

Recent Advances in the Study of Monolayers

THE most significant feature of the discussion on "Surface Phenomena—Films" held at the Royal Society on March 12 was the evidence it gave of the very considerable advance which has been made during the last decade in the direction of a synthesis of the biological and the more exact sciences. The opening address by Prof. E. K. Rideal was an illuminating summary of the present state of knowledge of molecular phenomena at interfaces. He emphasised the two fundamental aspects of the wide range of physical, chemical and biological work discussed, namely, the reality and far-reaching importance of molecular orientation at interfaces, and the great wealth of information which can be gained from studying the properties of complex organic molecules, particularly those of biological importance, when spread in monolayers at the surface of aqueous substrates.

In 1912, Sir William Hardy introduced the conception of molecular orientation in the boundary state, and his picture was strengthened and extended in 1916 by Langmuir's association of the asymmetrical parts of the molecular fields with the polar groups. From the evidence gained by the surface pressure method with the Langmuir-Adam trough, it is universally accepted that a film of an insoluble organic compound, such as stearic acid, on a water surface, consists of a two-dimensional monomolecular array or monolayer, of molecules oriented with their polar hydrophilic groups immersed in the water and the nonpolar hydrophobic portions (in this case the hydrocarbon chains) extended above the surface. The classical work of N. K. Adam has elucidated the essential physical factors responsible for film formation and the general properties of the various states of matter in monolayers—gaseous, vaporous, liquid-expanded, liquid-condensed and solid. The liquid-expanded state is of interest because it has no three-dimensional analogue. Its nature has been explained by Langmuir by his bold assumption of a duplex film, composed of a sheet of oil above and a layer of polar groups below. There can be little doubt that this conception is essentially true; but there is evidence that it may require extension by interposition between the two layers of a non-homogeneous oil phase containing entangled water molecules, thus imparting a triplex structure to the expanded monolayer. In 1931, Rideal and Schulman supplemented the force-area method of investigating monolayers by measurement of the change in phase boundary potential produced by the film molecules. This method gives detailed information about the vertical component of the resultant molecular electric dipole moment, and in addition, very considerable insight into the molecular orientation.

The value of the surface pressure and phase boundary potential methods, in conjunction with the X-ray crystallographic data, in elucidating the structure of large organic molecules of biological interest, is shown by the recent work of Dr. Adam and his collaborators on monolayers of sterols. Of singular interest is their finding that the surface potentials of cholestane-3-ol and its epimer are of opposite sign.

The general problem of chemical reactions in

monolayers is of great importance. A number of these reactions have now been studied, chiefly by Prof. Rideal and his collaborators, and include:

(1) Reactions between film molecules and ions or molecules in the substrate, for example, hydrolysis of esters by acids, lactones by alkalis, proteins by proteinases and polypeptidases, fats by lipases, lecithin by snake venom; oxidation of double bonds by permanganate ions.

(2) Oxidation of film molecules by atmospheric oxygen, for example, oxidation of double bonds, of $-SH$ groups.

(3) Reactions between the film molecules themselves. The only known example is the polymerisation of the unstable peroxide produced by autoxidation of the maleic anhydride compound of β -elæosterin. This reaction has been shown to have a typical chain mechanism.

(4) Photochemical decomposition of film molecules, for example, photochemical hydrolysis of the CO-NH linkage in proteins and in stearic anilide; photochemical splitting of carbon dioxide from organic acids.

In most of the cases studied, the apparent energy of activation is the same for the reaction at the interface as in bulk, but the molecular orientation present often controls the rate of reaction by controlling the steric factor. In the oxidation, by permanganate ions in the substrate, of the double bonds of molecules of oleic acid or petroselenic acid in the monolayer a rapid and striking decrease of reaction velocity is found when the films are compressed to the stage at which it is known that the double bonds are removed from the water surface. A similar reduction of reaction velocity is found in the hydrolysis of lecithin to lysolecithin by snake venom, when the double bond of the oleyl group is raised from the water surface.

In the drying of monolayers of the maleic anhydride compound of β -elæosterin, it was shown by G. Gee that in the polymerisation stage, which is a chain reaction, steric hindrance is responsible for stopping the growth of the polymer.

Photochemical reactions in monolayers were described by J. S. Mitchell. Photochemical hydrolysis of the CO-NH linkage in stearic anilide was found to occur in light of wave-lengths 2350–2483 Å. with a quantum efficiency of unity; the reaction velocity varies rapidly with molecular orientation in agreement with the theory given. Experimental evidence was brought forward suggesting that one of the most important actions of ultra-violet light of wave-length 2500 Å. on protein monolayers is to produce photochemical hydrolysis of those CO-NH linkages adjacent to the aromatic side chains, which are the only regions of the molecule where light absorption can occur.

Optical evidence of molecular orientation was found by Tronstad and Feachem in 1934 by investigating monolayers of myristic acid by measurement of the coefficient of ellipticity of plane polarised light reflected from the surface covered with film. The scattering index in the plane of the film is of the same order as in bulk, but is very much smaller in the direction normal to the surface.

An interesting related observation was described by A. H. Hughes. He has found that monolayers of the green dye, magnesium naphthalocyanine, were visible, and in conjunction with C. B. Allsopp, he showed that the molecular extinction coefficient in the film is of the same order as that in solution.

The recent work on protein monolayers is of great biological interest. F. A. Askew described the preliminary results obtained by surface pressure measurements on protein films at the liquid-liquid interface between water and bromobenzene. Evidence on two very important issues was brought forward by Prof. E. Gorter. By an ingenious experiment with pepsin and trypsin monolayers, he has shown that when these are spread at an air-water interface, only a negligible amount is lost into the substrate or by denaturation. He also found that myosin prepared below 0° C. does not spread, but can be made to do so by adding trypsin to the substrate. G. Philippi discussed some general theoretical considerations on the homalic state.

One of the most interesting papers read was that by J. H. Schulman on mixed unimolecular films. He described in some detail the phenomenon of 'film penetration'. If a very dilute solution of, for example, a long-chain acid is introduced into the substrate beneath a monolayer of an alcohol, complex formation occurs between the head groups, and the Van der Waals adhesion of the chains leads to formation

of a stable mixed film, composed of equal numbers of acid and alcohol molecules whatever the initial proportions. This complex formation is accompanied by a marked increase of surface pressure and a simple proportional change of phase boundary potential. When adsorption on to a protein film occurs without penetration, as in the case of tannic acid or silicic acid, there is no change of surface pressure but only a change of surface potential, although the film has become much more stable and can now resist displacement by fatty acids. The relationship of these phenomena to immunological specificity and to hæmolysis by saponin, fatty acids and complement was discussed.

J. F. Danielli, working with invertebrate ova, discussed the surface conditions of animal cells. O. Gatti described an investigation of the origin of electrical potentials in living tissues. By correlation of the potential difference across frog's skin with its electrical resistance and oxygen uptake, in the presence of various inhibitors, he brought forward strong evidence suggesting that bioelectric potentials have their origin in oriented monolayers and that the effective interfaces are occupied almost entirely by lipins and sterols, proteins being of much less importance.

The meeting was concluded by a beautiful demonstration of intertraction at liquid-liquid interfaces by Sir Almroth Wright.

Ionospheric Studies in India*

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SINCE the middle of the last decade, the study of the conducting upper atmosphere—the ionosphere—has been proceeding vigorously in various parts of the world. The countries where the study originated—England and the United States—are situated at high latitudes, far from the equator. In view of the fact that ionospheric conditions in a subtropical region of low latitude, like that of India, were likely to differ considerably from those in a region of high latitude—particularly with regard to the effect of meteorological disturbances of terrestrial or solar origin, such as thunderstorms, magnetic storms, etc.—the study of the ionosphere was taken up at Calcutta¹ (22° 34' N., 88° 22' E.) in 1930 and has been continued uninterruptedly since then. Recently, measurements have been made at Allahabad² (25° 26' N., 81° 50' E.) and Bangalore³ (12° 58' N., 77° 35' E.) on ionospheric heights—at the former on ionisation density as well—and at Dacca⁴ (23° 43' N., 90° 24' E.), on fading.

Measurement of the equivalent height of the lower *E* region, by the 'echo' method, carried out systematically at Calcutta according to the programme of the International Polar Year (1932-33), on a wave-length of 75 m. at normal incidence, gave the average value⁵ of the height as 90 km. This is lower by about ten per cent than the average value as obtained by the same method in England. Prior to this, measurement carried out with medium wave-length (370.4 m.) for oblique incidence, by the

'angle of incidence' method, had yielded the average value of the *E* layer equivalent height after sunset¹ as 80 km.

The Polar Year height measurements⁵, recording the appearance or disappearance of the echoes in different months of the year and at various hours of the day, indicated the nature of the seasonal and diurnal variation of ionisation at such low latitude as that of Calcutta. It was found that at midday in August and September the *E* ionisation density was greater than 2×10^5 equivalent electrons per c.c., that during October-November and April-May it was near this value, and that in the months December to March it was less. Direct measurement of ionisation density by observing the frequency of the wave which just pierces a particular region, after the method developed by Appleton, showed that during the summer solstice (1933) the *E* ionisation density at midday was more than 0.5 million (equivalent electrons) as compared with the corresponding average value in England of 0.18 million. At midnight, the *E* ionisation density was less than 0.2 million for the most part of the year, and the *F* density also less than 0.2 million in April, May and June. The maximum value of the *F* density was found by direct measurement to be more than 1.5 million, which is much greater than the value obtained at higher latitudes.

Records of diurnal variation of *E* ionisation density showed that the nature of the variation on a normal day, that is on a day not disturbed by thunderstorms or other causes, agrees with that

* Substance of a lecture delivered before the Maxwell Society at King's College, London, on January 30.