Some Applications of Surface Chemistry to Problems in Colloid Science.

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SURFACE chemistry, or surface physical chemistry as it might more appropriately be termed, is concerned with the study of interfaces, generally those of macroscopic area. The field is now an extensive one and for that reason this lecture will be restricted to the three interfaces air–water, oil–water, and solid–liquid, which are of particular relevance to typical colloidal systems such as foams, emulsions, proteins, pastes, bacteria, etc. One important aspect, namely, reactions at interfaces, was surveyed by Professor Rideal in his recent Liversidge Lecture.[1]

In order to appreciate the results an outline of the principal experimental techniques, particularly those of more recent development, is desirable.

The study of insoluble monolayers at the air–water surface, based upon the classical work of Langmuir and of Adam, and later extended by Rideal, Harkins, and many others, undoubtedly forms the basis of our present knowledge of surface phenomena. The principal measured quantities of the monolayer are its surface pressure, Π ($\Pi = \gamma_{water} - \gamma_{film}$), its surface potential, ΔV ($\Delta V = V_{water} - V_{film}$), and its mechanical properties (viscosity and elasticity), all measured as a function of the molecular area (A).

Several techniques for the automatic recording of Π–A and ΔV–A curves have been devised;[2] these are particularly useful for examining phase changes and stability ranges in condensed monolayers. A simple film balance recently described[3] makes the accurate study of Π–A curves readily accessible.

Condensed monolayers on water can frequently be transferred to a solid surface by a simple dipping process, and layers many molecules thick have thus been built up. These "multilayers," or "built-up films" as they are termed, find a number of applications, particularly where very thin layers of known thickness are required.[4]

Oil–water interfaces are clearly more directly related to emulsion and biological systems than are air–water interfaces, but the study of insoluble monolayers there has proved much less amenable. However, accurate Π–A curves can now be measured by means of a technique based upon the ring method for surface tension.[5] Some studies of "interfacial potentials" (ΔV) and of the mechanical properties of such films have also been carried out.[6]

With adsorbed films at mobile interfaces recent interest has been largely concerned with the study of rates of adsorption and desorption. Slow changes can readily be followed by any of the standard methods for boundary tension; for rapid adsorptions the oscillating-jet method recently developed and extended to oil–water interfaces,[7] and a method utilising surface potentials,[8] are available.

As regards adsorbed films at the solid–liquid interface, mention may be made of a recent simple method for surface-area determination of fine powders. It merely involves using long-chain polar compounds, in organic media, as adsorbates, and determining the concentration before and after adsorption by spreading as a monolayer on a film balance.[9] The adsorption isotherm and the saturation uptake, giving the specific surface, are obtained in the usual manner, a value of 20 A.^{2} per long-chain molecule being assumed at the saturation point.

Having outlined the basic techniques, it is now possible to survey those results which bear directly upon a number of problems in colloidal systems.

The first problem considered will be the proteins, or rather certain aspects connected with them. In addition to their obvious biological importance proteins are common stabilising agents for foams and emulsions, an aspect discussed in more detail below.

Despite their solubility in water, proteins can usually be spread quantitatively as homogeneous monolayers at both air–water and oil–water interfaces. Such monolayers have been extensively studied in the hope of throwing some light upon the structure of the native protein molecule, as well as upon the formation and structure of protein membranes. In addition, attempts have been made recently to determine the molecular weight of proteins from Π–A curves of monolayers in the gaseous state.[10] The technique here is not simple, since measurements have to be made at very large areas and therefore at minute surface pressures. As an illustration of the method, egg albumin has given values of 40,000 [10] and 44,000,[11] close to the

accepted value for this protein in solution. In the case of hæmoglobin the " surface molecular weight " of 12,000 at the air–water interface indicates splitting into some five or six fragments (cf. results for hæmoglobin at an oil–water interface, mentioned below).

At the air–water interface the monolayers from widely different proteins are remarkably similar as regards their Π–A curves, although their viscosity and elasticity characteristics may vary considerably. Spreading appears to be accompanied by the complete loss of solubility and, in general, of enzymatic and specific immunological properties, indicating very radical and irreversible changes in structure. Such changes are believed to arise from the polypeptide chains in the protein molecule, originally coiled in some way so as to give a corpuscular form, being unrolled and reorientated on the surface by the action of the very asymmetric field at the interface. Other notable features are the ready formation of two-dimensional elastic gels showing marked hysteresis, and the ease of compression to areas (often less than 10 A.^{2} per residue) which appear too small for a close-packed monolayer. Oil–water interfaces of high interfacial tension show very similar phenomena, but as the tension is reduced the protein molecules appear to suffer less drastic changes (see also below).

Early speculations concerning the molecular structure of protein monolayers were not very conclusive, largely because of insufficient knowledge of the behaviour of linear polymers at interfaces, and of the bonding between the polar groups present, particularly between $>C{=}O$ and $H{-}N<$ in the main chain, and groups such as $^{-}COO^{-}$ and $\overset{+}{N}H_3$ in the side chains. A recent study [12] of monolayers of synthetic linear polymers of known structure (*e.g.*, poly-acrylates, poly-methacrylates, nylons, etc.) has enabled the contribution from the first of the above factors to be assessed much more precisely. Collapse of such films, and probably therefore of proteins too, leads to the formation of a thickened layer or overfilm rather than to a looping of the chains beneath the surface as previously believed by some workers. It may be mentioned that films built up by the multilayer technique from monolayers of amorphous polymers have been shown by electron diffraction to possess a much higher degree of order than those formed by the more usual methods.[13]

The interaction between the polar groups in proteins, in particular the extent of hydrogen bonding between the $>C{=}O$ and $H{-}N<$ groups of adjacent chains, has been investigated by comparing monolayers of simple paraffin-chain compounds containing the $^{-}CO{\cdot}NH^{-}$ group (*e.g.*, acetamides, ureas) with the analogous esters and ketones, where intermolecular hydrogen bonding is impossible.[14] The replacement of $^{-}O^{-}$ or $^{-}CH_2^{-}$ by $^{-}NH^{-}$ brings about striking changes in monolayer properties, and the conclusion is reached that intermolecular hydrogen bonding is certainly of major importance in protein monolayers. This approach enables reagents known to bring about changes in native proteins (*e.g.*, urea) to be assessed as regards their action upon the keto-imino-hydrogen bonds.

Turning now to two closely related classical colloidal systems, namely, foams and emulsions, the principal problems arising are as follows : the adsorption of the stabilising agent during the dispersion process, the structure of the adsorbed film and its importance in relation to the gross stability, and finally the desorption of stabilising agent as re-aggregation occurs. Surface chemistry has been able to supply considerable information about all of these problems, although it must be confessed that the picture is by no means complete.

The rate of adsorption at an air–water interface, which is usually followed by surface-tension measurements, is found to occur much more slowly than predicted by classical diffusion theory.[15] In the case of soaps and dyes, for example, the ratio of the calculated to the observed rate may be 10^6 or more. The hindrance to diffusion has usually been ascribed to an electrostatic potential barrier at the surface, arising from the presence of the adsorbed layer of long-chain ions, but the fact that similar anomalies arise with un-ionised compounds (*e.g.*, β-phenylpropionic acid at pH 2) shows that this factor is certainly not the major one. The rate of attainment of equilibrium is accelerated by the presence of other surface-active substances, by insoluble monolayers, and by replacing the air by an oil phase.[8] Such experiments suggest that the main factor in these slow diffusions arises from the steric hindrance which a long hydrocarbon chain encounters when endeavouring to penetrate a comparatively close-packed monolayer. Anomalously slow adsorption of long-chain polar compounds can also occur from an oil phase to an aqueous interface, a phenomenon closely related to their well-known tendency to aggregate in organic media.[16]

Desorption, even with molecules of not particularly complex structure (*e.g.*, β-phenylpropionic acid), appears to be an equally hindered process, although little has been done on this aspect, particularly at oil–water interfaces. Compression of a film adsorbed at an air–

water interface may even lead to the adsorbate separating out on the surface as a crystalline or liquid aggregate.[17]

The structure of the stabilising film in foams and emulsions, in particular whether the thickness is uni- or multi-molecular, can frequently be inferred indirectly from surface studies. In the case of water-soluble compounds (*e.g.*, soaps, and the lower fatty acids or alcohols) an equation of state can be deduced from the study of homologous longer-chain compounds which form insoluble monolayers, and this enables the adsorption, if confined to a monolayer, to be calculated at both oil–water and air–water interfaces.[17] The values thus calculated for the two most accurately studied compounds are seen from the data below to agree closely with the experimental ones obtained by McBain and his co-workers using the microtome method.

Solute.	Adsorption. Calc.	Exptl.
β-Phenylpropionic acid	$8{\cdot}3 \times 10^{-8}$ g./cm.^{2}	$7{\cdot}7 \times 10^{-8}$ g./cm.^{2}
Laurylsulphonic acid	$5{\cdot}7 \times 10^{-10}$ g.-mol./cm.^{2}	$5{\cdot}2$—$5{\cdot}7 \times 10^{-10}$ g.-mol./cm.^{2}

The conclusion is therefore drawn that in foams, and by analogy also in emulsions (oil-in-water type), stabilised by water-soluble soaps, the interfacial films are no more than unimolecular in thickness, and are in a highly compressed gaseous (and hence fluid) state, with molecular areas of *ca.* 30 A.^{2} for simple straight paraffin-chain derivatives. Stabilisation arises chiefly from the marked reduction in the surface energy of the system, although other factors, particularly the surface viscosity of the adsorbed film, also play a part. The close connection between the lowering of interfacial tension and emulsion stability is shown particularly by systems stabilised by "interfacial complexes" formed between a water-soluble soap and organic compounds containing hydroxyl or amino-groups (*e.g.*, cholesterol, long-chain amines) dissolved in the oil phase.[18] The study of oil–water insoluble monolayers shows that in the case of stable oil-in-water emulsions the oil phase will be effectively displaced from the interface by the adsorbed monolayer of stabiliser.[5]

With the heavy-metal or oil-soluble soaps (*e.g.*, magnesium oleate) which stabilise the water-in-oil type of emulsion, the monolayers in equilibrium with the solid soap phase are also in a fluid, gaseous state, but the equilibrium spreading pressures are very much less than in the case of water-soluble soaps, which effectively rules out any stabilisation by a monolayer. The spontaneous formation of visible rigid films by reaction between heavy-metal cations and fatty acids at an oil–water interface indicates stabilisation by solid particles, in agreement with the observation that stable water-in-oil emulsions invariably contain solid soap.[19]

Protein solutions in contact with air–water and oil–water interfaces readily give rise to tough visible "skins", a phenomenon first recorded by Ascherson over a century ago, and still very imperfectly understood. In the case of an air–water interface this "surface denaturation" continues until all the protein present has been removed as a coagulum practically devoid of surface activity. At oil–water interfaces, the rate and the extent of these surface changes diminish with decreasing interfacial tension.[20] For example, if hæmoglobin is desorbed (by changing the pH) from the surface of a fine emulsion stabilised by sodium cetyl sulphate its molecular weight is unaffected but its ultracentrifuge disymmetry coefficient has increased from 1·16 to 1·33, indicating some, but not complete, unfolding of the molecule.[21]

The behaviour of monolayers of proteins at air–water and oil–water interfaces suggests very strongly that proteins stabilise foams and emulsions by the formation of multimolecular films or skins rather than by a monolayer, these conferring mechanical protection.

The question of elasticity in adsorbed films is important in relation to the question of thermodynamic stability of foams and emulsions. Monolayers only show elasticity when in the condensed state, and from the study of equilibrium spreading pressures of crystals it would appear that all *condensed* monolayers are unstable with respect to their bulk phase. Accordingly, if an *adsorbed* film exhibits elasticity (as with protein or saponin solutions, and with heavy-metal soaps formed by metathesis at an interface), it would seem probable that its structures is multimolecular rather than unimolecular, and that the system is not in thermodynamic equilibrium.

Mention may be made in passing of Hardy's technique for studying foam stability by measuring the life-time of an air bubble liberated beneath an insoluble monolayer. Appreciable stabilisation is only obtained with coherent monolayers (expanded or condensed), and the stability decreases in the highly condensed state where the monolayers become unstable.[22]

Passing now to a consideration of pastes (concentrated dispersions of finely divided solids in a liquid continuum), some recent work [9] has shed much light upon the influence of surface-

active substances upon their macroscopic properties, such as flow behaviour and sedimentation volume. The adsorption upon polar powders such as sodium nitrate, using paraffin-chain compounds with different polar groups, in benzene or organic solution, was found to be in the following order $\cdot NO_2 > \cdot CO_2H > \cdot OH > \overset{|}{\underset{|}{C}}{=}O$. Parallel measurements of the coefficient of friction between large crystals showed that the friction was lowered in the same order. With increasing adsorption the ease of flow increases and the sedimentation volume decreases. Adsorption in these systems takes place with the polar groups of the adsorbate molecules oriented towards the polar surface of the crystal, and the hydrocarbon chains extending into the organic liquid. This outer surface of hydrocarbon reduces the interaction between the polar crystals and leads to the observed changes in macroscopic properties.

Finally, brief reference may be made to the application of surface studies to problems of a biological nature. Two examples only will be considered here, although others have been studied in this way (*e.g.*, the mechanism of fat absorption).[23]

Hexylresorcinol is a well-known anthelmintic for *Ascaris* and other intestinal worms. *In vitro* tests showed its activity to be considerably affected by the presence of bile salts or other soap-like substances, low concentrations generally producing some activation, but very high ones complete inhibition. Measurement of the surface activities of the various mixtures showed that the inhibition arises from the colloidal soap micelles, which form at the higher soap concentrations, competing with the biological surface for the fixed amount of drug.[24] The activation produced by low soap concentrations is related to the increased surface activity of the mixture, leading to an increased rate of penetration.

Similar conclusions have been found to apply to the bactericidal action of phenols in the presence of soaps. Rideal–Walker tests, and measurement of the rates of killing, show that the bactericidal activity increases up to the point where soap micelles start to form, and thereafter decreases.[25]

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