

## The Spreading of Oils on Water Part II. Nonionized Molecules Having Only One Polar Group

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## The Spreading of Oils on Water

### Part II. Non-Ionized Molecules Having Only One Polar Group

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Experiments are described on the spreading upon water of drops of oil containing small amounts of alcohols, esters, ketones, phenols, non-ionized acids, and non-ionized amines. It is shown that such polar molecules do not cause spreading unless the molal concentration exceeds a certain value,  $c_0$ , which varies with the nature of the polar group, the chain length, the possible geometrical configurations of the molecule, and with the solubility in oil. The cause of their spreading is demonstrated to be a reversible adsorption at the oil-water interface associated with the osmotic pressure of the polar molecules dissolved in the oil. The average lifetime of adsorption of such molecules is shown to be only a small fraction of that of ionized molecules.  $A_0$ , the interfacial area per adsorbed molecule at the film pressure of 11.3 dynes per cm, is given for a considerable number of saturated and unsaturated straight- and branched-chain acids and alcohols. The observed changes of  $A_0$  with chain length and polar group are explained on the basis of structural and kinetic considerations. Certain new spreading phenomena due to the formation of colloidal suspensions and crystalline precipitates of the polar compounds are described, and use is made of the latter to measure the solubility in oils of the various straight chain saturated acids and alcohols.

#### 1. INTRODUCTION

IT was demonstrated in Part I<sup>1</sup> that open-chain fatty acids and amines having over 13 carbon atoms per molecule adsorbed completely at the oil-water interface if the pH of the water was adjusted to values greater than 10.5 or less than 3, respectively. Stated in another way, the lifetime of adsorption of the ionized polar molecule was found to be infinite.

The investigations here described were concerned with the spreading of oil drops containing non-ionized polar molecules. In order to obtain a theoretically acceptable interpretation, the alcohols were first observed, since in the pH range

used (pH 2 to pH 13) no ionization could occur at the interface. This was followed by the study of the spreading due to fatty acids on acid water and fatty amines on alkaline water with the pH adjusted in each case practically to stop ionization at the oil-water interface. Finally, the other non-ionizable molecules were studied.

The white mineral oil used throughout the experiments of Part I was also employed here.

#### 2. SPREADING DUE TO MONOHYDROXY ALCOHOLS

Each of the members of the open-chain saturated alcohols from hexanol ( $C_6$ ) to eicosanol ( $C_{20}$ ) was dissolved in the mineral oil and drops of each solution were spread on the clean surface

<sup>1</sup> W. A. Zisman, J. Chem. Phys. 9, 534 (1941).

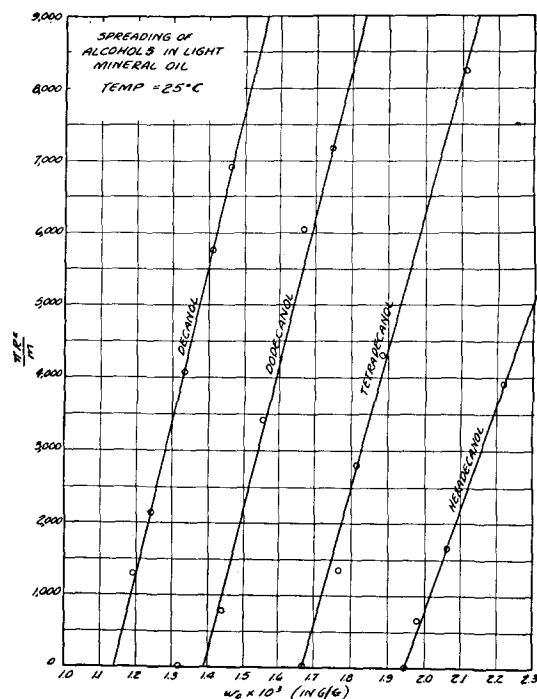


FIG. 1.

of distilled water at 25°C. It was found that spreading did not occur unless the weight concentration,  $w$ , exceeded a certain value  $w_0$ . The greater the difference  $w - w_0$ , the more rapid the rate of spreading and the greater the maximum area attained. For large values the films became thin enough to show uniform interference colors, in which case they broke up soon after attaining their maximum areas. The lower the molecular weight of the alcohol, the more rapid the rate of spreading, and the more violent the break-up of the oil disk. When the maximum spreading area per gram of oil ( $\pi R^2/m$ ) was plotted against  $w - w_0$ , a straight line was obtained for each substance studied (see Fig. 1).

These phenomena are manifestations of short-lifetime adsorption at the oil-water interface. Every molecule of alcohol which adsorbs at the interface does not remain there indefinitely, but, due to the effects of the oil solubility of the hydrocarbon chain of the molecule and to the effects of the collisions of the interfacial molecules with one another and with the neighboring water and oil molecules, it leaves after a brief stay and disappears into the volume of the oil drop. At any instant, however, the interfacial area will

contain adsorbed molecules, and their thermal agitation and mutual forces will result in the creation of a two-dimensional interfacial film pressure which will always act to increase the interfacial area. However, the spreading cannot commence until the film pressure,  $F$ , exerted by the adsorbed molecules exceeds the resultant of the surface tension forces acting on the thin oil disk. This resultant,  $F_0$ , was shown in Part I, Section 2 to be  $-11.3$  dynes/cm for the mineral oil used.

No disk spreading can occur when  $w$  is less than  $w_0$  because the film pressure due to the adsorbed molecules is too small. Once spreading of the oil drop can take place, the alcohol molecules adsorb as fast as new interfacial area is made available. The newly adsorbed molecules come from the alcohol distributed within the volume of the oil drop in the neighborhood of the interface, and the volume concentration in the drop decreases accordingly. Finally, the spreading ceases when the weight concentration in the drop has decreased to the value  $w_0$ , and equilibrium results. As evidence for the correctness of this description, when a multiple dropper (see Part I, Section 10) was employed to exert an external pressure on the oil drop, the disk contracted practically completely when the piston oil exerted an external pressure of only 15 dynes/cm. This is quite unlike the behavior under the same conditions of adsorbed films of ionized molecules, for they contracted only as much as necessary to obtain the closest packing of the adsorbed molecules.

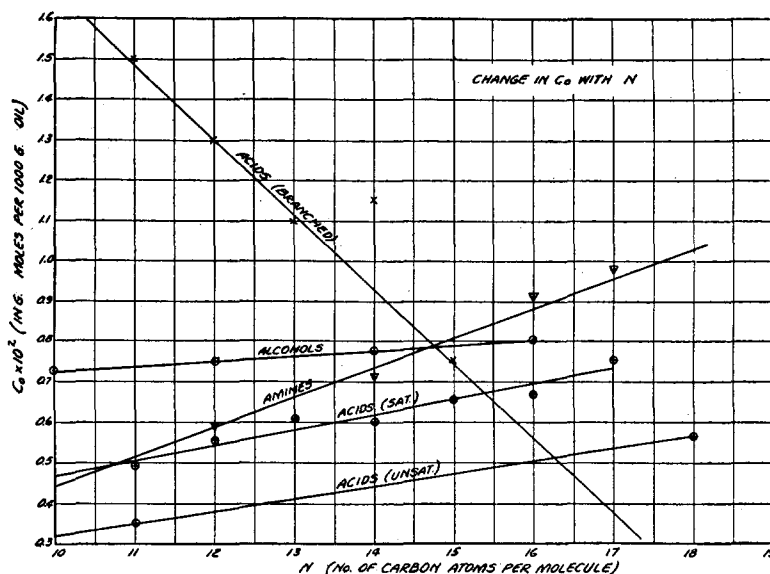
Now  $w - w_0$  is the amount of alcohol which had to flow from the oil drop to the interface to permit the disk to expand to its maximum spreading area  $S$ . Hence, if  $m$  is the mass of the oil drop, the number of alcohol molecules given up by the solution to form the film will be:

$$(w - w_0)m/M(6.06 \times 10^{23}), \quad (1)$$

TABLE I. *Aliphatic alcohols in mineral oil (temperature 25°C).*

ALCOHOL	$N$	$w_0$ IN G/G	$c_0$ MOLES/1000 G	$A_0$ IN CM <sup>2</sup>
Eicosanol	20	Too insoluble	—	—
Octadecanol	18	Too insoluble	—	—
Hexadecanol	16	$1.94 \times 10^{-3}$	$0.802 \times 10^{-2}$	$57.2 \times 10^{-16}$
Tetradecanol	14	$1.66 \times 10^{-3}$	$0.776 \times 10^{-2}$	$65.7 \times 10^{-16}$
Dodecanol	12	$1.39 \times 10^{-3}$	$0.749 \times 10^{-2}$	$56.2 \times 10^{-16}$
Decanol	10	$1.14 \times 10^{-3}$	$0.722 \times 10^{-2}$	$55.4 \times 10^{-16}$

FIG. 2.



where  $M$  is the gram molecular weight of the alcohol. If  $A_0$  is the area per interfacial molecule, and  $R$  is the maximum radius attained by the spreading oil disk, then  $S = \pi R^2$ , and the number of molecules in the interface must be:

$$\pi R^2 / A_0. \quad (2)$$

Since expressions (1) and (2) are equal;

$$\pi R^2 / A_0 = (w - w_0)m / M(6.06 \times 10^{23}). \quad (3)$$

Differentiating (3) with respect to  $w$  gives the relation:

$$d/dw(\pi R^2/m) = A_0/M(6.06 \times 10^{23}). \quad (4)$$

The left-hand side of (4) is the slope,  $\tan \theta$ , of the straight line whose equation is given by (3), and it can be obtained by plotting  $\pi R^2/m$  against  $w$ . Hence, the useful relation is obtained:

$$A_0/M = (6.06 \times 10^{23}) \tan \theta. \quad (5)$$

This quantitative treatment may be incorrect if all of the polar material in the oil is not in true solution. If the total weight concentration of polar material added to the oil is  $w$ , it may actually consist of a colloidal portion,  $w_c$ , and a non-colloidal portion,  $w_s$ , where  $w = w_c + w_s$ . In measuring  $A_0$  by diluting this solution and so measuring  $\pi R^2/m$  as a function of  $w$ , the colloidal part,  $w_c$ , may vary in a complex manner depending on the history of the dilution process. Hence the quantity  $(w - w_0)$  need not be the amount of

polar material adsorbed at the oil-water interface at concentration  $w$ . Therefore (5) can give incorrect values of  $A_0$  under such circumstances. This was found to be the case in studying solutions of tri-*p*-tert amyphenyl phosphate in oil.

Relation (5) does not require a precise knowledge of the state of molecular association of the polar material in solution, for so long as the value of  $M$  used is that of the unassociated molecule, the value of  $A_0$  obtained from a spreading oil drop analysis will be the area per unassociated molecule as adsorbed at the interface. For example, if hexadecanol is studied and the value of  $M$  used in (5) is that of a single molecule, then  $A_0$  is found to be  $57.2 \times 10^{-16} \text{ cm}^2$ . If it is assumed that association occurs in pairs,  $M$  is twice as great and so is  $A_0$ ; hence the area per chain is unchanged. Therefore no information is given as to whether or not the adsorbed molecules are also associated in pairs when adsorbed at the oil-water interface.

It was found that whereas  $A_0$  was not temperature sensitive,  $w_0$  was definitely so. Since  $w_0$  is the concentration at which  $F$  equals the resultant of all the surface tension forces acting on the rim of a flat disk of oil, and since the surface tensions of oil and water are affected markedly by temperature changes,  $w_0$  would be expected to be temperature sensitive. In fact the value of  $w_0$  for the long-chain alcohols was found to increase roughly 5 percent for a rise of  $1^\circ\text{C}$ .

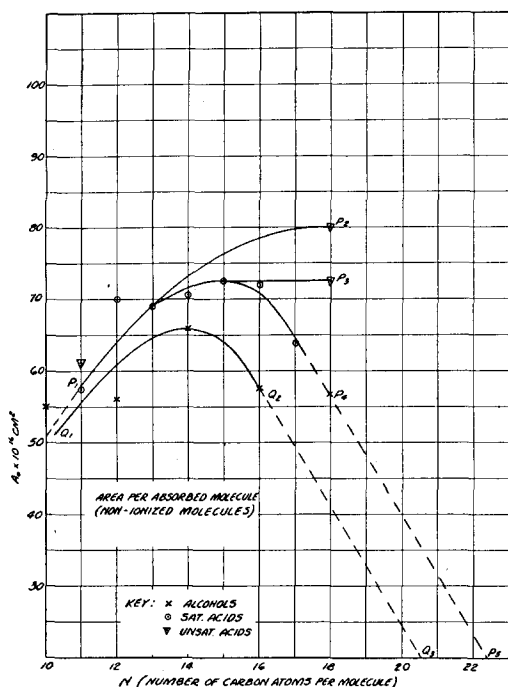


FIG. 3.

This change may be due in part to the increase with temperature of the solubility of the alcohol in oil.

The results obtained with the aliphatic alcohols are given in Table I and Fig. 1. In the third column  $w_0$  is expressed in grams of alcohol per gram of oil, while in the fourth column  $c_0$  is its value when expressed in gram molecules per 1000 grams of oil. In the fifth column is given,  $A_0$ , the area per adsorbed molecule.

One regularity shown by these data has been brought out in Fig. 2. Upon plotting  $c_0$  against  $N$ , the number of carbon atoms per molecule, it is found that  $c_0$  is a linear function of  $N$ .

Edge loss, or the edge diffusion phenomenon described in Part I, Section 4, also occurred here during and after the spreading of the oil disk. This effect became more pronounced the shorter the chain length of the molecule. The break-up effects were quite characteristic of the chain length and concentration of the polar molecules.

From the relation (5) a value of  $A_0$  can be computed; however, the existence of edge diffusion obviously may cause the calculated value to be too small, the error being greater the more rapid the rate of edge loss, or in other words,

the lower the molecular weight. That the value of  $A_0$  is nearly correct for all values of  $N$  of Table I will later be demonstrated by an independent method of measuring  $A_0$ . In Fig. 3 will be found a plot of  $A_0$  against  $N$ .

It might be thought that the lower values of  $A_0$  when  $N$  decreases beyond 14 are due to the increased solubility in the water of the interfacially adsorbed molecules. Adams' well-known rule<sup>2</sup> that monolayers of alcohols and acids at the air-water interface are insoluble if  $N$  exceeds 12 is not true for monolayers at the oil-water interface. This is to be expected since at the latter interface the polar molecule is attracted by both the water and the oil. To prove this point a very simple experiment was performed using octanol dissolved in oil at a concentration which did not cause spreading but did show a high rate of edge diffusion. When the boundary of the disk was compressed externally with an insoluble long-chain monolayer like eicosanol, or with a film of talc, it stopped the edge diffusion. After an hour the pressure was released and the edge diffusion commenced with undiminished intensity. If the octanol molecules adsorbed at the oil-water interface had been appreciably water soluble, all of them would have been dissolved in that time since an hour is much more than the time needed for all the octanol molecules to diffuse from the oil to the interface, adsorb, and finally dissolve in the water. On the other hand a monolayer of octanol adsorbed at the air-water interface dissolved in a few minutes.

Experiments were made with mineral oil to which progressively larger amounts of hexadecanol were added until  $w$  exceeded the solubility limit as evidenced by the subsequent precipitation of crystals. It was found that as long as the solubility limit was not exceeded uniformly colored films were obtained and the graph

TABLE II. Solubilities of alcohols in mineral oil (temperature 25°C).

ALCOHOL	$N$	IN SONNEBORN PETROLATUM	IN SQUIBB'S HEAVY PETROLATUM
Octadecanol	18	Less than $2 \times 10^{-3}$ g/g	Less than $2 \times 10^{-3}$ g/g
Hexadecanol	16	$2.5 \times 10^{-3}$	$2.6 \times 10^{-3}$
Tetradecanol	14	$6.1 \times 10^{-3}$	$4.4 \times 10^{-3}$
Dodecanol	12	$10.2 \times 10^{-3}$	$8.8 \times 10^{-3}$

<sup>2</sup> N. K. Adam, *The Physics and Chemistry of Surfaces* (Clarendon Press, Oxford, 1938), second edition.

of  $\pi R^2/m$  versus  $w$  was a good straight line. When  $w$  exceeded the value  $w_m = 2.5 \times 10^{-3}$  gram per gram, the graph was still a straight line, but numerous colored spots appeared in the oil film during the spreading. Experiments with tetradecanol furnished similar results when  $w$  exceeded the value of  $w_m = 6.1 \times 10^{-3}$ , and the colored spots spread more rapidly relative to the rest of the film. A similar experiment with dodecanol resulted in  $w_m = 10.2 \times 10^{-3}$ , but the incidence of the phenomenon was not as sharply defined as in the case of the other two alcohols.

Since experiments showed that precipitation of crystals occurred only when the hexadecanol concentration exceeded  $2.5 \times 10^{-3}$ , it was concluded that  $w_m$  which was defined by the incidence of spots was actually the solubility limit. The resulting solubilities are in agreement with the well-known fact that the solubility of long chain alcohols in oil increases as the number of carbon atoms ( $N$ ) decreases.

The appearance of these spots is due to the more rapid spreading of the oil disk in the vicinity of an undissolved crystal or of an undissolved droplet of the alcohol which has migrated to the oil-water interface under the influence of gravity. This change in the character of the spreading of oil drops in passing through the solubility limit can be used as a technique to measure the solubility of any slightly soluble polar substance which by itself is able to spread on water as a monolayer. However, it cannot be employed with much success if the solubility limit ( $w_m$ ) is great, since the rate of disk spreading increases with the difference  $w - w_0$ , so that before  $w$  has reached the value  $w_m$ , the speed of spreading will have become so great that it will be impossible to differentiate with the naked eye between the spreading in the locality of the undissolved crystal and that of the surrounding film. In Table II are listed the solu-

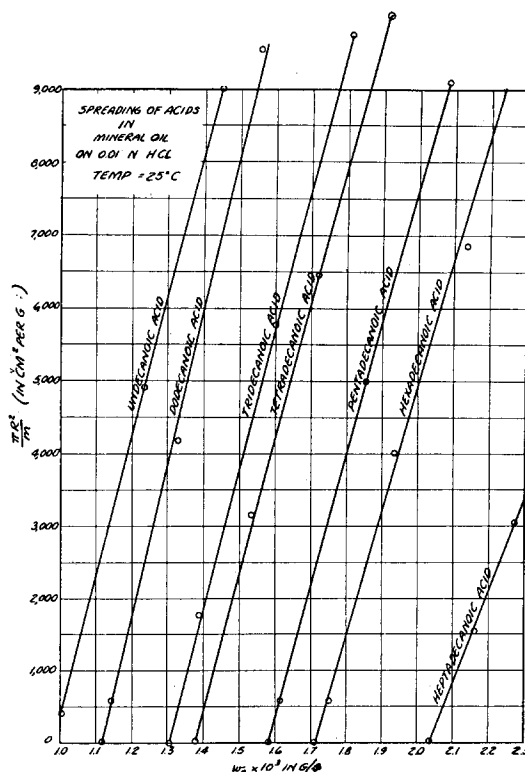


FIG. 4.

bilities of the three alcohols studied expressed in grams of alcohol per gram of oil. These measurements are probably correct to within  $\pm 3$  percent. Such accuracy was considered sufficient for the purpose of this work. A graph of the solubility,  $w_m$ , versus  $N$  is linear for Sonneborn light petrolatum, but is not for Squibb's heavy petrolatum.

The solubility data of the preceding paragraph permit an important experimental conclusion with regard to the mechanism involved in the spreading of non-ionized molecules. If the linear increase in the area of the spreading disk with increasing  $w$  were due to the fact that the intercept  $w_0$  was actually the solubility limit and  $w - w_0$  the excess undissolved alcohol, which in that way was made available to be adsorbed and cause spreading, then necessarily the solubility limit would have to be greater for hexadecanol than for dodecanol, since from Table I  $w_0$  increases with  $N$ . However, the solubility measurements of the preceding paragraph show that the reverse is actually the case. Hence  $w_0$  cannot be the solubility limit, but is less than that, and the

TABLE III. Cyclic alcohols in mineral oil (temperature 25°C).

ALCOHOL	$N$	$w_0$	$c_0$
Benzyl alcohol	7	$3.4 \times 10^{-3}$	$3.2 \times 10^{-2}$
Diphenyl carbinol	13	$0.9 \times 10^{-3}$	$0.55 \times 10^{-2}$
Phenyl benzyl carbinol	14	$1.0 \times 10^{-3}$	$0.51 \times 10^{-2}$
Cyclohexanol	6	$2.4 \times 10^{-3}$	$2.4 \times 10^{-2}$
1-Ethyl cyclohexanol	8	$2.7 \times 10^{-3}$	$2.1 \times 10^{-2}$

difference becomes rapidly greater as  $N$  decreases (compare Tables I and II). The only conclusion left is that the spreading of oil disks containing non-ionized molecules is a manifestation of interfacial adsorption from a true solution.

The lack of disk spreading found at 25°C for eicosanol and octadecanol has a simple explanation. From Table I it is evident that  $w_0$  increases as  $N$  increases, while from Table II the solubility,  $w_m$ , decreases as  $N$  increases. In the case of octadecanol or of homologous alcohols of still greater molecular weight,  $w_m$  is less than  $w_0$ ; that is, the low solubility does not permit dissolving enough alcohol for the adsorbed molecules to exert sufficient surface pressure to cause disk spreading.

As would be expected from the fact that the alcohols do not dissociate in water, the spreading effects of alcohols in oil were found to be uninfluenced by changes in the pH of the water or by the presence of metallic ions.

The spreading effects due to cyclic alcohols were studied much more briefly and the results are given in Table III. It will be noted that  $c_0$  is greater the greater the solubility of the alcohol in the oil. All these alcohols showed strong edge diffusion, the effect being greater the smaller the number of carbon atoms in the longest chain or branch of the molecule. In all cases the edge diffusion was too pronounced to permit accurate measurements of  $A_0$  by observation of the maximum spreading diameters. However,  $w_0$  could be approximately determined by seeking that concentration of alcohol in the oil which just caused the drop to begin to spread. Due to their insolubility in oil interesting alcohols like *p*-hydroxy diphenyl and triphenyl carbinol could not be studied.

TABLE IV-A. Saturated acids in mineral oil—temp. 25°C (spread on 0.01 N HCl).

ACID	$N$	$w_0$ IN G/G	$c_0$ MOLES/1000 G	$A_0$ IN CM <sup>2</sup>
Hexacosanoic	26	Too insoluble	—	—
Eicosanoic	20	Too insoluble	—	—
Nonadecanoic	19	Too insoluble	—	—
Octadecanoic	18	Too insoluble	—	—
Heptadecanoic	17	$2.05 \times 10^{-3}$	$0.752 \times 10^{-2}$	$63.8 \times 10^{-16}$
Hexadecanoic	16	$1.71 \times 10^{-3}$	$0.667 \times 10^{-2}$	$72.0 \times 10^{-16}$
Pentadecanoic	15	$1.58 \times 10^{-3}$	$0.653 \times 10^{-2}$	$72.6 \times 10^{-16}$
Tetradecanoic	14	$1.37 \times 10^{-3}$	$0.601 \times 10^{-2}$	$70.5 \times 10^{-16}$
Tridecanoic	13	$1.30 \times 10^{-3}$	$0.607 \times 10^{-2}$	$68.9 \times 10^{-16}$
Dodecanoic	12	$1.11 \times 10^{-3}$	$0.556 \times 10^{-2}$	$69.8 \times 10^{-16}$
Undecanoic	11	$0.98 \times 10^{-3}$	$0.530 \times 10^{-2}$	$57.4 \times 10^{-16}$

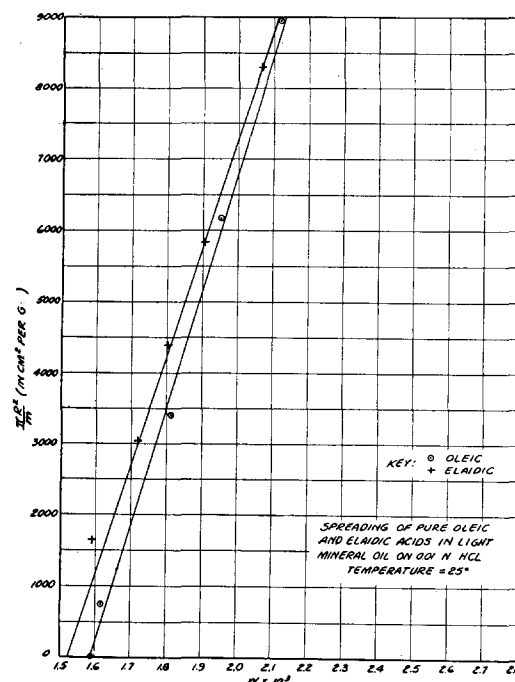


FIG. 5.

All of the alcohols described here were Eastman preparations except the 1-ethyl cyclohexanol which was kindly supplied by W. A. Mosher<sup>3</sup> of the Hercules Powder Company and the eicosanol which was prepared by Dr. Homer Adkins of the University of Wisconsin.

### 3. SPREADING DUE TO NON-IONIZED MONOCARBOXYLIC ACIDS

Each of the saturated open-chain acids described in Part I was also studied when spread on 0.01 normal HCl, and it was found in each case that precisely the same spreading phenomena occurred as have been described for the various alcohols. In Fig. 4 will be found graphs of  $\pi R^2/m$  against  $w$  for these acids, while the results suitable for comparison with those for the alcohols will be found in Tables IV-A and IV-B. The eicosanoic, nonadecanoic, and pentadecanoic acids were highly purified specimens supplied by Dr. Roger Adams of the University of Illinois; the oleic and elaidic acids were freshly prepared in a high state of purity by Dr. J. Kass of the University of Minnesota. The other acids were Eastman preparations.

<sup>3</sup> W. A. Mosher, J. Am. Chem. Soc. **62**, 552 (1940).

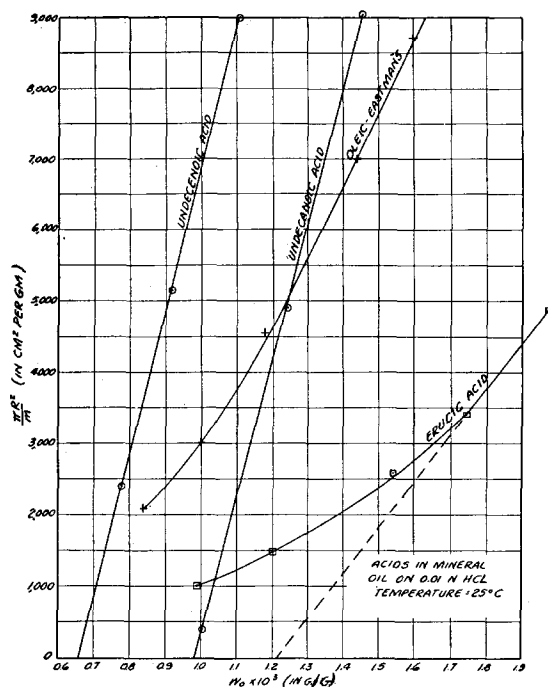


FIG. 6.

The preceding study of the spreading of alcohols furnished the clue as to the cause of the non-spreading of oil drops containing low concentrations of long-chain fatty acids on acid water (see Part I, Section 13). On acid water the fatty acids are not ionized, hence they adsorb like any other non-ionized molecules and cause disk spreading only when  $w$  exceeds a value  $w_0$  of the order of magnitude of  $10^{-3}$ . These conclusions evidently extend the earlier conclusion of Langmuir<sup>4,5</sup> which concerned the adsorption of stearic acid at the oil-water interface. Therefore, in contrast with the behavior of ionized molecules, all non-ionized polar molecules have very short lifetimes of adsorption.

A graph of  $c_0$  against  $N$  (see Fig. 2) is a straight line. Also the mean value of  $c_0$  for acids is  $0.613 \times 10^{-2}$  while for alcohols it is  $0.762 \times 10^{-2}$ . The lower value for the acids can be considered either as a manifestation of the smaller solubility in oil of the acids, or more likely, as evidence of the greater energy of adhesion of the carboxyl group to water, than of the hydroxyl group.

Upon comparing the value of  $A_0$  for each

alcohol and the corresponding acid, it is evident that it is always greater for the acid. This is not due to the effect of a slight dissociation of the fatty acid at the water interface for the same results were obtained using acid water varying in strength from 0.01 to 0.05 normal.

The lower values of  $c_0$  for the *cis*- and *trans*-isomers oleic and elaidic acids, as well as for undecenoic acid, than for the corresponding saturated acids (see Figs. 5 and 6) are noteworthy. An evident interpretation is that the presence of double bonds increases the average adsorption lifetime.

As an example of the great sensitivity of  $A_0$  and  $c_0$  to the state of purity of the acid preparation used, Eastman oleic acid gave a straight line graph of  $\pi R^2/m$  against  $w$  only for large values of  $w$ , and from this slope the values for  $A_0$  and  $c_0$  were calculated to be  $46 \times 10^{-16}$  and  $0.25 \times 10^{-2}$ , respectively. In contrast the pure acid prepared by Dr. Kass gave an excellent straight line for all values of  $w - w_0$ , and  $A_0$  and  $c_0$  were calculated to be  $79.8 \times 10^{-16}$  and  $0.564 \times 10^{-2}$ , respectively (compare Figs. 5 and 6). The values of  $A_0$  and  $c_0$  for oleic, elaidic, and undecenoic acids when plotted in Figs. 2 and 3 led to the suggestive curves shown. From the appearance of the graph for Eastman erucic acid (see Fig. 6) it was concluded that polar impurities were present.

Just as in the case of alcohols, the saturated fatty acids showed an increasing value of  $c_0$  as the number of carbon atoms per chain ( $N$ ) increased, and similarly it was found that the solubility in the mineral oil decreased as  $N$  increased. Thus the solubility of hexacosanoic acid ( $N=26$ ) was less than  $10^{-4}$ , that of eicosanoic acid ( $N=20$ ) was between  $0.4 \times 10^{-3}$  and  $1.0 \times 10^{-3}$ , that of octadecanoic acid ( $N=18$ ) was approximately  $1.0 \times 10^{-3}$ , and that of tetradecanoic acid exceeded  $3.0 \times 10^{-3}$ .

It was found that oil drops containing octa-

TABLE IV-B. *Unsaturated acids in mineral oil—temp. 25°C (spread on 0.01 N HCl).*

Acid	$N$	$w_0$ IN G/G	$c_0$ MOLES/1000 G	$A_0$ IN CM <sup>2</sup>
Erucic	22	$1.22 \times 10^{-3}$	$0.361 \times 10^{-2}$	$36.8 \times 10^{-16}$
Oleic	18	$1.59 \times 10^{-3}$	$0.564 \times 10^{-2}$	$79.8 \times 10^{-16}$
Elaidic	18	$1.53 \times 10^{-3}$	$0.541 \times 10^{-2}$	$72.7 \times 10^{-16}$
Undecenoic	11	$0.650 \times 10^{-3}$	$0.353 \times 10^{-2}$	$61.1 \times 10^{-16}$
Linolenic	18	$0.560 \times 10^{-3}$	$0.202 \times 10^{-2}$	$56.5 \times 10^{-16}$

<sup>4</sup> I. Langmuir, J. Frank. Inst. **218**, 143 (1934).

<sup>5</sup> I. Langmuir, Science **84**, 382 (1936).



decanoic acid did not spread on acid water at 25°C. This behavior was similar to that of octadecanol already described (Section 2) and had the same cause; i.e.,  $w_0$  for octadecanoic acid would of necessity, according to Table IV-A, be greater than for heptadecanoic acid, and therefore greater than  $2.0 \times 10^{-3}$ . Since the solubility of octadecanoic acid was less than  $1.0 \times 10^{-3}$ , disk spreading was impossible when using this mineral oil.

The results obtained with solutions in mineral oil of members of a homologous series of branched-chain acetic acid derivatives are presented in Table V. These were kindly supplied from preparations made some years ago under the direction of Dr. Roger Adams at the University of Illinois. The rapid decrease in  $A_0$  for the last four acids was due in greater part to the rapid increase in the rate of edge diffusion as the length of the longest branched chain ( $N_1$ ) decreased from 15 to 8 carbon atoms. It will be noted that  $c_0$  is approximately a linearly decreasing function of  $N_1$  (see Fig. 2). Due to the presence of small amounts of polar impurities, possibly formed in aging, more accurate measurements of  $w_0$  and  $A_0$  were not possible. As in the case of the oleic acid, already mentioned, the impurities caused sufficient departure of the  $\pi R^2/m$  vs.  $w$  curve from linearity for low values of  $w - w_0$  to make it difficult to measure accurately the intercept and slope and so obtain  $w_0$  and  $A_0$ .

Various acid molecules containing closed hydrocarbon chains were also studied and the limits of the oil solubility are given (Table VI). The chaulmoogric and hydnocarpic acids were pure, freshly prepared specimens obtained from Dr.

Roger Adams, while the other acids were Eastman chemicals. The low values of  $w_0$  obtained for the chaulmoogric and hydnocarpic are to be attributed, at least in part, to the low oil solubilities of the hydrocarbon tails of the molecules which consist of a cyclopentyl group at the end of a saturated straight chain. Since  $w_m$  was less than  $w_0$  it was not possible to measure  $A_0$ . As for the last three acids of this table, like the closed-chain alcohols of Table III, the edge diffusion effects were so pronounced as to prevent any accurate measurement of  $A_0$ .

A series of arylstearic acids already described in the literature<sup>6</sup> were kindly made available by Dr. Stirton of the Division of Industrial Farm Products Research of the Department of Agriculture. In Table VII will be found the results of measurements of  $w_0$  and  $c_0$  on 0.01 normal hydrochloric acid. It will be noted that  $c_0$  does not vary considerably, the mean value being  $0.23 \times 10^{-2}$ . The lower values of  $c_0$  as compared with those of the single chain molecules of Table IV-A cannot be due to the relative oil solubilities of the hydrocarbon portions of the acid molecules, for the arylstearic acids have the greater oil solubilities. It is suggested that either the lifetime of adsorption is greater for these arylstearic acids, or that they exert a greater surface pressure when adsorbed than does a monolayer containing the same number of stearic acid molecules per unit area.

#### 4. SPREADING DUE TO NON-IONIZED AMINES

Although oil drops containing concentrations of the order of magnitude of  $w = 10^{-5}$  of aliphatic amines were found to spread readily on acid water and not at all on alkaline water (see Part I, Fig. 8), spreading also resulted on water of high pH if  $w$  exceeded a critical concentration  $w_0$ . Values of  $w_0$  are given in Table VIII for various carefully purified primary aliphatic amines furnished generously by the chemical research laboratory of Armour and Company.

The concentration  $c_0$  is an increasing linear function of  $N$  as shown in Fig. 2. Evidently the behavior of the aliphatic primary amines on alkaline water is entirely similar to that of the

TABLE V. *Aliphatic branched chain acids in mineral oil—temp. 25°C (spread on 0.01 N HCl).*

ACID	$N$	$N_1$	$w_0 \times 10^3$	$c_0 \times 10^2$	$A_0 \times 10^{18}$ CM <sup>2</sup>
*N-Pentadecyl acetic	0+15+2	15	2.05	0.75	63.8
Methyl N-tetra- decyl acetic	1+14+2	14	(3.0–3.2)	1.15	(50–62)
Ethyl N-tridecyl acetic	2+13+2	13	2.9	1.1	55
N-propyl N-dodecyl acetic	3+12+2	12	(3.5–3.6)	1.3	(21–32)
N-butyl N-undecyl acetic	4+11+2	11	(3.9–4.2)	1.5	(15–26)
N-heptyl N-octyl acetic	7+8+2	8	4.9	1.8	13

\* This is heptadecanoic acid (see Table IV-A) written for purpose of comparison as an acetic acid derivative.

<sup>6</sup> A. Stirton and R. Peterson, Ind. Eng. Chem. **32**, 1137 (1940).

TABLE VI. Various closed-chain acids in mineral oil—temp. 25°C (spread on 0.01 N HCl).

ACID	<i>N</i>	<i>w</i> <sub>0</sub>	<i>c</i> <sub>0</sub> MOLES/1000 G	<i>w</i> <sub>m</sub> IN G/G
Chaulmoogric	18	$(1.0-1.5) \times 10^{-4}$	$(0.36-0.54) \times 10^{-3}$	$1.6 \times 10^{-4} < w_m$ $< 5.3 \times 10^{-4}$
Hydnocarpic	16	$5.5 \times 10^{-4}$	$0.22 \times 10^{-3}$	$w_m > 9.5 \times 10^{-4}$
Dibenzyl acetic	7+7+2	$1.4 \times 10^{-4}$	$0.58 \times 10^{-3}$	$w_m > 2.7 \times 10^{-3}$
Di- <i>n</i> -heptyl acetic	7+7+2	$3.6 \times 10^{-3}$	$1.4 \times 10^{-2}$	$w_m > 6 \times 10^{-3}$
Cyclohexane carboxylic	7	$(1.5-1.8) \times 10^{-3}$	$(1.2-1.4) \times 10^{-2}$	$w_m > 5 \times 10^{-3}$

aliphatic alcohols on water and of the aliphatic acids on acid water. In fact, so long as the polar end of the molecule cannot ionize while at the oil-water interface, all aliphatic polar molecules appear to behave analogously as regards the general character of the adsorption phenomena.

When a primary amine caused an oil drop to spread on alkaline water, it spread to a definite maximum diameter, stopped a few seconds, and then resumed spreading over a much larger area to make a thin colored film in which holes were formed during the final stages of spreading. Whereas the first stage of spreading was a characteristic effect due to the short lifetime of adsorption of undissociated amine molecules, the second stage was caused by a chemical reaction between the interfacial amine film and carbon dioxide dissolved in the water. This effect was first identified by noticing that blowing one's breath on the oil disk immediately accelerated the second stage of spreading. It was found not to be due to the air pressure, and it was concluded that the effect might be due to the carbon dioxide in the breath. Finally, when carbon dioxide vapor from a piece of "dry ice" was formed over the disk, the effect showed immediately in a most pronounced manner. When Na<sub>2</sub>CO<sub>3</sub> was dissolved in the water, the secondary spreading effects were not accelerated, but when NaHCO<sub>3</sub> was dissolved in the water that type of spreading was always greatly accelerated. Therefore, it was concluded that the effect was caused by a reaction between the amine molecules adsorbed at the interface and the high HCO<sub>3</sub> ion concentration in the water surface resulting in the formation of a highly adsorbed carbonate of that amine.

A number of secondary and tertiary aliphatic amines were investigated in a similar fashion and the results are presented in Table IX. The higher values of *w*<sub>0</sub> for these amines as compared

to the primary amines are possibly to be associated with their much greater oil solubilities. Similar experiments with various aromatic and naphthenic amines produced entirely similar results (see Table X).

Edge diffusion was found to a remarkable extent in secondary and tertiary amines. There is no doubt that in the case of the branched chain molecules the total number of carbon atoms per molecule *N* does not alone control the rate of edge diffusion, for there is a pronounced difference between branched chain and single chain molecules having the same value of *N*. This is in agreement with conclusions reached in Part I, Section 4.

### 5. SPREADING DUE TO ESTERS

Results of studying the spreading of solutions of esters are presented in Table XI. The effects were quite similar to those found for the other non-ionized molecules.

The tri-*p*-tert amylphenyl phosphate was a laboratory product of the Sharples Solvents Corporation and the tri-*p*-cresyl phosphate was an Eastman preparation. Both appeared to dissolve readily in the oil, but the very gradual formation of tiny holes in the otherwise stable colored oil films formed gave good evidence for concluding that some of the phosphates were present as a colloidal dispersion in the oil. The

TABLE VII. Arylsteoric acids in mineral oil—temp. 25°C (spread on 0.01 N HCl).

ACID	MOLE WT.	<i>w</i> <sub>0</sub>	<i>c</i> <sub>0</sub>
Phenylundecylic	263	$0.42 \times 10^{-3}$	$0.17 \times 10^{-2}$
Phenylstearic	360	$0.88 \times 10^{-3}$	$0.24 \times 10^{-2}$
Ethylphenylstearic	388	$1.05 \times 10^{-3}$	$0.27 \times 10^{-2}$
Diisopropylphenylstearic	430	$1.54 \times 10^{-3}$	$0.35 \times 10^{-2}$
<i>p</i> -Chlorophenylstearic	395	$0.66 \times 10^{-3}$	$0.17 \times 10^{-2}$
Xyllylsteoric	293	$1.26 \times 10^{-3}$	$0.32 \times 10^{-2}$
Pseudocumylstearic	406	$0.85 \times 10^{-3}$	$0.21 \times 10^{-2}$
Cymylstearic	416	$0.97 \times 10^{-3}$	$0.23 \times 10^{-2}$
Tetrahydronaphthylstearic	416	$0.87 \times 10^{-3}$	$0.21 \times 10^{-2}$
Xenylstearic	441	$0.48 \times 10^{-3}$	$0.11 \times 10^{-2}$

tri-amyl citrate and the tri-amyl borate were semi-commercial products of the Sharples Solvents Corporation, and each showed the high rate of edge diffusion to be expected from molecules containing only short hydrocarbon chains. The other esters were Eastman preparations.

A group of arylstearic acid esters obtained from Dr. Stirton<sup>6</sup> was also studied. These were methyl- and phenyl-undecylate, ethylphenyl stearate, ethylxylyl stearate, methylphenoxyphenyl stearate, butylphenoxyphenyl stearate, and butylxylyl stearate. All gave values of  $w_0$  in excess of  $5 \times 10^{-3}$ , which is from 5 to 10 times as great as the values for the corresponding arylstearic acids (see Table VII). This is presumably due to the shorter lifetime of adsorption of the ester group and to the much higher oil solubilities of esters than acids.

#### 6. SPREADING DUE TO KETONES

Oil solutions of various aliphatic and aromatic ketones gave results similar in their general nature to those already found for other non-ionized molecules, and the results are given in Table XII. The ketones, presumably due to their shorter lifetimes of adsorption and their higher solubilities in oil, had much larger values of  $c_0$  than did any of the long-chain acids or alcohols.

The solubilities in oil were measured only for the least soluble ketones, i.e., di-undecyl ketone ( $w_m = 15 \times 10^{-3}$ ) and di-heptadecyl ketone ( $w_m = 1.5 \times 10^{-3}$ ). In the case of the latter, it was not possible to dissolve enough of the ketone in the oil to reach the value  $w_0$ , and hence no oil spreading could be obtained.

All the ketones studied are Eastman preparations excepting the di-heptadecyl ketone which was obtained from the Chemical Laboratory of Armour and Company.

TABLE VIII. *Aliphatic amines in mineral oil—temp. 25°C (spread on 0.01 N NaOH).*

AMINE	N	$w_0$ IN G/G	$c_0$ IN MOLES/1000 G
Octadecyl amine*	18	Too insoluble	—
Heptadecyl amine	17	$2.5 \times 10^{-3}$	$0.98 \times 10^{-2}$
Hexadecyl amine	16	$2.2 \times 10^{-3}$	$0.91 \times 10^{-2}$
Tetradecyl amine	14	$1.5 \times 10^{-3}$	$0.71 \times 10^{-2}$
Dodecyl amine	12	$1.1 \times 10^{-3}$	$0.59 \times 10^{-2}$
Octadecenyl amine	18	$0.91 \times 10^{-3}$	$0.34 \times 10^{-2}$

\* Solubility,  $w_m$ , is between  $1.7 \times 10^{-3}$  and  $2.3 \times 10^{-3}$  g./g.

#### 7. SPREADING EFFECTS DUE TO PHENOLS AND NAPHTHOLS

Adding either phenols or naphthols to oil did not cause spreading unless  $w$  exceeded a critical value  $w_0$  which is listed in Table XIII. There was no observed effect of varying the pH of the water except at high pH (say pH 11) where it was found an increased rate of edge diffusion was occurring. The presence of metallic ions made no change in the phenomena of spreading or edge loss. These observations are not unexpected, since phenols are well known to behave as very weak acids. Oil soluble phenols of longer chain length might prove interesting but have not been obtainable.

The three chlorinated phenols listed in Table XIII are semi-commercial products of the Sharples Solvents Corporation, and as would be expected from their high oil solubilities the values of  $c_0$  were high. The other phenols and the two naphthols were Eastman preparations.

#### 8. THEORETICAL CONSIDERATIONS

A qualitative explanation of these adsorption phenomena at the oil-water interface can be given in terms of the kinetic concepts originated by Langmuir in developing the theory of monomolecular adsorption of gases on solids.<sup>7</sup>

Let  $\nu$  be the rate polar molecules strike unit area of the interface;  $\sigma_0$  be the actual cross-sectional area of an adsorbed molecule,  $\alpha$  be the coefficient of accommodation,  $\tau$  be the average lifetime of the adsorbed polar molecules, and  $n$  the average number of polar molecules adsorbed on unit area under equilibrium conditions, then:

$$\frac{n}{\tau} = \frac{\alpha \nu}{\sigma_0} (1 - n \sigma_0). \quad (6)$$

This relation is based on the assumption that no forces exist between the adsorbed molecules. It has already been suggested here and in Part I that forces did exist between the adsorbed polar molecules and oriented hydrocarbon molecules derived from the oil resulting in the formation of a compact mixed film at the oil-water interface. In addition, evidence will be given here for concluding that cohesive forces between the

<sup>7</sup> I. Langmuir, J. Am. Chem. Soc. **40**, 1361 (1918).

TABLE IX. *Aliphatic secondary and tertiary amines in mineral oil—temp. 25°C (spread on 0.01 N NaOH).*

AMINE	N	$w_0$	$c_0$
Di- <i>n</i> -amylamine	5+5	$w_0 > 2.2 \times 10^{-3}$ g/g*	$c_0 > 1.4 \times 10^{-2}$
Tri- <i>n</i> -amylamine	5+5+5	$w_0 > 2.6 \times 10^{-3}$ g/g*	$c_0 > 1.1 \times 10^{-2}$
Di-octylamine	8+8	$20 \times 10^{-3} < w_0 < 30 \times 10^{-3}$	$8.3 \times 10^{-2} < c_0 < 12.4 \times 10^{-2}$
Tri-octylamine	8+8+8	$w_0 < 13.8 \times 10^{-3}$	$c_0 < 3.0 \times 10^{-2}$

\* Pronounced edge loss.

hydrocarbon chains of the adjacent polar molecules become the most important forces when  $N$  exceeds 13 carbon atoms per molecule.

If the solution of polar molecules is dilute, there will apply the well-known Van't Hoff relation between osmotic pressure  $p$ , molal concentration  $c$ , and absolute temperature  $\theta$ . If the density of the oil is  $\rho$  and  $R$  is the gas constant, then:

$$p = (c\rho/1000)R\theta. \quad (7)$$

From the kinetic theory of ideal gases if  $M$  is the molecular weight:

$$\nu = kp/(M\theta)^{1/2}. \quad (8)$$

Even in dilute solutions relation (8) may be no more than a rough approximation. However, in dilute solutions  $\nu$  will certainly be proportional to  $p$ , and, although its variation with  $\theta$  may be complex, it will decrease as  $M$  increases, since the viscous resistance offered by the oil to the motion of polar molecules will vary with  $M$  and with the shape of the molecule.

It has been shown here that  $\tau$  is infinite if the long-chain molecule is ionized at the oil-water interface, and is a very small fraction of a second if it is not ionized. It is reasonable to assume that if there is cohesion between the adsorbed polar molecules  $\tau$  will be increased, while it will be less the greater the solubility of the polar molecule in the oil, other things being equal.

A quantity of importance here is  $A$ , the average area of interface occupied by the adsorbed polar molecules. Since by definition  $A = 1/n$ , Eq. (6) can be written:

$$A = \sigma_0/\alpha\nu\tau + \sigma_0. \quad (9)$$

Evidently the graph of  $A$  versus  $\nu$  is a rectangular hyperbola with a horizontal asymptote at  $A = \sigma_0$ . In these experiments  $\nu$  was increased either by increasing the concentration  $c$  of the polar molecules in solution, or by decreasing the chain

length  $N$ . Actually, for high values of  $\nu$  the curve may not be hyperbolic, since under such circumstances forces between polar molecules may become important.

The decrease in  $c_0$  with  $N$  for the saturated and unsaturated straight-chain acids (see Fig. 2) cannot be due to edge diffusion, for that would cause  $c_0$  to increase as  $N$  decreases. The most likely cause is the increased film pressure (for a given value of surface concentration) as  $N$  decreases. This is in conformity with the rule formulated in the study of adsorption at the air-water interface, to the effect that in a homologous series, provided mutual cohesive forces between the polar molecules are not important, as  $N$  decreases the film pressure rises at constant area per molecule.

The fact that the graph of  $c_0$  vs.  $N$  for acids is below that for alcohols can be attributed to a greater energy of adsorption of the non-ionized carboxyl group than the alcohol group (or a greater lifetime of adsorption). Therefore, for a given value of  $N$  a smaller molal concentration is needed to obtain the pressure  $F_0$ . The graph for the unsaturated acids is below that for the saturated acids, since, for a given value of  $N$  at the air-water interface, an unsaturated acid exerts a higher film pressure than a saturated acid at the same surface concentration. In other words, the unsaturated acids are less bound by cohesive or van der Waals forces between the hydrocarbon chains.

The acetic acid series of Table V is particularly

TABLE X. *Other amines in mineral oil—temp. 25°C (spread on 0.01 N NaOH).*

AMINE	N	$w_0$	$c_0$
Dicyclohexylamine	12	$w_0 > 3.6 \times 10^{-3}$ *	$c_0 > 2.2 \times 10^{-2}$
Diphenylamine	6+6	$w_0 > 2.9 \times 10^{-3}$	$c_0 > 1.7 \times 10^{-2}$
Triphenylamine	6+6+6	$w_0 > 3.9 \times 10^{-3}$	$c_0 > 1.6 \times 10^{-2}$
Dibenzylamine	7+7	$w_0 > 1.9 \times 10^{-3}$ *	$c_0 > 0.96 \times 10^{-2}$
Tribenzylamine	7+7+7	$w_0 > 6.9 \times 10^{-3}$ *	$c_0 > 2.4 \times 10^{-2}$

\* Pronounced edge loss.

TABLE XI. *Esters in mineral oil—temp. 25°C (spread on 0.01 N HCl).*

ESTER	<i>N</i>	<i>w</i> <sub>0</sub> IN G/G	<i>c</i> <sub>0</sub> MOLES/1000 G
Ethyl myristate	16	<i>w</i> <sub>0</sub> > 15.0 × 10 <sup>-3</sup>	<i>c</i> <sub>0</sub> > 5.9 × 10 <sup>-2</sup>
Methyl stearate	19	<i>w</i> <sub>0</sub> > 6.0 × 10 <sup>-3</sup>	<i>c</i> <sub>0</sub> > 2.0 × 10 <sup>-2</sup>
Ethyl stearate	20	<i>w</i> <sub>0</sub> > 6.1 × 10 <sup>-3</sup>	<i>c</i> <sub>0</sub> > 2.0 × 10 <sup>-2</sup>
Tri- <i>β</i> -cresyl phosphate	7+7+7	1.48 × 10 <sup>-3</sup>	0.4 × 10 <sup>-2</sup>
Tri- <i>β</i> -tert amyl-phenyl phosphate	11+11+11	1.5 × 10 <sup>-3</sup> < <i>w</i> <sub>0</sub> < 1.9 × 10 <sup>-3</sup>	0.28 × 10 <sup>-2</sup> < <i>c</i> <sub>0</sub> < 0.35 × 10 <sup>-2</sup>
Triamyl citrate	7+7+6+1	2 × 10 <sup>-3</sup> < <i>w</i> <sub>0</sub> < 2.5 × 10 <sup>-3</sup>	5.0 × 10 <sup>-2</sup> < <i>c</i> <sub>0</sub> < 6.2 × 10 <sup>-2</sup>
Triamyl borate	5+5+5	<i>w</i> <sub>0</sub> > 7 × 10 <sup>-3</sup> *	<i>c</i> <sub>0</sub> > 2.6 × 10 <sup>-2</sup>

\* Showed strong edge loss.

interesting. From Fig. 2 it is seen that the graph of  $c_0$  vs.  $N$  is a straight line with a negative slope. In plotting this graph the value of  $N$  used was the number of carbon atoms ( $N_1$ ) in the longest branched chain of the molecule (see column 3 of Table V). Upon constructing models of these molecules and considering various possible configurations of each, it was found that for any given member of this series some configurations were, for geometrical reasons, less likely to permit adsorption than others. Some configurations could be described roughly as various forms of the letter *Y* with the carboxyl group at the base, and others were like the inverted letter *V* with the carboxyl group hanging from the vertex between the open legs of the letter. The number of such poorly adsorbed configurations appeared greatest for the molecule  $N_1 > \text{CHCOOH}$  when  $N_1$  and  $N_2$  were nearly equal, and were least when  $N_1/N_2$  was greatest. Therefore the greatest molal concentration of acid molecules was necessary to cause oil disk spreading for the molecules having  $N_1$  and  $N_2$  most nearly equal. This was in agreement with the experimental results just described.

From Fig. 3 it is seen that the graph of  $A_0$  vs.  $N$  has a maximum at  $N=14$  in the case of the alcohols, and at  $N=15$  for the acids. Relation (9) makes it clear why the early increase of  $A_0$  with  $N$  is due to the decrease in  $\nu$  caused by the lowered speed of diffusion of the polar molecules in oil as  $N$  increases. The decrease in  $A_0$  after  $N$  exceeds 14 is due to the increased importance of the cohesive forces between adjacent hydrocarbon chains of the polar molecules, and this significantly happens when  $N$  approaches values for which the solubility in oil becomes low. This

also makes the parallel behavior of the curves of Fig. 3 for alcohols and acids readily understandable, since the mechanism essentially involves reactions between the hydrocarbon chains rather than the polar groups.

The curves  $P_1-P_2$  and  $P_1-P_3$  of Fig. 3 were obtained by plotting  $A_0$  for the unsaturated acids (undecylenic, oleic and elaidic). The graphical point for the first acid coincided within the experimental error with the point for saturated acids of that chain length, while the graphical points for oleic and elaidic acids were at  $P_2$  and  $P_3$ . Upon noting that the ordinates corresponding to points  $P_2$ ,  $P_3$ , and  $P_4$  had descending magnitudes in the order of *cis*-, *trans*-, and normal-saturated configurations for 18-carbon chains, it was concluded that the cause of these differences was in the greater tendency of the saturated chains to cohere. The *trans*-configuration would be expected to be intermediate in behavior since it is more nearly a straight chain than the *cis*-configuration. These geometrical differences are quite evident upon inspecting molecular models of these substances, and their application to the interpretation of film phenomena at the air-water interface was indicated by Adam and Jessop<sup>8</sup> and later by Marsden and Rideal.<sup>9</sup>

If the various types of polar compounds investigated here are arranged in the order of the values of  $c_0$  (as in Table XIV), they can be placed in three groups. The same grouping is obtained if values of  $c_0$  are arranged in their order of magnitude for polar molecules having the same value of  $N$ . It will be seen that the relative order of the three groups is the same as the relative order of the solubilities of these substances in the oil. This demonstrates the importance of the solubility in oil as a variable to

TABLE XII. *Ketones in mineral oil (temperature 25°C).*

KETONE	<i>N</i>	<i>w</i> <sub>0</sub> IN G/G	<i>c</i> <sub>0</sub> IN MOLES/1000 G
Methylnonyl ketone	10	12.2 × 10 <sup>-3</sup>	7.2 × 10 <sup>-2</sup>
Di- <i>n</i> -amyl ketone	10	15.1 × 10 <sup>-3</sup>	8.9 × 10 <sup>-2</sup>
Di-undecyl ketone	23	12.0 × 10 <sup>-3</sup>	3.6 × 10 <sup>-2</sup>
Di-heptadecyl ketone	35	Too insoluble	—
Di-phenyl ketone	13	13.4 × 10 <sup>-3</sup>	7.3 × 10 <sup>-2</sup>
Di-benzyl ketone	15	6.0 × 10 <sup>-3</sup>	2.9 × 10 <sup>-2</sup>
Phenylundecyl ketone	18	41.7 × 10 <sup>-3</sup>	16.0 × 10 <sup>-2</sup>

<sup>8</sup> N. K. Adam and G. Jessop, Proc. Roy. Soc. **A101**, 516 (1922).

<sup>9</sup> J. Marsden and E. Rideal, J. Chem. Soc. 1163 (1938).

be considered in the study of the oil spreading due to additive polar compounds.

A result of considerable interest is evident from an inspection of Fig. 3. All the saturated straight chain alcohols and non-ionized acids have values of  $A_0$  ranging from 50 to 72 square angstroms, whereas the same polar molecules at the same temperatures and film pressures would occupy only 20 to 25 square angstroms at the air-water interface. One would expect  $A_0$  to be higher in the former circumstances due to some degree of film disorganization resulting from the thermal agitation of the hydrocarbon molecules of the oil. However, at film pressures as high as 11.3 dynes/cm and in proximity to high molecular weight hydrocarbon molecules, a much closer packing would be more likely. This suggests the same conclusion given in Part I, i.e., the adsorbed polar molecules form a fairly closely

TABLE XIV. *Effect of solubility on magnitude of  $c_0$ .*

SUBSTANCE	$c_0$ RANGE	GROUP	MAGNITUDE OF $c_0$
Chaulmoogric and hydnocarpic acids	$(0.2-0.5)10^{-3}$	I	$10^{-3}$
Arylstearic acids	$(0.2-0.3)10^{-2}$	II	$10^{-2}$
Unsaturated acids	$(0.35-0.56)10^{-2}$		
Saturated acids (Straight-chain)	$(0.5-0.75)10^{-2}$		
Saturated alcohols	$(0.72-0.80)10^{-2}$		
Straight-chain amines	$(0.6-1.0)10^{-2}$	III	$10^{-1}$
Esters	$(0.2-.60)10^{-1}$		
Ketones	$(0.3-1.6)10^{-1}$		

packed mixed film with hydrocarbon molecules derived from the oil. Such a film can be considered a two-dimensional solution. Obviously the proportion of polar to non-polar molecules in the film will vary with  $c$ , and also with the intensity of the adhesional forces between the hydrocarbon chains of the polar molecules and of the non-polar molecules. The correctness of these conclusions will be demonstrated in Part III.

The cooperation of Dr. Roger Adams of the Department of Chemistry of the University of Illinois has been a source of encouragement, as well as the essential pure organic compounds already listed. A wealth of useful chemical information concerning hydrocarbons and polar additives was made available during the course of this work through numerous discussions with Dr. Parry Borgstrom.

TABLE XIII. *Phenols and naphthols in mineral oil—temp. 25°C (spread on 0.01 N HCl).*

PHENOL	N	$w_0$ IN G/G	$c_0$ IN MOLES/1000 G
<i>p</i> -tert-amyl phenol	11	$0.5 \times 10^{-3}$	$0.3 \times 10^{-2}$
<i>p</i> -cyclohexyl phenol	12	$0.5 \times 10^{-3}$	$0.3 \times 10^{-2}$
2-chloro-4-tert-amyl-phenol	5 + 6	$w_0 < 8.8 \times 10^{-3}$	$c_0 < 4.4 \times 10^{-2}$
2, 6-dichloro-4-tert-amyl phenol	5 + 6	$w_0 > 12.5 \times 10^{-3}$	$c_0 > 5.3 \times 10^{-2}$
2-chloro-4, 6-di-tert-amyl phenol	5 + 5 + 6	$w_0 > 40.0 \times 10^{-3}$	$c_0 > 1.5 \times 10^{-2}$
$\alpha$ -Naphthol	12	$1.0 \times 10^{-3}$	$0.6 \times 10^{-2}$
$\beta$ -Naphthol	12	$1.0 \times 10^{-3}$	$0.6 \times 10^{-2}$