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SURFACE CHEMICAL TECHNIQUES IN THE DESIGN OF COSMETIC PREPARATIONS

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Delivered at the Summer Conference of the Society on 25th August 1960.

Many of the methods used for the study of soluble and insoluble films at the Air-Water and Oil-Water interfaces are described. The possible applications for their use in the furthering of cosmetic products is given. It is suggested that much useful basic information can be obtained by the application of the results obtained from studies of this type.

WHETHER HE realizes it or not, the cosmetic chemist is intimately concerned with the properties of surfaces or interfaces of one type or another. His products are designed for application to the surface of the skin and the formulation chemist is constantly striving to improve and modify the physical and subjective properties of his preparations, usually by altering the mechanical properties of the interfaces existing in them.

Interfaces are the boundaries between two immiscible states of matter, e.g. Liquid/Liquid (emulsions), Gas/Liquid (foams), Gas/Solid (powders) and Solid/Liquid (toothpastes). It was realized before the time of Rayleigh that an interface is a region of high free energy and in consequence, has special properties of its own, some of them being two-dimensional analogues of a three-dimensional system.

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If a third substance is dissolved in one of the phases, it will tend to concentrate at the interface to a greater or lesser degree depending on its so-called "Surface Activity." This concentration at the interface is termed "adsorption" and the extent of adsorption will depend on relative affinity of the dissolved substance for the bulk phases. Adsorption results in a lowering of the free energy of the surface and hence it becomes easier to disperse one phase in the other. Thus, surface active agents are used as emulsifiers, detergents, foaming agents, etc., because they are able to modify the properties of multiphase systems. Many of the methods of surface chemistry and physics have been developed for studying the properties of adsorbed films, usually using model systems. Thus the Air/Water surface in a trough is a model for the interface existing in a foam, while the Oil/Water interface formed by placing oil on water is a model for the interface existing between the oil and water in an emulsion.

This paper is a review of the experimental methods that can be used to study Gas/Liquid and Liquid/Liquid interfaces, with an illustration of the type of result that can be obtained.

It is convenient to classify the experimental methods in terms of the type of interface being examined.

Gas/Liquid Interface

This interface and the Liquid/Liquid interface are probably the simplest to work with, since they are easy to form reproducibly. The experimental techniques are also fairly straightforward.

Adsorbed Films

It should be remembered when formulating a shampoo, that its ability to foam will depend on :—

(1) the surface tension being lowered sufficiently,

(2) a sufficiently rapid diffusion of the surface agent into the surface, especially during the rapid expansion of the surface as the foam is generated,

(3) the correct mechanical properties of the adsorbed film being achieved. If the film is too fluid or too rigid, it will be unstable and an unsatisfactory foam will be obtained.

The Determination of Surface Concentrations

(i) *Radio Isotopes*

This technique was introduced by Dixon *et al*[1] and Aniannsson and Lamm[2].

The kinetics and thermodynamics of adsorption have recently been studied using radio isotopes. Nilsson[3] studied the adsorption of sodium dodecyl sulphate using the tritiated compound, while Flengas and Rideal[4] studied the adsorption of C^{14}—tagged sodium stearate. They showed that the Gibbs Adsorption Isotherm predicted much lower surface concentrations than was found using the radio-tracer techniques. Their results suggested a molecular surface association of the solute.

(ii) *Surface Tension Measurements*

It is difficult to measure directly the surface concentration of adsorbed substances at the Gas/Liquid interface. This is usually determined indirectly by applying the Gibbs Adsorption Isotherm to the experimentally determined relationship between concentration of solute and surface tension of the solution :

The Gibbs Adsorption Isotherm is of the form :—

$$\Gamma = \frac{-c}{RT}\frac{d\gamma}{dc}$$

where Γ = the surface concentration.
c = the bulk concentration of the solute.
γ = the surface tension of the solution.

The equation is true for most practical purposes but strictly, concentration should be replaced by activity.

For solution of pure detergents the above equation is of the form :—

$$\Gamma = \frac{-c}{2RT}\frac{d\gamma}{dc}$$

When there is excess neutral salt present, the equation reverts to its original form without the factor of $\frac{1}{2}$.

The general validity of the Gibbs Adsorption Isotherm was demonstrated by McBain, who removed the surface of solution by a fast-moving microtome knife.

A. *Equilibrium Surface Tension Measurements*

The methods described here are most suitable for determining the surface tensions of solutions where the surface film has been allowed to reach equilibrium. Some of the methods can be adopted for systems where equilibrium is attained only slowly, e.g. dilute solutions of impure detergents reach their final surface tension slowly (1—24 h.).

(a) *Capillary Rise Method*

This can be a very accurate method. It depends on the measurement of the rise of the liquid in a capillary tube of known radius and

relies upon a zero contact angle between the tube and test liquid. This is sometimes difficult to achieve with dilute solutions of surface active materials.

(b) *Maximum Bubble Pressure Method*

This method depends on a measurement of the force required to blow a bubble of gas from a tube of known radius immersed in the test solution. This bubble must be blown sufficiently slowly to allow the equilibrium film to be established. The technique can be rendered simpler, by comparing the pressures for two tubes of differing diameters.

(c) *Drop Volume and Drop Number Method*

This is the most common and simplest method for determining surface tensions. The volume or weight of drops which fall from the tip of a vertical tube is determined. It is usual to calibrate the tip with solutions of known surface tension, e.g. ethyl alcohol, although absolute values may be determined using published correction factors. An Agla micro-syringe is a most convenient device with which to carry out Drop Volume determinations.

(d) *Ring Detachment Method*

The surface tension may be determined by measuring the force required to detach objects of various shapes from a liquid surface. If the object is wetted by the liquid (zero contact angle) some of the liquid comes up with it as it is lifted. At a certain height the liquid breaks away. The force at the break point is a function of the surface tension. The most commonly used shape for this method is a ring in conjunction with a du Nuoy tensiometer. It is always necessary to apply a correction factor, a table of which has been published by Harkins and Jordan[5].

The pull on a thin plate (Wilhelmy) is often quite satisfactory, especially when making quick comparative studies.

(e) *Sessile and Pendant Drop*

The shape of a large bubble or drop of liquid at rest on a plate or hanging from a suitable tip, is related quite simply to the surface tension of the liquid. The surface tension may be calculated from the height and maximum diameter of the drop or bubble.

A typical surface tension-concentration curve is shown in *Figure 1* for *n*-butyl alcohol. The Gibbs Adsorption Isotherm may be applied to this and the force (surface tension lowering)—area curve shown in *Figure 2* derived.

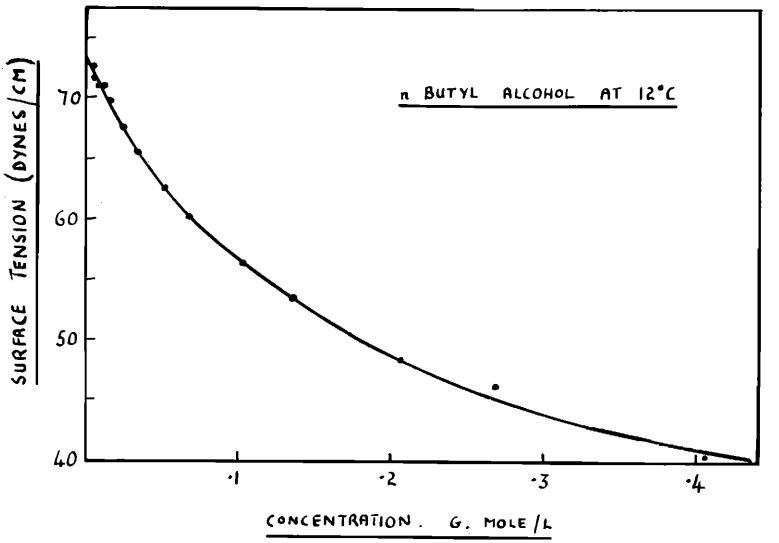

Figure 1

The surface tension concentration relationship for *n*-butyl alcohol at 12°C.

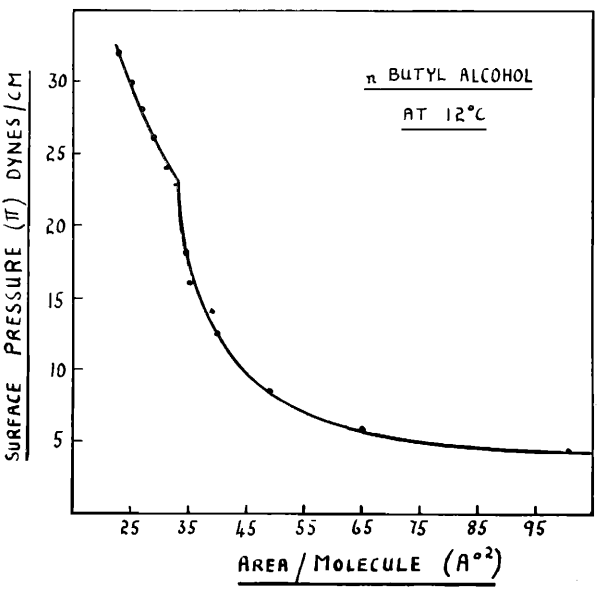

Figure 2

Force-area curve for *n*-butyl alcohol at 12°C calculated from *Figure 1*, using the Gibbs Adsorption Isotherm.

B. *Dynamic Surface Tension Measurements*

Where the ageing of a surface takes place over a long period of time, the hanging plate, Sessile Drop or Pendant Drop methods are probably the most suitable for studying the formation of adsorbed films.

One of the difficulties involved in formulating an aqueous spray formulation using a squeeze pack, say a wave-set, is the fact that the surface tension of water is very high and therefore a great deal of energy is required to be concentrated to break up the material into a satisfactorily fine spray. Additions of surface active agents may be made but they must be of the type, and be present in sufficiently large amounts, to bring the surface tension down to a low value (25—30 dynes/cm.) in a few milli-seconds. That is in the time required to form the droplet. Where high concentration of alcohol or mineral oil systems are used, the surface tension is naturally low and the problem is not so acute.

In order to investigate the surface tension of surfaces during the early moments of formation, special techniques have to be used.

1. *The Oscillating Jet*

One of the earliest methods developed for determining dynamic surface tensions is due to Rayleigh. He showed that when a jet of liquid issues from an elliptical orifice, oscillations are set up in the liquid, the wavelength of which is related to the surface tension at that point. Assuming that the jet moves *en bloc*, the age of the surface is related simply to the distance along the jet surface.

The relationship between wavelength and surface tension is a complex one and has not been fully resolved. Addison[6] attempted to resolve these difficulties but without complete success. Sutherland carried the mathematical analysis a stage further but considered that the whole system was complicated by indeterminate diffusion conditions under the surface, which rendered absolute interpretation of the results difficult.

2. *Surface Potential Measurements*

When two dissimilar surfaces are in contact with one another, an electrical potential difference known as contact potential is set up. If now a third material is introduced into the interface either by adsorption or by some other means, the potential changes by an amount known as the Surface Potential. The surface potential is related to the concentration of molecules at the surface, their orientation, dipole moment and the dielectric constant of the interface. If all the factors are constant then the surface potential is proportional to the surface concentration.

Because of the very high resistance involved at the Air/Water and Oil/Water interfaces, specialized techniques have to be used. The pioneers in the work at the Air/Water interface were Rideal and Schulman[7], who used a radio-active source (mesothorium or polonium) to irradiate the air gap between the surface and the electrode and hence increase its conductivity. The potential was then measured, using a valve electrometer. Much useful information has since been gained regarding the orientation of adsorbed and spread mono-layers using this technique.

Posner and Alexander[8] measured the surface potential along the surface of a cylindrical jet of fast-moving solution. They then related this measurement to surface tension by interpolation on a previously determined surface potential—surface tension curve obtained on an equilibrium surface. Examples of their results are shown on *Figure 3.*

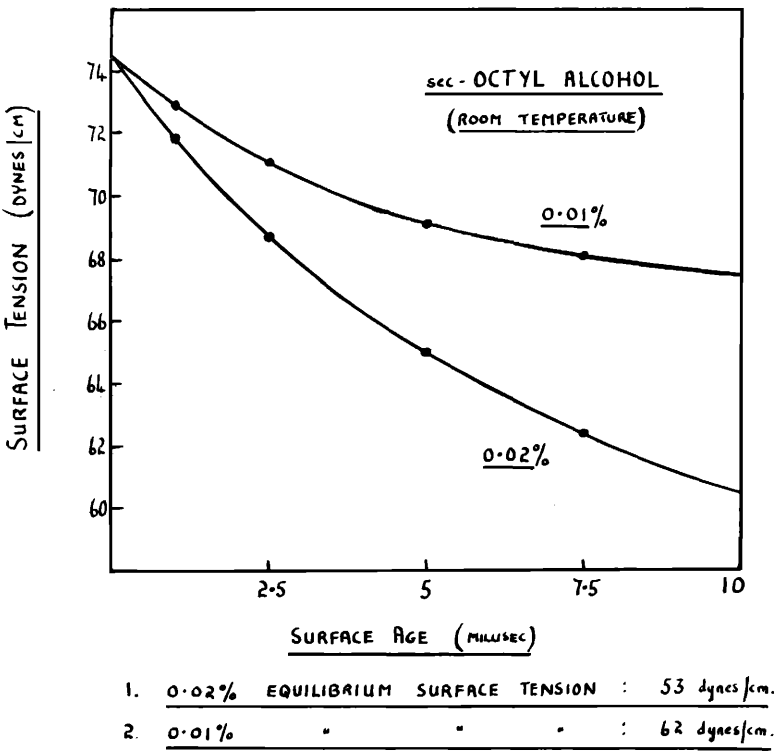

Figure 3

Surface tension plotted against surface age for solutions of sec-octyl alcohol.

3. *Hanging Plate Method*

Padday[9] has attempted to measure dynamic surface tensions by flowing solutions at various speeds upwards through a funnel, so that it overflows the top. This continuously generates a new surface and the tension is measured using a hanging plate. The surfaces studied are generally older than those studied by the techniques described earlier.

All the dynamic methods of studying surface tension suffer from the fact that the ages of the surfaces are uncertain because the hydrodynamic conditions at the surface are complex. The methods are therefore best used for making comparisons between different surface active agents and the effect of concentration. The results should therefore always be quoted back to the method used.

Insoluble Films

Surface Pressure Measurements at the Gas/Liquid Interface

Surface pressure is defined as the interfacial tension lowering produced by the spreading or adsorption of a material at the particular interface. Thus the measurement of surface tension described above also measures surface pressure.

The Langmuir trough is used to measure the surface pressure of insoluble monolayers spread at the Air/Water interface. A simple form of this apparatus has been described at Alexander[10]. It consists of a glass trough filled with the substrate (usually water). Lying in the surface of the water is a mica barrier, suspended from a torsion strip. The mica barrier extends to within 1 mm. of each edge of the trough and is sited about $\frac{1}{4}$ of the way along its length. The barrier is joined to the edge of the trough by silk or nylon threads coated with petroleum jelly. These joints must be carefully made to avoid leakage of the film past the barrier.

The apparatus must be scrupulously cleaned before use and the barrier and edges of the trough coated with paraffin wax to facilitate manipulation of the film.

Immediately before use, the surface of the trough, both behind and in front of the barrier is swept clean using waxed glass slides. The cleansing may be facilitated by sprinkling ignited talc on the surface. Any dirt is then sucked off the surface.

The material to be studied is dissolved in a suitable volatile solvent and about 0·02–0·05 cc spread from a micro-syringe. The surface film is then compressed with a glass barrier and the force read off on an optical lever system attached to the torsion strip. The strip should have previously been calibrated by the application of weights to a balance pan attached to a lever on the torsion head.

A typical force (π)—Area (A) curve is shown in *Figure 4.*

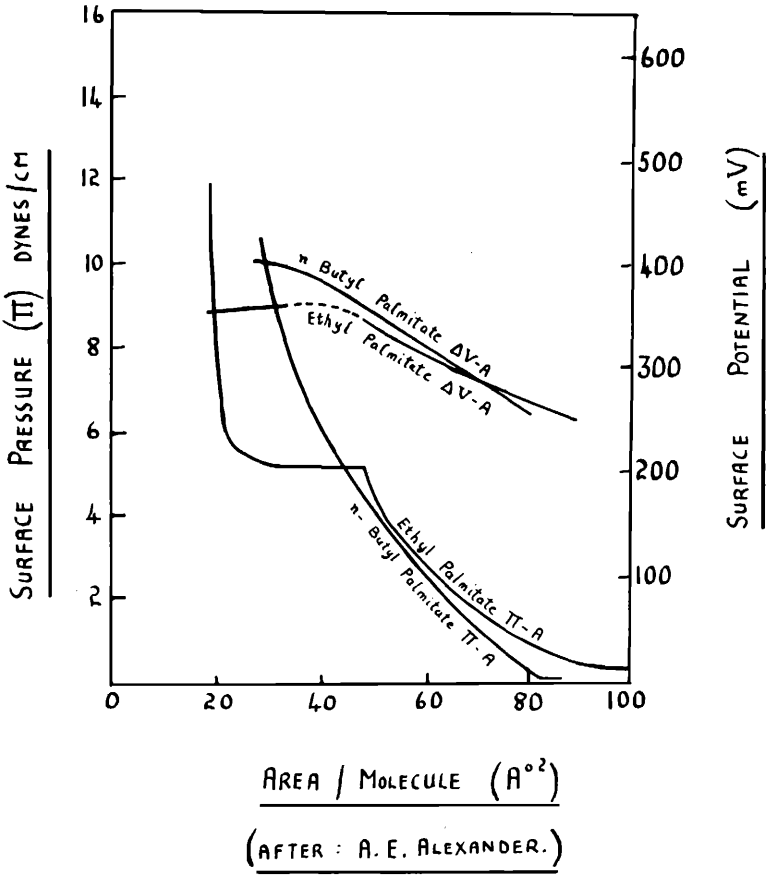

Figure 4

(a) Surface pressure/area relationship for methyl palmitate and *n*-butyl palmitate.
(b) Surface potential/area relationship for methyl palmitate and *n*-butyl palmitate.

Surface pressure is a two-dimensional analogue of gaseous pressure and obeys similar laws. Thus a dilute expanded film is termed gaseous and obeys a two-dimensional Boyles Law.

$$\pi A = kT$$

where k is the Boltzmann's Constant.

At higher concentrations the films deviate from this law and obey van der Waals and other modified equations of state. The films pass through various physical states including Liquid, Solid, Liquid Expanded and Liquid

Condensed. Well-defined melting points and phase transitions from one form to another can readily be detected from the force-area curves (*Figure 4*).

Very often surface pressure measurements are made in conjunction with surface potential measurements described above.

What use has this type of measurement for the cosmetic chemist? Many emulsion systems depend on the structure of the primary emulsifying layer; it should thus be possible to learn something about the physico-chemical properties and structures of emulsifying agents by spreading them at the Air/Water interface. The results at this interface are easier to interpret than those derived from adsorption measurements at the Oil/Water interface or Air/Water interface.

The author has used this technique for simplified detergency studies where the soil is spread at the interface and the detergent injected under the surface. The detergency is studied by examining the changes in surface pressure and potential with time.

Where this type of work is carried out, it is necessary to remove constantly the material diffusing into the surface behind the barrier by sweeping it clean. Unless this is done, low surface pressure readings will be obtained. Matalon and Schulman[11] overcame this difficulty by hanging a Wilhelmy plate behind the barrier. The plate was of such dimension that the pull on the plate was equal to the push on the free side of the barrier. The effect of molecules diffusing into the surface behind the barrier was therefore compensated by the pull on the plate.

Insoluble and Adsorbed Films

Surface Viscosities

The mechanical properties of a surface film often parallel the stability of a foam or emulsion. If the film is too rigid, the system will be unable to resist mechanical or thermal shock. If it is too fluid, rapid drainage of a foam or coalescence of an emulsion will take place.

Surface viscosities may be measured by timing the damping of a needle or disc placed in the surface. The effect of an adsorbed or insoluble film on the damping may thus be measured.

Alexander and Cumper[12] studied the surface viscosity of proteins which had been spread or adsorbed at the Air/Water and Oil/Water interface using an oscillating needle technique. The results indicated that the adsorption took place in two stages, (1) unrolling of the peptide chain and (2) coagulation.

Blakey and Lawrence[13] examined the surface viscosities of soaps and demonstrated the influence of surface viscosity on emulsion stability.

More recently Davies *et al* have introduced two new (viscous-traction) surface viscometers. One[14] is suitable for the Air/Water interface and the other[15] for the Oil/Water interface. The method involves measurement of the speed of rotation of talc particles placed in a narrow circular channel placed at the interface. Any viscosity developing at the surface retards the motion of the talc particles. Davies and Mayers[15] showed that the mixed film of adsorbed sodium lauryl sulphate and cetyl alcohol, which is well known as an efficient oil in water emulsifying system, becomes extremely viscous in the concentration regions where its emulsifying power is evident.

All the different rheological types known in three-dimensional systems can be shown in two dimensions.

Surface Rigidities

When the surface film condenses, it becomes solid and it is impossible to measure surface viscosities. Monquin and Rideal[16] and more recently Cumper and Alexander[17] measured the rigidity of a film by rotating a disc just beneath the interface. The displacement of a talc particle was then measured for a given speed of rotation and distance of the disc beneath the surface. It is thus possible to obtain some idea of the rigidity and elasticity of the film. The method can be used for both Oil/Water and Air/Water interfaces.

Contact Angles and Spreading

Useful information can often be obtained by measuring the rate of spreading, area of spreading and the contact angle of a liquid on a solid or a liquid on a liquid. Obviously, where good contact is wanted, the angle should be low and spreading easy.

It should be pointed out that contact angles are not the easiest of things to measure.

The Oil/Water Interface

Many of the methods described above for the Air/Water interface may be adapted to the Oil/Water interface. The Langmuir trough is difficult to use for this interface but the "hanging plate" or "pull on the ring" may be used. The properties of insoluble protein films have been studied in this way[18].

Davies[19] has measured interfacial potentials using a vibrating disc. This method is easier to use at the Oil/Water interface than the one involving a radio-active electrode. It has been used to study protein/detergent interactions.

Zeta Potential

When one phase is dispersed in another, electrical charge separation occurs either by adsorption of ions from one of the phases, or by an electrical dipole at the interface. These electrical charges play an important role in determining emulsion stability, especially of the water in oil type. The presence of such electrical charges may promote or hinder penetration of "active" ingredients through the skin.

The zeta potential at an interface may be determined by measuring the speed with which the dispersed phase migrates under an electrical potential. The particles are observed with an ultra-microscope. Thus, oil, water, skin or hair may be dispersed in suitable media and this migration determined using a micro-electrophoresis cell of the type described by Bradbury and Jordan[20]. The zeta potential and charge density on the particle may thus be calculated from the speed of migration and the applied potential.

The technique has been successfully used to gain insight into the mechanism of the salt precipitation of various colloids and dispersions. It has been shown that coagulation is due to a reduction in the thickness of the double layer and zeta potential.

Conclusion

The above descriptions of surface chemical techniques are by no means exhaustive. They have been collected together to direct thinking along such lines as might be found useful in determining some of the basic surface chemical and physical problems of cosmetic formulation and application. It must, however, always be borne in mind when interpreting this type of experiment, that quite often over-simplified model systems have to be used in order to make the measurements. Thus measurements on the Oil/Water interface described above neglect the interface/interface interaction which is always present in a concentrated emulsion and very often determines its physical properties.

Acknowledgment

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Introduction by the Lecturer

The classical division of matter into three forms or phases, namely gas or vapour, liquid and solid, is satisfactory as long as one is concerned only with a continuous phase or the gross properties of a number of phases in contact with one another. If, however, the region of transition from one phase to another is examined closely, one finds what are in effect new forms of matter with special properties existing at these boundaries. These regions of transition are termed surfaces or interfaces. The simplest interfaces are liquid/liquid and gas/liquid. This paper is primarily concerned with review of the methods of examining these latter two interfaces, although there are many features in common amongst the various types of interface.

Consider a pure water phase in which the molecules are all one kind. Each molecule will exert, as a result of its internal energy content, the same average force on its nearest neighbour. If an air/water interface is now formed, as for example by blowing a bubble or forming an Aerosol, those molecules at the surface will no longer be surrounded by molecules all exerting the same force. There will, in fact, be a resultant pull on the molecules at the surface directed towards the bulk tending to cause the surface to contract and take up a position of least energy content in which the area/volume ratio is at a minimum. Thus, a small drop of liquid or gas bubble will try to assume a spherical shape. The surface force involved here is known as the "Surface Tension".

In the case of solutions of one or more substances, whose molecules differ in the magnitude of the forces exerted on each other, the unbalanced forces at the surface may be diminished in another way. The molecules with the greatest affinity for one another will pass into the bulk, while those with the

smaller affinities will pass into the surface. This concentration of constituents is called "adsorption". Both positive and negative adsorption are possible, although the cosmetic chemist is almost always concerned with the positive adsorption of organic substances dissolved either in oil or in water, or in both.

Considering the various methods we have—

Static Methods at the air/water interface

1. The use of radio-isotopes.
2. Surface tension measurements.

Dynamic Methods

The formation of an adsorbed film at the usual concentrations of surface active material takes place very rapidly, often in less than a second. However, in the case of an aqueous formulation in pressurized or squeeze pack, the surface tension of the water is very high and therefore a great deal of energy is necessary to break the material into a satisfactorily fine spray. Surface active agents may be added but they must be of the type, and be present in sufficiently large amounts, to bring the surface tension down to a low value in a few milli-seconds. Where a high concentration of alcohol or mineral oil is used, the surface tension is naturally low and the problem is not so acute.

In order to investigate the surface tension of surfaces during the early moments of formation, special techniques have been used.

1. *Oscillating Jet*
2. *Surface Potention Measurements Along a Jet Surface*

Results are then interpolated on a previously determined calibration curve of surface potential against surface tension.

All dynamic methods of studying surface tension suffer from the fact that the true age of the surface is unknown because of the complex hydrodynamic conditions at the surface. The methods are therefore best used for making comparison between different surface active agents and the effect of concentration. The results should therefore always quote the method used.

Insoluble Films

Surface Pressure Measurements at the Gas/Liquid Interface

The Langmuir trough is used to measure the force/area of curves for insoluble mono-layers, although recently the hanging plate has been used in place of the barrier of the Langmuir trough which obviates the difficulty of leaks past the edges of the barrier. The hanging plate is probably satisfactory for all films except the most rigid.

Mechanical Properties of Insoluble and Adsorbed Films

Surface Viscosities

The mechanical properties of the surface film often parallel the stability of a foam or emulsion. If the film is too rigid, then the system will be unable to resist mechanical or thermal shock. If it is too fluid, rapid drainage of a foam or coalescence of the emulsion will take place. Davies has recently introduced two new surface viscometers which rely on the measurement of the speed of rotation of talc particles placed in a narrow circular channel placed at the interface, when the vessel containing the interface is rotated.

All the different rheological types known in three-dimensional systems can be shown in two dimensions.

The Oil/Water Interface

Many of the methods described for the air/water interface may be adapted to the oil/water interface.

Zeta Potential

When one phase is dispersed in another, electrical charge separation occurs either by adsorption of ions from one of the phases, ionic dissociation, or by an electrical dipole at the interface. This charge plays an important role in determining emulsion stability, especially of the oil-in-water type. The presence of such charges may promote or hinder penetration of active ingredients through the skin. The potential may be determined by measuring the speed with which the dispersed phase migrates under an electrical potential. Particles are observed with an ultra-microscope. The technique has been successfully used to gain insight into the mechanism of the salt precipitation of various colloids and dispersions. It has been shown that coagulation is due to the reduction in the thickness of the double layer and potential. You may well ask what use have these types of measurements for the cosmetic chemist ? Many emulsifying systems depend on structure of the primary emulsifying layer. It might be possible to learn something about the physio-chemical properties and structures of the diverse emulsifying agents by spreading them at the oil/water and air/water interface as has been done by Schulman and Cockbain. Similar remarks apply to the study of adsorbed films.

The above descriptions are by no means exhaustive. They have been collected together to direct thinking along such lines as might be found useful in determining some of the basic surface chemical and physical problems of cosmetic formulation and application.

Discussion

Dr. W. W. Myddleton : 1. Has anything been revealed of the emulsifying

properties of the natural and semi-synthetic gums apart from their effect in increasing viscosity of the aqueous phase ?

2. Dr. Posner regards the zeta potential as playing an important role in determining emulsion stability, *especially of the water-in-oil type.* To what type of emulsifier does this apply ? Is it only to a limited number like sodium dioctyl succinate ?
3. Do the methods reveal how alcohol in the aqueous phase affects emulsification and emulsion stability ?
4. Has anything been revealed of the behaviour at interfaces of "block polymers" in which a central hydrophobic zone of propylene glycol condensate is flanked by two hydrophilic zones built up by ethylene oxide condensation ?
5. What is the effect of adding *iso*propyl myristate to a refined white oil before emulsification ?

THE LECTURER: 1. I know of no work specifically directed at determining the emulsifying properties of the natural and synthetic gums using the techniques described in my paper. I have no doubt at all that such techniques can, and probably have, been used to reveal the surface chemistry of these materials. Interactions between emulsifying agents and gums might be studied by spreading a monolayer of the emulsifying agent at an interface and injecting the gum underneath. Alternatively, the emulsifying agent could be spread on a solution of the gum. Such changes in surface pressure and surface viscosity that may occur can quite easily be measured.

2. In so far as the zeta potential plays a part in stabilising an emulsion, there is an uncorrected error in my paper ; it mentions its effect in stabilising water-in-oil rather than oil-in-water. Nevertheless, I feel that a zeta potential will also play a part in the water-in-oil emulsion but to a lesser extent. A double-layer will undoubtedly exist inside the water droplet and there will be an image of the double-layer in the oil phase of a water-in-oil emulsion.

   I think, in the case of the oil-in-water emulsion, zeta potentials will play a part in stabilising almost all emulsions, in particular, of course, where there is ionisation of the primary layer. In the case where the emulsions are non-ionic, dipoles are likely to generate small stabilising zeta potentials, but these will not be of the same order of magnitude as those coming from ionic dissociation or adsorption.

3. I am certain that the methods described will reveal how alcohol in the aqueous phase affects emulsification and emulsion stability. Alcohol will

obviously affect the solubility of the emulsifying system and this in turn will be reflected in the surface activity of the emulsifying agent. There will also be a change in the mechanical properties of both adsorbed and insoluble films.

In the case of synthetic detergents, however, small amounts of long-chained alcohol form surface complexes which have considerable surface activity and viscosity. These complexes influence the behaviour of shampoos and other commercial detergents in which there is always some free fatty alcohol present. Thus, pure detergents have a poorer deterging power than the commercial ones containing free fatty alcohol.

4. A considerable amount of work has been done by Alexander and co-workers and many others on the behaviour of insoluble polymers at both the Air/Water and Oil/Water interfaces. I know of no specifically published work on the "block polymers" mentioned. Again, I know of no reason why those interested in examining surface chemical properties of these "block polymers" should not set up the type of experiments described.

5. If there is an effect due to *iso*propyl myristate, you will pick this up as an interfacial complex formation.

MR. G. E. NEU: The surface balance using a Wilhelmy plate is accurate for gaseous films as well as for more rigid films. I have worked with Professor Alexander using this type of balance, and spreading extremely rigid monolayers of polymer succrates and polyacrylates nitriles which were, up to that time, too rigid to spread. The surface tension results obtained are similar to the surface potential results and the theoretical results expected. Professor Alexander has used almost exclusively for the last 6-7 years Perspex troughs and Perspex barriers which eliminate waxing the sides of the bath and the barriers. The float used is a piece of mica sanded in a horizontal direction to eliminate any creep of the film.

THE LECTURER: I use a Teflon trough which has similar properties to those mentioned.

MR. H. CARTER: Is there an analogy between the Vant Hoff and Langmuir isotherms and the equation you gave for charged liquid surface phenomenon ?

THE LECTURER: The equations I have given are those of "state" and do not relate to isotherms. The latter determine the extent of adsorption, from one phase to another while the former defines the relationship between area and pressure in a single (surface) phase.

MR. J. B. WILKINSON: The normal touchstone of a theory is its ability to

make varifiable or refutable predictions. The techniques discussed assist in predicting short-term emulsion stability, but the practical cosmetic chemist is vitally interested in long-term stability, not minutes or hours, but weeks or months. At present he cannot find out empirically; if prophetic judgment can be made this would be most valuable. It is appreciated, of course, that such long-term stability may be affected in complex systems by migration of trace impurities to the interface, but could these techniques be of assistance?

THE LECTURER: The techniques I have described could give you the information you require provided the change taking place occurs at the interface. It is my experience that there is no substitute for time and one must therefore be prepared to set up the experiment to last for the required period. It may be that surface chemical techniques will detect changes much earlier than those detected by storage tests on the product. For instance, migration of divalent ions to a surface stabilised by a sodium soap will be manifest as a change in rigidity of the interface.

TECHNIQUES OF FOAM MEASUREMENT

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The physical properties of shampoo and toothpaste foams are characterised using seven different measurements. These measurements are easy to perform and yield reproducible results. A subjective assessment of the foam is correlated with the measurements described.

INTRODUCTION

FOAMING IS of major importance in shampoos and toothpastes, and the nature of the foam may be critical in determining the acceptability of these products. With toothpaste, the volume must be sufficient but controlled, and one of the chief qualities required is easy rinsing away; the foam is also important to the flavour which it disperses throughout the mouth to allow maximum contact with the taste buds.

The actual requirements of these two products are very different. A shampoo is normally expected to give a thick, creamy, voluminous foam, which is associated by the user with cleansing power and emolliency. Even if a shampoo has excellent cleansing properties and leaves the hair in very good condition afterwards but only provides a small amount of a thick,

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