

# Properties of Monolayers of $\omega$ -Monohalogenated Fatty Acids and Alcohols Adsorbed on Water

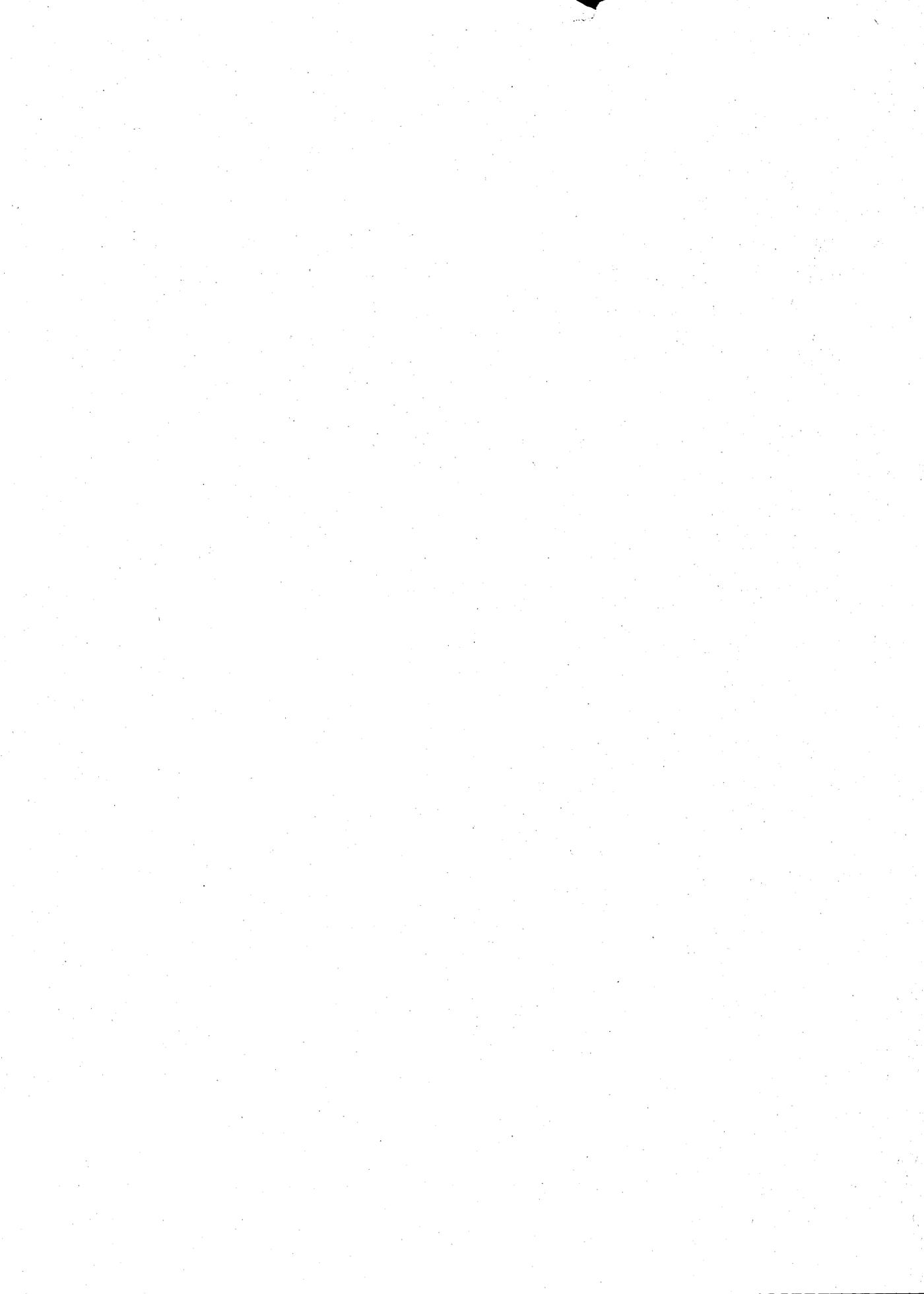
MARIANNE K. BERNETT, N. L. JARVIS, AND W. A. ZISMAN

*Surface Chemistry Branch  
Chemistry Division*

June 12, 1964



**U.S. NAVAL RESEARCH LABORATORY**  
Washington, D.C.



## CONTENTS

	Page
Abstract	ii
Problem Status	ii
Authorization	ii
INTRODUCTION	1
EXPERIMENTAL MATERIALS AND PROCEDURES	1
EXPERIMENTAL RESULTS	2
Force-vs-Area Relations for Monolayers on Distilled Water	2
Force-vs-Area Relations for Monolayers on Solutions of Polyvalent Metallic Ions	4
Effect of Temperature on Monolayer Stability	6
Electrical Properties of Monolayers	9
DISCUSSION	13
REFERENCES	15

## ABSTRACT

Relations between force and area, surface potential and area, and surface dipole moment and area for  $\omega$ -monohalogenated compounds spread as monolayers on aqueous substrates were studied at various pH values in the absence or presence of multivalent ions. The compounds investigated were  $\omega$ -monosubstituted bromo-, chloro-, and iodohexadecanoic acids, bromooctadecanoic acid, and fluorooctadecanol, along with their corresponding unsubstituted compounds. Mechanical properties of the substituted and unsubstituted alcohols were essentially the same and were not influenced by changes in pH or the presence of multivalent ions in the substrate. The halogenated hexadecanoic acids, however, gave unstable monolayers at all pH values on distilled and divalent ion-containing water at 20°C; it was necessary to add tetravalent ions and to lower the temperature to condense the monolayers to close-packed films. The change in surface potential of each substituted acid film was larger than that of any unsubstituted acid and showed the dipole orientation to be in the opposite direction. The vertical components of the apparent dipole moment were computed from the film potentials by use of the Helmholtz equation. Estimated values are given for the vertical components of the dipole contributed by the carbon-halogen bond. The results are discussed in terms of orientation and packing of the terminal polar groups and the resulting laterally induced polarization.

## PROBLEM STATUS

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

## AUTHORIZATION

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

Manuscript submitted March 26, 1964.

# PROPERTIES OF MONOLAYERS OF $\omega$ -MONOHALOGENATED FATTY ACIDS AND ALCOHOLS ADSORBED ON WATER

## INTRODUCTION

The physical properties of monolayers of fatty acids or alcohols on water are known to be greatly altered by the replacement of one or more of the "omega", i.e., terminal, hydrogen atoms by halogens. Various investigators (1-5) have reported that the presence of halogens on the omega carbon atom of a fatty acid or alcohol not only causes it to form more unstable monolayers but also to lower the electrostatic surface potential change  $\Delta V$  arising from monolayer adsorption. Gerovich and co-workers (1,2) determined that  $\Delta V$  for a condensed insoluble monolayer of 16-bromohexadecanoic acid, adsorbed at the air/water interface, can be as low as -0.87 volt, which is 1.26 volts less than that of the unbrominated acid under similar conditions. Davies (3) found that 16-bromohexadecanoic acid had a negative surface potential at both the oil/water and air/water interfaces. Fox (4) reported that a terminal  $-\text{CF}_3$  group on octadecanoic acid and octadecyl amine resulted in large and negative  $\Delta V$  values for condensed monolayers at the air/water interface. More recently Bernett and Zisman (5) found that condensed monolayers of a series of progressively fluorinated fatty acids would also give rise to large negative values of  $\Delta V$  at the air/water interface.

This report describes the mechanical and electrical properties of the following compounds adsorbed as monolayers at the air/water interface: the  $\omega$ -chloro-,  $\omega$ -bromo- and  $\omega$ -iodohexadecanoic acids,  $\omega$ -bromooctadecanoic acid, and  $\omega$ -fluorooctadecanol. The objective of the investigation was to examine the effect of each of the terminal halogens on the packing, orientation, stability, and surface potential of the monolayers spread on aqueous substrates at various hydrogen ion (pH) concentrations. From the changes in surface potential  $\Delta V$  it was proposed to determine the dipole contributions of each terminal methylene-halide group.

## EXPERIMENTAL MATERIALS AND PROCEDURES

Each organic acid and alcohol studied was a highly purified, white, crystalline solid. The n-hexadecanoic acid (m.p. 61.5°C) and n-octadecanoic acid (m.p. 69.5°C) were obtained from the Hormel Foundation, and the n-octadecanol (m.p. 59°C) from Lachat Chemicals, Inc. Pure specimens of 18-fluorooctadecanol (6) (m.p. 60.5°C) and 18-bromooctadecanoic acid (m.p. 72.0-73.0°C) were generously donated for this investigation by Prof. F. L. M. Pattison of the University of Western Ontario and by Dr. M. Stoll of Firmenich et Cie, Geneva, Switzerland, respectively. Pure 16-chlorohexadecanoic, 16-bromohexadecanoic, and 16-iodohexadecanoic acids (m.p. 61.0-61.5, 69.5-70.0, and 74.0-74.5°C, respectively) were prepared specially for this study by Fox and Price (7) of this Laboratory.

Spreading solutions of each polar compound in concentrations of  $5 \times 10^{-4}$  to  $7 \times 10^{-4}$  g/ml were prepared in n-hexane (Fisher grade "purified", freshly percolated through adsorptive columns of activated silica gel and alumina). Each solution was delivered dropwise to the clean water surface of the modified Langmuir-Adam film balance by a calibrated self-adjusting micropipet. The volume of solution was chosen to give a condensed film occupying an area from 200 to 240 cm<sup>2</sup>. The film balance used to measure the film pressure  $F$  vs the area per molecule  $A$  has been described in detail earlier (5).

It consisted of a shallow Pyrex glass trough with the rim lightly coated with paraffin, a paraffined mica float connected to the sides of the trough with end loops of thin polyethylene ribbon, and a Cenco duNuoy torsion head sensitive to a film pressure change of 0.05 dynes/cm. Surface potential measurements were made using essentially the same vibrating condenser apparatus described previously (5,8); this device was sensitive to a change of several millivolts (mv).

Aqueous substrates used in these experiments were prepared from water distilled once through a tin-lined still and then twice through an all-quartz still. The water thus produced had a conductivity of  $1 \times 10^{-6}$  ohm<sup>-1</sup> and a pH of 5.8 when in equilibrium at 20°C with atmospheric carbon dioxide. Variations in pH were made by appropriate additions of either C.P. grade sulfuric acid or potassium hydroxide. The source of bivalent metallic ions for certain aqueous substrates was C.P. calcium chloride, and the source of tetravalent ions was C.P. thorium nitrate. The pH of the latter at the concentration of  $5 \times 10^{-4}$  M was 3.4 at 20°C and 3.3 at 11°C. All film balance experiments were made at either  $20 \pm 0.2^\circ\text{C}$  or  $11 \pm 1^\circ\text{C}$ .

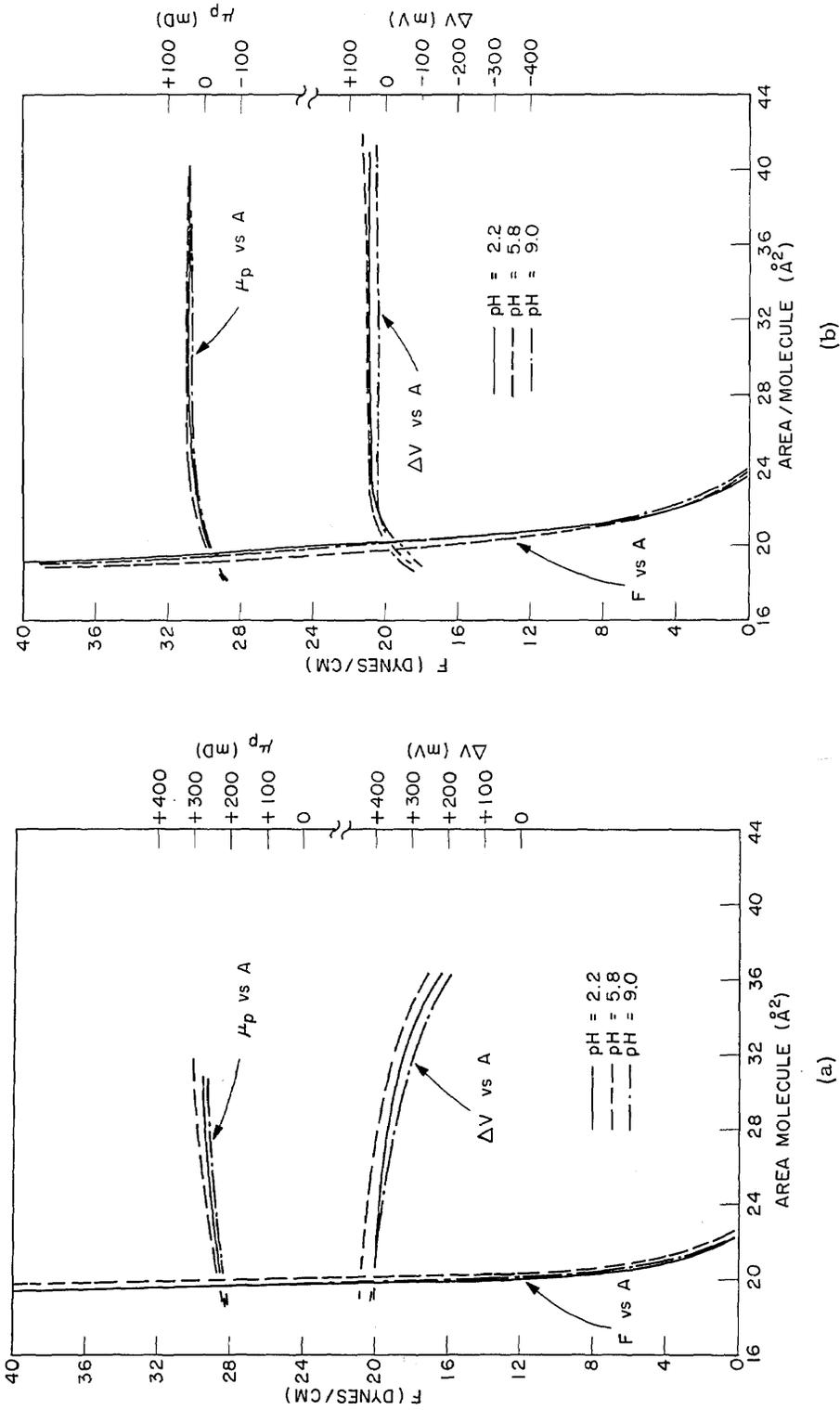
## EXPERIMENTAL RESULTS

### Force-vs-Area Relations for Monolayers on Distilled Water

Both octadecanol and 18-fluorooctadecanol formed stable insoluble monolayers on distilled water at three different pH values at 20°C (Fig. 1). These monolayers behaved reversibly with film pressure  $F$  up to 35 dynes/cm and formed very condensed films having limiting areas per molecule  $A_0$  from 20.2 to 21.0 Å<sup>2</sup>, depending upon the pH. The steep linear portions of the  $F$ -vs- $A$  curves above 12 dynes/cm indicated that both monolayers were solid-condensed at such film pressures. At lower film pressures the fluoroalcohol was somewhat more expanded than the octadecanol monolayer, which indicated that there was some repulsion between the terminal -CH<sub>2</sub>F groups. An examination of Stuart-Briegleb molecular ball models (Fig. 2) revealed that the substitution of a fluorine for a hydrogen atom on the terminal carbon atom did not cause a significant change in the molecular cross-section area. Therefore, the difference in size could not have caused the observed film expansion. The cause must be found elsewhere and will be discussed below. Varying the pH of the substrate over the range used had no significant influence on the  $F$ -vs- $A$  curve of the alcohol monolayers; this result is to be expected since the polar OH group was not ionizable under such conditions.

Monolayers of terminally chlorinated, brominated, or iodinated hexadecanoic acids collapsed at film pressures of only 2.0 to 5.5 dynes/cm on distilled water at all pH values. This instability may have been caused by either steric hindrance to molecular close packing caused by the presence of these halogen atoms, which are considerably larger than hydrogen, or by repulsive forces acting between the similarly oriented terminal electrostatic dipoles. Figure 2, which gives the respective cross-sectional areas of  $\omega$ -halogenated hydrocarbon chains (assuming the terminal carbon group does not rotate upon its axis), shows that the steric factor could be significant only with the  $\omega$ -iodo and  $\omega$ -bromo acids, and even then it could cause no more than a 10-percent increase in  $A_0$ . Hence, the observed instability in the acid monolayers must have been due to the repulsion between terminal dipoles; the same mechanism may have caused the expansion of the fluorooctadecanol monolayer mentioned before.

Gerovich, Frumkin, and Vargin (2) also found that monomolecular films of 16-bromohexadecanoic acid were remarkably unstable, and they attributed the instability to the repulsive forces acting between similarly oriented C-Br dipoles. They reported obtaining stable films of 16-bromohexadecanoic acid by mixing it with various concentrations of hexadecanoic acid. They also suggested that more stable films could be obtained in the presence of polyvalent cations, but they did not use this approach in their



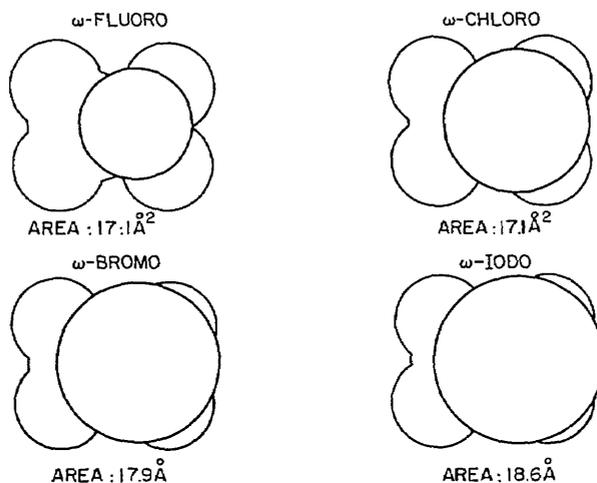


Fig. 2 - End views of terminally halogenated hydrocarbon chains

experiments, presumably because too little was known at that time about the structure of fatty acid films on neutral and alkaline solutions in the presence of polyvalent cations.

In our experiments with 16-iodohexadecanoic acid, it was found that the presence of iodide ions ( $I^-$ ) in the aqueous substrate (as 0.01N HI) did not alter the F-vs-A or  $\Delta V$ -vs-A relations. If hydrolysis of the C-I bond had taken place, the presence of the common iodide ion should have had a suppressive effect and there would have resulted a somewhat different monolayer behavior. Evidence that the observed film instability did not arise from the hydrolysis of the carbon-halogen bond can also be found in the literature. In his studies on monolayers of both 16-bromohexadecanoic acid and 16-hydroxyhexadecanoic acid on 1N NaOH, Davies (3) assumed that the molecules of each compound could not be compressed above 7 dynes/cm and that they tended to lie flat at the air/water interface up to those pressures. He obtained different surface potential values for each compound at equivalent areas per molecule, which indicated that the omega C-Br bond had not been cleaved by hydrolysis.

#### Force-vs-Area Relations for Monolayers on Solutions of Polyvalent Metallic Ions

It was our belief that the condensing effect of polyvalent ions on adsorbed monolayers of the higher fatty acids (9-12) could be used to stabilize and condense the monolayers of the terminally halogenated fatty acids. Each of the halogenated derivatives was therefore spread on  $10^{-2}$  M  $CaCl_2$  aqueous solutions at pH 2.2, 5.8, and 9.0. As expected, the F-vs-A relations for octadecanol and 18-fluorooctadecanol monolayers on this substrate were identical with those obtained on distilled water. Although the stability of the halogenated acid monolayers was somewhat improved on the  $CaCl_2$  solutions, they were still too unstable (even at pH 9.0) to give reliable F-vs-A relations.

An increase in the length of the hydrocarbon chain usually increases the stability of fatty acid monolayers. Accordingly, octadecanoic and 18-bromooctadecanoic acids were spread on  $10^{-2}$  M  $CaCl_2$  solutions at pH 3.9, 6.2, and 8.5 (Fig. 3). The F-vs-A relations obtained for octadecanoic acid agreed well with the results of Spink and Sanders (12). The monolayer of 18-bromooctadecanoic acid was stable and reproducible at pH 6.2; at pH 8.5 it was close packed with a value of  $20.4 \text{ \AA}^2$  for  $A_0$ , the same as that of the

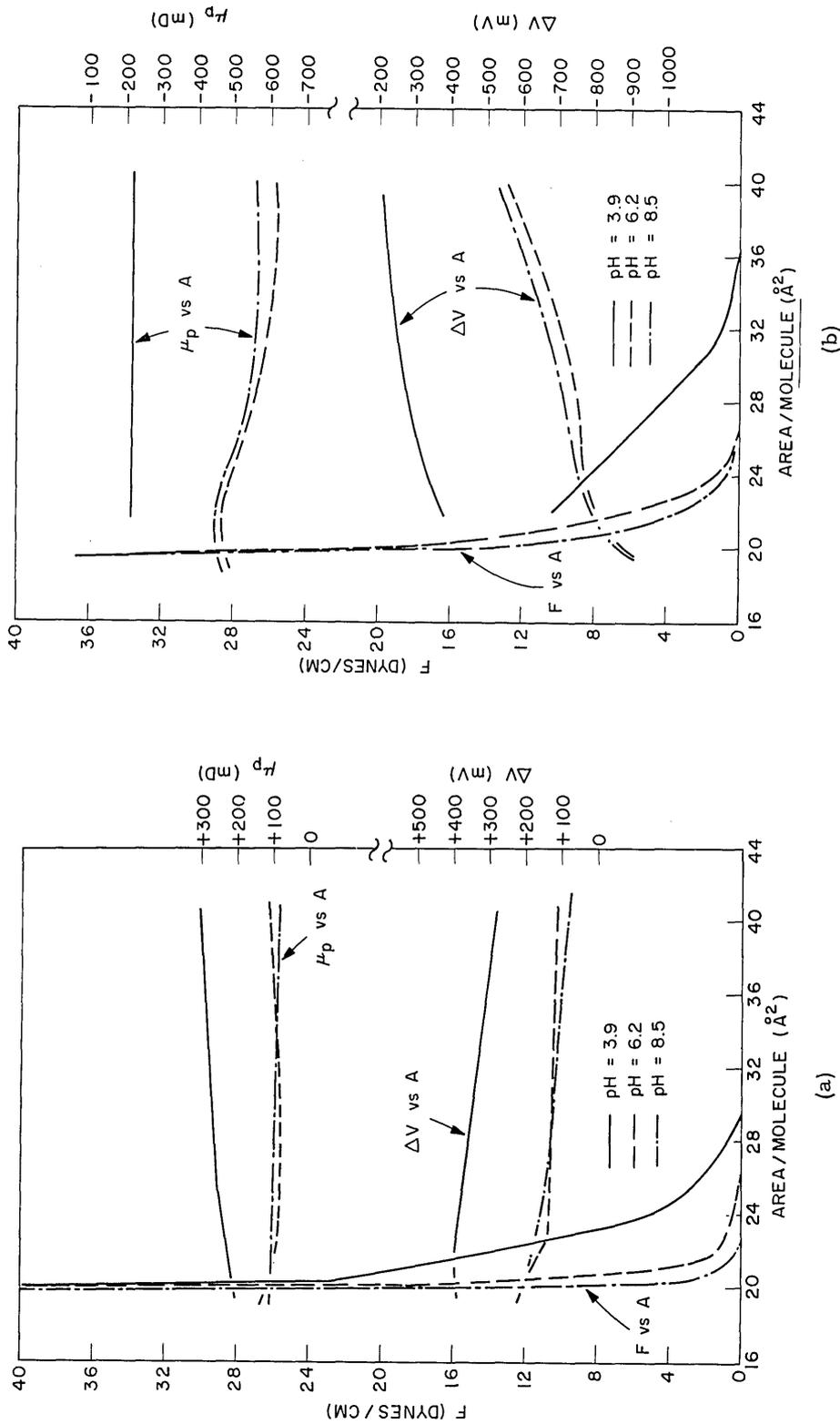


Fig. 3 - Properties of monolayers of (a) octadecanoic acid, and (b) 18-bromooctadecanoic acid spread at 20°C on substrate containing 10<sup>-2</sup> M CaCl<sub>2</sub>

unbrominated acid. Hence, increasing the length of the hydrocarbon chain from 16 to 18 carbon atoms increased the intermolecular cohesion sufficiently to stabilize the monolayer at the alkaline pH value in the presence of divalent calcium ions. In a recent study of monolayers of progressively fluorinated fatty acids, each of which contained a terminal  $-CF_3$  group (5), an 18-carbon aliphatic chain was the shortest which permitted formation of stable monomolecular films on water at  $20^\circ C$ .

Since the condensing effect of divalent ions in the aqueous substrate was not enough to overcome the large repulsive forces caused by terminal halogenation in the hexadecanoic acid monolayers, tetravalent thorium ions were added to distilled water to try to stabilize each monolayer. Many years ago Zisman (10) had shown that thorium salt solutions were able to solidify monolayers of straight-chain acids even at the oil/water interface and to condense branched-chain aliphatic acids having 10 or more carbon atoms per molecule. Abramson and Ottewill (13), in a recent study of hydrolysis in thorium salt solutions, found that a concentration of  $5 \times 10^{-5} M$  thorium nitrate was sufficient to completely condense monolayers of myristic acid. Therefore, a substrate containing  $5 \times 10^{-4} M$  thorium nitrate at the equilibrium pH value of 3.4 was used to determine the ability of tetravalent thorium ions to stabilize the monolayers of the  $\omega$ -halogenated hexadecanoic acids. As would be expected, the F-vs-A relations for octadecanol or 18-fluorooctadecanol on this substrate were not significantly different from those obtained on distilled water or on  $10^{-2} M CaCl_2$ . The 18-fluorooctadecanol was again slightly more expanded than the octadecanol at lower film pressures and appeared to collapse at a somewhat lower area per molecule. Figure 4 shows the F-vs-A relations of hexadecanoic acid and its  $\omega$ -halogenated derivatives on the thorium salt substrate. All of the F-vs-A curves have the same shape and approximately the same value of  $A_0$  (28 to  $29 \text{ \AA}^2$ ). Whereas the monolayer of hexadecanoic acid supported film pressures up to 35 dynes/cm, the chloro-, bromo-, and iodo-hexadecanoic acid monolayers each collapsed at a lower film pressure (16, 12, and 8 dynes/cm, respectively). It should be noted that all  $A_0$  values are still 60 percent greater than the cross-sectional areas per molecule determined from molecular models (Fig. 2). Thus, these  $\omega$ -halogenated hexadecanoic acid monolayers were condensed and stabilized by the presence of  $Th^{+4}$  ions in the aqueous substrate, even though they had not been condensed to the closest possible packing.

#### Effect of Temperature on Monolayer Stability

It is well known that lowering the temperature will condense monolayers of paraffin derivatives (14-16). Figure 5 gives the F-vs-A relations of these acids on the thorium nitrate solutions at  $11^\circ C$  and shows that the monolayers remained stable at higher film pressures with lower values of  $A_0$  (19 to  $20 \text{ \AA}^2$ ) than at  $20^\circ C$ , i.e.,  $A_0$  approached the value for closest packing given in Fig. 2. The F-vs-A curves for octadecanol and 18-fluorooctadecanol in Fig. 6 show that whereas the monolayer of fluorinated alcohol behaved on this substrate very much like on other substrates, octadecanol was more expanded by about  $1 \text{ \AA}^2/\text{molecule}$  at lower film pressures.

Since decreasing the temperature from  $20^\circ C$  to  $11^\circ C$  effected the desired condensation and stabilization of the  $\omega$ -halogenated hexadecanoic acid monolayers in the presence of thorium nitrate, F-vs-A curves were also determined at  $11^\circ C$  for each of these compounds on  $10^{-2} M CaCl_2$  at a pH of 1.8, as well as at a pH of 10.0. At pH 1.8 the F-vs-A curves were nearly identical with those observed on acid substrates at  $20^\circ C$ , while at pH 10.0 significant differences were found. F-vs-A curves are given in Fig. 7 for those monolayers exhibiting changes in film properties, as the temperature was reduced from  $20^\circ$  to  $11^\circ C$ , at a pH of 10.0. At  $20^\circ C$  and pH 9.0 the 16-bromo- and 16-iodo-acids were too unstable to give reliable data; at  $11^\circ C$  and pH 10.0, however, they formed close-packed reproducible films which were stable up to pressures of 10 dynes/cm. The areas per molecule for the  $\omega$ -halogenated hexadecanoic acids at collapse pressure were in

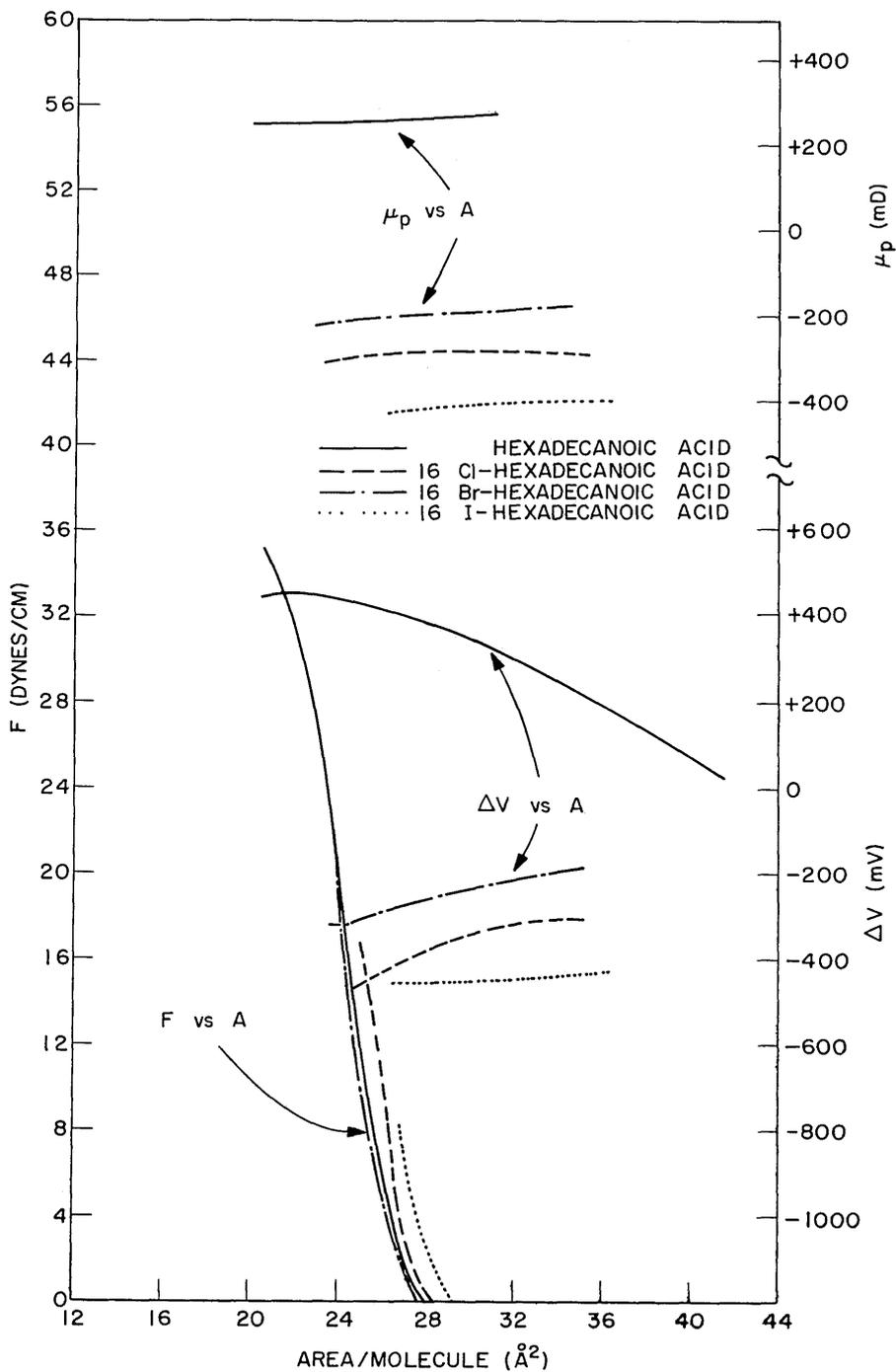


Fig. 4 - Properties of monolayers of 16-halogen hexadecanoic acids spread at 20°C on a substrate of  $5 \times 10^{-4}$  M  $\text{Th}(\text{NO}_3)_4$  and at a pH of 3.4

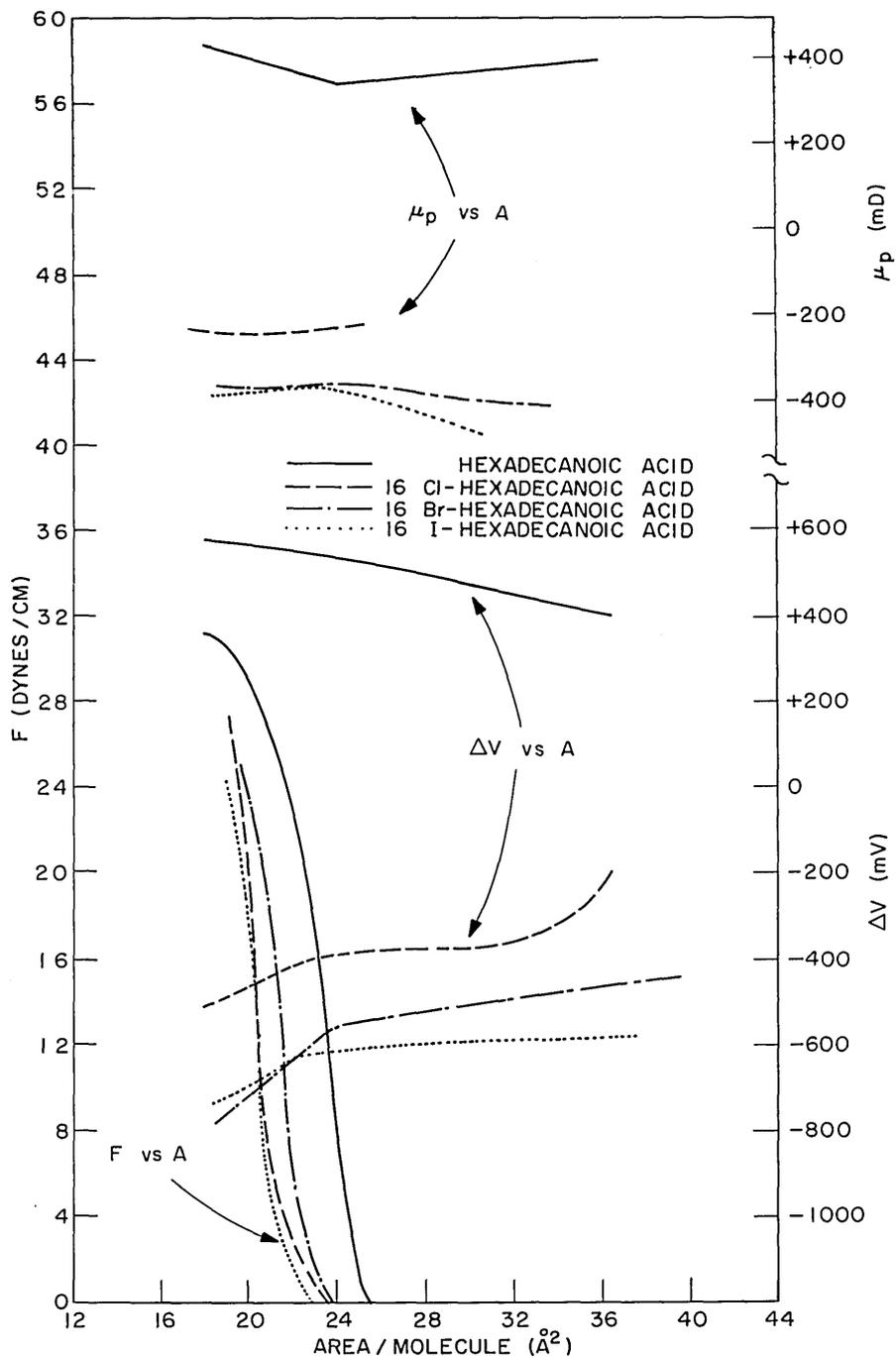


Fig. 5 - Properties of monolayers of 16-halogen hexadecanoic acids spread at 11°C on a substrate of  $5 \times 10^{-4}$  M  $\text{Th}(\text{NO}_3)_4$  and at a pH of 3.3

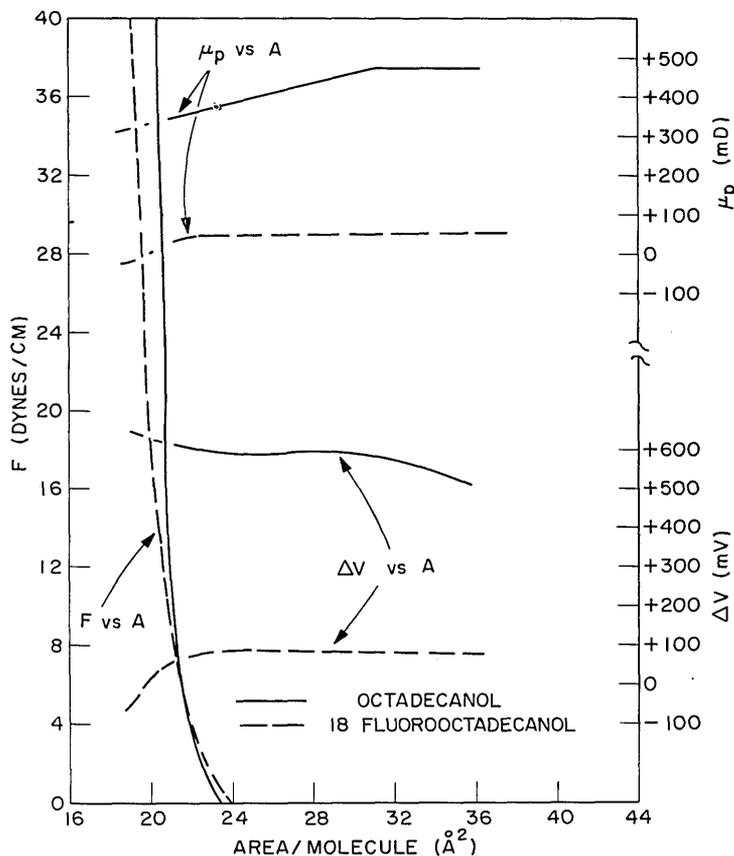


Fig. 6. - Properties of monolayers of octadecanols spread at  $11^{\circ}\text{C}$  on a substrate of  $5 \times 10^{-4}$  M  $\text{Th}(\text{NO}_3)_4$  and at a pH of 3.3

each case approximately  $19 \text{ \AA}^2$ , which is comparable to the values obtained on the thorium nitrate substrate at  $11^{\circ}\text{C}$ . Thus the divalent calcium ions were ineffective in condensing monolayers of these halogenated acids at  $20^{\circ}\text{C}$ , but became effective when the temperature was lowered to  $11^{\circ}\text{C}$ .

#### Electrical Properties of Monolayers

The difference  $\Delta V$  in the electrostatic potential between a clean water surface and the surface covered by a monolayer is known to be dependent upon the structure of the adsorbed molecules and, with adsorbed acidic or basic compounds, upon the pH and salt content of the aqueous substrate as well (12,14,17,18). The  $\Delta V$ -vs- $A$  relations for each of the compounds studied have been plotted, along with the corresponding  $F$ -vs- $A$  curves, in Figs. 1 and 3 through 7. Values of  $\Delta V$  are given along the right-hand vertical scale in each figure. Values of  $\Delta V$  for octadecanol and 18-fluorooctadecanol monolayers were independent of substrate pH or composition, except for octadecanol on  $5 \times 10^{-4}$  M  $\text{Th}(\text{NO}_3)_4$  at  $11^{\circ}\text{C}$  (Fig. 6), where  $\Delta V$  was 200 mv higher than on any of the other substrates. The  $\Delta V$ -vs- $A$  curves for hexadecanoic and octadecanoic acids varied with the pH and the salt content of the substrate, the effect of varying pH alone being in good agreement with the results of Spink and Sanders (12,17).  $\Delta V$  was always positive for the unsubstituted acid or alcohol monolayers and, as expected,  $\Delta V$  was always negative for each  $\omega$ -halogenated

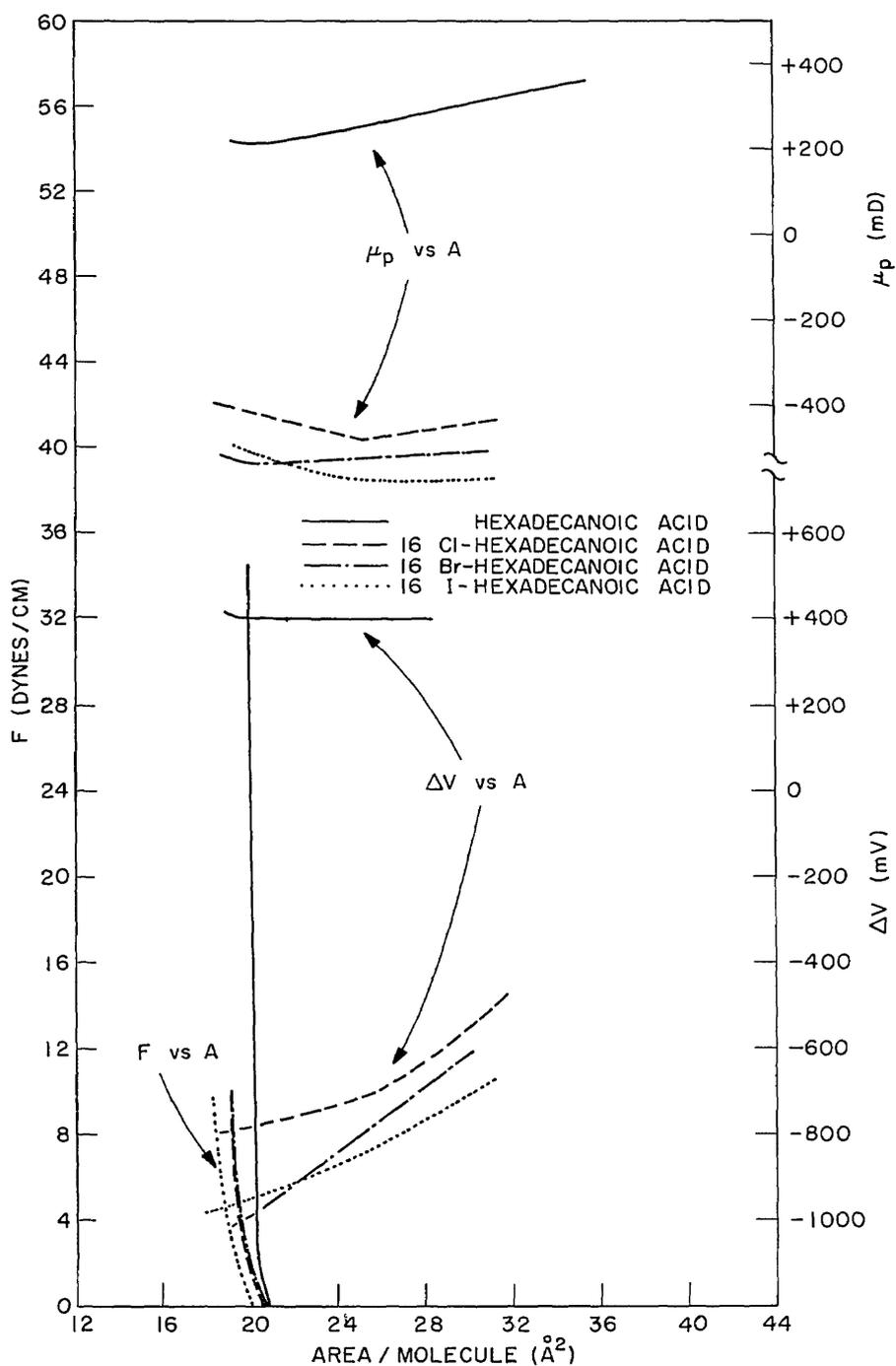


Fig. 7 - Properties of monolayers of 16-halogen hexadecanoic acids spread at  $11^\circ\text{C}$  on a substrate of  $10^{-2}$  M  $\text{CaCl}_2$  and at a pH of 10.0

compound; at molecular close packing it was at least 1000 mv less for the halogenated than for the unhalogenated acid.

The normal component of the molecular dipole moment  $\mu_p$  was calculated from  $\Delta V$  by using the classic equation of Helmholtz,

$$\Delta V = 4\pi\eta\mu_p, \quad (1)$$

where  $\eta$  is the number of adsorbed polar molecules per  $\text{cm}^2$ . Resulting values of  $\mu_p$  have been plotted against  $A$  along the right-hand vertical scale of each figure. It has long been realized that the value of  $\mu_p$  so calculated is the resultant of several contributing dipoles in, or associated with, each molecule of the adsorbed film. These dipoles are: (a) the permanent dipole in the adsorbed organic molecule, (b) the resultant arising from the reorientation of the surface water dipoles in the immediate vicinity of the polar hydrophilic group of the adsorbed organic molecule, and (c) the contribution of any ionic double layer present at the water/air interface. As is well known, contribution (a) can be considered the sum of vector contributions from each bonded pair of atoms in the organic molecule. In computing (a) it will be assumed (as is usual) that the net contribution from each unsubstituted polymethylene chain is zero; hence, the organic molecule contributes two moments, one due to the terminal polar  $-\text{CH}_2\text{X}$  group (where X is a halogen atom) at one end of the paraffin chain, and the other due to the hydrophilic polar group at the other end. It can also be assumed that contribution (b) and (c) do not alter the  $-\text{CH}_2\text{X}$  dipole located at the outermost end of the paraffin chain because of its distance from the surface of the water substrate. Since at present it is impossible to separate the contributions of the hydrophilic polar group located in the water/air interface (from a), the water layer polarized by it from (b), and the adjacent ionic double layer from (c), it is usual to combine the three terms into the single term  $\mu_{(o)p}$ . Consequently,  $\mu_p$  for the unhalogenated adsorbed molecule can be expressed as

$$\mu_p = \mu_{(o)p} + \mu_{(\text{CH}_3)_p}, \quad (2)$$

where  $\mu_{(\text{CH}_3)_p}$  is the contribution of the terminal  $\text{CH}_3$  group. When the adsorbed molecule has a halogen atom X on the  $\omega$  carbon atom, then

$$\mu_p = \mu_{(o)p} + \mu_{(\text{CH}_2\text{X})_p}. \quad (3)$$

From the assumptions made, it follows that  $\mu_{(o)p}$  at a given value of  $\eta$  should be the same for the halogenated and unhalogenated adsorbed compounds.

In Table 1 values of  $\Delta V$  are given for closely packed monolayers, at areas per molecule (second column) from  $19.5$  to  $20\text{A}^2$ , of each of the compounds studied in the present investigation. Values of  $\Delta V$  for monolayers of both  $\omega$ -substituted and nonsubstituted hexadecanoic acids and octadecanols were obtained on  $5 \times 10^{-4}\text{M}$   $\text{Th}(\text{NO}_3)_4$  at  $11^\circ\text{C}$  and a pH of 3.3, while those for octadecanoic acid and 18-bromooctadecanoic acid were measured on  $10^{-2}\text{M}$   $\text{CaCl}_2$  at  $20^\circ\text{C}$  and a pH of 8.5. From the measured value of  $\Delta V$  (given in the third column) the corresponding value of  $\mu_p$  was calculated from Eq. (1) for each compound and is given in the fourth column. The value of  $\mu_{(o)p}$  (given in the fifth column) for each unhalogenated compound was calculated from Eq. (2) by using  $-0.3$  Debye (D) as the vertical component of the dipole moment of the terminal methyl group,  $\mu_{(\text{CH}_3)_p}$ , on the hydrocarbon chain, the terminal C-H bond being directed at an angle of  $54^\circ 44'$  from the water surface. The best literature value for the dipole moment of the terminal  $-\text{CH}_3$  group is approximately  $0.4$  Debye, with the polarity being  $\text{C}^+ - \text{H}^-$  (19), the same polarity as the carbon-halogen bond. Equation (3) was then used to compute the value given in the sixth column for each halogenated compound by assuming that  $\mu_{(o)p}$  was the same for the halogenated and unhalogenated compounds.

Table 1  
Electrical Properties of Fatty Acids, Fatty Alcohols, and  
Their  $\omega$ -Monohalogenated Derivatives

Compound	Area/ Molecule ( $\text{\AA}^2$ )	$\Delta V$ (mv)	$\mu_p$ (D)	$\mu_{(O)_P}$ (Calc. from Eq. 2)* (D)	$\mu_{(CH_2X)_P}$ (Calc. from Eq. 3) (D)	$\mu_{(CH_2X)_P}$ (Calc. by Davies' method) (D)
On Aqueous Substrate: $5 \times 10^{-4} M$ $\text{Th}(\text{NO}_3)_4$ at pH 3.3 and $11^\circ \text{C}$						
Hexadecanoic acid	19.5	+565	+0.29	+0.59	--	--
16-Chlorohexadecanoic acid	19.5	-480	-0.25	+0.59	-0.84	-0.54
16-Bromohexadecanoic acid	19.5	-705	-0.37	+0.59	-0.96	-0.66
16-Iodohexadecanoic acid	19.5	-730	-0.38	+0.59	-0.97	-0.67
Octadecanol	20.0	+620	+0.35	+0.65	--	--
18-Fluorooctadecanol	19.5	-55	-0.03	+0.65	-0.68	-0.38
On Aqueous Substrate: $1 \times 10^{-2} M$ $\text{CaCl}_2$ at pH 8.5 and $20^\circ \text{C}$						
Octadecanoic acid	19.8	+200	+0.10	+0.40	--	--
18-Bromooctadecanoic acid	19.8	-910	-0.48	+0.40	-0.88	-0.58

\*  $\mu_{(CH_3)_P} = -0.30$  D from literature dipole moment  $\text{C}^+ - \text{H}^-$ .

The values of  $\mu_{(CH_2X)_P}$  ranged from -0.68 to -0.97 Debye in going through the series of halogens from fluorine to iodine. In Fig. 8 the values of  $\mu_{(CH_2X)_P}$  are plotted against the covalent radii of the halogen atoms, and a linear graph results. This should be expected since the polarizability of an atom increases with the radius of its outer electron shell. It will be noted that the value of  $\mu_{(CH_2X)_P}$  for  $X = \text{F}$  was determined using a terminally halogenated alcohol, whereas for the other halogens the calculation was based on measurements on the terminally halogenated acids. Nevertheless, the deductions made should be valid because of the large number of carbon atoms separating the polar hydrophilic group and the polar  $\text{CH}_2\text{X}$  group. If one plots in Fig. 8 the value of  $\mu_{(CH_2X)_P}$  for the limiting case where  $X$  is replaced by a hydrogen atom (0.3 Debye), the graphical point falls close to the extrapolated straight-line plot defined by the halogen family.

Surface potential data for terminally halogenated derivatives have been treated in a somewhat different manner by both Gerovich (2) and Davies (16). They used the Helmholtz relationship to calculate  $\mu_p$  for the halogenated and nonhalogenated compounds and then determined the values of each  $\mu_{(CH_2X)_P}$  from the amount that each of the halogens reduced  $\mu_p$ . The last column in Table 1 shows the values for  $\mu_{(CH_2X)_P}$  obtained by their calculations. It can be seen that their results for the value of  $\mu_{(CH_3)_P}$  are lower by 0.3D than those obtained by our calculations. In other words, they have assumed that the contribution of the terminal  $-\text{CH}_3$  group can be neglected. Hence, except for the difference in the value assigned to  $\mu_{(CH_3)_P}$ , the results of Gerovich and co-workers (2) for 16-bromohexadecanoic acid agree well with ours.

With an angle of  $54^{\circ}44'$  between the terminal C-X bond and the water surface, the apparent dipole moment of each  $-\text{CH}_2\text{X}$  group, as determined from  $\Delta V$  measurements, would be  $\mu_{(\text{CH}_2\text{X})_p} / \sin 54^{\circ}44'$ . In the third column of Table 2 the dipole moments obtained in this manner for each terminal halogen bond are compared with the values (fourth column) reported in the literature for the same dipoles (20,21). It is apparent that our values are only about 50 percent of the literature values, which were obtained from measurements on appropriate halogenated compounds in the gaseous state, or in dilute solution in a nonpolar solvent. The conclusion is unavoidable that the close packing of the similarly oriented polar molecules in the condensed monolayer caused mutual, lateral, induced polarization and thus lowered by 50 percent the contribution of the terminal  $-\text{CH}_2\text{X}$  groups to the dipole moments.

## DISCUSSION

The results of this investigation demonstrate that the replacement of a hydrogen atom on the terminal carbon atom of a fatty acid or alcohol by a halogen atom will greatly reduce the stability of closely packed monolayers of the compounds. It was also found that the effect of the substituted chloro-, bromo-, and iodo-atoms on monolayer stability is of approximately the same magnitude. Unlike the effect of  $\omega$ -chloro-, -bromo-, and -iodo-substitution on fatty acid monolayers, the substitution of fluorine on the  $\omega$  carbon of a fatty alcohol did not cause noticeable monolayer instability.

If the instability of the  $\omega$ -halogenated hexadecanoic acid monolayers arose from steric hindrance to close packing due to the larger diameter of the terminal halogen atom as compared to hydrogen, one would expect the 16-iodohexadecanoic acid monolayer

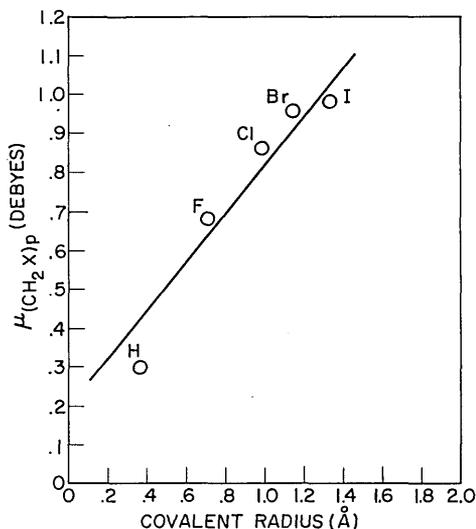


Fig. 8 - Relation between perpendicular dipole moment of methylene-halogen group and the covalent radius of its respective halogen atom

Table 2  
Comparison of Observed Values of Dipole Moments for  
 $\text{CH}_2\text{X}$  Group with Literature Values

Compound	$\omega$ Terminal Group	Values of $\mu_{\text{CH}_2\text{X}}$ (D)	
		$\mu_{(\text{CH}_2\text{X})_p} / \sin 54^{\circ}44'$	Literature (20,21)
18-Fluorooctadecanol	$-\text{CH}_2\text{F}$	0.80	1.9 to 2.1
16-Chlorohexadecanoic acid	$-\text{CH}_2\text{Cl}$	1.02	1.8 to 2.2
16-Bromohexadecanoic acid	$-\text{CH}_2\text{Br}$	1.15	1.9 to 2.2
18-Bromooctadecanoic acid	$-\text{CH}_2\text{Br}$	1.07	1.9 to 2.2
16-Iodohexadecanoic acid	$-\text{CH}_2\text{I}$	1.16	1.8 to 2.0

to be the most expanded and to collapse at lower film pressures than the bromo- and chloro-derivatives. However, if the disruptive influence was caused by an electrostatic repulsion between the large dipole moments of the terminal  $-\text{CH}_2\text{X}$  groups in the neighboring adsorbed molecules, then each of the 16-halogen hexadecanoic acids should have roughly the same monolayer stability, for the literature values of the  $-\text{CH}_2\text{X}$  bond dipole moments are approximately the same (Table 2). All of the F-vs-A data presented in this report strongly suggest that the monolayer instability arose primarily from mutual repulsion between the terminal dipole moments and not from steric hindrance related to the size of the halogen atoms. It was also shown in this investigation that the instability of the monolayers of terminally halogenated hexadecanoic acids could be overcome by decreasing the temperature of the system and by adding multivalent thorium or calcium ions to the aqueous substrate in order to take advantage of the condensing effect arising from their reaction with the adsorbed acid molecules.

Monohalogenation of the  $\omega$  carbon atoms also caused marked changes in the surface potential difference  $\Delta V$  of condensed monolayers of fatty acids and alcohols adsorbed on water. Substitution of chloro-, bromo-, or iodo- for a terminal hydrogen atom in hexadecanoic acid was found to decrease  $\Delta V$  by 1100 to 1300 mv in a close-packed monolayer. However, the change in  $\Delta V$  caused by replacement of the  $\omega$  hydrogen in octadecanol by fluorine was only 675 mv, appreciably less than the change caused by the substitution of the other halogens on hexadecanoic acid. From the literature values of the C-F dipole moment, which is equivalent to the dipole moment of the  $-\text{CH}_2\text{F}$  group when obtained from a paraffin compound (21), one would expect the decrease of  $\Delta V$  to be as large as for the other halogens. The reason that the values of  $\Delta V$  are not the same for each halogen may be that the dipole moment of each carbon-halogen bond in a closely packed monolayer is modified to a different extent by mutual lateral polarization. This possibility is reinforced by Fig. 8 which shows that the perpendicular component of the apparent dipole moment  $\mu_{(\text{CH}_2\text{X})\text{p}}$  varies with the covalent radius (or polarizability) of the halogen atom.

The term  $\mu_{(\text{o})\text{p}}$  used in this report for the contribution of the polar adsorbing group to the molecular dipole moment is analogous to the term  $\mu_{(\text{COOH})\text{aq}}$  used previously by Bennett and Zisman (5). The values reported here for  $\mu_{(\text{o})\text{p}}$  do not agree with those determined previously (5) because here we have assumed a different polarity for the dipole moment of the terminal  $-\text{CH}_3$  group. Bennett and Zisman used a value of 0.3 Debye for the vertical component of the  $-\text{CH}_3$  dipole moment, assuming a bond polarity of  $\text{C}^-\text{H}^+$ . In the present study a value of 0.3 Debye was also used, but we assumed the reverse polarity,  $\text{C}^+\text{H}^-$ ; this was done because values obtained by theoretical and spectroscopic methods (19) indicate that the true polarity of the C-H bond in a saturated aliphatic compound is  $\text{C}^+\text{H}^-$ , giving the C-H bond the same polarity as the C-X bonds.

## REFERENCES

1. Gerovich, M., and Frumkin, A., *J. Chem. Phys.* 4:624 (1936)
2. Gerovich, M., Frumkin, A., and Vargin, D., *J. Chem. Phys.* 6:906 (1938)
3. Davies, J.T., *Trans. Faraday Soc.* 49:949 (1953)
4. Fox, H.W., *J. Phys. Chem.* 61:1058 (1957)
5. Bennett, M.K., and Zisman, W.A., *J. Phys. Chem.* 67:1534 (1963)
6. Pattison, F.L.M., Howell, W.C., McNamara, A.J., Schneider, J.C., and Walker, J.F., *J. Org. Chem.* 21:739 (1956)
7. Fox, R.B., and Price, T., *J. Chem. Eng. Data* 8:612 (1963)
8. Zisman, W.A., *Rev. Sci. Instr.* 3:367 (1932)
9. Langmuir, I., and Schaefer, V.J., *J. Am. Chem. Soc.* 58:284 (1936); 59:2400 (1937)
10. Zisman, W.A., *J. Chem. Phys.* 9:534 (1941)
11. Wolstenholme, G.A., and Schulman, J.H., *Trans. Faraday Soc.* 46:475 (1950)
12. Spink, J.A., and Sanders, J.V., *Trans. Faraday Soc.* 51:1154 (1955)
13. Abramson, M.B., and Ottewill, R.H., *J. Colloid Sci.* 17:883 (1962)
14. Adam, N.K., "The Physics and Chemistry of Surfaces," London:Oxford University Press, pp 59-63, 72-74 (1941)
15. Harkins, W.D., "The Physical Chemistry of Surface Films," New York:Reinhold Publishing Corp., pp 111-112 (1952)
16. Davies, J.T., and Rideal, E.K., "Interfacial Phenomena," New York:Academic Press, pp 70-71 (1961)
17. Spink, J.A., *J. Colloid Sci.* 18:512 (1963)
18. Goddard, E.D., and Ackilli, J.A., *J. Colloid Sci.* 18:585 (1963)
19. Gent, W.L.G., *Quart. Rev. (London)* 2:383 (1948)
20. Smith, J.W., "Electric Dipole Moments," London:Butterworths, pp. 92, and 119-125, (1955)
21. Smyth, C.P., "Dielectric Behavior and Structure," New York:McGraw-Hill, pp. 240-245, (1955)

\* \* \*