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THE SHAPES OF GROUP MOLECULES FORMING THE SURFACES OF LIQUIDS

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In a recent paper[1] I have developed a theory according to which all the forces involved in the structure of solids and liquids, are similar in nature to the forces causing chemical combination. Thus condensation, evaporation, adsorption, cohesion, crystallization, liquefaction, viscosity, surface tension, etc., are manifestations of the forces already known to the chemist. In all these cases the range of the forces is limited to atomic dimensions except in so far as their effects may be transmitted from atom to atom. According to this theory, every atom in a solid or liquid is chemically combined to every adjacent atom. This chemical union may be strong or weak and may be characterized either by primary or secondary valence (Werner).

In most inorganic solid or liquid substances of the strongly polar type, the identity of the molecule is wholly lost, but in organic compounds the groups of atoms constituting the chemical molecule usually have a real existence even in the liquid or solid state. These group molecules are held together by primary valence forces while the forces acting between the group molecules, although no less chemical than the others, are to be characterized as secondary valence forces.

From this viewpoint the forces involved in adsorption and surface tension do not originate from the group molecule as a whole, but rather from certain atoms in the molecule.

This theory leads inevitably to the conclusion that adsorbed films on plane surfaces of solids or liquids should, in general, be one atom or group molecule in thickness. Considerable experimental evidence has already been presented that this is the case with films of gases adsorbed on solids.

Miss A. Pockels[2] showed, in 1891, that very small amounts of oil on the surface of water have no appreciable effect on the surface tension, but that the surface tension begins to *decrease suddenly* when the amount of oil per unit area is increased beyond a certain sharp limit.

Lord Rayleigh,[3] Devaux,[4] and Marcelin[5] have made similar experiments and have concluded that the amount of oil needed to produce an appreciable effect on the surface tension corresponds to a layer one molecule deep. Devaux finds with triolein that a film $11. \times 10^{-8}$ cm. thick just begins to lower the surface tension of water. From the density and molecular weight of the oil and from Perrin's value of the Avogadro constant, he calculates that the diameter of the molecule would be 11.3×10^{-8} cm. if this be assumed spherical in shape.

According to my theory, however, molecules should not be regarded as spheres, since such a supposition would not be consistent with the chemical nature of the forces. The fundamental question immediately arises: What causes the spreading of an oil upon the surface of water? If we regard molecules as spheres, any attraction between the water and the oil should cause the oil to dissolve in the water instead of spreading on the surface. From the chemical viewpoint, however, the force causing the spreading should be a force between atoms, not between molecules. Evidently, then, some atom or atoms in the oil must have an affinity for the water. Now it is known that the presence of the $-COOH$, $-CO$, or $-OH$ groups in an organic molecule tends to render the substance soluble in water, while the hydrocarbon chain decreases the solubility. On the other hand, hydrocarbons are soluble in each other. Therefore the $-COOH$, $-CO$, and $-OH$ groups have more affinity for water than for hydrocarbons, while hydrocarbons have more affinity for each other than for water.

Thus, when an oil is placed on water, the $-COO-$ groups combine with the water, while the hydrocarbon chains remain combined (secondary valence, of course) with each other. This process leads directly to the spreading of the oil on the surface. If only a limited amount of oil is placed on a large surface, the spreading ceases as soon as all the available $-COO-$ groups have come into contact with the water, for any further spreading would separate the hydrocarbon chains from each other.

According to this conception, pure hydrocarbon oils would not spread on water. Experiment shows that this is actually the case.[6]

The theory furthermore indicates that the hydrocarbon chains in the oils must be placed above the $-COO-$ groups on the surface. Thus, in a series of homologous compounds, as the length of the chain increases the thickness of the oil film should increase in proportion, while the area occupied by each molecule should remain constant.

Now the area occupied by each molecule, which we will designate by a, is readily calculated. If w is the weight of oil placed on the surface and A is the area to which the film must be compressed before the surface tension changes, then the area a covered by each molecule is evidently $a = AM/wN$, where M is the molecular weight of the oil (oxygen = 16), and N is the Avogadro constant (6.06×10^{23} molecules per gram molecule). Furthermore, we may calculate τ the length of the molecule (measured vertically), as follows: the volume of each molecule is $M/\rho N$, where ρ is the density of the oil. By dividing this volume by a, the cross-section of the molecule, we obtain the length of the molecule, thus $\tau = M/a\rho N = W/\rho A$.

To measure A, a new method has been developed. A strip of paper, floating on the water in a long tray, is fastened to a horizontal balance. Oil is placed on the water on one side of the strip only, and leakage of oil past the ends of the strip is prevented by localized blasts of air from two small tubes. Thus the force tending to cause spreading of the oil is measured for different values of A. By plotting these results it is easy to extrapolate to zero force and thus obtain the maximum area completely covered by the oil film.

TABLE 1

CROSS SECTIONS AND LENGTHS OF MOLECULES

SUBSTANCE	M	CROSS SECTION a	$\sqrt{a}$	LENGTH τ
		sq. cm. $\times 10^{-16}$	cm. $\times 10^{-8}$	cm. $\times 10^{-8}$
Palmitic acid $C_{15}H_{31}COOH$	256	24	4.9	19.6
Stearic acid $C_{17}H_{35}COOH$	284	24	4.9	21.8
Cerotic acid $C_{25}H_{51}COOH$	396	25	5.0	29.0
Cetyl alcohol $C_{16}H_{33}OH$	242	21	4.6	21.9
Myricyl alcohol $C_{30}H_{61}OH$	536	29	5.4	35.2
Tristearin $(C_{18}H_{35}O_2)_3C_3H_5$	891	69	8.3	23.7
Cetyl palmitate $C_{15}H_{31}COOC_{16}H_{33}$	482	21	4.6	44.0
Oleic acid $C_{17}H_{33}COOH$	282	48	6.9	10.8
Triolein $(C_{18}H_{33}O_2)_3C_3H_5$	885	145	12.0	11.2
Trielaidin $(C_{18}H_{33}O_2)_3C_3H_5$	885	137	11.7	11.9
Ricinoleic acid $C_{17}H_{32}(OH)COOH$	297	90	9.5	5.8
Linoleic acid $C_{17}H_{31}COOH$	280	47	6.9	10.7
Linolenic acid $C_{17}H_{29}COOH$	278	66	8.1	7.6
Castor oil $(C_{17}H_{32}(OH)COO)_3C_3H_5$	929	280	16.8	5.7
Linseed oil $(C_{17}H_{31}COO)_3C_3H_5$	875	143	11.9	11.0

Table 1 gives the values of a and τ found for a number of different solid and liquid films on distilled water at 16°C. Palmitic, stearic, and cerotic acids all occupy the same area ($24. \times 10^{-16}$ sq. cm.) per molecule. The length of the molecule in the vertical direction (τ) increases about in proportion to the number of carbon atoms in the chain. This is a direct proof that the molecules are oriented on the surface with the COOH groups in contact with the water, and the hydrocarbon groups placed vertically above them. Dividing the value of τ by the number of carbon atoms in these molecules, we obtain an average of 1.19×10^{-8} cm. It is not likely that the carbon atoms in a hydrocarbon molecule are closer to each other than in a diamond, so that we must conclude that the carbon atoms in the chain are not arranged along a straight line, but in a zigzag fashion. The cross-section a is ample for such an arrangement.

The data for tristearin show that the three $-COO-$ groups are all located on the surface of the water and that each occupies the same area as it does in the stearic acid molecule. The three chains are placed side by side. Cetyl palmitate occupies actually less space than palmitic acid. The two chains lie side by side, each having less than one-half the cross-section, but twice the length, that it has in palmitic acid or cetyl alcohol.

These results prove that the areas are determined by the space on the water required by the active groups $-COO-$ or $-OH$ and not by the cross-section of the hydrocarbon chain itself.

The unsaturated acids and esters occupy much larger areas than the saturated ones, and have correspondingly shorter lengths. This is clearly due to the double bond (and the $-OH$ in ricinoleic acid) itself occupying a space on the water. Marcelin[5] has shown that when a globule of oleic acid is placed on a water surface, the film obtained is twice as thick as one which just alters the surface tension of water. Marcelin concludes that such a film is two molecules thick. The above data show that when the thin film of oleic acid is doubled in thickness, each molecule then occupies the same area as does one of stearic acid. Clearly, when an excess of oleic acid is added, the $-COOH$ groups displace the double bonds and the chains assume an erect position on the surface.

These facts prove that the hydrocarbon chain is extremely flexible and has no definite shape of its own. The term 'chain' thus describes its properties admirably.

The above method makes it possible to determine the lengths and cross-section of molecules of non-volatile, insoluble substances. Devaux has shown that oils spread on clean mercury surfaces as well as on water, so that it may be possible to study many substances soluble in water by this method.

For volatile or soluble substances, however, there is another method by which the cross-sections and lengths of molecules in the surfaces of liquids may be determined.

According to Gibbs' equation

$$q = -\frac{c}{RT}\frac{d\gamma}{dc} \tag{1}$$

we may calculate q the amount of material adsorbed per square centimeter in the surface of a liquid, by determining the rate at which the surface tension, γ, changes as the concentration of a dissolved substance, or that of a vapor above the liquid, is altered. It has been pointed out by Milner[7] that when substances strongly depressing the surface tension are added to water, the surface tension varies linearly with the logarithm of the concentration for all except extremely dilute solutions. If we write equation (1) as follows:

$$q = -\frac{1}{RT}\frac{d\gamma}{d\ln c} \tag{2}$$

it is evident that under these conditions q is independent of the concentration. Milner thus calculates from Whatmough's data for acetic acid solutions, that q is 3.8×10^{-10} grams mol. per square centimeter over a rather wide range of concentrations. This should correspond to a monomolecular film. Multiplying the above result by N, we find that it corresponds to $23. \times 10^{13}$ molecules per square centimeter. The area occupied by each molecule is the reciprocal of this, or 43×10^{-16} sq. cm. per molecule. If the whole of this area were covered by a single molecule of acetic acid, the value of τ would be only 2.2×10^{-8} cm. It is therefore probable that the group molecule forming the surface layer contains water adsorbed around the acetic acid group. The polar character of the $-COOH$ group should exert its influence on the CH_3 radical, causing it to pack into the surface layer surrounded by a definite number of water molecules. This hypothesis is in accord with the fact that acetic acid mixes in all proportions with water.

Still more conclusive evidence in support of the new theory is furnished by a paper by Szyszkowski,[8] in which surface tension data for water solutions of propionic, butyric, valeric, and caproic acids are given. The results are found to be given quite accurately by the purely empirical relation

$$1 - \frac{\gamma}{\gamma_0} = b \log_{10}\frac{c+a}{a} \tag{3}$$

where γ is the surface tension of the solution and γ_0 is that of water; a and b are constants. Szyszkowski found that b had the same value, namely 0.411, for all the fatty acids investigated, while the constant a had a different value for each substance. Over a large part of the range of concentrations investigated, a was negligible compared to c so that the empirical equation 3 is equivalent to the relation found by Milner. That is, if we neglect a in (3) and differentiate, we obtain

$$\frac{d\gamma}{d\ln c} = -\,0.434\,\gamma_0\,b. \tag{4}$$

Comparing this with (2),

$$q = \frac{0.434\,\gamma_0\,b}{RT}. \tag{5}$$

Since b was found to have the same value for all the fatty acids, this equation indicates that the same number of molecules of acid are adsorbed in the surface layer in each case. Placing $\gamma_0 = 73$ dynes per centimeter; $b = 0.411$, $R = 83.2 \times 10^6$ ergs. per degree and $T = 290°K$ we find $q = 5.4 \times 10^{-10}$ gram mols. per square centimeter. This corresponds to a value of a of 30.6×10^{-16} sq. cm. per molecule. This agrees even better with our value of $24. \times 10^{-16}$ sq cm. per molecule for palmitic acid.

Donnon and Barker[9] have measured the amount of nonylic acid adsorbed in the surface of its water solutions and have compared the result with that calculated from surface tension measurements by Gibbs' equation. Both methods gave approximately the same results, averaging about 1.1×10^{-7} grams per square centimeter (independent of the concentration over a wide range). This corresponds to a value of a of 23.7×10^{-16} sq. cm. per molecule, practically identical with the values for the fatty acids given in table 1.

We may therefore conclude that in moderately concentrated solutions of all substances which strongly depress the surface tension, the surface consists of a layer, *one molecule deep*, of the dissolved substance, and that there is never a transition layer in which the concentration varies progressively as we go further from the surface into the solution. The amount of solute required to form the monomolecular layer can be calculated from Gibbs' equation. The length and cross-sections of the molecules forming the surface layer may then be found.

In the case of solutions of inorganic salts, such as NaCl, the surface tension is greater than that of pure water and increases linearly with the concentration. Milner[7] pointed out, according to Gibbs' equation, that there is a deficiency of solute in the surface proportional to the concentration. Now this is exactly what we should expect if the surface layer of these solutions consists of a single layer of group molecules of water. Milner shows that the deficiency of salt is 4.1×10^{-11} gram molecules of salt per square centimeter for a normal solution ($c = 0.001$). Hence we may place $q/c = -4.1 \times 10^{-8}$.

This result can be explained if we assume that there is a layer 4.1×10^{-8} cm. thick on the surface which contains no salt. This then should represent the length of the water group molecule. It is interesting to note that practically this same value is obtained with solutions of all the different inorganic salts.

Taking the molecular weight of water in the surface to be 18, we find the cross-section of the water molecule to be 7.3×10^{-16} sq. cm.

It is believed that this method of studying the structure of liquid surfaces will prove to be of very general application. The writer is undertaking experiments to measure the cross-sections of molecules adsorbed on water surfaces from vapors. Thus, benzol vapor greatly lowers the surface tension of water, and in this way some knowledge may be obtained as to the shape of the benzol molecules under different conditions. Of course other liquids than water may also be used.

There is a great deal of available data on surface tension of solutions in the literature which can serve this same purpose. I hope to refer to as many of these cases as possible, in a paper on the constitution of liquids which will soon be submitted for publication in the *Journal of the American Chemical Society*.

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THE IMPORTANCE OF THE WATER CONTAINED IN THE DEEPER PORTIONS OF THE SUBSOIL

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The most extreme views are entertained as to the importance of the water contained in the deeper portions of the subsoil—that below the depth penetrated by the roots of crop plants. Thus while McGee[1]