STUDIES ON MONOLAYERS

by

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A Thesis submitted to the University of Glasgow for the Degree of Doctor of Philosophy in the Faculty of Science.

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August, 1952.

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ACKNOWLEDGMENT.

The author wishes to express his gratitude to Professor P.D. Ritchie, Ph.D., F.R.I.C., for the great interest he has shown in this work, and to Dr. C.H.Giles, Ph.D., F.R.I.C., for his constant and invaluable guidance.

Thanks are also due to the Staff of the Technical Chemistry Department Workshop for the construction of the Langmuir Film Balance.

The author is greatly indebted to the Directors of Imperial Chemical Industries Limited, Dyestuffs Division, for their financial assistance, and also the gift of intermediates.

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SUMMARY.

As a preliminary to the ultimate photo-chemical study of monolayers, aromatic azo-compounds (with one hydroxy-group either o- or p- to the azo-group in most cases) quinones, acid amides and a hydro-quinone derivative have been examined for monomolecular film-forming properties on water by means of the Langmuir film balance. The largest group of compounds examined was that of the azo-compounds. These are found to form condensed films in all cases where a hydroxy-group is present and the alkyl chain has at least 16 C atoms; and also in many cases where the chain has only 12 C atoms.

In absence of a hydroxy-group, at least two azo-groups appear to be required to give the necessary water attraction for film formation. The molecules appear to be oriented in the film with the plane of the aromatic nuclei vertical but the longer axis of this plane is in many cases tilted from the perpendicular at an angle depending on the nature and relative position of the various substituent groups. The azo-group appears to be at or near the water surface in all cases.

The orientations of the other compounds were also studied and it was found the angles of orientation to the water surface seem to lie between 40° and 90°.

The tautomeric equilibrium of azo-compounds in monolayers has been studied by determining their apparent molecular areas and/

and compressibilities on dilute acid and alkali. In accordance with published data, the p-hydroxy compounds appear to exist almost completely in the azo-form. The o-compounds contain much of the hydrazone form but the results do not give decisive evidence of the presence or absence of the azo-tautomer in this series, except in one case where an o:o'-dihydroxyazo-compound appears to contain the azo-form. One purpose of the work being the study of the photochemical decompositions of azo-compounds, which is believed to result in the formation of phenols, selected azo-compounds were examined by the film balance technique using solutions of various phenolic substances as substrates in place of water. By this means, azo-, hydroxy-, and quinone groups in monolayers of aromatic compounds were found to form hydrogen bonds with the hydroxy-groups in phenols. The increased water attraction imparted thus, e.g., to the azo-group, may cause an expansion of the film by a change in the angle of tilt of the molecules therein. Dihydric phenols in the substrate appear to behave in two ways:

(a) If there are two suitably placed bonding groups in the monolayer molecule, a 1:1-complex may be formed, in which each group is bonded with one hydroxy-group in the solute molecule; two molecules probably stand parallel side by side and the area of the film increases slightly.

(b) If the solute hydroxy-groups are too far apart for (a) to occur they may form cross-links between monolayer molecules leading/

leading to a considerable increase in film area and compressibility.

These experiments were extended in order to study the combination between dyes and fibres, e.g., proteins, acetate rayon and cellulose, by the use of "model" compounds in the substrate. The hydrogen bond is found here to be of great importance, as has previously been suggested. In several cases the dependence of hydrogen bonding power on pH was demonstrated.

Preliminary fading experiments were performed on azo-dye monolayers and other substances. These showed that fading in monolayers is slow and that powerful light sources will have to be employed for significant results to be obtained.

A surface potential measuring apparatus was also constructed for future work on the irradiation of monolayers.

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INTRODUCTION

The work described in this thesis was undertaken with the ultimate view of contributing to an understanding of the mechanism of the fading of dyestuffs. No satisfactory solution to this problem has as yet been advanced. This is not surprising in view of the fact that as the fading of a dye depends on the substrate on which it is applied, the discovery of each new synthetic fibre gives rise to fresh problems. In addition, no satisfactory theory has as yet been produced to account completely for the connection between colour and constitution. To understand a fading mechanism fully, it will be necessary to define the degree of degradation at which a molecule of dye may be regarded as faded.

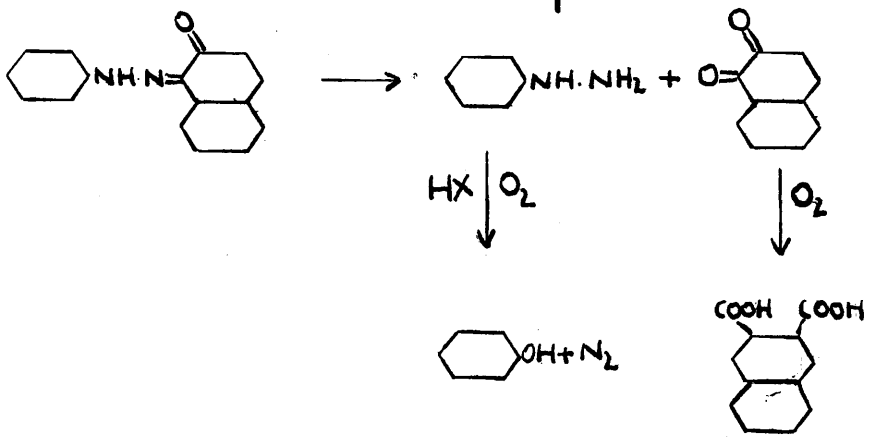
The fading of a dyestuff often takes the form of decomposition at the chromophoric group, this being generally the most reactive part of the molecule. It is believed that fading is normally initiated by oxidation. Desai and Giles (J. Soc. Dyers and Col., 65, 639, (1949)), suggested an oxidation mechanism for the fading of azo dyes and, more recently, Couper (Text. Res. J., 21, 720, (1951)), has shown that a typical anthraquinone dye is also oxidised when faded.

These workers have been able to investigate only the final completely faded oxidation products, as it is very difficult to arrest the fading process at any definite stage, and examine the intermediates. In addition, fading was produced by chemical means which may be quite different from fading initiated by ultra-violet light.

It/

It was thought that the Langmuir film balance technique could furnish a new approach to the problem. Films of suitable dyestuffs could be examined and the areas and other characteristics compared before and after irradiation, for various periods of time, with ultra-violet light. This would furnish a method for the continuous observation of the fading process. It would also be possible to ascertain the effects of substrates, chosen to simulate the various types of fibres, on the behaviour of the dye films. This, it was hoped, would throw additional light on the dye-fibre link.

Giles and Desai postulated the following oxidation mechanism for the dye aniline→β-naphthol.



This mechanism could be checked by the film balance technique if instead of the above, the dye (Fig. 1) were employed.

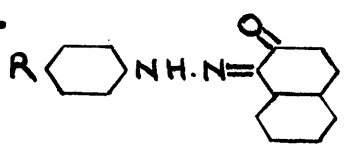


Fig. 1.

(Where R is a long linear aliphatic chain of 12 C atoms or more)

If/

If the postulated mechanism were correct, then on irradiation we should obtain a long chain phenol and an o-quinone, or ultimately a dibasic acid, the latter being soluble in the substrate. Hence, if the surface area of the original dyestuff should reduce to 24 sq. A. per molecule (Area occupied by long chain phenols; Adam, Proc. Roy. Soc., A, 103, 676 (1923)), it would be reasonable to conclude that the above reaction mechanism were correct.

It can be seen from the above that the degradation of a dyestuff would involve a change in the composition of the substrate. Anderson, Harbins and others, (J. Amer. Chem. Soc., 2195, (1937)), have shown that small concentrations of ions can have a marked effect on monolayer characteristics. The rate of the photochemical reaction is also profoundly influenced by changes in the substrate. (Mitchell et. al., Nature, 139, 625, (1937)).

The azo-group is the point in the molecule at which photochemical attack is believed to commence. Hence, it was important to determine whether this group would be in a position accessible to the radiation when the molecules were spread as monolayers.

The work of this thesis therefore falls into several sections:

(a) The orientation of the dyes at the water surface.
(b) The effect of changes in the substrate.
(c) Irradiation studies.

Unfortunately/

Unfortunately Sections (a) and (b) proved to be more complex than was initially envisaged, and hence it was only possible to perform some preliminary experiments in Section (c).

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INTRODUCTORY SECTION.

In this section it is proposed to review, in the light of present day knowledge, those subjects which are closely connected with the matter contained in this thesis, e.g., the structure of azo compounds, surface films and hydrogen bonding.

AZO DYES

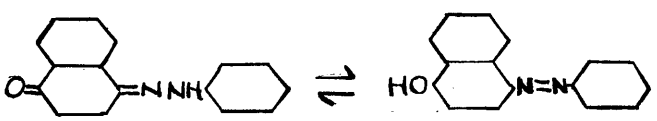
AZO DYES.

No azo-compounds occur in nature; they have been prepared mainly by coupling aromatic diazo compounds with phenols or amines in slightly alkaline or acid solution respectively. They form the largest of all known groups of organic compounds and more than one half of all dyestuffs used at the present time are azo compounds.

Because of their unique importance in the dyestuffs industry and the relative ease with which they can be prepared, it was decided to employ them mainly throughout these investigations.

Structure of Hydroxyazo-compounds.

The hydroxyazo-compounds exhibit keto-enol tautomerism, and controversy about their structure has raged since 1883, when T. Zincke obtained the same compound by the action of phenylhydrazine on α-naphthaquinone as was formed by coupling diazobenzene with α-naphthol, thus demonstrating the existence of the tautomerism.



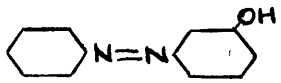
This is confirmed by the fact that when a p-quinone-monoxime is used, the above tautomerism is prevented and the product is a hydrazine derivative. (Borsche, Annalen, 357, 171, (1907)).

Smith and Mitchell (J.C.S., 93, 842, (1908)), by observing the number of mercuriacetate groups taken up by various

o-/

o- and p-hydroxyazo-compounds, decided that all these substances exist in the hydroxyazo-form.

Some authors claim that o-hydroxyazo-compounds exist only in the quinonoid form, while the p-derivatives are in the azo-form. The following m-hydroxyazo compound has been prepared. (Jacobson and Hoenigsberger, Ber., 36, 4102, (1903)).



This compound must be in the azo form as m-quinones cannot be formed. It resembles the p-isomer closely; both compounds are alkali soluble and act as true acids, forming an ammonium salt with ammonia in dry toluene. The o-isomer differs in all these particulars.

Experimental evidence also suggests, however, that the products obtained by coupling aromatic diazonium compounds with aliphatic ketones have the hydrazone configuration.

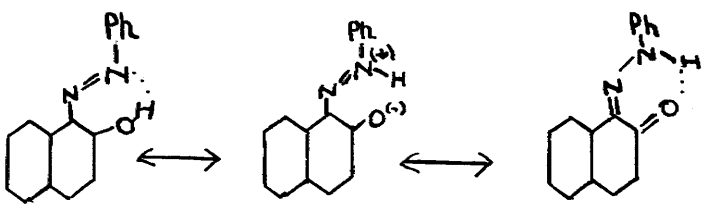
Baker states ('Tautomerism,' p.129) that it is a general rule that a hydroxyazo-compound will exist in the azo or hydrazone form, according to whether its oxygenated precursor is an enol or a ketone respectively.

Recently it has been shown, however, that a Diels-Alder condensation takes place between 2:4-dinitro-4'-hydroxyazobenzene and cyclo-pentadience (Lauer and Miller, J. Amer. Chem. Soc., 52, 520, (1935)). This is a reaction typical of a quinone and is not shown by a benzenoid compound. Hence, it is seen that there is/

is evidence that the p-compounds, in spite of their resemblance to the meta series, have the quinone structure. O-methyl and other O-derivatives of dinitro-4-hydroxyazobenzene did not give a Diels-Alder condensation, showing as would be expected, that these derivatives can exist only in the azo-form.

The mononitro and other substituted compounds of this series did not, however, condense in this manner. Fierz-David, Blangley and Kaul, (Helv. Chim. Acta., 29, 1765, (1946)), from a study of N-substituted derivatives decided that o-hydroxyazo compounds do not have a quinone structure. Mason (J. Soc. Dyers and Col., 48, 293, (1932)) showed by isolating a boroacetate derivative that p-nitrophenylazo-β-naphthol contains a chelate ring, but could not decide whether it was part of an azo- or hydrazone structure.

For the o-hydroxyazo series, resonance of both forms with a third zwitterion configuration may occur. Benzeneazo-β-naphthol would be represented thus:



(Kuhn, Naturwiss., 20, 618, (1932)).

Burawoy and Markowitsch-Burawoy (J.C.S., 36, (1936)), following studies of absorption spectra, state that the similarity between 2-benzeneazo-α-naphthol and its N-phenyl derivative, and the/

the difference between these two on the one hand and the corresponding O-methylether on the other, exclude the interpretation of the structure of the o-hydroxyazo-compounds as resonance hybrids.

The above evidence is based on chemical reactions and thus may be misleading because the equilibrium state may be disturbed by the progressof the reaction itself. Physical measurements might be expected to yield more decisive evidence. The conclusions drawn from physical properties, however, are equally at variance.

From light absorption spectra, Burawoy and Markowitsch (Annalen, 503, 180, (1933): 504, 71, (1933)), Kuhn and Bär (Annalen, 516, 143, (1935)), and Ramart-Lucas et.al. (Bull. Soc. Chim., 10, 127, 223, (1943); Ibid., 12, 814, (1945)), are said to show beyond doubt that the o- series are quinone-hydrazones and their O-acyl derivatives only in the azo-form. Molecular refractivities seem to support the view that they are azo-phenols (von Auwers and Walter, Annalen, 487, 79, (1931)). Phenylazoanthranol was similarly found to be quinonoid and its acetate and benzoate in the azo form (Shingu Scientific Papers of the Institute of Physical and Chemical Research, Tokyo, 35, (870), 78, (1938)). Kuhn and Bär also demonstrated that phenylazo-α-naphthol compounds exist as tautomeric mixtures, the preponderance of one form or the other depending on the solvent. Ramart-Lucas and Mastynoff, however, consider them to be azo compounds, like their O-ethers and esters.

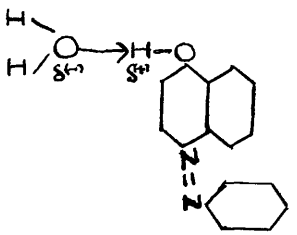
Yet molecular refractivity measurements show that the

o/

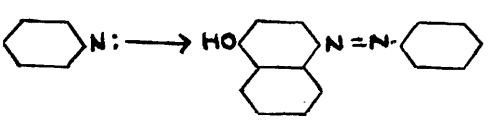
o-series exists in the azo-form. (Auwers and Walter, Annalen, 487, 79, (1931)). Again, dipole measurements carried out by Bergmann and Weizmann (Trans. Faraday. Soc., 32, 1318, (1936)), demonstrate that o-hydroxyazo-compounds are probably quinonoid and that the p-hydroxyazo-compounds have an azo structure with a tautomeric mixture existing in certain solvents.

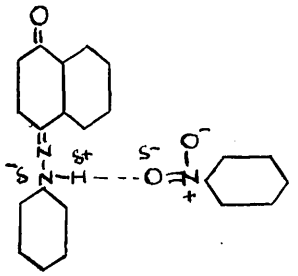
From the above evidence, it may be taken as well established that a tautomeric equilibrium can exist, though the evidence regarding the nature of the prevailing structure in normal hydroxyazo dyes is very conflicting. It is probable that the state of the system will depend on the surrounding medium. Hodgson and Marsden (J. Soc. Dyers and Col., 60, 121, (1944)) have discussed the mobility of the hydroxyazo-hydrazone system. They conclude that in aqueous solution the azo-form is usually predominant. In pyridine benzeneazo-α-naphthol is mainly in the azo-form, while in nitrobenzene it is mainly the hydrazone and in benzene there is a 50 per cent. equilibrium mixture. They have advanced the following explanation.

In aqueous media the azo tautomeride is usually predominant due to stabilisation by polarised water molecules, thus:



Similarly, pyridine will produce still greater stabilisation by attaching itself to the phenolic hydrogen atoms by means of its lone pair of electrons, thus:





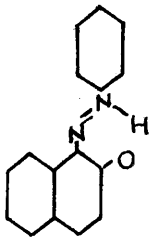
and so entirely preserving the azo-structure by means of hydrogen bonds. Dipolar nitrobenzene will more readily attach itself to the hydrogen atom of the hydrazone form with incipient salt formation by analogy with the salt formation of nitrobenzene with concentrated sulphuric acid. (Mason, J.C.S., 3200, (1931). The almost inert (feebly anionoid) benzene will tend to promote some salt formation, by anology with its double salt formation with picric acid, with the hydrazone tautomeride and thereby bring about an equalisation of the azo-hydrazone concentrations.

A further proposal other than simple tautomerism has been made with regard to the structure of the o-hydroxyazo compounds by Pfeiffer, (J.pr.Chem., 126, 108, (1930)), and Mason (J. Soc. Dyers and Col., 48, 293, (1932)). These authors pointed out that in the o-series there is the possibility of the formation of a chelate ring, such hydrogen bond formation being impossible in the p-series. The following indicate that this chelation actually occurs.

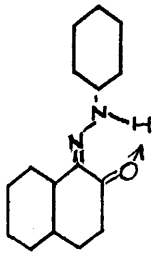
(a) o-compounds do not show the absorption in the infra-red characteristics of either the -OH or the -NH group. (Hendricks et al., J. Amer. Chem. Soc., 58, 1995, (1936)).

(b) The o-compounds form stable complexes with certain metals, these are typical chelate compounds being insoluble in water and soluble in benzene and chloroform. One atom of the metal unites with two or three molecules of the azo compound according to its valency/

valency, replacing the hydrogen atom shown in formula (a) and (b)



(a)



(b)

(c) Recent work (unpublished) on hydrogen bonding carried out in these laboratories has shown that phenol has a consistent tendency to form a bond with another phenolic hydroxy group and that two phenol molecules can bond with an azo-group. Presumably one attaches to each nitrogen atom, yet only one phenol molecule appears to unite with a molecule of benzeneazo-β-naphthol. Probably this unites with the one free nitrogen atom of the azo-group, the other nitrogen and the hydrogen atom of the hydroxy group being unable to unite with phenol by virtue of their intramolecular chelate bond.

If these compounds can form chelate metallic complexes, then judging from similar cases, it is very probable that (a) itself forms hydrogen bonds. The insolubility in alkali of the o-compounds cannot be quoted as evidence for chelation, however, since o-nitrophenol is acidic, although chelated. (Sidgwick's, "The Organic Chemistry of Nitrogen," p. 268, 443). It is almost certain that if the chelate ring actually exists in the o-compounds it can only do so by virtue of resonance between structures (a) and (b), the compounds having neither individual structure.

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It would appear to the present author that in light of present day knowledge of these compounds, the p-hydroxyazo series should, in most cases, be regarded as having the azo structure. For the o-series resonance between the two chelate forms (a) and (b) and Kuhn's Zwitterion structure, which differs only in the electron distribution and not in the position of the constituent atoms, would appear to be the most reasonable. This at any rate explains why the o-series cannot be satisfactorily represented by any one formula, thus accounting for the many confusing and contradictory results obtained.

HYDROGEN BOND.

THE HYDROGEN BOND.

A great deal of theoretical speculation put forward in this thesis, as well as the theories concerning the dye-to-fibre bond, depend to a large extent on the hydrogen bond, viz., the ability of hydrogen to exhibit bivalency. It is hence proposed to review its properties and the conditions of its formation.

The hydrogen bond is a weak bond depending somewhat on the natures of the atoms joined by it, say X and Y. The work needed to break it is about 5-8 kg.cals. The length of the bond also varies considerably, the distance between X and Y generally lying between 2.5-3Å. The hydrogen atom itself cannot be located in X—H-Y but there is some evidence to show that it is generally nearer to Y. The presence of the hydrogen atom and hence of the hydrogen bond can readily be inferred from the following type of consideration. Taking the ice crystal as an example, it has been shown by X-ray analysis that every oxygen atom has four equidistant neighbours at a distance of 2.76 Å. This distance is too great for a direct covalent O-O link and too small for two unbound oxygen atoms. This fact, and the necessity for placing the hydrogen somewhere in the crystal, leads to the conclusion that a hydrogen bond must exist between each pair of oxygen atoms.

Nature of the Bond.

Latimer and Rhodebush (1920) wrote the formula of dimerised hydrofluoric acid as being $\ddot{H}:\ddot{F}:H:\ddot{F}:$ This implies the formation of a dative covalency and an increase of the electrons round the hydrogen/

hydrogen atom from the normal two to four. This would, however, involve a breach of the Pauli principle and is hence not in accordance with modern valency theory. Two explanations have been advanced to overcome this difficulty.

The first is based on the concept of resonance. It is supposed that resonance occurs between the two structures X—H-Y and X-H—Y and that the true state of affairs is not represented by either structure but is a hybrid of the two.

The second suggestion invokes an electrostatic mechanism. If X is negatively charged (a full unit charge is not required - a partial charge suffices) and if a sufficiently strong dipole is associated with $H^{\delta+}$- $Y^{\delta-}$, then the arrangement (Fig. 2 pp15) may give a net attraction strong enough to account for the observed strength of the bond.

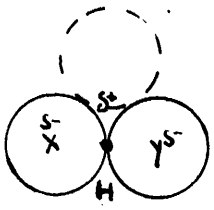


Fig. 2

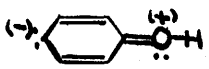
This also demonstrates how an anion is prevented from close approach to the proton and thus the co-ordination number of hydrogen is restricted to two. Both these factors may play their part in giving rise to the hydrogen bond but it is not known in what proportion.

Conditions Favouring Formation of Hydrogen Bond.

From the first suggested mechanism of hydrogen bond formation/

formation, only the most electronegative atoms should form hydrogen bonds and the strength of the bond should increase with increase in the electronegativity of the two bonded atoms. From the electronegativity scale, it would be expected that the strength of the bonds would decrease in the following order: F, O, N and Cl. This is borne out in practice, except for chlorine which, although it has the same electronegativity as oxygen, yet forms much weaker hydrogen bonds. This may be attributed to the relatively large size of the chlorine atom leading to a reduced electrostatic interaction.

Generally, increasing the electronegativity of one or both of the bonded atoms increases the power of hydrogen bond formation, e.g., the phenols form stronger hydrogen bonds than the aliphatic alcohols because of the increase in electronegativity of the oxygen atom resulting from resonance with structures such as:



COLOUR AND CONSTITUTION.

The phenomenon of adsorption is associated with vibrations of electrons in the molecule responsive to stimulation by light rays of specific frequency. Firmly bound electrons will respond to and absorb light of short wave-length and high frequency. As the electrons become more mobile, with increase in the number of conjugated centres of unsaturation, they can absorb light of longer wavelength, viz., the substance becomes coloured. The more complicated a molecule or the greater the number of absorbing centres, the more complex will be the absorption spectrum. The colour of organic compounds is said to deepen as the absorption bands are shifted to the longer wavelengths.

It must be noted that colour may be a resultant effect of light absorption in two or more regions of the spectrum. Thus, while one substance may appear green because it absorbs both the red and blue regions, another may be so due to absorption in the region complementary to blue and yellow, and since the eye cannot distinguish individual wavebands, the visible colour of substances is no accurate guide to the spectral composition of the light they reflect or transmit. It may hence be futile to seel a correlation between constitution and colour - the only exact basis for comparison is absorption spectroscopy.

The first effective theory was advanced by Witt (Ber., 9, 522, 950, (1876)). On surveying the dyestuff known at the time, he noted that they all contained an unsaturated group responsible for the colour. This he called the chromophoric group. Amongst these are the azo, thio, carbonyl and nitro groups. Increase in the number of chromophoric groups intensifies the colour of the substance.

Witt also recognised another type of group - the auxochrome/

auxochrome. This cannot confer colour on an otherwise colourless molecule, but can augment the action of the chromophore. Typical examples are the NH_2 and OH groups.

There were, however, substances, e.g., indigo, which did not seem to fit into this classification and Witt's theory gave no explanation as to why chromophoric and auxuchromic groups should be able to make a molecule coloured. Dilthy noted that salt formation can intensify the colour, e.g., o-nitrophenol, colourless in neutral solution, becomes yellow in alkaline solution.

Yet, many molecules are highly coloured but incapable of forming salts. Kuhn (Naturwiss, 20, 618, (1932)), has suggested that some of these substances should be formulated as dipolar molecules or internal salts.

Indigo, the conventional formula for which is shown in Fig.3.

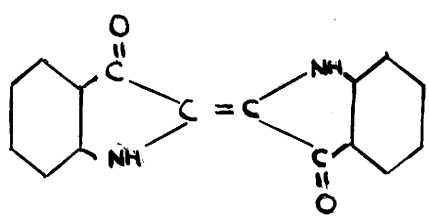


Fig. 3

contains a system of conjugated double bonds similar to that in the p-quinones. This was at one time considered to be the reason for its intense colour, yet 2:5-Diphenyl-1:4-benzoquinone Fig. 4 pp19. contains a similar/

similar conjugated system, but is only a pale yellow.

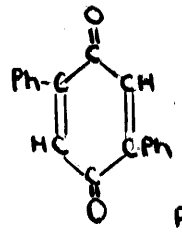


Fig.4.

In addition, the formula does not account for the high melting point of indigo. Hence Kuhn formulated it as a tetrapolar molecule, Fig. 5.

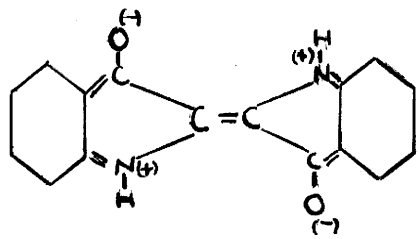


Fig.5.

The conjugated system is more extensive than in Fig. 3. and at the same time it also accounts for the high melting point.

Stieglitz advanced a theory (Proc. Nat. Acad. Sci., 9, 303, (1923)) which may be said to be the precursor of the resonance theory of colour. He was particularly concerned with the colour theory in relation to absorption in the visible spectrum, and wished to ascertain which of the electrons in the dye molecule are subject to vibrations leading to absorption and further to establish a connection between those electronic vibrations and the then known facts relating to colour and constitution.

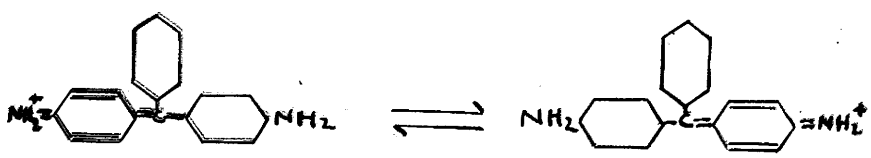
Reduction of a dye to the leuco compound destroys the colour, while gentle oxidation causes it to reappear. The dye itself may thus be in an intermediate state of oxidation and must/

must contain both oxidising and reducing groups. These groups were identified with chromophores and auxochromes respectively.

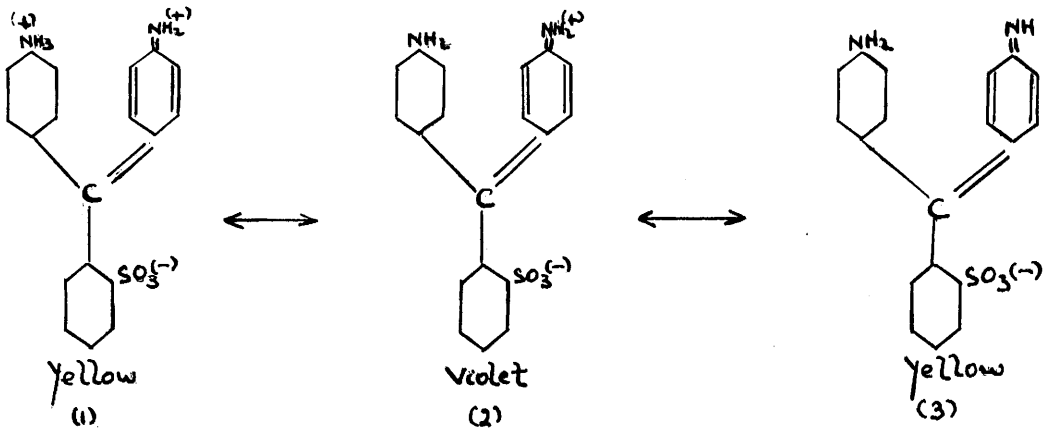
In strong reducing groups, electrons tend to be liberated from intra-atomic restraint, whereas oxidising groups attract electrons from their surroundings. When both types of groups are present in the same molecule one would expect intramolecular electron-transfer to occur. The shift of absorption bands from the ultra-violet to the lower frequencies of the visible spectrum involve lessened electronic restraint, hence Stieglitz drew the conclusion that colour was due to the oscillation of electrons, which would be involved in such an intramolecular oxidation-reduction process.

The latest developments in the field of quantum mechanics have led to a satisfactory colour theory based on the concept of resonance.

The following two structures may be written for Doebner's Violet.



Here we have complete resonance. The auxochrome NH_2 is acting as an electron source and the chromophore as the electron acceptor. Further evidence for a resonance colour theory emerges from the fact that the predicted influence of symmetry on resonance is readily correlated with its effect on colour depth. (Bury, J. Amer. Chem. Soc., 57, 2115, (1935)). This is shown in the following example.



In (2) there is a possibility of complete resonance, thus the colour is deep. When this symmetry, however, is destroyed by taking up of a proton (1) or loosing one (3), the resonance effect will be diminished and the substances will be less intensely coloured.

It is now recognised that there are two restricting principles which must be imposed on the resonance theory to make it fit into an adequate colour theory. These are:

(a) High resonance energy does not always imply a large absorption of light, e.g. the non-contributing Kekulé forms

of/

of benzene. G. N. Lewis states:

The electron mobility is small in a molecule whose properties correspond to a formula in which all the electrons are paired, and there is no formal charge on any atom. When such a structure is the major contributing form of a resonating molecule, the mobility is still small. When, however, the actual state of the molecule differs considerably from a classical or ideal structure, the mobility is greatly increased. In other words, displacement from the ideal structure makes further displacements easier. Strong colour is obtained when two important forms are such that the changes from one to the other involves the movement of an electronic charge.

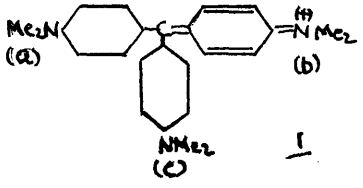
(b) From various data, it has become clear that changes in total resonance do not necessarily parallel the changes in the resonance responsible for colour.

G. N. Lewis has proposed that oscillations responsible for the fundamental absorption must be in one direction only, e.g., in a triphenylmethane skeleton.

If the oscillation is only effective in colour production when it traverses the horizontal path ((a)⟶(b)), then only two-thirds of the charge in (1) contributes to colour production. In (2) the charge cannot be relayed to (c), so the whole charge oscillates horizontally and the colour should be deeper. This is actually found in practice.

From/

From this brief review, it will be seen that the present-day trend is to do away with those theories which seek to explain colour by way of some particular constitutional peculiarity. These theories may be quite useful in a practical way but we have to look to the resonance theory for the ultimate solution of this problem.



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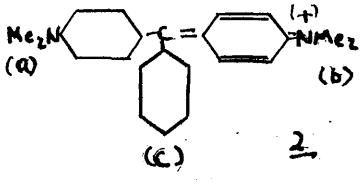


2

THE BONDING OF DYESTUFFS TO FIBRES.

The Langmuir trough technique has also been found suitable as a means of isolating the effects of groups thought to be responsible for causing the bonding of dyes to fibres. The object of this part of the work has been to throw additional light on the dye to fibre bond, and if possible to verify and enlarge on existing theories concerning the bond.

CELLULOSE.

Haworth and others have shown that cellulose is made up of very long chains of glucose residues linked together as shown. (Fig. 6 pp.25)

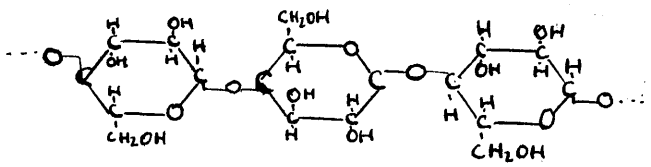


Fig. 6.

From the Figure it is seen that since the glucose units in the chain are arranged in an alternating manner, any particular group is in the same position every second unit, which corresponds to a spacing of 10.3Å. The lengths of the cellulose chains vary in the different fibres, regenerated fibres having the shorter chain lengths.

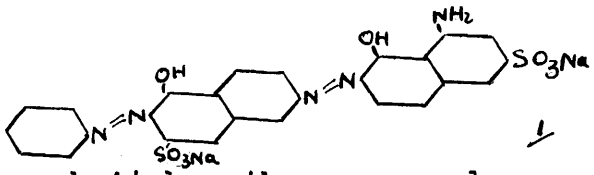
The cellulose fibre is usually assumed to consist of a continuous network of cellulose chains which in certain regions form an ordered arrangement, termed a micelle or crystallite. This is embedded in the matrix, a chemically identical though less ordered material. However, Astbury has recently pointed out that electronmicrographs of natural cellulose membranes show only an arrangement of parallel smooth rods with no evidence of amorphous regions.

The pore-size of cellulose (viz., the space between the micelles in the water-swollen material) has been estimated at/

at about 26 $\mathring{A}$(rad.) (Manegold Viet and Morton Kolloid-Z., 56, 7, (1931)). This is important as it governs the size of the dye molecule which can penetrate the fibre.

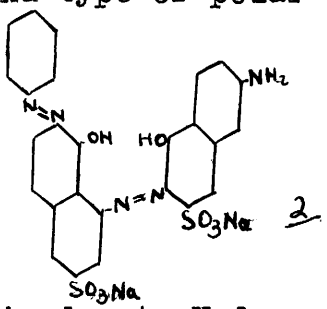
Dyeing Mechanism.

Meyer (Textilber., 9, 573 (1928)), pointed out that the dyes which would dye cotton most readily had a linear configuration, when considered in the trans-form, e.g., (1) is linear and substantive.



1

but (2) although it has the same number and type of polar groups and is not of equal molecular weight is not.

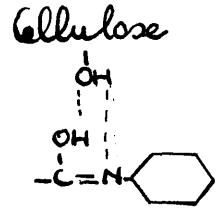


2

A further advance in this theory is due to Hodgson, who suggested that all the various benzene and naphthalene nuclei in the dye must be capable of lying in one plane. This is supported by the fact that of the dyes containing a disubstituted benzidence nucleus only those derivatives containing the substituents in the 3:3-position would yield substantative dyes. None of the dyes derived from 2:2-benzidene derivatives are substantative. This is attributed to the fact that in the case of the 2:2-derivatives the two benzene rings are prevented from becoming coplanar by the substituent groups.

It/

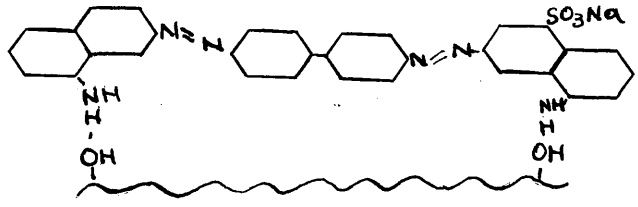
It is now generally supposed that the dye is bound to the cellulose by means of the hydrogen bond. In the case of substantive amide groupings the mode of union is visualised thus:



(The results of recent work in these laboratories on hydrogen bonding suggests that the amide group behaves as an enol, in forming hydrogen-bond complexes).

The effect of solubilising groups, e.g., sulphonic groups, is considered to reduce the substantivity as they are negatively charged, thus causing the dye molecule to be repelled from the cellulose, which itself has a negative charge in water.

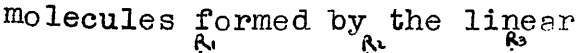
The final concept arrived at from the above and the dichroism of cellulose fibres is of the dye molecule lying lengthwise along the cellulose chains, having the hydrogen bonding and solubilising groups lying on opposite sides of the molecule.



Adsorption of Congo Red on Cellulose.

Proteins.

Protein fibres consist essentially of polypeptide chain molecules formed by the linear condensation of amino acids

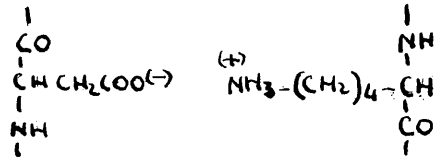


The nature of the protein depends on the side group R. These may be divided into four sections (1) Non-reactive; (2) Basic; (3) Acidic; and (4) Cross-linking. Of the types(1- 3)there are numerous examples: of type (4) there is only one example derived from the amino acid cystine.

As in other natural fibres, the polymer chain molecules in protinoid fibres appear to lie with their length roughly along the fibre axis and to be oriented in the crystalline parts and arranged in a random fashion in the amorphous regions.

Adjacent chains are linked by hydrogen bonds through the carbonyl group.

Speakman and Hirst have further suggested that salt linkages are present between adjacent chains due to the positively charged basic groups and the negatively charged carboxyl groups, thus:



Absorption of the Dye on the Fibre.

The experimental data on the dyeing of wool is very varied and complex. It is now believed that from an acid solution, hydrogen and chloride ions (in the case of hydrochloric acid) are adsorbed by the basic and acidic groups respectively of/

of the dye. The larger and more slowly diffusing dye ions then displace the chloride ions from their sites. The dye ions must have greater affinity for the absorption sites than the chloride ions: this is believed to be due to the fact that in addition to the ionic link of the chloride ion, the dye anion is further able to form hydrogen bonds with the fibre.

Cellulose Acetate.

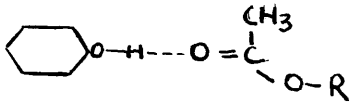
The material used as a fibre is the di-acetate. It has been shown that the distribution of the acetyl-groups along the cellulose chain is very uniform, each glucose residue containing an average of two acetyl groups. The commercial rayon has a low degree of orientation.

Dyeing Properties.

The dyeing properties of cellulose acetate are completely different from those of the cellulose fibres. Direct cotton and acid dyes leave the fibre nearly unaffected. This is thought to be largely due to changed surface characteristics, whereas cellulose is highly hydrophilic cellulose acetate is hydrophobic. This is shown among other things by the low water absorption of the fibre.

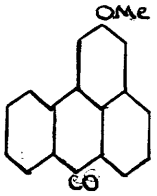
From the work of Marsden and Urquhart (J. Text. Inst., 33, T105, (1942)), on the absorption and swelling effect of phenol on cellulose acetate, it appears that the bonding force between the dye and the fibre is again the hydrogen bond. For phenol/

phenol this may be written:



The dyeing mechanism may hence be visualised as consisting of diffusion of the dye through intermicellar channels followed by adsorption on the micellar surfaces, brought about by hydrogen bonding.

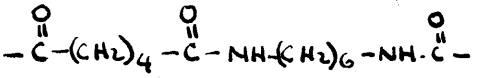
Some questions are difficult to account for on this basis - for example, why dyes such as Duranol Brilliant Yellow 6G,



which has no groups capable of forming a hydrogen bond with an acetyl group, should nevertheless dye cellulose acetate.

NYLON.

This is obtained commercially by condensing hexamethylenediamine and adipic acid; the product $HOOC(CH_2)_{14}.CONH(CH_2)_6NH_2$ further condenses to form a linear polymer of average molecular weight 10,000-12,000.



It is important to note that nylon has the peptide link in common with the protein fibres, but does not contain the complicating side chains. Nylon also contains a small proportion of free carboxyl and amino groups. The strength of the fibre is attributed to hydrogen bonds between the regularly spaced amide groups.

Nylon is usually dyed with dispersed acetate rayon dyes or acid dyes. The former are readily applied but are not very fast to light; the latter have much better fastness properties but are also much more difficult to apply.

The mode of dye attachment to the fibre has not been studied in great detail. The mechanism is thought to be similar to that involved in acetate rayon dyeing, the carbonyl groups of the main chains of nylon playing the same role as the ester groups in cellulose acetate. The dyes are most likely attached by means of hydrogen bonds to the amide group in the fibre.

The direct evidence for this postulated mechanism is not very great; it has been deduced in the main from the work on cellulose-acetate.

SURFACE FILMS.

SURFACE FILMS.

Early History.

The fact that all films have the abilfty to prevent waves from breaking, thus protecting ships in rough seas, has been known from the earliest times.

With the establishment of the idea of surface tension came the observation that any contamination lowers this tension. It was first measured accurately by Rayleigh (Proc. Roy. Soc., 47, 364, (1890)) for olive oil on water.

In 1891 Fraulein Pöckels (Nature, 43, 437, (1891)), introduced the idea of varying the area of the surface occupied by a film by confining it between strips or "barriers" resting everywhere on the water and the edges of the trough and extending the whole width of the latter filled to the brim with water. The variation in the lowering of surface tension with change in film area was investigated. Provided the area exceeded a certain critical amount for a given quantity of oil, the surface tension of water was not changed perceptibly, and the movement of the barrier had no effect. When the area was decreased below this critical value, the surface tension fell very rapidly.

The Structure of Monolayers.

Rayleigh (Phil. Mag., 48, 337, (1899)), confirmed Pöckels' observations, and suggested further that at the critical point the molecules form a layer of one molecular thickness with all the/

the molecules in contact.

This introduces two important points:

(a) The molecules are floating objects repelling one another when in a single layer in contact, so that the first point at which surface tension is reduced is when the film is one molecule thick.

(b) The diminution in surface tension is the repulsion between the film molecules, i.e., the resistance to lateral compression. This resistance to compression can be measured by enclosing the film between boundaries.

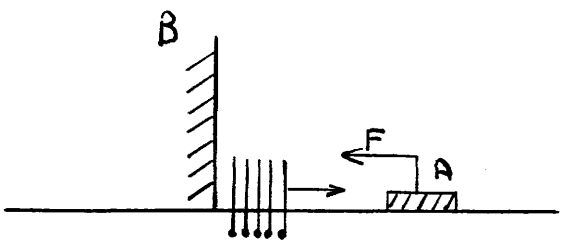


Fig. 7.

Surface Pressure and Surface Tension.

The resistance to compression of an insoluble monolayer can be measured by enclosing the film between barriers, which it cannot pass. A, is a light floating strip connected to some instrument whereby the outward pressure F exerted on it by the film can be measured. This force is called the surface pressure. At the other end, the film is bounded by a heavy barrier B.(Fig.7)

Surface tension is the free energy per sq.cm. of the surface, or the work necessary to increase the area of the surface by one sq.cm.

Let the float A be displaced to the right by a distance dx/

dx, then the work done on it by the surface pressure F is Fldx, where l is the length of the float. The γ is the surface tension of pure water and γ' that of the film covered surface, an area ldx of free energy γ has been replaced by one of free energy γ' and the work done must be $(\gamma-\gamma')$ ldx. The two expressions for the work done must be equal

$$\therefore \quad F = \gamma - \gamma'$$

The surface pressure is hence equal to the diminution of the surface tension of the water caused by the film.

This concept of surface pressure is very definite and convenient in terms of the molecule. It is exactly analogous in two dimensions to osmotic pressure in three. The film barriers constitute the most perfect semi-permeable membrane, for the film molecules cannot pass it at all, while the water molecules pass it almost instantaneously from below, and to a certain extent above in the vapour.

Devaux (Proc.-verb. Soc. Phys. Nat. Bordeaux, 19 Nov., 3 Dec., 1903; 7 Jan., 14 Apr., 1904; 28 Mar., 1912. J. Phys. Radium, 3, 450, (1904); 2, 699, 891, (1912). Ann. Rep. Smithsonian Inst., 261, (1913)), carried out numerous experiments with light powders sprinkled on the surface. He confirmed the results of Pockels and Rayleigh and, on calculating the thickness of the films, found them to be of the same order as the known dimensions of the molecule.

Modern quantitative work on surface films was begun by Langmuir/

Langmuir (J.A.C.S., 39, 1848, (1917)). He measured the outward pressure directly by means of a floating barrier connected to a device for measuring the force on it. His apparatus has now been largely modified but the principle of measuring the surface pressure directly is still the most useful method of investigating surface films. Langmuir also employed pure substances of known constitution in place of oils, and the effects of changes in constitution on the films were observed. The technique used consisted in dissolving the pure substance in a clean volatile solvent, usually benzene, allowing time for the film to spread (about one minute), and measuring the area. The results were expressed as Å^2 per molecule.

Langmuir showed that the normal saturated fatty acids and alcohols all gave stable films and did not increase the surface pressure until they occupied an area of approximately 22 Å^2 per molecule; at 20.5 Å^2 per molecule the pressure increased very rapidly. (Fig. 9 pp.41). He also found that his results were independent of the length of the hydrocarbon chain as long as the latter was greater than about 12 carbon atoms. This shows that the molecules are steeply orientated to the surface and are all inclined at the same angle within the films.

By simple calculation, it can be shown that the film molecules are generally greatly elongated in one direction, e.g., palmitic acid is at least 4-5 times as long as it is thick. It

was/

was further seen that to form a film the substance had to contain a water soluble group, usually OH or COOH (long chain paraffins will not form surface films). Hence, the general picture which emerges is that the end group dissolves in the substrate, the rest of the molecule refusing to be dragged in owing to the long chain.

Experimental Techniques Employed in the Study of Surface Films.

The Langmuir film balance technique commenced by Langmuir and improved upon by Adam, Jessop and others, is still the approach which reveals most concerning the properties of surface films. However, other useful methods of studying these films have been developed recently and these will be briefly discussed below.

Surface Pressure Measurements.

Recently another direct experimental method for determining surface tensions has been developed by Derivichian (J. Phys. Radium, 6, 221, 429, (1935)), and by Harkins and Anderson (J. Amer. Chem. Soc., 59, 2189, (1937)).

The method consists of a direct measurement of the surface tension by observing the downward pull on a clean glass plate held vertically in the surface. This method is now rivalling the ordinary film balance technique both in accuracy and convenience. A sensitivity approaching 0.01 dyne per cm. has been claimed.

Surface/

Surface Potential Measurements.

This method ranks second in importance to surface pressure measurements. The difference in surface potential of a clean surface and the film-covered surface is measured.

If the film should not be uniform, viz., incompletely spread, then on exploring the surface with the air electrode, (see below, p. 64.) a fluctuation of the surface potential will be noted. It is hence very useful to employ a surface potential technique, simultaneously with surface pressure measurements, to detect incomplete spreading.

The change in surface potential (ΔV) may be written thus: $\Delta V = 4\pi n \mu$.

("The Adam Physics and Chemistry of Surfaces," 3rd Edition, p. 38). Where n=number of molecules in the film, and μ would be the vertical component of the dipole moment of one film molecule, if all the surface potential were due to the dipole moments of the film molecule in a plane and if the dielectric constant of the film could be treated as unity.

The interpretation of surface potential results is more complex than that of surface pressure results. The following points have, however, been established:

With compounds of similar end groups and similar constitution, a rise in the value of μ probably indicates an increasing tilt of the dipole to the surface. Further chemical changes, especially those leading to ionisation of the end group, may/

may lead to large changes in the value of μ. When, as sometimes occurs, surface potentials are negative, this indicates that the negative end of the total dipole of the molecules in the film is uppermost.

Surface potential measurements may thus furnish useful information regarding the changes of orientation of the film molecules. The technique is useful for following chemical reactions in films and it is largely employed for this purpose.

Ultramicroscopic Examination of Surface Films.

This was introduced by Zocher and Stiebel (Z. Physikal. Chem., 147, A, 401, (1930)), and modified by Adam (Trans. Faraday Soc., 29, 90, (1933)). A powerful dark-ground illuminator of the cardioid type was fixed in the bottom of the trough and focussed sharply on the water surface. With a powerful light source, it is normally easy to detect whether any of the film-forming material is not spread. A monomolecular film scatters no light under these conditions, and appears dark. Any unspread material shows up as a brightly illuminated region, different in appearance from any dust which may settle on the surface.

Although this method yields no information as to the structure of the films, it is a valuable accessory technique in that it reveals whether or not the film is properly spread. Furthermore, it is essential when kinetic studies of reactions in monolayers are undertaken - as may become necessary at a later stage of the work - to provide additional evidence that accidental/

accidental contamination has not occurred. (Adam, "The Physics and Chemistry of Surfaces," 3rd Edition, p.402). Ultramicroscopic examination of the films would then be highly desirable.

Examination of Light Reflected from Surface Films.

Freundlick et.al. (Z.physikal.Chem., 130, 289, (1927)), Bouhet (Ann.Physique., 15, 5, (1931)), as well as other workers, describe apparatus for measuring the ellipticity of polarisation of the light reflected from surfaces covered with monolayers.

The nature of the reflected light depends on the structure of the surface films. Interpretation of the results in terms of the molecules and their orientation is unfortunately too difficult; hence this approach has so far made no significant contribution to the elucidation of the structure of surface films.

Requirements for Spreading.

When a drop of a non-volatile liquid is placed on the surface of another liquid immiscible with it, it may either remain as a drop or proceed to spread out as a film. This is entirely determined by the surface tensions of the two liquids and the interfacial tensions between them.

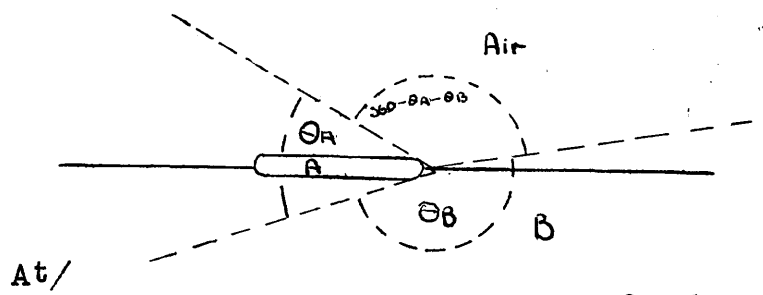


Fig. 8.

At the edge of the drop, three fluid surfaces meet and equilibrium is maintained only if the three surface tensions are in equilibrium. Hence, from Neumann's triangle, we obtain:-

$$\frac{\gamma_B}{\sin\theta_A} = \frac{\gamma_A}{\sin\theta_B} = \frac{\gamma_{AB}}{\sin(360-\theta_A-\theta_B)}$$

where γ_A and γ_B are the surface tensions of the upper and lower liquids and γ_{AB} is the interfacial tension between them. θ_A and θ_B are the angles in liquids A and B respectively.

If the surface tension of B is increased, θ_A will tend to zero, then,

$$\gamma_B \geq \gamma_A + \gamma_B$$

and equilibrium is impossible. The energy will be diminished by a spreading of A on B, liquid A will hence spread on B if

$$\gamma_B > \gamma_A + \gamma_{AB}$$

But W_{AB} (the work of adhesion) = $\gamma_A + \gamma_B - \gamma_{AB}$

$\therefore W_{AB} \geq 2\gamma_A$ (Dupré, "Théorie Mécanique de la Chaleur," p. 368; Hardy, J.C.S., 623, (1930)).

$W_{AB} - 2\gamma_A$ has been called the spreading coefficient of A on B. Now $2\gamma_A$ is the cohesion of A. Hence we see that the condition of spreading is that the two liquids A and B must adhere more strongly to each other, than to themselves.

Spreading on Liquids.

Reynolds observed that when an oil is spread on a dust covered surface, the dust does not move until the oil reaches it, when it proceeds to crumple up and is swept along before the advancing oil.

The constant motion of the water molecules beneath the drop/

drop cause it to expand. The oil molecules adhere to the water and are carried by their motion along the surface, viz., the oil is spread. If the liquid is one which spreads stably, then the potential energy of the film is lower than that of the drop, and spreading will continue. The molecules just being spread drive the already spread molecules ever farther from the initial drop. If the liquid is a non-spreading one, a few molecules may diffuse outwards from the drop but, being more stable in the drop than on the surface, they will tend to return to the drop.

Spreading occurs in the following stages. First a film of visible thickness is formed. When the surface is completely covered, the film commences to break up and finally settles down to a monomolecular film in equilibrium with droplets of the liquid.

The monomolecular films thus obtained are an interesting and useful state of matter. They are capable of existence in various forms, corresponding in two dimensions to the three principal states of matter in three dimensions. The molecules in these films are often arranged in a simple manner, thus giving a means whereby the shape and size of individual molecules may be studied. The state of these monolayers depends very largely upon the amount and distribution of the lateral adhesion of the film molecules for each other and the perpendicular attraction between the film molecules and the substrate.

THE TYPES OF SURFACE FILMS.

It has now been established that a number of forms of surface films of long chain aliphatic substances can exist. The type of film depends to a great extent on the lateral adhesion between the film molecules.

The present research is concerned mainly with condensed and liquid-expanded films, although some of the results obtained would indicate the formation of gaseous films. These most important types of films will be reviewed in the light of present day knowledge.

Condensed Films.

These are the most important types of films. The molecules have a great amount of lateral adhesion, and if the surface is greater than can be covered by the adhering molecules, a two-phase system results which is detectable by surface-potential measurements.

With condensed films, we obtain the following type of force-area curves: (Fig.9.)

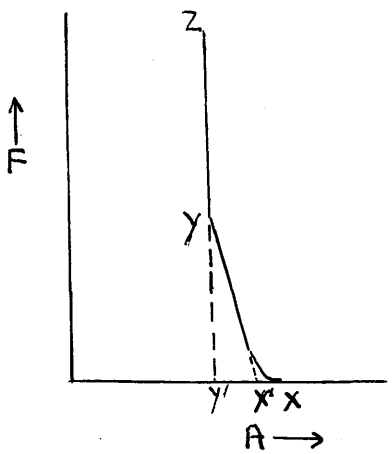


Fig.9.

In some cases XY and YZ both occur, in others only one of the portions occurs. The area at Y' is always 20.5$\mathring{A}^2$ for straight alkyl chains at no compression; while the area at X' may extend even over 30$\mathring{A}^2$. (Adam

and/

and Jessop, Proc. Roy. Soc., A, 112, 362, (1926)).

There have been numerous attempts to draw analogies between the two dimensional condensed films and solid matter. It has been suggested that the regions YZ and YX correspond to the solid and liquid states respectively. This cannot, however, be correct, as some compounds, e.g., the alcohols give fluid films in both regions.

Adam suggested (Proc. Roy. Soc., A, 99, 336, (1921)), that the two parts XY and YZ could be ascribed to the close-packed heads and close-packed chains respectively. Lyons and Rideal (Proc. Roy. Soc., A, 124, 322, (1929)), proposed that the chains were inclined at an angle of 26.5° or 45° to the vertical, since this tilt would allow the chains to interlock, if the cross section of the latter is taken as 18.5 $\mathring{A}^2$ (Müller, Proc. Roy. Soc., A, 114, 542, (1927); 120, 437, (1928)), this would give areas of 20.7 and 26.2 $\mathring{A}^2$ for Y' and X' respectively.

Adam, however, pointed out (Proc. Roy. Soc., A, 126, 526, (1930)), that though there may be some evidence for the first interlocking position, there is none for the second. This author stated that the question is still open as to whether the area of 20.5 $\mathring{A}^2$ for the films of close-packed chains is due to the chains being packed exactly as in crystals, at a tilt of 26.5°, or to the chains being vertical and packed less closely, owing to the influence of the water molecules. ("The Physics and Chemistry of Surfaces," 3rd Edition, p. 52). With regard to the XY/

XY portions, Adam concludes (Loc.cit., p.53-54) that these give a measure of the cross section of the head groups as packed in the films and that these latter could be divided into two groups, according to whether they are, or are not, rearranged by compression. Those with high compressibility, e.g., fatty acids on acid solution and nitriles belong to the first class; those with much lower compressibilities, e.g. phenols, ureas, fit into the second.

Schulman and Hughes (Proc.Roy.Soc., A, 138, 430, (1932)), have criticised the concept of head compression along XY on the basis of their potential measurements, since they found that the vertical component of the apparent dipole moment remained almost constant throughout this region. They suggested the expulsion into the substrate of solvent molecules orientated between the polar groups.

Derivichian (J.Chem.Physics, 7, 931, (1939)), has drawn very close analogies between monolayers and three dimensional matter. He states: "The lattice structure and the tilt of the molecules in the different forms are the same in two and three dimensions." Alexander (Trans.Faraday Soc., 37, 426, (1941)), has criticised this theory severely. He points out, among other things, that if Derivichian's theory were correct, then substances solid at room temperature should also give condensed monolayers at this temperature. This is known to be incorrect in numerous cases. He supports the view (Proc.Roy. Soc., A, 179, 486, (1941)), that in the YZ region the long chains /

chains are close packed, but not so tightly as is possible in the crystalline state, and vertically arranged in all cases. Amongst other data, he shows that the surface moment of condensed films of ethyl stearate requires vertically oriented chains (Alexander and Schulman, Proc. Roy. Soc., A, 161, 155, (1937)).

Alexander (Proc. Roy. Soc., A, 179, 486, (1941)), maintains that the structure in the more compressible region XY is a composite effect, depending both upon the packing of the hydrocarbon chain (Lyons and Rideal), and on the packing of the heads. (Adam). He classifies the condensed monolayers according to the factors primarily responsible for the limiting area X. These factors are as follows:

(a) The size of the head group

The p-alkyl phenols anisoles and anilines fall into this group, if the ring is taken as part of the head group.

(b) Cross hydrogen bonding.

Alexander believes this to be a factor in the limiting area of unsubstituted fatty acids, ureas, amides and others. In certain cases, where hydrogen bonding was expected but was prevented by steric factors, he postulates a hydrogen bond through a single water molecule. (Alexander, Proc. Roy. Soc., A, 179, 470, (1941)).

(c) Packing of the chains.

This is believed to be the deciding factor in the case of cis, and trans-unsaturated compounds methylketones and others.

In/

In these cases, any attractive forces between the head groups arising e.g., from hydrogen bonding, are unlikely.

Alexander finally summarises his view as follows:

"The most general statement possible would appear to be, that for the usual chain lengths of 14-20 carbon atoms the configuration of minimum energy at the limiting area X, is determined both by the orientation of the dipole with respect to the surface and by the long chain packing. The area at X may correspond either to that of the hydrocarbon chain depending upon which occupies the larger area in their respective orientation at this point."

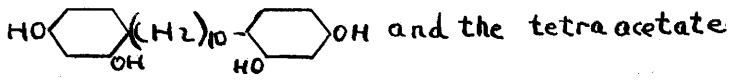
Gaseous Films.

This is by far the simplest type of film; ideally it consists of molecules of negligible size, having no lateral adhesion, but being attracted by the water surface. The theoretical behaviour of such a film can be readily calculated and is closely approached in some actual cases. The film is considered to consist of molecules lying flat on the surface moving in a random fashion. The surface pressure is due to continuous collisions between the moving film molecules and the float.

In the evidence outlined by Adam ("The Physics and Chemistry of Surfaces," 3rd Edition, p. 57-58) to show that molecules of this type of film lie flat on the surface, he points out that it is often possible to convert a coherent film into/

into a gaseous one by introducing a second water-attracting group some distance from the first. The following compounds are cited as forming good gaseous films:

$C_2H_4OOC(CH_2)_{11}COOC_2H_4$



and the tetra acetate

Adam and Jessop (Proc. Roy. Soc., A, 110, 423, (1926)), have shown that for an idea gaseous film FA=kT, (cf. PV RT) where k is the gas constant (1.372 x 10 ergs. per degree). The proof follows that for the ordinary gas laws very closely. At room temperature kT = 400 (in terms of A). Hence a perfect gaseous film would give a FA/F curve as shown (Dotted line Fig. 10 pp.48). A gaseous film can always be recognised by giving a curve similar to that in Fig. 10 pp.48 (Full line).

Liquid Expanded Films.

This type of film has properties intermediate between those of the gaseous and the condensed film forms. It frequently occurs with long chain aliphatic substances. Langmuir's explanation (Adam, Ann. Rep., 33, 103, (1936)); Langmuir, J. Chem. Phys., 1, 756, (1933)), of the properties of these films, and in particular of the fact that the limiting area does not correspond to any definite orientation of the molecules but is intermediate between that of the molecules standing upright and lying flat, is generally accepted.

Transition Temperature.

This is generally a fairly well defined point, although not quite so sharp as the melting point of a solid, at which a film

film changes its state, e.g., from solid to liquid.

From a study of duplex films, (Alexander, Colloid Science, 523, (1949)), and from the shape of the Force-area curves of the expanded films, (Adam, "The Physics and Chemistry of Surfaces," 3rd Edition, p. 63-70), Langmuir suggested that the monolayer in the expanded state should be regarded as a duplex oil film of extreme thinness (15-20 Å). The upper surface being hydrocarbon in contact with air was regarded as the liquid phase. The lower surface of polar head groups in two dimensional kinetic agitation was regarded as a gaseous film. This is regarded as being possible, although one end of the molecule will be restricted in its movement as it is anchored in the water surface by the hydrophilic group.

The type of curve obtained with these films is as shown (Fig. 11 pp.48). For actual examples, see N. K. Adams, "The Physics and Chemistry of Surfaces," 3rd Edition, p. 59.

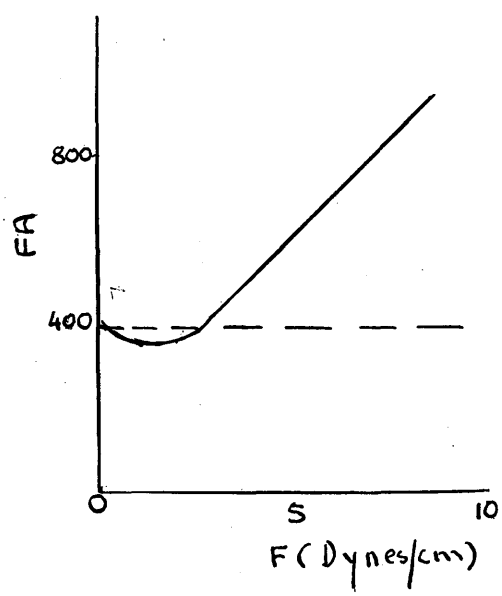


Fig 10.

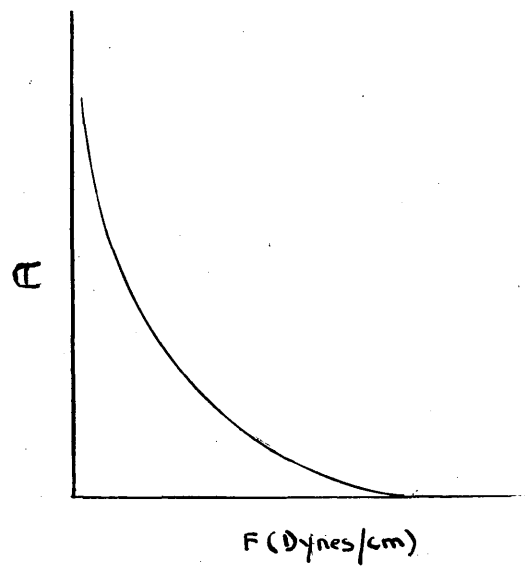


Fig. 11.

Influence of the Substrate.

In this thesis, the author has been largely concerned with structural changes in the monolayers due to variations in the nature of the substrate. It is therefore deemed necessary to outline present day views on these effects.

Effect of pH.

There is a decrease in the lateral adhesion of the film molecules when the end groups are ionised by a suitable pH change in the substrate. This was first shown by Adam (Proc. Roy. Soc., A, 101, 516, (1922)), who found a decrease in the expansion temperature of fatty acids on alkaline solutions.

Adam and Miller (Proc. Roy. Soc., A, 142, 401, (1933)), also discovered that the molecular areas of long alkyl-chain phenols increased when 2N-sodium carbonate or 2N-sodium hydroxide solutions were used as substrates. Whereas all the phenols tended to give a molecular area of 24 $\overset{o2}{A}$ on water, those of p- dodecyl and p-hexadecyl phenol increased to ca.42.5 $\overset{o2}{A}$ and ca. 28.5 $\overset{o2}{A}$ respectively on 2N-sodium carbonate solution at 16°.

Since then, many further examples of this type of behaviour have been found. Condensed films became expanded, and expanded films gaseous. The decrease in adhesion between the molecules is due to the repulsion between the end groups, which become ions of like charge.

In several instances, as with long chain amines (Adam, Proc. Roy. Soc., A, 126, 526 (1930)), the pH changes do not seem to be as important as the nature of the acid radicles of the buffer/

buffer solutions used to change the pH. The amines appear to form salts with the acid radicles, and the area changes are dependent to a large extent on the bulkiness of these groups.

Effect of Long Chain Compounds on the Expansion of Monolayers.

Adam and Jessop (Proc. Roy. Soc., 120, 473, (1928)), found that cholesterol and other bulky molecules can cause an expanded film to condense. Various explanations for this were offered (Adam, "The Physics and Chemistry of Surfaces," pp. 70-71), but it is now believed to be due to hydrogen bonding between the original film and the added molecules. (Alexander, Proc. Roy. Soc., A, 179, 470, (1941)). This author also remarks that condensation will not occur unless there is a possibility of hydrogen bonding. It would appear that the attractive forces between polar groups in mixed films may be interpreted upon the hypothesis that they are due to Coulomb forces, acting between polar groups, in systems in the following order, graded by the energy of association.

Ion^{+}-ion^{-} > ion^{+}-dipole > ion^{+}-ion^{-} (Schulman, Ann. Reps., 36, 110, (1939)).

Double Bonds.

Langmuir, and more recently Adam and Jessop (Proc. Roy. Soc., A, 112, 362 (1926)), have shown that double bonds (C=C) cause films to expand. Langmuir ascribed this to the increased attraction for the water caused by the double bond. Doubtless this/

this is partly true, as unsaturated hydrocarbons are more soluble than the saturated ones. The effect will also be partly due to configurational changes caused in the molecule by substituting a double for a single bond.

Reactions in Monolayers.

The study of reactions at the air water inferface by means of the monolayer technique is due in the main to Rideal and his co-workers. Reactions have been followed by change of surface area and/or surface potential. In nearly all cases the reaction velocity is found to depend upon the molecular orientation at the interface. This steric factor may modify the reaction velocity by a power of 10 or more.

Oxidation of unsaturated compounds by permanganate, esterifications and many other types of reaction have been investigated by this means.

Dissolved Salts in the Substrate.

The effect of small traces of salts in the substrate on monolayers has been investigated by Anderson Harkins (J. Amer. Chem. Soc., 2195, (1937)), and others. The effect is not fully understood, but it is believed that any substance in solution which can link the film molecules by their heads will tend to make the films more rigid, usually decreasing the area (a similar effect to hydrogen bonding). The concentration of ions required is very small, 10^{-8} molar concentrations of aluminium having a noticeable effect.

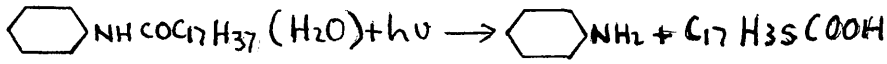
Irradiation/

Irradiation of Monolayers.

Studies of irradiated monolayers were first undertaken by Mitchell and Rideal (Proc. Roy. Soc., A, 159, 206, (1937)). These authors studied the photochemistry of the keto-imino linkage. They state that with a large number of compounds, photochemical changes will not occur at a sufficient rate to allow accurate determinations of the change of the monolayer to be made - very slow reaction rates being observed with hydroxystearic acid, stearic acid and methylstearamide.

Preliminary photochemical experiments were carried out, using quartz mercury vapour lamps of standard design. These, however, proved to be inadequate, producing insufficiently large photochemical changes. Finally, intense radiation in the region of 2,300 to 2,500 $\mathring{A}$ from a quartz hydrogen discharge tube had to be employed.

Monolayers of stearic anilide were then found to undergo photochemical decomposition. Stearic acid and aniline were produced thus:



$$C_6H_5NHCOC_{17}H_{37}(H_2O) + h\upsilon \longrightarrow C_6H_5NH_2 + C_{17}H_{35}COOH$$

The aniline is believed to diffuse away from the surface. There was no evidence of any further reaction, and this was supported by the fact that the collapse area of the final film always lay between 21 and 22 $\mathring{A}^2$.

Photochemical reactions in monolayers were found to be very sensitive to traces of metallic ions, sometimes in amounts too/

too small to be accurately measured.

Mitchell and Rideal found that the velocity of the decomposition depended very largely on the acidity of the substrate, from which they concluded that the actual photolyte was an ionisation complex of the ammonium or oxonium type. They also demonstrated the importance of molecular orientation in controlling the rate of the photochemical reaction.

This was followed up by a study of the photochemistry of gliadin, zein and other proteins (Proc. Roy. Soc., A, 167, 342, (1938)). These papers constitute the most important contributions so far made in the application of the monolayer technique to photochemistry.

Role of Hydrogen Bonding in Monolayers.

In mixed monolayers of two long chain components, the tendency towards solidification and condensation is well shown in those examples where cross hydrogen bonding would be expected, e.g., octadecylaminehydrochloride and octadecylmethylether, (Marsden and Schulman, Trans. Faraday Soc., 34, 748, (1938)), cetyl alcohol and sodium cetyl sulphate (Schulman and Stenhagen, Proc. Roy. Soc., B, 126, 356, (1938)). Sodium cetyl sulphate shows a powerful interaction with cholesterol but a weak one with cholesterol acetate. (Schulman and Rideal, Proc. Roy. Soc., B, 122, 29, (1937)). This is readily explained in the hydrogen bonding theory, since no such bond can occur in the latter case. The rather sharp transition temperatures shown by condensed monolayers/

monolayers of substituted ureas, acetamides and acetanilides (Adam, Proc. Roy. Soc., A, 101, 452, (1922); ibid, 103, 676, (1923); Adam and Dyer, ibid., 106, 694, (1924)), can also be readily explained. Again, a comparison between substituted amides and analogous esters with very similar head groups but when the latter cannot form cross linkages shows many striking differences

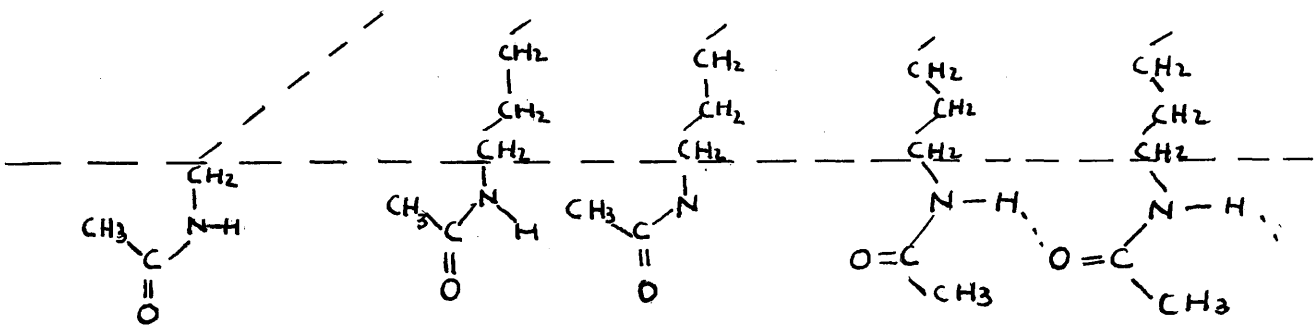
Alexander (Proc. Roy. Soc., A, 179, 470, (1941)), discusses films of acetamides, ureas, amides, acetanilides, aldoximes, unsubstituted and α aminoacids on the basis of the hydrogen bonding theory. He states: "From general reasoning, it might be anticipated that two factors would determine the extent of hydrogen bonding in a monolayer, the first and foremost being the steric one. Since in monolayers the minimum cross-sectional area occupied by an unsubstituted hydrocarbon chain is 19-20 $\overset{o}{A}^2$, the polar groups cannot approach more closely than 4.5 $\overset{o}{A}$. Consequently, such simple groups as OH are prohibited from forming direct intermolecular bonds and can only form hydrogen bonds with water. (They may, of course, form cross-linkages through the intermediary of a water molecule). Larger groups, however, such as COOH, CONH, etc. can bridge distances of this size and often tend to do so."

Condensed films of acetamides were found by Adam and Dyer (Proc. Roy. Soc., A, 106, 694, (1924)), to exist in two forms with a definite transition temperature - the high temperature form being liquid with a limiting area of ca. 24.2 $\overset{o}{A}^2$., the low

temperature/

temperature form solid with a limiting area of 20.5 $\mathring{A}^2$.

Alexander explains these changes readily on the basis of a hydrogen bonding theory. The diagrams and condensed explanations from his paper are reproduced below.



Configuration 1. Configuration 2. Configuration 3.

(Water surface parallel to horizontal dotted line)

Configuration 1.

Expanded form area $> 47\ \mathring{A}^2$. No cross hydrogen bonding, although there will be hydrogen bonds with water. The film is liquid.

Configuration 2.

High temperature condensed form area ca. 24 $\mathring{A}^2$. Hydrogen bond distance ca. 4 $\mathring{A}$., hence there are no direct hydrogen bonds/

bonds, although Alexander believes that there may be cross linking through the OH group of a single water molecule. This bond, however, would still be rather weak and thus the film is in the liquid state.

Configuration 3.

This represents the low temperature condensed form with area < 21 A^{o2}. There are strong hydrogen bonds (with bond distance ca. 2.8 $\mathring{A}$.) The film is solid and rigid with normal area of close packed vertical chains.

It is evident that solidification of the film is brought about by hydrogen cross-bonding.

Calculations of the difference in energy of the CONH group when forming hydrogen bonds with water molecules as in the expanded films (Configuration 1) and when cross-linked as in the low temperature condensed form (Configuration 3) show that the increase in free energy is approximately 840 cal./gram. molecule. This is evidence that intermolecular hydrogen bonding brings about an appreciable increase in stability.

EXPERIMENTAL SECTION.

THE LANGMUIR FILM BALANCE.

Construction and Setting of the Instrument.

The first instrument for the direct measurement of surface pressure was introduced by Langmuir in 1917. An improved form was constructed by Adam in 1926 (Adam and Jessop, Proc. Roy. Soc., A, 110, 423, (1926)), followed by many other simplifications and refinements. The instruments used in this work were constructed according to a later type designed by Alexander, (Nature, 159, 304, (1947)). This new type of apparatus appears at first sight to be rather simple when compared with the usual torsion head film balance of the Adam-Jessop type. However, Alexander claims: "This apparatus appears to give an accuracy fully equal to that of the usual torsion balance, with the additional advantage that measurements can be carried out much more rapidly." The present author has found that this claim is fully justified.

A general view of the apparatus is shown in fig. 12. The monolayer is compressed by a waxed glass slide (B) against a float consisting of duraluminium sheet. The resulting deflection of the float is amplified optically by a system of lenses and mirrors.

Two instruments were used in this research and the earlier one will be described first.

The Trough and Barriers.

The trough containing the water consisted of a pyrex baking dish 50 x 25 x 5 cm. The edges were specially ground to/

to give a level and flat surface. The barrier (B) consisted of quarter-inch glass plate, 3/4 inch wide, and 12 inches long. Barrier (A) was made of duraluminium sheet. Before use, a thin strip of mica was fixed beneath it by means of wax so as to keep all metal out of contact with the solution. The float was 25.3 cm. long.

The Balance System.

This is shown in detail in the fig. 12. The duraluminium barrier (A) is turned up at the edge and attached to an arm (G) to which a watch spring (L) is clamped. The latter is held taut at both ends by two fixed arms (N), carrying the dented clamps shown in Fig. 13.

To the upper part of the arm (G), a small mirror (C) was fixed by means of wax. Below the mirror and at the level of the spring, an arm (F) was fixed perpendicularly to the plane formed by (L) and (G). This arm carried a small pan (E) at one end, and a counterweight at the other. The counterweight can be screwed along the arm (F) until a horizontal position is reached for the zero reading.

The Optical Lever.

The optical lever was designed to amplify the deflections of the barrier (A). It consists of a light source, an image forming lens (I) and a mirror (C) which transmits the movements of the barrier to the beam of light. A second reflecting mirror (D) and a scale was placed two metres away.

The/

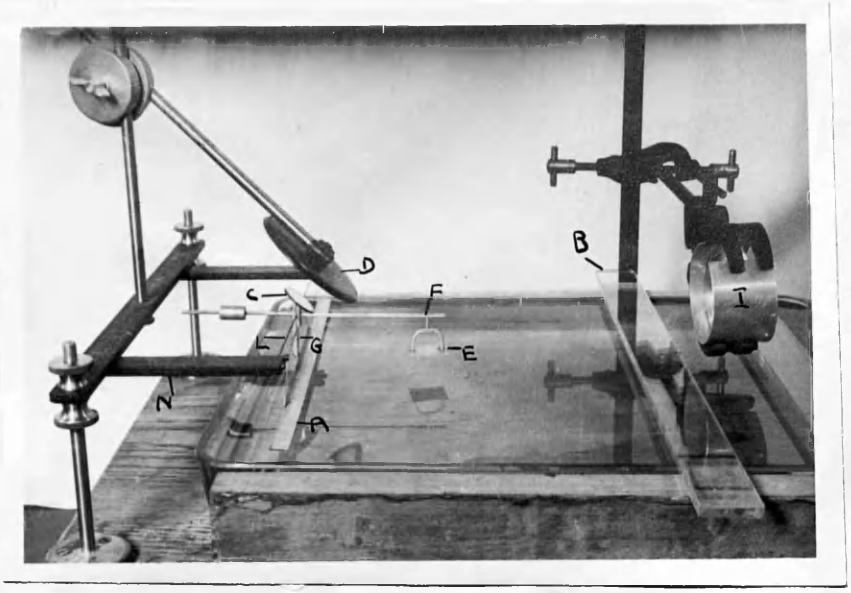


Fig. 12

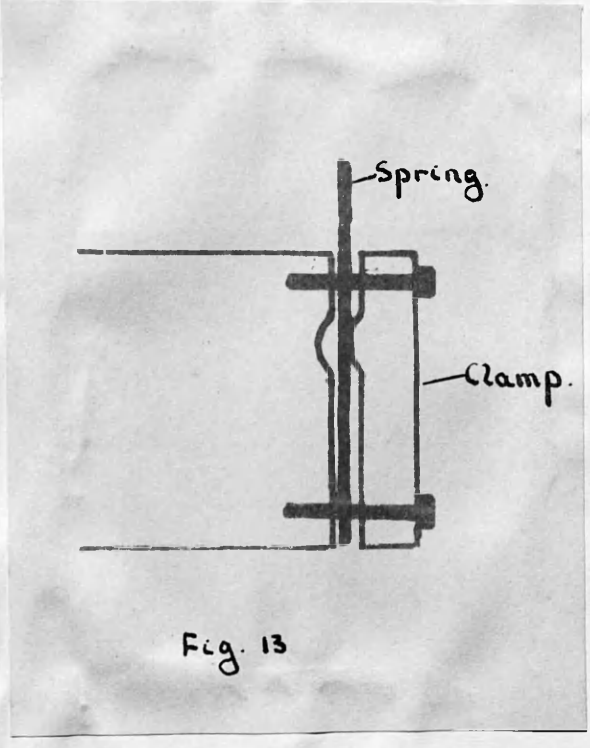


Fig. 13

The lens used was a combination of two biconvex lenses placed side by side. The focal lengths were 20 and 50 cm. respectively, and the lenses were 4 cm. in diameter.

The reflecting mirror (D) is a flat, circular mirror 5 cm. in diameter, and mounted on an adjustable arm. Mirror (C) is also a flat circular mirror, 1 cm. in diameter.

The instrument described above was constructed by Messrs. Thomson, Skinner and Hamilton. It suffered from two disadvantages. The first of these was the large size of the pyrex trough. This involved the handling of large volumes of liquid (5 litres), which was inconvenient and expensive when another substrate was used in place of water. Secondly, no provision had been made to enable the moveable barrier (B) to be operated from a distance, thus allowing the whole instrument to be enclosed.

The second instrument, constructed at first by the author and subsequently re-built by the Technical Chemistry Department Workshop, is shown in Fig. 14. . This instrument differs from the one described above in having a smaller trough (22.5 x 10.0 x 0.6 cm), and a shorter float (9.6 cm). The arm (F) was shortened to 5 cm. and the balance pan used was much lighter than in the first instrument. A screw mechanism for advancing the perspex bridge (see below) and the prongs carrying the moveable barrier were introduced. Twenty turns of the screw advanced these mechanisms by 2.5 cm. Enclosed in an aluminium case/

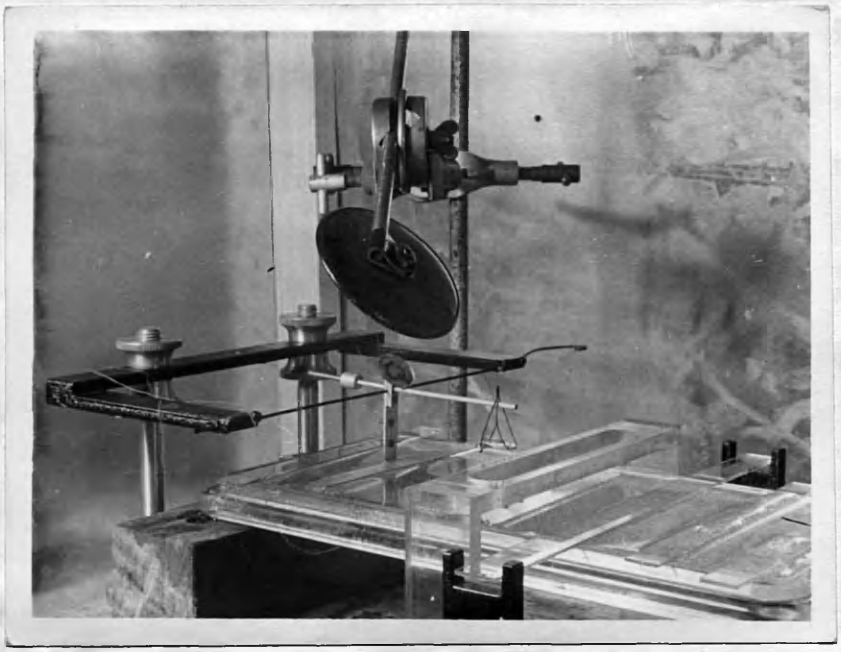


Fig. 14.

case, the instrument rests on a heavy slate block, fitted underneath with hard rubber blocks to minimise vibration.

Operation of the Film Balance.

To ensure accuracy in the operation of a film balance, the following essential points require attention. (Adam, "The Physics and Chemistry of Surfaces, 3rd Edition, p. 27-28).

(1) The barriers used to confine the film must be proof against the leakage of the film under any surface pressure, and must be heavy enough not to move under this pressure.

(2) Leakage of the film past the ends of the light floating barrier on which pressure is measured must be prevented in such a way as to interfere as little as possible with the sensitivity of the measuring instrument.

(3) Sufficiently sensitive means for measuring the force on the float must be provided.

(4) All the apparatus must be as clean as possible, and means must be provided for measuring the amount of contamination of the surface, which is inevitably present to some extent.

(5) An accurate means of measuring the amount of film-forming substance put on the surface must be available, and the solvents used for dissolving the substance must be carefully purified until there is no appreciable trace of film forming impurity present.

Cleaning of the Apparatus.

The trough and glass slides were periodically cleaned with chromic acid, then allowed to stand in distilled water, and finally rinsed with warm distilled water.

Waxing.

The trough and glass slides were dried in the 100° oven and while still hot, a solution of paraffin wax in benzene was painted on by means of a camel-hair brush or a swab of cotton-wool. The apparatus was then allowed to stand for several hours so as to allow the wax to harden. Finally, the apparatus was washed out again with distilled water. The float was cleaned by periodically removing the mica strip and cleaning it carefully. It was completely waxed in the same manner as the trough and the barriers.

Silk Threads.

The space between the edge of the trough and the end of the float was closed by means of thin silk threads. These were fixed between the bottom of the float and the mica strip. They were lightly vaselined to prevent wetting. Before use they were carefully washed out in distilled water. The threads were renewed frequently, new ones always being used when the substrate was changed.

Cleaning of the Surface.

The U-shaped arm carrying the float was removed, leaving only the glass barriers on the water surface. These barriers were moved over the surface one behind the other, and the film that had been on the surface was pushed to the edge of the trough, and there wiped off with cotton-wool. This was repeated several times. Finally, the barriers were moved to the/

the edge of the trough behind the float, and the latter was again placed in position.

Testing of Cleanliness of the Surface.

This was tested frequently by moving the moveable barrier towards the float with no film on the surface. The surface was assumed to be clean when the surface pressure developed on reducing the surface by 3/4 was less than .06 dynes cm. Very frequently the pressure recorded would be less than this. These checks were essential owing to the dusty atmosphere that sometimes prevailed in the laboratory.

Leakage.

The final force area curves were always an average of 5-6 determinations carried out on different amounts of the substance to be spread. In one of these determinations, a light powder was usually dusted on to the surface behind the float in the vicinity of the silk threads. Any movement of the powder made leaks readily apparent.

Spreading of the Film.

The substances were nearly always spread from benzene solution. In several cases when the substances were not sufficiently soluble, they were spread from petroleum ether or a mixture of absolute alcohol and benzene. About 0.010 gms. of the material to be spread was weighed out accurately and dissolved, being made up to 10 c.c. with AR-benzene. The solutions were kept in Quickfit test-tubes in the refrigerator. Usually two solutions of the same material were made up to ensure/

ensure against errors in weighing out.

The solutions were spread on the surface by means of the Agla Micrometer Syringe (Messrs. Burroughs Wellcombe & Co., cf. Trevan Biochem.J., 19, 1111, (1925)). This instrument is now in general use for measuring out accurately small volumes of solutions. It is composed of a glass cylinder and piston of total capacity 0.5 c.c. The syringe in turn is held by a rigid metal clamp fitted with a piston attached to a micrometer. The whole course of the micrometer is covered by 50 turns and one complete turn delivers 0.01 cc. Moreover, each turn is sub-divided into 50 graduations, allowing a delivery of 0.0002 c.c. to be read.

After the film had been spread, one or two minutes were allowed to elapse to allow the benzene to evaporate completely.

Direct Calibration of the Instrument.

This had to be carried out to ascertain what one unit movement of the optical lever was equivalent to in dynes/cm. pressure at the float. It was found that within short periods of time little variation in the sensitivity of the instrument occurred, and hence calibration was normally carried out before and after each set of readings, and an average sensitivity taken. Variations over one day would be about 1.0 per cent. Once a film had been spread, the actual determinations for the force area curves would only occupy a few minutes. However, much time was spent in cleaning the surface and in setting up the balance for measurement.

SURFACE POTENTIAL MEASUREMENTS.

SURFACE POTENTIAL MEASUREMENTS.

Chemical reactions in monolayers are nearly always studied by carrying out simultaneous surface pressure and surface potential measurements. Such instruments have been described by Adam and Harding, (Trans. Faraday Soc., 29, 837, (1933); Harkins (J. Chem. Physics, 1, 852, (1933); 3, 693, (1935), and other workers.

To carry out surface potential measurements, a precision potentiometer is essential. Unfortunately, the author was only able to procure this instrument on loan for a short time. Preliminary tests carried out with this precision potentiometer and the apparatus as shown in Figs. 16 – 18 , showed that the arrangement to be described below was adequate.

The author feels sure that when a potentiometer is obtained, the apparatus described could give results to within 2 mv.

The arrangement generally used for measuring the surface potential, i.e., the effect of the surface film on the potential difference between the water and air, is shown diagrammatically in Fig. 15 pp. 64 .

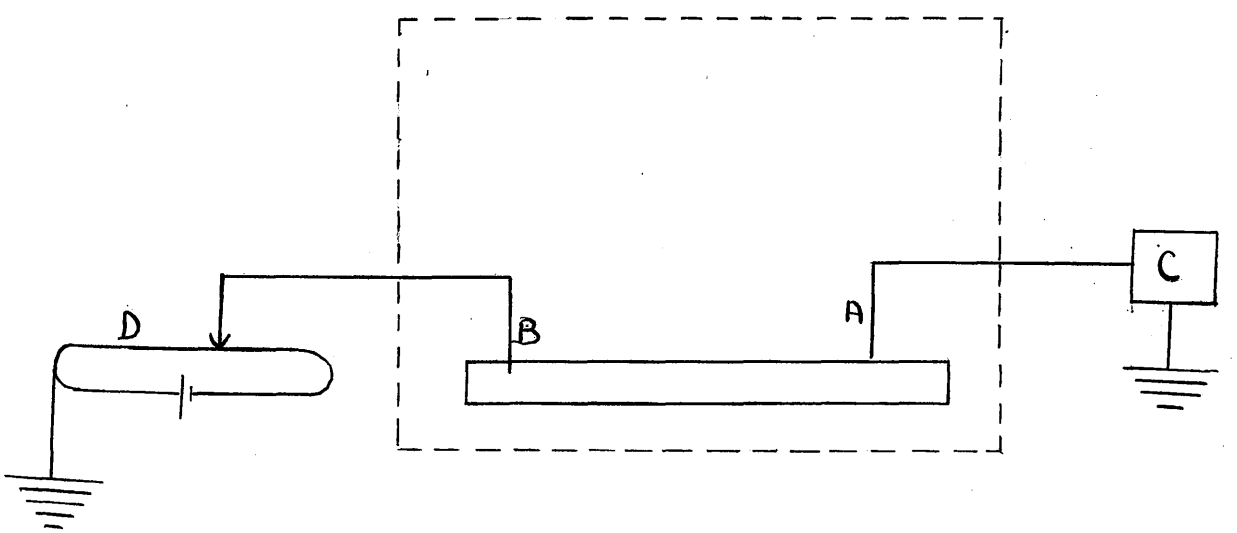


Fig. 15.

BLOCK DIAGRAM.

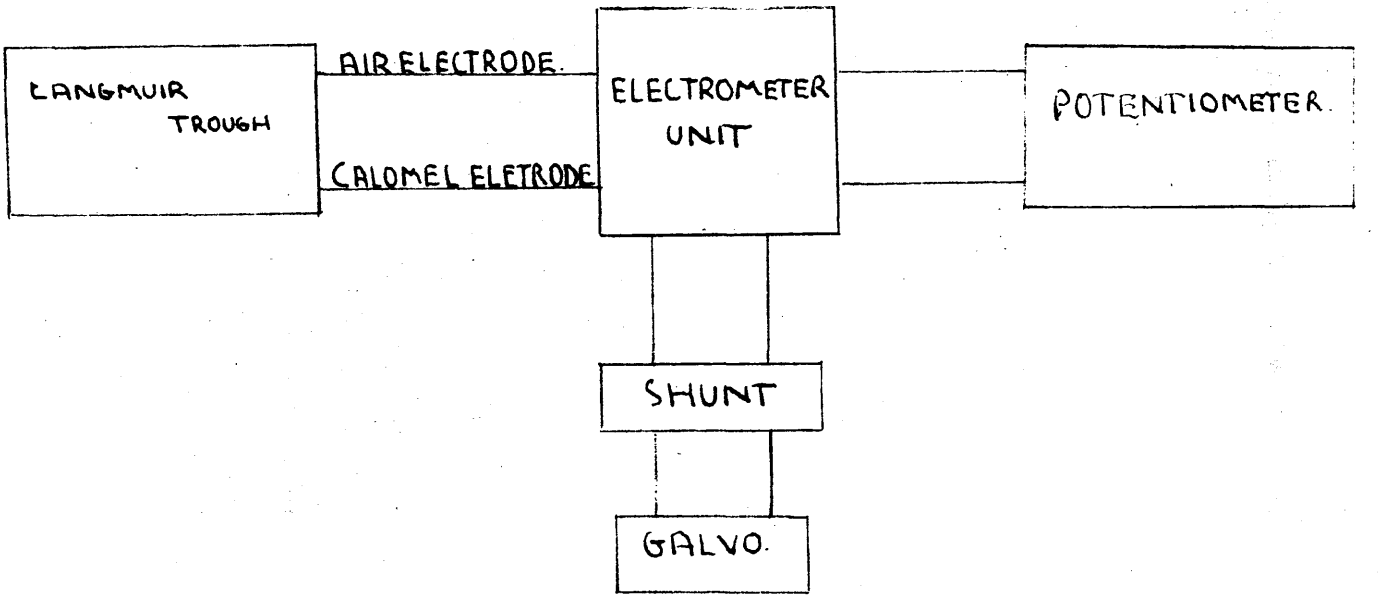


Fig 16.

(A) and (B) represent the air and calomel electrodes and (C) and (D) the electrometer unit and precision potentiometer respectively. (E) represents an earthed case.

The entire arrangement constitutes a rather complex electrolytic cell with two electrolytes, the liquid in the trough and the ionised air (see below) and three surfaces - the reversible electrode in the liquid, the air liquid surface and the surface of the air electrode. Only one of these, the air-liquid surface, can have its potential difference affected by the presence of an insoluble and non-volatile film on the liquid. Measurements of the surface potential of the film are therefore taken by first noting the emf. of the cell with the liquid surface clean, then putting on the film and noting the emf. at various areas per molecule. The difference between the emf. of the cell with a film covered surface, and the emf. with a clean surface of liquid is defined as the surface potential of the film.

Surface Potential Apparatus.

A general view is shown in Fig. 15 pp. 64 . The Line Diagram shows the various connections. (fig. 16)

The Air Electrode (A).

The electrode used is shown in Fig. 17 pp. 66 . It consists of a glass tube through the bottom of which a piece of platinum wire is fixed. The small air gap between the electrode and the water surface is rendered conducting by means of/

AIR
ELECTRODE.

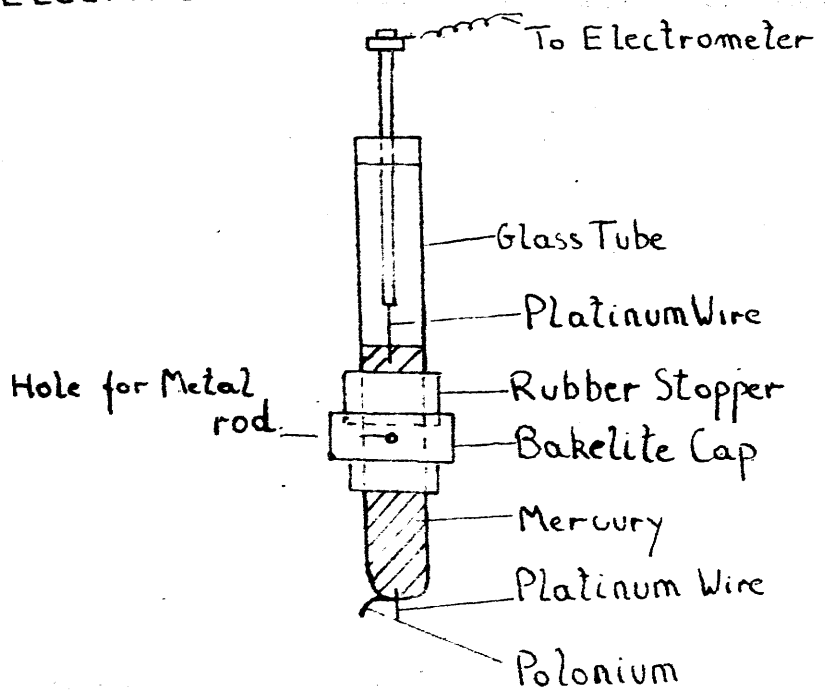


Fig. 17

of a small silver disc coated with polonium. This was glued to the bottom of the glass tube in the position indicated. An attempt was made to place the foil in such a position that the greatest concentration of alpha particles in the air gap was achieved.

It is essential to insulate the air electrode as completely as possible. This was achieved by carrying it on a perspex bridge, on which it was held in position by means of the bakelite cap and rubber stopper as is shown in the Figure. Screened co-axial cable was used to connect the electrode to the electrometer unit. This cable was further sheathed in polythene in the narrow gap between the earthed case and the electrometer unit.

The electrode could explore the surface by moving the perspex bridge. It could also be moved in a direction at right angles to this by sliding along the perspex bridge by means of a rod screwed into the bakelite cap.

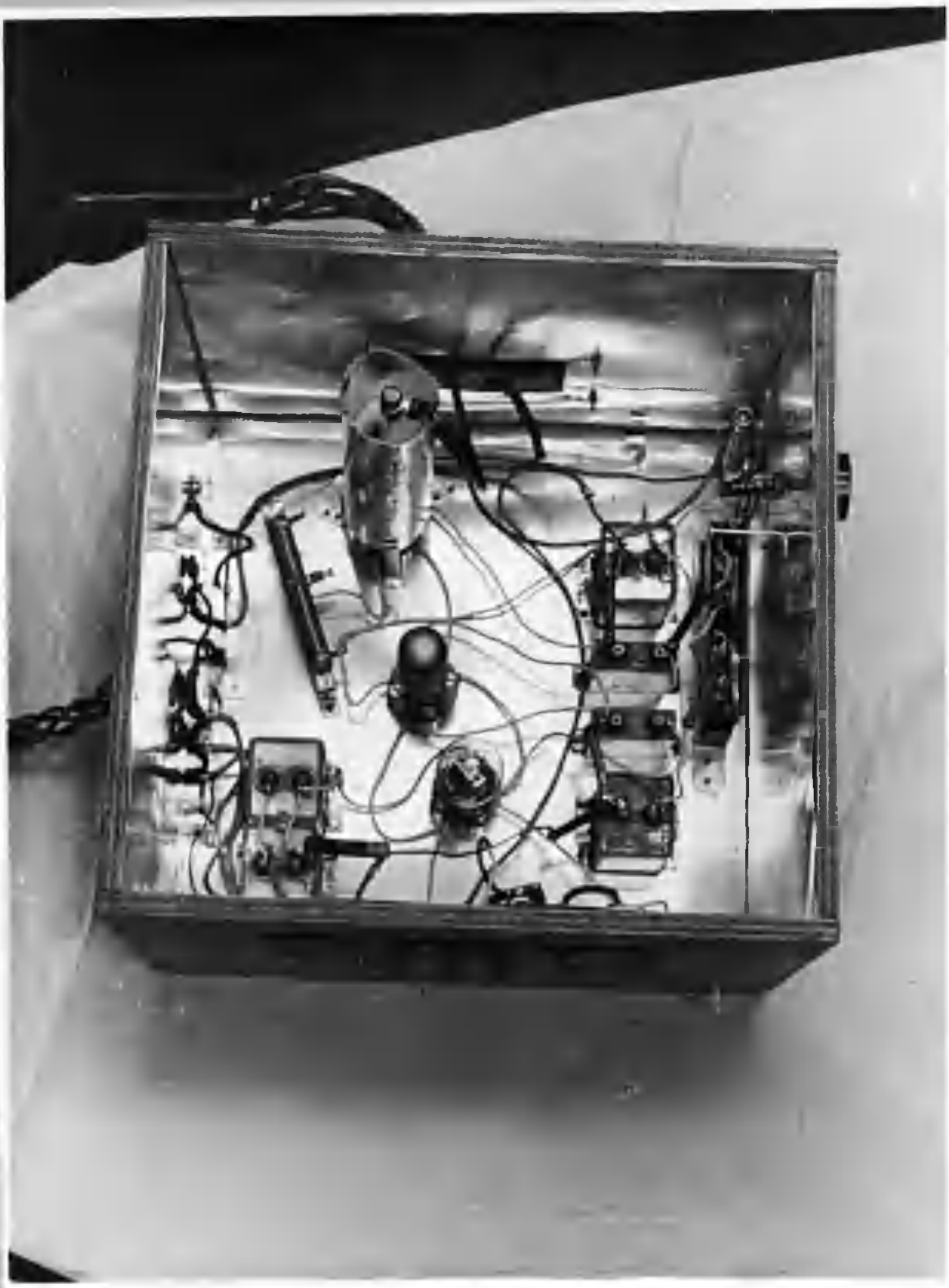
Reversible Electrode (B).

For this purpose the calomel electrode from the Marconi pH meter was employed.

Electrometer Unit (C).

This unit was constructed by the author with the kind assistance of Mr. E. Marchand, B.Sc. It consists essentially of a two-stage amplifier incorporating an electrometer triode with a high input resistance.

The/



ELECTROMETER UNIT.

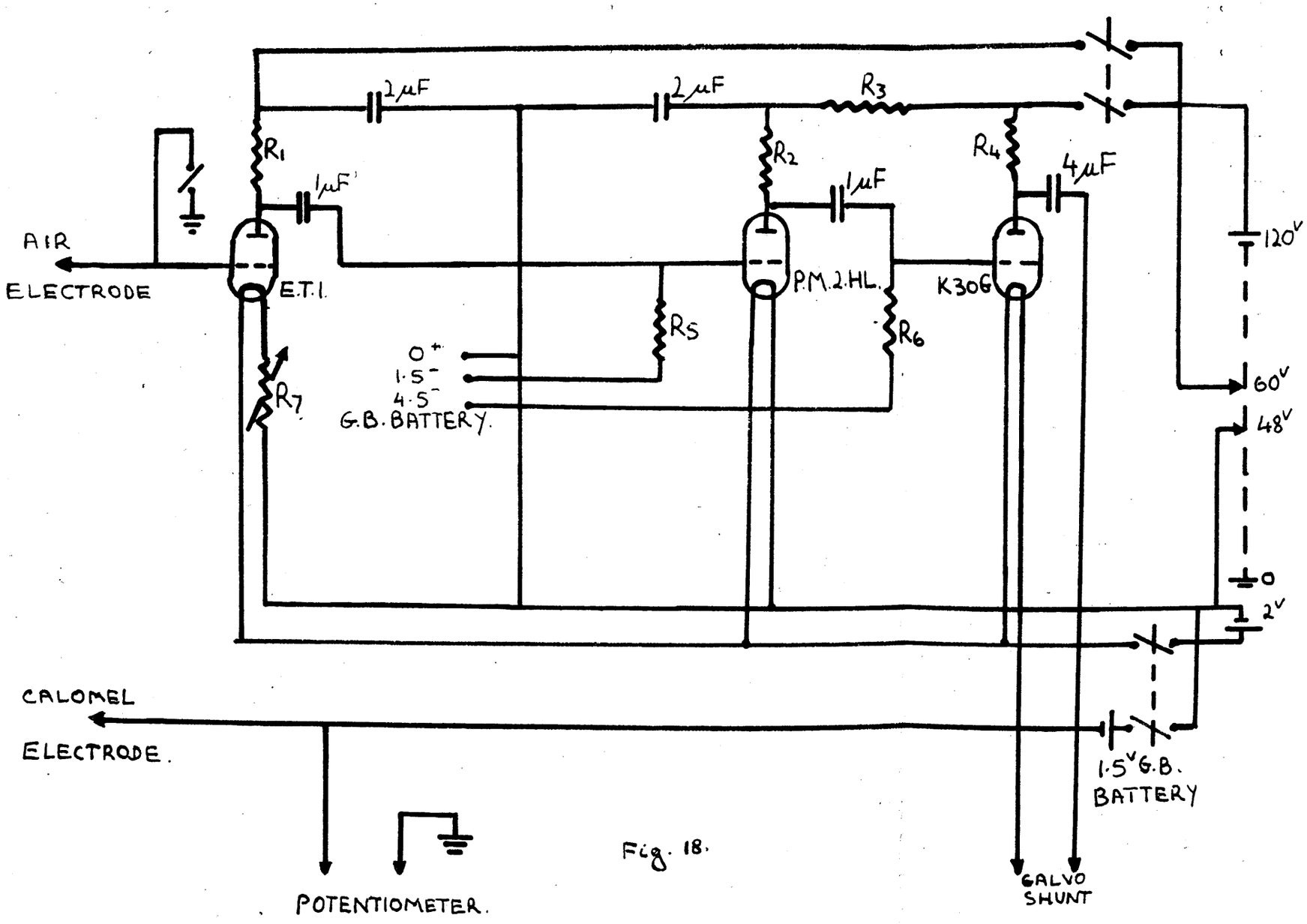


Fig. 18.

Fig. 18

COMPONENTS.

Resistances.

R_1-20,000Ω

R_2-400,000Ω

R_3-20,000Ω

R_4-20,000Ω

R_5-2MΩ

R_6-4MΩ

R_7-Variable resistor 0-12Ω

Valves.

Osram ET1

Mullard PM2HL

Ever REady K30G

Batteries.

Drydex H1006-120 volt

Drydex H1001-9 volt

Siemens Type T-15 volt

Accumulator-2 volt.

The relatively great resistance of the ionised air gap necessitates the use of an electrometer circuit. If an ordinary radio valve with a low input resistance were used, a path of low resistance would be shunted across the air gap and this would lead to erratic readings. This was found to be the case when the author attempted to use the Marconi pH meter instead of the unit described. The meter has a circuit very similar to the one described, except that the input resistance of the valve is much lower.

A circuit diagram and a list of the components employed are shown in Fig. 18 pp67 ; these latter being of ordinary radio quality. The resistors had a tolerance of 10 per cent. and the condensers were of the non-electrolytic type.

The whole unit was housed in a wooden box (28 x 28 x 29 cm.) lined with aluminium foil.

The Potentiometer (D).

As already indicated above, (p. 64) the necessary potentiometer could not be obtained. First an attempt was made to use the Marconi pH meter as a potentiometer [illegible], but this arrangement did not produce satisfactory results.

Finally, some preliminary measurements were carried out with a Tinsley No. potentiometer (See p. 64). The results obtained with this instrument gave promise of ultimate success.

The Earthed Case.

This consisted of a wooden framework covered with aluminium/

aluminium sheeting. (See Fig. 14 pp. 59). It had various slots cut in it to allow the passage of the light beam and enable the balance to be operated from the outside. The front of the case opened out.

PREPARATIVE WORK.

The nature of the work described in this thesis required that the substances used should be capable of forming surface films. The high degree of insolubility necessary for this is normally achieved by attaching a long alkyl chain to the molecule under consideration. In some cases, however, very complex substances may form surface films without having a long chain incorporated in the molecule, e.g., the proteins.

AZO COMPOUNDS.

A large number of azo dyes containing long alkyl chains have been described in the literature. (See Knight, J. Soc. Dyers and Col., 66, 34, (1950)), and several are in commercial use. The long alkyl chain generally increases the rubbing and light fastness of azo dyes. These however are all solubilised by sulphonic acid groups. Water insoluble long chain azo compounds, of the type used in the present work, do not appear to have been studied or prepared previously.

It was expected that alkylaryl-azo-compounds with at lease C_{12} chains and containing hydroxy-groups would be firm-forming. The phenolic group is sufficiently hydrophilic to lead to film formation, e.g. p-alkyl phenols with straight chains of at least 12 carbon atoms form condensed films. (Adam, Proc. Roy. Soc., A, 103, 676, (1923)); Adam, Berry and Turner, ibid, 117, 532, (1928)).

In view of the fact that the first few dyes prepared with a linear chain of 12 carbon atoms had adewuate film-forming properties and that, in addition, p-dodecylaniline was readily available, many of the dyes prepared were made using this amine. The difficulties encountered in the purification of azo dyes are well known. All of the compounds prepared were boiled up with charcoal and recrystallised repeatedly, in many cases from more than one solvent. In a few instances, final purification by chromatography was resorted to.

A description of the preparation of the azo compounds and the necessary intermediates is set out below.

p-Dodecylaniline, hexadecyl m-aminobenzoate, p-hexadecyloxyaniline.

These were supplied by Imperial Chemical Industries Ltd. (Dyestuffs Division). They were all recrystallised before use from ethanol, m.p. 34° 52° and 70° respectively.

Micro-analyses were by Drs. Weiler and Strauss, Oxford, and Dr. A. C. Syme, Royal Technical College, Glasgow. M.p.s. are uncorrected.

p-Dodecylazobenzene. This was prepared by Mill's method (J.C.S., 67, 925, (1895)) for azobenzene. Nitrosobenzene (.1 mol.) was dissolved in glacial acetic acid and then added to p-dodecylaniline (.05 mol.) dissolved in the minimum volume of glacial acetic acid. The mixture was kept for several days, with occasional shaking; red crystals of the azo-compound separated, having m.p. 72° (from acetic acid). (Found: C, 82.0; H, 9.5; N, 7.9; $C_{24}H_{34}N_2$ requires C, 82.3; H, 9.7; N, 8.0 per cent.)

4-Hexadecyloxyazobenzene. Benzeneazophenol (1 mol.) was dissolved in ethanol and refluxed for several hours with hexadecyl iodide (2 mol.) and sodium (2.1 mol.). The ether separated, after concentration, as yellow prisms (from benzene) Yield 60 per cent. (Found: C, 79.5; H, 9.7; N, 6.8; $C_{28}H_{42}ON_2$ requires C, 79.8; H, 10.0; N, 6.7 per cent.)

4'-Hexadecyloxybis(phenylazo)benzene. p-Aminoazobenzene (1 mol.) was diazotised and coupled with phenol (1 mol.) in dilute aqueous sodium hydroxide. Next morning, the precipitated bisazo-compound was recrystallised from ethanol (orange prisms, m.p. 184°) and refluxed (6 hours) with hexadecyl iodide (2 mol.) and sodium (2.1 mol.) in ethanol. The ether was separated by filtration and concentration and formed orange prisms (from benzene/

(benzene). (Found: C, 77.6; H, 8.9; N, 10.4. $C_{34}H_{46}ON_4$ requires C, 77.8 H, 8.8; N, 10.6 per cent.)

Hexadecyl p-Aminobenzoate. p-Nitrobenzoyl chloride (1 mol.) and hexadecyl alcohol (1 mol.) were refluxed for 6 hours in dry toluene, and the solvent was then removed by distillation under reduced pressure. The crude hexadecyl p-nitrobenzoate (.8 mol.) was reduced by refluxing it for 12 hours with ethanol, concentrated hydrochloric acid, water and iron dust. The product was separated by filtration followed by dilution with water.

Diazotisation. (i) p-Dochecylaniline and p-hexadecylaniline. A mixture of the base (0.05 mol.), concentrated hydrochloric acid (16 c.c.) and water (150 c.c.) was stirred for 15 minutes at 50°, then cooled to 0°, and sodium nitrite (0.51 mol.) in a little water slowly stirred in. The suspended hydrochloric dissolved to give a yellowish diazo-solution, which was filtered and used for coupling.

(ii) Hexadecyl m- and p-aminobenzoates and p-hexadecyloxyaniline. The amino-compound (0.4 mol.) was well ground with water (45 c.c.) and concentrated hydrochloric acid (6.25 cc.) 2N-Sodium nitrite solution (12.5 cc.) was slowly added and Diazotisation was complete after 30 minutes. The esters were diazotised at 5 - 10°, and the ether at 15 - 20°.

1-Hydroxyanthracene. The mixture of anthracene-1- and -2-sulphonic acids, obtained by treating anthracene (0.27 mol.) dissolved in glacial acetic acid (100 cc.) with 20 per cent./

cent. oleum (65 g.) at 95° for 5 hours (Battegay and Brandt, Bull. Soc. chim., 33, 1667, (1923)), was separated by fractional crystallisation of the sodium salts from hot water. The yield was poor.

p-Hexadecylaniline. Hexadecyl alcohol (1 mol.), aniline (1 mol.), aniline hydrochloride (0.3 mol.), and zinc chloride (0.66 mol.) were heated together at 270° for 10 hours, while the water formed was allowed to distil off, and thereafter for a further 12 hours (Coffey, Haddock, and I.C.I. Ltd., B.P. 468 226). The product, a zinc chloride double salt, was cooled, broken up, and heated for 4 hours with 50 per cent. aqueous sodium hydroxide. The oil thus formed was dissolved in ether, washed with dilute hydrochloric acid, then with water, and dried ($CaCl_2$). After the ether had been distilled off, the dry oil was distilled in vacuo; it had b.p. 240°/11 mm.

p-Hexadecyl- and p-Octadecyl-phenol. Hexadecanoyl or octadecanoyl chloride (0.1 mol.) was refluxed for 5 hours with anisole (0.1 mol.). The ketones thus obtained were subjected to Clemmensen reduction and then demethylated by boiling these products for 24 hours with hydriodic acid (8 mols.); the yield was 25 per cent.

3-Hydroxyphenanthrene. Phenanthrene (0.27mol.), recrystallised from ethanol, was stirred into concentrated sulphuric acid (32.7 c.c.), the temperature then being raised to 120-125° and kept thereat for 4 hours. The mixture was then cooled/

cooled to room temperature and carefully stirred into a large volume of cold water. Excess of sodium hydroxide was then added; phenanthrene-2-and-3-sulphonates were slowly precipitated and were separated by the difference in solubility of the barium salts (Fieser, J. Amer. Chem. Soc., 51, 2460, (1929)); the 3-sulphonate was then converted into 3-hydroxyphenanthrene by alkali fusion (Smith, J.C.S., 109, 569, (1916)); this formed colourless crystals (from ligroin), m.p. 118-119°.

Azo-compounds from Alkylaniline Derivatives. These were prepared by slowly stirring the diazonium salt solution, previously neutralised with sodium acetate, into a solution of the calculated quantity of the phenol in ice-cold dilute aqueous sodium hydroxide; the azo-compounds were crystallised from the solvents stated and dried. The p-isomers were recrystallised several times to ensure complete removal of any o-isomers (checked by chromatography on alumina).

Azo-compounds from Long-chain Alkylphenols. p-Hexadecyl- and p-octadecyl-phenol were dissolved in alcoholic sodium hydroxide, for coupling.

Azo-compounds from Hexadecyl m- and p-Aminobenzoates and p-Hexadecyloxyaniline. The diazo-compounds were coupled with o- or p-cresol or β-naphthol in aqueous sodium hydroxide solution. To couple diazotised hexadecyl m-aminobenzoate with α-naphthol, the latter was dissolved in 75 per cent. aqueous ethanol and added carefully to the diazo-solution.

p-Dodecylaniline/

p-Dodecylaniline ⟶ p-cresol. Owing to the low m.p., some difficulty was experienced in crystallising this compound which, when warmed with acetic acid, tended to form oily globules. These were removed by settling and decantation and by charcoal treatment, to enable the dissolved portion to be recrystallised: it gave small orange needles, m.p. ca. 35-40°. (Found: C, 79.0; H, 9.2; N, 7.1. $C_{25}H_{36}ON_2$ requires C, 78.9; H, 9.5; N, 7.4 per cent.)

p-Dodecylaniline ⟶ β-naphthol formed scarlet needles (from ethanol), m.p. ca. 75°. (Found: C, 80.5; H, 8.7; N, 6.7. $C_{28}H_{36}ON_2$ requires C, 80.8; H, 8.7; N, 6.7 per cent.) p-Dodecylaniline ⟶ 3-hydroxyphenanthrene formed crimson needles (from ethanol), m.p. 74°. (Found: C, 82.2; H, 8.1; N, 6.0. $C_{32}H_{38}ON_2$ requires C, 82.4; H, 8.15; N, 6.0 per cent.) p-Hexadecylaniline ⟶ β-naphthol was obtained as orange-red prisms (from glacial acetic acid), m.p. 97-98°. (Found: C, 81.1; H, 9.2; N, 6.2. $C_{32}H_{44}ON_2$ requires C, 81.1; H, 9.3; N, 5.95 per cent.), and aniline ⟶ p-hexadecylphenol as orange-yellow prisms (from glacial acetic acid and then ethanol), m.p. 84°. (Found: N, 6.5. $C_{28}H_{42}ON_2$ requires N, 6.65 per cent.) Aniline ⟶ p-octadecylphenol formed orange-yellow prisms (from glacial acetic acid and then ethanol), m.p. 87°. (Found: C, 80.1; H, 10.1; N, 6.4. $C_{30}H_{46}ON_2$ requires C, 80.0; H, 10.2; N, 6.25 per cent.), and hexadecyl m-aminobenzoate ⟶ p-cresol orange prisms (from ethanol), m.p. 82°. (Found: C, 74.8; H, 9.1; N, 5.9. $C_{30}H_{44}O_3N_2$ requires C, 75.0; H, 9.2; N, 5.9 per cent.) Hexadecyl m-aminobenzoate ⟶ β-naphthol orange/

orange prisms, m.p. 84°. (Found: C, 77.0; H, 8.9; N, 5.11. $C_{33}H_{44}O_3N_2$ requires C, 76.8; H, 8.5; N, 5.4 per cent.), and the p-amino-analogue, orange-red prisms, m.p. 80°. (Found: C, 76.5; H, 8.7; N, 5.6 per cent.), were both crystallised from ethanol. p-Hexadecyloxyaniline → p-cresol formed yellowish-orange needles (from glacial acetic acid and then ethanol, m.p. 67°. (Found: C, 77.2; H, 9.8; N, 6.5. $C_{29}H_{44}O_2N_2$ requires C, 77.0; H, 9.75; N, 6.2 per cent.), and the β-naphthol analogue formed dark red prisms (from ethanol) m.p. indef. (Found: C, 78.5; H, 9.1; N, 5.5. $C_{32}H_{44}O_2N_2$ requires C, 78.7; H, 9.0; N, 5.7 per cent.). p-Dodecylaniline → o-cresol, orange prisms, m.p. 48° (Found: C, 79.0; H, 9.9; N, 7.3. $C_{25}H_{36}O_2N_2$ requires C, 78.9; H, 9.5; N, 7.4 per cent.), and its α-naphthol analogue dark red prisms, m.p. 120° (Found: C, 80.7; H, 8.4; N, 6.5. $C_{28}H_{36}ON_2$ requires C, 80.8; H, 8.7; N, 6.7 per cent.) were both crystallised from ethanol. The 1-hydroxyanthracene analogue formed bluish-red prisms (from glacial acetic acid) m.p. 60°. (Found: C, 82.1; H, 8.4; N, 5.9. $C_{32}H_{38}ON_2$ requires C, 82.4; H, 8.2; N, 6.0 per cent.). Hexadecyl m-aminobenzoate → o-cresol formed orange-yellow prisms (from glacial acetic acid), m.p. 103°. (Found: C, 74.7; H, 9.1; N, 6.1. $C_{30}H_{44}O_3N_2$ requires C, 75.0; H, 9.2; N, 5.9 per cent.), and its α-naphthol analogue crystallised from ethanol, then purified by alumina chromatography from benzene solution containing 0.5 per cent. of ethanol/

ethanol. Two bands emerged, a small light red band, and a much larger dark red one. The small band was presumed to be the o coupled dye, while the larger red band was assumed to be the p coupled substance required. The compound was finally crystallised from ethanol; it formed dark red prisms, m.p. 90° (Found: C, 76.6; H, 8.3; N, 5.6. $C_{35}H_{44}O_3N_2$ requires C, 76.8; H, 8.55; N, 5.4 per cent). Hexadecyl p-aminobenzoate → o-cresol crystallised in orange prisms (from glacial acetic acid), m.p. 96°. (Found: C, 74.8; H, 9.5; N, 6.0. $C_{30}H_{44}O_3N_2$ requires C, 75.0; H, 9.2; N, 5.9 per cent.). p-Hexadecyloxyaniline → o-cresol formed orange prisms (from glacial acetic acid), m.p. 58°. (Found: C, 76.7; H, 10.0; N, 6.1. $C_{29}H_{44}O_2N_2$ requires C, 77.0; H, 9.75; N, 6.2 per cent.), and the α-naphthol analogue purified as dark red prisms, m.p. 108°. (Found: C, 78.6; H, 8.8; N, 5.6. $C_{32}H_{44}O_2N_2$ requires C, 78.7; H, 9.05; N, 5.75 per cent.)

o-Aminophenol → p-hexadecylphenol. o-Aminophenol (1 mol.) was diazotised by Reisenegger's method (Annalen, 221, 314, (1884)), and coupled with p-hexadecylphenol (1 mol.) in aqueous sodium hydroxide. The solutions were stirred very vigorously while being mixed, red prisms (from glacial acetic acid and ethanol successively), m.p. 84–85°. (Found: C, 76.5; H, 9.3; N, 6.2. $C_{28}H_{42}O_2N_2$ requires C, 76.0; H, 9.6; N, 6.4 per cent.).

ADDITIONAL LONG CHAIN COMPOUNDS.

In the course of the investigation it became desirable to determine whether it is possible to detect hydrogen bond formation, both with azo-compounds and other classes of dyestuffs by experiments on monolayers. In the compounds described below, various groups which were capable of and believed to be responsible for hydrogen bond formation were incorporated. Each substance contains only one type of group, thus allowing the effects to be studied separately.

N-Methylstearamide.

Methylamine hydrochloride (1.1 mol.) was suspended in dry chloroform and to this was added during 5 minutes stearoyl chloride (1 mol.) in dry chloroform at room temperature, with stirring and cooling. N-methylmorpholine (2.3 mol.) dissolved in chloroform was then added during 30 minutes. After a further hour, the solution was filtered, and washed with dilute hydrochloric acid, sodium carbonate and water successively. After drying (Na_2SO_4) the chloroform was distilled off and the residue recrystallised from alcohol, Yield 70 per cent. Colourless prisms, m.p. 91° (Found: C, 76.7; H, 12.8; N, 4.4. $C_{19}H_{39}ON$ requires C, 76.8; H, 13.1; N, 4.7 per cent.)).

This compound has been previously investigated by Mitchell (Tabulae Biologicae, 19, 292, (1939)).

N-Octadecylacetamide hydrochloride.

n-Stearamide was prepared by carefully dropping stearoyl chloride (.16 mol.) from a dropping funnel into an ice cold solution of ammonia(0.88)(Vogel "Organic Preparations," p.396, as for n-caproamide). The amide was filtered off, washed with water, and dried.

The n-stearamide (0.15 mol.) was reacted with thionyl chloride (0.3 mol.) to yield the low melting n-stearonitrile.

It was then reduced by refluxing with excess sodium in/

in ethanol for several hours. On addition of hydrochloric acid and cooling, the amine hydrochloride crystallised out. This was distilled with quicklime, the distillate warmed with acetic anhydride a few minutes, and the product crystallised from acetic acid with the aid of charcoal, m.p. 79°. (Adam and Dyer, J.C.S., 127, 70, (1925)).

N- n-Butylstearamide.

Stearoyl chloride (1 mol.) was added slowly with cooling (in ice water) to n-butylamine (1 mol.). A solid mass resulted. This was washed with dilute hydrochloric acid to remove any amine, and recrystallised from alcohol followed by ether. White needles, m.p. 70°. (Found: C, 78.2; H, 13.5; N, 4.3. $C_{21}H_{43}ON$ requires C, 77.9; H, 13.3; N, 4.1 per cent).

2-(p-Dodecylphenyl)benzoquinone.

This was prepared by Kvalnes method (J. Amer. Chem. Soc., 56, 2478, (1934)). p-Dodecylaniline (.1 mol.) was diazotised as described above, and added to a cooled, equimolar solution of benzoquinone, (purified by sublimation) in alcohol. An excess of sodium acetate was added immediately afterwards. Nitrogen was evolved, and the quinone slowly separated from the solution. Pale yellow prisms, m.p. 76°, from glacial acetic acid. Yield good. (Found: C, 81.6; H, 9.2; $C_{24}H_{32}O_2$ requires C, 81.8; H, 9.1 per cent.).

2-(p-Dodecylphenyl)hydroquinone.

2-(p-Dodecylphenyl)benzoquinone was reduced by boiling

under/

under reflux for 2 hours with zinc dust and glacial acetic acid. The red solution turned a pale yellow, and the product was then precipitated in water. Colourless prisms (from acetic acid) m.p. 80°. (Found: C, 81.6; H, 9.4; $C_{24}H_{34}O_2$ requires C, 81.4; H, 9.6 per cent.).

3-(p-Dodecylanilinomethyl)-2-naphthol.

This was obtained by the reduction of the corresponding keto-compound, prepared by dissolving 2.3-hydroxynaphthoicacid (1 mol.) in a small volume of toluene to which p-dodecylaniline (1 mol.) dissolved in toluene and phosphorous trichloride (1.4 mol.) were added. The mixture was refluxed several hours, and the product, m.p. 160°C. recrystallised from benzene and then reduced. A solution of lithium aluminium hydride (2 mol.) in 30 c.c. of ether was placed in a three necked flask fitted with a stirrer, and a solution of the acid-amide (1.8 mol.) in ether was added gradually, with stirring, to produce a gentle reflux. On completion of the reaction, water was added cautiously and the mixture was finally poured into ice and water acidified with sulphuric acid. The aqueous layer was extracted with ether, evaporated, and the product recrystallised from benzene. Colourless prisms, m.p. 114°. (Found: C, 83.7; H, 9.2. $C_{29}H_{39}ON$ requires C, 83.5; H, 9.35 per cent.).

This method was first used by Finholt and Band(J. Amer. Chem. Soc., 69, 1199, (1947)).

1-Stearamidonathraquinone.

1-aminoanthraquinone (1.0 mol.) and stearoyl chloride

(1.0/

(1.0 mol.) were dissolved in nitrobenzene and refluxed for 5 hours. (Newton and F. Bayer & Co., B.P. 3055/1909). On cooling, crystals separated from the mother liquor. Yellow needles from pyridine, m.p. 120°. (Found: C, 78.3; H, 8.7; N, 3.1. $C_{32}H_{43}O_3N$ requires C, 78.4; H, 9.0; N, 2.9 per cent.).

2-Stearamidoanthraquinone.

This was prepared as 1-stearamidoanthraquinone, using 2-aminoanthraquinone. Yellow needles from pyridine, m.p. 182°. (Found: C, 78.3; H, 9.1; N, 3.0. $C_{32}H_{43}O_3N$ requires C, 78.4; H, 9.0; N, 2.9 per cent.) The yields in both cases were practically quantitative.

2-Anthraquinonyl stearate.

A solution of stearoyl chloride (1.0 mol.) in nitrobenzene was added to a hot solution of 2-hydroxyanthraquinone (1.1 mol.) in nitrobenzene. Heating was continued for 30 minutes at 180°C. The product separated on cooling. Colourless prisms from ethanol, m.p. 85°. (Found: C, 78.6; H, 8.6; $C_{32}H_{42}O_4$ requires C, 78.4; H, 8.6 per cent.)

Stearoyl-2-(2-naphthoyl)propionate.

β-2-naphthoyl propionic acid and heptadecanol were refluxed for 2 hours in dry pyridine, and the mixture then poured into excess 2 N sulphuric acid. The precipitate was boiled in ethanol. White needles, from ethanol, m.p. 74-75°.

n-Stearyl ethyl ketone.

This was synthesised according to the method of Gilman

and/

and Nelson (Rev. Trav. chim., 55, 518, (1936)). Methylmagnesium bromide was first prepared (Hickinbottom, "Organic Compounds", p.) by reacting magnesium (0.35 mol.) with ethylbromide (0.3 mol.) in ether in the usual manner for preparing a Grignard reagent. The Grignard solution was then decanted from any unreacted magnesium. Powdered anhydrous cadmium chloride (0.16 mol.) was added gradually, with stirring, to the Grignard reagent, cooled in an ice bath, and when all the cadmium chloride had been added, the ice bath was removed and stirring continued for 1/2 hour.

Stearoyl chloride(.05 mol.) dissolved in 40 c.c. of ether was added gradually, followed by a further (0.16 mol.) of the undiluted acid chloride, and stirring was continued for an hour in the cold, and for a further 2 hours on the water bath. Crushed ice was carefully added to the flask, followed by water and sufficient dilute sulphuric acid to dissolve any white precipitate. The ether layer was separated off, washed with alkali and water, and then evaporated to dryness. The white solid residue was heated with concentrated caustic soda solution, and filtered off in the cold. It was finally washed by dissolving in ether and shaking up the ether layer with water. The solid obtained from the ether layer was recrystallised twice from ethanol, m.p. 53°.

The following reactions are involved in the preparation:

$$EtBr + Mg = EtMgBr$$

$$2EtMgBr + CdCl_2 = EtCdEt + MgBr_2 + MgCl_2$$

$$EtCdEt + 2C_{17}H_{35}COCl = 2EtCO\ C_{17}H_{35} + Cd\ Cl_2$$

Cetyl acetate.

Dry hydrochloric acid gas was bubbled through a mixture of ethyl alcohol (0.3 mol.), and glacial acetic acid (0.6 mol.). The mixture was then heated for several hours on the water bath. The acetate was isolated from the reaction mixture by a vacuum distillation. Bp. 200°, 15 mm. m.p. 22°.

Substrate.

The substrate described below was employed in dilute solution, as a substrate for surface films of several of the long-chain compounds described previously. This material is not new, but had to be synthesised as it was not readily available.

N-n-Butyl acetamide.

Acetyl chloride (1.0 mol.) was added cautiously to an ice-cold solution of n-butylamine (1.0 mol.), diluted with four times its volume of dry ether. The reacted mixture was diluted further with ether, and washed with dilute hydrochloric acid, followed by water. The ether layer was dried (Na_2SO_4). The ether was then removed on the water bath and the methyl N-n-butyl acetamide was purified by vacuum distillation.

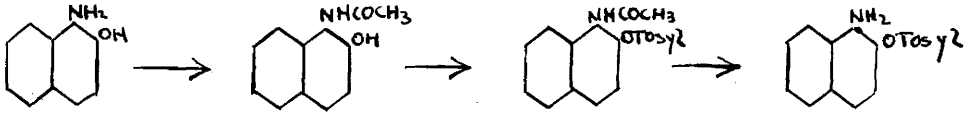
ATTEMPTED PREPARATIONS.

This section deals with attempts to prepare various types of compounds which were thought necessary for the prosecution of the research by virtue of the reasons indicated below. In several cases, suitable alternative substances more readily prepared were found later., e.g., 1-amino-2-naphthol→ p-dodecylphenol was adequately replaced by o-aminophenol→ p-hexadecylphenol.

1-Amino-2-naphthol→p-dodecylphenol.

To prepare this compound, it was sought to couple 1-amino-2-naphthol with p-dodecylphenol. Various patents describe the diazotisation of 1-amino-2-naphthol sulphonic acids (B.P.15025/1904, 10323/1906 and 7029/1906).

None of these methods, however, proved successful, as the 1-amino-2-naphthol was too rapidly oxidised by the nitrous acid. At the suggestion of Mr. A.H.Knight, (I.C.I.Limited), the following synthesis was attempted:

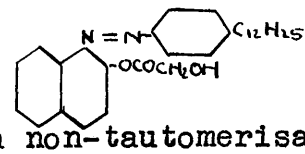


Followed by diazotisation and coupling with the long-chain phenol and subsequent removal of the tosyl radicle, 1-amino-2-naphthol was prepared by the reduction of benzene-azo-β-naphthol. (Organic Synthesis Collective. Vol.2, p.33).

1-/

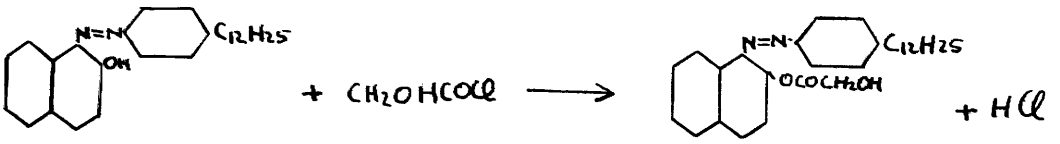
1-Acetylamino-2-naphthol was obtained by partial hydrolysis of the diacetal derivative. (Michel, Ber., 25, 3429, (1892)). The p-toluenesulphonylchloride derivative was obtained from a concentrated pyridine solution of the reactants. (Vogel, "Practical Organic Chemistry," p. 654). Removal of the acetal group was achieved by hydrolysis with 5N. hydrochloric acid containing a small amount of alcohol.

The tosyl derivative thus obtained coupled readily with β-naphthol in alkaline solution. It would hence be expected to couple with long-chain phenols, yielding an o:o'-dihydroxyazo-dye on heating with alkaline caustic soda. This synthesis was not carried through the two concluding stages as a simpler method of preparing o:o'-dihydroxyazo-dyes was found (see p. 78). It will prove a useful general method, however, of preparing o:o'-dihydroxyazo-dyes containing various aromatic nuclei. This would be desirable if it should prove necessary to compare the effect of variation in the size of aromatic nuclei on the area of surface films of these dyes.

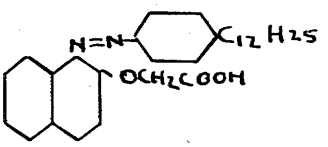


This would be a non-tautomerisable azo-dye, permanently in the azo form.

It was hoped to proceed as is shown in the equation below:



The acid chloride of glycollic acid was prepared (D.-R.P. 584,216, Chem. Zent., 3, 728, (1931)). It is very likely that such an acid chloride, if indeed capable of separate existence as is claimed, would readily react with itself forming a closed ring compound. On mixing (a) with the acid chloride, only the unchanged azo-dye was recovered. (Shown by mixed melting point).



This would constitute a surface active dye which would be in the hydroxyazo-form with no possibility of tautomerism.

β-naphthoxyacetic acid was prepared by heating equimolar quantities of β-naphthol and chloroacetic acid with caustic potash solution. (Spica, Gazzetta, 16, 441, (1886)). The β-naphthoxyacetic acid was isolated, by allowing the solution to cool when the required acid separated in an almost pure state and in large yield. (Lees and Sheddon, J.C.S., 83, 750, (1903)).

Attempts/

Attempts were made to couple this with p-dodecylaniline. All the usual coupling methods for coupling diazotised amines with phenols were attempted, but none of them produced the desired compound.

p-Dodecylaniline-α-naphthylamine-β-naphthol.

This compound would have proved useful to ascertain why certain o-hydroxyazo-compounds expand on alkali. The reason for this might be that the o-OH group does not chelate with -N=N- in water, i.e., it might bond preferentially with water. The C_{12} compound expands on alkali (pH 7), while the C_{16} compound does not. This may be due to the C_{16} chain bringing the OH-group too high above the water. This point could be proved by preparing a compound with a C_{16} chain, in which the OH-group would certainly be well below the water surface. This substance would then have the properties of a C_{12} o-hydroxyazo-compound.

As p-dodecylaniline was readily available, it was used first to save the p-hexadecylaniline, which could have been prepared in quantity had the synthesis proved successful with p-dodecylaniline. p-Dodecylaniline was coupled with α-naphthylamine. An attempt was made to further diazotise the compound thus obtained by the chloro compound method (Troeger, Arch. Pharm., 255, 161, (1917)). That this was not accomplished was not surprising, for whereas 4-benzeneazo-α-naphthylamine diazotises readily, 4-p-tolueneazo-α-naphtylamine does so only with the greatest difficulty, large amounts of water insoluble by-products being formed. (Beilstein, 16, (325)).

FADING EXPERIMENTS.

FADING EXPERIMENTS.

In the Introduction (p.4.) it has already been indicated that these experiments were of a preliminary nature. Although fading was not achieved with any of the monolayers investigated, the experimental data will however be included for future reference.

Lightfastness of Dyes Investigated.

The lightfastness of two of the dyes prepared was investigated. p-Dodecylaniline → 3-phenanthrol (an o-hydroxyazo-compound) and p-dodecylaniline → α-anthranol (a p-hydroxyazo-compound) were dyed on wool from a solution in glacial acetic acid. The samples were then faded in a mercury vapour lamp fadometer. In both cases the light fastness exceeded standard 5 (S.D.C. Light Fastness Standards).

Apparatus.

The Langmuir film balance described on p. 57 was used. To fade the monolayers, the following light sources were employed:

(A) A Mazda 250 V. 240W "Compact Source" mercury vapour lamp, clamped about 12 cm. above the water surface.

(B) The same lamp fixed outside the aluminium case, the light being focussed on the surface by means of a lantern slide projector.

(C) A small carbon arc, outside the aluminium case, viz., 22 cm. above the water surface.

(D) The same arc focussed on the surface as in (B) above.

Results/

Results Obtained.

In all cases the irradiation was carried out on monolayers occupying a surface area well beyond the critical one. It is almost certain that fading will be much more difficult on compressed monolayers.

With the Mazda lamp as in (A), no change in surface area was ascertainable when the films were irradiated for short periods of time (5-30 minutes). The irradiated films, when wiped off the surface, were still intensely coloured. When the exposure time was increased much beyond 1/2 hour, the temperature of the water rose to such an extent (to approximately 50°) as to make the observed area increases meaningless. The film, even after prolonged exposure (10 hours), still wiped off the surface highly coloured.

When the lamp was employed as in (B), the water in the trough did not heat up to any appreciable extent, but no changes in the monolayers were detected even after 18 hours exposure. Light sources (C) and (D) as described above gave no changes in the monolayer, even after prolonged exposure (24 hours).

In addition to the two azo dyes mentioned above, hexadecyl m-aminobenzoate o-cresol on water as the substrate was subjected to the fading treatments indicated above. The results were similar to those already observed.

N-Methylstearamide and p-dodecylaniline → β-naphthol monolayers on 0.1 N phenol were subjected to irradiation for various/

various periods of time. The behaviour of the monolayers was as found previously without irradiation, viz., the N-methyl-stearamide film did not alter in area, while the film of p-dodecylaniline→β-naphthol expanded considerably. On water, these monolayers again exhibited no change.

In view of the experimental evidence it must be concluded that, contrary to expectation, fading is not accelerated when the dye is spread as a monolayer, although it was expected that as the azo group is known to be at the water surface (see p. 103 below) it would be more readily accessible than when the dye is adsorbed on a fibre and hence more readily faded.

Evidently, therefore, to produce satisfactorily rapid decomposition, a very much stronger light source will have to be employed. This is in agreement with the results of Rideal and Mitchell in their work on proteins. (See p. 51). N-Methyl-stearamide, which was found to undergo slow photochemical decomposition in their apparatus was not affected by the weaker light source employed by the present author.

FORCE-AREA MEASUREMENTS ON THE LANGMUIR FILM BALANCE.

FORCE-AREA MEASUREMENTS ON THE LANGMUIR FILM BALANCE.

Force-area determinations on the film balance were carried out on the compounds, of which the synthesis has been described on p.70-85 of this thesis. The manner in which these measurements were carried out has been described on p.60-63 and requires no further comment.

The curves shown were obtained from 5-6 separate determinations on differing amounts of the film-forming substance. A set of readings was taken, and the force-area curve drawn. Generally, the points from second and subsequent determinations were also on this curve or were, at any rate, very close to it. In several cases, the curves shown were obtained by using the data obtained from two separate determinations. The curves were then extrapolated to the X-axes (molecular area $\overset{o}{A}^2$/molecule) and did not vary by more than 2 $\overset{o}{A}^2$ units/molecule over the range of the 6 determinations carried out. The slopes of the curves were practically identical in each case. The curve chosen was the one midway between the two outside limits.

This method had to be adopted since in the earlier stages of the work a great deal of inconvenience was caused by vibrations set up by an A.C. converter, and by the large amount of dust in the atmosphere of the laboratory. Macauley (J. Roy. Tech. Coll., 3, 357, (1935)), in a study of solid surfaces and boundary lubrication/

lubrication has shown that inconsistent results could be traced to impurities in the atmosphere). Frequently this led to unreliable results, so that it was often necessary to carry out far more than the stipulated number of determinations before satisfactory results were obtained.

Force-area measurements were carried out on distilled water and various other substrates as specified below. These were unbuffered 0.1 N solutions of the compounds in distilled water. The graphs shown are the usual Force-Area curves. The Tables (4-22) give the data from which these curves were plotted.

Direct Calibration of the Instrument.

As already indicated above (p.63), this had to be carried out from time to time to ensure accuracy of the readings. One specimen calculation of the determination of this sensitivity is given below.

The distance between the pan (E) and the spring (L), i.e., length of arm (F) = 5.0 cm.

The distance between spring (L) and float (A) = 2.7 cm.

This gives a ratio of 5/2.7

∴ 1 mg. placed in (E) will exert a force along float (A) given by $\frac{5}{2.7}$ = 1.85 mgm.

But length of the float (A) = 9.6 cm.

∴ 1 mgm. in the pan = $\frac{1.852}{9.8}$ = .189 mg/cm. of float (A)

= $\frac{.189 \times 980}{1000}$ = .185 dynes/cm.

Now/

Now 100 mgm. in the pan gave a deflection on the scale

$$= 15 \text{ cm.}$$

$$\therefore \quad 1 \text{ cm.} = \frac{100}{15} \text{ mgm.}$$

$$= 6.67 \text{ mgm.}$$

Since each mgm. in (E) corresponds to a pressure of .187 dynes/cm. on the float,

$$1 \text{ cm.} = 6.67 \times .185$$

$$= 1.24 \text{ dynes/cm.}$$

$$\text{or} = 1.24 \text{ dynes/scale division.}$$

Spreading of the Films.

The substances were nearly always spread from A. R. benzene, except in the cases mentioned below, when other solvents had to be resorted to owing to insolubility of the surface-active compounds in benzene.

Octadecylamine hydrochloride spread from a 1:1-mixture of benzene and ethanol. (Adam, Proc. Roy. Soc., A, 126, 526, (1930)).

1 and 2-stearorlaminoanthraquinone spread from a mixture of chloroform and benzene.

DISCUSSION OF THE RESULTS.

This section is concerned with the theoretical interpretation of the experimental results obtained. All conclusions are necessarily of a tentative nature because surface pressure measurements only were carried out.

The areas of molecules in films are best determined by means of molecular models. Adam states: "It is found that the horizontal cross-section of the rectangular parallelapiped just enclosing these molecular models is usually a close approximation to the area actually occupied by the molecules in the film; the area occupied in the film is practically never less than this. If it is much greater, the cause is usually to be found in a tilt of the molecules."

In this research models were used not only to determine the areas of the molecules and to see whether they are in agreement with the experimental values, but also to ascertain the orientation of the molecules at the water surface which would result in the molecule occupying the area found experimentally. This was done in the following manner. Two Stuart-type models of each molecule were placed flat on squared paper and oriented at different angles to a line representing the water surface, until a position was found satisfying the following requirements. The two models were just in contact, and each at the same level, oriented at the same angle relative to the surface-line. The azo- and hydroxy-groups were slightly below the surface-line (see p.103). It was found that in nearly all cases there was one such position where the repeat distance is a minimum. (p.104)

DETERMINATIONS ON WATER.

All the substances investigated had primarily to be measured on water as the substrate. The area as determined on distilled water was used as a basis for comparison when other substrates were employed. It could also be taken as a general rule that a substance which was unable to form a film on water would not be likely to form a film on any other substrate, unless this substrate was of a very special nature. (See below).

The effect of an azo-group on monolayer formation has not so far been investigated. It was therefore essential to determine whether the azo-group is strongly hydrophilic. If this had been the case, it would have had a profound effect on the orientation of the molecules in the surface. (See below). The azo-group would not then have acted as a pivot near the water surface but would have been buried deeply in the substrate. Another consequence of this would have been that the inaccessibility of the azo-group to ultra violet radiation might have given rise to additional difficulties when the fading experiments (see above) were commenced. Although the film areas and molecular orientations discussed appertain only to compressed monolayers, yet if the hydrophilic effect were great enough it might well be that even in the expanded state of the monolayer, the azo-group would be well below the water surface. Hence,

at/

Hence, at the outset of the research, the three compounds (xx), (xxi) and (xxii) were prepared.

Compound (xx) did not form a film, thus showing that one azo-group by itself is not sufficiently hydrophilic to give rise to film formation. Compound (xxi) was also non-film forming, demonstrating that an azo-group - even in conjunction with an ether grouping which might be expected to be slightly film forming by virtue of the ether oxygen (see below) - does not possess sufficient water attraction to render the substance film forming.

The fact that Compound (xxii) gives a surface film shows that the azo-group has a certain, although weak, attraction for the aqueous phase. This attraction is much less than that of the hydroxy-group, but it may be compared with that of the ether grouping.

It would seem from the probable angle of orientation to the water surface and the area occupied ( ) (Table), that the additional azo-link in the head group converts the latter into a solubilising group, thus plunging one of the azo-groups below the water surface. (Fig. 19 p. 100).

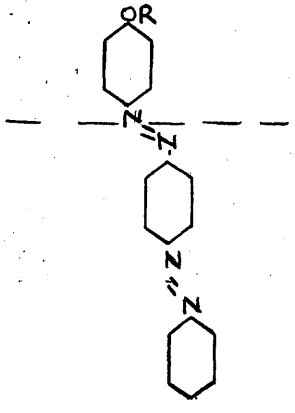


Fig. 19

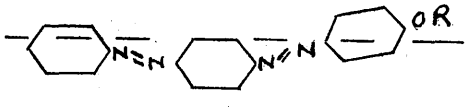


Fig. 20.

This was not what the author had expected to find. It was thought that if the azo-group had a slight anchoring effect then the two azo-groups would behave as shown (Fig.10 p.100). This would, however, have given rise to a very large increase in surface area as well as a possible expansion of the film to the gaseous state.

Cis-and Trans-Isomerism.

Azo-compounds are capable of existing in two forms. Thus, azo-benzene exhibits cis- and trans-isomerism.

(On fusion cis- azobenzene is converted into the trans-form. The separation of cis-azobenzene from irradiated solutions is normally achieved by chromatographic adsorption on an alumina column. This method has been applied successfully to other azo-compounds. (Cook, J.C.S., 876, (1938); 1309, (1939)); Zechmeister, Frehden and Jorgensen, Naturwiss., 26, 495, (1938)).

In general, the trans-form is the most stable and hence occurs most commonly.

The azo-compound investigated were all of the trans-configuration. When models were constructed, it was found that only when the trans-configuration was chosen could the area occupied by the model be reconciled with the experimental evidence.

The other azo-compounds (i), (xix), and (xxiii), have been chosen partly for the availability of the intermediate products, and partly for their suitability in showing the effect upon/

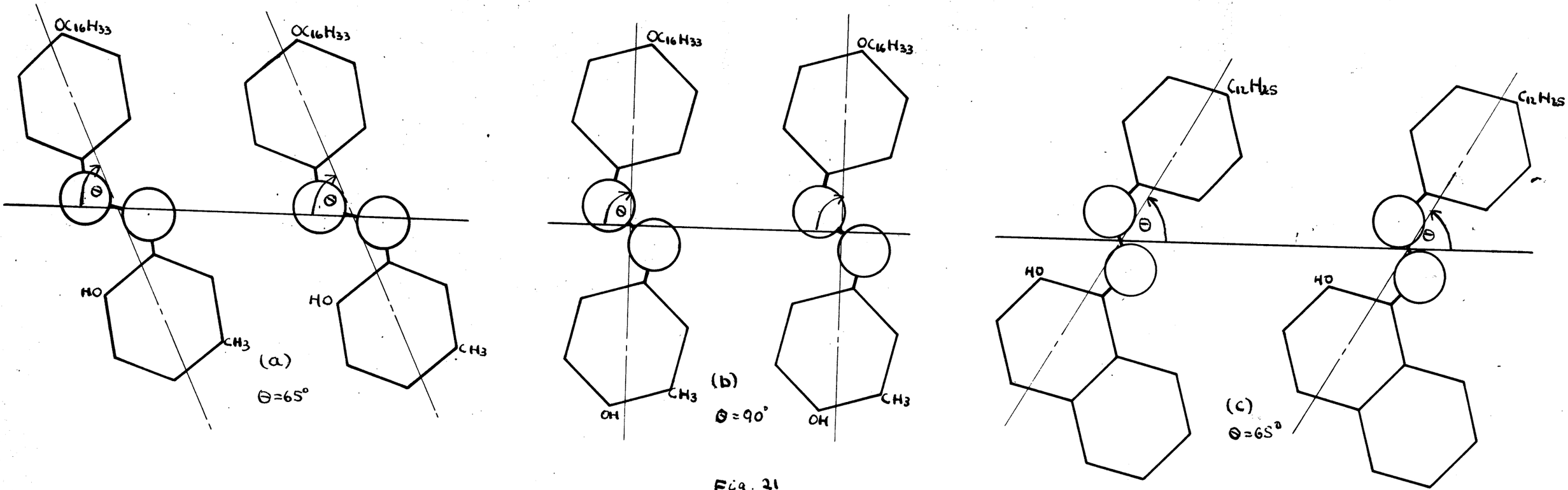

OC16H33
OC16H33
Θ
Θ
HO
HO
CH3
CH3
(a)
Θ=65°
OC16H33
OC16H33
Θ
CH3
CH3
OH
OH
(b)
Θ=90°
C12H25
C12H25
Θ
Θ
HO
HO
(c)
Θ=65°

Fig. 21

upon orientation of: (a) the length of the alkyl chain attached to one of the aromatic nuclei; (b) the presence of hydroxy-groups o- or p to the azo-group; (c) the presence of condensed ring systems in the molecule; and (d) the presence of water-attracting groups in the alkyl chain. The results are given in Tables 1, 3 and 4) and graphs 1-4.).

Adam and his co-workers (See p.) found that the long chain p-alkyl phenols in monolayers have a molecular area of about 24 $\overset{o2}{A}$, consistent with close vertical packing of the benzene rings. The areas of the compounds investigated in this work lie in the range 30-55 $\overset{o2}{A}$, and it is evident from a study of the models that in these monolayers also the molecule is so oriented that the plane of the aromatic nuclei is vertical. The molecules are thus stacked side by side like slices of toast in a rack. Whatever substituent groups may be present, the plane of the rings remains vertical, but the whole molecule may be tilted in this plane at an angle depending on the nature and relative position of the substituent groups.

In illustration, the probable orientations of pairs of molecules of three typical members of the series are shown in Fig. 21 p. 102, which is drawn to scale from the molecular models. (For simplicity, the position of the nitrogen atoms only are shown in full; the benzene rings have been drawn through the centres of the carbon atoms. These molecules are actually close-packed when oriented as shown, but owing to the omission of the full carbon and hydrogen atoms this is not immediately obvious).

The

The probable angles of orientation given in Tables 1 and 3 have all been measured from molecular models. They represent the angle to the water surface of the axis joining the two benzene nuclei lying on either side of the azo-group. (See Fig. 21 p.102).

From a survey of the results obtained by measurement on water, the following conclusions have been drawn.

AZO-COMPOUNDS.

In agreement with published information, it is found that the hydroxy-group penetrates into the aqueous phase as far as possible, consistent with structural relationships, i.e., the hydrophobic long-chains must be as far removed from the surface as possible. In some instances, it is necessary in order to satisfy structural relationships, to place the OH-group near the water surface.

From work on the models it became apparent that the azo-group, with its slight but definite attraction for the aqueous phase, lay below but close to the water surface. This has received additional confirmation from the fading experiments (p. 91). If the azo-group were above the water surface, the fading with ultra-violet radiation should have been quite rapid. The difficulties encountered with the fading are believed to be due largely to the fact that the azo-group lies below the surface, even in the expanded state of the film.

In/

In compounds having only two benzene nuclei, the azobenzene axis stands vertically to the water surface if the water attracting groups, e.g., N=N, OH, O, lie along a straight line. (Fig.21(b) p. 102). Compounds (vi), (xv) and (xvi) fall into this category.

In the benzeneazo-β-naphthol series of dyes, closest packing is achieved when the OH- group is oriented close to the water surface as shown (Fig.21(c) p. 102) All the dyes in which β-naphthol is the coupling component are in this group, viz., (ii), (xix), (viii), (xiv) and (xi).

When the water-attracting groups do not lie along a straight line (as in Fig.21(a) p. 102), the axis is usually tilted in the plane of the nuclei, as is demonstrated in Fig. 21(a). Save for a few exceptions (see below), all the remaining dyes follow this type of orientation. This group includes compounds (i), (iii), (vii), (xiii) and (ix).

The molecules appear to stand about 6 $\mathring{A}$ apart, measured in a direction at right angles to the plane of the rings. This is consistent with each molecule being separated from its neighbour by a water molecule, which could join adjacent azo-groups by means of hydrogen-bonds as shown in Fig.22 p. 104.

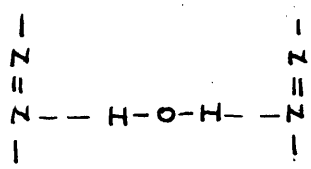
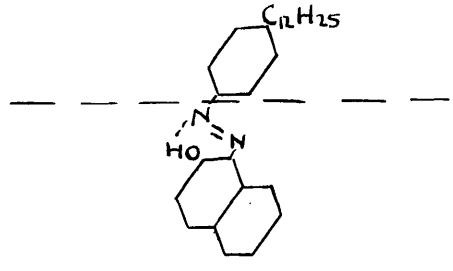


Fig. 22.

In/

In the case of an o-hydroxyazo dye, one of the azo-nitrogen atoms would be bonded intramolecularly, while the second nitrogen might not be expected to bond intermolecularly as it does not do so intramolecularly. Miss E. McLure has, however, found (B.Sc. thesis, Glasgow, 1952), by means of refractive index measurements, that the dye sulphanilic acid→β-naphthol will bond with one molecule of phenol, thus demonstrating that the second azo-nitrogen must be available for intermolecular cross-bonding.

The compounds with the long-chain alkyl benzoate group in the opposite nucleus to the hydroxy-containing group show evidence of an increased tilt due to the water attraction of the ester group. Thus, the p-azobenzoic acid esters are more tilted to the surface than the corresponding ethers or alkylbenzene compounds (e.g., compare (xii) and (xv).).



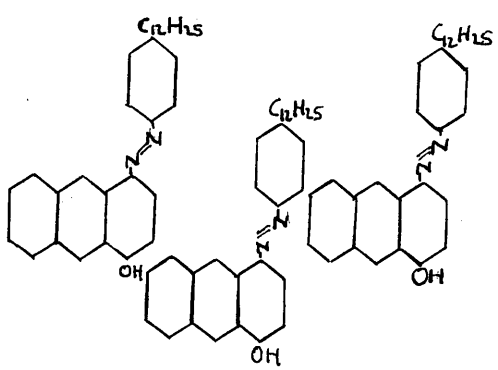
Orientation of (ii) on water.

The azo-group appears to behave as a pivot, about which the molecular axis seems to be able to rotate. The powerful tendency for the hydroxy-group on one side to be immersed as deeply/

deeply as possible in the acqueous phase is somewhat counteracted by the water-attraction of the ester group at the opposite end of the molecule, thus setting up a see-saw effect, due to the creation at opposite ends of the molecule of two hydrophilic centres. This accounts for the greater tilt with the ester group in the p-position than in the m-position, as in the former case. The greater distance of the group from the point of pivot enables it to exert a greater moment.

The Compounds (v) and (xii) should, on the above reasoning, be vertical - the relevant groups lying on a straight line while compounds (xvii) and (xviii) are vertical, although their configuration is not linear. The following explanation may account for these apparent anomalies.

Compound (v) has the short p-dodecyl chain between which adhesion is not so great as in the case of the p-hexadecyl chain. Hence, these chains tend to bend over to the water surface filling up the spaces above the molecules and assuming an inclined orientation. It may be said that the same conditions pertain to Compound (vi) where the configuration is vertical. In this case, however, it must be assumed that all the molecules do not stand in the same horizontal plane but that some are being pushed upwards to allow closer packing, with the bulky anthranol head being accommodated in the following manner:



It is therefore apparent that this compound assumes the vertical configuration in quite a different manner from, e.g., (xvi) where all the molecules lie in one horizontal plane.

Compound (xii) does not assume the vertical orientation due to the moment exerted by the hydrophilic ester grouping. (See above).

Compounds (xvii) and (xviii) are vertical for the same reasons as Compound (vi). Here again, the molecules cannot all lie in the same horizontal plane.

o:o'-hydroxy-azo dye (xxiii)

From the area occupied by this Compound, the orientation shown in Fig. 23 with $\theta = 80^{\circ}$, each molecule being separated from its neighbour by a water molecule, has been arrived at.

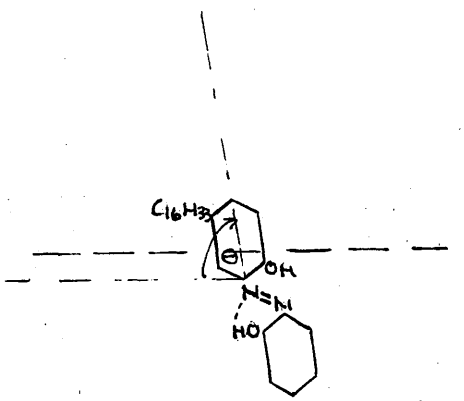


Fig. 23

Compounds Not Containing An Azo-Group.

At a later stage of the research, a group of compounds was examined which did not contain an azo group. (Compounds (xxiv), and (xxvi) (xxviii)).

Compound/

Compound (xxvi) does not form a surface film on water. This is undoubtedly due to the fact that the hydrophilic-CONH- group is prevented from penetrating the water sufficiently by virtue of the hydrocarbon groups on either side. (cf., Adam, "The Physics and Chemistry of Surfaces," 3rd Edition, Chap. 2). That the effect is purely a steric one is borne out by the fact that (xxiv) does form a surface film; apparently the methyl group is not able to prevent the -CONH-group from penetrating the surface as the butyl group does. From similar reasoning, it can be seen why (xxxiii) does not form surface films.

Compound (xxiv) undoubtedly assumes the configuration shown in Fig. 25 p. 108, with the MeCONH-group acting as the hydrophilic head group.

Compound (xxvii). Closest packing is achieved in this case when the molecule is tilted as shown in Fig. 24 p. 108. Here it is assumed that the benzene ring to which the hydrophobic alkyl chain is attached is above the water surface, as shown.

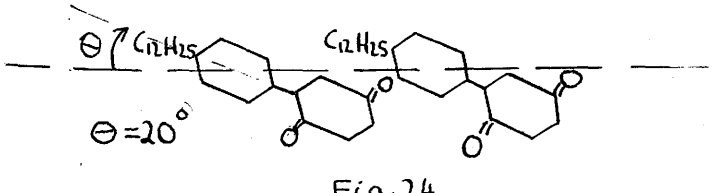


Fig. 24.

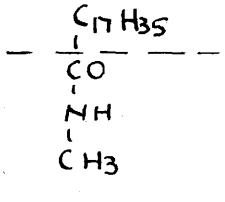


Fig. 25.

This corresponds to a repeat-distance perpendicular to the plane of the aromatic rings of 3.5-4 Å, which appears to be rather/

rather small to accommodate a bridging water molecule as postulated above for azo-compounds.

The hydroquinone derivative (xxviii) oxidises too readily in the surface film to allow reliable measurements to be made. A quinhydrone may be formed because when the film is wiped off the surface it is of a dark green colour, while the original hydroquinone is colourless. This seems an unexpected result as the oxidation must be entirely caused by the small amounts of oxygen dissolved in the distilled water. The shape of the Force-Area curve for the quinone (xxvii) would seem to exclude the possibility that at any time even one of the -OH groups of the hydrophilic ring was lying on the water surface and be liable to be attacked by atmospheric oxygen.

Compound (xxxii) appears to stand with its anthraquinone nuclei vertical, with some of the molecules forced slightly above the rest as shown (Fig.26 p.109), to assist the close packing of the quinone groups.

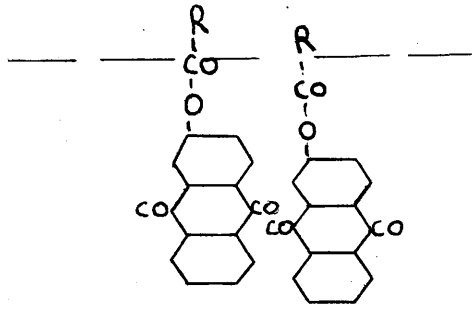


Fig.26.

The repeat distance perpendicular to the rings is thus about 4.5 A^{o}. This is greater than the value for (xxvii). The reason/

reason may well be that greater separation is required to accommodate the -O-C-O group which cannot lie in the same plane as the rings.

The water attraction of the amide group in (xxx) and (xxxi) causes a pronounced tilt (see long-chain ester azo-dyes above, p.105-106), and the molecules are probably less closely packed than in the case of Compound (xxxii). (See Fig.27 p.110)

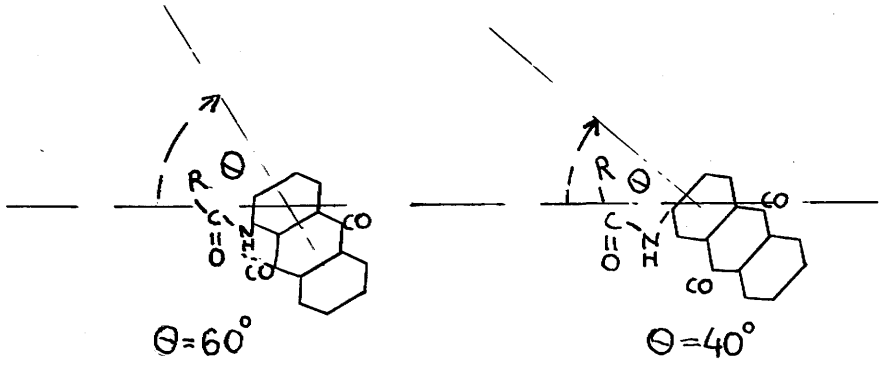


Fig. 27.

Probable Orientation of Anthraquinonoilstearamides.

That hydrogen bond formation occurs with the α and not with the β derivative is shown by the fact that the α derivative has a much lower melting point. (See p.83).

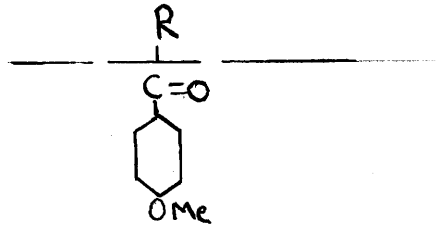
n-Stearyl ethyl ketone (xxxiv).

This compound will float in a nearly vertical position with the $>C=O$ group well submerged and several of the links of the long-chain below the water surface. As in the above case, the molecules are not as closely packed as possible owing to the interposition of water molecules.

p-Methoxy/

p-Methoxy-stearoylphenone (xxxvi).

The most strongly hydrophilic group, the OMe group, will be well submerged and the >C=O group is believed to be at or near the water surface just as the azo-group in the dyes discussed above.



p-methoxy-stearoylphenone was used to study the hydrogen bond forming properties of the C=O and OMe groups in surface films. A film of (xxxvi) was accordingly floated on water and hydroquinone (See below, p. 124). The fact that stearyl ethyl ketone (xxxiv) gave the same graphs on water and hydroquinone (Graph 17) showed that in monolayers of simple aliphatic ketones the CO group is unable to form hydrogen bonds. With aromatic ketones, however, the additional electronegativity emparted to the structure due to resonance (Pauling, Nature of the Chemical Bond, p. 287)) enables hydrogen bonds to be formed. (See Compound (xxxi), p. 127).

The increase in area of (xxxvi) on hydroquinone must be attributed to a composite effect, bonding being possible in this case both with the CO and OMe groups.

THE EFFECT OF ACID AND ALKALI ON MONOLAYERS.

The controversy regarding the structure of azo-compounds has already been dealt with. (p. 6). It has also been pointed out that the evidence is rather conflicting, the use of different solvent media appearing to give rise to different conclusions.

When investigating structural changes in monolayers, it would appear very desirable to know in what state the various substances would be expected to be. To give only one example, if the dye aniline→β-naphthol were completely in the azo-form then the fading mechanism postulated (p. 2) could not possibly take place.

The apparent molecular areas and compressibilities of selected hydroxy-azo compounds were therefore measured on acid and alkali. The film compressibility is expressed as the tangent of the angle (α), to the vertical of the upper part of the Force-area curve. The results are shown on tables 2, 6 and 7 and graphs 5-9.

In accordance with the results of earlier work (see p.6-13), the p-hydroxyazo-compounds seem to exist nearly completely in the azo-form. The o-compounds appear to contain much of the hydrazone form, but the results do not give decisive evidence of the presence or absence of the azo-tautomer, except in the case of the Compound (xxiii), which does seem to contain the azo-form.

The/

The effect of ionisation on the areas of monolayers has been stressed. (See p. 49). Unbuffered solutions (0.1N) of hydrochloric acid and sodium carbonate were employed as substrates. Buffers were not used in view of the fact that anomalous effects have been observed with them. (See p.47-50). Sodium carbonate was found to be more suitable than the hydroxide, as the latter was attacked by atmospheric carbon-dioxide. It had also been previously pointed out by Adam and Miller that some films tend to collapse on 0.1N sodiumhydroxide solution, perhaps owing to excessive solubility of the monolayer molecule.

The pH value of the sodium carbonate solution is close to the probable pK values of the compounds examined and hence, if the azo-form is present, there may be roughly equal proportions of the ionised and the un-ionised forms present in the monolayer. Marsden and Schulman, (Trans. Faraday Soc., 34, 748, (1938)), found that under these conditions the apparent molecular areas of certain fatty acids, amines and esters were at a minimum. The results of this work show in most cases a definite increase in molecular area on alkali solution as compared with water alone.

If ionisation takes place, then the hydroxy-group of the azo-form would be expected to ionise on alkaline solutions and the imino-group of the quinone might ionise on acid solutions.

Some or all of the following changes might occur in the monolayer/

monolayer if ionisation occurred at either an OH- or an NH-group:

(a) Mutual repulsion of the surface-active ions in the monolayer, leading to an increase in both apparent molecular area and compressibility.

(b) A change in the balance of forces determining the orientation of the monolayer molecules relatively to the water surface, caused by changes in solubility of the ionisable groups. Thus the -OH group should be reduced in solubility by acid and increased by alkali, and the -NH group should behave in the reverse manner. The molecular orientation might then change, and either a decrease or an increase in molecular cross-section at the water surface would take place, depending, e.g., upon the bulkiness of the under-water "head" group and the orientation of the several substituent groups. Such a change might mask, or be masked by, film expansion due to ionic repulsion, but if so, the latter would still be made evident by an increase in compressibility.

(c) Partial collapse of the shorter (C_{12}) alkyl-chain present in many of the compounds used, if ionic repulsion forces the molecules apart. Its length is so near the minimum required to form solid films that if the "head" groups are mutually repelled the chains may have insufficient cohesion to prevent partial collapse into intermolecular gaps, towards the water surface. If this occurred, the result might be an increase in film area without increase in compressibility.

(d)/

(d) In addition, the presence of alkaline solution may cause some degree of hydrolysis of the ester groups in (viii), (ix), (x) and (xii). This would lead to a decrease in film area without change in compressibility, because the azo-molecule would be replaced by a long-chain alcohol with a smaller "head" group. The following more detailed discussion of the results shows that most of them can be explained on the basis of one or more of these four effects.

As would be expected, considerable differences in behaviour were displayed by the o- and p- hydroxyazo-compounds. The effect of alkali in particular showed great differences in the two series.

o-Hydroxyazo-compounds on acid.

Compounds (i), (xix), (viii) and (xiv) show little or no increases in molecular area, but large increases in compressibility. (See Table 2.). This is probably due to ionisation and subsequent re-orientation of the molecule. These compounds are probably predominantly in the quinone form.

Compound (i) on water has configuration (Fig. 21(a) p.102) where $\theta = 45^{\circ}$. If now the solubility of the hydroxy-group is decreased on the acid substrate, the molecule would tend to assume a more vertical orientation, the azo- (or hydrazo-) group acting as a pivot, and the hydroxy-group exerting the required upward force. This substance would hence be expected to exhibit a substantial increase in compressibility.

The/

The same effect is shown by compounds (xix), (viii) and (xiv), although the effect here is not so marked, the substances all having larger head groups than (i) where it is only a benzene ring and is hence able, for the reasons indicated above, to occupy much less space on the surface.

The small compressibility change of (ii) may be due to collapse of the alkyl chain as discussed above (p.114). The larger compressibility increase of (iii) may be caused by the fact that it has a larger and hence more unsymmetrical under water head than (ii) which leaves greater intermolecular gaps at the surface.

(xvii) and (xviii) are nearly vertically oriented on water, (p.106), so that the decreased solubility of the OH-group could not cause any change in the orientation. The C_{16} chain also would not be expected to collapse, so that the observed increase in area and compressibility must be due largely to intermolecular repulsion caused by ionisation.

On Alkali. The area increases of this series, coupled with their mostly rather small increases in compression, could be accounted for by re-orientation due to decreased solubility of an -NH group in the hydrazone tautomer and they are therefore not certain evidence of the presence of an azo-form. The increase of compressibility of (i) would then be due to the greater mobility of the small "head" group, and that of (xiv) to re-orientation caused by the solubility of the ether group increasing relatively to that of the -NH group. Hydrolysis

of/

of the ester group in (viii) can account for the decreases in area and compressibility.

The evidence, however, is not decisive enough to exclude the possibility that the hydroxyazo-form is present in this series. If it is present, then the effect of alkali is evidence of an increased solubility of the hydroxy-group, which in that case is not chelated with the adjacent azo-group. In the monolayer, each molecule is in direct contact with water and thus if any azo-tautomer is present, the hydroxy-group may be prevented from bonding with the proximate azo-group by preferential linkages with water.

Compound (xix) which differs from (ii) only in having a longer alkyl chain, shows an increase in compressibility but a slight decrease in area. The differences could be explained by a re-orientation of the molecule of (xix) masking the intermolecular repulsion caused by ionisation of the hydroxy-group and a partial collapse of the alkyl chain in (ii) interfering with such a change.

The difference here evident in the behaviour of (ii) and (xix) is therefore more easily explained by assuming that a hydroxy-form is present, so that on the whole it is not possible to state that <u>no</u> hydroxy-form is present in the o-hydroxyazo-series.

The case for the view that the hydroxyazo-form is absent derives some support from the improbability of the azo-group forming/

forming preferential hydrogen bonds with water.

As already indicated above (p.105) the dye, sulphanilic acid→β-naphthol unites with one molecule of phenol in an aqueous solution of the latter. If preferential bonding occurred with water (or in this case, phenol), three molecules of the latter would combine with one of the dyestuff.

Compound (xxiii) shows a great increase in area and compressibility on alkali, evidently due to ionisation. Rather smaller changes were observed on acid. (Even if this compound were completely in the quinone-hydrazone form, one free hydroxy-group would still remain).

A study of the structure of (xxiii) and its orientation at the surface shows that the hydroxy-groups are symmetrically placed in a horizontal line on either side of the azo-group. If, therefore, the compound were completely in the azo-form, the effect of the acid substrate in reducing the solubility of the hydroxy-groups relative to that of the azo-group should cause no change in orientation or in area. The observed changes must, hence, be evidence that the substance is not wholly an azo structure.

p-Hydroxyazo-compounds. - On Acid. These compounds display very small area increases((v) in fact, decreases), and with the exception of the o-cresol compounds (ix), (xii), (xv), where re-orientation would be most expected, no appreciable increase/

increase in compressibility occurs. It would appear, therefore, that very little of the quinone hydrazone tautomer is present in this series of compounds.

On Alkali. All the compounds examined increase considerably in area, especially (xv) and (xvi), which also increase appreciably in compressibility. The small compressibility change of (ix) and (x) and their lower degree of expansion are probably due to partial hydrolysis. Compound (v) has a very large and unwieldy under-water "head" and re-orientation of this may account for the smaller change in compressibility compared with (xv) and (xvi), though it has been found difficult to demonstrate the effect on models.

The behaviour of the two p-dodecylaniline→cresol compounds may be additional evidence for the preponderance of the hydrazone form in the o-hydroxyazo-series. p-Dodecylaniline→ o-cresol, which has the hydroxy-group p- to the azo-group, is too soluble to form a film. The film-forming properties of the o-hydroxy-isomer (from p-cresol), however, might be attributed to the absence of a hydroxy-group and the consequent reduced water-solubility, or the reduced solubility might be due to chelation of the azo- and the hydroxy-group.

CONCLUSIONS.

It may hence be concluded that the water-insoluble p-hydroxyazo-compounds exist practically wholly in the azo-form, while the corresponding o-hydroxyazo-compounds contain the hydrazone form. The evidence for the presence of the azo-form in the latter series is equivocal, except for (xxiii) where the evidence is positive.

These conclusions are in general agreement with published data. It is therefore practically certain that the spreading of azo-dyes in monolayers does not affect the normal tautomeric equilibrium to any marked extent.

MOLECULAR AREAS ON PHENOLIC COMPOUNDS.

Phenols will very probably be formed when monolayers of azo-compounds are irradiated. (p. 2). It is hence important to study the interaction of these substances with surface films so as to be able to account for the area changes.

In the case above (p. 2), the area of the film would be expected to decrease considerably on irradiation. However, the fact that the final product is a phenol might lead to a much larger area than initially expected. This may become particularly evident when in the above case the long chain were attached to the dicarboxylic part of the molecule.

During the fading process, which is in most cases liable to be very slow (see p.93), the area changes which will take place due to, e.g., the interaction of a phenol with unreacted azo/

azo-compound will be better understood if the studies discussed below are considered.

The azo-group, besides acting as a chromophoric centre in the molecule, is believed to be partly responsible for adsorption on fibres by reason of hydrogen-bond formation with suitable groups, e.g., hydroxy-groups in cellulose, and the peptide link in protein fibres. (See above, p.27-28).

If the behaviour of azo-compounds on phenols could be elucidated, it would furnish an excellent method whereby the influence of the bonded substrate on the rate of photolysis could be studied.

Monolayers on Phenol.

The results are given in Tables 3, 3a and 9, and Graphs 10 and 13.

The effect of a hydrogen bond between the phenolic hydroxyl-group and an azo-nitrogen atom is sufficient to enable a stable film to be formed on phenol solutions, but the bond between the azo- and the phenol group alone is not sufficient to promote film formation. This is shown by the fact that Compound (xx) is not film-forming either on water or on phenol. Compound (xxi) however does form a film on phenol, while it will not do so on water. The only essential difference between this substance and (xx) lies in the etheric oxygen atom. It is difficult to see what effect this would have on solubility relationships, as the ether oxygen will not be at the water surface. The latter may however

modify/

modify the properties of the azo-group by an electromeric mechanism, thus causing it to be more reactive towards the phenol.

Compounds (xxvi) and (xxxiii) form no films on phenol solutions. This indicates that steric factors are preventing anchorage to the water surface as is the case when water is the substrate. (See. p.108). This inability to form films could also be said to show that the increase in solubility caused by using phenol as the substrate is insufficient to render the head group hydrophilic enough to convert the substance into a film-forming one, e.g., in the case of (xxvi) the presumed bonding of phenol to the -CONH-group (see p.30,31) is not powerful enough to overcome the effect of the hydrophobic butyl-chain.

Phenol causes a large increase in the apparent area of the o-hydroxyazo-compound (ii) but only a small increase in that of the p-hydroxy-azo-compound (xii). The p-compound is already tilted at a considerable angle (see above, p. 107), so that any further tilt which might follow a greater solubilising action upon the hydroxy-, azo- or ester groups would have little effect upon the molecular area. The observed area increase can in fact be accounted for by an additional tilt of approximately 10^{o}.

In the case of the o-hydroxyazo-compound (xii), the additional attraction of the azo- and hydroxy-groups for the aqueous phase, caused by the presence of phenol, must cause a considerable change in tilt. The observed area increase on

phenol/

phenol might be accounted for by a change in tilt of about 90°, which would allow the azo-group to be more exposed to the aqueous phase and at the same time allow the hydrophilic hydroxy-group to penetrate more deeply into the substrate.

Orientation of (ii) on (a) water; (b) phenol.

The high compressibility values of the azo-compounds on phenol solutions seems to be an indication of an increased tilt of the molecules, viz., an increase in solubility. This increased tilt could also be accounted for in the following manner. Phenol molecules could penetrate the monolayer, and on compression of the film these could be progressively displaced from the surface, where they were only loosely held within the monolayer.

(xxiv) and (xxvii) however are almost unaffected both in area and compressibility by phenol. This suggests that the film molecules are too closely packed to allow ready penetration by the phenol molecules.

From this it would also appear that the azo-group does confer very special properties on a molecule for, while substances not containing the azo-group such as (xxiv) and (xxvii) which contain acid-amide and keto-groups respectively, are unaffected, yet compounds containing the azo- and ether groups (xxi) and (xxii) and the azo and ester groups (xii) are all affected by phenol.

Monolayers on Hydroquinone.

The results are shown on graphs 11, 17, 18 and tables 3, 3a and 8

Hydroquinone causes a considerable increase in area and relative compressibility of (ii) and (xxiv), and a small expansion, with a small increase in compressibility, in the case of (xii) and (xxiii). Compounds (xxx) and (xxxi) show a small increase in area and no significant change in compressibility. Compounds (xxvii), (xxix) and (xxxii) show little change with hydroquinone as the substrate.

The considerable expansion with (ii) can be attributed to a cross-linking of the hydroxy-groups via a hydroquinone molecule, as shown in the figure; the OH-group in the 2-position on the naphthalene nucleus probably being chelated with one azo-nitrogen atom as shown, leaving one nitrogen atom free to form the intermolecular bond.

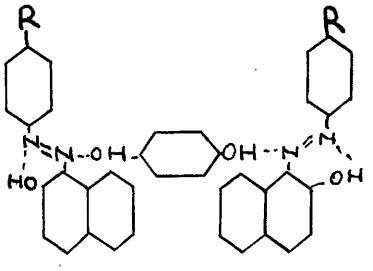


Fig. 28.

Cross linking of (ii) with hydroquinone.

The/

The increased compressibility of the film could be accounted for by the folding of the cross-links, viz., the gradual forcing of the hydroquinone molecules out of the surface film (as with phenol, see p.123). This has been confirmed by dielectric constant measurements in solutions of benzeneazo-β-naphthol and phenol, in which the existence of a 1:1-complex of the same nature as discussed above is evident. (Ogilvie, B.Sc. Thesis, Glasgow, 1952).

Hydroquinone has a much smaller effect on the molecular area and compressibility of this compound than would be expected if cross-links occurred. It is possible that hydrogen bonding does occur but that the hydroquinone molecules lie parallel with the lines of the stearamide molecules, forming a type of chain linkage rather than at right angles to them, as they would do in cross-linking.

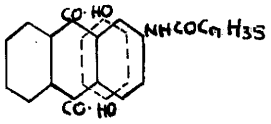
Giles, Rose and Vallance (Paper accepted for publication in J.C.S.), by means of dielectric constant measurements, have detected bonding of both CO and -NH-groups in the amide linkage by two hydroquinone molecules in parallel. If this also occurs in the monolayer then the hydroquinone molecule must lie on either side of the stearamide molecules, in a staggered formation.

The smaller expansion of (xii), (xxiii), (xxx) and (xxxi) may be accounted for by assuming that hydroquinone has no effect on monolayers of these substances, or by postulating another/

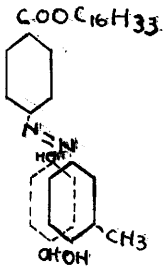
another type of complex between the hydroquinone and the compounds under consideration. A study of the structure of these molecules shows that each has a pair of groups so placed that they could simultaneously bond with the two hydroxy-groups of hydroquinone, thus giving rise to a 1:1 complex.

In Compound (ii), the azo- and the p-hydroxy-groups are the relevant pair. (Fig.28 p. 124). One o-hydroxy-group and an azo-nitrogen atom would be available for bonding in Compound (xxiii) . (Schetty has shown that in an o,o'-dihydroxyazo-compound only one hydroxy-group is chelated with an azo-nitrogen atom. Textil-Rundschau, 5, 399, (1950)). The quinones could react in a similar manner to form complexes of the quinhydrone type. From a study of the models, it is clear that in such a complex the hydroquinone molecule must lie flat against the quinone or azo-molecule and hence film expansion is much less than if cross-bonding occurred. (Figs. 28, p. 127)

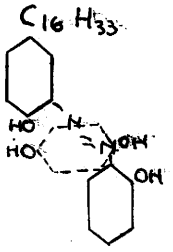
The compressibility of the quinones (xxx) and (xxxi) is slightly reduced by this complex formation, but that of the azo-compounds (xii) and (xxiii) is increased. It would therefore appear that readily ruptured cross-links must be formed in the two latter cases.



(XXXI)



(XII)



(XXIII)

Fig. 29.

1:1 Complex formation of (xxxi), (xii) and (xxiii) with hydroquinone.

Penetration of the film (xxvii) appears to be limited. Some reaction does, however, occur in this case as is shown by the deep green colour of this film when it is wiped off the hydroquinone solution (quinhydrone formation).

Virtually no penetration occurs with (xxxii), presumably due to the close packing of the molecules. This is confirmed by the fact that the probable angle oforientation of (xxxii) on water is 90°, while Compound (xxvii), films of which do appear to be slightly affected, has an orientation angle of 80°.

MONOLAYERS ON SOLUTIONS OF POLYHYDROXY COMPOUNDS OF LARGE MOLECULAR SIZE.

1:5-Dihydroxynaphthalene.

1:5-Dihydroxynaphthalene produces great increases both in area and compressibility of films of (ii), (xii), (xxiv) and (xxx). This must be due to cross-linking of two molecules of the film by one molecule of the phenol, (Fig. 28 p. 124), in much the same manner as with hydroquinone. Compound (xxxii) is also almost unaffected (cf. on hydroquinone, p. 124). The small increases produced in area and compressibility may be due to a limited degree of cross-linking. Another, although less probable cause of the area increase might be that 1:1-complex formation occurs across the ester group and the most remote quinone group.

1:2:4:5:6:8-Hexa-hydroxyanthraquinone-3:7:disodium-sulphonate.

A greater expansion even than with the 1:5-dihydroxy-naphthalene should be produced by the above compound, which has phenolic hydroxy-groups still more widely separated in the molecule.

The expected large increases in area and compressibility of Compounds (ii) and (xii) were observed. The only conclusion that can be drawn from this is that the bonding occurs, as with 1:5-dihydroxynaphthalene, across two hydroxy-groups situated far apart, e.g., the 1:6 hydroxy-groups.

No satisfactory explanation can be advanced to show why bonding should not take place across two hydroxy-groups situated more/

more closely together (e.g., the 1:4-hydroxy-groups). In this case, area increases would still be larger than with 1:5-dihydroxynaphthalene, but the differences would not be so marked.

The area of (ii) and (xii) may, however, increase on acid solution. With the former, the increase is quite considerable (see table 2.). The combined effect of the slight acidity and the size of the molecule may change the film from a solid to a liquid expanded type (see above, p. 47). This may also account for the large slope of the graphs.

Monolayers on Ethylene Glycol.

Films of Compounds (xxvii) and (xxxii) appear to be too closely packed to allow the ethylene glycol to penetrate. The latter probably produces an increased tilt in the molecules of the azo compounds (xii), and the stearamidoanthraquinone (xxx), by increasing the solubility of the hydroxy- and the ester groups.

The large area and compressibility increase of azo-compound (ii) indicate that in this case a certain amount of cross-linkage, which largely folds up on compression, occurs.

Monolayers on Catechol Solution.

The results are given in Tables 3, 3a and 13 and graph 16.

The large increases in area and compressibility of (ii) show that cross-linking is taking place. (Fig. 30 p. 130)

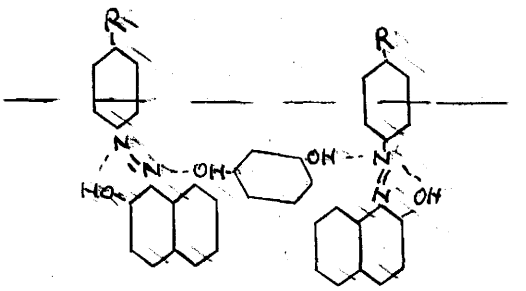


Fig. 30.

Compound (xii) increases considerably in compressibility, but the increase in area is small. This indicates that re-orientation occurs due most probably to a change in the relative solubility of the ester group in the molecule. This may mask any increase in film area which would otherwise occur.

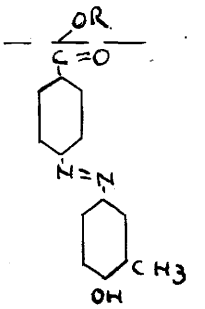


Fig. 31.

This increase in solubility may cause the molecule to become much more submerged, as shown in Fig. 31 p. 130 . The area/

area increases caused by the interposition of the catechol would then be masked, the film molecules fitting closer together (as for Compounds (xxiv) and (xxvii), p.).

Monolayers on Pyridine.

The results are given in Tables 3, 3a and 11 and on Graphs 16 and 17.

This was an essential part of the investigation in that it gave a means of confirming that the effects shown above are actually due to a bonding between the film molecule and the solute (viz., hydrogen bonding) and not merely to a penetration of the film by molecules of the latter. If hydrogen bonding alone is responsible for the increases in the apparent molecular area and compressibility of e.g., (ii), produced by hydroquinone, then the films of this substance on pyridine solution should have the same characteristics as on water, for if the hydroxy group in (ii) is chelated with one of the nitrogen atoms in the azo-group, none is left capable of forming a hydrogen bond with pyridine. This furnishes additional evidence of chelation in Compound (ii).

The data show that pyridine has in fact no significant effect on the areas of films of (ii) or of (xxii). There is only a small increase in compressibility.

With a compound such as (xii), which has a free hydroxy-group, pyridine increases the compressibility, but slightly decreases the molecular area. These effects can be attributed to bonding between the solute and the hydroxy-group in the film molecule/

molecule. This would cause increased solubility of the latter and possibly a consequent change in orientation.

CONCLUSION.

It may be concluded from the above that if compounds containing hydroxy-groups are produced on irradiation of monolayers of azo-compounds, then this will lead to an expansion of the monolayer, at any rate during the period in which any of the original material is still present. Expansion will not occur if the molecules are too tightly packed to allow penetration of the solute, viz., when the probable angle of orientation on water is about 90°.

If the solute (or split-product) is a monohydric compound, the effect is to increase the attraction of the film-forming substance for water, often with a change in the orientation of the molecules in the monolayer and an expansion of the film.

Solutes (or split-products) having two hydroxy-groups, may utilise both of these in forming bonds with suitable groups in the monolayer molecule. This they may do in either of two ways:

(a) They may form cross-links between the two monolayer molecules, thus considerably expanding the film and increasing its compressibility, or,

(b) If the two hydroxy-groups in the solute or reaction product are at a distance apart corresponding with that of two hydrogen-bonding groups in the monolayer molecule, they may form a 1:1 molar complex with the latter, in which the two molecules are/

are flat-packed side by side. The film is then only slightly expanded and its compressibility may be somewhat reduced.

These conclusions are also valid for the quinone and amide groups, with which similar experiments were carried out. The importance of the latter lies in the fact that this group occurs in protein fibres. It was interesting to be able to confirm that the bond-forming properties of this group can also be detected by the film balance method. Further work in connection with this and the dye fibre bond mechanism will be discussed below. (p. 135).

The bond in all cases is the hydrogen bond, the effects recorded being in no case due to simple penetration of the film by solute molecules. This was confirmed by the use of pyridine.

It has been shown (p. 51) that extremely minute traces of substances dissolved in the substrate can have very marked effects on monolayer characteristics. In several cases, experiments on acid and alkali were carried out on 1N solution instead of the usual 0.1N. The observed effects were as expected for the 0.1N solutions. There is hence no reason to believe that the above mechanism would be invalidated in irradiation experiments, because the amounts of material involved would be very small. At any rate, concentration of the solute is generally greater at the surface than in the body of the solution and as these substances are formed at the surface there may well be little or no tendency for them to diffuse into the bulk of the solution.

EXPERIMENTS USING GLUCOSE, GLYCINE AND N-n-BUTYL-ACETAMIDE AS SUBSTRATES.

These experiments were performed to determine whether it would be possible, by using the film balance technique, to add to the knowledge of the dye/fibre bond. Present day views on this subject have been discussed above (p.24-31), and it is seen that the concept of the hydrogen bond plays a predominant role in this field, as in many others.

Glucose.

This is the basic building unit of the cellulosic fibres (see p.25). The results are given in graphs 20-22 and tables 17, 19, 20 and 21.

As was expected, Compounds (xxx), (xxvii), (xv) and (ii) all increased in area when glucose was used as the substrate. The fact that (xv), which has a vertically oriented and tightly-packed film, also increases in area indicates a very strong tendency to form cross-hydrogen bonds. On compression, these bonds will be mostly disrupted, but residual bonds, coupled with the increases solubility caused by the glucose, will result in an increase in area.

Glycine.*

The area of (ii) is not altered but it increases in compressibility. It is therefore possible that the increased solubility caused by the glycine results in a re-orientation of the molecule, thus masking any area increase. Similar reasoning applies in the case of (xxx) which does not increase in area but only/

(* For results see graphs 20-22 and tables 17 and 19-21)

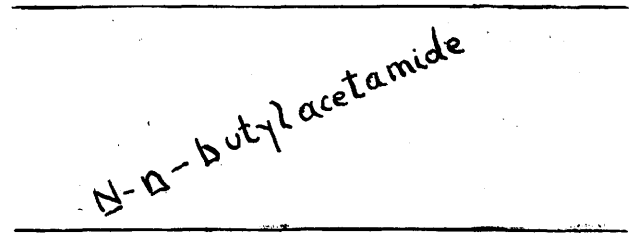
only in compressibility.

Compounds (xxvii) and (xv) do show an area increase. This suggests that the internally-chelated azo-group and the >C=O group in the quinone ring are more powerful hydrogen-bonding agents in monolayers than chelated azo-groups, as in (ii), or a normal C=O group in an alkyl-chain. The -NHCO- of (xxx) does not appear to be active, due to chelation (see above, p.).

In the case of Compound (xxvii), the high relative increase in area coupled with the low compressibility could be interpreted as permanent cross-bonding between the CO groups and the $-NH_2$ and -COOH groups of the glycine molecule. With (xv) the rather smaller area increase and the large rise in compressibility indicates increases solubility accompanied by re-orientation.

N-n-Butylacetamide.

This gave fairly large increases both in area and compressibility in all cases. It is probable that the N-n-butyl-acetamide loosely links two of the monolayer molecules lying between them, thus:



The link being able to fold up as the pressure is increased.

From/

From the above, it may be concluded that the -CONH- group which occurs in the protein fibres has a very powerful tendency to form hydrogen bonds, being able to break down the internal chelation of the OH- to the azo-group, which the $-NH_2$ and -COOH groups, separated as in the glycine molecule, do not appear capable of doing.

From a comparison of the areas, it can be said that the -CONH group is at least as effective a bonding agent as the OH-group. The CO group, however, appears only to bond with the separated CO and $-NH_2$ groups, as in glycine, when it is activated in a quinone ring.

The Effect of pH on the Dye-to-Fibre Bond.

From the above (p.28), it is evident that the mechanism of the dye to fibre link in wool is considred to be an ionic link, strengthened by hydrogen bonding. Peters (J. Soc. Dyers and Col., 61, 95, (1945)) advanced the following theory for the wool fibres:

When wool is placed in an acid solution, hydrogen ions enter the fibre and repress the ionisation of the carboxyl groups, thus enabling dye anions to combine with the ammonium groups. Saturation of the fibre would be reached when all the carboxyl groups are un-ionised and dye ions are attached to an equivalent amount of ammonium groups.

Experiments were carried out to confirm these current ideas, using the substances and techniques described above.

N-Methyl/

N-Methylstearamide (xxv).

This compound was chosen as it incorporates the -CONH- group, so important in protein fibres. The molecule is also very simple, thus permitting the study of this group alone, which is not often possible in actual fibres except perhaps in the case of nylon.

The results are given in the Table 16 and Graph 18

2-Nitro-naphthalene-4:8-disulphonic acid at pH 4.4 increases the area. This must be due to a limited amount of cross-bonding and to an increased solubility in the substrate.

At the lower pH of 1.45 the power of the -CONH-group to form hydrogen bonds is increased, and the disulphonic acid may be able to form cross-links. The compressibility of the monolayer also increases, which is as expected, the comparatively weak link being able to fold up like a joiner's rule. (See above, p. 136).

1:4-diaminoanthraquinone-2-sodiumsulphonate also increases the molecular area but to the same extent at both high and low pH values. The area increase is also of the same numerical order as in the case of the disulphonic acid at pH 4.4. This indicates that this area increase, which in this case cannot be due to cross-bonding, must be a simple extra-solubilising effect.

The effect of hydroquinone on this compound has already been discussed. Acidification did not alter the curve. It seems probable/

probable that OH-groups can bond with either the CO or -NH group of the -CONH-grouping, as is shown above (p.), over a wide range of pH.

These experiments hence confirm in a quantitative manner that the bonding of sulphonic groups with acid-amide groups is sensitive to pH changes. Bonding of the -OH-group appears to be unaffected.

Stearylaminehydrochloride (xxxvii).

This compound was investigated on the monosulphonic acid in the same manner (see p. 138). It was hoped to be able to elucidate further the effect of acidity on the hydrogen bonding power of the $-NH_2$ group by the Langmuir film technique.

The area increases, which were large, were all found to lie in the same region. (Adam, Proc. Roy. Soc., A. 126, 526, (1930)) points out that the area increases of this substance on acid substrates depend not so much on the acidity of the latter as on its nature, e.g., the areas obtained on a phthalate buffer of pH 4 were entirely different from those obtained on an acetate buffer of the same pH. Adam believes that in these cases amine phthalates and acetates are formed. This is likely to have occurred with the sulphonic acid, otherwise the pH change would have caused a larger change in the area.

Cetyl Acetate (xxxv).

The substantivity of dyes on acetate-rayon is almost exclusively explained on the basis of hydrogen bonding, which is supposed to take place between the dye molecule and the O-C-O group/

group (see above, p.30). Cetyl acetate was employed in a series of experiments to study this bonding, because it was the simplest long chain compound containing the required group. The results obtained are given in table 15 and graphs 23 and 24. These show that in all cases where hydrogen bonding is possible, the area increases are large.

The cross-bonding effect observed with the disulphonic acid (p.138) was confirmed. Cetyl acetate increases greatly in area on the disulphonic acid, while on the monosulphonic acid it is almost unaffected.

Orange I and Acid Magenta, with both of which cross-bonding is possible, give rise to large area and compressibility increases.

Crystal Violet, which has no group in its molecule which could form a hydrogen bond, does not give an increase in area. The compressibility increase is most probably due to the large substrate molecules penetrating the surface to be subsequently forced out of the monolayer when the film is compressed.

On 1:5-dihydroxynaphthalene, with which hydrogen bonding is also possible, the area does not increase to the same extent as in the other cases. The other substrates used, however, all contained the sulphonic group. It seems likely, therefore, that in monolayers a compound containing an ester group will form the strongest hydrogen bonds with molecules containing the sulphonic group. The large compressibility may also indicate a folding up of the cross-links.

SUMMARY.

This section of the work has served to demonstrate that the hydrogen bonding which is believed to be responsible for the dye-to-fibre link also occurs when long chain substances containing these groups are floated on selected substrates.

The interdependence of pH and hydrogen bonding power has also been confirmed.

When the irradiation technique has been perfected, these experiments will furnish a useful means whereby the breakdown of the dye-to-fibre link on irradiation (viz., fading) can be studied.

****

LIST OF COMPOUNDS EMPLOYED IN THIS THESIS.

The following constitutes a list of all compounds utilised in this research work. The numbers given in the text refer to those given below. Those compounds marked with an asterisk have been previously prepared.

(i) p-Dodecylaniline → p-cresol.

(ii) " β-naphthol.

(iii) " 3-phenanthrol.

(iv) " o-cresol.

(v) " α-naphthol.

(vi) " α-anthranol.

(vii) Hexadecyl m-aminobenzoate → p-cresol.

(viii) " β-naphthol.

(ix) " o-cresol.

(x) " α-naphthol.

(xi) Hexadecyl p-aminobenzoate → β-naphthol.

(xii) Hexadecyl p-aminobenzoate → o-cresol.

(xiii) p-Hexadecyloxyaniline → p-cresol.

(xiv) " β-naphthol.

(xv) " o-cresol.

(xvi) " α-naphthol.

(xvii) Aniline → p-hexadecylphenol.

(xviii) " p-octadecylphenol.

(xix) p-Hexadecylaniline → β-naphthol.

(xx) p-Dodecylazobenzene.

(xxi)/

(xxi) 4-Hexadecyloxyazobenzene.

(xxii) 4'-Hexadecyloxybis(phenylazo) benzene.

(xxiii) o-Aminophenyl→ p-hexadecylphenol.

(xxiv) N-Methylstearamide.

(xxv) N-Octadecylacetamide hydrochloride.

(xxvi) N-n-Butylstearamide.

(xxvii) 2-(p-Dodecylphenyl)benzoquinone.

(xxviii) 2-(p-Dodecylphenyl)hydroquinone.

(xxix) 3-(p-Dodecylanilinomethyl)-2-naphthol.

(xxx) 1-Stearamidoanthraquinone.

(xxxi) 2-Stearamidoanthraquinone.

(xxxii) 2-Anthraquinonylstearate.

(xxxiii) Stearoyl-2(2-naphthoyl)propionate.

(xxxiv) n-Stearyl ethyl ketone. *

(xxxv) Cetyl acetate. *

(xxxvi) p-Methoxy-stearoylphenone. *

(xxxvii) Stearylamine hydrochloride. *

* Compounds previously prepared.

Table 1.

Molecular Areas and Orientation angles

Compound	Limiting Area (A^{o2})	Area at zero compression (A^{o2})*	Probable angle of orientation to water surface.
Azo-Compounds without hydroxy-groups			
(xx)	No film formed		
(xxi)	No film formed		
(xxii)	48	38	90°
o-Hydroxyazo-compounds			
(i)	49	44.5	45°
(ii)	45	42.5	60°
(iii)	51	50	65°
(xix)	46	44.5	60°
(xvii)	33	32	90°
(xviii)	33	32	90°
(vii)	59	55	80°
(viii)	60	57	55°
(xi)	41.5	41	45°
(xiii)	37	35.5	65°
(xiv)	39	38	55°
p-Hydroxyazo-compounds			
(iv)	No film formed.		
(v)	48	48	70°
(vi)	ca. 46	41	90°
(ix)	63	53	60°
(x)	77	55	60°
(xii)	45	44	50°
(xv)	37	36	90°
(xvi)	47	38	90°

* Extrapolated value.

Table 2.

Effect of acid and alkali compressibilities and apparent molecular areas of hydroxyazo-compounds in monolayers.

Compound.	Apparent molecular area at zero compression(A^{o2}) and compressibility($\tan\alpha$)** on:						ΔA^{o2}(%) and $\Delta \tan\alpha$			
	Water		0.1N-HCl		0.1N-Na_2CO_2		0.1N-HCl		0.1N-Na_2CO_3	
	$\theta^{\S}$	A^{o2} $\tan\alpha$	A^{o2}	$\tan\alpha$	A^{o2}	$\tan\alpha$	ΔA^{o2}(%)	$\Delta\tan\alpha$	ΔA^{o2}(%)	$\Delta\tan\alpha$
o-Hydroxyazo-compounds.										
(i)	45°	44.5 0.11	44	0.97	51	0.33	0	0.86	15	0.22
(ii)	60	42.5 0.16	53	0.25	58	0.21	24	0.09	36	0.05
(iii)	65	50 0.23	59	0.53	55	0.18	18	0.30	10	-0.05
(xix)	60	44.5 0.05	43	0.65	44	0.33	-4	0.60	-1	0.28
(xvii)	90	32 0.07	40	0.27	36	0.09	25	0.20	12	0.02
(xviii)	90	32 0.07	40	0.27	36	0.09	25	0.20	12	0.02
(viii)	55	57 0.28	57	0.43	56	0.21	0	0.15	-2	-0.07
(xi)	55	38 0.05	39	0.21	41	0.19	2.5	0.16	8	0.14
o:o'-Dihydroxyazo-compound.										
(xxiii)	80	47 0.09	47	0.19	70	0.43	0	0.10	49	0.34
p-Hydroxyazo-compounds.										
(vi)*	90(?)	41 0.07	40	0.11	75	0.18	-3	0.04	83	0.11
(ix)	60	53 0.25	56	0.45	68	0.33	6	0.20	28	0.08
(x)	60	55 0.36	56	0.23	82	0.40	2	-0.13	49	0.04
(xii)	50	44 0.09	46	0.51	-	-	5	0.42	-	-
(xv)	90(?)	36 0.07	37	0.40	65	0.49	2.5	0.33	80	0.42
(xvi)	90(?)	38 0.18	41	0.25	75	0.36	8	0.07	97	0.18

* The data for this compound were obtained on 1N-solutions of HCl and Na_2CO_3.

** Where α is the deviation from the vertical of the upper portion of the F/A curves in Figs. 5-9.

§ Where θ is the probable orientation angle on water alone.

Table 3.

Compound.	Probable angle of orientation on water of Longest aromatic axis	Molecular area (A^{02}) at zero compression and (in brackets) compressibility[5] on ** 0.1N aqueous solution of						
		Water alone	a	b	c	d	e	f	g
(xx)			no film formed						
		Azo-compounds without hydroxy-groups.							
(xxi)	70 *	no film formed	37.0 (0.23)						
(xxii)	90°	38.0 (0.13)	48.0 (0.36)						
		o-Hydroxy-azo-compound							
(ii)	60°	42.5 (0.16)	102.0 (0.42)	113.0 (0.42)	152.0 (1.23)	198.0 (1.33)	44.0 (0.12)	80.0 (0.29)	110.0 (0.38)
		p-Hydroxyazo-compound							
(xii)	50°	44.0 (0.09)	51.0 (0.40)	52.0 (0.19)	122.0 (0.65)	175.0 (1.23)	42.0 (1.29)	48.0 (0.12)	50.0 (0.30)
		o:o'-Dihydroxyazo-compound							
(xxiii)	80°	47.0 (0.09)		51.0 (0.14)					
(xxiv)		21.0 (0.03)	23.0 (0.05)	29.0 (0.08)	44.0 (0.36)				
(xxvi)		no film formed							no film formed
(xxvii)	80°	26.0 (0.02)	27.5 (0.04)	27.0 (0.0)	54.0 (0.31)			25.0 (0.0)	
(xxviii)		oxidises							
(xxix)	90°	31.0 (0.19)		31.0 (0.18)					

Table 3. (cont)

Compound	Probable angle of orientation on water of Longest aromatic axis	Molecular area (A^{o2}) at zero compression and (in brackets) compressibility§ on ** 0.1N aqueous solution of						
		Water alone	a	b	c	d	e	f	g
(xxx)	60°	48.0 (0.09)		55.0 (0.05)	69.0 (0.60)			53.0 (0.11)	
(xxxi)	40°	42.0 (0.09)		53.0 (0.05)				50.0 (0.14)	
(xxxii)	90°	33.0 (0.03)		34.0 (0.0)	39.0 (0.16)			34.0 (0.01)	
(xxxiii)		no film formed							

§ Expressed as the tangent of the angle (α) to the vertical of the upper portion of the F/A Curve.

* On phenol solution.

** a = Phenol
b = Hydroquinone
c = 1.5-Dihydroxynaphthalene
d = Alizarin Cyanin W.R.S.
e = Pyridine
f = Ethylene glycol
g = Catechol.

Table 3a.

Change in Area (ΔA^{o2}) (%)) and Change in compressibility.

(Tan α (on a, b, c, d, e, f and g) - Tan α (water) - in brackets)

Compound	a	b	c	d	e	f	g
(xxii)	+26.0 (+0.23)						
(ii)	+141.0 (+0.26)	+167.0 (+0.26)	+256.0 (+1.07)	+366.0 (+1.17)	+4.0 (-0.04)	+89.0 (-1.3)	+159.0 (+0.22)
(xii)	+16.0 (+.31)	+18.0 (+.10)	+177.0 (+.56)	+300.0 (+1.14)	-5.0 (+0.20)	+9.0 (+0.03)	+14.0 (+0.27)
(xxiii)		+9.0 (+0.05)					
(xxiv)	+10.0 (+0.02)	+38.0 (+0.05)	+110.0 (+0.33)				
(xxvii)	+6.0 (+0.02)	+4.0 (-0.02)	+108.8 (+0.29)				
(xxix)		0 (-0.01)					
(xxx)		+15.0 (-0.04)	+49.0 (+0.51)				
(xxxi)		+26.0 (-0.04)					
(xxxii)		+3.0 (-0.03)	+18.0 (+0.13)				

Table 4.

Substrate WATER Substance	Area/Molecule ($A^{\circ 2}$).	Scale Reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(v)	47.9	17.0	2.41	0.0
	44.7	16.1		2.17
	40.8	15.0		4.82
	36.8	14.3		6.51
	30.3	12.8		10.12
	25.5	11.5		13.24
	18.6	9.8		17.35
(xvi)	47.0	14.0	2.55	0.0
	44.2	13.9		0.26
	40.1	13.8		0.51
	36.9	13.1		2.30
	34.5	11.6		6.12
	32.6	10.7		8.39
	30.9	9.8		10.70
(xv)	37.2	16.0	2.48	0.0
	36.0	15.5		1.24
	35.1	15.1		2.20
	34.0	14.3		4.22
	33.2	13.2		6.94
	32.4	12.5		8.69
	31.4	10.9		12.64
	31.0	9.3		16.60
	29.2	7.4		21.36
	27.6	5.2		26.79
(ix)	63.0	17.0	2.61	0.0
	58.8	16.4		1.57
	55.4	16.0		2.61
	51.2	15.6		3.66
	47.0	14.8		5.74
	42.4	13.1		10.19
	39.5	12.1		12.8
	35.9	10.8		16.17
	32.4	9.2		20.16

Table 4. (cont)

Substrate WATER Substance	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(x)	77.2	12.0	2.41	0.0
	72.3	11.8		0.48
	67.6	11.7		0.72
	63.5	11.7		0.96
	56.2	11.3		1.69
	51.3	10.6		3.37
	46.4	9.2		6.74
(v)	45.5	17.0	2.62	0.0
	41.4	16.7		0.79
	39.6	15.2		4.71
	38.8	13.5		9.16
	37.1	11.9		13.35
	35.0	8.7		21.7
	33.3	6.9		26.40
	31.2	4.1		33.8
(xii)	45.3	15.0	2.60	0.0
	44.4	14.7		0.78
	43.1	14.0		2.60
	41.9	11.8		8.32
	39.8	10.5		11.70
	39.0	9.2		15.1
	37.5	7.8		18.75
	36.0	5.7		24.2
	34.3	4.5		27.32
(xiii)	37.0	17.0	2.61	0.0
	33.1	16.0		2.61
	30.8	15.2		4.69
	29.4	14.6		6.26
	27.6	14.2		7.30
	26.2	13.4		9.40
(xiv)	39.5	15.0	2.57	0.0
	37.4	13.2		4.63
	36.1	11.6		8.75
	34.0	8.7		16.20
	33.0	6.3		22.4
	32.5	5.2		25.21
	31.5	3.5		29.6

Table 4. (cont)

Substrate WATER Substance.	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(xi)	41.5	16.0	2.53	0.0
	40.5	14.3		4.31
	39.8	10.5		13.91
	39.7	9.0		17.70
	38.8	6.2		24.81
(viii)	60.0	17.0	2.60	0.0
	57.2	16.6		1.04
	56.1	16.4		1.56
	53.7	15.7		3.38
	51.0	14.6		6.24
	49.0	13.9		8.05
	46.2	12.9		10.65
	44.1	12.3		12.20
	38.9	10.6		16.60
(vii)	59.2	17.0	2.45	0.0
	56.4	16.9		.25
	54.3	15.8		2.94
	53.4	15.3		4.16
	52.9	14.0		7.35
	52.2	13.2		9.30
	51.2	12.8		10.3
	51.0	12.3		11.5
	58.0	11.8		12.72
(xvii)	33.4	16.0	2.58	0.0
	31.2	14.4		4.13
	30.9	12.9		8.0
	29.5	11.4		11.88
	28.5	9.6		16.52
	27.2	7.4		22.2
	26.8	6.6		24.29
(ii)	44.9	13.0	2.63	0.0
	42.8	12.8		0.53
	41.9	12.5		1.33
	39.5	11.4		4.21
	37.4	10.0		7.89
	35.0	8.4		12.1
	33.5	7.5		14.46

Table 4 (cont)

Substrate WATER Substance	Area/Molecule (A^{o2})	Scale reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(i)	48.8	13.0	2.49	0.0
	45.0	12.7		0.75
	41.4	10.7		5.73
	37.2	7.7		13.2
	37.4	6.9		15.20
	36.5	6.1		17.19
(xix)	46.0	17.0	2.44	0.0
	43.5	15.7		3.17
	42.8	14.5		6.1
	42.0	13.4		8.78
	41.1	11.4		13.65
	40.7	10.7		15.35
(iii)	51.0	16.0	2.56	0.0
	48.1	15.2		2.05
	45.2	14.0		5.12
	44.1	13.5		6.40
	42.4	12.8		8.19
	41.0	12.0		10.24
	40.4	11.9		10.50
	39.4	11.3		12.05

Table 5.

Substrate WATER Substance.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(xxix)	30.9	16.0	1.18	0.0
	28.8	13.7		2.72
	25.7	10.7		6.25
	22.2	7.3		10.28
	19.7	4.8		13.22
	18.5	3.5		14.75
(xxiv)	22.8	17.0	1.24	0.0
	21.0	15.4		1.99
	20.2	7.3		12.01
	20.0	5.2		14.6
	19.5	0.1		20.9
	19.1	-1.5		22.85
(xxvii)	30.0	17.0	1.16	0.0
	27.6	16.6		0.47
	25.7	9.2		9.04
	25.5	4.5		14.50
	25.1	-5		25.50
	24.8	-7.8		28.80
	24.7	-9.4		30.60
(xxxii)	36.5	16.0	1.22	0.0
	34.9	15.2		0.98
	33.6	11.9		5.00
	33.0	9.1		8.41
	32.8	4.5		14.00
	32.5	-3.7		24.00
	32.00	-8.0		29.21
	31.9	-10.0		31.70
(xxxi)	43.9	15.0	1.26	0.0
	43.0	14.6		0.54
	41.1	12.7		2.9
	38.7	7.0		10.1
	36.0	1.0		17.65
	34.8	-2.5		22.0

Table 5. (cont).

Substrate WATER Substance	Area/molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm.)
(xxx)	54.0	16.0	1.30	0.0
	51.1	15.0		1.30
	47.0	13.3		3.51
	45.8	6.3		12.60
	44.7	1.4		19.0
	43.0	-4.3		26.41
	42.9	-6.5		29.22
	42.6	-7.6		30.64
	42.0	-8.8		32.2

Table 6.

Substrate HYDROCHLORIC ACID. Substance.	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in.)	Pressure (Dynes/cm).
(xviii)	49.6	14.0	2.53	0.0
	47.2	13.9		0.25
	43.9	13.5		1.27
	43.1	13.1		2.28
	40.4	13.0		2.53
	37.7	12.9		2.78
	35.8	12.3		4.30
	34.0	11.6		6.06
	32.3	11.0		7.59
	31.2	10.6		8.60
	29.9	10.1		9.86
	27.0	9.3		11.9
(iii)	49.3	17.0	2.49	0.0
	44.9	16.7		0.75
	41.5	16.3		1.74
	39.1	15.9		2.74
	38.0	15.0		4.98
	37.6	14.5		6.23
	37.2	14.3		6.72
	34.2	12.1		12.22
(ii)	56.3	17.0	2.62	0.0
	54.0	16.9		0.26
	49.2	15.5		3.93
	45.1	14.0		7.86
	42.8	13.3		9.95
	37.9	11.5		14.4
	35.6	10.6		16.73
(xxiii)	51.7	14.0	2.56	0.0
	48.6	13.7		0.77
	44.9	12.4		4.11
	44.0	12.0		5.12
	43.2	11.4		6.65
	41.2	10.5		8.95
	39.6	9.6		11.29
	36.9	8.3		14.6
	36.0	7.8		15.84
	35.7	7.4		16.9
	33.3	6.4		19.46

Table 6. (cont)

Substrate HYDROCHLORIC ACID. Substance.	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm).
(iv)	43.8	16.0	2.47	0.0
	38.5	15.5		1.24
	30.0	14.6		3.46
	25.9	14.2		4.45
	23.7	13.9		5.18
	16.8	13.2		6.92
(xix)	47.4	14.0	2.60	0.0
	43.6	13.8		0.52
	40.0	13.5		1.29
	37.1	13.1		2.34
	32.7	12.5		3.9
	27.8	11.7		5.98
	22.2	10.8		8.25
	20.1	10.5		9.10
	18.3	10.3		9.64
(xii)	50.4	17.0	2.63	0.0
	47.1	16.9		0.26
	44.2	16.7		0.79
	42.9	16.4		1.58
	39.9	15.9		2.88
	36.1	15.2		4.73
	33.0	14.6		6.30
	26.9	13.4		9.45
	26.0	13.2		10.0
(x)	59.4	12.0	2.44	0.0
	56.8	11.8		0.49
	54.1	11.3		1.71
	52.0	10.4		3.90
	47.9	8.5		8.55
	45.7	7.6		10.74
	44.8	7.2		11.71

Table 6. (cont)

Substrate HYDROCHLORIC ACID. Substance.	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in.)	Pressure (Dynes/cm).
(xv)	39.9	15.0	2.47	0.0
	37.6	14.9		0.25
	32.2	13.8		2.98
	30.0	13.2		4.45
	26.5	12.4		6.42
	21.7	11.2		9.40
	17.6	10.2		11.85
(xiv)	43.0	13.0	2.52	0.0
	39.1	12.8		0.51
	35.4	11.4		4.03
	32.8	10.1		7.31
	32.1	9.8		8.05
	30.0	9.0		10.01
	24.9	6.8		15.62
	23.0	6.0		17.64
	22.2	5.5		18.9
(iii)	61.2	15.0	2.58	0.0
	59.7	14.9		0.26
	55.4	14.3		1.81
	50.4	13.5		3.87
	38.2	11.3		9.55
	35.3	10.8		10.82
	33.0	10.5		11.60
(ix)	61.7	17.0	2.43	0.0
	57.6	16.4		1.45
	53.4	16.0		2.43
	47.5	15.0		4.86
	40.0	13.3		9.0
	32.9	11.7		12.9
	29.8	11.0		14.58
	25.0	10.0		17.0
(viii)	60.4	16.0	2.48	0.0
	57.4	15.8		0.5
	52.1	14.9		2.73
	44.0	13.0		7.43
	39.2	12.0		9.93
	34.5	10.9		12.62
	32.0	10.3		14.12
	29.4	9.8		15.36

Table 7.

Substrate SODIUM CARBONATE Substance.	Area/Molecule (A^{o2})	Scale Reading (inches)	Sensitivity (Dynes/cm/in.)	Pressure (Dynes/cm.)
(xv)	71.4	13.0	2.42	0.0
	67.1	12.8		0.48
	62.0	12.4		1.45
	57.9	11.5		3.64
	54.8	10.9		5.10
	49.2	9.8		7.75
(xxiii)	73.2	15.0	2.58	0.0
	65.8	13.9		2.84
	60.1	12.7		5.94
	57.2	12.0		7.75
	51.0	10.5		11.60
	49.9	10.3		12.10
(xvi)	92.8	15.0	2.52	0.0
	84.5	14.9		0.25
	79.3	14.5		1.26
	74.8	14.1		2.27
	68.7	13.2		4.54
	66.4	12.6		6.04
	63.0	11.6		8.56
	56.2	10.0		12.61
	52.1	8.9		15.38
(x)	99.6	17.0	2.47	0.0
	86.1	16.5		1.23
	81.1	16.0		2.47
	75.6	15.3		4.19
	72.3	14.6		5.92
	68.8	13.7		8.14
	64.0	12.6		10.90
	59.2	11.4		13.8
	53.6	10.1		17.0
(iii)	58.1	15.0	2.62	0.0
	56.1	14.8		0.52
	53.3	14.2		2.10
	51.1	13.0		5.25
	47.0	10.7		11.25
	44.9	9.6		14.18
	43.8	8.9		16.00

Table V. (cont)

Substrate SODIUM CARBONATE Substance.	Area/Molecule (A^{o2})	Scale Reading. (inches)	Sensitivity. (Dynes/cm/in).	Pressure. (Dynes/cm.)
(ii)	66.0	16.0	2.54	0.0
	61.0	15.7		0.76
	55.4	14.8		3.05
	53.2	13.9		5.33
	52.1	13.4		6.62
	50.9	13.0		7.62
(ix)	82.0	13.0	2.70	0.0
	78.7	12.7		0.81
	74.6	12.5		1.35
	70.4	12.3		1.89
	67.0	12.0		2.70
	62.1	11.5		4.05
	59.0	10.8		5.95
	56.5	10.1		7.84
	53.2	9.1		10.50
	46.8	7.6		14.58
	43.0	6.7		17.0
(w)	89.0	16.0		0.0
	80.8	15.6		1.06
	74.0	14.9		2.84
	71.0	14.2		4.64
	69.5	13.4		6.71
	68.8	13.0		7.75
	66.0	11.8		10.8
	63.4	10.3		14.70
	61.0	9.1		17.15
	59.0	8.2		20.15
(xviii)	41.0	17.0	2.46	0.0
	37.9	16.8		0.49
	36.5	16.5		1.23
	35.8	16.2		1.97
	34.5	14.8		5.42
	33.6	13.7		8.13
	32.4	12.3		11.51
	31.4	11.1		14.50
	31.0	10.6		15.70

Table 7. (cont)

Substrate SODIUM CARBONATE Substance.	Area/Molecule ($A^{o\,2}$)	Scale Reading (inches)	Sensitivity (Dynes/cm/in).	Pressure (Dynes/cm.)
(xix)	43.5	14.0	2.51	0.0
	43.0	13.8		0.50
	41.8	13.5		1.25
	39.0	12.7		3.26
	35.7	11.7		5.77
	33.0	10.9		7.78
	30.6	10.2		9.55
(xiv)	46.6	17.0	2.53	0.0
	44.8	16.7		0.76
	42.0	16.4		1.52
	41.2	16.2		2.03
	36.1	14.5		6.33
	33.6	13.3		9.35
	31.5	12.3		11.88
(viii)	66.2	13.0	2.40	0.0
	63.0	12.9		0.24
	57.2	12.6		0.96
	53.5	11.9		2.64
	50.9	10.5		6.00
	48.3	9.2		8.86
	47.1	8.7		10.32
	46.3	8.4		11.0
	43.1	7.1		14.12
	39.9	5.3		18.45
(i)	60.1	15.0	2.42	0.0
	57.7	14.9		0.24
	54.8	14.8		0.49
	50.9	14.5		1.21
	47.2	13.9		2.66
	45.1	13.2		4.35
	43.4	12.7		5.56
	41.2	12.0		7.25
	38.9	11.4		8.70
	37.0	10.8		10.15

Table 8.

Substrate HYDROQUINONE Substance.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(ii)	130.1	14.0	1.24	0.0
	126.0	13.1		1.14
	112.8	10.4		4.46
	105.6	8.9		6.32
	101.3	9.0		7.44
	97.9	6.7		9.05
	86.5	1.0		16.11
	81.0	-1.7		19.44
(xxxii)	42.0	16.0	1.25	0.0
	39.1	15.6		0.50
	36.6	14.4		2.0
	33.5	6.8		11.5
	32.7	-1.2		21.50
	31.8	-10.0		32.5
	31.1	-13.2		36.5
(xii)	60.1	16.0	1.30	0.0
	56.2	14.5		1.95
	54.7	13.7		2.99
	51.0	12.1		5.06
	48.8	11.2		6.25
	46.0	9.8		8.06
	40.8	4.5		14.95
	36.9	0.6		20.0
	33.0	-3.6		25.5
	30.1	-6.3		28.95
(xxiii)	53.0	15.0	1.28	0.0
	46.9	9.5		7.03
	45.1	7.1		10.08
	41.5	2.1		16.5
	37.2	-4.0		24.25
	34.6	-7.5		28.82
(xxxi)	57.2	16.0	1.29	0.0
	53.4	14.8		1.55
	51.5	11.2		6.20
	48.8	2.4		17.55
	47.6	-3.7		25.41
	46.8	-6.9		29.58
	46.2	-9.2		32.50
	45.5	-11.3		35.28
	44.7	-14.0		38.76

Table 8. (cont)

Substrate HYDROQUINONE Substance.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(xxix)	31.5	16.0	1.23	0.0
	29.7	19.8		1.48
	27.0	10.7		6.53
	25.8	9.5		8.00
	25.9	7.0		11.08
	22.4	5.4		13.01
	21.0	3.18		15.00
	36.8	15.0	1.14	0.0
	34.0	14.6		0.57
	31.5	13.7		1.48
	26.5	7.1		9.00
	24.8	1.4		15.50
	23.7	-1.6		18.90
(xxvii)	32.0	17.0	1.32	0.0
	30.0	16.2		1.06
	28.5	15.5		1.98
	26.5	10.9		8.05
	26.2	10.2		9.00
	26.0	4.9		16.0
	25.8	-1.2		23.92
	25.5	-6.0		30.40
	25.2	-11.0		37.00
	25.0	-14.4		41.40
(xxx)	57.5	16.0	1.32	0.0
	54.1	11.4		6.06
	52.5	5.4		13.98
	51.0	-2.5		24.04
	50.4	-3.4		25.60
	49.9	-5.2		28.00
	49.0	-9.0		33.00
	48.5	-10.3		34.70

Table 9.

Substrate PHENOL Substance	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(iv)	68.0	17.0	1.27	0.0
	63.5	16.4		0.76
	58.7	15.8		1.53
	54.9	15.2		2.28
	51.0	14.6		3.04
	48.0	14.2		3.56
	43.8	13.7		4.20
	41.5	12.7		5.46
	34.8	9.5		9.53
	32.0	8.3		11.05
	29.4	7.2		12.48
	27.2	6.2		13.70
	24.1	4.8		15.50
(xxii)	60.0	14.0	1.19	0.0
	51.1	13.3		.84
	45.4	11.8		2.62
	40.5	9.5		5.35
	39.0	8.7		6.31
	37.5	7.8		7.39
	35.5	6.5		8.94
(xxiv)	29.0	17.0	1.18	0.0
	25.8	14.9		2.48
	24.6	14.5		2.95
	22.4	12.8		4.96
	21.0	11.7		6.30
	20.2	6.4		12.51
	19.4	3.4		16.07
	18.9	2.0		17.7
	17.7	-3.4		25.21
(xxvii)	32.8	16.0	1.31	0.0
	27.6	14.5		1.97
	26.1	11.8		5.50
	25.5	8.8		9.45
	25.0	5.7		13.50
	24.2	1.5		19.0
	23.5	-1.9		23.4
	23.0	-4.6		27.00

Table 9. (cont).

Substrate PHENOL substance.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(xxi)	57.0	16.0	1.24	0.0
	45.0	15.6		0.45
	38.0	14.6		1.74
	32.5	12.4		4.46
	30.2	10.3		7.06
	27.4	8.3		9.54
	23.9	5.5		13.00
	21.1	3.1		16.00
(ii)	113.2	16.0	1.14	0.0
	108.7	15.0		1.14
	101.0	13.3		3.18
	96.0	12.3		4.23
	89.7	10.0		6.84
	83.5	6.6		10.77
	78.3	4.1		13.60
	72.6	1.1		17.00

Table 10.

substrate ETYLENE-GLYCOL substance.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm./cm.)	Pressure (Dynes/cm.)
(xxvii)	29.1	17.0	1.26	0.0
	26.0	16.5		0.76
	24.9	15.4		2.0
	24.6	10.8		7.82
	24.0	5.5		14.50
	23.8	3.2		17.41
(xxxi)	39.0	16.0	1.27	0.0
	37.9	15.5		0.64
	35.4	14.4		1.90
	33.6	11.9		5.20
	33.3	9.2		8.63
	32.8	5.4		13.45
	32.5	1.8		17.90
(xii)	51.9	17.0	1.18	0.0
	48.6	16.5		0.59
	46.4	14.5		2.93
	44.0	10.8		7.26
	43.4	9.6		8.68
	42.5	7.7		10.90
(xxxi)	52.8	13.0	1.22	0.00
	50.3	12.4		0.73
	48.9	11.4		1.96
	46.8	9.5		4.28
	47.0	8.5		5.50
	44.9	5.3		9.41
(xxx)	56.6	15.0	1.14	0.0
	54.0	14.7		0.34
	52.3	13.4		1.82
	51.0	10.6		5.02
	48.8	7.3		8.78
	47.0	3.6		13.00
(ii)	80.0	16.0	1.28	0.0
	79.5	15.6		0.51
	75.5	12.7		4.22
	73.5	11.3		6.01
	71.2	9.9		7.80
	68.0	7.5		10.9

Table II.

Substrate PYRIDINE Substance	Area/Molecule (A^{o2})	Scale Reading (cm)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(xii)	46.5	17.0	1.24	0.0
	42.1	16.8		0.25
	38.9	15.4		1.98
	34.8	12.5		5.58
	30.9	9.5		9.30
	26.6	7.1		12.29
	25.4	6.0		13.64
(ii)	49.8	15.0	1.27	0.0
	47.3	14.8		0.25
	44.3	14.1		1.14
	42.2	12.9		2.67
	40.8	10.4		5.84
	39.2	8.5		8.25
	38.1	6.6		10.68
	37.0	4.6		13.20
	35.1	2.1		16.39
(xxii)	48.2	15.0	1.28	0.0
	40.7	14.5		0.64
	36.1	14.1		1.15
	31.9	11.7		4.22
	29.3	9.4		7.16
	26.6	7.2		9.97

Table 12.

Substrate 1.5 DIHYDROXY NAPHTHALENE Substance	Area/Molecule (A^{o2})	Scale Reading (cm).	Sensitivity (Dynes/cm/cm).	Pressure (Dynes/cm.)
(xxiv)	53.3	17.0	1.31	0.0
	49.8	16.2		1.05
	46.0	15.3		2.22
	41.9	14.3		3.54
	40.1	13.8		4.18
	36.8	13.2		4.97
	35.9	12.5		5.90
	34.1	11.6		7.06
	33.0	11.0		7.85
	30.2	9.6		9.70
	27.8	7.4		11.28
	25.1	6.9		13.22
(xxxii)	58.9	17.0	1.14	0.0
	45.8	15.9		1.25
	41.3	15.2		2.05
	35.9	12.8		4.79
	34.2	10.2		7.75
	32.0	7.5		10.83
	30.4	5.3		13.31
	28.5	3.0		16.00
(xxvii)	60.0	13.0	1.27	0.0
	54.1	12.1		1.15
	48.2	9.4		4.57
	46.5	8.3		5.98
	42.9	5.7		9.26
	40.4	4.3		11.1
	36.4	1.7		14.35
	33.0	-1.0		17.0
(xxx)	80.2	17.0	1.32	0.0
	70.9	16.3		0.93
	61.4	14.6		3.16
	57.1	13.2		5.02
	50.1	10.9		8.05
	44.0	9.1		10.41

Table 12. (cont).

Substrate 1.5 DIHYDROXY NAPHTHALENE Substance.	Area/Molecule (A^{o2})	Scale Reading (cm).	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
(xii)	134.0	15.0	1.30	0.0
	126.5	13.6		1.82
	120.2	12.4		3.38
	114.1	11.3		4.81
	108.0	10.2		6.24
	102.7	9.2		7.53
	96.8	7.9		9.24
	89.5	5.9		11.80
	79.3	3.0		15.60
	70.0	0.4		18.95
(ii)	168.1	15.0	1.26	0.0
	165.1	14.7		0.38
	151.8	13.6		1.77
	142.5	12.9		2.65
	135.2	12.4		3.28
	132.0	11.8		4.04
	125.4	10.8		5.29
	112.8	8.6		8.06
	101.5	6.9		10.20
	94.3	5.9		11.50
	82.0	3.9		14.00

Table 13.

Substrate CATECHOL Substance	Area/Molecule (A^{o2})	Scale Reading (cm)	Sensitivity (Dynes/cm/cm).	Pressure (Dynes/cm.)
(ii)	112.9	16.0	1.31	0.0
	107.9	15.0		1.31
	106.0	14.2		2.36
	103.3	12.6		4.44
	98.5	10.3		7.46
	94.8	8.7		9.56
	91.2	6.8		12.05
	88.8	5.7		13.5
	86.2	4.7		14.81
(xii)	56.0	17.0	1.26	0.0
	50.8	16.5		0.63
	46.6	15.1		2.39
	42.8	12.6		5.54
	36.9	8.8		10.32
	33.3	6.5		13.21
	31.1	5.4		14.60

Table 14.

Substrate ALIZARIN CYANIN W R S. Substance	Area/Molecule (A^{o2})	Scale Reading (cm).	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm).
(ii)	219.2	16.0	1.21	0.0
	200.7	14.5		1.82
	188.4	13.3		3.26
	174.0	12.3		4.48
	159.0	10.0		7.25
	150.9	8.6		8.95
	143.0	7.5		10.28
	134.8	6.1		12.00
	124.0	4.4		14.01
(xii)	178.5	15.0	1.16	0.0
	173.8	14.6		.47
	166.5	13.5		1.74
	159.2	12.0		3.48
	150.0	10.9		4.74
	144.2	9.6		6.26
	135.0	8.2		7.86
	127.0	6.8		9.53
	121.0	5.7		10.8

Table 15.

Compound Tested(xxxv) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm).	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm)
1.5 Dihydroxy-Naphthalene	58.9	16.0	1.17	0.0
	56.8	15.6		0.47
	53.5	15.1		1.05
	50.6	14.7		1.52
	43.9	13.4		3.04
	40.7	12.9		3.62
	37.5	12.3		4.33
	35.4	11.7		5.02
	32.2	10.3		6.76
	27.7	9.2		7.95
	24.6	7.5		9.95
Crystal Violet (.1N)	72.4	12.0	1.21	0.0
	61.7	116.		0.48
	54.6	11.4		0.73
	49.0	11.2		0.97
	41.5	10.7		1.57
	29.0	9.1		3.50
	25.6	8.1		4.72
	22.0	7.4		5.50
Acid Magenta (.1N)	129.0	16.0	1.24	0.0
	127.0	15.6		0.5
	115.8	15.2		0.99
	104.7	14.8		1.49
	94.2	14.1		2.36
	83.0	13.1		3.6
	73.6	12.1		4.85
	61.2	10.7		6.57
	55.0	9.6		7.94
Orange I (.1N)	69.1	17.0	1.22	0.0
	67.0	16.8		0.24
	57.2	16.6		0.49
	51.6	16.0		1.22
	46.0	15.4		1.95
	40.7	15.0		2.44
	35.0	14.5		3.06
	30.0	13.7		4.03
	24.8	12.9		5.1

Table 15. (cont).

Compound Tested(xxxv) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm).	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
1.4 Disulphonic acid. pH=1.45	96.0	17.0	1.24	0.0
	92.8	15.8		1.49
	90.9	13.8		3.96
	88.3	13.0		4.95
	86.5	12.2		5.94
	84.5	11.0		7.43
Alizarin Cyanin W R S (.05N)	115.5	14.0	1.31	0.0
	114.0	13.7		0.39
	108.2	13.4		0.79
	103.0	12.4		2.10
	98.0	12.0		2.62
	87.0	10.9		4.05
	82.2	10.5		4.58
	71.1	8.6		7.06
	65.3	7.5		8.51

Table 16.

Compound Tested(xxv) Substrate.	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm).	Pressure (Dynes/cm.)
Water	39.8	15.0	1.31	0.0
	34.2	14.2		1.05
	30.1	13.1		2.49
	27.2	11.9		4.06
	23.9	10.3		6.15
	22.9	8.0		9.16
	21.7	5.0		13.1
	20.6	2.2		16.75
Naphthalene Mono-Sulphonic acid pH = 1.85	48.0	13.0	1.16	0.0
	44.2	12.1		1.04
	42.1	11.2		2.09
	39.8	10.2		3.25
	36.5	8.2		4.86
	33.7	7.4		6.48
	27.0	4.4		9.95
Naphthalene disulphonic acid pH=4.4	45.2	14.0	1.24	0.0
	40.8	11.8		2.73
	38.9	10.0		4.96
	36.8	7.9		7.56
	35.0	6.3		9.54
	34.2	5.3		10.80
	32.0	3.5		13.0
	30.6	1.9		15.0
	27.7	-1.3		18.98
Hydroquinone (at various pH values).	51.4	17.0	1.19	0.0
	46.7	16.4		0.71
	45.0	16.2		0.95
	40.7	13.8		3.80
	38.8	12.2		5.70
	38.3	11.8		6.18
	36.1	10.0		8.33
	35.1	9.4		9.04
	34.0	7.8		10.94

Table 16. (cont).

Compound Tested(xxv) Substrate.	Area/Molecule (Å^{02})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
Monosulphonic Acid pH=2.6	49.5	17.0	1.23	0.0
	46.4	15.6		1.72
	44.7	14.3		3.32
	42.4	12.9		5.04
	41.3	11.9		6.27
	39.3	10.3		8.25
	36.0	7.2		12.08
	31.4	3.3		16.85
Disulphonic acid pH=1.45	60.4	13.0	1.17	0.0
	55.9	12.5		0.59
	49.4	10.6		2.81
	46.2	8.8		4.91
	43.1	7.0		7.01
	40.0	5.4		8.89
	37.3	3.9		10.62
	33.5	1.7		13.22

Table 17.

Compound Tested (xxvii) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm)
Glycine (.1N)	49.1	17.0	1.22	0.0
	48.0	16.8		0.24
	44.2	16.2		.98
	42.0	15.0		2.44
	41.6	14.3		3.30
	40.3	12.6		5.25
	39.0	11.1		7.20
	38.5	9.5		9.16
	37.9	8.6		10.26
	36.0	6.1		13.31
Glucose (.1N)	56.6	16.0	1.19	0.0
	51.3	15.0		1.19
	49.0	13.6		2.86
	45.8	11.6		5.24
	43.0	10.1		7.02
	41.2	9.0		8.33
	38.6	7.4		10.23

Table 15.

Compound Tested OCTADECYLAMINE HYDROCHLORIDE Substrate	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm).	Pressure (Dynes/cm).
Water	58.9	16.0	1.27	0.0
	51.7	15.5		0.64
	47.0	15.0		1.27
	40.8	13.5		3.28
	35.8	11.6		5.59
	32.6	9.4		8.38
	27.1	6.0		12.70
Disulphonic Acid pH = 4.4	88.0	13.0	1.35	0.0
	79.9	12.4		0.81
	77.7	12.2		1.08
	72.6	11.6		1.88
	69.6	11.0		2.70
	65.0	10.3		3.64
	62.3	9.7		4.45
	60.0	9.1		5.27
	56.1	8.2		6.48
	54.0	7.4		7.29
Disulphonic Acid pH = 1.45	100.0	11.0	1.18	0.0
	94.1	10.4		.71
	89.5	9.9		1.30
	79.0	8.6		2.83
	74.0	7.6		4.01
	68.8	6.7		5.07
	59.0	4.2		8.03
	54.0	2.6		9.9
	48.7	.7		12.14
Monosulphonic Acid pH=1.85	89.2	15.0	1.23	0.0
	87.0	14.4		.74
	85.1	13.8		1.48
	76.4	11.3		4.55
	74.0	10.5		5.53
	68.6	9.0		7.37
	85.7	14.0	1.31	0.0
	82.4	13.5		0.6
	77.4	11.9		2.75
	72.8	9.6		5.77
	69.2	7.9		8.0
	66.0	6.4		9.95
	62.3	4.6		12.31
	57.0	2.4		15.2

Table 19.

Compound Tested (xxx) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm)
Glycine (.1N)	52.9	17.0	1.22	0.0
	51.7	16.8		0.24
	48.8	15.9		1.34
	46.4	12.6		5.37
	45.0	8.3		10.61
	43.9	6.1		13.30
	43.2	4.9		14.75
Glucose (.1N)	89.8	16.0	1.18	0.0
	85.2	14.3		2.03
	82.4	13.3		3.18
	78.6	11.8		4.96
	68.5	7.9		9.55
	62.0	5.5		12.39

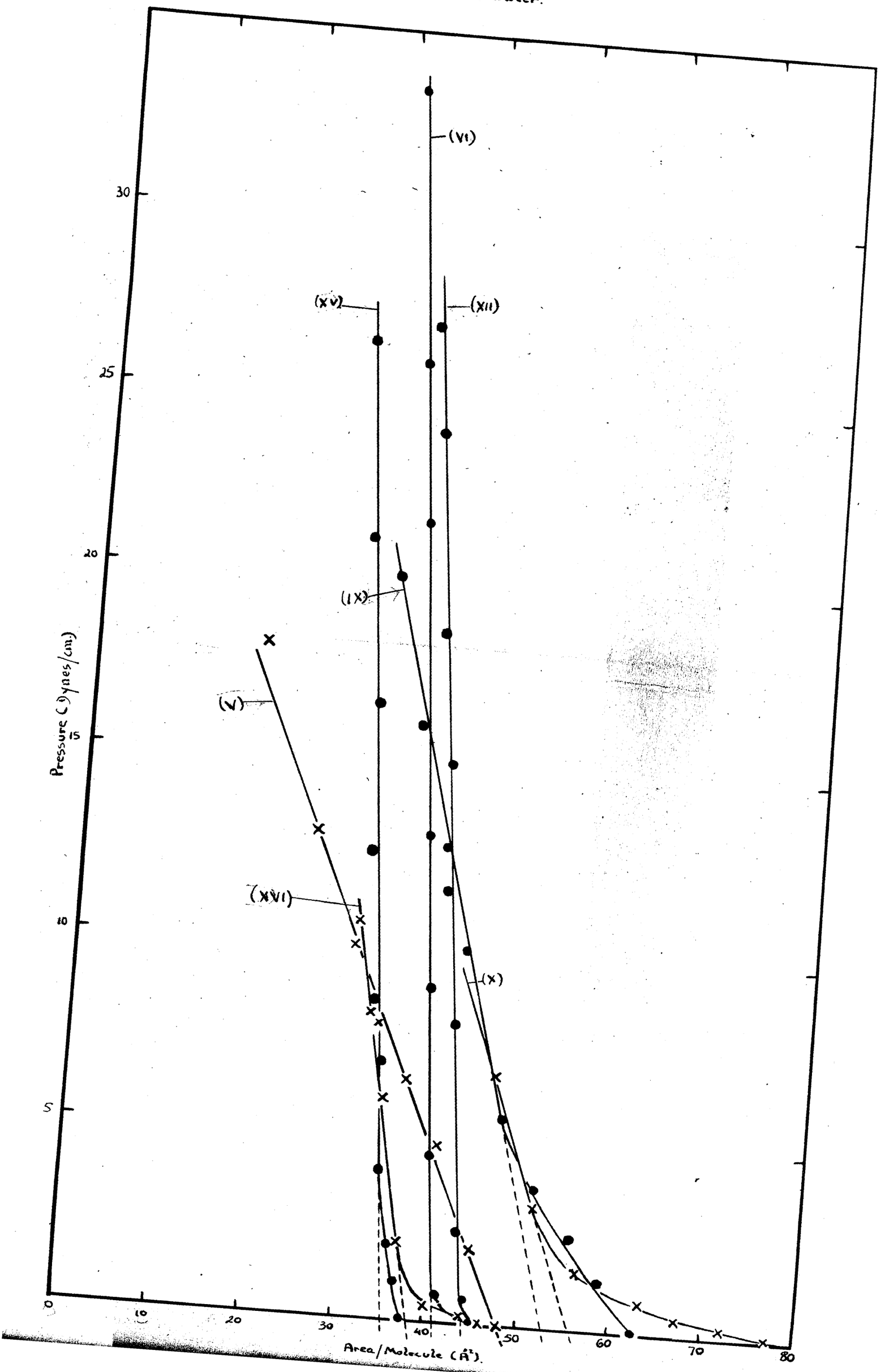
Table 20.

Compound Tested (xv) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
Glycine (.1N)	58.7	13.0	1.33	0.0
	53.2	12.7		0.4
	50.0	12.4		0.8
	46.1	11.1		2.52
	43.0	9.7		4.38
	40.9	8.2		6.37
	47.4	6.3		8.91
	45.5	5.1		10.5
Glucose (.1N)	55.6	17.0	1.29	0.0
	52.8	16.3		0.91
	49.7	15.1		2.46
	47.0	13.2		4.90
	44.2	11.6		6.96
	42.8	11.0		7.75
	41.0	9.7		9.42
	38.0	8.3		11.22

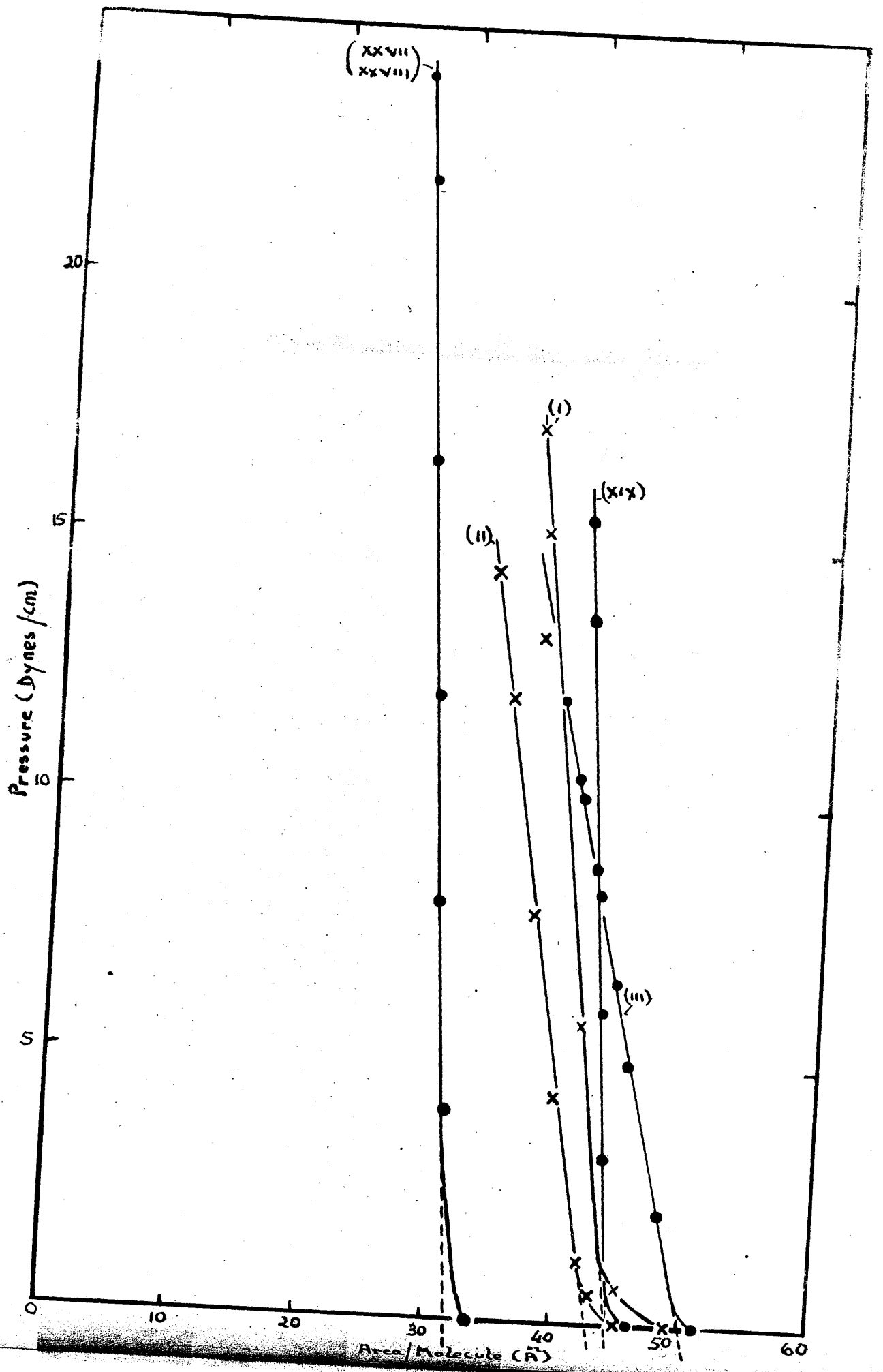
Table 21.

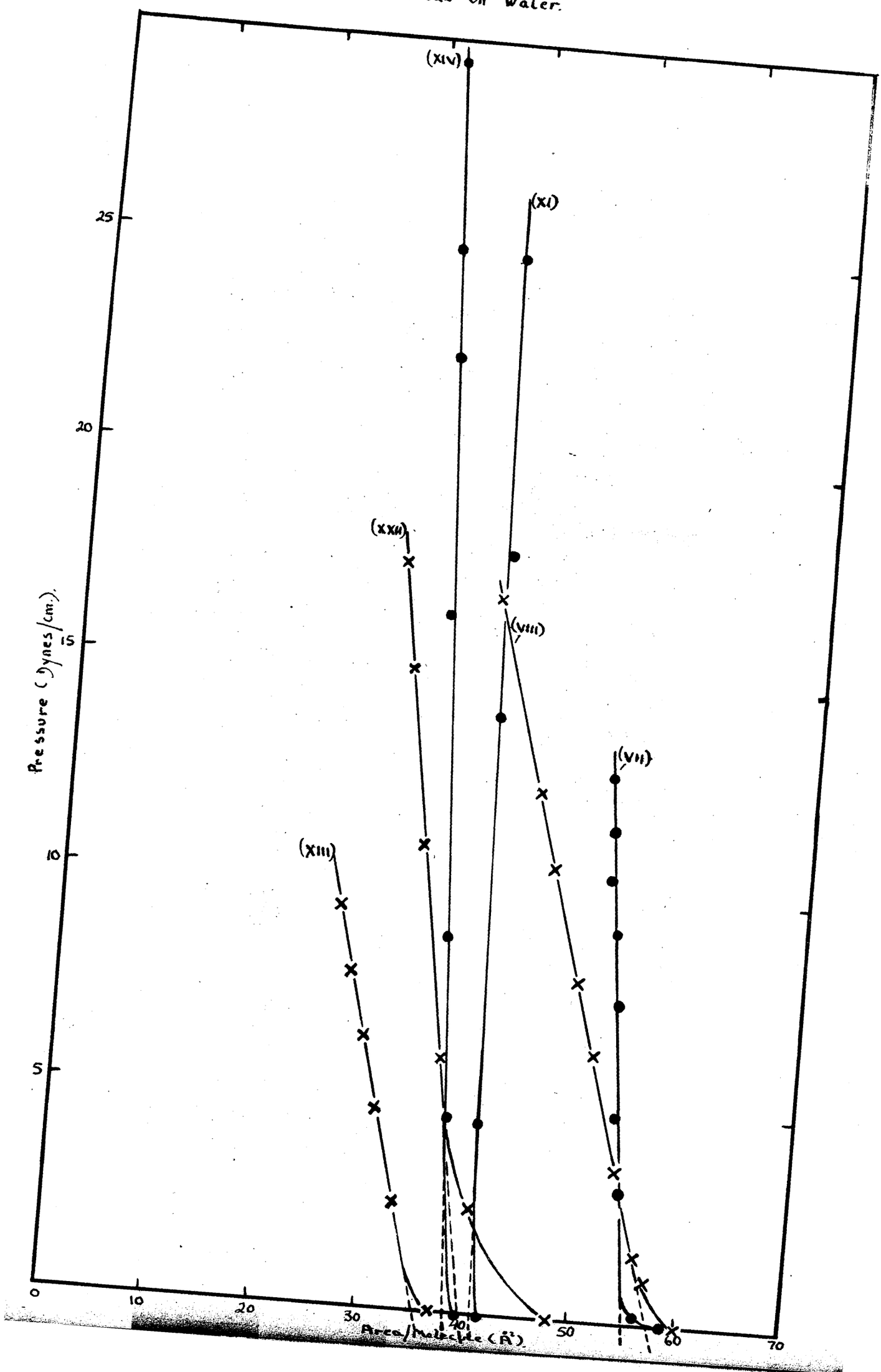
Compound Tested (ii) Substrate	Area/Molecule (A^{o2})	Scale Reading (cm.)	Sensitivity (Dynes/cm/cm.)	Pressure (Dynes/cm.)
Glycine (.1N)	55.6	17.0	1.26	0.0
	53.0	16.4		0.76
	49.0	15.7		1.64
	45.7	15.2		2.27
	42.0	14.4		3.28
	38.9	13.8		4.03
	35.7	12.4		5.80
	33.8	11.6		6.81
	31.0	10.8		7.82
Glucose(.1N)	64.2	17.0	1.25	0.0
	60.3	16.4		.75
	55.4	15.2		2.25
	53.9	14.4		3.25
	50.8	12.8		5.25
	47.0	11.2		7.25
	45.0	10.0		8.75
	43.6	9.2		9.75

Areas on Water.

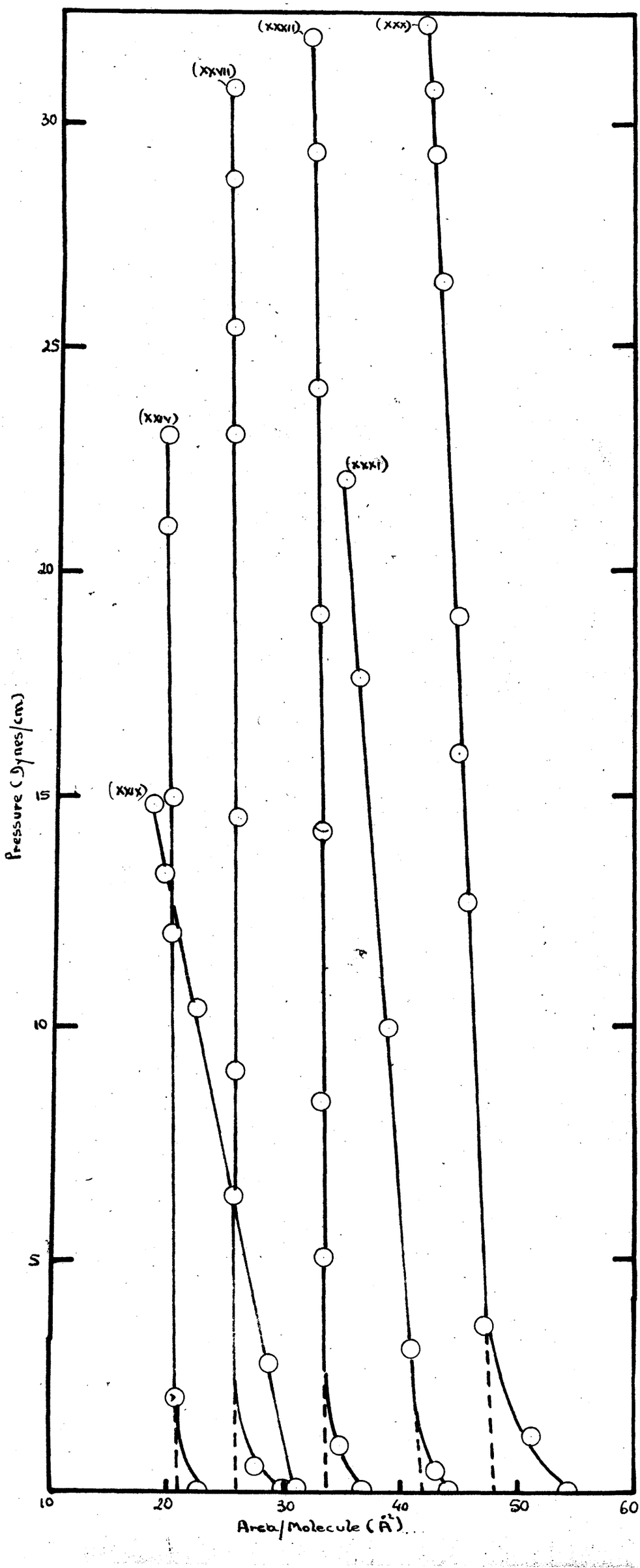


Areas on Water

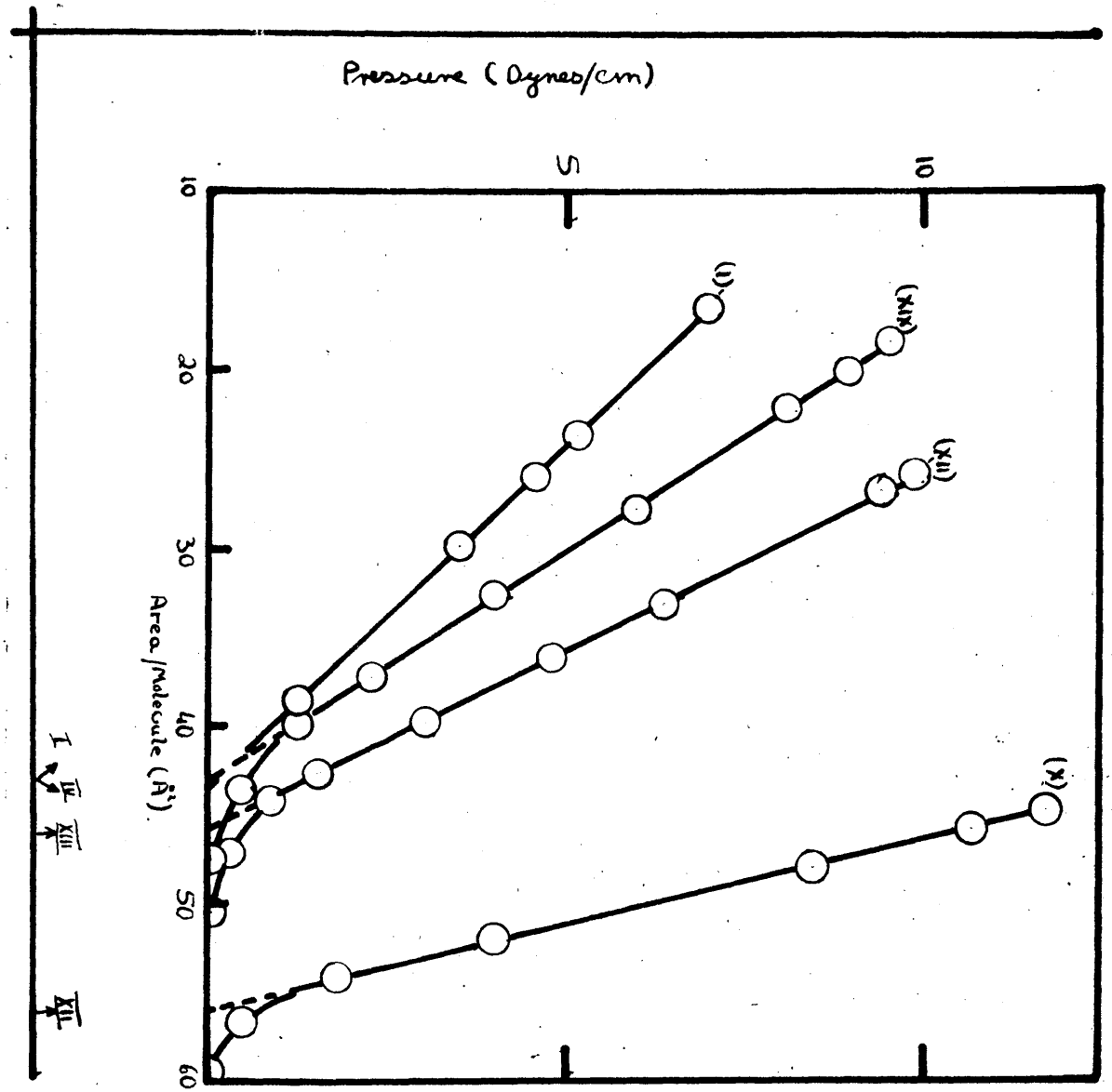



Areas on Water.
(XIV)
(XI)
(XXII)
(VIII)
(VII)
(XIII)
Pressure (Dynes/cm.).
25
20
15
10
5
0
10
20
30
40
50
60
70
Area/Molecule (Å²).

Areas on Water.

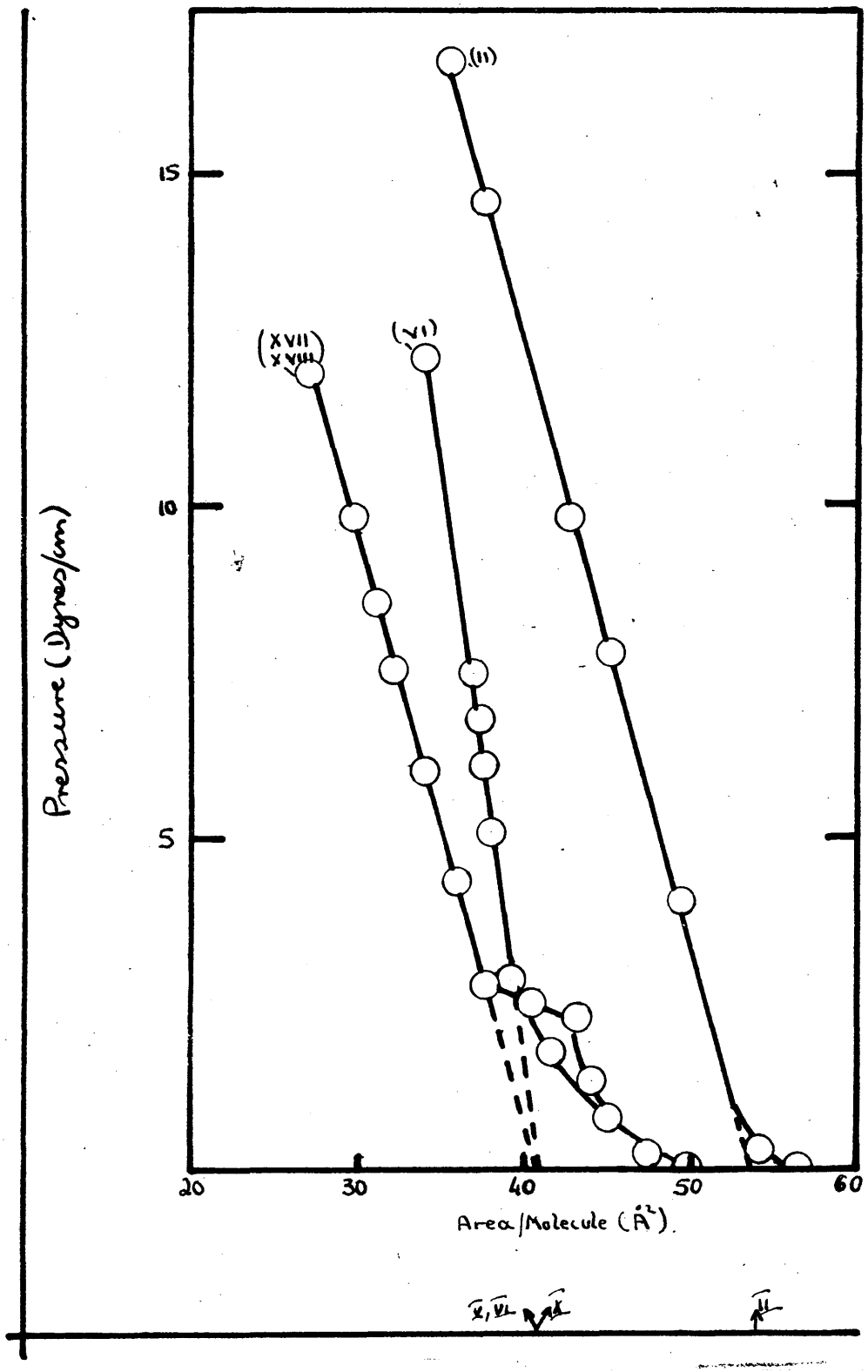


Graph 5

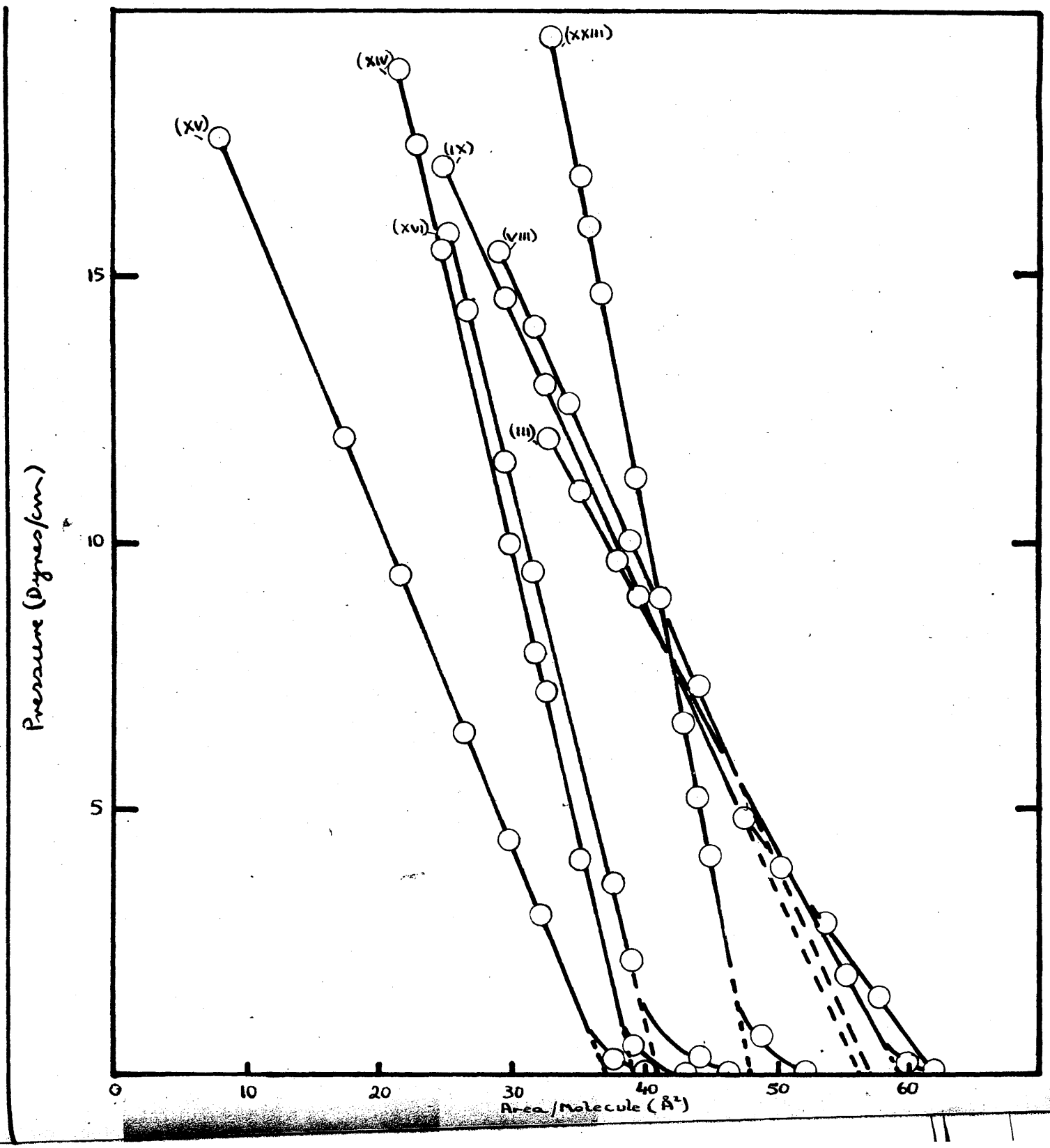


Area on N/10 HCl.

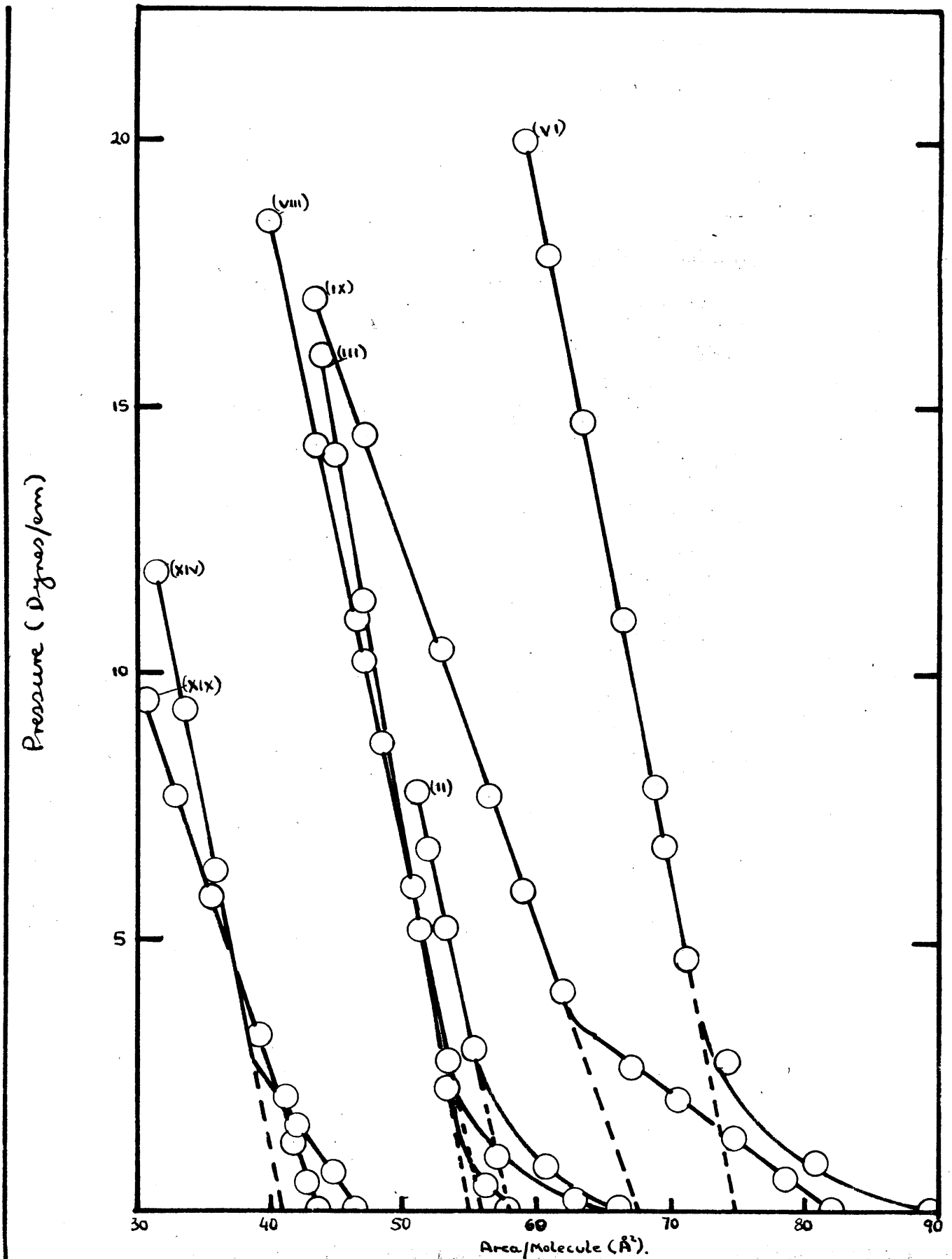
Areas on N/10 HCl



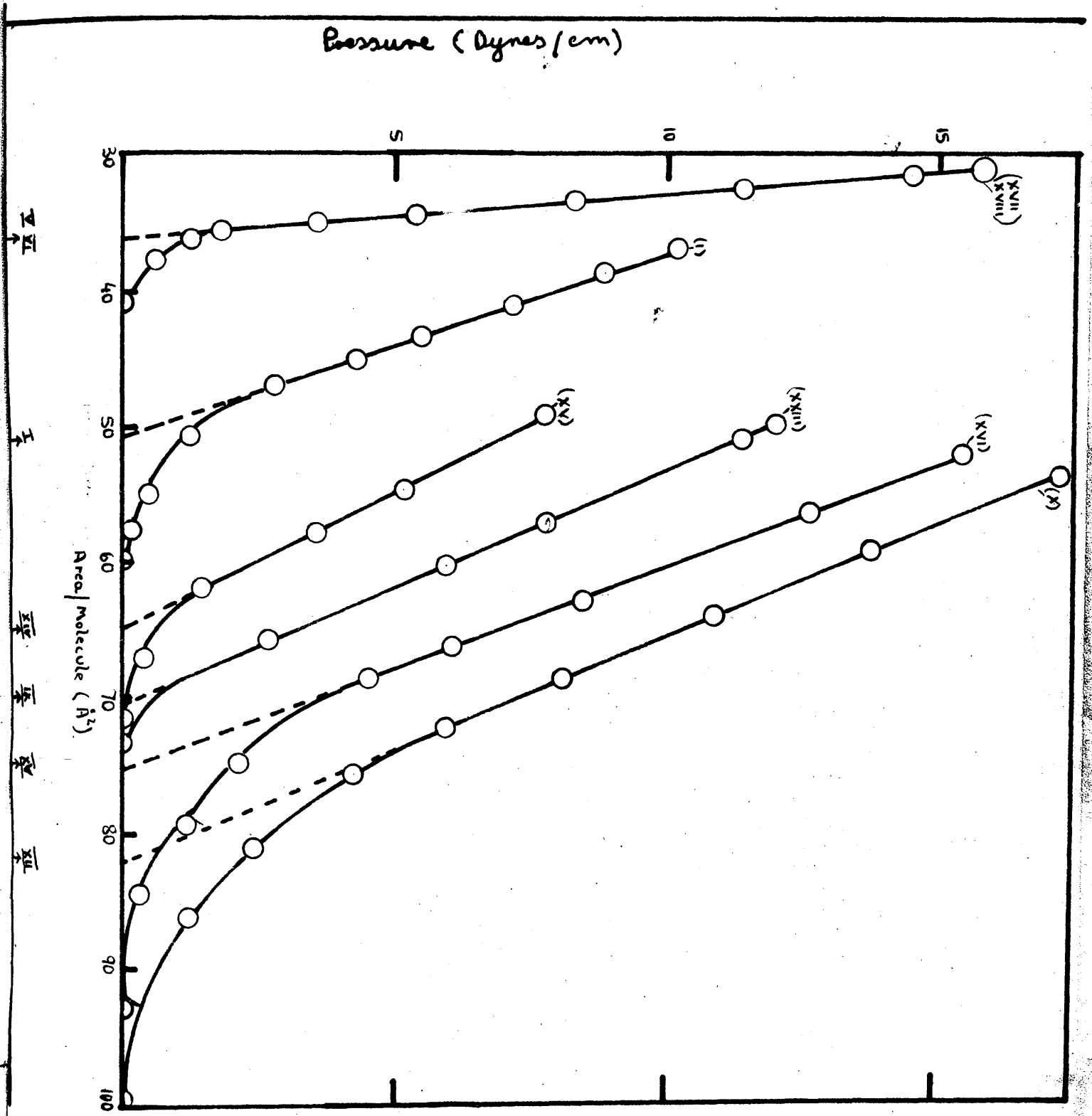
Areas on N/10 HCl.



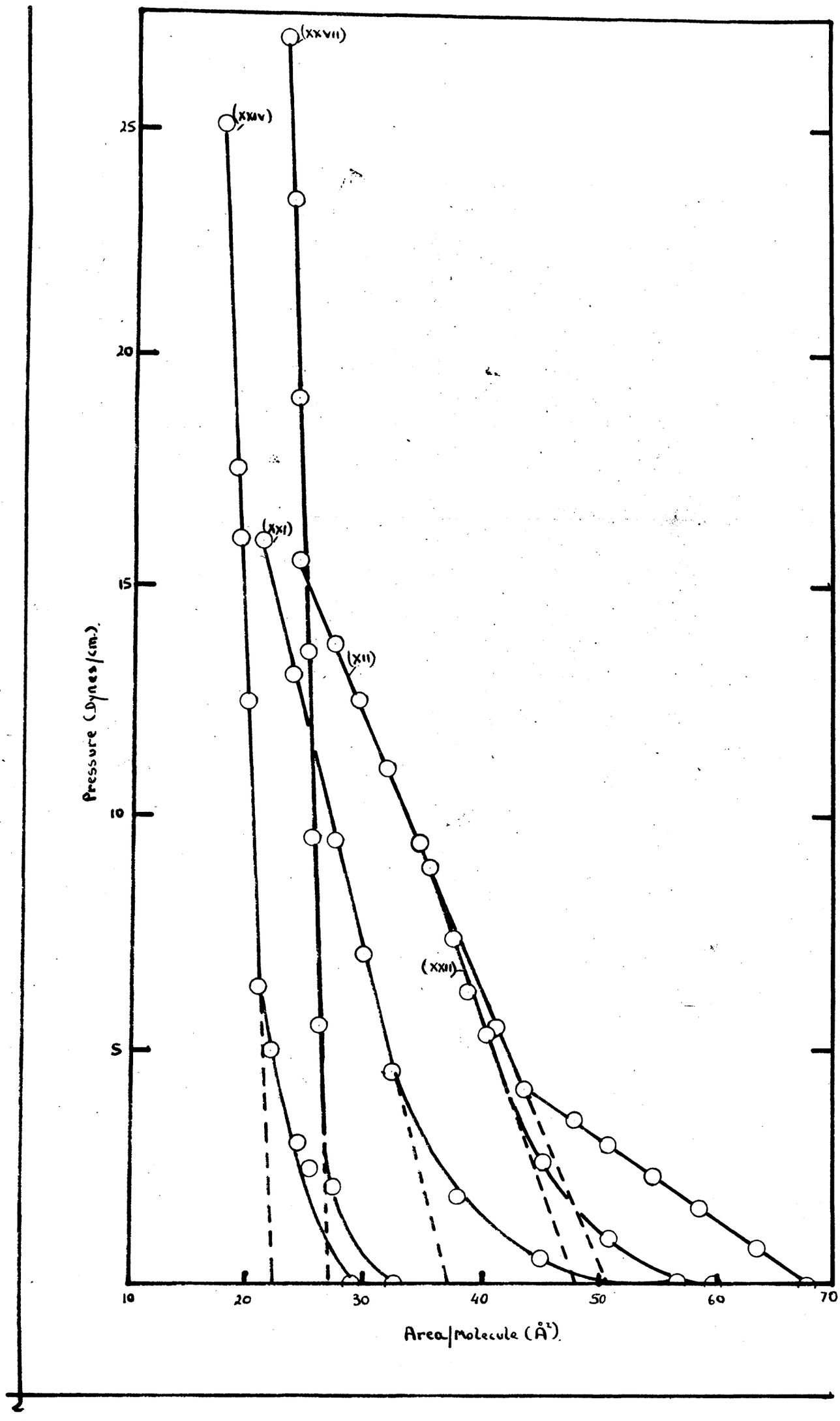
Areas on N/10 Na_2CO_3



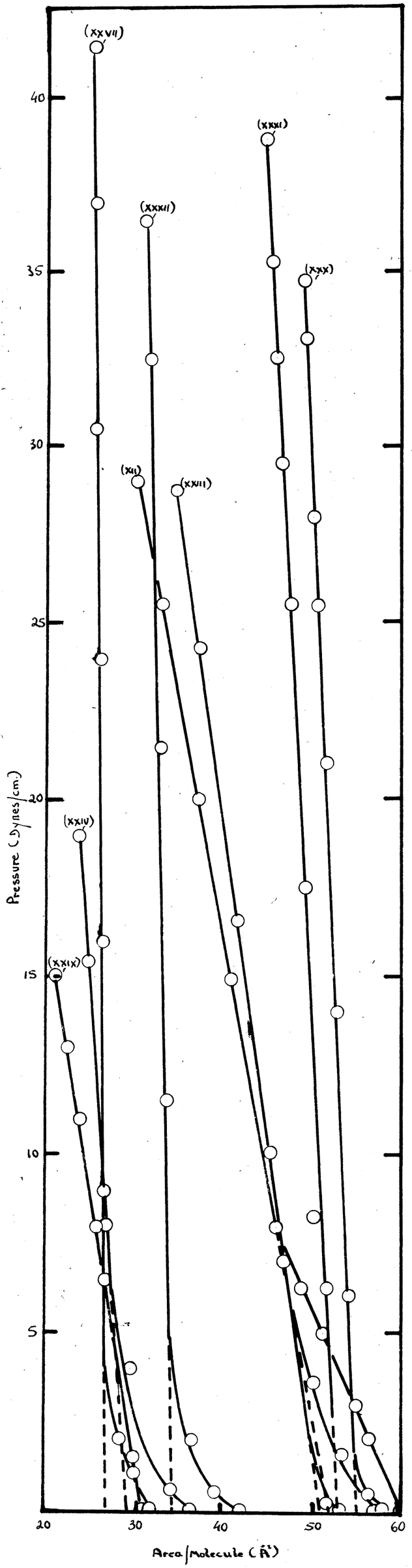
Graph 9


Pressure (Dynes/cm)
5
10
15
30
40
50
60
70
80
90
100
Area/Molecule (Å²)
(XVII)
(XVIII)
(XIX)
(XX)
(XXI)
(XXII)

Areas on Phenol.

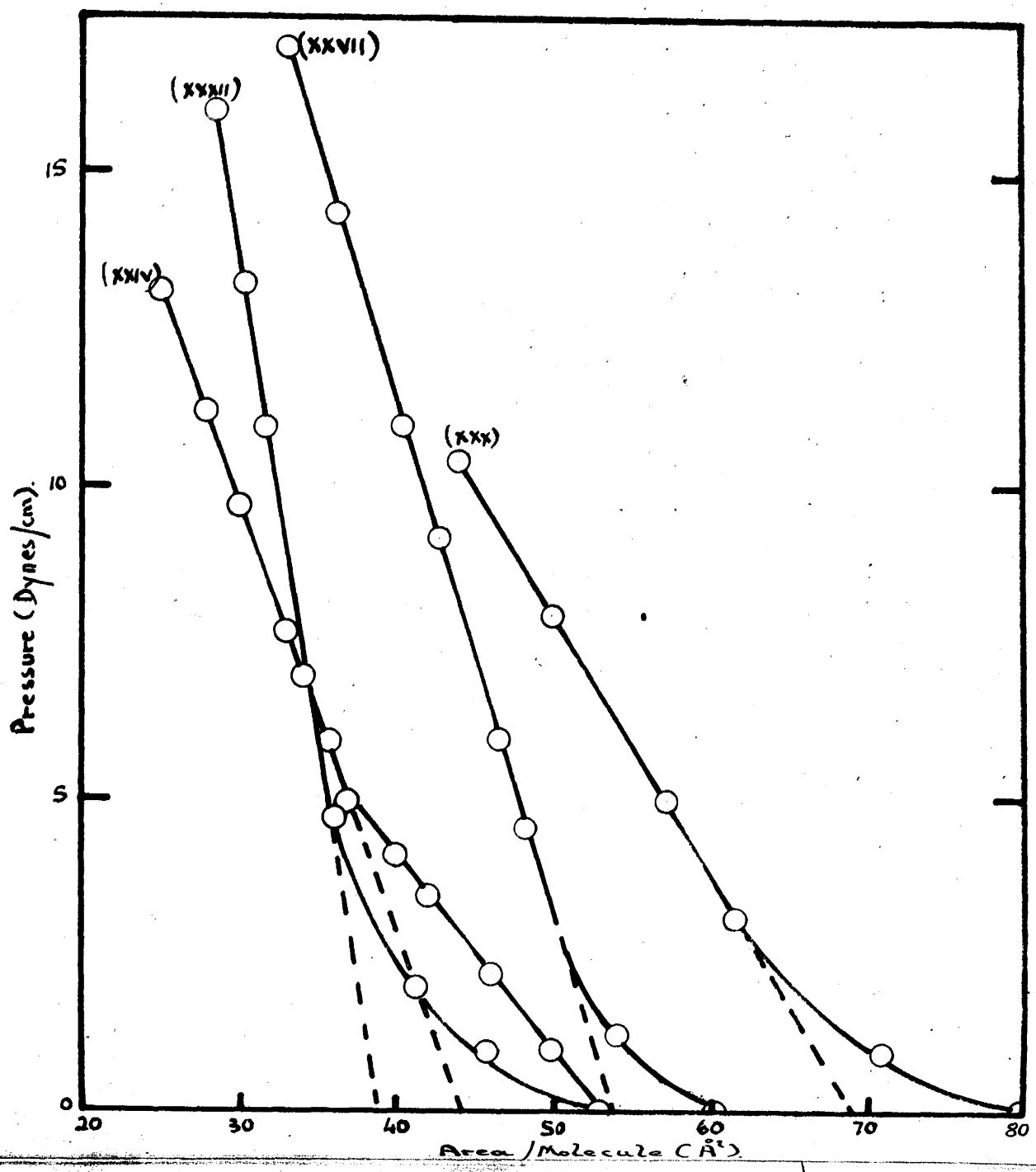


Areas on Hydroquinone.

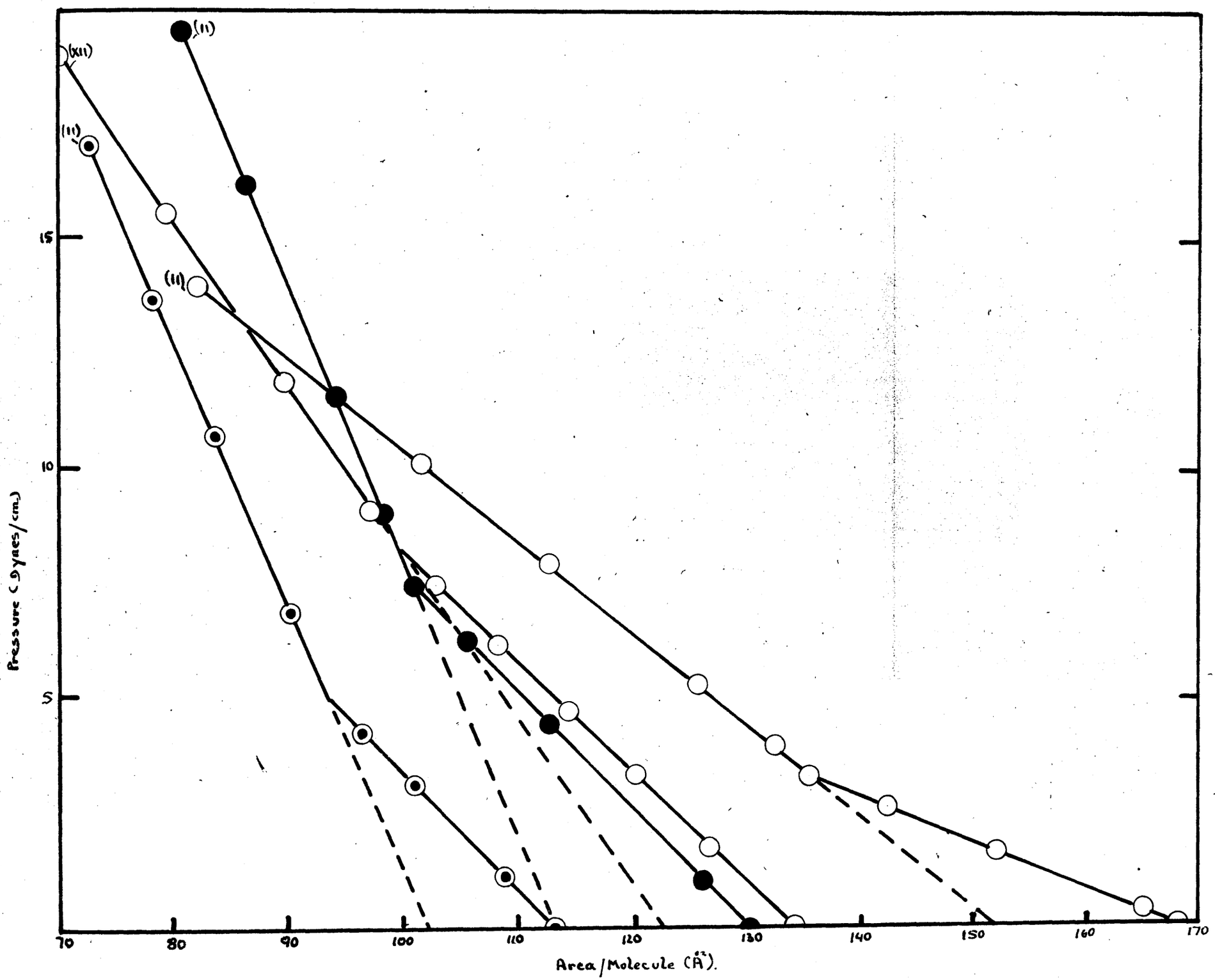


Graph 12

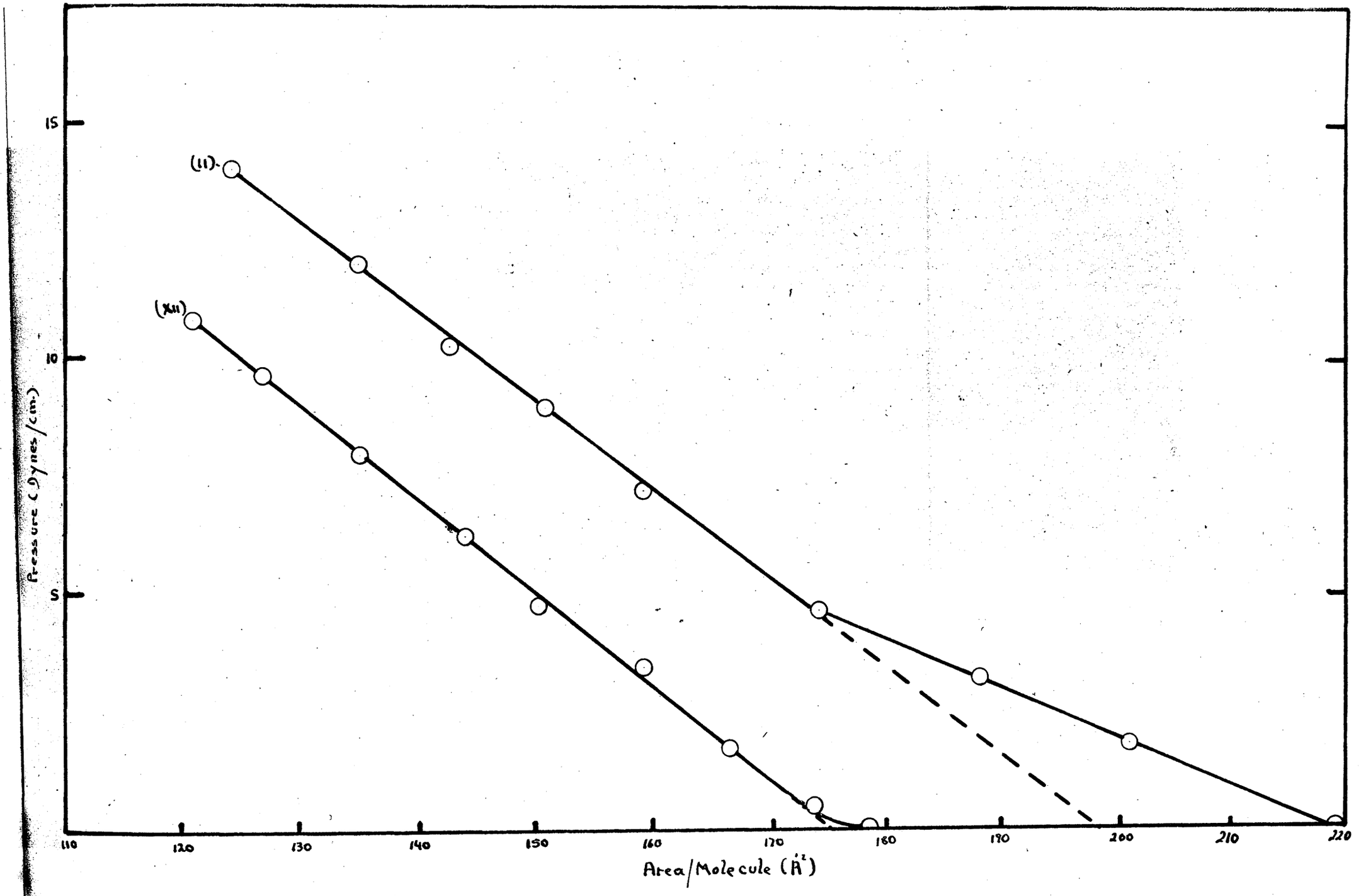
Areas on 1:5-Dihydroxynaphthalene.



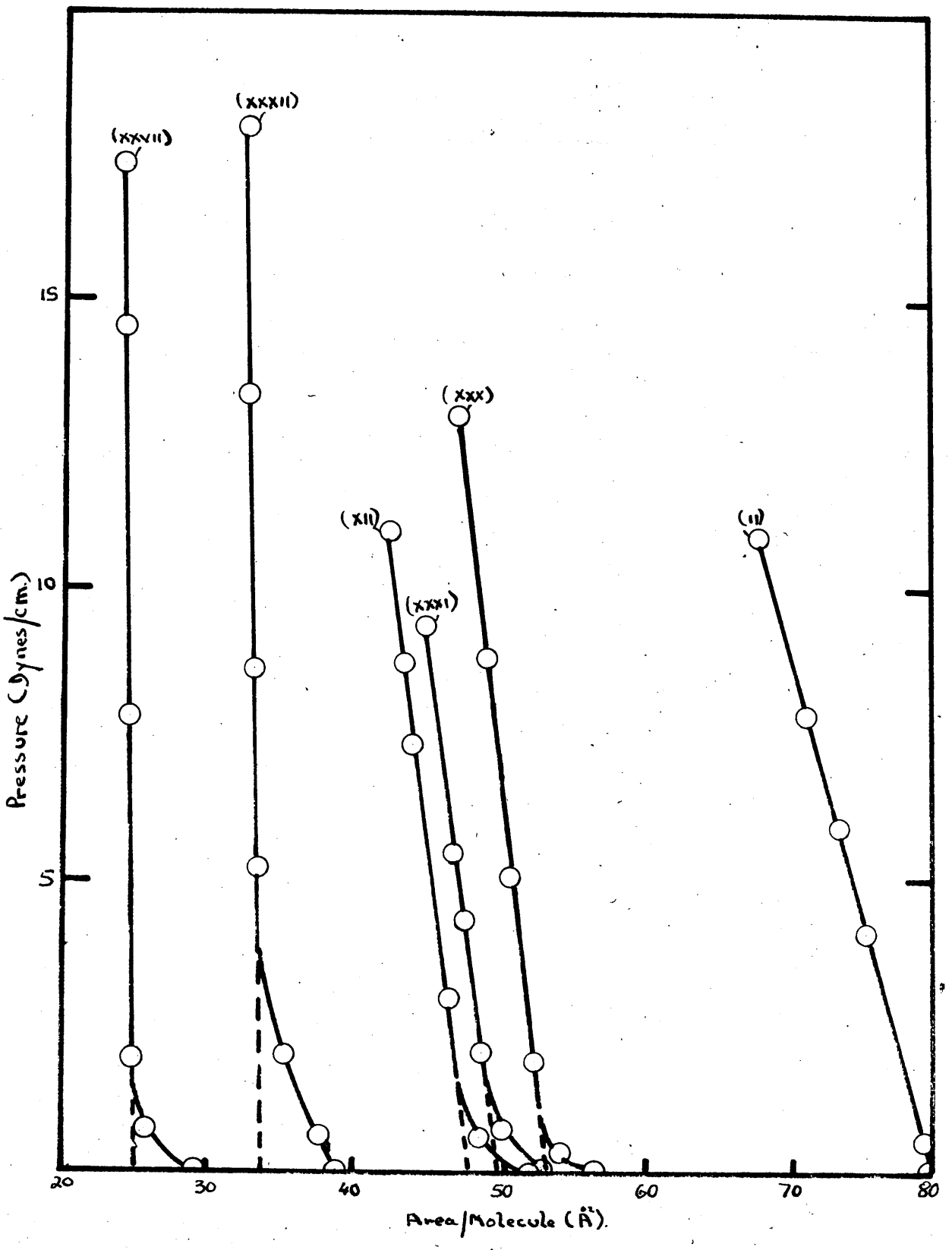
o- Dihydroxynaphthalene, • - Hydroquinone, ⊙ - Phenol.



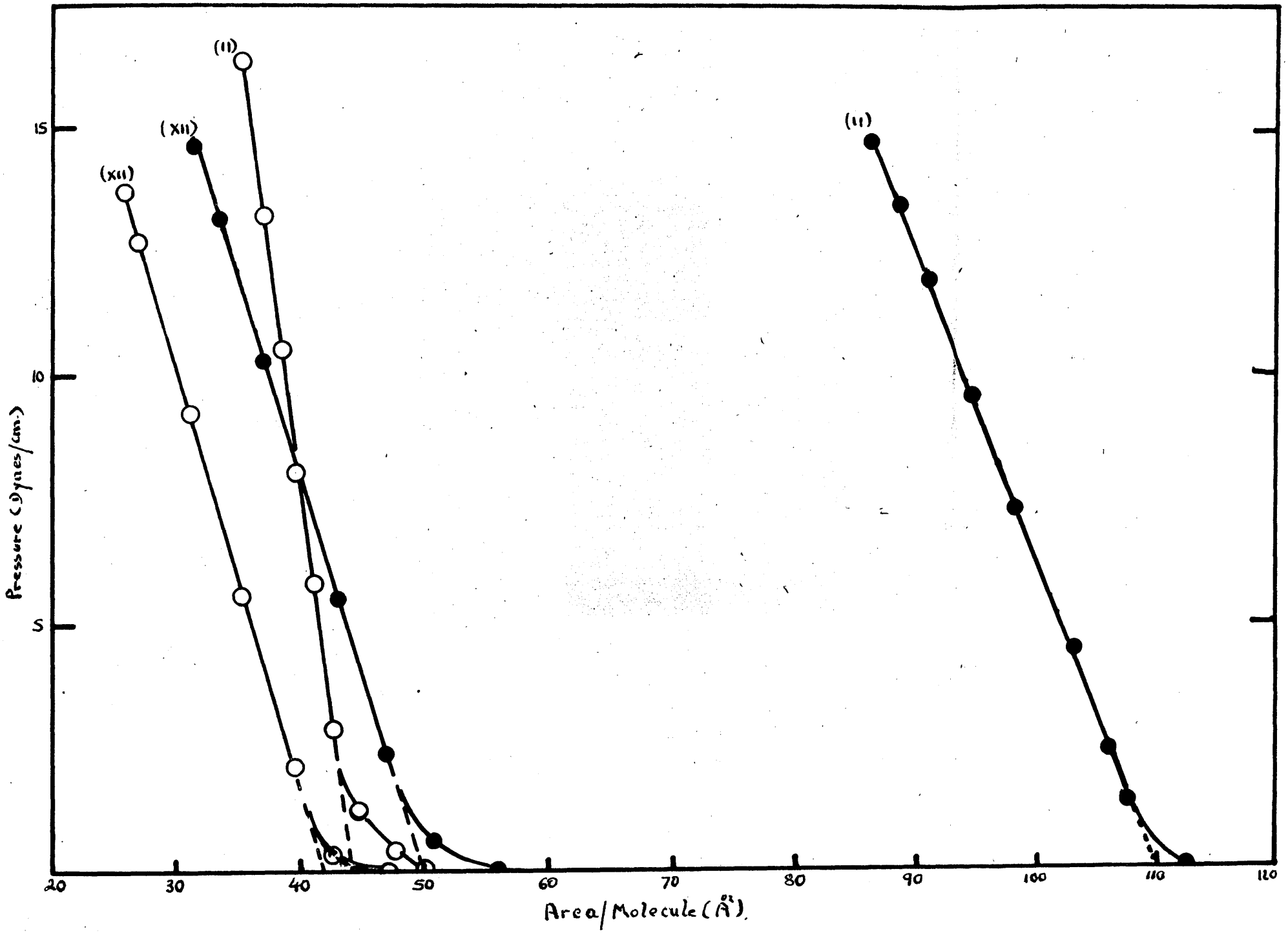
Areas on Alizarin Cyanin W.R.S.

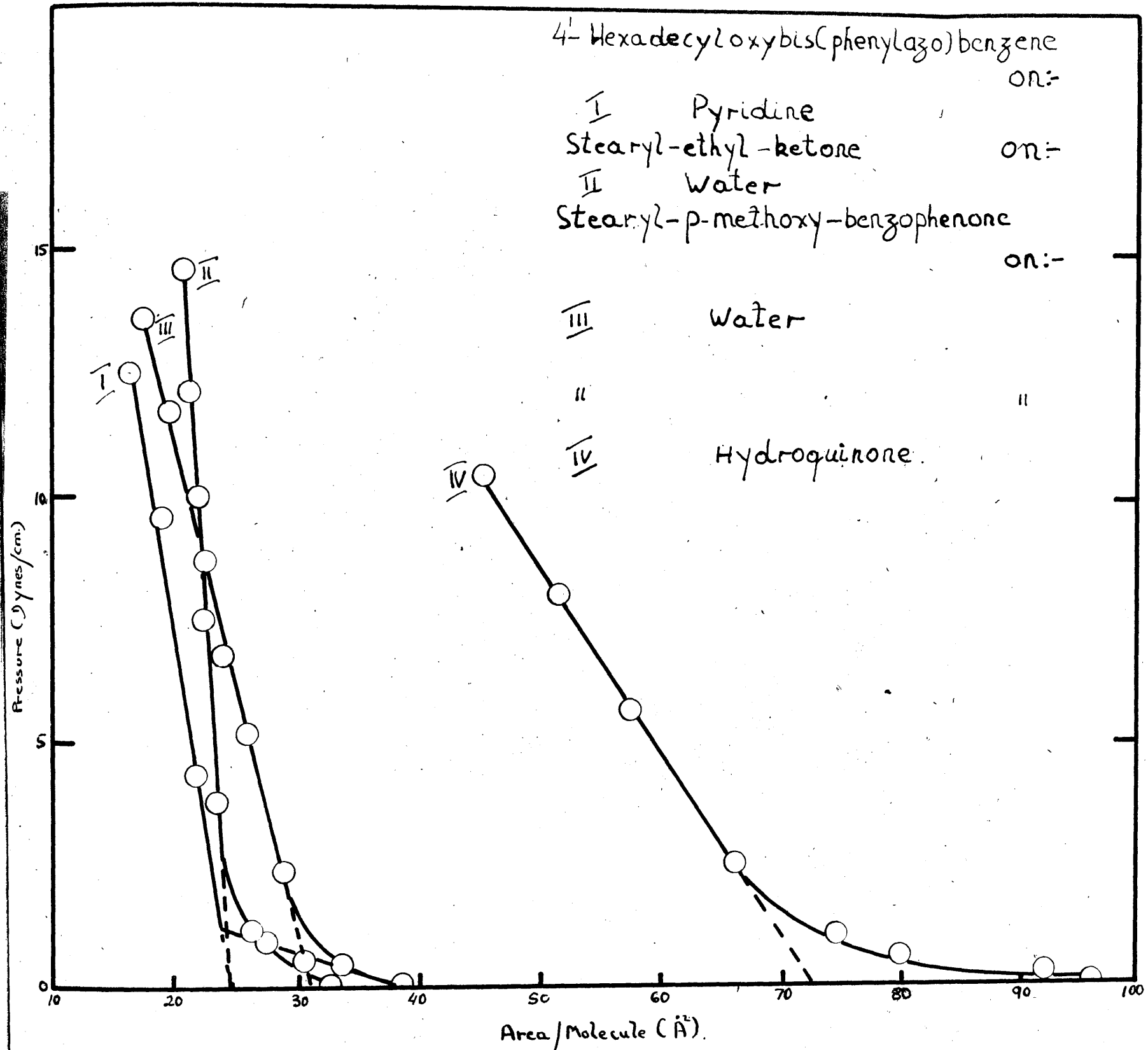


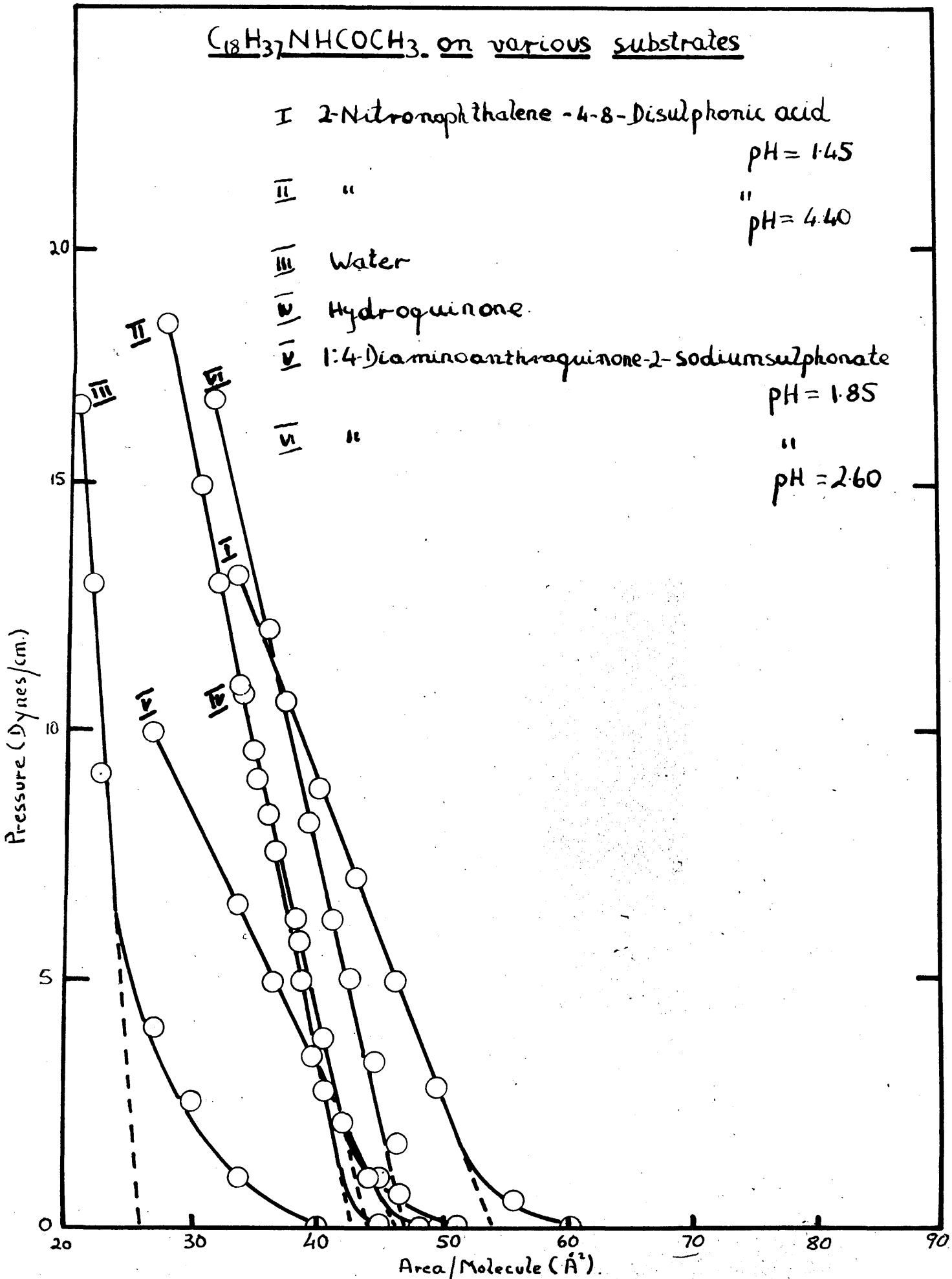
Areas on Ethylene Glycol.

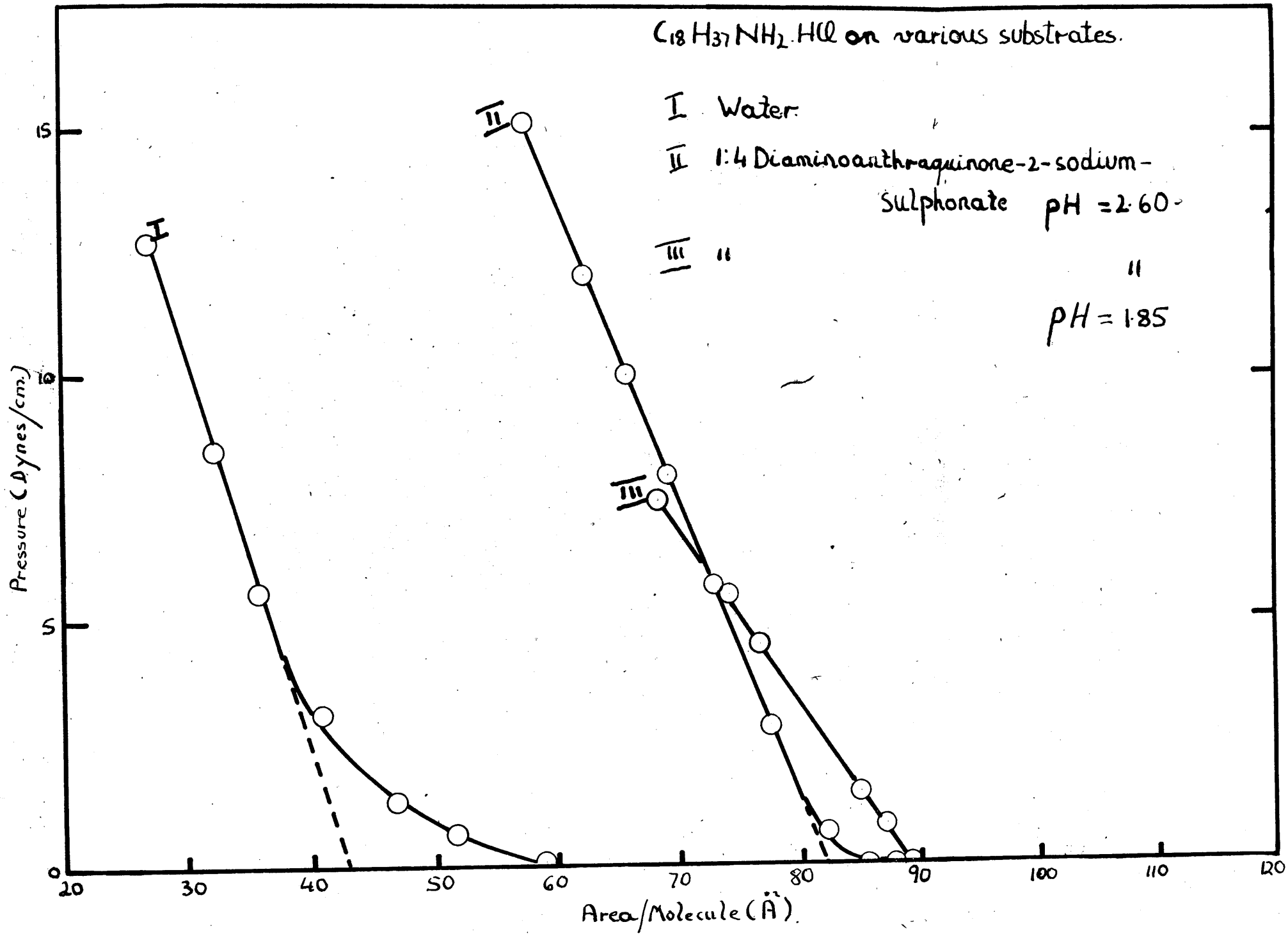


o- Pyridine, •- Catechol.




4'- Hexadecyloxybis(phenylazo)benzene
on:-
I Pyridine
Stearyl-ethyl-ketone
on:-
II Water
Stearyl-p-methoxy-benzophenone
on:-
III Water
II "
IV Hydroquinone.
Pressure (Dynes/cm.)
Area/Molecule (Å²)
0
5
10
15
10
20
30
40
50
60
70
80
90
100


$C_{18}H_{37}NHCOCH_3$ on various substrates
I 2-Nitronaphthalene-4-8-Disulphonic acid pH = 1·45
II " " pH = 4·40
III Water
IV Hydroquinone
V 1:4-Diaminoanthraquinone-2-sodiumsulphonate pH = 1·85
VI " " pH = 2·60
Pressure (Dynes/cm.)
0
5
10
15
20
20
30
40
50
60
70
80
90
Area/Molecule (Å²).


$C_{18}H_{37}NH_2.HCl$ on various substrates.
I Water
II 1:4 Diaminoanthraquinone-2-sodium-sulphonate pH = 2·60
III "
pH = 1·85
Pressure (Dynes/cm.)
Area/Molecule (Å²)
0
5
10
15
20
30
40
50
60
70
80
90
100
110
120

P-dodecylaniline → β-naphthol on:-

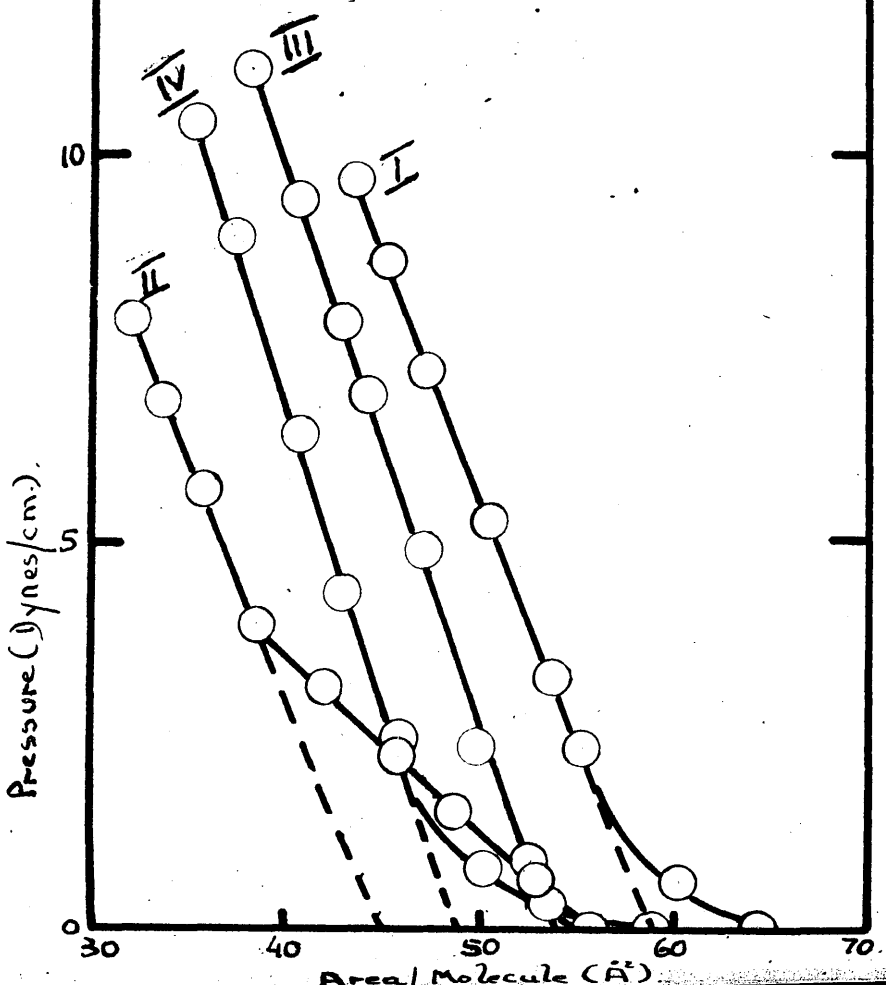
I Glucose.

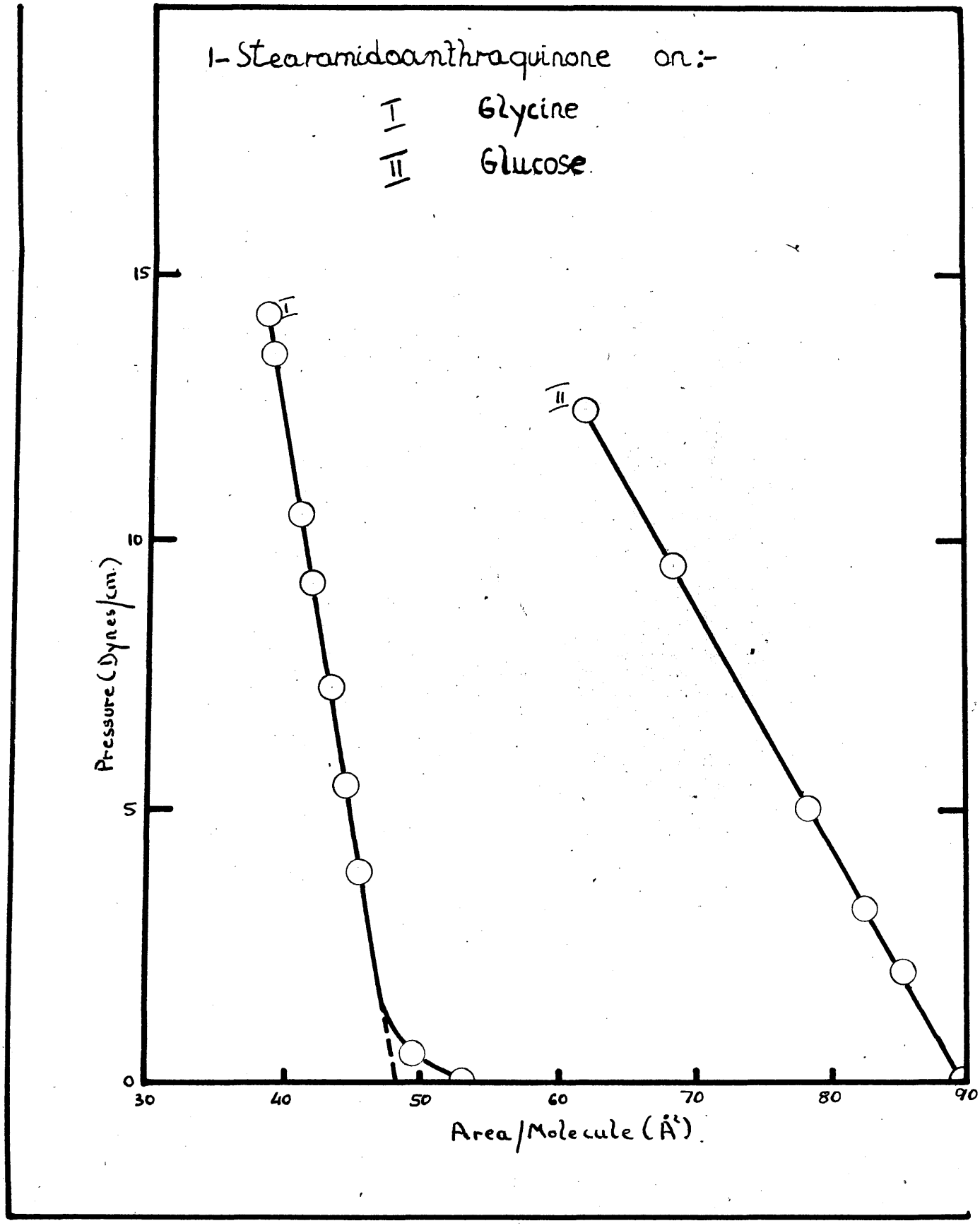
II Glycine

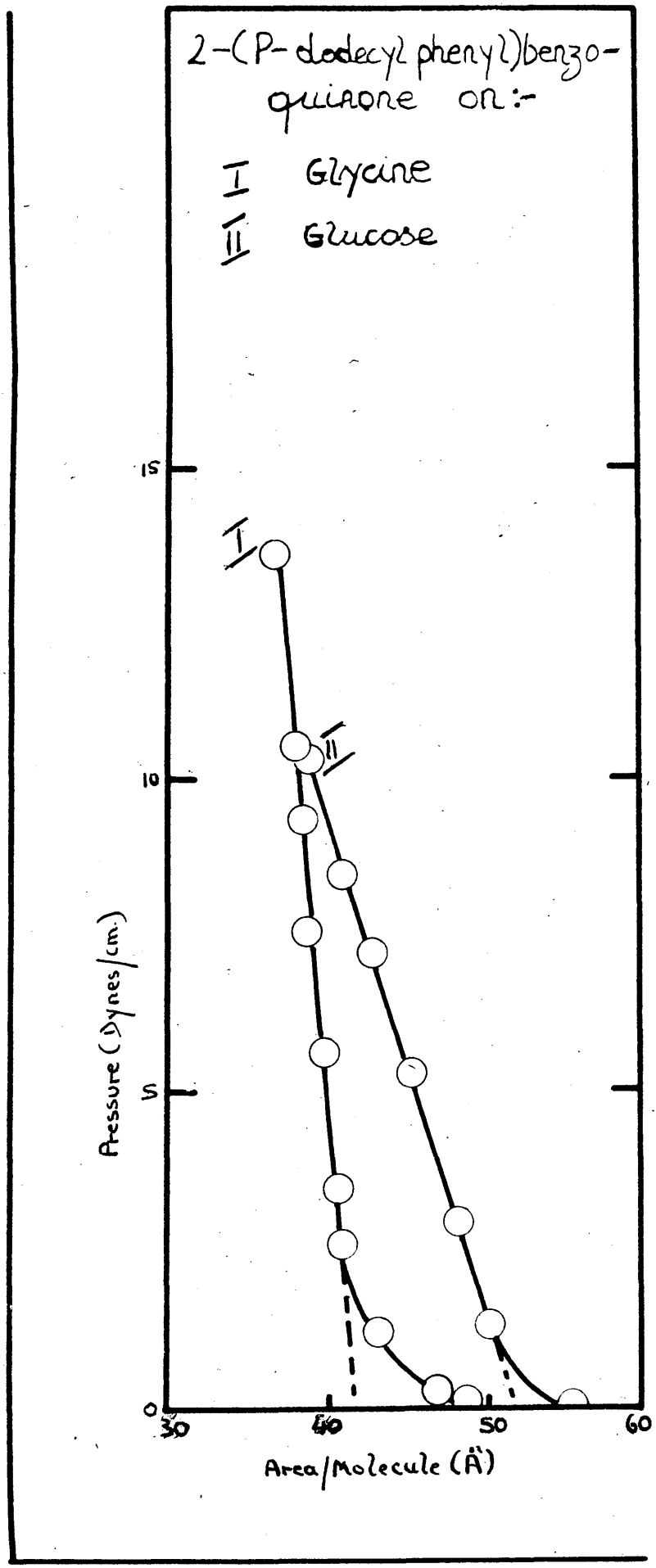
P-Hexadecyloxyaniline → o-creol on:-

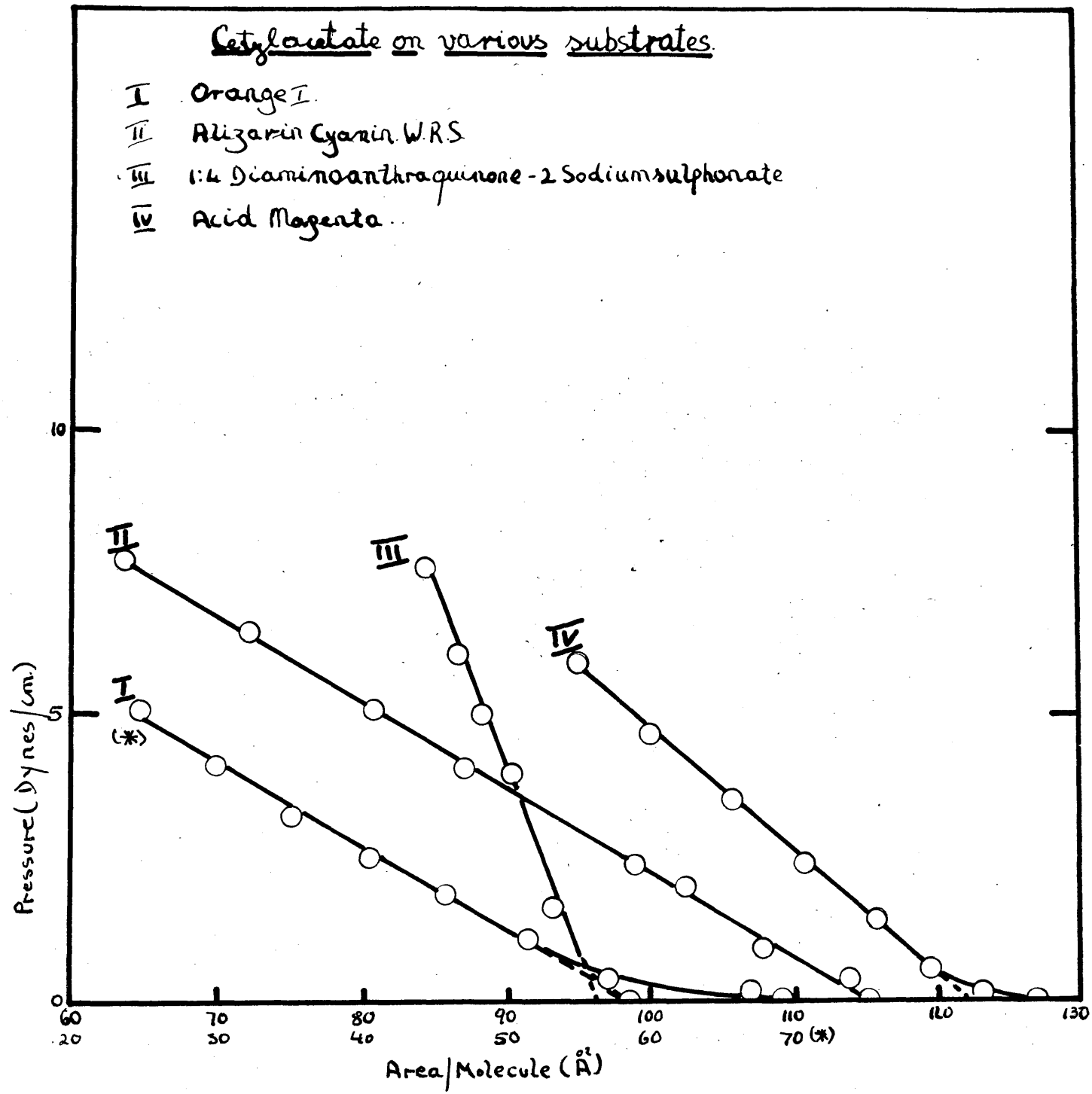
III Glucose

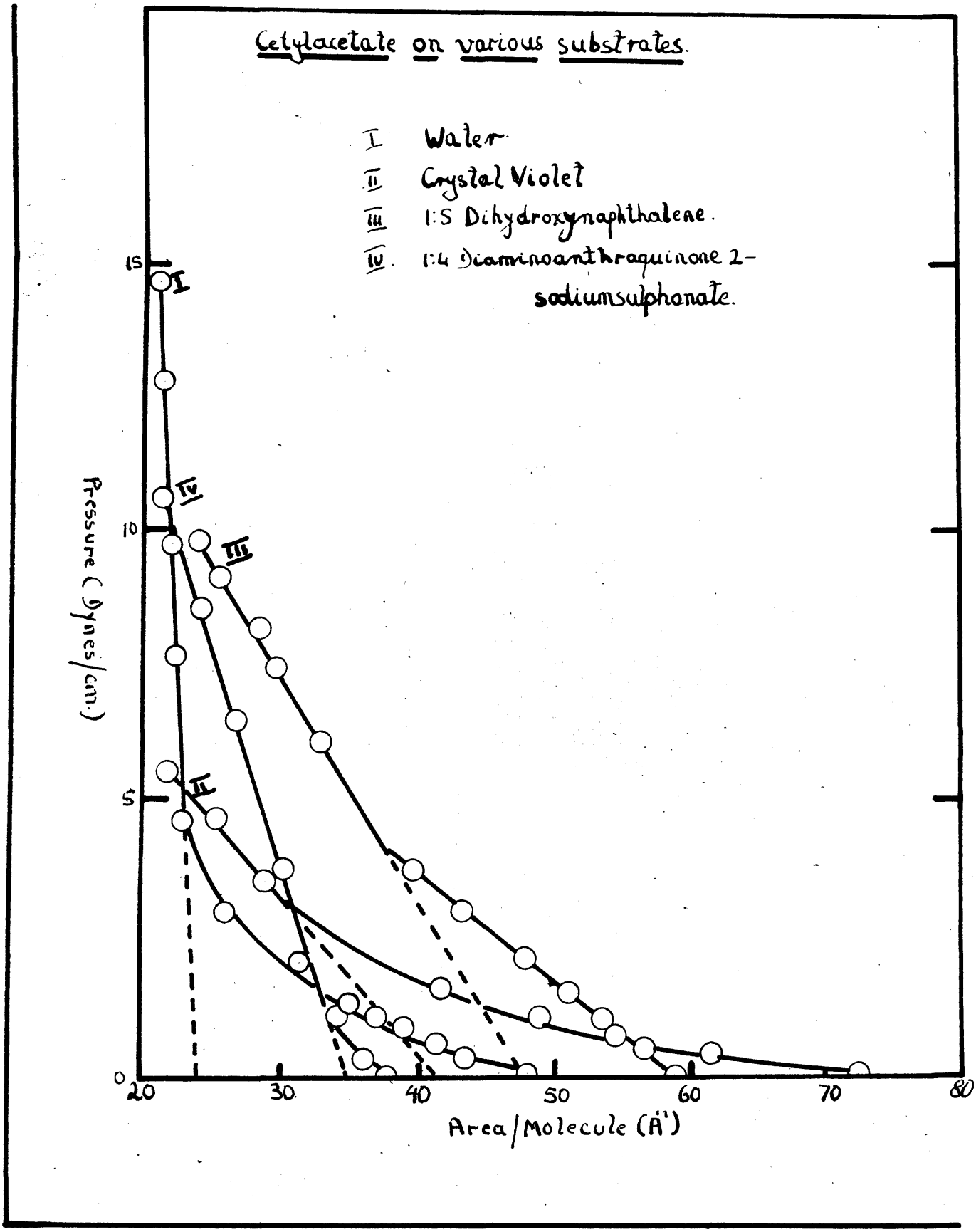
IV Glycine.




1- Stearamidoanthraquinone on :-
I Glycine
II Glucose.
15
10
5
0
I
II
Pressure (Dynes/cm.)
30
40
50
60
70
80
90
Area/Molecule (Å²)


2-(P-dodecyl phenyl)benzo-quinone on:-
I Glycine
II Glucose
15
10
5
0
I
II
Pressure (Dynes/cm.)
30
40
50
60
Area/Molecule (Å)


Cetylacetate on various substrates
I Orange I
II Alizarin Cyanin W.R.S
III 1:4 Diaminoanthraquinone-2 Sodiumsulphonate
IV Acid Magenta
Pressure (Dynes/cm.)
Area/Molecule (Å²)
(*)
0
5
10
60
70
80
90
100
110
120
130
20
30
40
50
60
70 (*)


Cetylacetate on various substrates.
I Water
II Crystal Violet
III 1:5 Dihydroxynaphthalene.
IV 1:4 Diaminoanthraquinone 2-sodiumsulphonate.
Pressure (Dynes/cm.)
Area/Molecule (Å²)
0
5
10
15
20
30
40
50
60
70
80
I
IV
III
II