

## **Molecular Interaction in Mixed Monolayers on Aqueous Subsolutions I. Mixtures of Alcohols, Acids and Amines**

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## Molecular Interaction in Mixed Monolayers on Aqueous Subolutions

### I. Mixtures of Alcohols, Acids and Amines

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Mixed films are of fundamental importance in biological systems, so mixtures of long chain alcohols, acids, and amines on acidic and basic subsolutions have been investigated. The principal effect of mixing is to change the conditions with respect to the pressure, area, and temperature at which one surface phase changes into another.

In general a mixture of two liquid films gives a monolayer of the same type, with the mean molecular area: a liquid expanded film is made more condensed by admixture of a substance which gives a condensed film, and the condensing action increases with the length of the hydrocarbon chain; an alcohol condenses an acid more than the

corresponding acid. The interaction, or departure from the mean value may be either positive or negative, and on acid subsolutions is greatest when one of the components is an amine. Only in amine-acid mixtures is there an indication of chemical action. The 1 : 1 mixture of stearyl alcohol and stearic acid "freezes" at a much larger area than the film given by either component, so the area of the solid mixed film is abnormally high. The area interaction with an amine present is negative, and the potential interaction has a high value and is positive. Calcium ions in a basic subsolution condense a Type II to a solid Type I monolayer.

#### 1. INTRODUCTION

THE properties of mixed films, that is those which consist of two or more components in addition to water, are of fundamental importance for biology, since membranes are undoubtedly structures built up on one or more mixed monolayers as a foundation. Indeed, the first investigation of mixed films was undertaken by Leathes<sup>1, 2</sup> on account of the supposed importance in biology of monolayers of this type. He found that when the proportions were one (large) molecule of lecithin to two to four of myristic or another fatty acid which gives an expanded film, the effect of the large molecules was to condense the film.

The mutual effect of alcohols and stearic acid in mixtures was one of the topics in an investigation by Harkins and Morgan,<sup>3</sup> and in the present work mixtures of alcohols, acids, and amines of from 14 to 18, and in some cases up to 20 carbon atoms, per molecule have been studied both on acidic and basic subsolutions. A paper by Marsden and Schulman,<sup>4</sup> received after our communication was written, considers two of the mixtures investigated by us, but in no case

did they vary the length of the hydrocarbon chain. That we were able to do so is due to the generosity of Emmet E. Reid and Jane E. Meyer, who contributed the large number of extremely pure organic compounds used in this work.

#### 2. APPARATUS

The film balance, polonium electrode, and dark field microscope used in the investigation of the mixed films were similar to those used in earlier work in this laboratory.

#### 3. MIXTURES OF COMPONENTS EACH OF WHICH GIVES A CONDENSED FILM

For convenience the different types of films are, in this paper, designated by number as follows: I. Condensed film of very low compressibility, usually solid. II. Condensed liquid film of higher compressibility. III. Transition film with a very high compressibility near the transition point. IV. Liquid expanded. V. Vapor expanded. VI. Gaseous.

The pressure-area relations of a mixed monolayer which consists of two components, each of which forms when alone a condensed film, may be illustrated by the behavior of an equimolar mixture of stearic acid (H St) and stearyl alcohol (St OH) as presented in Fig. 1, and as described below:

<sup>1</sup> Leathes, *Zeits. f. Physiol. Chemie* **130**, 113 (1923).

<sup>2</sup> Leathes, *Lancet* **2**, 853 (1925).

<sup>3</sup> W. D. Harkins and J. W. Morgan, *Proc. Nat. Acad. Sci.* **11**, 631 (1925).

<sup>4</sup> J. Marsden and J. H. Schulman, *Trans. Far. Soc.* **34**, 748 (1938).

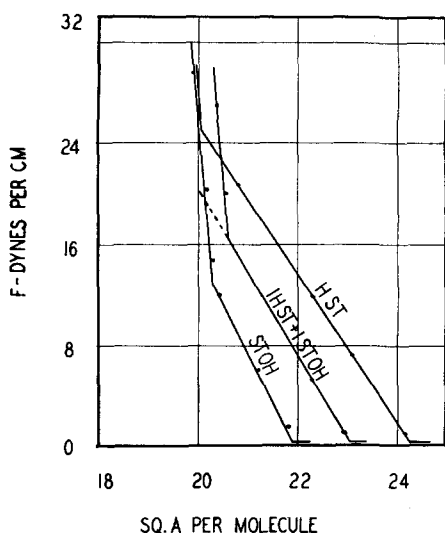


FIG. 1. Mixtures (1 : 1) of condensed films of alcohol and acid ( $pH=3$ ) exhibits expansion in solid film only. Note: The experimental points obtained in this work for the first compression of each film lie within the widths of the lines drawn, the dots represent curves obtained by a reduction of the pressure to a low value for one hour and a subsequent recompression of the film.

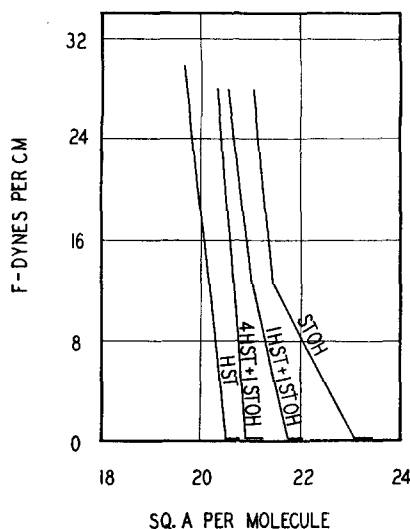


FIG. 2. Mixtures of condensed films of alcohol and calcium stearate ( $pH=9.5$ ). The Type II film is eliminated with 80 equivalent percent of calcium stearate, and only the Type I film exists.

1. The Type II, or less condensed film, exhibits a molecular area which is the mean of that given at the same pressure by the pure components. Thus the "limiting areas at zero pressure" as obtained by extrapolation are at  $25^{\circ}C$ : stearic acid = 24.3, octadecyl alcohol = 21.9, mean value calculated = 23.1, determined = 23.1.

2. The Type I, or more condensed film, has almost exactly the same molecular area in films of either the acid or the alcohol, but for the equimolar mixture the area is much higher (by about 0.75 sq. A). This seems to be due to the fact that the transition II $\rightarrow$ I occurs in the mixture at a pressure which is much (1.4 dynes) below the mean of the kink points for the films of one component. If the films of Class I are considered as two dimensional solids, then it may be said that the mixed film freezes at a larger molecular area than that of either component.

The experimental points obtained in the work represented by Fig. 1 lie very exactly on the straight lines when these are obtained in the original compression. In order to simplify the figure these points are not given. The dots, which lie very close to, but not so exactly on the lines, were obtained by an additional operation. After the original compression, which gave the linear

relations, was completed, the barriers which confined the film were separated widely and the film was allowed to expand for one hour. It was then compressed for a second time, and this recompression gave the data represented by the dots. It is remarkable that the pressure-area relations are so closely the same in the original and the later compression.

#### 4. EFFECT OF BIVALENT IONS AND OF BASIC AQUEOUS SUBSOLUTIONS ( $pH=9.5$ )

While calcium stearate monolayers have been investigated extensively,<sup>5</sup> the pressure-area relations have been given, so far as we are able to find, in only one paper<sup>6</sup> which presents values for the molecular area which are not sufficiently accurate for our purpose. A more accurate and extensive set of data is presented in this section.

The effect of a basic subsolution which contains sodium without calcium ions is to give not only a condensed film of Type I, but also a lower second limb of the  $F-A$  curve which indicates a

<sup>5</sup> R. J. Meyers and W. D. Harkins, *Nature* **139**, 368 (1937). J. S. Mitchell, E. K. Rideal and J. H. Schulman, *ibid.* **139**, 626 (1937). J. H. Schulman, *ibid.* **139**, 626 (1937). C. Robinson, *ibid.* **139**, 626 (1937). I. Langmuir and V. J. Schaefer, *J. Am. Chem. Soc.* **59**, 2400 (1937).

<sup>6</sup> W. D. Harkins and T. F. Anderson, *J. Am. Chem. Soc.* **59**, 2181 (1937).

higher compressibility (Type II). The effect of calcium ion is to eliminate this second type of film and to change it to Type I. With a sub-

TABLE I. Increase of area or of surface potential (interaction) above the mean value for mixtures of acids, alcohols, and amines.

MIXTURE pH	AREA INTERACTION AT LIMITING AREA (Å <sup>2</sup> )	LIMITING AREA (Å <sup>2</sup> )	DIPOLE INTERACTION IN MV
<i>Alcohols</i>			
+Acids (1 : 1)			
18-18 3	+0.02		+33
18-18 9.5	-0.05		+20
18-15 3	-9.6		+2
15-15 3	-4.5		+50
14-15 3	+7.1		+28
18-14 3	-3.7		+29
15-14 3	+5.8		+63 (+3)
14-14 3	+9.5		+42
<i>Acids + Acids (1 : 1)</i>			
20-15 3	-4.3		-27
20-14 3	+2.5		-35
18-14 3	+4.5		—
<i>Alcohol</i>			
+Amine (1 : 1)			
18-18 3	Approx. -25	21.45	+60
16-18 3	Approx. -25	22.20	+30
14-18 3	Approx. -25	23.60	+26
18-16 3	Approx. -25	22.90	+200
16-16 3	Approx. -25	23.20	+100
14-16 3	Approx. -25	26.25	+200
<i>Acid + Amine (1 : 1)</i>			
18-18 3	Approx. -25	21.6	+200
16-18 3	Approx. -25	(20.4)	+240
15-18 3	Approx. -36	22.8	+105
14-18 3	Approx. -36	22.8	—
18-16 3	Approx. -25	(20.4)	—
16-16 3	Approx. -25	(20.4)	—
14-16 3	Approx. -36	21.6	—
<i>Pure Components</i>			
Alcohols 3		22.0	
18 and 16 acids 3		24.5	
15 and 14 acids 3		47	
18 and 16 amines 3		(Area = 70 Å <sup>2</sup> at ½ dyne)	

#### STEARIC ACID—STEARYL AMINE MIXTURES ON SUBPHASE OF pH = 3

6 MOL. S+NH <sub>2</sub> : MOL. HSt	AREA AT F = 2 DYNES (Å <sup>2</sup> )	DIPOLE INTERACTION IN MV
(pure StNH <sub>2</sub> )	55	—
4 : 1	29.2	+140
2 : 1	22.2	+112
1 : 1	20.1	+200
2 : 3	20.8	+103
1 : 3	21.3	+125
1 : 6	23.1	+108
0 (pure HSt)	23.9	—

#### OCTADECYL ALCOHOL—STEARYL AMINE MIXTURES ON SUBPHASE OF pH = 3

MOL. StNH <sub>2</sub> : MOL. StOH	AREA AT F = 2 DYNES (Å <sup>2</sup> )	DIPOLE INTERACTION IN MV
(pure StNH <sub>2</sub> )	55	—
2 : 1	24.5	+ 30
1 : 1	21.1	+ 60
1 : 2	21.9	+ 60
0 (pure StOH)	21.85	—

solution with 10<sup>-3</sup> m NaHCO<sub>3</sub>, 10<sup>-4</sup> m CaCl<sub>2</sub>, and NaOH to give a pH of 9.5, the compressibility is reduced to 0.0013 (Fig. 2).

The molecular area of this calcium stearate film at 25°C and 0.1 d/cm pressure is 20.5 sq. Å, which is practically the same as the extrapolated area at zero pressure for a Type I film of stearic acid (20.6) at the same temperature. On the average each calcium ion attracts two stearate ions but is probably coordinated with the oxygen of four of the carboxyl groups of these ions to give a definite solid lattice. Below the transition pressure of 25 dynes per cm (Fig. 2) the calcium ions have the effect of an increase of pressure on the stearic acid film. Above this pressure the stearic acid and calcium stearate films have practically the same area per equivalent (Figs. 1 and 2).

A monolayer formed from an equimolar mixture of stearic acid and octadecyl alcohol exhibits on this basic subsolution both Types I and II, with the transition pressure at 12.8 dynes at 25°, or practically that of the alcohol. The compressibility of the Type II film is, however, halved, that is from 0.0057 for the pure alcohol to 0.0026 for the mixture. The presence of four molecules of the acid to one of alcohol is sufficient to give enough calcium stearate to eliminate the Type II film, and the compressibility is approximately that found for calcium stearate alone.

At 20 dynes per cm the equivalent mixture of calcium stearate and octadecyl alcohol exhibits an area of 20.8 which is 0.2 sq. Å greater than the mean, while the four to one mixture has an area of 20.5 while the calculated area is 20.2.

It is found in general that the liquid film of stearic acid of Type II does not undergo a transition into a Type I (solid) film at pH 3 if the compression is made slowly, since the liquid film collapses at about the transition pressure. However a sufficiently rapid compression seems to give a Type I film in practically every instance.

#### 5. THE CONDENSING EFFECTS OF ALCOHOLS UPON EXPANDED MONOLAYERS OF ACIDS (pH = 3)

In mixed films of acids and alcohols the principal types of forces involved are those classified as (1) dipole-dipole, (2) dipole-induced dipole, and (3) van der Waals. Early investigations by

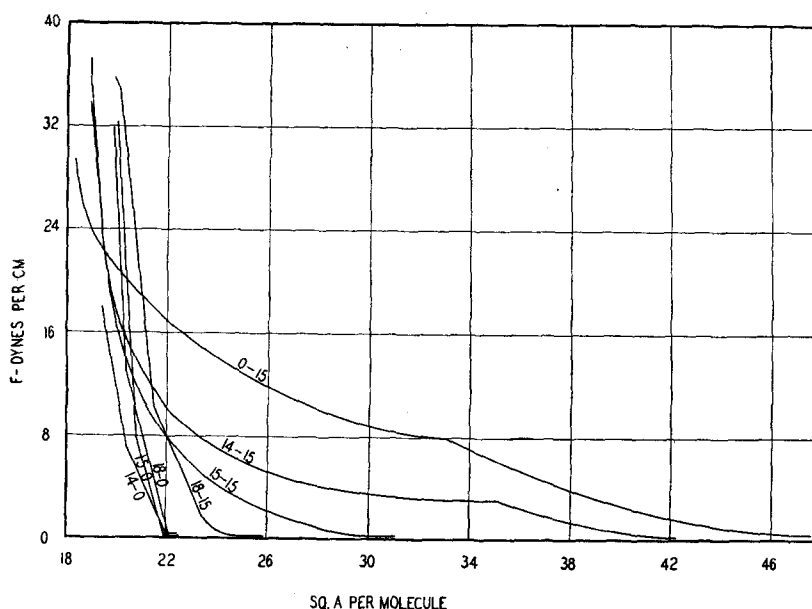


FIG. 3. Mixtures (1 : 1) of condensed alcohol and expanded films of pentadecylic acid. Pentadecylic alcohol eliminates the expanded film of pentadecylic, but not that of myristic acid. The first number gives the number of carbon atoms in the molecule of alcohol, and the second, in the acid.

Harkins and his collaborators<sup>7</sup> indicate that the van der Waals energy of interaction between hydrocarbon chains is, for unit area, of the general order of half that for the dipole-dipole interaction, and that the induced dipole energy is relatively small between hydroxyl or carboxyl, or water, and a hydrocarbon chain. For example, at room temperature the free energy of separation of a hydrocarbon (e.g., octane) from itself, in which van der Waals forces are involved, is the same per unit area as that for the separation of water from octane. The van der Waals forces in the case of water are lessened by the smallness of the water molecules so that van der Waals energy<sub>H<sub>2</sub>O-Octane</sub> + dipole-induced dipole energy<sub>H<sub>2</sub>O-Octane</sub> = van der Waals energy<sub>Octane-Octane</sub>.

The dipole-dipole interaction between the polar groups of either the acid or the alcohol binds the film firmly to the water. The interaction between the dipoles in the film varies greatly with the relative position of the dipoles. For example, with two equal dipoles the mutual

energy is  $V = (\mu_1\mu_2/R^3)(\cos \nu - 3 \cos \theta_1 \cos \theta_2)$ , where  $\mu$  is the dipole moment,  $R$  the distance between the centers of the dipoles,  $\nu$  the angle between the vectors of the dipoles and  $\theta_1$  and  $\theta_2$  are the angles between the straight line connecting the centers of the dipoles and their directions. With dipoles oriented in the same direction in a plane the effect is a repulsion.

Even if the total dipole moments for the alcohol and acid were the same, the orientation and length of the dipoles may be expected to be different, and the size of the group is also different, which affects the value of  $R$ . Also the grouping of water molecules around the carboxyl group is undoubtedly different from that around the hydroxyl group.

From this point of view, it is to be expected, especially when one of the substances forms an expanded film, that the molecular interaction will be different in mixtures from that in the one-component monolayers. Thus the molecular area for the mixture may be expected to be either greater or less than that which corresponds to the proper mean value. That there is also a departure from the mean produced by differences in the lengths of the hydrocarbon chains is shown in the figures and in Table I.

<sup>7</sup> W. D. Harkins, F. E. Brown and E. C. H. Davies, *J. Am. Chem. Soc.* **39**, 354 (1917). W. D. Harkins, G. L. Clark and L. E. Roberts, *J. Am. Chem. Soc.* **42**, 700 (1920). W. D. Harkins and Y. C. Cheng, *J. Am. Chem. Soc.* **43**, 35 (1921).

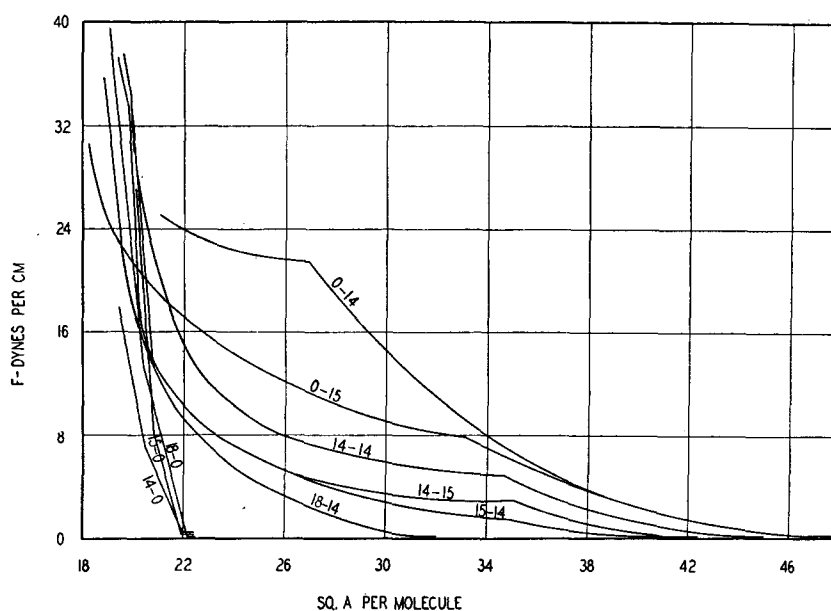


FIG. 4. Mixtures (1 : 1) of condensed alcohol films and expanded films of myristic acid ( $pH=3$ ). The curve for myristyl alcohol with pentadecylic acid (14-15) is added for comparison with the effect produced with interchange of number of carbon atoms in the alcohol and acid. Stearyl alcohol does not condense the myristic acid, while it does the pentadecylic acid film (Fig. 3).

The same type of reasoning indicates that the surface potentials ( $\Delta V$ ) should not in general be additive in mixtures.

Relations of this general type are explained by Schulman and Hughes<sup>8</sup> and Schulman and Rideal<sup>9</sup> as due to compound formation; but that is not the view expressed here.

Alcohols with 14 or more carbon atoms per molecule form highly condensed films of Type I, at high, and II at low pressures. These substances reduce greatly the extent of the expansion in expanded (Type IV) and transition (Type III) films. However, the mixture may exhibit an area either higher (+) or lower (-) than the mean value, and in Table I this is represented as the interaction in sq. A at the limiting area for the film. This is the area at which the pressure begins to rise rapidly above that of the vapor from the film.

In both Table I and Figs. 3 and 4 the number in the first column or on the curve represent first the number of carbon atoms in the hydrocarbon chain of the alcohol, and second, of the acid. Thus 18-15 represents a mixture of octadecyl alcohol and pentadecylic acid. As compared with

the mean value the relations which are obtained may be noted as follows:

- (1) A contraction occurs if in mixtures with pentadecylic acid the alcohol chain is of the same length or longer than that of the acid.
- (2) Expansion is exhibited if the alcohol chain is the shorter.
- (3) With myristic acid there is contraction if the alcohol chain is much longer (i.e. 18-14) but expansion if the alcohol chain is one atom longer or of the same length.

It is of considerable interest that in an equimolecular mixture any alcohol of greater length than 14 carbon atoms eliminates the expanded film and leaves only the transition film (15-15, Fig. 3) or the liquid (II) film (18-15). That is, the transition pressure (IV→III) or kink, is depressed to negative film pressures.

It is found (Fig. 4) that equimolecular mixtures of the 14 alcohol with 15 acid, and of 15 alcohol with 14 acid, give the same pressure-area curve for the transition film over a considerable region, but the expanded film exhibits a considerably higher pressure if the acid chain is the longer.

<sup>8</sup> Schulman and Hughes, *Biochem.* p. 29, 1243 (1935).

<sup>9</sup> Schulman and Rideal, *Proc. Roy. Soc. B122*, 29 (1937).

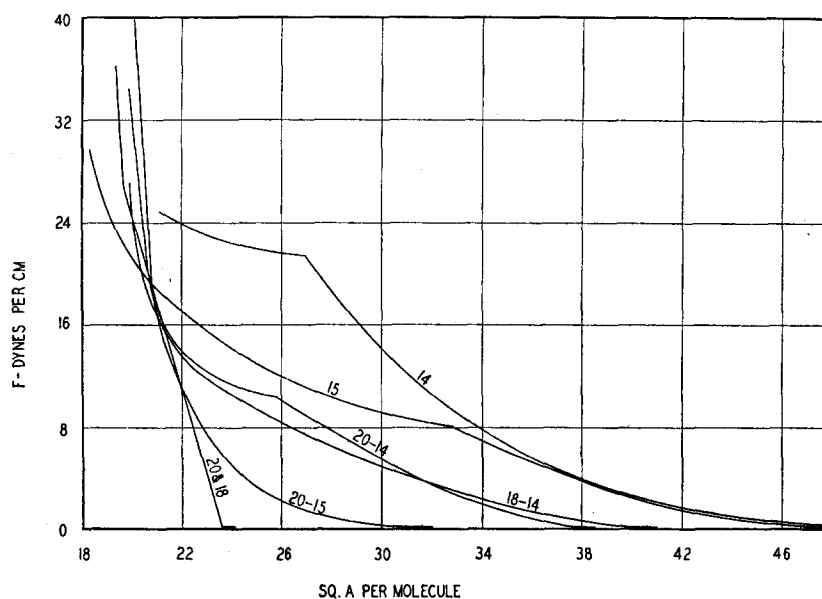


FIG. 5. Mixtures of condensed and expanded acid films ( $pH=3$ ). Arachidic, stearic, pentadecylic, and myristic acids. The pressure-area values for the 20-14 and 18-14 mixtures are almost the same, but the position of the transition point expanded transition (IV $\rightarrow$ III) is affected by an extremely large shift.

With myristic acid stearyl alcohol inhibits the expanded film, but pentadecyl alcohol permits its existence.

Since the molecular interaction is expressed in sq. A at the limiting area it is not surprising that there is an expansion with reference to the mean when the mixed film at this area is an expanded one, and a contraction when the film is of either Class II or III.

If the mixed film is of the transition type and that of the acid expanded, the relation is reversed. Thus at 7 dynes the interaction is  $-6.2$  sq. A for the 14-15 mixture while it is  $+7.1$  at the limiting area.

Thus the sign and magnitude of the interaction, depends upon the effect of the mixing upon the state or class of the film which is produced.

Increasing the chain length of the condensing agent has the same effect as a lowering of temperature even though this effect is not apparent with the pure alcohols with from 14 to 18 carbon atoms. Increasing the chain length of the expanded acid has a similar effect.

The deviation from the mean of the surface potential for the alcohol-acid monolayers is positive in all cases, and is smallest in magnitude when the difference in chain length is greatest.

The greatest interaction in mv is 63 for the 15 alcohol-14 acid, and 50 for the 15-15 mixture. These are the largest interactions as measured by the potentials.

## 6. FILMS OF MIXED ACIDS

Films of mixed acids (Fig. 5) exhibit the same general relations as those which consist of an acid and an alcohol except that long chain acid condenses an expanded film of an acid much less than the alcohol with the same number of carbon atoms. For example, at an area of 26 sq. A the equimolecular mixture of the 18 and 14 acids gives a film pressure of 8.5 dynes/cm, while with the 18 alcohol the 14 acid it is only 3.3 dynes. This is related to the fact that Type II alcohol films are much more condensed than those of the same type with acids.

One component films of arachidic (20) or stearic (18) acid exhibit practically the same pressure area relations for the liquid film, and when mixed in equimolecular proportions with myristic acid give almost the same values. In the case of the mixtures the interaction in terms of the surface potential is negative (Table I), which is the opposite sign from that for alcohol-acid mixtures.

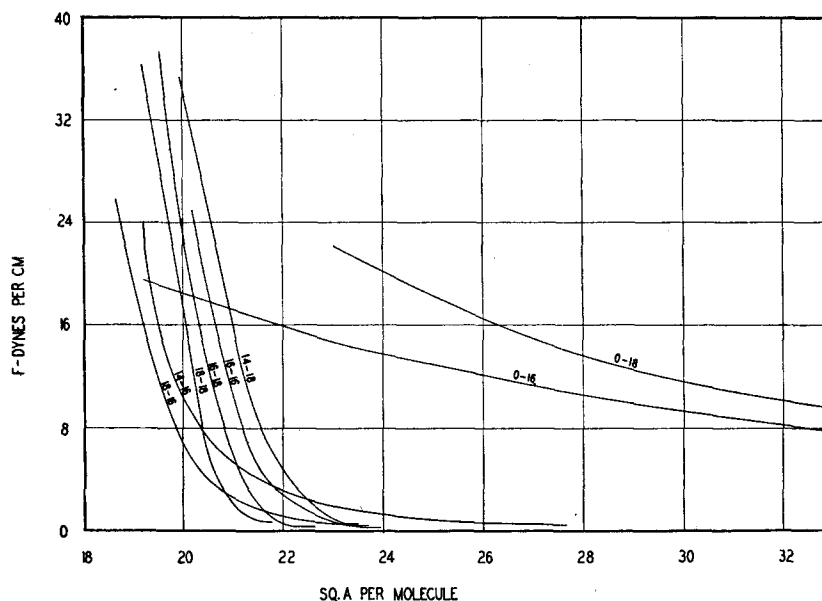


FIG. 6. Mixtures (1 : 1) of condensed alcohol and vapor-expanded amine films ( $pH=3$ ). For the one-component alcohol films see Fig. 3 or Fig. 4. The curves at the lower pressures are of the transition type. The first number gives the number of carbon atoms in the alcohol, and the second in the amine, molecule. The 14-16, and 18-16 mixtures have a high compressibility.

In mixtures of the 22-14 acids Adam and Jessop<sup>10</sup> were unable to detect an appreciable condensation but in this work the 20-15 mixture gave a decrease from the mean of 4.3 sq. A at the limiting area, but only 0.25 sq. A at 8 dynes per cm. These involve comparisons of expanded films for the pure 14-component and the mixture. At 12 dynes the condensation is 6.3 sq. A, but here the mixture is in the transition state. These facts indicate that for an understanding of the relations between the films of pure components and the mixtures in all of this work it is essential to study the entire curves as presented in the figures.

#### 7. POSITIVE IONS IN MIXED FILMS ( $pH=3$ )

##### Alcohol-amine mixtures

The use of amines on dilute acid subsolutions ( $pH=3$ ) gives an opportunity to investigate the effect of a positive ion of an organic type. In alcohol mixtures this gives rise to an ion-dipole effect. The pure amines on acids give vapor-expanded films of extremely high expansion, but these are very greatly condensed by the addition of an equal number of molecules of the 14 to 18 alcohols (Fig. 6). Of the mixtures that in which

both the amine and the alcohol have 18 carbon atoms gives the closest approach to a solid film of Type I, with an extrapolated area at zero compression of 20.7 sq. A, which is the normal value for solid condensed films. All of the other mixtures give curves of the general type exhibited by transition films of Type III.

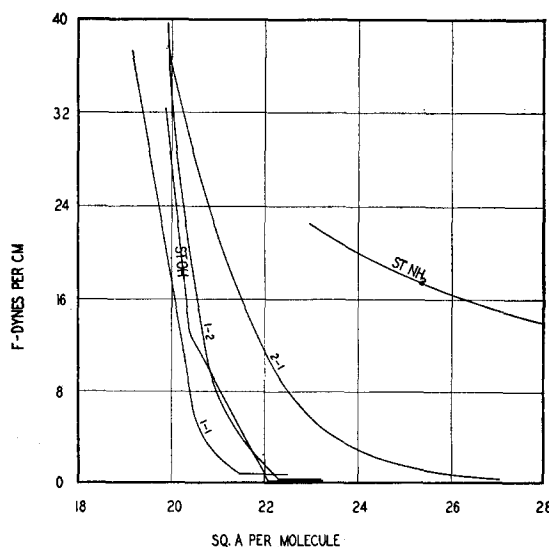


FIG. 7. Effect of proportions in mixed stearyl alcohol and amine films ( $pH=3$ ). The first figure gives the number of molecules of amine and the second of alcohol. The 1 : 1 mixture exhibits the greatest condensation.

<sup>10</sup> N. K. Adam and G. Jessop, Proc. Roy. Soc. A120, 473 (1928).



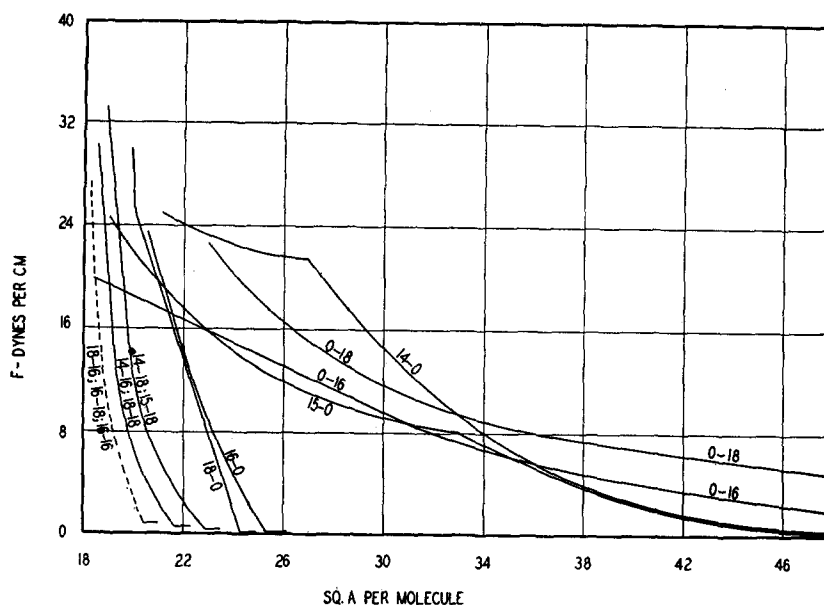


FIG. 8. Mixtures (1 : 1) of acids and amines ( $pH=3$ ). The first figure gives the number of carbon atoms in the acid, and the second in the amine, molecule. All of the seven mixtures exhibit pressure-area curves of the same form, and with not very widely differing and very low areas. At the lower pressure all the mixtures give curves of the transition form.

At the low pressure of the limiting area the 14 alcohol and the 16 amine give the highest, and the 18-18 mixture the lowest area, as might have been predicted, but at the higher pressures the order is shifted on account of the fact that the 14-16 mixture is by far the most compressible, as is normal.

Mixtures which contain the amine not only give abnormally low areas at the high pressures, but they also exhibit extremely high positive deviations  $\Delta(\Delta V)$  of the surface potential from the mean values. Thus (Table I) the interaction was +200 mv for the 18-16, 100 mv for the 16-16, and 200 mv for the 14-16 mixture, if the first number of each pair refers to the alcohol and the second to the amine. The mixtures with octadecyl (stearyl) amine give potential deviations of the same sign and order of magnitude as those found with alcohol-acid mixtures, that is 25 to 60 mv. The large deviations with cetyl amine as listed above were the maxima, and it is not certain that the films were molecularly homogeneous. This will be investigated later by the use of our ultramicroscopic equipment.

The effect of changing the proportions in the alcohol amine mixtures is exhibited in Fig. 7. It may be noted that the 1 : 1 mixture gives

the lowest area, and that one molecule of stearyl alcohol to two of the stearyl amine was not sufficient to give a Type I solid film, though in Fig. 6 it has been shown that 1 : 1 produces the transformation.

#### Acid-amine mixtures ( $pH=3$ )

When an organic acid is present in the mixture there is the possibility of a chemical action with the positive ion of the amine, so an even more powerful condensing action is to be expected. Thus it is not surprising that a mixture of myristic acid with either cetyl or stearyl amine, both of which when alone form very highly expanded films at  $25^\circ C$ , gives a highly condensed film, but in no case is the relation between film pressure and molecular area linear (Fig. 8). The positive deviation of the surface potential from the mean is very high (Table I) of the order of 200 mv, and is highest for the equimolar mixture.

In the acid : amine mixtures examined, 14-18, 15-18, 16-18, 18-18, 14-16, 16-16, 18-16, there is no evidence of a definite effect of chain length. All of the curves for the mixtures are seen to be practically parallel, and of the same form, and the difference in area is not very significant.

The effect of a change of the relative propor-

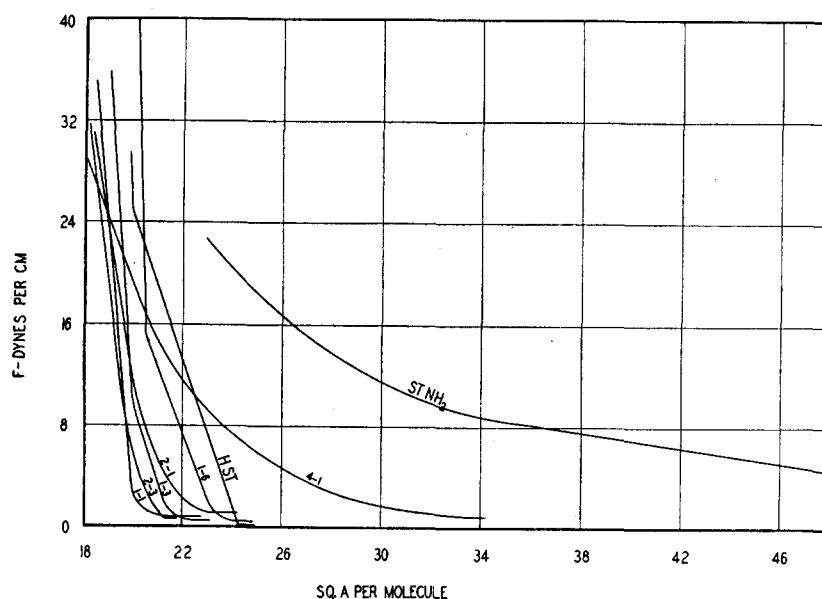


FIG. 9. Effect of proportions in mixed films of stearyl amine and stearic acid ( $pH=3$ ). The numbers on the curves give the ratio mole of amine to acid. The 1 : 1 mixture exhibits the greatest condensation with very low molecular areas, and above 3 dynes the low compressibility 0.0023 (at  $F=0$  extrapolated) or a Type I film, while the similar value for one-component stearyl alcohol I film is 0.0024. With 75 molar percent of acid the sharp transition II $\rightarrow$ I or liquid to solid is preserved, but seemingly not with 66 $\frac{2}{3}$  percent.

tions of stearyl amine and stearic acid is presented in Fig. 9, where for example 4 : 1 means 4 molecules of amine to one of acid. The 1 : 1 mixture is found to give the minimum area and the greatest interaction of the potentials (200 mv).

The pressure of the transition for the mixtures Phase II $\rightarrow$ Phase I is lowered, as the proportion of the amine is increased, from 25 dynes/cm for the pure acid, to 15.4 for one-seventh amine, to 9.8 for one-fourth amine, and the transition point disappears for two-fifths amine or more.

The effect of changes of the proportions in a mixed film of stearic acid and stearyl amine, as given in Fig. 9, is to give a maximum in the potential interaction and a minimum in that of the area for a 1 : 1 proportion.

## 8. DISCUSSION

It was believed by Adam and Jessop<sup>11</sup> that the condensing action of cholesterol upon expanded films of myristic acid, is due to the "mechanical" action of its large molecules upon the motions of

<sup>11</sup> N. K. Adam and G. Jessop, Proc. Roy. Soc. **A120**, 474 (1928).

the smaller ones. They found this effect to be small when myristic acid is replaced by substances which give vapor expanded films.

It has been found in our work that shortening the hydrocarbon chain of either the molecules which give condensed or expanded one-component films, increases the expansion of the mixture, as is to be expected on account of the increase in the van der Waals forces with the length of the chain, except when long chain acids and amines are mixed, when the effect disappears, presumably due to compound formation. The condensing effect is greatest with the 1 : 1 mixture and in the potential interaction. This last effect is also a maximum for the 1 : 1 mixture of the amine with the alcohol.

For equal chain length, the acid is found to have a greater condensing effect on the amine than does the alcohol, even though the alcohol itself is more condensed. This is presumably due to compound formation. But with expanded saturated acids the alcohol has a greater condensing effect than an acid; the amine has again the greatest effect, which suggests that a compound may be formed.