

PENETRATION AND COMPLEX-FORMATION IN MONOLAYERS*

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IF A MONOLAYER OF an insoluble substance is spread at an air-water interface, and a soluble substance containing a polar or ionized group attached to a non-polar structure (e.g., organic acids, soaps) is introduced into the underlying solution, in low concentrations ($1 - 10 \times 10^{-6}$ g./cc.), there may be considerable changes in the surface pressure and potential of the film. If this is so, the soluble substance is said to *penetrate* the monolayer (1, 2). Because of the chemical nature of the substances concerned, it is clear that there may be interaction between the polar head groups, or between the non-polar portions (van der Waals forces), or between both portions, and the nature of the

phenomenon is determined by the

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relative importance of the two kinds of forces (3).

In the first place, there may be strong polar interaction associated with weak van der Waals forces, as when benzoic acid is injected be-



Dr. Schulman addressing the Society of Cosmetic Chemists of Great Britain, November 9, 1949.

neath a film of a long-chain amine (4). In this case a process of solution of the soluble substance in the monolayer takes place, which may be reversed by compressing the film,

when ejection of the penetrating molecules occurs, followed by their adsorption under the monolayer, which is thus stabilized, by polar forces. No stoichiometric association is observed between the two components, and fairly large concentrations of the penetrating substance are required.

If there is no interaction between the two components of the system, the behavior depends on their relative surface activities. If the monolayer substance is the more active, nothing happens above the collapse pressure of the soluble compound, but if not, it is displaced from the surface, with the formation of a monolayer of the soluble substance. This occurs when soaps are injected beneath films of triglycerides, and consequently accounts for the detergent action of soaps (5).

When both van der Waals and polar forces are strong, definite stoichiometric complexes are formed, often analogous to complexes formed in bulk solution, e.g., between cholesterol and digitonin (1). The extent of penetration of the film is shown by a sharp rise in the surface pressure of the film at constant area. On compression of the film, the pressure rises still more, and it is found that compression can be carried to a pressure higher than the collapse pressures of the components. For example, a complex of cetyl alcohol and sodium cetyl sulfate will stand a pressure of 60 dynes/cm. compared with the collapse pressures of cetyl alcohol (40 dynes/cm.) and sodium cetyl sulfate (15 dynes/

cm.). Similarly, the collapse pressure of the cholesterol-digitonin complex is 60 dynes/cm. compared with those of its components (40 and 20 dynes/cm., respectively). When the film of the complex collapses, it may do so as a unit (e.g., elaidyl alcohol-sodium cetyl sulfate) or by

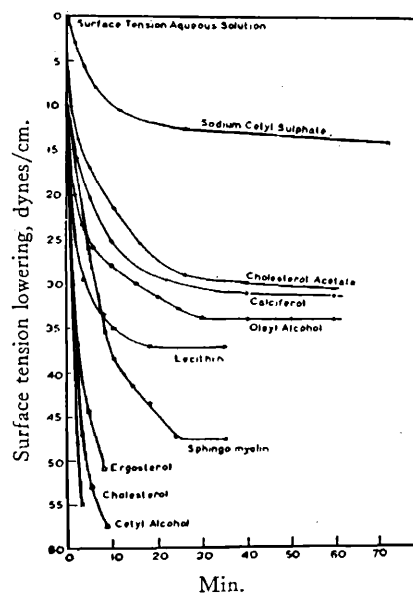


Figure 1.—Sodium cetyl sulfate $3.3 \times 10^{-4}\%$ injected at pH 7.2 under various films, at 10 dynes surface pressure.

ejection of one component (e.g., oleyl alcohol-sodium cetyl sulfate, the latter being ejected). The stability of the complexes is increased by the adsorption of a layer of soluble component beneath the mixed film.

The formation of complexes shows remarkable specificity. Saponin, for example, forms a complex with cholesterol but not with cholesteryl acetate, because of the considerably reduced hydrogen-bond activity of

the ester group compared to the hydroxyl. Similarly, oleyl alcohol forms a complex with sodium oleate but not with oleic acid. Specificity is thus related to the polar group, and also to steric hindrance and the presence of double bonds. The effects of the polar group is shown by the variation in the equilibrium surface pressure of substances penetrating a cholesterol monolayer, the

on penetration at an area of 78 \AA^2 per molecule, whereas the elaidyl alcohol film (trans) is liquid down to 60 \AA^2 per molecule, and the oleyl alcohol film (cis) never solidifies. It is clear that the trans-isomer conforms more closely to the shape of the saturated alcohol than does the cis-isomer, and consequently the van der Waals attraction for the long chain salt is greater. Iso-morphism between the molecules plays an important part in the penetration phenomenon.

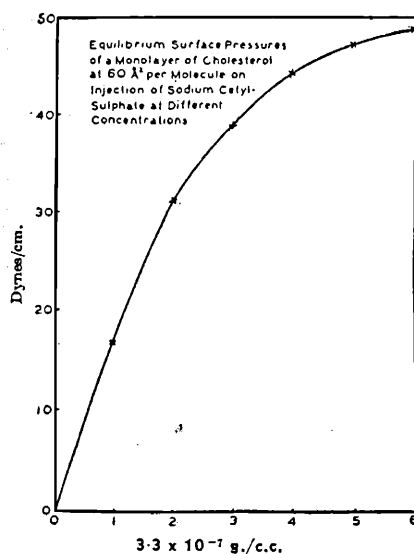


Figure 2.—This shows that $FA = RT \log C_1/C_2$. A = area of cetyl sulfate molecule.

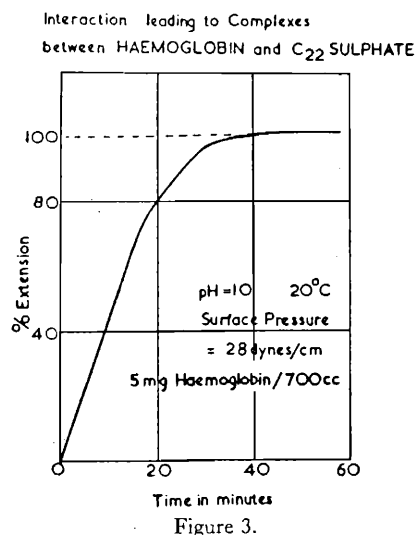
order being: $R-NH_3^+ > R-SO_4^- > R-SO_3^- > R-CO_2^- > R-NMe_3^+ >$ bile salt anion. The effect of the presence of a double bond is shown strikingly by the effect of sodium cetyl sulfate on monolayers of the unsaturated C_{18} alcohols, as compared with the saturated C_{18} alcohol. As will be seen, a cetyl alcohol film solidifies

METHODS OF INVESTIGATION

Several methods are available for the study of the penetration phenomenon. It may be studied either at constant area of the film, when changes are revealed by increasing surface pressure, or by keeping the pressure constant, when the film expands as penetration proceeds (21). Finally, the film may be expanded to a large area, injection carried out, and the mixed film compressed, the force-area curve being plotted. From the existence of kinks in the force-area curves of various penetrating systems, Schulman and Stenhagen concluded that 1:1 and 1:3 complexes existed, and that 1:2 complexes were unstable. Work by Matalon and Schulman (6) has since shown that owing to the rigidity of some of the films studied (e.g., cetyl alcohol-sodium cetyl sulfate) hysteresis effects are involved which make some of the conclusions doubtful. However, work done by these authors using an expansion tech-

nique at constant pressure shows that in the systems cetyl alcohol-sodium cetyl sulfate, cholesterol-saponin and cholesterol-sodium cetyl sulfate, 1:1 complexes definitely

water caused an immediate increase in surface pressure. However, it was also found that during compression of a mixed film, higher pressures were attained, due to closer packing in the film, than during spontaneous penetration.



exist irrespective of the pressure of expansion and concentration of the penetrating substance in the underlying solution (22).

The influence of salts in the underlying solution is very important. Harkins and his co-workers, using distilled water, were unable to repeat the results of Schulman and Stenhagen (2) for the system cetyl alcohol-sodium cetyl sulfate, which had been obtained on M/500 phosphate buffer at pH 8. They ascribed the discrepancy to defects in the earlier workers' technique, but Schulman and Matalon (6) showed that injection of phosphate beneath a mixed film of cetyl alcohol and sodium cetyl sulfate on distilled

BIOLOGICAL APPLICATIONS

The concepts described above have important biological applications. In the first place, Schulman and Rideal showed (1) that hemolytic activity is closely associated with the equilibrium penetration pressure of the dissolved substance when penetrating a cholesterol monolayer, the order of activity being the same as that given above for the latter phenomenon. Some hemolytic substances, such as the long-chain alcohols, have a strong dispersing action on protein films, and it seems that hemolysis is also due to the penetrating substance displacing the protein portion of the cell wall. The specificity mentioned earlier, namely that of cholesterol with saponin or long-chain sulfates, and long-chain hydrocarbons polyethylene oxides or alcohols for protein films can be used to distinguish between the components of cells. Thus, lysis of cells can be obtained by penetration of the available cholesterol portion by cholesterol-penetrating substances or dispersion of the available protein portion by protein-penetrating or -dispersing substances.

A protein monolayer collapses at a surface pressure of about 16 dynes/cm., and so substances that

lower the surface tension by about 20 dynes/cm. will lyse cells if protein is available and if the agent is in sufficient concentration to lower the surface tension to that extent. The cholesterol-active substances are effective in concentrations below 10^{-3} per cent and so, are active at concentrations which lower the surface tension approximately 5 dynes/cm. or less. Substances which adsorb on to protein monolayers, and do not penetrate, are all agglutinating agents, as they render the hydrophilic surfaces of the cells hydrophobic.

The chemistry of the cell surfaces can thus be established by the nature of the substances which attack them. Further, some cells can be shown to be resistant to both these types of agent, and consequently to be composed of chitin or other polysaccharide material. It is also of interest that active substances in sublytic doses can induce a permeability of the cell to materials which are not normally taken up or given out by the cell.

SUMMARY

The penetration and adsorption phenomena may be summarized under the following headings: (a) constant area, (b) variable area and pressure, (c) constant pressure.

1. Weak Interaction. (a) If the surface pressure of the soluble agent is π_S , and the collapse surface pressure of the film-forming molecules is π_F , then if $\pi_S > \pi_F$, displacement of the film material will take place, if there is no association by polar

forces between the two molecules. The resultant surface pressure will be π_S .

(b) Ejection of a compound in a mixed film will take place at its collapse pressure if there is no polar interaction.

2. Strong Interaction. (a) If there is strong association by van der Waals forces between the film-forming molecules and the soluble molecules in the underlying solution, the resultant surface pressure of the mixed film will approach $\pi_S + \pi_F$, well above the collapse pressure of either of the components.

(b) No ejection occurs from a mixed monolayer of the two associated molecules, but a 1:1 complex of very high collapse pressure is formed. Ejection of the excess of dissolved molecules from the 1:1 complex monolayer can be followed experimentally. Phase diagrams obeying a two-dimensional phase rule can be plotted for these mixed monolayers.

1 and 2 (c). The percentage increase in area of a monolayer on penetration by soluble molecules from the underlying solution, at constant pressure and below the resultant equilibrium surface pressure of the monolayer at constant area, is directly related to the ratio of the molecular areas of the interacting species at their collapse pressures. Thus, a cholesterol monolayer with an area of 40 \AA^2 per molecule on being penetrated by sodium cetyl sulfate (20 \AA^2) will expand by half

the original area. This can be shown to be independent of the surface pressure or concentration of the penetrating molecules in the underlying solution (2). Similarly, a cholesterol monolayer expands to double its area on penetration by saponin, showing that the area per molecule of saponin is also 40 \AA^2 . Surface solution effects shown at low surface pressures by excess of penetrating agent (above the amount required to form the 1:1 complex) can be taken into account by extrapolation of the expansion-time curve to the starting time (7, 22).

ADSORPTION AND TANNING

If in the underlying solution the soluble interacting molecule has two or more appropriately spaced polar groups, the penetration of the non-polar portion of the molecule is prevented, and adsorption in the form of a double layer takes place. This results in the film-forming molecules becoming spaced on the lattice of the polar groups of the adsorbed molecules, producing a solid film of the insoluble film-forming molecules at very large areas, usually at least twice the normal area of solidification of the monolayer alone [e.g., tanning of an amine film (4, 23)].

Should the area of the film-forming molecule be greater than the area taken up by two of the spaced polar groups in the adsorbed molecule, no expansion of the insoluble film takes place, but a marked increase in rigidity is observed, due to

intermolecular interlacing by the adsorbed molecules [e.g., tanning of proteins (1)].

Adsorption results in big changes of surface potential of the insoluble monolayer, either a rise or a fall according to the nature of the adsorbed dipole.

REVERSIBILITY OF ADSORPTION

Proteins may adsorb on to lipid monolayers, either at the air-water or at the oil-water interface, in the latter case as protein-stabilized emulsions. Since this adsorption is pH-conditioned, it can be easily reversed. The structural changes of the protein molecule before adsorption, as an adsorbed monolayer and after desorption are very interesting, especially in relation to the biological activity of protein molecules in the three structural forms (7-9).

THE OIL-WATER INTERFACE

Analogous molecular interactions to those at the air-water interface can be shown by an emulsion technique to exist at the oil-water interface. The stability and ease of formation of emulsions are related to complex-formation, surface viscosity and rigidity and surface charge. As has been shown, complex-formation at the interface between an oil-soluble agent in the oil phase and a water-soluble agent in the aqueous phase can radically alter all these factors (10). Since the resultant interfacial tension depends on the

surface tensions of both components, very low interfacial tensions are obtained when complex-formation is observed between the oil-soluble and water-soluble stabilizing agents (11).

At the oil-water interface, there are interesting phenomena which suggest similar associations resulting in mixed-film formation (12). In the first place, it is known that the interfacial tension between an aqueous soap solution and a hydrocarbon is independent of the oil used. This indicates the presence of a monolayer of the soap alone at the interface. On the other hand, the interfacial tension between an oil solution of oleic acid and water is strongly dependent on the oil used. The lowering of the interfacial tension between the oil and water is least with benzene, intermediate with cyclohexane and decalin and greatest with hexane and long-chain paraffins. This effect is shown very definitely, particularly in the difference between the aromatic and saturated hydrocarbons. In the case of the latter, minima occur in the surface-tension-concentration curves, the explanation of which is doubtful. If they are due to the presence of two components in the interfacial film, the second component can only be an oxidation product of oleic acid or the hydrocarbon itself. Now, it is known that benzene is the best solvent for long-chain alcohols, to which undissociated fatty acids would no doubt approximate in their intermolecular inter-

actions, and it is noticeable that it produces the least effect in these experiments, perhaps because of a low surface-bulk partition ratio of the surface-active oleic acid.

In the case of emulsification, the inversion of phase continuity from oil- to water-continuous, occurs in decreasing order of readiness in the sequence benzene, cyclohexane, hexane, higher paraffins. This may be due to the fact that this is the descending order of interaction energy between solvent and solute, so that penetration of the polar heads by water becomes more pronounced than penetration of the hydrocarbon chains by the solvent, which would favor oil-continuity from steric considerations.

If we now take a three-component system consisting of oil, water, and a soap such as potassium oleate and add to it a substance which from monolayer experiments would be expected to form a complex with the soap (and penetrate the soap monolayer), the mixture liquefies and, on adding sufficient of the fourth component, clears giving a transparent, fluid dispersion, which does not show streaming birefringence. A suitable complex-forming agent is an alcohol such as hexyl alcohol or (best) *para*-methyl cyclohexanol. If benzene is used as the oil, the dispersions are oil-continuous; if nujol (long-chain paraffins), they are water-continuous, as judged by their electrical conductivity. It is possible to make such systems containing equal volumes of oil and water, and indeed their sta-

bility is greatest in such a case, becoming less when the volume of the continuous phase is increased (13).

It is interesting that if we take as the hydrocarbon one which is between benzene and nujol in the hydrophobic series, two transparent systems can be prepared. This has been done, for example, in the case of decalin and of a petroleum fraction of the approximate formula $C_{15}H_{32}$ containing a high proportion of naphthenes. These give first very viscous, almost gel-like systems, which are water-continuous, with conductivities, however, less than that of a liquid dispersion. They show pronounced streaming birefringence. When more *para*-methyl cyclohexanol is added, they break and, on adding still more, liquid dispersions like those previously described are formed. If a hydrocarbon such as decalin or hexane is used, the final dispersion is oil-continuous, but if a mixture containing higher paraffins is used, the system remains water-continuous, but has a lower conductivity than if no gel had formed (14).

Formation of the two types of dispersion is consistent with the views outlined above. As more alcohol is added, above the amount required for an equimolecular mixed film with the soap, it will pass into the oil phase, rendering it less hydrophobic by virtue of the hydroxyl groups so introduced. This will weaken the interaction between the oil and the paraffin chains of the soap relative to that between the polar groups and water. This will favor an inversion

of the dispersion from water- to oil-continuity, but whether the inversion actually takes place or not depends on the degree of hydrophobic character possessed by the oil. Thus, nujol is sufficiently hydrophobic to prevent it, but decalin is not. These phenomena can also be expressed in terms of the wettability of the interface by the oil phase and the water phase. The phase which has the lower contact angle with the interfacial film will be continuous, and as the alcohol is added to the oil, it causes its contact angle to approach that of water. If the angle is lowered sufficiently by this means, inversion to an oil-continuous system occurs; in the case of nujol the lowering is not sufficient to bring this about.

STRUCTURE OF THE TRANSPARENT DISPERSIONS

In view of their properties, it is clear that the structure of these isotropic dispersions must be different from that of concentrated solutions of soaps and of so-called "solubilized oils." It has been shown by the x-ray studies of Hess (15), McBain (16), Harkins (17), and their collaborators, that a soap micelle can swell with oil, and a soap crystallite with water, only within certain definite limits. In the present instance, much more of the disperse phase is incorporated, and it is thought that the alcohol molecules penetrate between the soap molecules in the crystallites introducing disorder into the lattice,

which then breaks up and forms a spherical shell in order to enclose a given volume of water or oil in a surface of minimum area (13, 19).

the soap alcohol molecules, several hundred Angstrom units in diameter separated by the continuous phase. Confirmation of the postulated

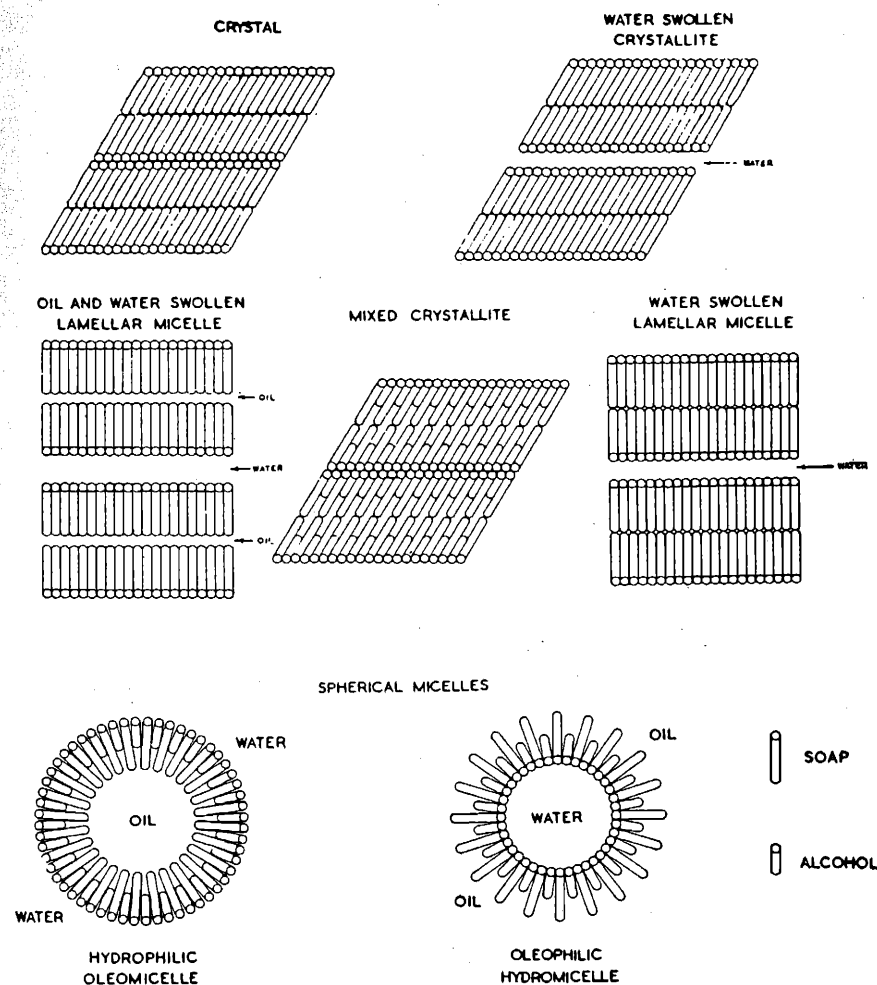


Figure 4.—The phenomena of solubilization of soap crystal lamellae by non-polar oils and penetration of the monolayer lattice by polar oils in the formation of micelles and emulsions.

Thus, Schulman and Hoar (18) suggested that these transparent, fluid dispersions consisted of droplets, surrounded by a mixed monolayer of

structure of the fluid dispersions was sought in three ways. In the first place, the area occupied at the air-water interface by a molecule of po-

tassium oleate is known, and so is that occupied by an alcohol molecule. Further, the area of the cross-section of a soap molecule can be derived from the side spacing of 4.8 Å. found in the liquid crystal. As a result of these two lines of evidence, the most probable area of a bimolecular complex in the oil-water interface is about 70 Å.² Accepting this as the area per oleate residue, the total area of the interface can be calculated, and since the total volume of the disperse phase is known, the radius of the supposed droplets can be found. Assuming that all the oleic acid is in the interface, the radius of a water droplet in oil is given by the formula

$$r = 3V_w/\sigma,$$

where V_w = volume of water, and σ = total interfacial area of the droplets and is given by

$$\sigma = N_0 ws/M,$$

where $N_0 = 6 \times 10^{23}$, w = weight of oleic acid, $s = 70 \text{ Å.}^2$ and M = mol. wt. of oleic acid. The overall radius of the droplet is $r + 25 \text{ Å.}$ as the oleic acid molecule is about 25 Å. long. The dimensions of oil droplets in water can be calculated in a similar way, but the method is slightly more complicated. Calculations were also made assuming short cylinders and lamellae for the droplets. When this was done, results could be compared with experimental data obtained by the two following methods.

X-RAY STUDIES (19)

The solutions were subjected to examination in an x-ray camera designed to study low-angle scattering. Because the ratio of disperse to continuous phase was nearly 1.0, the spheres were expected to be arranged, almost in contact, on a three-dimensional hexagonal lattice. One would expect therefore, low-angle scattering from adjacent planes, and these Bragg spacings when corrected by multiplying by the Ehrenfest-Prins factor for liquids (1.23) would give the distance between the centers of adjacent droplets. Diffraction bands of this type were in fact found. They were diffuse, corresponding to liquid-type scattering, and after allowance had been made for the gap between spheres the resulting diameters were in good agreement with those calculated. By suitably adjusting the oil-water ratio, it was possible to bring the spheres almost into contact, and then the spacings were very nearly equal to the diameters of the droplets.

Bands of this type were obtained with both oil- and water-continuous dispersions. In nearly all the oil-continuous systems, agreement was better with the spherical model than with either lamellar or cylindrical micelles. However, the case of the water-continuous systems containing comparatively large quantities of oleic acid is not so clear, and it may be that a cylindrical model is better for them.

It is obvious that the gels, which

show streaming birefringence, cannot be treated as aggregates of spheres, but must contain cylindrical or lamellar aggregates which are long compared to their other dimensions. As would be expected, they give sharper bands, and the spacings are nearer to those expected for lamellae. Examination of them is still in progress.

LIGHT-SCATTERING STUDIES (20)

In order to obtain more direct evidence of the existence of micellar aggregates in the dispersions, investigations were carried out by a light-scattering method, using Rayleigh's formula to determine the droplet size. This is

$$\frac{i}{I_0} = \frac{9\pi^2}{2r^2\lambda^4} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 NV^2$$

for right-angle scattering of a beam of unpolarized light of intensity I_0 and wave-length λ in the solution, in which there are N particles of volume V and refractive index m relative to the solute, per cc., and the distance from the scattering solution to the observer is r . In these experiments, NV was known, being the total volume of the disperse phase, and so V and hence the radius of the droplets, assumed spherical, could be calculated.

When the formula was applied to systems prepared as described, it was found that the diameters calculated were far too small, values

of 10–20 Å. being indicated. This is easily explained, as Rayleigh's formula assumes that the total scattering is the sum of the scattering from the individual units. This is true for a gas, but is manifestly false when the scattering units are separated by less than their diameter, as we have here. Alternatively, if we regard scattering as due to concentration fluctuations in neighboring volume elements (Einstein, Smoluchowski, Debye) it is clear that fluctuations are hindered in

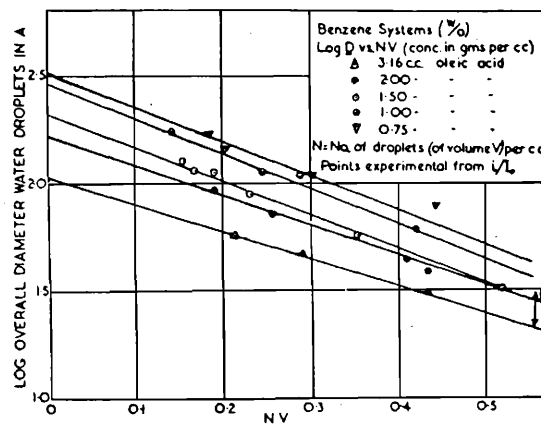


Figure 5.

highly concentrated solutions, as has indeed been shown for tobacco mosaic virus and sucrose solutions. In order to overcome this difficulty, series of solutions containing the same volume of disperse phase in increasing volumes of the oil (benzene) were examined. In all cases the intensity of the scattered light increased as the solutions were diluted. The apparent droplet diameter was calculated in each case, and it was found that the log d -con-

centration plots were linear; extrapolation to infinite dilution gave the ideal droplet diameters. As will be seen from the table, these agreed well with the calculated values, and indicate the general correctness of

TABLE 1

Volume of Oleic Acid, Cc.	Droplet Diameters, Å.		
	Calc.	X-ray	Light- Scattering
0.75	363	480	330
1.00	280	300-350	285
1.50	201	185-235	210
2.00	164	125-190	165
3.16	120	100-125	107

the hypothesis. The diameters in the last column were derived assuming that the paraffin chains of the soap form part of the scattering unit. If, as is possible, they do not, calculations must be made without the monolayer, and 50 Å. added to the result. If this is done, the results are: 365, 295, 220, 155, 128 Å., also in good agreement with the calculated values. If the two sets of experimental values are used to derive the thickness of the monolayer, a value of 22 Å. is obtained. Of course, the fact that the lowest concentration that could be investigated was about 10 per cent lays the accuracy of the extrapolation open to criticism, but it seems to be justified by the results.

We have also examined the system benzene - water - cetyltrimethylammonium bromide-chloroform, which forms dispersions completely analogous to the others. However, interpretation of the results must be made on a different basis, be-

cause the area occupied per CTAB molecule could not be determined *a priori*. Again, x-ray and light-scattering results agreed, and in this case it proved possible to carry light-scattering measurements down to a concentration of 6 per cent. It will be seen that the area per CTAB molecule is found from the light-scattering results to be 35-45 Å.², which is not much more than the area per molecule in a close-packed monolayer of CTAB (28-30 Å.²). This indicates that the area available for the chloroform is not more than about 18 Å.² The chloroform will alter the hydrophobic-hydrophilic balance of the oil phase, and must be associated in some way with the positively charged nitrogen atoms of the soap.

TABLE 2

Wt. of CTAB, Gm.	Light- Scattering Diameter, A.	X-ray Spacing, A.	Area per CTAB Mole- cule, Å. ²
1.50	320	369	45
2.25	280	Ca. 270	35
3.00	200	...	40

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