-F dipole moment also caused 18-fluoro-1-octadecanol to have a much lower value of ΔV than octadecanol (-55 millivolts as compared with 620 millivolts).

Ellison and Zisman (62,63) found that it was possible to spread certain fluorocarbon derivatives, as well as silicones and organosilicates, as insoluble monomolecular films on a variety of organic liquids. Using an all-PTFE (polytetrafluoroethylene) version of Langmuir's early film balance, they spread monolayers on such liquids as hexadecane, white mineral oil, and tricresyl phosphate. They proved that these films were oriented, adsorbed monomolecular films which obeyed the same surface-chemistry laws already established for conventional surface-active agents adsorbed at the water-air interface. Their work clearly pointed to the promise of high fluorochemical surface activity with respect to a variety of organic liquids, but the need was also obvious for a study of the surface tensions of solutions of similar compounds.

SURFACE ACTIVITY OF FLUOROCHEMICALS IN NONAQUEOUS SOLUTIONS

In seeking compounds which would be surface active when dissolved in nonaqueous liquids, it was realized that the mechanism causing solute adsorption should be most effective when the adsorbed film caused the surface-energy decrease to be a maximum. Therefore, for a given solute there should be a greater surface-active effect, the higher the solvent surface tension. For this reason, a great variety of common polar-nonpolar organic compounds are surface-active agents in water because water has the highest surface tension of all common liquids at ordinary temperatures (72.8 dynes/cm at 20°C). Most of the liquid organic compounds, however, have surface tensions at 20°C between 30 and 45 dynes/cm. Thus it should be difficult to find an effective surface-active solute for hexadecane, because its surface tension is only 26.7 dynes/cm at 20°C. One must turn to derivatives of the silicones or highly fluorinated hydrocarbons for suitable solutes for an organic liquid having such a low surface tension. In turn, one would be hard pressed to find a suitable surface-active agent for use in perfluorocarbon solvent.

How should a surface-active molecule be designed so that it will be an efficient surface-tension depressant for organic liquids? An answer has been found (64-68) by reasoning as follows. It is well known that surface-active agents for water systems have a characteristic hydrophobic-hydrophilic structure such that the hydrophilic portion of the molecule can be dissolved in or associated with the water in the bulk or surface phase, with the hydrophobic portion of the molecule remaining essentially out of the water. Similarly, a surface-active agent for an organic liquid should have an asymmetric structure such that one extreme portion of the molecule is made up of one or more organophobic groups and the opposite extreme portion is made up of one or more organophilic groups. Structural diagrams of three of the many such organic structures synthesized at NRL by O'Rear and Sniegoski (69) are given in Fig. 16. For example, in the third compound there are two organophobic $CF_3(CF_2)_6CH_2$- groups. The organophilic portion of the molecule opposed to it is a benzene ring containing two ester groups and four covalent chlorine atoms. Chlorine was also desirable in this structure to decrease its volatility. Incidentally, this molecular design is an application of the previously mentioned conclusion that covalent chlorine substitution has an effect on the surface energy of the molecule opposite to covalent fluorine.

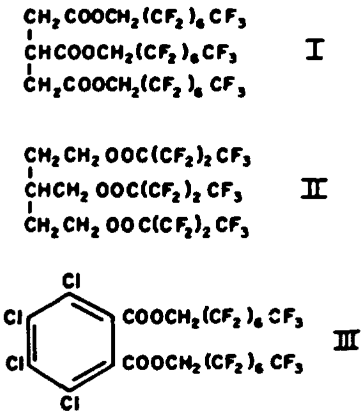


Fig. 16 - Structure of several fluorine-containing compounds used as additives for certain organic liquids and polymers

Some of the interesting results of the investigation of these compounds in various organic liquids are summarized in Figs. 17, 18, 19, and 20. Thus, Fig. 17 illustrates the fact that the higher the surface tension of the solvent, the greater the surface activity of a given solute. The higher surface activity is indicated by the steeper initial slopes. Figure 18 illustrates the effect of varying the surface-active solute on the surface tension vs concentration curves in propylene carbonate. Figure 19 is the result of using the Gibbs' adsorption relation to compute from the surface-tension-vs-concentration curves in Fig. 18 the adsorption of the surface-active agents. Figure 20 is a plot obtained from the data in Fig. 18 in terms of F, the film pressure (total surface tension lowering), vs the area A occupied per adsorbed nolecule. These calculations are based on the assumption that the solute adsorbs as a monomolecular film. These F-vs-A graphs are very much like those obtained with conventional surface-active agents adsorbed at the water-air interface. Finally, in Fig. 21 are the results of fitting the previous curves to Langmuir's early ideal gas-law relation (70) in two dimensions

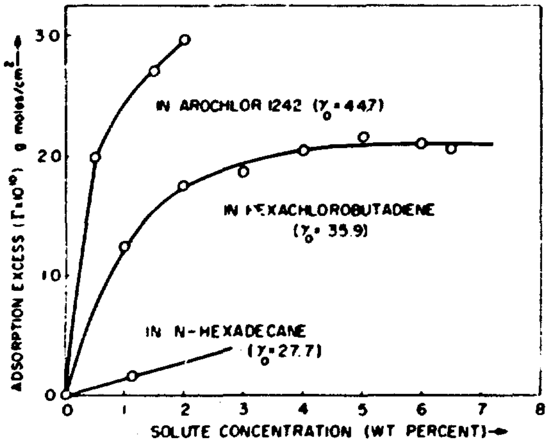


Fig. 17 - Adsorption excess vs concentrations of 1H,1H,9H-hexadecafluorononyl butyrate in various solvents (all data at 20°C)

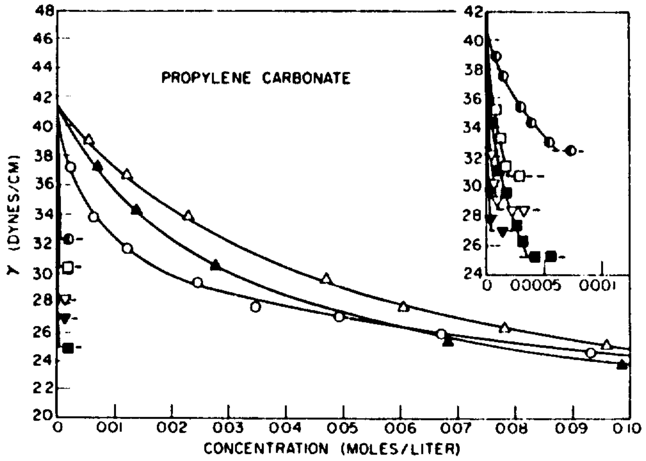


Fig. 18 - Surface tensions of partially fluorinated compounds in propylene carbonate: △, 1,H,1H-pentadecafluorooctyl alcohol; ▲, 1H,1H pentadecafluorooctyl ethanesulfonate; ▽, bis-(1H,1H-pentadecafluorooctoxy)-bis-(t-butoxy) silane; ▼, tris (1H,1H-pentadecafluorooctoxy)-t-butoxysilane; □, bis-(1H,1H-pentadecafluorooctyl) tetrachlorophthalate; ○, tris-(1H,1H heptafluorobutyl) tricarballylate; ●, tris-(1H,1H-pentadecafluorooctyl) tricarballylate; ■, bis-(1H,1H-pentadecafluorooctyl) dodecenyl succinate; ◐, bis-(1H,1H-pentadecafluorooctyl) toluene dicarbamate; ⊗, hexyl perfluorobutyrate; ⊠, 1,2,3-trimethylolpropane tris (perfluorobutyrate); ◓, bis-(1H,1H-undecafluorohexyl)-3-methylglutarate; ◒, bis-(1H,1H-pentadecafluorooctyl) 3-methylglutarate

$$(F + F_0)(A - A_0) = kT \tag{5}$$

and to the relation obtained recently by Hedge (71) from the more general equation of state derived for gaseous monolayers on water by Phillips and Rideal (72).

$$F + \left(\frac{a}{A^2}\right)(A - A_0) = kT. \tag{6}$$

If one considers a plastic solid to be either a supercooled liquid or a liquid of extremely high viscosity, one would expect many partially fluorinated compounds to show surface activity when dissolved in various polymers. The rate at which these surface-active agents adsorb will be primarily determined by the rate of diffusion in the bulk polymer phase. Jarvis, Fox, and Zisman (73) found that a variety of fluorine-containing additives, such as those listed in Fig. 16, would adsorb very strongly at the polymer-air interface when incorporated in the bulk polymer. It was shown that the additives upon adsorption caused remarkable changes in the surface properties of the polymer. Just 0.5 percent of tris(1H,1H-pentadecafluorooctyl) tricarballylate reduced the γ_c of poly(methyl methacrylate) from 40 dynes/cm to less than 19 dynes/cm, approximately that of a polytetrafluoroethylene surface.

In addition to reducing the oil and water wettability of polymer surfaces, the adsorbed fluorochemical additives should also influence the surface in other ways, such as reducing adhesion and reducing its coefficient of friction. In this regard, Bowers, Jarvis, and

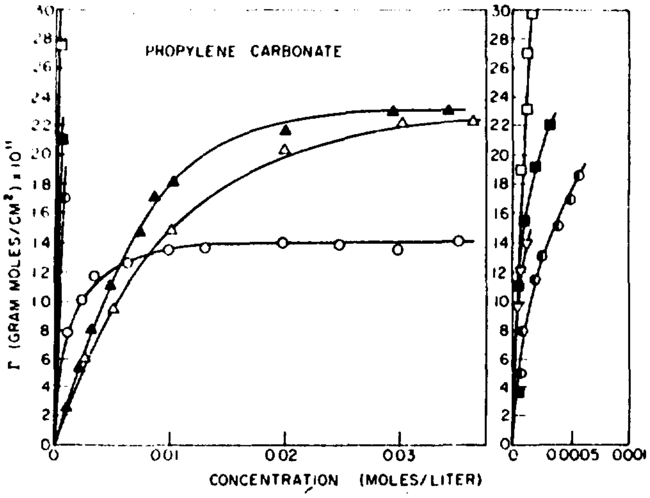


Fig. 19 - Surface excess of partially fluorinated compounds in propylene carbonate: △, 1H,1H-pentadecafluorooctyl alcohol; ▲, 1H,1H-pentadecafluorooctyl ethanesulfonate; ▽, bis-(1H-1H-pentadecafluorooctoxy)-bis-(t-butoxy) silane; □, bis (1H,1H-pentadecafluorooctyl) tetrachlorophthalate; ○, tris-(1H, 1H-heptafluorobutyl) tricarballylate; ●, tris-(1H,1H-pentadecafluorooctyl)tricarballylate; ■, bis-(1H,1H-pentadecafluorooctyl) dodecenyl succinate; ◐, bis-(1H,1H-pentadecafluorooctyl) toluene dicarbamate

Zisman (74) reported that the coefficient of friction of poly(methyl methacrylate) and several of its copolymers with vinylidene chloride could be reduced to 0.10 or less by the incorporation of only 1 percent of a suitable fluorochemical additive in molded polymer discs. An interesting and important property of these systems is the ability of the adsorbed fluorocarbon film to be self-repairing. If the initially adsorbed fluorocarbon film is removed, other molecules of the surface-active additive will diffuse into the interface and restore the original surface behavior.

ADHESIVE AND ABHESIVE BEHAVIOR OF FLUOROCHEMICALS

In ancient times it was found that solids could be made to adhere strongly by wetting each surface to be joined with a thin layer of a liquid which hardened or solidified gradually during contact. Until this century the selection of suitable adhesives and application techniques was an art, depending on the use of glue formulations made from fish and animal products or cements made from inorganic slurries or solutions.

Pioneering studies of adhesion by McBain and Hopkins (75) led them to report that "Any fluid which wets a particular surface and which is then converted into a tenacious mass by cooling, evaporation, oxidation, etc., must be regarded as an adhesive for that surface." McBain and Lee (76) soon afterward added the requirement that the adhesive must be able to deform during its solidification to release elastic stresses developed in the forming of the joint. Their work made evident the following three requirements for an adhesive: (a) wetting, (b) solidification, and (c) sufficient deformability to reduce the buildup of elastic stresses in the formation of the joint. Hull and Burger (77) found the

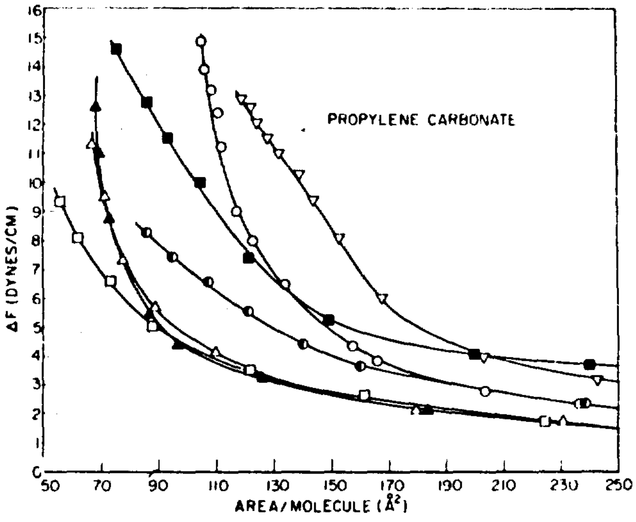


Fig. 20 - Force-area isotherms of partially fluorinated compounds in propylene carbonate: △, 1H,1H-pentadecafluorooctyl alcohol; ▲, 1H,1H-pentadecafluorooctyl ethanesulfonate; ▽, bis-(1H,1H-pentadecafluorooctoxy)-bis-(t-butoxy)-silane; □, bis(1H,1H-pentadecafluorooctyl) tetrachlorophthalate; , tris-(1H,1H-heptafluorobutyl) tricarballylate; ●, tris-(1H,1H-pentadecafluorooctyl) tricarballylate; ■, bis-(1H,1H-pentadecafluorooctyl) dodecenyl succinate; ◐, bis-(1H,1H-pentadecafluorooctyl) toluene dicarbamate

same rules necessary for good glass-to-metal joints. The second and third requirements have been fully investigated and reported. The first requirement was studied much later by deBruyne (78) and Zisman (79,80).

When a liquid adhesive solidifies, the reversible work of adhesion of the adhesive to the adherend would still be close to the value computed in the calculations shown in Eqs. (5) and (6) for the adhesive in the liquid state if it were not for the development of stress concentrations. This conclusion follows from the highly localized nature of the attractive field of force causing adhesion. Since this attractive force is effective little more than the depth of one molecule in both the adhesive and the adherend, it will be unaffected by changes of state so long as allowance is made for any resulting alteration in the surface density or molecular orientation occurring at the joint interface (79,80). The former can be estimated from the change of density on solidification, but the latter may be difficult to compute, since reorientation effects could originate through a crystallization process starting from some nucleus not located in the interface. Internal stresses and stress concentrations usually develop on solidification of the adhesive, the most common cause being the difference in the thermal expansion coefficients of the adhesive and adherend. In many applications of adhesives this matching process is not readily done or is neglected because it is not critical. However, in general, the theoretical strength of the adhesive joint is considerably decreased by the development of internal stress concentrations.

Effects of internal stresses developed on solidification and of stress concentrations during applications of a joint have been given much attention; an excellent discussion of this area of research has been given by Sneddon (81). Photoelastic studies by Mylonas (82) and Mylonas and deBruyne (83) led to the conclusion that in a lap joint, poor wetting

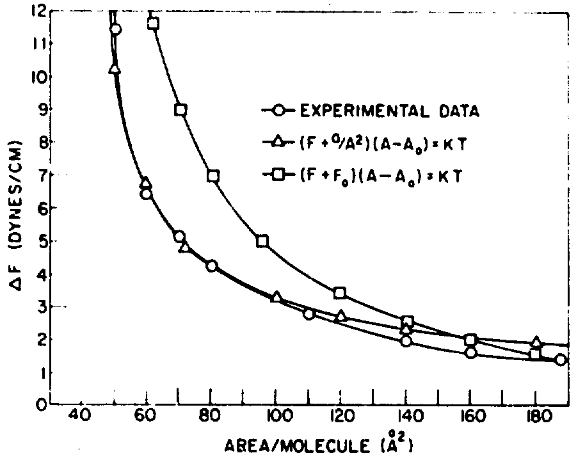


Fig. 21 - Force-area isotherms of bis-(1H, 1H-heptafluorobutyl)-3-methylglutarate adsorbed at the propylene carbonate-air interface

of the adherend tends to produce a greater stress concentration at the free surface of the adhesive where failure is most likely to be initiated. As the contact angles become large, the maximum stress concentration increases and moves toward the lineal boundary, where the adhesive and atmosphere make contact with the adherend, the stress concentration factor increasing from about 1.2 to 2.5. Griffith (84) had shown that failure of the adhesive may occur at a relatively small applied stress if there are bubbles, voids, inclusions, or surface defects; it occurs because stress concentrations result which are much higher than the mean stress applied across the specimen.

Griffith's conclusion is especially important when considered in terms of the probable effect of poor wetting on the development of air pockets at the adhesive-adherend interface. It has already been shown that if [illegible] = 0, the theoretical joint strength far exceeds the tensile strength of most adhesives. In practice, the theoretical joint strength is not attained; evidently, one major cause is the development of stress concentrations during solidification of the adhesive. When [illegible] = 0, there may be gas pockets formed at the adhesive-adherend interface around which stress concentrations can build up, for if the adhesive is too viscous when applied, it may never penetrate the accessible surface pores before polymerizing. Of course, this situation is aggravated if [illegible] ≠ 0.

In adhesives technology it is common practice to roughen the surface of each adherend, or "give it tooth," and so obtain a stronger joint. This practice can be justified theoretically with reservations by the following considerations. If gas pockets or voids in the surface depressions of the adherend are all nearly in the same plane and are not far apart (as on the upper adherend of Fig. 22), there may be crack propagation from one pocket to the next, and the joint may break as if it has a built-in "zipper." Therefore, if roughness must be accepted, the kind of roughness shown on the lower adherend would be preferable because crack propagation along a plane would be less probable (79,80).

An adequate theory of adhesive action should be able to explain poor as well as good adhesion; hence, a test of any theory is its ability to explain the properties of abhesives (79,80). "Abhesives" are films or coatings which are applied to one solid to prevent—or greatly decrease—the adhesion to another solid when brought into intimate contact with it. Abhesives are employed in molding, casting, or rolling operations; therefore, it is common

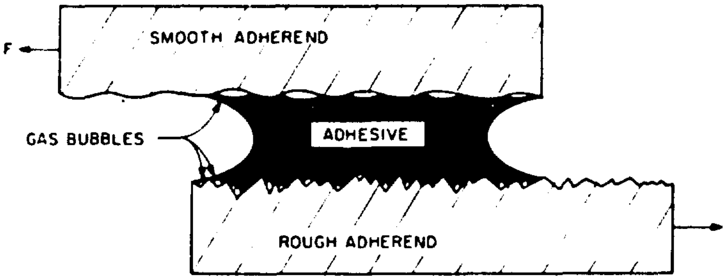


Fig. 22 - Effect of surface roughness on coplanarity of gas bubbles

to refer to the film as the parting, mold-release, or antistick agent. Examples of materials commonly used for such purposes are the polymethylsiloxanes, the high-molecular-weight fatty acids, amines, amides, and alcohols; various types of highly fluorinated fatty acids and alcohols; and polytetrafluoroethylene or films or copolymers of polytetrafluoroethylene and hexafluoropropylene deposited by coating the mold with an aqueous dispersion of the polymer, drying it, and finishing with a brief bake at a high temperature. Usually a condensed monolayer of the agent is sufficient to cause the optimum parting effect. Table 4 gives the values of γ_c of each of these films. Evidently, each abhesive coating converts the solid into a low-energy surface, and any liquid placed on such a coated surface will exhibit an equilibrium contact angle which will be larger as $\gamma_{LV} - \gamma_c$ increases. When θ is large enough, such poor adhesion results that the application of a modest external stress suffices for effective mold release. However, the excellent and easy parting action observed needs additional explanation.

It was pointed out earlier that the value of W_A for the various low-energy surfaces reported here exhibits a maximum variation of threefold in going from the least to the most adhesive materials. This range is much too small to explain the effectiveness and easy parting action caused by a film of a good abhesive. Note that the value of W_A is for a flat, nonporous, smooth surface. The roughness factor r of the uncoated surface of the mold could suffice to raise W_A by a factor of from 1.5 to 3 or more, depending on the surface finish; however, if the material to be molded is (or becomes) viscous rapidly during injection or application, poor wetting will cause pockets to be produced at the interface between the material molded and the abhesive, and thereby the adhesion will be greatly decreased through stress concentrations by some unknown fraction 1/g. Also, when $\theta > 30^\circ$, the resulting stress-concentration factor of from 1.2 to 2.5 at the abhesive-plastic interface acts to decrease adhesion accordingly. Therefore, the adhesional work per unit area of the apparent or envelope area at the molding interface will be $(r/g)W_A$. For the best abhesive action, the release agent should have the largest possible value of θ for the substances to be molded against it. The large values of θ encountered with the various types of organic liquids on such low-energy surfaces as those shown in Table 4 make it evident why these film-forming materials are so effective as abhesives. As a general proposition, any low-energy surface will be more effective as a release agent (or abhesive), the lower its value of γ_c or the lower W_A (79,80). It also can be concluded from the preceding discussion that the smoother the finish of the outer coating of the abhesive, and the lower the surface tension and viscosity of the material being molded (or the lower its contact angle with the adhesive), the greater will be the external stress required to cause the parting action.

Evidently, for optimum joint strength, it is essential to keep the contact angle between the liquid adhesive and the adherend as small as possible in order to minimize buildup of stress concentrations and to obtain good spreading into pores and cracks. In applying the liquid adhesive, its viscosity should be as low as possible to increase the rate of spreading and penetration before polymerization causes solidification. Maximum spreading and capillarity will be obtained with adhesives having the highest surface tensions compatible with obtaining a zero (or small) contact angle. When conditions of complete wetting and freedom from the formation at the interface of gas (or vacuum) pockets and occlusions prevail, adhesion will usually be ample, and joint failures generally will be cohesive. But because pores and cracks always exist in the surfaces of real solids, surface occlusions and pockets will always be formed to some extent on applying the adhesive; the resulting loss in joint strength can be so large as to allow a failure in adhesion to occur—as happens readily in the presence of an adsorbed parting agent. It is possible that the strongest joints obtainable in practice will be found when the surface tension of the adhesive is slightly less than the value of γ_c of the adherend. In other words, more may be gained by minimizing the tendency to form interfacial occlusions than by maximizing the specific adhesion W_A.

An adhesive with a very low γ_{LV} would seem to be advantageous for most adherends. Inasmuch as fluorination of a polymer lowers its liquid surface tension, Sharpe and Schonhorn (85) recently concluded that a highly fluorine-substituted polymer would be an all-purpose adhesive. As a matter of fact, some of the copolymers of tetrafluoroethylene and hexafluoroethylene have low melt viscosities and hence have been used for some years as adhesives for highly fluorinated plastics like polytetrafluoroethylenes. Unfortunately, as the surface tension of the liquid adhesive is made lower by fluorination, its cohesive strength (W_C) is also lowered, since $W_C = 2\gamma_{LV}$. Thus the strength of the solid is also lowered. If the adhesive is prepared as a thermosetting polymer, or becomes highly crystalline on solidifying, some cohesive strength is thereby gained. When the adherend is a highly fluorinated polymeric solid, its cohesive strength will usually not be so great as to necessitate use of an adhesive of great cohesive strength. But if the adherend is a plastic or other solid of high strength, the use of a low-strength adhesive is too limiting. Therefore, there are serious problems to be overcome in making any general-purpose adhesive from high fluorinated polymers.

There has been much discussion about the necessity for using adhesives capable of chemically combining with the adherend, but the energy of adsorption involved in the physical adsorption to the adherend of the adhesive molecules has been proved more than sufficient to form joints which are stronger than the cohesive strength of the solidified bulk adhesive. Chemical bonding may prove desirable in order to obtain greater heat, water, or chemical resistance, but it should not be necessary to increase the specific adhesion. However, it is usually a great advantage to be released from the very limiting requirement of finding an adhesive capable of chemically combining with the adherends.

CONCLUSIONS

This very condensed review of the surface properties of fluorochemicals has led to a number of generalizations which deserve a brief summation here.

1. The most nonwettable and nonadhesive solid is one whose surface consists of fully fluorinated aliphatic hydrocarbons, the composition of the outermost layer being made up of perfluoromethyl groups in closest packing.

2. Langmuir's principle of localized action, which he applied to conventional hydrocarbon monolayers many years ago, has proved true provided that ions or unbalanced dipoles near the surface are avoided.

3. Whereas the polar hydrophilic group of a "conventional" surface-active agent determines its solubility, ionizability, and adsorptivity, it is the hydrophobic portion of the molecule that determines the minimum surface energy it can impart to a liquid in which it is dissolved or to a solid surface on which it is adsorbed.

4. An analogous rule to the preceding one holds for the surface-active agents used in organic solvents which have perfluoroalkyl organophobic groups arranged in opposition to organophilic groups (such as hydrocarbon, ester, or chlorocarbon groups).

5. Perfluoroalkyl derivatives are the most surface active of all materials yet studied, whether relative to water or other liquid systems.

6. A great future is predicted for surface-active materials made from partially fluorinated compounds, and also for highly fluorine-substituted monomers, and polymers, especially for protective coatings.

7. The extreme surface properties of perfluoro aliphatic compounds arise from the extraordinarily weak field of force existing in the vicinity of covalently bonded fluorine atoms and their neighbors. Although this result agrees with the fact that fluorine has the lowest polarizability of the halogens, the fact that the field of force is so much weaker, even than that around the covalent hydrogen, deserves more investigation. Probably the explanation is in the values of the octapole moment or higher terms of the cohesive field of force rather than simply the polarizability. Another way of stating the case is that the local attractive fields of force giving rise to cohesive effects in perfluoromethane, the perfluoromethyl group, and in the perfluoromethylene group, are more like those of the inert gases than the fields of force around the CH_4,-CH_3, and -CH_2- groups, respectively.

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13 ABSTRACT

Research on the surface chemistry of fluorochemicals, including the related development of new fluorine-containing compounds, polymers, and surface treatments, has progressed to the stage where a review of the subject is appropriate. A report has been prepared in the hope that it will serve not only as a record of progress, but will also clarify much of the fundamental information that is available, and will serve as a guide for future investigations and applications.

With the advent of the highly fluorinated organic compounds, it has been possible to prepare surfaces having extremely low free surface energies, much lower than had previously been possible with hydrocarbon derivatives. Because of their low surface energies, fluorinated solids have the most nonwettable and nonadhesive surfaces known. It has been proved that only the outermost molecules of the surface of a solid need be highly fluorinated in order to achieve such low surface energies. In fact the most nonwetting surfaces studied to date were those covered with an adsorbed monolayer of closely packed perfluoro acids, with the perfluoromethyl ($-CF_3$) groups outermost.

It has likewise been found that surface-active agents containing perfluorocarbon terminal groups will lower the surface tension of water far below the values obtainable with hydrocarbon-type wetting agents. Certain fluorinated hydrocarbon derivatives have also been synthesized that show very high surface activity in a wide variety of organic liquids, the extent of surface activity being dependent upon the organophilic-organophobic balance in the fluorine-containing amphipathic molecule.

It is predicted that fluorine-containing monomers and fluorocarbon-substituted surface-active materials will find increasing application in polymers and plastics, as additives for liquids, and as protective coatings on solids.

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
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Polymers						
Surface properties						
Organic compounds						
Surface-active substances						
Surface tension						

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