90. *The Behaviour of Surface Films of Unsaturated Compounds.*

By ARTHUR H. HUGHES.

THE early experiments of Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848) led him to conclude from the force–area curves of oleic acid on a water surface that both the central double bond and the terminal carboxyl group remained in the aqueous surface on compression of the film, the dipole system of the double bond having a greater adhesion to the water than has the non-polar hydrocarbon chain.

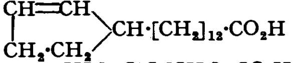
Labrouste's discovery (*Ann. Physique*, 1920, **14**, 164) of the phenomenon of film expansion with increase of temperature led to the recognition of the two types of film, condensed and expanded. From the force–area characteristics of oleic acid films, Adam (*Proc. Roy. Soc.*, 1922, *A*, **101**, 516) concluded that at ordinary temperatures they were of the liquid expanded type, similar to that of an expanded film of myristic acid, with a limiting area of about 55 Å.^{2} per mol., the polar carboxyl heads being attached to the water surface and the chains being in violent thermal agitation. Adam and Jessop (*ibid.*, 1926, *A*, **112**, 362) further noticed a marked expansion of the film of oleic acid on solutions of potassium permanganate at 0·85% concentration or greater, the force–area curves showing that the limiting area of the film was now certainly greater than 100 Å.^{2} per mol. They concluded that the film was now gaseous in character, and that the molecule was attached to the water surface both by the carboxyl head and by the double bond, now strongly anchored to the surface. In general, they found that films formed of molecules with two widely separated points of attachment were of this gaseous type.

Whilst Langmuir's original suggestion does not appear tenable in the light of the work of Labrouste and Adam, yet it is clear that the double bond does exert a very marked influence on the character of the film. Not only does oleic acid give a more highly expanded film than does myristic acid with four less carbon atoms, under the same conditions (limiting area *ca.* 45 Å.^{2} per mol.), but it gives a totally different type of film from that of stearic acid, the corresponding saturated acid, which gives a condensed film with much smaller areas per mol. (*ca.* 25—20 Å.^{2}).

The method of surface potentials (Schulman and Rideal, *ibid.*, 1931, *A*, **130**, 259) permits us to investigate in some detail the polarity of the various portions of the molecules forming the unimolecular film, and to observe any changes in orientation occurring therein. This method has been applied in conjunction with force–area measurements to a study of various types of unsaturated long-chain aliphatic compounds of special interest (see Table I).

The behaviour of a conjugated double-bond system in a long-chain molecule has been studied for α- and β-elæostearic acids and for their addition compounds with maleic anhydride.

TABLE I.

Acid.	Structure.	M. p.
Oleic	$CH_3\cdot[CH_2]_7\cdot CH\colon CH\cdot[CH_2]_7\cdot CO_2H$	11°
cis-Petroselinic	$CH_3\cdot[CH_2]_{10}\cdot CH\colon CH\cdot[CH_2]_4\cdot CO_2H$	30
Δ^α^-*iso*Oleic	$CH_3\cdot[CH_2]_{14}\cdot CH\colon CH\cdot CO_2H$	59
Chaulmoogric		68
Stearolic	$CH_3\cdot[CH_2]_7\cdot C\vdots C\cdot[CH_2]_7\cdot CO_2H$	48

EXPERIMENTAL.

Oleic, cis-*Petroselinic, and* Δ^{α}-iso*Oleic Acids.*—A comparison of the unimolecular films of these three acids on aq. solutions is of interest in illustration of the effect of a double bond in different positions along a hydrocarbon chain on the properties of the mol. In Fig. 1 the change in air–liquid *P.D.* (ΔV), due to the presence of a unimolecular film, is plotted against n, the number of mols. per sq. cm., for the three acids concerned. The corresponding surface-press. values are plotted in Fig. 2.

FIG. 1.

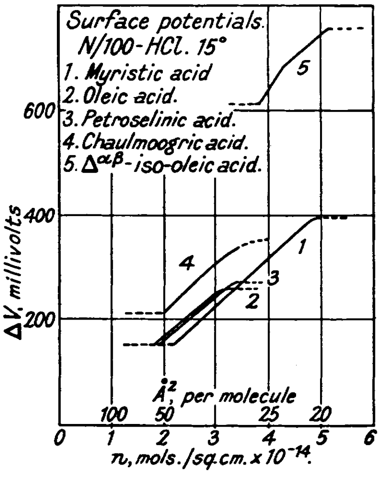
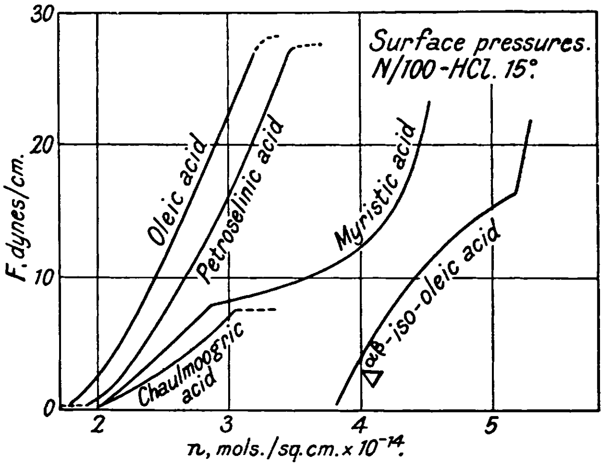


FIG. 2.



Oleic and petroselinic acids both form liquid expanded films on dil. acid solutions with limiting areas of transition to a vapour film at 55 and 52 Å.^{2} per mol. respectively; the curves for myristic acid are included for comparison in Figs. 1 and 2. Oleic and petroselinic acids do not form a condensed film under these conditions, the films collapsing at about 30 Å.^{2} per mol. On compression, an approx. linear ΔV–n graph is obtained. The values of the total vertical component of the electric moment per mol. (μ), calc. from the Helmholtz equation $\Delta V = 4\pi n\mu$, are given in Table II for the various acids.

TABLE II.

Acid.	State.	Area per mol., Å.^{2}.	$\mu \times 10^{19}$, e.s.u.	Acid.	State.	Area per mol., Å.^{2}.	$\mu \times 10^{19}$, e.s.u.
Myristic	Expanded	45·0	1·8	Δ^{α}-*iso*Oleic	Liquid condensed	26·4	4·2
Oleic	,,	55·0	2·1				
Petroselinic	,,	52·0	2·1	Stearolic	Vapour expanded	80·0	3·6
Chaulmoogric	,,	50·0	2·5				

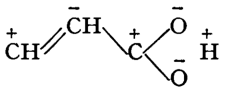
At the limit of the expanded state the value of $\mu = 2{\cdot}1 \times 10^{-19}$ e.s.u. is very nearly the same for oleic and petroselinic acids, but is, however, rather larger than that for myristic acid in the same state, *viz.*, $1{\cdot}8 \times 10^{-19}$ e.s.u. The contribution of the double bond to the vertical component of the dipole moment of the mol. seems thus to be small in comparison with that of the polar head, but is not negligible; and further, the contribution is in the same sense as that of the carboxyl group, *viz.*, positive above, negative below.

At the highest compression with an area per mol. of about 30 Å.^{2}, when there are presumably on the average very few double bonds in the surface, it will be seen that ΔV approaches the value of 260 mv. obtained for myristic acid, implying that the electric moment of the double bond when removed from the water surface is very small.

The behaviour of *iso*oleic acid is in striking contrast to that of oleic or petroselinic acid. As shown by Adam (*Proc. Roy. Soc.*, **1922**, *A*, **101**, 452), the force–area characteristics of this acid are those of a liquid condensed film with a limiting area of 28·7 Å.^{2} per mol. The surface–press. curve was repeated in the present work (Fig. 2) and the limiting area obtained is rather smaller, *viz.*, 26·4 Å.^{2} per mol. The latter value agrees with the point on the surface–potential curve (Fig. 1) at which the film becomes uniform in potential all over the surface. At larger areas the film is composed of large islands of the condensed film in equilibrium with the vapour film which gives a very small surface potential.

The main significance of the surface–potential curve of *iso*oleic acid lies in the very large values of ΔV. The value of the electric moment per mol. (μ) at 26 Å.^{2} is approx. twice that of oleic or petroselinic acid in the expanded state, as shown in Table II.

The close proximity of the double bond to the strong dipole system of the carboxyl head has clearly caused a marked distortion of the former, resulting in a dipole moment in the sense indicated :



Closer examination of the surface–press. and surface–potential curves shows that there is a definite change in each case at about 23 A.^{2} per mol., resulting in a decrease of electric moment per mol., which is probably associated with a change in orientation of the double bond on compression of the film.

Chaulmoogric Acid.—This acid, although not an isomeride of oleic acid, was examined as presenting two points of interest, the double bond being (i) in a ring system, and (ii) remote from the terminal carboxyl group. It might be expected that the adhesion of the double bond would be sufficient in this case to make the molecule lie flat on the surface. Actually this does not occur, as may be seen from the surface–potential and surface–press. characteristics (Figs. 1 and 2), for a film spread on N/100-HCl or -H_2SO_4. An expanded film is obtained with a limiting area of transition to the vapour at 50 Å.^{2} per mol. The film is very unstable and collapses at about 33 Å.^{2} per mol. at 7 dynes/cm., a much lower press. than that for oleic or petroselinic acid. Examination of the surface potentials shows that the film is uniform over the range 50—33 Å.^{2} per mol. The corresponding value of the vertical component of the electric moment per mol. (μ) is $2{\cdot}5 \times 10^{-19}$ e.s.u., which is considerably larger than that for oleic or petroselinic acid under the same conditions, and indicates that the double bond here present in a 5-membered ring is definitely more polar than when occurring in a straight chain (cf. Table II).

The range of existence of the expanded film, 50—33 Å.^{2} per mol., precludes the possibility that the 5-membered ring, and thus the double bond, of all the molecules can be in the surface throughout the compression. The area found by Adam for a simple *p*-substituted benzene ring was 24 Å.^{2} in the surface film; the area of a 5-membered ring under the same conditions is probably, therefore, about 20 Å.^{2}, which, together with the area of 20 Å.^{2} for a carboxyl group, gives a min. area of 40 Å.^{2} for chaulmoogric acid if oriented with the double bond and the terminal carboxyl group both in the surface. It is difficult to draw any clear picture as to the structure of the film in this case.

Stearolic Acid.—The effect of a triple bond on the properties of a long-chain molecule was examined with reference to stearolic acid. The surface–press. and surface–potential curves are shown in Fig. 3. This acid forms a vapour expanded film and is uniform at the largest areas per mol. investigated, *viz.*, 300 Å.^{2}, whereas oleic acid is an expanded film with a limiting area of 55 Å.^{2} per mol.

The ΔV–n curve remains linear down to 80 Å.^{2}, the electric moment per mol. being const. over this range at $3{\cdot}6 \times 10^{-19}$ e.s.u. At 80—75 Å.^{2} a break occurs in the graph, and a second straight line of smaller slope is maintained down to film collapse (30 Å.^{2} per mol. at 260 mv.). The surface–press. curve shows a large decrease of compressibility at about 80 Å.^{2} per mol.

The molecular mechanism involved in compression of a film of stearolic acid would appear to be as follows. In the most expanded state the molecules are lying flat in the surface and move about independently. On compression, the first portion of the molecule to leave the surface is the non-polar hydrocarbon chain $CH_3\cdot[CH_2]_7$ remote from the carboxyl group, which can slip over a neighbouring molecule. This needs only a relatively small surface press. of at most 2 dynes/cm., and results in no change of electric moment per mol. until a mean mol. area of 80 Å.^{2} is reached. Further compression results in the gradual removal of triple bonds from the surface. The surface press. increases more rapidly and the mean electric moment per mol. decreases. At the highest compressions the film is very similar to that of oleic acid, the surface potential of the latter being 256 mv. at 30 Å.^{2}.

Three main facts emerge from a comparison of oleic and stearolic acids. First, a triple bond lying in the aq. surface has a much higher dipole moment than a double bond, the values for stearolic and oleic acids in their most extended states being $3{\cdot}6 \times 10^{-19}$ and $2{\cdot}1 \times 10^{-19}$ e.s.u. per mol., of which $1{\cdot}8 \times 10^{-19}$ e.s.u. may be ascribed to the carboxyl group. Secondly, the triple bond has a correspondingly larger adhesion to the aq. solution than the double bond, *i.e.*, a much greater tendency to expand the film and to cause the molecules to lie flat in the surface. Finally, on compression, when the triple bonds are largely removed from the surface, the triple bond, as also the double bond, has only a small contribution to the total vertical component of the electric moment per mol.

FIG. 3.

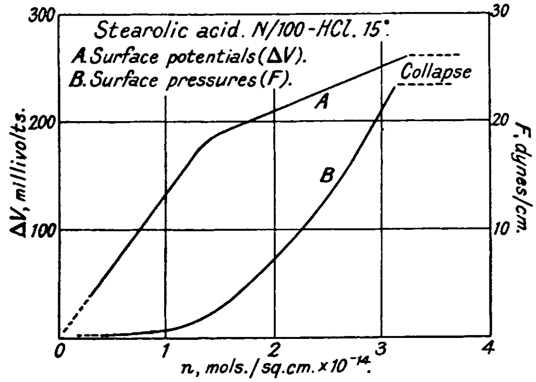
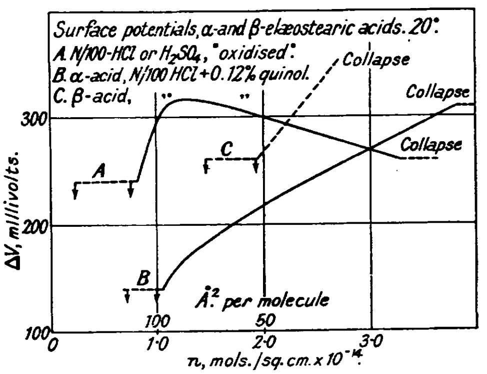


FIG. 4.



It is of interest that from 75 to 33 Å.^{2} per mol. the relation between ΔV and n for stearolic acid is still linear, although not passing through the origin. We may therefore write $\Delta V = K_1 n + K_2$ or $\Delta V/4\pi n = \mu = K_1/4\pi + K_2/4\pi n$, K_1 and K_2 being const. Since $1/n$ is proportional to A, the mean area per mol., we find that $\mu = a + bA$, a and b being constants, or the decrease of the total vertical component per mol., μ, due to expulsion of the triple bonds from the surface is proportional to the mean area per mol.

In conclusion, it is instructive to compare the behaviour of oleic and stearolic acids with that of stearic acid, the corresponding saturated acid, on dil. acid at room temp. Stearic acid gives a close-packed liquid condensed film with limiting area of 25 Å.^{2} per mol., oleic acid an expanded film with limiting area of 55 Å.^{2} per mol., while stearolic acid gives a vapour expanded film with no limiting area. We may thus place the systems $\cdot CH_2\cdot CH_2\cdot$, $\cdot CH{:}CH\cdot$, and $\cdot C\vdots C\cdot$ in that order of increasing adhesion for H_2O.

Systems with Conjugated Double Bonds.—*α- and β-Elæostearic acids.* The recent work of Morrell and Samuels (J., 1932, 2251) has confirmed the accepted formulæ for these two acids: they are respectively the complete *cis-* and *trans-*modifications of the conjugated system $CH_3\cdot[CH_2]_3\cdot CH{:}CH\cdot CH{:}CH\cdot CH{:}CH\cdot[CH_2]_7\cdot CO_2H$. C_6H_6 was used as solvent in spreading the films.

On dil. acid solutions, both the α- and the β-acid spread to a unimolecular film whose properties change with time. The surface–potential curve of the film rises over a period of about 15 min., rapidly at first and then more slowly to a final steady value represented by points on curve A (Fig. 4). The initial values of the surface potential approximate to curve B (Fig. 4). Both these acids are known to undergo oxidation on exposure to air. It is reasonable, therefore, to connect this observed rise in potential, and its implicit increase in molecular dipole moment of the film, with an atmospheric oxidation of α- or β-elæostearic acid. The product, provisionally termed "oxidised elæostearic acid," appears to be identical in its film characteristics whether derived from the α- or the β-acid. The oxidised acid forms a stable film with a limiting area of about 125 Å.^{2} per mol. At larger areas, fluctuations in potential are observed over the surface, showing that the film is non-uniform. This limiting area corresponds closely with the area to be expected for the mol. lying flat in the surface.

The vertical component of the electric moment per mol. remains const. and high, $\mu = 8{\cdot}0 \times 10^{-19}$ e.s.u., over a short range of compression from 125 to 100 Å.^{2} per mol. On further compression, the surface potential reaches a max. and then falls to a value of *ca.* 255 mv. at 30 Å.^{2} per mol.

The relation between μ and A is of the same form as that for stearolic acid, μ decreasing uniformly as the oxidised double-bond system is removed from the surface by compression of the film. The range 125—100 Å.^{2} over which μ is const. presumably corresponds to the removal from the surface of the non-polar $CH_3{\cdot}(CH_2)_3{\cdot}$ hydrocarbon chain remote from the terminal carboxyl group. The final value of μ at film collapse is very close to that for stearolic, oleic, and petroselinic acids, indicating that the oxidised double-bond system, when removed from the surface, has little contribution to the total vertical component of the electric moment per mol.

Some conclusions may be drawn as to the nature of the oxidation product. It has been shown that the electric moment per mol. of the oxidised α- or β-acid is $8{\cdot}0 \times 10^{-19}$ e.s.u. in its most expanded state, *i.e.*, when lying flat in the surface. Of this, one may assume that approx. $2{\cdot}0 \times 10^{-19}$ e.s.u. is due to the terminal carboxyl group, leaving $6{\cdot}0 \times 10^{-19}$ e.s.u. for the oxidised double-bond system. If, therefore, oxidation is due to the addition of OH groups across one or more double bonds, it is probable that two of the double bonds have been oxidised, but certainly not all three, the electric moment of a hydroxyl group in a long-chain alcohol being $2{\cdot}0 \times 10^{-19}$ e.s.u. in the expanded state, while unpublished work on the oxidation of a film of oleic acid indicates that the value of μ for two *adjacent* hydroxyl groups is $3{\cdot}0 \times 10^{-19}$ e.s.u.

FIG. 5.

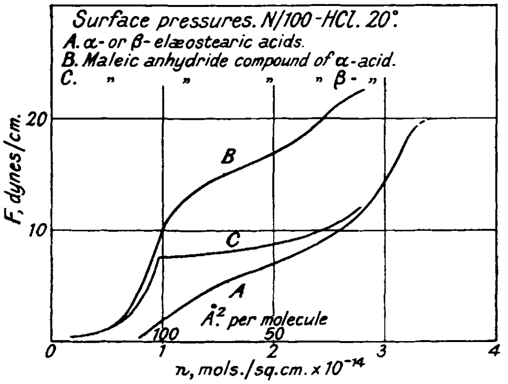
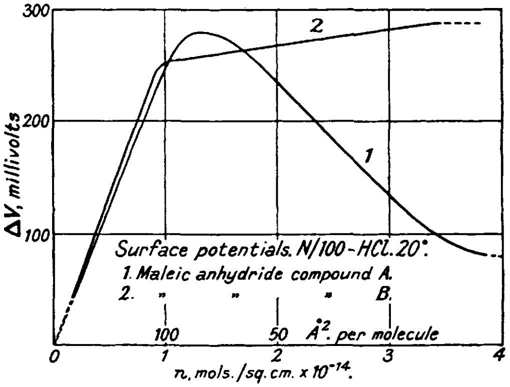


FIG. 6.



Further, on compression of the oxidised film, the first decrease in μ occurs at 100 Å.^{2} per mol. This must be due to the removal from the surface of some polar portion of the molecule, and the area corresponds to 18 × 100/125, *i.e.*, 14 carbon atoms lying in the surface, 125 Å.^{2} being taken as the area occupied by the whole molecule lying flat. Thus the oxidation concerns, at any rate, the double bond in the molecule remote from the terminal carboxyl group, and either of the following structures may be tentatively assigned to the oxidation product:

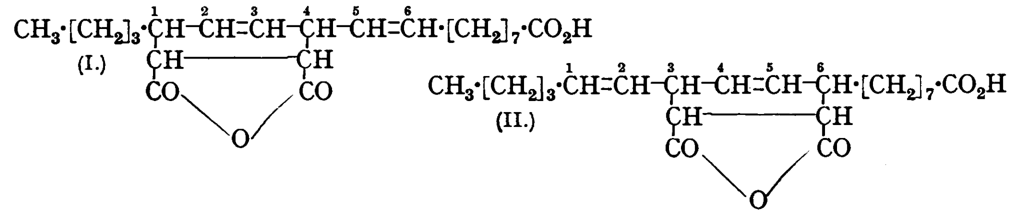
(1) $CH_3{\cdot}[CH_2]_3{\cdot}[CH(OH)]_4{\cdot}CH{:}CH{\cdot}[CH_2]_7{\cdot}CO_2H$;
(2) $CH_3{\cdot}[CH_2]_3{\cdot}[CH(OH)]_2{\cdot}CH{:}CH{\cdot}[CH(OH)]_2{\cdot}[CH_2]_7{\cdot}CO_2H$.

In order to examine more closely the nature of the observed initial rise in potential with time, the acids were spread on N/100-HCl containing quinol. The values of ΔV, with a concn. of 0·12% quinol in the underlying solution, are perfectly steady with time, but whereas for the α-acid (Fig. 4, B) the film thus obtained has the characteristics to be expected for the unoxidised unsaturated acid, and is comparable to that of oleic acid, yet for the β-acid the film in the presence of quinol has a higher surface potential than has the α-acid and only approximates to uniformity in potential (± 15 mv.) over the range 50—35 Å.^{2} per mol. (Fig. 4, C). This is the only difference so far observed between the unimolecular films of the *cis*- and the *trans*-form of elæostearic acid. The behaviour of the β-acid may be due to the formation of an unstable addition product with the quinol, which cannot be formed with the α-acid.

The action of quinol as an antioxygen is dependent on its concn. in the underlying solution: with 0·001%, autoxidation proceeds unchanged, while at 0·01% its rate is approximately halved.

The surface–press. curves for oxidised α- or β-elæostearic acids are shown in Fig. 5 (A) and are of an unusual type. The compressibility increases markedly below about 90 Å.^{2} per mol. and only decreases again at areas below about 40 Å.^{2} per mol. It appears that the removal of the polar oxidised double-bond system from the surface is assisted by those already removed, due to their strong mutual cohesion.

The Maleic Anhydride Addition Compounds of α- and β-Elæostearic Acids.—These compounds, recently isolated by Morrell and Samuels (*loc. cit.*), have been assigned the structures (I) and (II), corresponding to the compounds derived from the α- and the β-acid respectively; for convenience they are referred to as A and B.

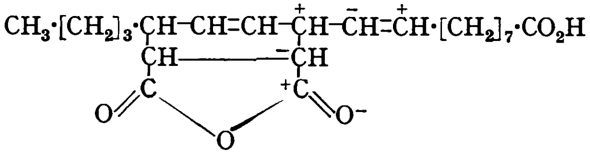


(I.)

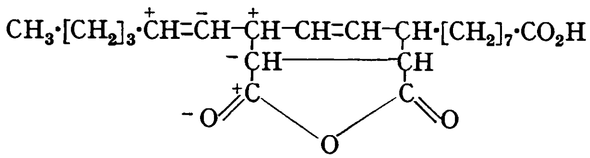
(II.)

Films of these two substances spread (from solution in C_6H_6) on dil. acid showed a very similar behaviour on compression from large areas down to 100 Å.^{2} per mol., the films being uniform up to at least 500 Å.^{2}. On further compression, a remarkable change is apparent in the characteristics of the film, and this change is very different for the two derivatives (Fig. 6; 1, 2). For compound A the surface potential of the film *falls* from 280 mv. to 80 mv. on compression from 80 to 30 Å.^{2} per mol.; for compound B, it *rises* from 260 mv. to 285 mv. The only difference in the structures of these two derivatives, as far as the unimolecular film is concerned, lies in the position of the double bond outside the ring. The results obtained for $\Delta^{\alpha\beta}$-*iso*oleic acid (p. 340) indicate a very marked increase in the polarity of the double bond due to the proximity of the carboxyl group, in the sense that there is an electron displacement from the β- to the α-carbon atom. In the present case, if one traces the polarity which would be induced in the 5 : 6-double bond for (I), and in the 1 : 2-double bond for (II), due to the polarity of the neighbouring maleic anhydride residue, it is seen that the polarity will be the same in magnitude but opposite in direction along the chain, thus:

Compound A.



Compound B.



On compression of the film from the state where the molecules are lying flat in the surface to that where the terminal carboxyl groups alone remain in the surface, it follows that the moment of the 5 : 6-double bond in (I) is ∓ when it is removed from the surface and tending to vertical orientation. This will oppose the ± vertical component of the carboxyl group and tend to decrease the total vertical component of the electric moment per mol. much more than in (II), where the electric moment of the 1 : 2-double bond is now in the same sense as that of the carboxyl group on compression of the film. This affords at least a qual. explanation of the obs. differences between the two compounds.

The surface-press. curves of the two compounds are shown in Fig. 5 (B, C) and bear general similarity to those of the elæostearic acids, but are more expanded. Compression from large areas down to about 100 Å.^{2} per mol., as for the ΔV–n curves, follows the same course for both compounds. For (II) the compressibility increases enormously at this point with a surface pressure of some 7½ dynes/cm. For (I), however, the increase in compressibility is not noticed until a press. of nearly 12 dynes/cm. is reached, and the film only collapses at about 26 dynes/cm., as compared with 12 dynes/cm. for (II). These differences in compressibility are difficult to account for unless they are due to the fact that compression of (I) involves raising the bulky anhydride residue by a distance of two carbon atoms further from the surface than in the case of (II).

SUMMARY.

(1) A study has been made of the effect of various types of unsaturation on the behaviour of long-chain aliphatic molecules as unimolecular films on aqueous solutions. The films were examined by the methods of surface pressure and of surface potentials.

(2) In the series oleic, petroselinic, and Δ^{α}-*iso*oleic acids it is shown that the dipole system of the double bond has a marked adhesion for the aqueous surface as compared with a saturated hydrocarbon chain. The dipole moment of the double bond is much larger when the latter is adjacent to a carboxyl group than when it is separated therefrom by several CH_2 groups. The double bond present in a five-membered ring, as in chaulmoogric acid, is shown also to have a larger dipole moment than when present in a straight hydrocarbon chain.

(3) A triple bond has a greater dipole moment than a double bond; the adhesion to the aqueous surface is correspondingly greater for stearolic than for oleic acid.

(4) The behaviour of a conjugated double-bond system has been examined in α- and β-elæostearic acids and their maleic anhydride compounds. Both the α- and the β-acid undergo autoxidation in the unimolecular film. The autoxidation is completely inhibited by the presence of 0·12% quinol in the underlying solution.

Thanks are due to Professor T. P. Hilditch for a specimen of *cis*-petroselinic acid, to Dr. N. K. Adam for a specimen of Δ^{α}-*iso*oleic acid, and to Mr. H. Eyde for a specimen of chaulmoogric acid. The author is especially indebted to Dr. Morrell for the provision of samples of α- and β-elæostearic acids and of their maleic anhydride compounds.

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