

## Molecular Interaction in Mixed Monolayers II. Unstable Mixtures with Unsaturated Acids

Robert T. Florence and William D. Harkins

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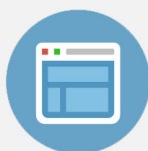
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## Molecular Interaction in Mixed Monolayers

### II. Unstable Mixtures with Unsaturated Acids

ROBERT T. FLORENCE AND WILLIAM D. HARKINS

*George Herbert Jones Chemistry Laboratory, University of Chicago, Chicago, Illinois*

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This investigation concerns the effect of the form of a molecule, with otherwise identical composition and structure, on its binding to the acidic or basic water of the sub-phase and to the molecules of the film itself. The binding to the water by the carboxyl group should be approximately the same for stearic acid and for the unsaturated acids, oleic and elaidic acid, with the double bond in the middle of the hydrocarbon chain. By compression of the film oleic acid may be squeezed out practically completely, from a mixed monolayer in which a saturated long chain alcohol, acid, or amine is the other constituent. Thus the energy of binding of the oleic acid to the other molecules in the film is weaker than that between the saturated molecules. However, earlier work in this laboratory has shown that the presence of the double bond does not decrease, but very slightly increases, the attraction between molecules.

Thus it seems to be the shape of the molecule which reduces the energy of binding of oleic acid in the film.

Oleic acid is a *cis* form, so a nine carbon atom chain  $R_2$  is bent backward with respect to the other 9C chain  $R_1$  which ends in the carboxyl group. It may be assumed that the whole molecule is free to rotate, with the carboxyl group in contact with the water, and that the group  $R_2$  is free to vibrate or "flagellate." Thus the oleic acid molecule would occupy a larger area than a saturated acid and this increased distance together with a lessening of the length of the contact between this and the other molecules in the film, decreases greatly the energy of binding. Space models of oleic and elaidic acid have been used in the study of these relations.

By a greater straightening of the chain, as in the trans-compound, elaidic acid, the energy of binding should become intermediate between that of oleic and stearic acid, and much above that for oleic acid. On this basis compression should segregate elaidic acid slightly from the mixed film, but by no means completely, and this is what the experiments demonstrate.

#### 1. MIXTURES WITH OLEIC ACID ON ACID SUBSOLUTIONS

MIXTURES of oleic acid with cetyl alcohol, tripalmitin, and triolein have been investigated by Schulman<sup>1</sup> who found that in every case the film was unstable above the collapse pressure of the component which has the lower collapse pressure. Our investigation was undertaken in order to extend the observations to a considerable number of other mixtures, and in an attempt to find an explanation for the phenomenon.

The pressure area relations for mixtures of oleic acid on 0.001*N* sulphuric acid with stearyl alcohol, stearic acid and stearyl amine are presented in Fig. 1.

At a pressure of 5 dynes/cm the molecular area of the mixture is somewhat larger than the mean value (Table I). With any of the mixtures the pressure rises only very slowly as the area is decreased after the collapse pressure of oleic acid is reached. At about this pressure (Fig. 1) lenses,

presumably of oleic acid, appear in the field of the dark field microscope used for observation. In a 1:1 mixture the pressure begins to rise abruptly at an area of about 10.5 sq. A for the mixture, which is about 21 sq. A for the substance, stearic acid, stearyl amine, or stearyl alcohol, left in the film. At areas at which lenses begin to be squeezed out, the surface potential ( $\Delta V$ ) remains constant at the mean value for the mixtures which contain the stearic acid or stearyl alcohol. With stearyl amine the potential was 85 mv above the mean value.

After the abrupt rise in pressure obtained after all of the oleic acid had been squeezed out of the mixed film, the potential obtained was very nearly that of the pure stearic acid, stearyl alcohol or stearyl amine, respectively. This is in accord with the hypothesis that the oleic acid has been squeezed out. For example at this final collapse the surface potential for the mixture is 686 mv which is practically the value found for a film of pure stearyl amine.

Before this work was begun a hypothesis was developed to explain the squeezing out of oleic

<sup>1</sup> J. H. Schulman, *J. Biochem.* **29**, 1243 (1935).

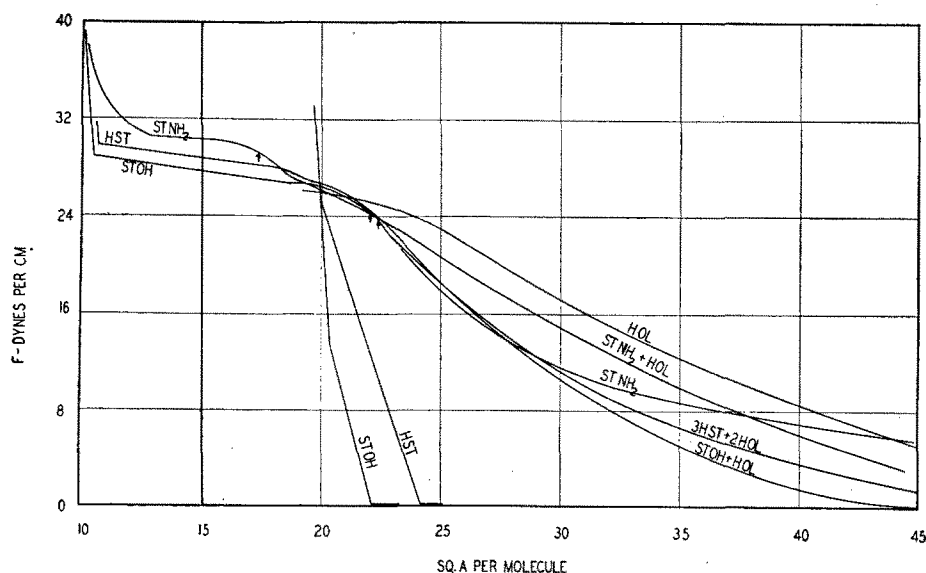


Fig. 1. Pressure-area relations of an oleic acid monolayer, and of mixtures of oleic acid (HOL) with stearyl alcohol (StOH), stearic acid (HSt), and stearyl amine (StNH<sub>2</sub>) on a sub-solution of pH 3. The arrows represent the points at which lenses of oleic acid become visible in the ultramicroscope. Since at the extreme left all of the oleic acid has been squeezed out, the figure has been drawn in such a way that the values of the area multiplied by two give the areas for the constituent left in the film: e.g. the almost vertical line at 10.5 sq. A for the mixture of oleic acid and stearyl alcohol indicates that the molecular area for the alcohol left alone in the film is 21 sq. A.

acid from these films. Now oleic acid is a *cis* form of acid with the double bond in the middle of the chain, and elaidic acid is the corresponding *trans* form. The hypothesis predicted that elaidic acid would be squeezed out from similar mixtures with more difficulty and much less completely. Before the relations are discussed it will be convenient to have available the data for mixtures with this acid.

## 2. MIXTURES WITH ELAIDIC ACID ON ACID SUBSOLUTIONS ( $pH = 3$ )

Elaidic acid which is the *trans* form is a solid at ordinary temperatures. Its geometric isomer is the *cis* form, or oleic acid, which is a liquid. Both acids form expanded films at 25° on 0.001N sulphuric acid. The limiting areas are 61 sq. A for oleic and 51.5 sq. A for elaidic acid. At a molecular area of 30 sq. A the film pressure is 17 dynes/cm for oleic, and 18.4 dynes/cm for elaidic acid, but the latter suffers a more definite collapse. The pressure attained at collapse is well known to depend upon the rapidity of compression, but in the special experiment with elaidic acid this occurred at 22 dynes/cm, and 28.6 sq. A

(Fig. 2), whereas with oleic acid the collapse was at a much lower area and a higher pressure (Fig. 1). The expansion temperatures have been estimated by Adam<sup>2</sup> as -30° for oleic and +6° for elaidic acid. That collapse occurred with elaidic acid at the values given was indicated by the appearance of a point structure in the field of the ultramicroscope.

The mixtures with elaidic are much more condensed than those with oleic acid. The extremely striking difference appears in the mixtures with stearyl amine. Thus, of the mixtures investigated, those of stearyl amine are the least condensed with oleic, and the most condensed with elaidic acid, and at 5 dynes/cm the area of the former mixture is 1 sq. A greater, and the latter 23.6 sq. A less, than the mean value. This is a remarkable condensing action in which the mixture of two highly expanded films gives a highly condensed film though the condensation is not so great at low pressures as with the saturated acids which form expanded films. At the same pressure the mixture of elaidic acid with stearyl alcohol gives a condensation of 4.6 sq. A, while

<sup>2</sup> Adam, Proc. Roy. Soc. A101, 516 (1922).

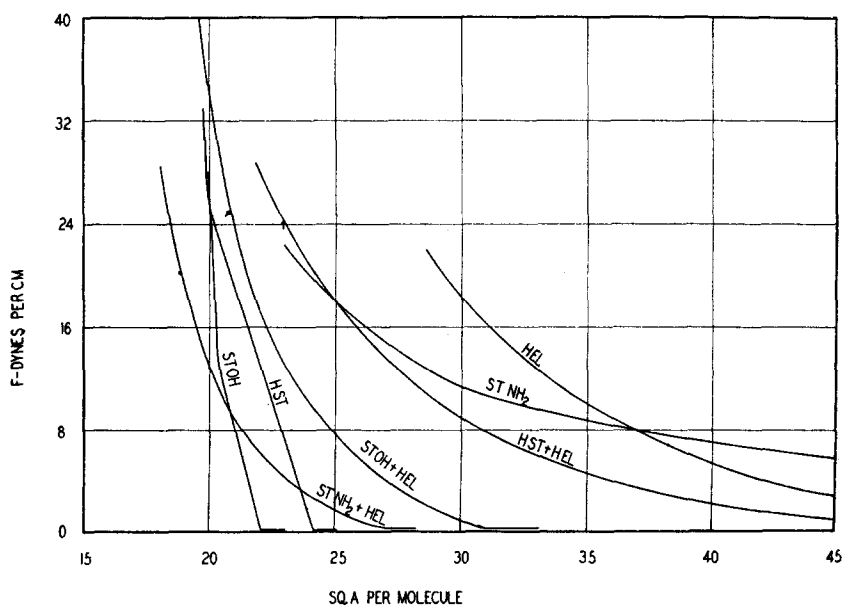


FIG. 2. Mixtures (1 : 1) of elaidic acid with stearyl alcohol, amine, and stearic acid on a subsolution of pH 3.

the action of oleic acid is always an expansion: equal to 3 sq. A with stearic acid (2 : 3), 1.7 with

TABLE I. *Equimolar\* mixtures of elaidic or oleic acid with stearyl alcohol, stearic acid, or stearyl amine at pH=3.*

MIXTURE	AREA INTERACTION AT $F=5$ DYNES (A <sup>2</sup> )	LIMITING AREA (A <sup>2</sup> )	DIPOLE INTERACTION AT LENS PT. (M.V.)	$\Delta V$ AT FINAL COLLAPSE (M.V.)
HOI		61.2		+310
*HOI+HSt (2 : 3)	+3.0	50.0	+5	+365
HOI+StOH	+1.7	44.0	+7	+440
HOI+StNH <sub>2</sub>	+1.0	55.0	+85	+686
HEL		51.5		+250
HEL+HSt	+3.0	47.5	+50	+370
HEL+StOH	-4.6	30.9	+30	+385
HEL+StNH <sub>2</sub>	-23.6	27.2	(+100)	—

† Same mixtures on pH=9.5.

HOI		41.0		+225
†HOI+HSt (1 : 1)	+0.5	32.0	+100	+150
HOI+StOH	-1.5	32.0	+20	+347
HOI+StNH <sub>2</sub>	+6.0	42.0	+5	+525
HEL		(35)		-70
HEL+HSt	Appr. 0	(33)	+60	+230
HEL+StOH	-4.8	23.5	+6	—
HEL+StNH <sub>2</sub>	-6.1	22.4	+215	+510
HSt		24.3		+385
StOH pH=3		22.1		+455
StNH <sub>2</sub>		∞		+680
HSt		20.5		-85
StOH pH=9.5		23.0		+410
StNH <sub>2</sub>		23.0		+660

octadecyl alcohol, and 1.0 with stearyl amine.

The increase of surface potential for mixtures with elaidic acid is 50 mv for stearic acid, 30 mv for octadecyl alcohol, and about 100 mv for the amine.

The behavior of the mixture of the amine with elaidic acid suggests a chemical combination of the two, but that of the mixed film with oleic acid gives no such suggestion.

### 3. MIXTURES WITH OLEIC ACID ON BASIC SUBSOLUTIONS (pH=9.5)

The subsolution used for these experiments contained  $10^{-3}$  m sodium bicarbonate,  $10^{-4}$  m calcium chloride, and sodium hydroxide to give a pH of 9.5. When oleic acid is spread on this solution, the effect of the calcium ions is not great enough to condense the film of oleate ions, although the expanded film is much less expanded than that of oleic acid on an acidic subsolution. Stearyl amine spreads in a molecular form and at low pressures forms a condensed film of Type II, which at 19.4 dynes and 20.8 sq. A transforms into Type I.

The most remarkable feature exhibited by the mixtures is that although a stearyl amine film is highly condensed, its presence in the oleate film expands the latter even more (Fig. 3). Mixtures

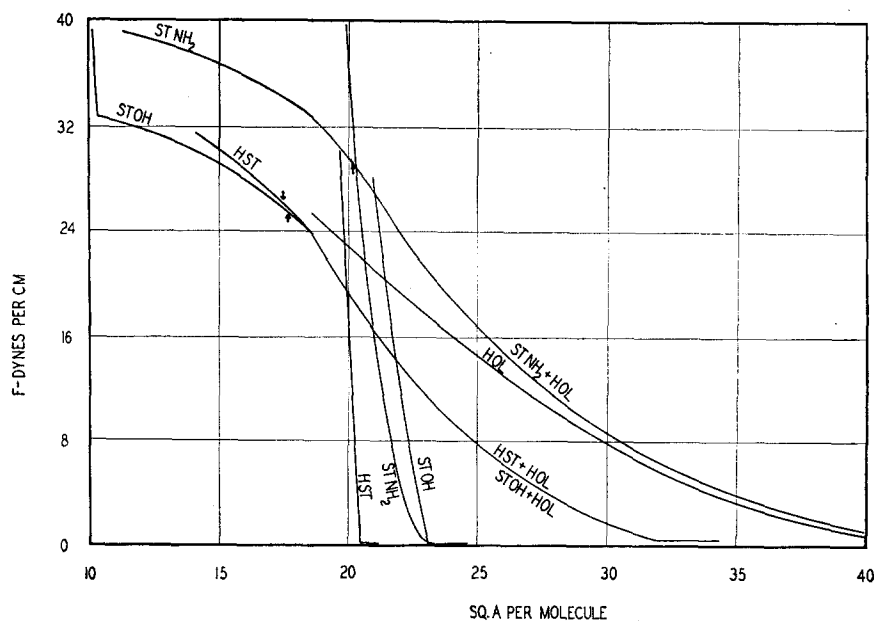


FIG. 3. Mixtures (1 : 1) of oleic acid with stearyl alcohol, amine, and stearic acid on a subsolution of pH 9.5 ( $10^{-3}$   $\text{NaHCO}_3$ ,  $10^{-4}$   $\text{CaCl}_2$  plus  $\text{NaOH}$ ).

with stearic acid or stearyl alcohol are slightly less expanded than on acid subsolutions.

The surface potentials of the mixtures with stearyl alcohol and stearyl amine exhibited almost no departure from the mean, but that with the stearate was 100 mv higher, and passed through a maximum at the lens point for oleic acid. On this subsolution the surface potential is +230 for the oleate, and -85 for the stearate, so forcing the oleic acid out of the film lowers the surface potential.

On further compression the oleic acid was apparently squeezed out of the film, since the pressure began to rise very abruptly in all cases between 20 and 25  $\text{A}^2$  when calculated as if the stearate, stearyl alcohol, or stearyl amine is the only constituent present. Thus the values are practically those for these pure one-component films.

#### 4. MIXTURES WITH ELAIDIC ACID ON BASIC SUBSOLUTIONS (pH=9.5)

If elaidic acid is spread on the same basic subsolution, the 1 : 1 mixed film with stearyl amine is highly condensed, with even smaller areas than that of the pure amine (Fig. 4) instead of being more expanded than the expanded component,

or than the mixed film with oleic acid. The elaidate film is itself less expanded (limiting area 35 sq. A) than that of the oleate (41 sq. A). The mixture of the elaidate and stearate is nearly as much expanded as the pure elaidate, but the other mixtures, with the alcohol and the amine are, in contrast with those with the oleate, highly condensed.

The pure elaidate on this subsolution, even although calcium ion is present, is quite soluble, so it is not easy to obtain accurate values for the molecular area, but the film collapses at about 20 to 25 dynes per cm. The surface potential is about -70 mv, while that of the oleate is +230 mv. Neither pressure-area nor the potential *versus* area curve shows a horizontal portion below 40 dynes.

The elaidate-stearate mixture (expanded) is soluble, but the mixtures which form condensed films are only very slightly soluble. Schulman<sup>1</sup> found earlier that one somewhat soluble component may become much less soluble when a stable mixed film is produced.

The potential interaction is +215 mv for the stearyl amine-elaidate mixture, or of the same order as with a saturated acid, but even although the stearyl alcohol-elaidate mixture is highly condensed the interaction is only +6 mv.

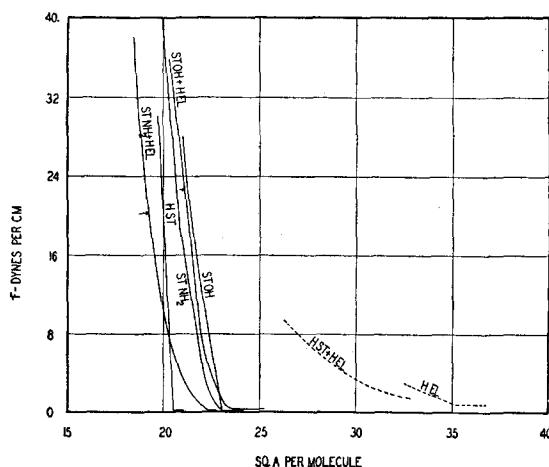


FIG. 4. Mixtures 1 : 1 of elaidic acid with stearyl alcohol, amine, and stearic acid on a basic subsolution (same as for Fig. 3).

While Fig. 4 indicates that the elaidate constituent begins to separate out from the mixtures, as shown by a point structure shown in the dark-field microscope, at 20 dynes/cm with stearyl alcohol, the relations are very different from those in which oleate is present, since this does not bring about a collapse of the film. Obviously very little elaidate separates. It is possible that the extent of the separation would be greater if the film were compressed with extreme slowness.

## 5. DISCUSSION AND CONCLUSIONS

The fact that oleic acid is easily squeezed out from its mixtures with substances which give condensed one-component films, was explained by Schulman<sup>3</sup> as due to a "reduction of the adhering qualities between hydrocarbon groups" caused by the presence of a double instead of one single bond in the chain. Since, however, both the work of Harkins and his collaborators<sup>4-6</sup> and modern

theory indicate a very slight increase in the primary attraction due to the increased polarity, it is important to see if the difference is due instead to the space relations involved.

Since oleic acid is a ciscompound, it seemed that the bending back of the hydrocarbon chain must increase the distance between an oleic acid molecule and its neighbors, which lessens the attraction between it and the hydrocarbon chains, particularly since the molecule is free to rotate and the doubled-back portions of the hydrocarbon chain may in the mixed film sweep out a larger area. The various orientations which the different groups in both the molecule of oleic and that of elaidic acid may assume by rotation and vibration have been studied by the use of space models, and while the relations are complicated, they seem to justify the conclusion that on the average a molecule of oleic should occupy more area in a monolayer than one of elaidic acid. The plane formulas on paper give a misleading picture as compared with that presented by the space models.

From this standpoint it seemed that the use of the transcompound, elaidic acid, should reduce the effect, but not eliminate it, and the experimental work showed, as has been seen, that this is true. The most marked difference was found on a basic solution with calcium ion, on which the mixture of the two expanded films gave with the elaidate and stearyl amine a highly condensed film, while the oleate-amine mixture was even more expanded than the oleate alone.

On an acid subsolution the film of pure elaidic acid is less expanded at low and more expanded at high pressure than that of oleic acid, that is the former is much less compressible than the latter. The mixtures with elaidic acid are very much the more condensed, and with stearyl amine seems to indicate compound formation, while that with oleic acid does not. As found with saturated expanded acids in the preceding paper, the amine has the greatest condensing effect and the acid the least, with the alcohol intermediate.

<sup>3</sup> J. H. Schulman, *Trans. Faraday Soc.* **33**, 1118 (1937).

<sup>4</sup> W. D. Harkins, F. E. Brown and E. C. H. Davies, *J. Am. Chem. Soc.* **39**, 354 (1917).

<sup>5</sup> W. D. Harkins, G. L. Clark and L. E. Roberts, *J. Am. Chem. Soc.* **42**, 700 (1920).

<sup>6</sup> W. D. Harkins and Y. C. Cheng, *J. Am. Chem. Soc.* **43**, 35 (1921).