

THE ACTIVITIES OF SOME WATER-IN-OIL EMULSIFYING AGENTS

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A lecture delivered before the Society on 22nd March 1962.

From the results of measurements of several properties of cholesterol and its esters, it is deduced that the water-in-oil emulsifying power of a compound is determined almost entirely by the mechanical properties of the interfacial film it forms. The properties of interfacial films cannot be deduced from measurements of the effect that a compound has on the water-oil interfacial tension, nor can the results for one oil phase be used to predict the interfacial properties of a system containing a different oil phase. The importance of other relevant factors is discussed.

Wool wax and its constituents are among the most effective W/O emulsifying agents so that it is not surprising that many workers have been interested in discovering the source of the emulsifying power¹⁻⁴. Although a considerable amount is known about the chemical constitution and properties of wool wax⁵, there are still many unexplained problems concerning the mechanism by which these emulsifying agents act.

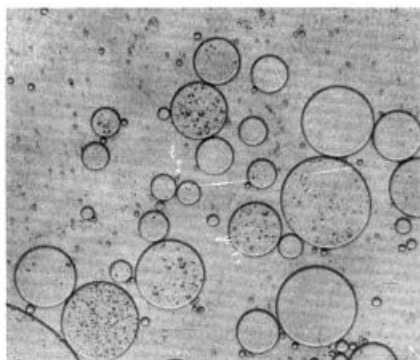


Figure 1. A woolscouring liquor at 45°C. containing double emulsions

Wool wax is the lipid material found in the sheep's fleece. In the first stage of processing wool, the wax or grease is washed off the wool with soap and water. Although the object of this process is to remove the grease as an O/W emulsion, the remarkable W/O emulsifying powers of wool wax are already evident. Figure 1 shows that a typical woolscouring liquor contains

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double emulsions ; globules of wax are dispersed in the soapy water while smaller droplets of water are to be found in many of the wax globules. In the subsequent processing, the wax is recovered from the aqueous liquors by mechanical or chemical means⁵, and after it has been refined and bleached, it is marketed as lanolin.

Chemically, wool wax is a mixture of esters which, after saponification, can be resolved into two roughly equal fractions of wax acids and wax alcohols. *Table 1* summarises the compositions of the two fractions ; further details of the composition can be found in the literature^{5,6}.

Table 1
The Constitution of Wool Wax

Acidic Fraction Type of acid :—	Percentage
<i>n</i> Acids 15 members, C10 to C32 even numbered carbon chains C13 to C17 odd numbered carbon chains	} 7
<i>iso</i> Acids 12 members, C10 to C32 even numbered carbon chains	23
<i>anteiso</i> Acids 12 members, C9 to C31 odd numbered carbon chains	30
α -Hydroxynacids 13 members, C12 to C24 even numbered carbon chains C13 to C23 odd numbered carbon chains	} 15
α -Hydroxyisoacids 6 members, C14 to C24 even numbered carbon chains	11
α -Hydroxyanteisoacids 7 members, C13 to C25 odd numbered carbon chains	4
ω -Hydroxynacids 5 members, C26 to C34 even numbered carbon chains	3
ω -Hydroxyisoacids 2 members, C30 and C32 carbon chains	0.5
ω -Hydroxyanteisoacids 4 members, C27 to C33 odd numbered carbon chains	1
Total identified :—	94.5
Unsaponifiable fraction :—	
<i>n</i> Hydrocarbons 21 members, C14 to C32 even numbered carbon chains C13 to C33 odd numbered carbon chains	} 1
<i>iso</i> Hydrocarbons 10 members, C14 to C32 even numbered carbon chains	
<i>anteiso</i> Hydrocarbons 8 members, C15 to C29 odd numbered carbon chains	

Table 1 (*continued*)
The Constitution of Wool Wax

Unsaponifiable fraction :—	Percentage
<i>n</i> Alcohols 11 members, C16 to C30 even numbered carbon chains C19 to C23 odd numbered carbon chains	} 4
<i>iso</i> Alcohols 6 members, C16 to C26 even numbered carbon chains	6
<i>anteiso</i> Alcohols 9 members, C17 to C33 odd numbered carbon chains	7
<i>n</i> Alkane-1,2-diols 10 members, C14 to C24 even numbered carbon chains C17 to C23 odd numbered carbon chains	} 4
<i>iso</i> Alkane-1,2-diols 6 members, C16 to C26 even numbered carbon chains	
<i>anteiso</i> Alkane-1,2-diols 6 members, C15 to C25 odd numbered carbon chains	
C27-Sterols :	
Cholesterol	30
7-Oxcholesterol	3
Cholestan-3,5,6-triol	2
Cholestenol	1
Cholesta-3,5-dien-7-one	1
C30-Sterols :	
Lanostadienol	16
Lanostenol	16
Agnostadienol	1
Agnostenol	3
7-Oxolanostenol	2
7,11-Dioxolanostenol	1
Total identified :—	98

There is a fundamental difference in the physico-chemical requirements for the formation of emulsions of the O/W and W/O types. For invert emulsions (W/O), the interfacial film must be electrically neutral and it should possess some degree of rigidity⁷. The necessity for electrical neutrality is evident from the observation that invert emulsions are best formed from non-ionic compounds, but this does not mean that non-ionic compounds must necessarily give rise to invert emulsions. That the interfacial film possesses a great deal of rigidity can be inferred from the non-spherical shape of the droplets of the dispersed phase (*Fig. 2*).

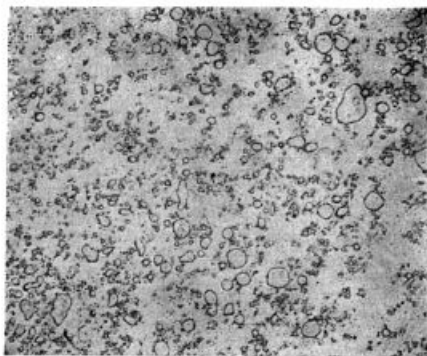


Figure 2. Irregularly shaped globules of a W/O emulsion stabilised with 2.5% cholesterol + 2.5% cholesteryl palmitate ; photographed after dilution with liquid paraffin

MEASUREMENT OF THE EMULSIFYING POWER

The normal criterion of the activity of an emulsifying agent is the extent to which it can lower the oil/water interfacial tension. For W/O emulsifying agents, however, the reduction in interfacial tension is not a satisfactory measure of the emulsifying power. In general, a good W/O emulsifying agent will lower the benzene/water interfacial tension to 10-30 dynes/cm which, by the normal standards of surface activity, is very poor. As will be seen later, the ability of the emulsifying agent to form a viscoelastic interfacial film is a more important property but so far no serious attempt has been made to correlate interfacial viscosity with emulsifying activity.

The most generally used quantitative measure of the emulsifying power of a W/O emulsifying agent is the *water number* which is defined by Casparis and Meyer⁸ as the maximum weight of water that can be emulsified in a hydrophobic base containing a specified concentration of the emulsifying agent. Later workers have found it more convenient to measure the water number in volume units (ml/100g). The experimental technique affects the accuracy of the results. The most accurate method is to add small volumes of water from a burette to a known weight of oil and emulsifying agent contained in a beaker. Between the additions, the emulsion is well stirred (by hand) until no more water can be emulsified, i.e., until the presence of unemulsified water is unmistakable. Observations made by this method are reproducible to $\pm 5\%$, but the process is tedious.

In an attempt to simplify the technique, some workers have stirred the emulsions mechanically^{3,9}; they have also adopted the procedure of adding different volumes of water to a series of samples of the hydrophobic base contained in a boiling tube and stirring the mixture with a high-speed (2200 r.p.m.) glass or stainless steel stirrer for an arbitrary time. Sub-

sequently, the samples are classified into two categories : in one, all the water has been emulsified and in the other, some water still remains unemulsified.

The uncertainty of the results obtained by methods in which a mechanical stirrer is used is so large that the water number must be determined statistically. For example, Worrell *et al*⁹ have determined the water number of cholesterol (3%) in petrolatum by adding different volumes of water, in 1 ml steps, to a series of 3g samples of the hydrophobic base. Twenty observations were made for each volume of water. *Figure 3* shows the number of samples in which the water was completely emulsified as a

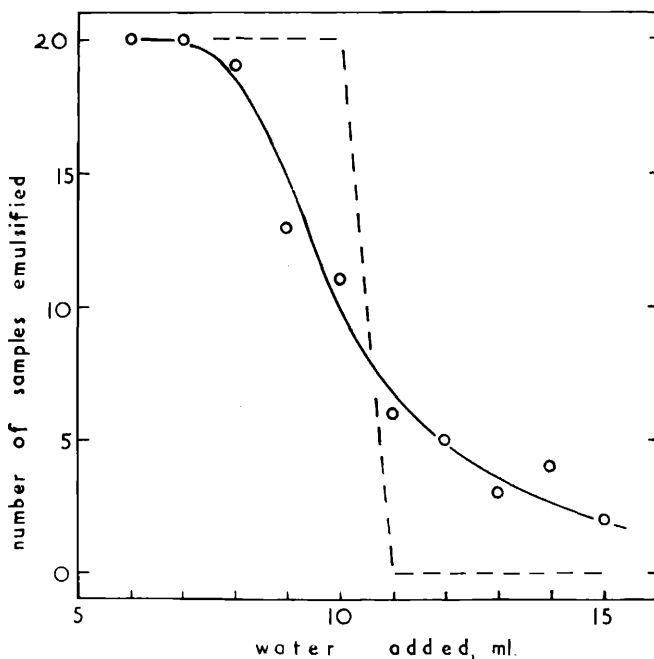


Figure 3. The number of samples (out of 20) in which all the water was emulsified plotted as a function of the volumes of water. The deviation from the broken line indicates the inaccuracy of the results obtained using a mechanical stirrer

function of the volume of water added. Statistically, the best result is that for which 50% of the samples are completely emulsified. If the mechanically stirred emulsification could be carried out with the same degree of reproducibility as can the hand-stirred emulsification, an ideal curve such as that shown by the broken line in *Figure 3* would be obtained.

Another undesirable feature of the method employing a mechanical

stirrer is that the water number depends on the size of the sample. *Table 2* shows that as the size of the sample increases, so too does the water number.

Table 2

Dependence of the water number on the size of the sample (3% cholesterol in petrolatum) when the emulsions are stirred mechanically.

Sample weight in grams	Water number
1	300
2	375
3	450
4	500
5	500
6	550

EMULSIFYING POWER OF LANOLIN

It has long been known that lanolin has the power to emulsify considerable amounts of water without losing its characteristic properties. For a long time it was believed that the constituent esters had the power to hold water in the form of a W/O emulsion but it is now known that the emulsifying agents are the free alcohols and to a lesser extent, the free acids⁴. By chromatographing commercial lanolin on alumina and examining the various fractions, it was established that the esters of lanolin were devoid of emulsifying power. As *Table 3* shows, the emulsifying activity of lanolin lies mostly in its free alcohols.

Table 3

Water numbers of lanolin fractions obtained by chromatography on alumina.

Sample	Water number
100% commercial lanolin	355
100% lanolin esters obtained by chromatography	16
5% commercial lanolin*	145
5% lanolin esters*	5
5% lanolin alcohols*	710
5% lanolin acids*	235
2.5% lanolin alcohols*	255
2.5% lanolin alcohols + 2.5% lanolin esters*	650
2.5% lanolin acids + 2.5% lanolin esters*	190

*In liquid paraffin.

Although the entire composition of the alcohols is not known, 59 individual compounds have already been identified. Using the relatively new technique of thin film chromatography, *Hartolan* (commercial wool wax

alcohols) can be shown to contain at least 18 groups of compounds (*Fig. 4*). Most of the unidentified compounds are steroids. The known composition of Hartolan has been effectively summarised in *Table 1*, but in addition to the alcoholic compounds listed, there is also a small amount of unsaponified ester.

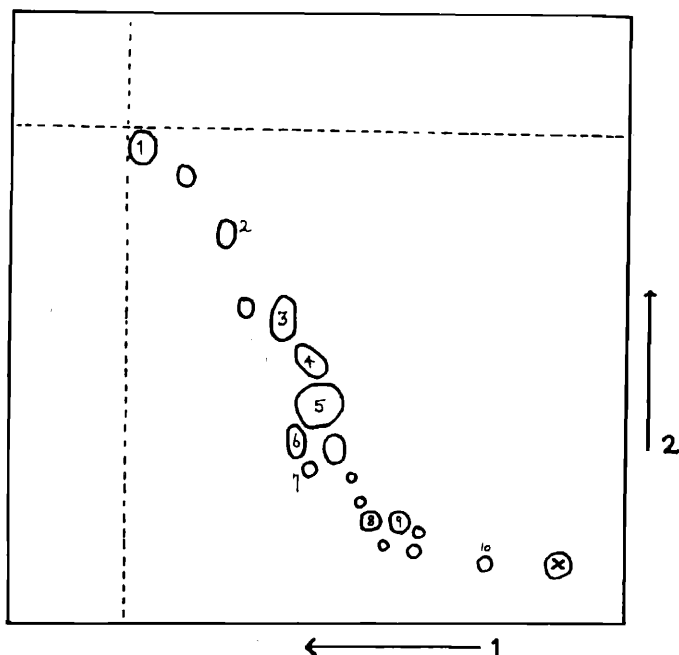


Figure 4. Two-dimensional thin film chromatographic pattern of Hartolan (kindly provided by B. Bush, Esq.). Developing solvents:—

1. cyclohexane/benzene/acetone : 3/1/1 2. benzene containing 12% ethanol

Key:—

- | | |
|----------------------------|-------------------------|
| 1. esters and hydrocarbons | 6. 7-oxolanostenol |
| 2. cholesta-3,5-dien-7-one | 7. 7,11-dioxolanostenol |
| 3. isocholesterol | 8. 7-oxocholesterol |
| 4. aliphatic monols | 9. aliphatic diols |
| 5. cholesterol | 10. cholestane triol |

Hartolan is not easily resolved into its individual components so that ideas about its emulsifying power are based on the behaviour of representative pure compounds. Three main groups of compounds can be distinguished: aliphatic alcohols, steroids containing 27 carbon atoms per molecule and steroids (sometimes referred to as triterpenes) containing 30 carbon atoms per

molecule. The emulsifying powers of representatives of each group are shown in *Figure 5*.

Comparison of the emulsifying powers of the crude fractions obtained from *Hartolan* with those of the representative compounds shows that the

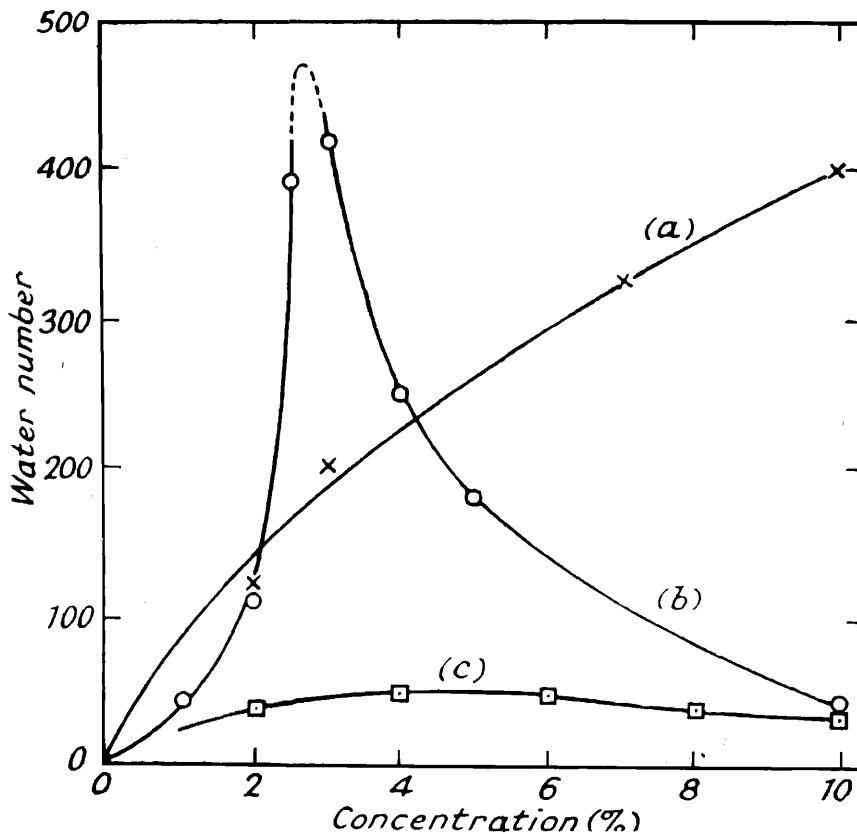


Figure 5: Water numbers of alcohols as a function of their concentrations in liquid paraffin (a) cholesterol ; (b) isocholesterol ; (c) neicosanol

impure materials usually have the greater water numbers. Although it is well known that a mixture of related surface-active agents is usually more effective than a single compound, *Table 3* also reveals that it is possible to obtain an enhancement of the emulsifying power by mixing an emulsifying agent with a non-surface-active compound of the right type. It may be seen that for 2.5% lanolin alcohols in liquid paraffin, the water number is 255 while that of the lanolin esters is negligible. If, however, the two materials

are used in equal proportions, the resultant water number is 650, a value which is much greater than the sum of the individual contributions.

EMULSIFYING POWER OF BINARY MIXTURES OF ALCOHOL AND ESTER

Using pure compounds, Powers *et al*³ found that a mixture of cholesterol with one of its aliphatic acid esters has a much higher water number than has cholesterol by itself; the ester alone is, of course, without activity. They also made the surprising discovery that the magnitude of the effect depends on the length of the acid chain in the ester. *Figure 6* shows the dramatic increase in the water number of equal weights of cholesterol plus ester as the homologous series of *n* acids is ascended.

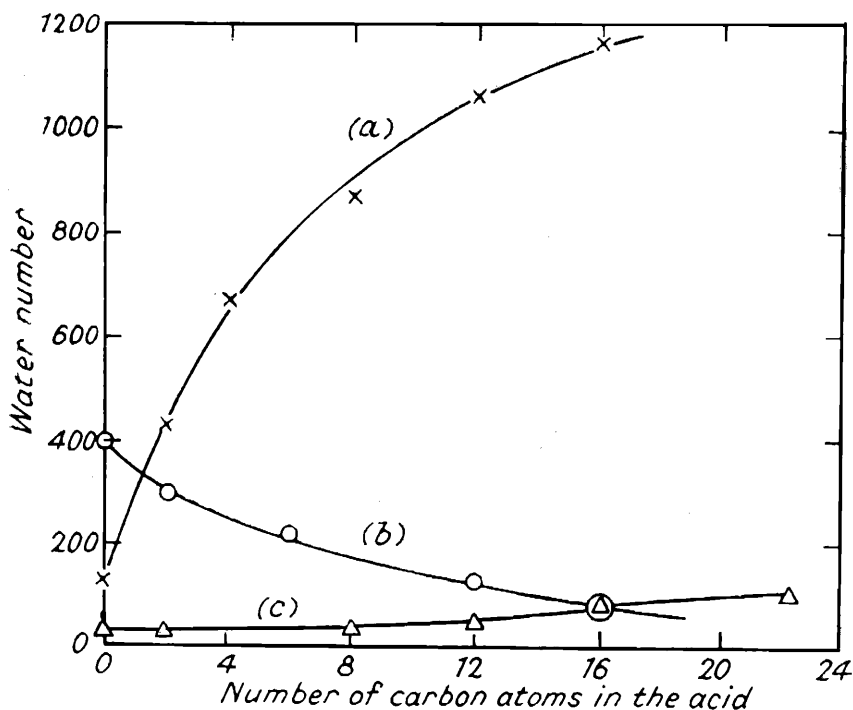


Figure 6. Effect of lengthening the acid chain of an ester upon the water number of a mixture of an alcohol and its esters (2.5% of each in liquid paraffin). (a) cholesterol + cholesteryl esters; (b) *iso*cholesterol + *iso*cholesteryl esters; (c) *noctadecanol* + *octadecyl* esters.

The observation that the water number of a mixture of two compounds is not the sum of their separate contributions has been made for several series

of compounds. For example, an enhancement of the water number is observed with mixtures of

- (a) cholesterol with its aliphatic di-esters,
- (b) cholesterol with aliphatic esters and di-esters of hexadecanol,
- (c) cholesten-3-carboxylic acid with its aliphatic esters,
- (d) 3-homocholesterol (3-methylol-cholestene) with its aliphatic esters, and
- (e) noctadecanol with its aliphatic esters.

For mixtures of *isocholesterol* with its esters, on the other hand, the emulsifying power is less than the sum of the individual contributions (*Fig. 6*).

Although a considerable number of experiments have been directed towards elucidating the mechanism of the synergistic process, so far no altogether satisfactory explanation has been found. The most obvious conclusion is that an association complex is formed at the interface, between the alcohol and its ester, and that the complex has a greater (or for the complex formed between *isocholesterol* and its esters, a lower) emulsifying power than either of its components. Examination of the behaviour of mixtures of octadecanol and octadecyl laurate, and of cholesterol and cholesteryl stearate suggests that the maximum enhancement of the water number is observed when the molecular ratio is 1 : 1. Hence, the interfacial complex would appear to arise from a 1 : 1 association of alcohol and ester. It is surprising, therefore, that none of the evidence obtained in related fields supports the concept of the formation of a molecular complex of definite composition.

It is a tenet of the theory of surface activity that, if a compound is surface-active, its concentration in the interface must be different from its concentration in the bulk solution. Consequently, the interfacial tension must depend on the bulk concentration of the surface-active solute. Measurement of the interfacial tensions of solutions of cholesterol and cholesteryl stearate in benzene against water, shows that cholesteryl stearate is not surface active and that mixtures of cholesterol and its stearate produce the same lowering in interfacial tension as does cholesterol alone (*Table 4*)¹⁰. Hence, cholesteryl stearate cannot be adsorbed at the benzene/water interface either by itself or in association with cholesterol.

Similar results for hexadecanol and hexadecyl palmitate showed that the ester is not surface-active nor does it form an interfacial complex with the alcohol. The interfacial tension between benzene and water is 34.4 dynes/cm, that for 0.03 molar lanostenol is 28.9 dynes/cm, and that for 0.03 molar hexadecanol is 32.0 dynes/cm. The interfacial tensions of 2.5% solutions of cholesterol, lanostenol and hexadecanol in benzene against water are 19.2, 23.5 and 28.2 dynes/cm respectively. It should be noted that the differences

Table 4

Interfacial tensions of benzene solutions of cholesterol and mixtures of cholesterol and cholesteryl stearate against water.¹⁰

Temp.	Cholesterol moles/litre	Ester moles/litre	γ dynes/cm.	γ for cholesterol at the conc. shown in column 2
20	0.0300	0.0100	25.9	26.1
	0.0200	0.0200	29.6	29.4
	0.0100	0.0300	32.7	32.5
40	0.0300	0.0100	29.6	29.3
	0.0200	0.0200	31.1	30.8
	0.0100	0.0300	31.9	31.7

between these values do not explain the observed differences (*Fig. 5*) in the emulsifying powers.

These observations may not be strictly comparable with the emulsification experiments because the paraffin has been replaced by benzene. The latter is used for interfacial measurements as a matter of convenience because it is a better solvent and it has a clearly defined chemical composition. If the enhancement of the water number is caused by the formation of an interfacial complex, it is hard to see how the large effect caused by mixtures of cholesterol and its stearate can be completely eliminated merely by substituting benzene for liquid paraffin.

To eliminate the possibility of interference by benzene, two other properties of the cholesterol/cholesteryl stearate system may be investigated. First, their behaviour at the air/water interface may be examined on a Langmuir trough. Cholesterol forms a "solid" monomolecular film whereas cholesteryl stearate does not form a real interfacial film. At very low interfacial pressures the stearate forms an expanded monolayer, but as the pressure is increased above about 0.1 dyne/cm the molecules pile up to form a multilayered film, showing that the stearate has no spontaneous tendency to remain at the air/water interface. Mixed films of cholesterol and its stearate behave like films of cholesterol alone. Because the presence of cholesterol makes no difference to the ease with which the ester is squeezed out of the interface, there cannot be an association between the two types of molecules.

Secondly, it is reasonable to suppose that the association between cholesterol and cholesteryl stearate should be most evident in the absence of all diluents, i.e., the phase diagram should show the formation of a complex. Once again, however, there is no evidence of any association; the phase diagram shows no unexpected features. The eutectic mixture has the composition 3 molecules cholesterol : 1 molecule cholesteryl stearate.

A brief summary of the evidence so far shows that there is some sort of

association between cholesterol and cholesteryl stearate in the presence of water and liquid paraffin, but there is no indication of association when the compounds are studied by themselves, or in the presence of water or in the presence of water and benzene. It must follow, therefore, that a simple molecular complex is not formed; it must also follow that the liquid paraffin is involved in some way.

Measurements of the interfacial viscosity confirm this conclusion; the films formed by 2.5% cholesterol and 2.5% cholesterol + 2.5% cholesteryl stearate at the benzene/water interface have no viscosity, but the viscosity of the film formed by cholesterol at the liquid paraffin/water interface is appreciable (42.7 surface poises after 3 min) and after a slight fall, it increases steadily as the interface ages until it is too high to measure; it exceeds 10^6 s.p. after 16 h. The viscosity of the paraffin/water interface is, of course, nil and so too is the viscosity of the interface formed between 2.5% cholesteryl stearate in liquid paraffin and water, but the viscosity of the interfacial film formed by 2.5% cholesterol + 2.5% cholesteryl stearate follows the same trend as that formed by cholesterol alone, but the former is lower throughout. After 1 min it is 3.5 s.p., and after 16 hours it is 53,000 s.p.

CONCLUSIONS

What general conclusions can be drawn from these observations about the nature of the interfacial film in W/O emulsions, and in particular, what can be learned about the mechanism underlying the change in emulsifying power brought about by the inclusion of an ester?

When water is stirred into an oil to produce an emulsion, there is a point of dynamic equilibrium at which water is being emulsified as fast as the emulsion is being broken down. The amount of water that can be emulsified depends on the extent of the interface that can be formed by the emulsifying agent and also on the stability of the interfacial film. A very approximate calculation based on the water number of cholesterol and the size of the water droplets in the emulsion, shows that there is space in the interface for only one cholesterol molecule out of about forty. Hence, the interfacial film must be either a multilayer about 40 molecules thick, or the cholesterol is present in the form of very small but discrete solid particles. These solid particles can be accommodated in the hydrocarbon medium enclosing the water droplets which has an average thickness of about 6μ . In the alcohol/ester emulsion the specific surface area is about seven times larger, so the thickness of the multilayer of cholesterol is reduced to about 6 molecules, or the size of the solid particles must be correspondingly smaller. The enhancement of the water number must, therefore, be attributed to some property of the ester which enables the cholesterol to be spread more thinly. In either case, the interfacial film is more properly regarded as an interfacial phase.

The observations do not support the theory that there is a specific association of the ester and the alcohol into pairs, nor is the ester to be found in the aqueous part of the interface, nor does it increase the extent to which cholesterol is adsorbed at the interface. That the length of the acid chain in the ester plays a very important part in determining the water number suggests that the packing of the molecules in the interfacial phase can be influenced from the hydrocarbon side. In liquid paraffin, 2.5% cholesterol or 2.5% ester form almost saturated solutions at room temperature so that the interfacial phase has no tendency to be dissolved. In better solvents, however, the interfacial film is probably an expanded monolayer having a negligible surface viscosity. It is likely then, that the ester in liquid paraffin acts as a plasticizer and *reduces* the interfacial rigidity or viscosity. This deduction implies that the maximum water number is observed at an optimum value of the interfacial viscosity. If the interfacial phase is too rigid, the water number is low but the emulsion is stable; when it is too fluid, the water number is low and so too is the stability of the emulsion. The ideal W/O emulsifying agent should give rise to a viscoelastic, semi-ordered interfacial phase. As its name implies, a viscoelastic film has both elastic and viscous properties. Because of its elasticity it can be stressed without rupturing, and if it should rupture, its plasticity enables it to reform. This hypothesis is an attractive one when applied to the cholesterol/ester system, particularly as cholesteryl esters are known to possess the property of forming liquid crystalline phases.

Microscopical examination, in polarised light, of emulsions formed with sterol/ester mixtures in petrolatum reveals that the entire hydrocarbon phase is of the liquid crystalline type; it is possible that the interfacial phase and the hydrocarbon phase are not separate entities.

Although the observational data are still lacking, it seems likely that a rational basis for classifying W/O emulsifying agents could be developed from a correlation of the water numbers with the interfacial viscosities.

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DISCUSSION

DR. E. L. NEUSTADTER : (1) What is the effect of branched chain esters on the emulsifying properties of wool wax alcohols ?

(2) Is the surface viscometer actually a flat plate or a cone ?

THE LECTURER : (1) So far as I am aware, this point has not been investigated. It seems unlikely that replacement of the normal chains by slightly branched chains such as *iso*- or *anteiso*-end groups would make any marked difference to the water number.

(2) It is a circular plate about 3 mm thick. Calculation of the surface viscosity requires knowledge of the radius of the viscometer plate and the radius of the container. If a cone is used, it would have to be immersed to exactly the same depth in each experiment or the radius of the cone at the level of immersion would have to be determined in each experiment.

DR. A. W. MIDDLETON : (1) You have referred to the rate of change of surface viscosity reading, sometimes say 50,000 surface poise in a short while, whilst in other cases 500,000 surface poise. How reproducible is the rate of change ?

(2) *Figure 3* showed us a sigmoid curve of the number of stable emulsions produced with increasing amounts of water to a constant amount of emulsifier. With some amounts of water, say 3 out of 20 tests given an emulsion. What chance occurrence caused these three to be stable ?

THE LECTURER : (1) I have not made any systematic measurements of the *rate* of change of surface viscosity. Comparison of the viscosities of replicate samples of the same age shows that the high values referred to are reproducible to about 20 per cent.

(2) It is difficult to be sure, but the formation of "superhydrated" emulsions would provide one explanation. When water is progressively stirred into some emulsions (e.g., those containing cholesterol + cholesteryl caprylate in liquid paraffin) the normal end-point may be passed without any indication that the emulsifying capacity of the system is being exceeded. Suddenly, the next addition of water causes the emulsion to collapse, and the system separates into water + emulsion. If the quantity of free water is measured, it is found that the amount of water that remains emulsified corresponds, within acceptable limits, to the expected water number. Although "superhydrated" emulsions cannot be produced to order, when they are formed, they appear to break at a fairly reproducible water content, i.e. it seems as though some systems have a higher, secondary water number. If the addition of water to a "superhydrated" emulsion is discontinued before the secondary water number is reached, the product has sufficient short-term stability to be wrongly classified.

MISS E. E. CHAMPION : *W/O emulsions*. I refer to the stability of hand stirring with a glass rod against the instability of an American experiment using a mechanical stirrer. Had any air been incorporated during the manual action using a glass rod, hence any bearing on the stability ?

THE LECTURER : I have never observed the inclusion of air in hand-stirred emulsions. With a high-speed mechanical stirrer air might well be included in the emulsion but I do not believe that it would affect its stability.

MR. K. H. STEINITZ : At what temperature were the hand-stirred emulsions prepared ?

THE LECTURER : All emulsification experiments have been conducted at room temperature. I have observed that some emulsions break very readily as the temperature is raised. Moreover, the breaking temperature is fairly reproducible which suggests the possibility of a phase change in the system.

DR. J. J. MAUSNER : Please comment on the relative stabilities of cholesterol versus cholesterol/ester emulsions.

THE LECTURER : There is nothing to choose between them. Both types of emulsion are stable for four weeks at room temperature.

PHOTO-CONTACT DERMATITIS FROM SOAPS

C. D. CALNAN, M.R.C.P.*

A lecture delivered before the Society on 26th January 1962.

The studies which led to the discovery of the photo-contact sensitizing property of tetrachlorosalicylanilide are described.

ABNORMAL HYPERSENSITIVITY to light is a phenomenon that has interested biologists, veterinarians and physicians for at least a century, although the most intensive studies have been made over the past twenty or thirty years. It has been appreciated for a long time that certain chemicals have the capacity to make animals and men more sensitive to light, not as an exceptional phenomenon but as a normal inherent property. The use of some such chemicals has been discontinued in medical therapeutics entirely because of their photosensitizing properties. The first medicaments to be used on a large scale in recent years which frequently produced light sensitivity were the sulphonamides. Various sulphonamide derivatives used for other than anti-bacterial action have been found to have a similar effect.

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