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THE RELATION BETWEEN ADSORPTION ISOTHERM SHAPES AND THE MECHANISM OF SOME VAPOUR PHASE AND SOLUTION ADSORPTION PROCESSES.

by

IAN ALEXANDER EASTON.

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CONTENTS.

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PUBLICATIONS.

The work describing the adsorption of alizarin on alumina powder, given in Section II, Part II, is included in the paper:-

Datye and Giles, *Trans. Inst. Metal Finishing*, in press.

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GENERAL INTRODUCTION

ADSORPTION.

Adsorption[1,2] may be defined as the concentration of molecules of phase A at the surface of phase B. Phase A is known as the adsorbate and phase B the adsorbent or substrate. Adsorption of gases by charcoal was first recorded by Scheele[3] in 1773 and later by the Abbe Fontana in 1777. It was not until 1785, however, that Lowitz noted that charcoal also removed colouring matters from solution. Although these cases were the first to be given some scientific explanation they were not the first to be observed. Some 3000 years ago, perhaps the first recorded vapour phase adsorption experiment was unknowingly reported in the scriptures[4] and has since been partially explained by Brunt[5] and recently more fully explained by Giles[6].

Although adsorption occurs essentially at the surface of a body, unless this body is suspended in a vacuum, it would be more correct to use the term interface since a solid is generally in contact with a gas, a liquid or another solid.

Interface.

The interface between a solid and liquid or gas which is of great importance in the study of surface chemistry especially from an adsorption point of view, is only one or two molecules thick[7] (*ca.* 100A) but spreads macroscopically over /...

over the surface. Thus the interface can be considered as a two dimensional region with the accompanying restrictions of movement of the molecules within this region. As well as the solid:gas, solid:liquid and solid:solid interfaces there are two others, namely the liquid:liquid and gas:liquid.

Interfaces may be conveniently divided into two broad classes - mobile and immobile.

Mobile interfaces. - Mobile interfaces are represented by liquid:liquid and gas:liquid and are characterised by their ability to contract spontaneously to the smallest possible area. Unlike the molecules of a solid which have only vibrational and rotational movement, the molecules of a liquid can move relative to each other but are kept close together by cohesional forces. The movements of molecules in liquids are more restricted than in gases and the intermolecular attraction prevents more than a small number escaping into the vapour. Thus molecules at a mobile interface are continually being shuffled back and forth and so form a dynamic equilibrium. Because of this continual movement the phases are homogeneous parallel to the interface.

Immobile interfaces. - The immobile interface, on the other hand, which is represented by solid:gas, solid:liquid and solid: solid, cannot contract spontaneously owing to the rigidity of the solid surface which forms at least one phase. Because of its /...

its rigidity an immobile interface is normally heterogeneous. The molecules of the solid surface are in the random arrangement in which they were left when the surface was formed. Unless it has received some treatment, such as polishing, to remove irregularities the surface will consist of crystal faces and edges randomly arranged and protruding in all directions giving regions of different adsorption characteristics.

Only immobile interfaces of the type, gas:solid and liquid:solid, will be considered further in this work.

FORCES OF ADSORPTION.

A solid, which consists of atoms or molecules, is held together by several forces:- van der Waals, electrostatic or Coulombic, exchange or homopolar valence forces. Several of these can act simultaneously although one usually predominates. Particles at the centre of a solid are subject to equal forces in all directions whereas the particles at the surface experience unbalanced forces, being attracted inwards and on all sides, but having no attraction in an outward direction. The surface is therefore in a state of unsaturation. These unsaturated forces can attract the molecules or ions of a gas or liquid (which also have unbalanced forces) and so adsorption can be thought of as the interaction of the fields of force of the surface particles of a solid with those of a gas[8], a liquid or another solid. When a solid is immersed in a gas or liquid the molecules tend to migrate towards the surface to balance the unsatisfied forces and so reduce the free energy.

Forces Involved in the Adsorption of Gases.

Gases can be adsorbed by a solid by either physical or chemical adsorption.

Physical Adsorption.

Physical adsorption of a gas can be likened to the condensation of a vapour on a solid. The process is completely reversible /...

reversible simply by increasing the temperature or decreasing the pressure since no chemical bonds are formed or broken. The heat of adsorption is small, being about 2-3 kcal./mole.

The forces involved in physical adsorption, normally grouped under the term "van der Waals" consist of electrostatic, dispersion, dipole moments and polarisation forces.

Electrostatic forces. - Ionic solids give rise to an electrostatic field which decreases rapidly with distance from the surface. For a homogeneous solid the electrostatic charge should alternate over the surface according to the charge of the ion beneath any point. A solid surface, however, unless a true crystal face, is very inhomogeneous, having randomly arranged crystal faces, edges and corners. The electrostatic charge will vary in intensity, being greatest for a crystal corner, less for an edge and least for a face. Thus no ordered pattern of charge can be expected. Verwey[9] has shown theoretically that negative ions are displaced preferentially to the surface.

If the adsorbate has a permanent dipole the forces will interact such that the dipole is correctly oriented. If the adsorbate does not have a permanent dipole the electrostatic field will induce a weak dipole.

Dispersion forces. - Dispersion forces are caused by the fluctuating electrical moment produced by the movement of electrons /...

electrons in their orbits which produces a corresponding moment in a neighbouring atom or ion thus leading to attraction.

London[10] first evaluated these forces by quantum mechanics as a function of the distance between two isolated molecules and later the expression was integrated by Polanyi and London[11] to cover the entire surface.

These forces are always present, although sometimes they may be obscured by some stronger force.

Chemical Adsorption.

If physical adsorption is considered to be similar to the condensation of a gas to a liquid then chemical adsorption (chemisorption) may be likened to a chemical reaction. In fact a localised chemical reaction, confined to the surface, actually takes place between the gas and the solid with the accompanying transfer of electrons. The heat of adsorption is high and similar to the heat of a chemical reaction (20-30 kcal/mole). This high heat is caused by the energy of activation which must be overcome before the reaction (adsorption) can take place.

Unlike physical adsorption, which is completely unspecific if the temperature is low enough, chemisorption occurs at much higher temperatures and is very specific, e.g. hydrogen is chemisorbed by tungsten and nickel but not by alumina or copper[8], and oxygen is chemisorbed by charcoal but not by magnesia /...

magnesia or gold. A gas is chemisorbed only to the extent of a monolayer (any further layers being held by physical adsorption) whereas physically adsorbed gases can form multilayers.

The sharing of electrons between a metal and an adsorbed gas may be unequal[8] causing the formation of a dipole, e.g. hydrogen on platinum forms a dipole with the positive charge away from the metal whereas hydrogen on nickel has the negative end of the dipole away from the metal.

Forces Involved in the Adsorption of Liquids and Solutions.

Several of the forces already mentioned in connection with gaseous adsorption take part in the adsorption of liquid mixtures or solutes from solution.

Van der Waals forces. - As in the case of physical adsorption of gases van der Waals attraction is purely physical since no chemical bonds are formed.

Several instances of van der Waals attraction have been observed:-

Acid wool dyes are appreciably adsorbed by graphite[13]. Since graphite has no chemically active groups adsorption must be by van der Waals attraction. This is supported by the fact that adsorption decreases with increased sulphonation of the dye molecule since the molecules then have greater attraction for water.

The dyeing of cellulose by direct dyes was thought to be due /...

due to hydrogen bonding[13], but cellulose consists of many hydroxyl groups in close proximity to each other, which, in aqueous solution, will strongly attract an atmosphere of water thus perhaps preventing dyes from forming hydrogen bonds. In a non-polar solvent, however, the hydroxyl groups of the cellulose will not be bound by water and are thus free to form hydrogen bonds with a suitable solute. Phenol is not adsorbed from water by cellulose but it is adsorbed by chitin[14] (an amino-acetyl derivative of cellulose) which does not have a strong protecting layer of water. Cellulose in _iso_-octane is not surrounded by water and so is free to adsorb phenol. Although some sulphonated acid dyes are adsorbed from water by cellulose, the mechanism cannot be attributed to hydrogen bonding since there are no potential hydrogen bonding groups present in the molecules of several of these dyes. It was found[15], however, that the affinity of these dyes increases with the logarithm of the longest chain in the molecule, which supports the theory of van der Waals bonding.

Further evidence against the theory of hydrogen-bond dyeing of cellulose is given by Giles[16] in a study of the dyes Orange I and Bordeaux Extra. The molecule of Orange I has three potential bonding groups whereas that of Bordeaux Extra has only two, yet Orange I is not substantive to cellulose and Bordeaux Extra is. The latter, however, has a longer conjugate chain system in its molecule, which is planar and larger /...

larger than that of Orange I, and these tendencies according to Hodgson[17] should increase its substantivity.

It was also shown by Giles[16] that anthracene α-sulphonic acid, which has no hydrogen bonding groups in its molecule has a higher affinity for cellulose than haematoxylin which has four strong and two weak hydrogen bonding groups. Anthracene α-sulphonic acid, however, has a longer conjugate chain than haematoxylin and will be adsorbed by physical forces.

Ion exchange. - The process of ion exchange was first observed by Way[18] in 1850 when solutions of electrolytes were passed through certain naturally occurring earths and zeolites. Ion exchange has since been observed in several adsorption processes of dye cations on powders such as silica[19] and graphite[12] and anions on acidified alumina[20]. The reactions involve exchange of dye anions and cations usually with sodium, hydrogen or chlorine. They are characterised by a very low heat of adsorption and rapid attainment of equilibrium. The surface is completely covered by the adsorbed layer and in many cases the ions adsorbed are much in excess of a monolayer. This has been explained by the formation of ionic micelles or clusters of ions which are adsorbed as aggregates at the surface.

Silica has a negative charge in water[21] due to the ionisation of some silicic acid at the surface and readily adsorbs./...

adsorbs dye cations. Basic dyes are adsorbed by graphite by ion exchange with the hydrogen ions in the double layer[12]. Acid dyes (anionic), although also adsorbed by graphite, are adsorbed by physical forces such as van der Waals forces between the graphite and the aromatic nuclei of the dye molecules[12]. Commercial alumina is alkaline in water[20] due to the presence of sodium carbonate left from a manufacturing stage. It was shown by Schwab and Jockers that cations are adsorbed by ion exchange[22] with the sodium ions at the surface. Alumina acidified by hydrochloric acid has a positive surface[23] which contains covalently bound chlorine atoms as well as some ionised chlorine. Anionic dyes are adsorbed by ion exchange with the ionised chlorine. Giles et al.[24] have shown that sulphate esters are adsorbed by ion exchange by the anodic film on aluminium.

Hydrogen bonding. - Hydrogen bonding has been shown to occur between compounds with a free hydrogen atom and a polar solid such as alumina if internal chelation does not take place. Thus, alumina[20] adsorbs phenols, amines and aldehydes and silica adsorbs phenols and amines from both aqueous and non-aqueous solvents[19]. As discussed above cellulose cannot form hydrogen bonds with solutes in water but it can form them in non-polar solvents.

Arshid et al.[25] have shown that haematein and brazilein which are poly-hydroxy compounds and weak acids are adsorbed probably /...

probably by hydrogen bonding on wool and nylon, and Chipalkatti[26] has suggested that hydroxy compounds form hydrogen bonds with the enolic forms of the amide and peptide groups in nylon and wool, respectively. Phenols and amines seem to form hydrogen bonds when adsorbed from non-polar solvents on the anodic film of aluminium[24].

Covalent bonding. - A covalent bond occurs between the adsorbed molecule and the substrate when a transfer of electrons takes place. Covalent bonding has been shown to occur between mordant dyes[27] and certain metals and it was thought to take place directly between alizarin and the atoms of the anodic film of aluminium[24]; although this latter action has recently been shown to be unlikely by Datye and Giles[28]. They suggest that the aluminium:alizarin complex is preformed in solution and adsorbed by ion exchange as ionic micelles.

Perhaps the most important type of covalent bonding molecules discovered in the field of colour chemistry is the class known as reactive dyes[29]. A typical reactive dye molecule has a triazinyl nucleus which is thought to form a covalent bond, in the presence of alkali, with the secondary hydroxyl groups of cellulose.

It has been stated[30] that at least some of the p-nitrophenol adsorbed on alumina forms a covalent bond and cannot be removed completely by rinsing.

FACTORS INFLUENCING ADSORPTION.

1. Properties of the Solid.

Physical properties. - A solid surface being more rigid than a liquid cannot contract spontaneously and as a result it has the atoms arranged in the same random manner as when the surface was formed[7], for example by breaking. This random arrangement and non-mobility of the surface particles results in the surface being rough because of projecting crystals, aggregates of small crystals and even crystal fragments. Unless some attempt has been made to smooth the surface by polishing, the roughness will prevent easy spreading of liquids, even if the liquids have some affinity for the surface.

The surface properties of a solid can be altered by changing the degree of disorder or the conditions of formation of the surface. In a study of the reactivity of copper surfaces Palmer[31] and Constable[32] found that electrolytically deposited copper and polished copper mirrors are inactive in the dehydrogenation of alcohols to aldehydes whereas copper formed by the reduction of the oxide or the rapid condensation of the vapour is active. Thus catalysis only seems to occur if the metal is not arranged in a regular space lattice. The fact that only some parts of the catalyst surface have active sites on which reaction occurs was put forward by Taylor[33] and has now become generally accepted.

Carbon blacks vary enormously in their properties depending on the conditions used in forming them[34]. Spheron 6, a low temperature carbon black, contains bound oxygen giving the surface a polar character, whereas if the same carbon is heated to 2700°C the surface becomes similar to graphite and is almost completely non-polar. Gasser and Kipling[35] have studied the adsorption of alcohol:benzene mixtures on these two carbons as well as on a coconut charcoal. The more polar Spheron 6 carbon adsorbs the alcohol preferentially from solution over part of the concentration range whereas non-polar Spheron 6 (2700) adsorbs benzene preferentially over the whole concentration range.

Solids may be classed as crystalline or non-crystalline. The crystalline solids have a regular arrangement of atoms in the form of a lattice and they have reproducible properties such as melting point. The non-crystalline solids may be considered as having a distorted lattice whereas amorphous solids do not have any regular arrangement of particles.

Even a true crystal has varying regions of activity since the corners, being more exposed than the edges have more unsaturated forces and a higher free energy than the edges which in turn have a higher free energy than a crystal face. Different faces of the same crystal have different adsorption activity. This was illustrated by Gaubert[36] who found that Methylene Blue and picric acid were adsorbed on different respective /...

respective faces of urea nitrate. In fact if urea nitrate is crystallised in the presence of a mixture of Methylene Blue and picric acid (yellow in colour) the dyes will be occluded in different parts of the crystal, making some faces blue and some yellow. The shape of a crystal may be altered by the adsorption of solutes on particular faces since the growth of these faces will be inhibited and so will predominate in the final crystal. Butchart and Whetstone[37] have studied the crystal modification of salts such as ammonium nitrate, ammonium sulphate and potassium nitrate, by the inclusion of dyes. They found that different dyes modified different crystals, e.g. Acid Magenta modified ammonium nitrate while Tartrazine, which had no effect on ammonium nitrate, modified ammonium sulphate and potassium nitrate. No relationship between the dye structures and their ability to modify different crystals could be found although for ammonium nitrate the dye molecule had to contain sulphonate substituents as well as at least one cationic substituent such as a hydroxy or a primary amino group.

In a study of the caking properties of salts Whetstone[38] found that the dyes which successfully modified the crystal structures also enhanced the free-flowing properties of the salts. The caking of water-soluble salts is caused by partial dissolution of the crystal surfaces in the presence of moisture, followed by the formation of inter-granular bridges

by /...

by recrystallisation of the dissolved salt. The strength of these bridges determines the caking properties of the salt. Crystals having weak inter-crystalline bridges are free flowing because the bridges are easily broken by mechanical shock. Ammonium nitrate cakes strongly in the presence of moisture but when the crystal is modified by the inclusion of a dye the new crystal shape does not form strong bridges and so the salt becomes free flowing.

Bunn[39] showed that ammonium chloride, which normally forms skeletal growths by rapid growth along axial directions, formed cubic crystals in the presence of urea. The urea was adsorbed on certain faces which had crystal lattice spacings similar to urea itself and thus the rapid growth in axial directions was reduced.

Solid surfaces may be porous like silica gel or non-porous like silica dust. Most of the surface of porous solids (some carbon blacks) forms the walls of the pores and interstices and can really be considered as an internal surface. The presence of pores may assist gaseous or vapour adsorption since adsorption is strong inside the pores, which are molecular in diameter, due to the close proximity of two adsorbing surfaces which may eventually lead to capillary condensation. Adsorption, especially from solution, may be hindered as the size of the solute molecules increase since only the smallest molecules will be able to penetrate the finest /...

finest pores. Thus much of the available surface will be inaccessible to large molecules. Traube's rule states that in a homologous series adsorption increases with the number of carbon atoms[40]. Bruns[41], however, has shown that the adsorption on charcoal of a series of long chain fatty acids, ranging from one to six carbon atoms, decreases as the size of the molecules increase. Although this is in apparent disagreement with Traube's rule Brun's explanation was that the adsorption is controlled by the porosity of the charcoal. In fact if the pores are broken by further grinding of the charcoal then there is a tendency for the fatty acids to obey Traube's rule.

The rate of diffusion of vapours and liquids is controlled by the porosity of the surface and so as the size of the adsorbing molecule increases the rate of adsorption decreases. In the case of some powders, such as carbon blacks, which are extremely porous the attainment of equilibrium may take several days.

Chemical properties. - Solids may be divided chemically into polar and non-polar classes. Polar solids such as silica, alumina and titania adsorb by electrical or polar charges, the dispersion forces, described above being relatively small. Non-polar surfaces such as graphite adsorb mainly by dispersion forces.

Polar solids having dipolar molecules react with dipolar adsorbates /...

adsorbates in such a way that the dipoles are opposed causing increased attraction. It has been shown by Arnold[42] that the adsorbate containing the largest number of isolated dipoles is the more strongly held, e.g. picric acid is more strongly adsorbed from petroleum ether on alumina than is o-nitrophenol, although o-nitrophenol has the larger permanent dipole. Karrer and Nielson[43] found that the order of appearance of nitrophenols on an alumina column is para, meta, and ortho. This order is not due to basicity or acidity but is due to the decreasing permanent dipoles in the molecule and Cook[44] has shown that cis-azobenzene is more readily adsorbed on alumina than is trans-azobenzene. This has been confirmed by Giles et al.[20]. Thus isomeric molecules containing the same number and kinds of groups are more strongly adsorbed by a polar solid as their dipoles increase.

If no permanent dipole exists in the adsorbate molecule then the adsorbent will induce a weak dipole and the adsorbate molecule with the highest polarisability (ease of formation of an induced dipole) will be adsorbed to the strongest extent.

2. Properties of the Gas.

The adsorption of a gas by a solid is not only dependent on the surface properties of the solid but is, to some extent, dependent on the nature of the gas. Several correlations between the amount of gas adsorbed by a given adsorbent and certain characteristics of the gas have been reported.

Perhaps /...

Perhaps the earliest was by de Saussure[45] in 1814 when he showed that the most easily condensible gases are adsorbed to the greatest extent. This is hardly surprising when physical adsorption is considered to be similar to the condensation of a vapour on a surface.

The graph in Fig. 1. is plotted from data by Hene[46] and shows the relation between the volume of gas adsorbed by charcoal and its boiling point. A similar relationship is obtained by using the critical temperature of the gases which is in fact related to the boiling point.

Arrhenius[47] found a relationship between the volumes of different gases adsorbed by charcoal and their van der Waals constants "a" and Schmidt[48] showed that there is a relationship between the heats of vapourisation of gases and the amount adsorbed.

All the above correlations are dependent on purely physical adsorption, which is entirely non-specific. No such relationships can be found for chemisorbed gases which are usually specific for certain substances.

3. Properties of Solutions.

As the solubility of a solute increases, the molecules become more firmly held in solution and so they cannot be adsorbed to the same extent by a solid. Cassidy[49] illustrated this effect with the adsorption of fatty acids from ligroin and petroleum ether on charcoal. The fatty acids were adsorbed /...

adsorbed by charcoal to a lesser extent from ligroin in which they have a higher solubility. It was pointed out, however, by Bartell and Fu[50] that the decrease in adsorption due to increased solubility could only be strictly compared using two solvents which have the same wetting ability for the surface, e.g. benzene and carbon tetrachloride on silica.

Hydrolytic adsorption was defined by Bartell and Miller[51] as the preferential adsorption of an anion or cation from solution. The most striking example of hydrolytic adsorption is shown by the preferential adsorption of large basic dye cations, making the solution acid and the adsorption of large acid anions making the solution alkaline.

Broda and Mark[52] have shown by calculation that adsorbability of long chain molecules increases with chain length. There are more degrees of freedom in the desorbed than in the adsorbed state, since the ~~the~~ adsorbed molecule has only rotational and vibrational movement, but no translational movement. It is known that molecules usually prefer the state with the largest number of degrees of freedom and so will prefer the desorbed state. The difference, however, between translational and vibrational degrees of freedom decreases with increasing chain length. This theory of Broda and Mark[52] was verified by Baum and Broda[53] who studied series of paraffin waxes and carbohydrate derivatives. They found that although equilibrium adsorption increased with chain /...

chain length the rate of adsorption decreased. The smaller adsorption rate of the longer chain molecules may cancel the effect of the greater absorbability on the final equilibrium.

If solute molecules tend to associate together they become less soluble and as a result adsorption increases. Acetic acid is less adsorbed at high temperature on charcoal than at room temperature[54]. The reason for this is that acetic acid, which forms dimers at room temperature, is dissociated by heat.

4. Effect of Temperature.

Adsorption is governed thermodynamically by the equation:-

$$\Delta F = \Delta H - T\Delta S.$$

Since adsorption results in a decrease of the free energy of a surface ΔF must be negative. At the surface the adsorbed molecules move from a three dimensional region to a two dimensional one with a resulting increase in the degree of order of the system, thus ΔS is positive and so ΔH must be negative to balance the equation. If ΔH is negative then adsorption is an exothermic reaction and will decrease with increase in temperature.

The adsorption of gases and vapours decreases with increase in temperature. The adsorption of solutes from solution usually does so but not always. The adsorption of hydrogen bonding and physical van der Waals bonding solutes follow the exothermic principle but ion exchange reactions which /...

which have a very low heat of adsorption (ΔH) show no change in the amount adsorbed at two temperatures except in special cases. Giles et al.[55] have shown that ion exchange adsorption involving large ionic micelles actually increases with increased temperature and this has been confirmed by McKay[56]. The explanation given is that the ionic micelles break down at high temperature and the larger percentage of monomer present in solution can build (at the surface) into larger aggregates. This matter will be discussed in more detail later.

SECTION I.

VAPOUR PHASE ADSORPTION.

INTRODUCTION.

As shown in the General Introduction adsorption occurs as a result of the interaction between the field of force of the surface of a solid and that of a gas or vapour molecule. Perhaps the best method of studying adsorption is by means of the adsorption isotherm. This is merely a plot of the amount of gas or vapour adsorbed at various pressures by a given solid at a constant temperature. Usually when the adsorbate is a vapour the amount adsorbed is plotted against the relative pressure rather than the actual pressure. The relative pressure is the actual pressure of the vapour divided by the saturated vapour pressure at the temperature of the isotherm. Although hundreds of isotherms have been reported on many different adsorbents, Brunauer[57] divided them all into five separate classes depending on the various shapes obtained. Only types I, II and V will be considered in this work and these are represented in Fig. 2.

According to Langmuir[58] when the forces of attraction are strong, as in the adsorption of a polar vapour on a polar solid, adsorption proceeds readily even at low vapour pressures, giving a type I isotherm. As the available sites are filled it becomes progressively more difficult for a molecule to be adsorbed until finally a monolayer is complete. Since the range of force is only about 10^{-8} cm., which is less than /...

than the diameter of the molecule, a large molecule will orientate itself such that the attracting group is towards the surface. Sometimes a second layer of molecules begins to form on top of that already present, as shown by a second rising part in the isotherm (Brunauer type II, Fig. 2b). A simplified pictorial representation of adsorption is given in Fig. 3, which shows the relationship between the stages of a Langmuir-type isotherm and the amount of surface covered. Types I and II isotherms correspond closely to types L2 and L3 of the Giles _et al._ classification[59] of isotherms for adsorption from solution and are the most common types encountered in both vapour and solution adsorption work. A simplified classification of the four main types of solution adsorption isotherm is shown in Fig. 4.

When the attraction of the solid surface for a vapour is low compared with the attraction between the vapour molecules themselves then it will require a considerable vapour pressure before any molecules are adsorbed. The first molecules will be adsorbed only by a few active sites on the surface and subsequent adsorption will be assisted by those initially adsorbed molecules. This type of adsorption results in a type V isotherm (Fig. 2c). A type V isotherm corresponds to the S isotherm of Giles _et al._[59] (Fig. 4a) for adsorption from solution and must not be confused with the term "sigmoid isotherm" incorrectly used in some textbooks to describe a type II /...

type II vapour adsorption isotherm. As in the case of type V vapour adsorption isotherms the molecules adsorbed from solution (usually having a vertical orientation) assist the adsorption of further molecules until the surface is completely covered.

Using the knowledge of the shape of the adsorption isotherms the affinity of a vapour for a solid can be easily ascertained. For example, if a vapour gives a type I isotherm on one solid and a type V on another solid then at low vapour pressures the solid which gives type I must have a higher affinity for the particular vapour. The theory of vapour adsorption isotherms has recently been applied to a study of the mechanisms involved in atmospheric pollution.

A STUDY OF ATMOSPHERIC POLLUTION.

INTRODUCTION.

The study of air pollution is attracting widespread attention as the natural fuels such as coal and oil are consumed in ever-increasing quantities both for domestic and industrial use. Excellent reviews have been written on the subject by Rogan[60], Meetham[61] and Cohen and Ruston[62] and it has been discussed at several symposia both in this country and in the United States[63-67].

Atmospheric pollution, defined as the impurities present in air, may be divided into two broad classifications; natural pollution and artificial pollution, both of which contribute, in varying extents, to the general condition of the atmosphere.

Natural Pollution.

The two main sources of natural pollution are plants and dust from eroded rocks. During the summer months grasses, trees and fungi liberate pollen or spores into the atmosphere. These microscopic particles are extremely light and are thus readily held in suspension by turbulent air. They may be dispersed hundreds of miles from their original source, e.g. pollens from certain trees grown only in Alaska were detected near Washington and Oregon in America[68] and aeroplanes often collect samples of pollen far out over the oceans both at high and low altitudes. The presence of these fine particles, especially /...

especially near grass fields, gives rise to the well known allergy "hay fever" suffered by many individuals. This is merely an irritation of the respiratory tract of certain people who are allergic to grass pollen, causing symptoms similar to a heavy head cold, and after prolonged exposure leading to an asthmatic condition. Although this type of pollution is almost impossible to control, modern drugs of the anti-h~~y~~istamine type may be prescribed to reduce the effects of the allergy.

Rocks eroded by wind and rain cause fine dust which is carried aloft into the atmosphere by wind. Depending on the turbulence of the air and the size of particles, this dust may remain suspended for some time. Pollution of this type cannot be controlled but since it causes no immediate danger to health, as do poisonous gases, then it can be ignored although long exposure to such dust would probably cause "silicosis" - a lung irritation caused by fine silica particles.

Other sources of natural pollution are salt crystals, smoke from natural fires, and dust and fumes from volcanic eruptions. Since Britain is an island the atmosphere will contain fine salt crystals formed by the evapouration of sea spray. The presence of these crystals will greatly increase the corrosion of metals especially near the coast. Dust from natural fires and volcanic eruptions is normally localised

and /...

and its occurrence of short duration and so it will not be considered further. It is probable that the concentration of natural pollutants will be virtually constant over the years and so will not cause any increasing hazard to health.

Artificial Pollution.

Since the time man first learned to make fire he has been producing smoke. Until modern times, however, this smoke was overshadowed by the natural forms of pollution described above and therefore did not present any serious problem. During the last hundred years cities have sprung up around certain industries and the increased use of coal and more recently oil fuel has led to a serious pollution problem in these areas. Certain industrial processes such as cement manufacture, mining, smelting, quarrying and crushing of rocks give rise to airbourne dust and obnoxious gases. These, however, can be controlled to a great extent by physical and chemical means and therefore only present a problem of a localised nature.

In this work only pollution such as smoke, sulphur compounds, and other products of fuel combustion will be considered.

HISTORICAL SURVEY OF THE USE OF MINERAL FUELS.

Until the eighteenth century the major fuel for both industrial and domestic use was wood or wood charcoal. The reserve of timber, however, by the time of the industrial revolution in the late eighteenth and early nineteenth century had dwindled considerably and since the improved steam engines and the new blast furnaces required better fuel, attention was directed towards the use of coal. Coal has long been known in this country[60,62]. Cinders were discovered at the site of the Roman wall in Northumberland dating back to before the time of the Roman conquest of England around 54 B.C. The Bishop of Durham has described coal-mining operations around that city in 1180. As early as 1273 the fumes from burning coal in London caused Parliament to pass an act forbidding the use of coal within the city limits and in 1306 an artificer was actually tried, condemned and executed for this offence. The Act seems to have been repealed, however, before the reign of Elizabeth, since coal was then being used in certain industries. In 1578 the Company of Brewers offered to burn only wood in the breweries near the palace because the Queen was annoyed by the taste and smoke from burning coal. About the same time a deputation of women went to Westminster and complained to the Queen about "the filthy, dangerous /...

dangerous, poisonous use of coal".

John Evelyn, the diarist, was perhaps the first person to suggest a remedy for the increasing pollution of London air by coal smoke. In his famous pamphlet "Fumifugium"[69] written in 1661 he proposed that the factories of brewers, dyers, lime-burners and other industries using coal should be moved lower down the Thames and that the area around central London should be made a green belt planted with trees and flowers. Not only did Evelyn point out the soiling properties of smoke, but he also stated the danger to building materials from sulphur oxides and more especially the "spirits of sulphur". It is difficult to understand how Evelyn detected sulphur dioxide, since the odour only becomes apparent above 3 p.p.m.[70] - a much higher concentration than in normal polluted air. The presence of the "spirits of sulphur" or sulphuric acid may have been an inspired guess, after he had observed the decay of metal, which as it happens, was alarmingly accurate.

No further action appears to have been taken in the control of air pollution for nearly 200 years until the real danger of pollution by burning fuel became serious at the time of the industrial revolution. Increased industrial activity required large quantities of coal for the manufacture of coke, which could be used in the new type of blast furnace. Coal, too, was required for the steam engine which came into widespread /...

widespread operation in factories and mills. Wood, which had become scarce, was much too expensive and mechanically unsuitable for modern industrial use. For domestic purposes, wood was too expensive and so coal for heating and cooking came into general use. Towns collected round the new iron and textile industries and in these areas the pollution of the air from smoke became serious.

Within recent years the rapid increase in the use of motor transport, family motor cars and small internal combustion engines for drainage pumps and garden machinery has introduced another form of air pollution - exhaust fumes. These fumes are just as dangerous as smoke, containing as they do carbon monoxide, sulphur compounds and carcinogenic compounds such as 3,4-benzpyrene. The pollution from exhaust fumes, unlike smoke from chimneys, originates near ground level where, at a busy road junction, a pedestrian is exposed to an atmosphere containing dangerously high proportions of poisonous material.

It was not until 1912, however, that a committee was set up to make a scientific investigation of air pollution. In 1927 the D.S.I.R. took over the general supervision of pollution measurement and in 1945 the Atmospheric Pollution Research Committee became a constituent member of the Fuel Research Board. As a result of the recent interest in air pollution many large cities including London and Glasgow have made /...

made "smokeless zones" within which only smokeless fuels may be burned. Thus it has taken some 300 years to put Evelyn's revolutionary idea of smokeless zones into operation, and his idea of a green belt is now being applied.

THE MECHANISMS INVOLVED IN ATMOSPHERIC POLLUTION.

The analysis of town air has shown[71] that 85% of the suspended matter is smoke. Smoke is the general term used to describe the visible effluent from a fire or chimney. It consists mainly of incompletely burned fuel and gaseous products of combustion, the most important of which are carbon dioxide, sulphur dioxide and some higher aromatic hydrocarbons, such as benzpyrene. Mixed with this there will be a small percentage of ash entrained in the hot gases. In factory chimneys smoke rises at about 40 ft./sec.[71], a speed which is capable of carrying particles of ash as large as 0.1 in. After leaving the chimney, however, these particles will settle rapidly to earth and cause no nuisance apart from a deposit of dust on surrounding buildings. The gases in domestic chimneys travel at a speed of about 5 ft./sec.[71] and so can carry particles of ash only up to a size of 0.003 in., but these will also settle quickly compared with smoke.

Meetham[72] has estimated from fuel consumption and meteorological data that each year 800,000 tons of smoke and 3.9 million /...

3.9 million tons of sulphur dioxide are deposited in Britain while about 1.5 million tons of smoke and 1.1 million tons of sulphur dioxide are blown out to sea.

Industrially prepared carbon for various purposes is formed either from solid or liquid fuels. Carbon blacks are usually prepared by the combustion of oils at a controlled temperature. The properties of the carbons vary enormously with the temperature of preparation[34]. A low temperature carbon black, Spheron 6, prepared at about 700°C. is similar in physical and chemical properties to Sterling MT (another low temperature carbon black) shown in Fig. 5. These carbon blacks are similar in appearance to actual smoke particles collected during a Glasgow fog (Fig. 6). Beebe and Dell[73] have studied the adsorptive properties of sulphur dioxide on two carbon blacks. One is the low temperature carbon Spheron 6 which has a polar surface, due to the presence of surface oxides[34]; the other, Graphon (Spheron 6 heated to 2700°C.) has a non-polar graphite-like surface[34]. The isotherms obtained for the adsorption of sulphur dioxide are of two different types according to the Bruneuer classification[57] and are shown in Fig. 7. Sulphur dioxide is adsorbed strongly by the polar low temperature carbon giving a typeII isotherm, whereas the non-polar carbon has only a few scattered adsorption sites, leading to a typical type V isotherm. At very low sulphur dioxide vapour pressures (as found in atmospheric /...

atmospheric conditions) the low temperature carbon will adsorb sulphur dioxide strongly, whereas the high temperature carbon, being non-polar, will not adsorb it at all. Since the majority of town smoke is domestic in origin it will be a low temperature carbon and so will have similar chemical properties to Spheron 6. It will therefore adsorb the atmospheric sulphur dioxide strongly. On this arguement the sulphur dioxide concentration in the atmosphere, measured daily at all D.S.I.R. testing stations, is due to the excess unadsorbed gas since all carbon particles, including any adsorbed sulphur dioxide they carry, are filtered from the air before being passed to a hydrogen peroxide solution[74]. In fact Herd (private communication) found that if the air was not filtered before testing, the apparent sulphur dioxide concentration increased considerably, showing that there was sulphur dioxide adsorbed on the smoke particles which was desorbed by the test solutions.

The adsorption of sulphur dioxide by carbon will obey normal thermodynamic principles and be exothermic, i.e. the amount adsorbed will decrease with rise in temperature. The D.S.I.R. Warren Spring Laboratories issue annual reports giving exact figures for the daily concentrations of smoke and free sulphur dioxide measured at over one hundred testing stations throughout Britain. The author plotted the average summer and winter values of free sulphur dioxide for 1960[75] against /...

against the corresponding values for smoke shown in Fig. 8. Since an approximately even distribution of stations throughout Britain was required the excessively large number of stations in the London area was omitted. The values were statistically analysed by D. Smith (Table I) and two lines, one for the summer and one for winter values were obtained as shown in Fig. 8. The regression coefficients of these lines are different at the 10% level of significance. Normally regression coefficients are accepted as being different at the 5% level, but in this case the observations being spread over the entire country, the lines are accepted as being different at the 10% level. These two lines may be considered as being equivalent to isotherms from two enormous adsorption tests. The line for the winter data lies above that for summer. This shows that for the same smoke concentration the amount of free sulphur dioxide in the atmosphere in winter is less than in summer. Conversely, the amount of sulphur dioxide adsorbed in winter (low temperature) is greater than in summer, in accordance with theory. Thus the carbon is definitely adsorbing sulphur dioxide since, if it was not, there would be no difference between the summer and winter values. It is the opinion of the author that it is this _adsorbed_ sulphur dioxide and not the _free_ sulphur dioxide which causes the damage to the various systems described below.

Since low temperature carbon black has a polar surface[34], it /...

it was thought that water would be adsorbed strongly in preference to sulphur dioxide. Anderson and Emmett[76] have studied the adsorption of water vapour on the same carbon, Spheron 6, used by Beebe and Dell[73]. Their results are plotted relative to those of Beebe and Dell (Fig. 7, broken line) and it is immediately obvious that Spheron 6 has a much higher affinity for sulphur dioxide than it has for water.

The Effect of Atmospheric Pollution on Animals.

The irritant substances present in polluted air which cause respiratory diseases are as yet unknown, although Firket[77], Roholm[78] and Regan[60] have suggested that sulphur dioxide, carbon monoxide from automobile exhaust fumes, and certain fluorine compounds are the culprits; and recently 3,4-benzpyrene, a product of combustion, has been found to be a powerful carcinogen.

Particularly high concentrations of atmospheric pollution occurred during the fogs in London of 1948 and 1952 and in the Meuse Valley, Belgium in 1930. Although no accurate analyses are available for those fogs they were found to attack very young and very old people, and in particular people suffering from respiratory diseases. Post mortem examination of the victims showed that death was due to the presence of an irritant substance in the lungs.

Laboratory experiments have been carried out on both humans and animals using known fog constituents in an attempt

to /...

to discover the irritating mechanisms of certain substances which make polluted air dangerous. Pattle and Cullumbine[79] treated mice with a 8 p.p.m. concentration of sulphur dioxide. This concentration had no apparent effect on the animals although with humans 1 p.p.m. sulphur dioxide can cause broncho-constriction and a feeling of discomfort - an effect which would not be immediately apparent with mice. In smog atmospheres sulphur dioxide always appears with carbon particles and moisture. Meetham[80] has suggested that sulphur dioxide could be adsorbed by carbon smoke particles. This is supported by the fact that a low temperature carbon has a higher affinity for sulphur dioxide than it has for water, as discussed above. The adsorbed sulphur dioxide would not be detected in the gas analyser and smoke particles which are mainly less than 5μ in diameter[81] and in many cases less than 1μ will be carried deep into the lungs. Larger dust particles (>5μ) will be caught in the mucous tract and expelled.

Sulphur dioxide gas, unadsorbed on carbon, is highly soluble in water and so when inhaled will dissolve in the fluids of the upper respiratory tract and will not reach the lungs. The inhaled gas causes some immediate discomfort but is not toxic at normal concentrations. The adsorbed sulphur dioxide, however, will be carried on the carbon into the lungs where increase in temperature and presence of moisture will slowly desorb the gas which can then cause an irritation "in situ". /...

"in situ". Pattle and Cullumbine[79] treated the mice with sulphur dioxide mixed with smoke from a kerosene lamp (i.e. a low temperature carbon). The smoke itself was shown not to be lethal in the concentration used but the number of fatalities of the mice when the gas was present increased considerably showing that both sulphur dioxide and smoke are required to have a toxic effect. If the mice are given an initial treatment with a high concentration of smoke (much higher than in atmospheric conditions) followed by treatment with sulphur dioxide they appear to have an increased resistance to the toxic effects of sulphur dioxide. This has not been satisfactorily explained although the smoke must be having a shielding effect on the lung surfaces.

The fact that the presence of smoke is required along with sulphur dioxide before small concentrations of sulphur dioxide become deadly, supports the hypothesis outlined above that sulphur dioxide is adsorbed on low temperature carbon. Sim and Pattle[82] have shown that the restricting effect of sulphur dioxide on breathing is greatly suppressed by the presence of finely divided magnesium oxide (from flash bulbs) since the sulphur dioxide is apparently adsorbed by the magnesium oxide. Sulphuric acid mist had an even stronger effect on breathing, especially as the droplet size increased. In this case, however, magnesium oxide had no beneficial effect.

Clifton et al.[83] have used the frequency with which bronchitis sickness certificates were issued as an index of air pollution. For all cases of fog in London from November 1956 to January 1959 they found that there was a corresponding increase in the number of bronchitis certificates issued. The increase in smoke concentration during all these fogs was greater than the rise in sulphur dioxide concentration. Since the source of smoke and sulphur dioxide is common the concentration should increase together, unless the sulphur dioxide is being adsorbed by the smoke, when its apparent concentration would be low. During each period of fog there was a marked decrease in temperature which would assist the adsorption of sulphur dioxide by the smoke. Bronchitis was not due merely to a decrease in temperature since during cold spells without the presence of fog there was no increase in the number of bronchitis patients. Thus the sulphur dioxide adsorbed on the carbon is probably causing the irritation of the lungs.

Fog is usually caused by the presence of a meteorological temperature inversion. Instead of the temperature of the atmosphere decreasing with increase in altitude, a layer of cold air collects near ground level ranging in depth from a few feet to several thousand feet. Within this belt of cold air there is very little turbulence and so any pollution, such as smoke, entering the region will increase in concentration /...

concentration since it is not dispersed by wind. Such a temperature inversion took place at the time of the December fog in 1952. In this case the inversion only reached a height of 500 ft.[80] and stretched over most of the London area. The fog lasted for six days during which time there was a steady increase in smoke and sulphur dioxide concentrations[84] as shown by Fig. 9. The concentration of sulphur dioxide appears to have continued to rise for about one day after the smoke concentration began to decrease. A possible explanation is that the point when the smoke began to decrease marked the beginning of the breakdown of the temperature inversion. At that time the temperature started to rise and desorbed some of the adsorbed sulphur dioxide from the smoke so maintaining the rise in sulphur dioxide concentration. After this initial stage, however, the inversion was completely dispersed and both the smoke and sulphur dioxide concentrations fell together.

The graph of the number of deaths recorded in London during the 1952 fog is also shown with the smoke and sulphur dioxide graphs (Fig. 9). It is surprising that the increase in deaths coincides with the increase in smoke and sulphur dioxide. This suggests that death was almost instantaneous after exposure to fog, which is unlikely. The most probable reason is that many people, who had been suffering from bronchial disorders such as asthma caused by long exposure to low /...

low concentrations of pollutants, finally succumbed to the sudden rapid increase in pollution.

Recently the fog in London during December 1962 was compared with the 1952 fog[85]. Both fogs were similar from a meteorological point of view and the 1962 fog lasted only one day less. The atmospheric concentration of sulphur dioxide, which has not changed much during the last ten years, was similar in both fogs but possibly because of the increasing number of smokeless zones in London (introduced since 1952) the amount of smoke has decreased by about 37%. It is significant that the number of deaths during the 1962 fog was less than the corresponding number in 1952. This can be explained by the fact that since there is less smoke there will also be less adsorbed sulphur dioxide capable of causing damage. Kelly[86] has pointed out that the decrease in deaths during the 1962 fog may not be due entirely to the reduction of smoke. He suggests that from experience gained during the 1952 fog people were better educated on what counter measures to take in order to combat the fog.

Humans and animals may be affected indirectly by the presence of polluted air. The fine particles of smoke and suspended matter will reduce radiation from the sun, especially in the ultra-violet region; such radiation is necessary for the photolysis of vitamin D. In urban districts which are normally under a pall of smoke the number of cases of rickets is /...

is higher than in rural areas; rickets is caused by a deficiency of vitamin D. In recent years this disease has been prevented by the use of synthetic vitamin D capsules and the supply of free cod liver oil to young children.

The Effect of Pollution on Building Materials.

Soot particles, although consisting mainly of low temperature carbon, are covered by sticky tar residues and so adhere strongly to the stone and metalwork of buildings. This soot deposit not only causes buildings to have a dirty appearance but because of the adsorbed sulphur compounds on the carbon, metal and certain types of stone are attacked chemically.

Vernon[87] has studied the corrosion of iron under laboratory controlled conditions and his results are shown in Fig. 10. In pure air free from carbon particles, particles of ammonium sulphate and sulphur dioxide the corrosion is negligible. When the air contains only sulphur dioxide the corrosion is increased but in the presence of ammonium sulphate or especially in the presence of carbon corrosion is rapid probably due to the adsorption of the sulphur dioxide on the particles.

Vernon[87] was of the opinion that carbon increased the concentration of the sulphur dioxide only at the surface, by physical adsorption. Regan[60], however, thought that the sulphur dioxide adsorbed would be oxidised by air to sulphur trioxide /...

trioxide and then in the presence of water to sulphuric acid, which has an even stronger corrosive action.

It has been found[88] that sulphur dioxide in the presence of oxides of nitrogen and hydrocarbons, found in normally polluted atmospheres, is photolytically converted to aerosols containing sulphuric acid. The sulphur dioxide - nitrogen oxide - olefin reaction is fast enough to account for the high sulphate and organic contents of the particulates found in, for example, the Los Angeles basin. The high rate of nuclei formation shows that photooxidation of very small amounts of sulphur dioxide can supply enough acidic nuclei for physical or chemical condensation of other materials present in the atmosphere.

Recently Commins[89] suggested that moisture adsorbed on small particles of iron and manganese will dissolve sulphur dioxide, which will then be catalytically oxidised to sulphuric acid. He also pointed out that nitric oxide, which has a half-life of 100 hours and is present to a concentration of 1 p.p.m. in the atmosphere, (possibly formed by electrical discharge during thunderstorms) may take part in a "quasi lead chamber" process, thus forming sulphuric acid directly.

From the above discussion it is apparent that the carbon acts as a carrier both for sulphur dioxide and for sulphuric acid, but it is the opinion of the author that carbon will play an equally important role in metal corrosion as one pole

of /...

of an electrolytic cell. Iron and aluminium may be considered typical construction metals, and carbon is more "noble" than them, i.e. lower in the electrochemical series. When carbon and iron are in contact with each other in the presence of pure water no corrosion should take place. If, however, a solution of sulphur dioxide or sulphuric acid is also present as a strong electrolyte then a very efficient electrolytic cell will be formed, the iron acting as the anode and being attacked.

Prati[90] has studied the corrosion of aluminium in the presence of carbon and various electrolytes. She found that when the aluminium and carbon (graphite) were connected in the presence of sodium chloride there was some corrosion of the aluminium, but if an oxidising agent such as hydrogen peroxide was also present then the corrosion was extremely rapid. This cell is chemically and physically similar to that formed by the adhesion of smoke on iron or aluminium in the presence of sulphur dioxide and sulphuric acid (as electrolyte) and so corrosion is rife in polluted air.

Thus three conditions must be fulfilled for corrosion to take place at a metal surface. There must be moisture, sulphur oxides as electrolytes and carbon, all present simultaneously. The carbon may act as a carrier but it more likely forms the cathode of an electrolytic cell as discussed above.

Baines[91] stated that when sulphuric acid is brought into contact with stone either by moisture or in tarry soot deposits, a chemical reaction is set up in which part of the calcium or magnesium carbonate is changed to sulphate. The softer building stones, which are easier to work, are often limestones or dolomites and because of their chemical composition are readily attacked by sulphuric acid. Sandstones, which consist of silica particles bound together by calcium carbonate, corrode at the surface where the calcium carbonate has been converted to the sulphate and the silica particles released, thus exposing fresh surface for attack.

The surface of many porous stones is caused to flake by either the action of sulphuric acid or of frost. When sulphuric acid converts calcium and magnesium carbonates to the corresponding sulphates the volume increases are respectively 1.7 and 4 times[92]. These volume increases, especially in cracks and fissures, cause an exfoliation of the surface. Everett has shown thermodynamically that certain stones are split by frost, not merely by the expansion of freezing water, but by the growth of ice crystals. When a water saturated porous material freezes, macroscopic ice crystals form in the coarser pore spaces and water is withdrawn from the finer pores to feed the growing crystals. Thus stones with poor resistance to frost, such as Portland stone and Bath stone, consist of a macroporous structure embedded in a microporous matrix /...

matrix and it is the presence of the two sizes of pores which causes the damage. Sandstones have good resistance to frost damage, although they have lower mechanical strength than, for example, Bath stone. The reason is that they have only a coarse pore structure without the accompanying presence of fine pores. The action of frost is only intermittent whereas the chemical action from air pollution is present throughout the year.

The Effect of Pollution on Plants.

The effects of various pollutants on plants has been studied for some time. Meetham[94] states that plants are more sensitive to smoke and sulphur dioxide than are animals; smoke clogs the stomata through which the plant collects carbon dioxide. The effect of various concentrations of sulphuric acid on several types of grasses and on radishes has been studied at Leeds[95]. As the acidity of the water increased, the yield of both the grass and radishes decreased steadily and the effect of the acid appeared to be cumulative. Acid and acid gases not only attack the leaves and foliage but destroy or inhibit the growth of necessary ammonia-producing bacteria and nitrifying organisms.

Research in Canada has shown[94] that lucerne is injured by as little as 0.3 p.p.m. (v/v) of sulphur dioxide and barley by 0.8 p.p.m. Thus plants which are dormant during winter months when pollution is at a maximum suffer less from the effects /...

effects of sulphur compounds and carbon deposits than does, for example Timothy grass, which has an active growth throughout the year.

CONCLUSIONS.

The above discussion illustrates the harm caused to several systems by the direct action of air pollution. In all cases one fact predominates - carbon must be present before the action of sulphur gases and acids becomes serious. The carbon in the case of lung infections merely acts as an inert carrier of sulphur dioxide which enables the sulphur dioxide to penetrate regions of the lung where it can do most harm. It is difficult to determine whether long exposure to low concentrations of pollutants or short exposure to high concentrations is more serious. Perhaps the low concentration will start an irritation in the lungs which is greatly aggravated, to a lethal extent, by a sudden increase in the pollutants.

Carbon appears to play a dual role in the corrosion of metals. It first of all acts as a carrier on which catalytic oxidation of sulphur dioxide to sulphuric acid may occur and the sticky surface of the soot holds the acids in contact with the metal surface. Carbon on metals can also act as a half-

cell /...

cell in the electrolytic corrosion mechanism.

Plants are attacked in two ways by air pollution. Carbon simply acts as a mechanical block to the stomata of the leaves and sulphur acids attack the roots and plant nutrients.

It is obvious, therefore, that all city local authorities should attempt to reduce the amount of smoke released into the atmosphere. This has had some beneficial effects in London between 1952 and 1962. Although a reduction of carbon in the atmosphere will reduce the intensity of fogs and also reduce the potential carrier effects for sulphur gases, the output of sulphur dioxide must also be reduced since free sulphur dioxide will still be a danger especially during a temperature inversion.

The pollution from domestic grates (many of which already burn smokeless fuel) in a particular area decreases in summer and during holiday periods whereas industrial furnaces run continuously day and night all the year round. The pollution output from industry, especially power stations, will be greatly decreased when the use of nuclear powered generators comes into general practise.

SECTION II.

ADSORPTION OF SOLUTES FROM SOLUTION.

INTRODUCTION.

In section I the relation between three types of vapour adsorption and their corresponding Brunauer[57] adsorption isotherms (Fig. 2) was described. A similar comparison can be made of the various types of solution adsorption on solid surfaces and the isotherms encountered. A solution adsorption isotherm is simply a plot of the amount of solute adsorbed by a solid against the residual solute concentration in the solution.

Adsorption from solution is complicated by the fact that there is more than one component present in the liquid phase, either a mixture of liquids or a solid dissolved in a solvent, which can compete with each other for the available sites on the adsorbent surface. Mixtures of completely miscible liquids (A and B) can be thought of as a solution of A in B or B in A, where B and A are in excess respectively. Kipling and Wright[96] have studied the adsorption of stearic acid from four organic solvents on carbon blacks over a limited range of solubility. They have shown that when the solubility is low the adsorption of the solvent by competition seems to be low. In dilute solutions the composite isotherm is a close approximation to the isotherm for the adsorption of the solute alone, but the two isotherms diverge with increasing concentration. The present work is confined to dilute solutions /...

solutions of various solutes. Sometimes, however, the competition of solvent, especially a polar solvent, such as water, in presence of a polar solid such as silica or titania can reduce considerably the amount of solute adsorbed. This has been illustrated by Giles and Nakhwa[97] in the adsorption of p-nitrophenol from water on silica, where the amount adsorbed is small, and on titania, where it is zero.

The adsorption of large solute molecules, often complex organic dyes, unlike that of small almost spherical gas molecules is complicated by the fact that the orientation of the molecule at the surface is difficult to establish with certainty. In fact the use of dyes or large solute molecules, except long chain fatty acids and alcohols[98], for the measurement of surface area, has been limited because of the lack of knowledge of the exact orientation of the adsorbed molecule.

Dye molecules have large, often flat, aromatic nuclei around which are distributed different hydrogen bonding, ionic or polar groups. The orientation of the molecule at the surface will depend, therefore, on the chemical nature of the adsorbent and also the types and numbers of substituent groups in the solute.

Consider the adsorption of phenol on a polar solid such as alumina. The hydroxyl group of the phenol can form hydrogen bonds with oxygen atoms or hydroxyl groups at the alumina surface and the aromatic nucleus which has no attraction /...

attraction for a polar solid will be left projecting into solution. Since the phenol molecule is planar, the adsorbed molecules will pack together standing upright and forming a stable layer. The initially adsorbed molecules will assist the adsorption of further molecules until the monolayer is complete. This type of adsorption is very similar to that necessary to give type V isotherms in the Brunauer[57] classification (Fig. 2c) and the same S-shaped isotherm is obtained in solution adsorption (Fig. 4a), e.g. phenol on silica. Possibly the same effect would be produced by a solute being adsorbed initially by a few active sites on the adsorbent surface (the solute need not have a vertical orientation). If there was association of the solute at the surface around the initially adsorbed molecules then the same shape of isotherm would probably be obtained, even if the molecules were adsorbed with a flat orientation on the surface.

If the phenol molecule has another hydroxyl substituent e.g. in the para position, i.e. quinol, then on a polar surface both hydroxyl groups will be attracted to the surface groups, and so will force the molecule to lie flat. In this type of adsorption, as the sites are used up it becomes progressively more difficult for a molecule to be adsorbed. The isotherm obtained is therefore similar in shape to the typical Langmuir isotherm (Brunauer type I, Fig. 2a) for the adsorption of gases.

The /...

The phenol molecule itself when adsorbed on graphite does not stand upright, since there is no attraction between the hydroxyl group and the non-polar surface. The aromatic nucleus of the phenol molecule is attracted by van der Waals forces to the condensed ring system of the graphite surface, thus the phenol molecule lies flat and again a Langmuir-type isotherm is obtained (Fig. 4b).

Another important type of adsorption is that encountered in the study of ionic detergents. The long hydrophobic hydrocarbon chains of detergent molecules, which have no attraction for water, bond together by van der Waals attraction into a large aggregate with the charged hydrophilic ends of the molecule pointing outwards forming a large spherical micelle with charges spread over its surface. In the case e.g., of negative surfaces, positive micelles of this type are attracted so strongly by the surface that the solute is entirely removed from dilute solutions. This type of micellar adsorption gives rise to a 'high affinity' isotherm (H isotherm) which starts at a positive value on the ordinate (Fig. 4c). Sometimes a Langmuir type (L) isotherm (Fig. 4b) is obtained in the adsorption of micelles when the amount adsorbed is much in excess of a true monolayer of molecules in a flat orientation.

One other main type of adsorption from solution which will only be considered briefly later is that of "solid solution". Many /...

Many hydrophobic polymers such as cellulose triacetate and Terylene polyester fibre, which have very low attraction for water have high attraction for certain non-polar organic solutes, such as disperse dyes. Disperse dyes in aqueous suspension will thus be taken up by Terylene in preference to water; in fact the dye molecules will penetrate the surface of the Terylene exposing more and more adsorption sites. A constant partition of dye in the substrate will result and the adsorption isotherm will be a straight line (Fig. 4d), the amount of dye adsorbed being proportional to the dye concentration up to the solubility limit when a flat plateau is obtained.

Thus four main types of adsorption have been identified, each being represented by a different shape of isotherm (Fig.4). In the classification proposed by Giles et al.[59] the initial shape of the isotherms determines the nature of adsorption and the later changes in shape denote the formation of multilayers or a reorientation at the surface.

Significance of the Plateau.

The first plateau of the isotherm indicates the formation of a monolayer of adsorbed molecules at the surface. The length of plateau signifies the ease with which a second layer can form. If the adsorbed species presents a surface greatly different in properties to the original surface it will be difficult for a second layer to form e.g. the adsorption of a

layer /...

layer of cationic micelles on a negatively charged surface will change the charge of the surface making it effectively positive. These positive charges will repel cationic micelles and so prevent further adsorption. Thus the plateau will be long.

If the adsorbed species in the monolayer presents a surface similar in adsorptive properties to the original surface, then the adsorption of multilayers will be relatively easy and so a short plateau or in some cases no plateau but just a point of inflection will be obtained.

Significance of Second Rise and Second Plateau.

Some isotherms display a second rise and second plateau beyond the "monolayer" plateau. If the initial shape of the isotherm indicates that the molecules are adsorbed end-on to the surface (S-isotherm, Fig. 4a) then a second rise suggests that a second layer is forming on top of that already present, an example is the adsorption of monosulphonated aromatic compounds on graphite[99]. If, however, the initial shape of the isotherm shows the molecules to be adsorbed flat (L-isotherm, Fig. 4b) then the second rise and second plateau can indicate one of two possible mechanisms. The second rise could simply indicate the build-up of a second layer on top of the first as with the S-isotherm; e.g. the adsorption of cyanine dyes on silver halide[99]. The second rise could, in some cases, indicate a change of orientation at the surface. If /...

If the amounts adsorbed, corresponding to each plateau, are in the same ratio as the cross-sectional areas of the molecule in the respective orientations then this shows that the molecules forming a monolayer in a flat orientation have been forced, by entry of more of the adsorbed molecules, into a monolayer of vertically oriented molecules. This occurs with p-nitrophenol on organic pigments.[99]

Thus from a study of the adsorption isotherms obtained from solution the possible mechanism of adsorption can be determined since the orientation of the adsorbed molecule is known and the type of bonding is often apparent, e.g. normal ion-exchange adsorption is temperature independent.

PART I.

THE ADSORPTION OF BASIC DYES ON ALUMINA.

INTRODUCTION.

The adsorption mechanisms of different classes of organic solute have previously been studied on several different types of aluminium oxide. The anodic film formed by acid electrolysis of aluminium has a positive charge in water[24] and so will attract anionic solutes such as sulphonated dyes. It has been suggested that each sulphonate group replaces a hydroxy group attached to the aluminium and there is also some ion exchange adsorption of anionic micelles[100]. Acid treated chromatographic alumina powder has been shown to have a positive surface containing both covalently bound and ionised chloride[20,23] according to the reaction:-

$$Al—OH + H^+Cl^- \rightleftharpoons Al—Cl + H_2O \rightleftharpoons Al^+ + Cl^-$$

Anionic solutes such as sulphonated dyes are adsorbed by acidified alumina powder by ion exchange with the ionised chloride, in the form of anionic micelles[20]. In fact the author found it possible to detect the displaced chloride ion (in a qualitative test). The density of a silver chloride precipitate was visibly stronger in the supernatant liquor after the adsorption of an anionic dye (C.I. 62055) compared with the same treatment of the powder with the same volume of de-ionised water.

It has been suggested that the adsorption of basic dyes on negatively charged alumina powder will take place by adsorption /...

adsorption of cationic micelles[20] as in the case of basic dyes on silica[19], although until now no quantitative work had been reported on this type of adsorption.

Buchanan _et al._[23] have examined the effects of various pretreatments such as grinding, heating and treatment with acids, alkalis and salts on the electrokinetic properties of natural alumina (corundum). The corundum lattice, which consists of hexagonal close packed γ-alumina, will be damaged, especially near the surface, by grinding or abrasion. This damage to the surface will expose positively charged aluminium atoms and negatively charged oxygen atoms. The surrounding atmosphere of water is of course ionised, and the H^+ and OH^- ions will be adsorbed by the O^- and Al^+ atoms respectively in the lattice to form surface hydroxyl groups which will be partially covalently bound or partly ionised depending on the extent of the damage to the surface. Extensively damaged parts of the surface will be generally hydrated:-

$$Al_2O_3 + 3\ H_2O \longrightarrow 2\ Al(OH)_3$$

while less damaged parts will not be so completely hydrated:-

$$Al(OH)_3 \rightleftharpoons Al(OH)_2^+ + OH^- \quad \ldots \quad \ldots \quad (i)$$

$$Al\ O.OH \rightleftharpoons Al\ O.O^- + H^+ \quad \ldots \quad \ldots \quad (ii)$$

Chromatographic alumina when obtained commercially consists mainly of γ-alumina mixed with a little monohydrate, having /...

having been formed by heating aluminium trihydroxide at a temperature below 700°C[20]. Commercial alumina contains some sodium carbonate left from the final manufacturing stage and when shaken with de-ionised water gives a solution of pH 9-9.5. This favours equation (ii) above resulting in a negative charge at the surface.

Freshly prepared alumina is very active but because of the adsorption of water when it is exposed to damp air, it becomes less active since the water molecules occupy some of the available adsorption sites. In fact when alumina is being studied in non-polar solvents it is usually graded by the Brockmann[101] test into one of five possible grades depending on the adsorbed surface water. Since all the present work was carried out using aqueous solutions it was not necessary to grade the alumina for activity.

EXPERIMENTAL.

Dyes.

The basic dyes, listed in Table II were obtained as commercial "batch" samples without the addition of diluent and were recrystallised (with the exception of Victoria Blue BN, Victoria Pure Blue BO, Rhodamine 6GB and Rhodamine 3B) from aqueous hydrochloric acid, concentrated hydrochloric acid diluted 10:1 with water. The dyes were dried first at 40-50°C. in air and then in a vacuum dessicator over potassium hydroxide, overnight. In the presence of alkaline alumina, Malachite Green and Victoria Blue BN (Figs. 11 and 12) precipitated, and so could not be studied further. Elementary analyses of the dyes were obtained by the author's colleague R. B. McKay, and the values are given in Table III. The dyes are between 85 and 95% pure. The remainder was assumed to be traces of water and hydrochloric acid (a test with Safranine T solution showed that even with twice the amount of hydrochloric acid likely thus to be present in the strongest dye solution used, the pH of the liquid after shaking with alumina fell *only* from 6.9 to 5.6). An exception is Methylene Blue; its analytical data can only be explained if a homologue is present equivalent to an additional C_2H_4 group. Rhodamine 6GB was used without purification and its extinction coefficient showed it to be about 90% pure.

One dimensional paper chromatography with a solvent mixture /...

mixture of benzyl alcohol, di-methylformamide, methyl-ethyl ketone and water showed no coloured impurities in any of the dyes.

The proton donor solute, p-nitrophenol (recrystallised four times from water), was also used for comparative tests.

Substrate and Adsorption Procedure.

The alumina used for the experiments was taken from a sample marketed by May and Baker*. It was found to have a specific surface area of 4.8 m^2/g. measured by the adsorption of dye C.I. 62055 (Fig. 15) according to the method of Giles and Nakhwa[97] and $5m^2/g$. by the adsorption of p-nitrophenol[97] calculated by the author's colleague C. C. Patel.

When shaken with de-ionised water it gave a solution of pH 9-9.5 and so was used without any pretreatment.

The adsorption procedure was exactly the same as described previously[20] using end-over-end agitation of the solutions[102]. No rate curves were determined since a preliminary experiment showed that adsorption was complete in a few minutes. 0.05 g. alumina in 10 ml. solution were used in all cases except for the Rhodamine dyes for which the liquor ratio was shortened to make the experiment more sensitive, when 0.1 g. alumina in 10 ml. solution were used. The /...

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* In the adsorption-desorption experiment of p-nitrophenol, B.D.H. alumina was used (Fig. 14a).

The temperature of adsorption was controlled to ±1°C. in the thermostatic tank by means of a Sunvic control (Sunvic Controls Ltd., London).

Desorption was carried out using a modified technique. First an adsorption isotherm was obtained in the usual way[20], then the solution of initial strength corresponding to one particular point on the isotherm (usually a point on the plateau) and the corresponding weight of powder were placed in a Quickfit test-tube (B.14), cut to fit an M.S.E. centrifuge and agitated as before[102]. When adsorption was complete the tube was centrifuged and 50% (5 ml.) of the supernatant liquor removed for spectrophotometric comparison with a set of standard solutions. 5 ml. of water were now added to the test tube and tumbling resumed. The removal of dye and addition of water was repeated several times, all solutions being analysed (after dilution if necessary).

After the initial adsorption the strength of solution in the tube is found from the calibration graph. This solution is diluted 50% by the addition of water and so its strength (X say) is known. After desorption has taken place, the solution strength (Y say) is again found from the calibration graph. The difference Y-X gives the amount of dye desorbed.

All tubes and glassware were rinsed in a surface active agent, cetyl trimethyl ammonium bromide, Lissolamine A, (ICI) to neutralise the negative charge of glass and so prevent the adsorption /...

adsorption of the basic dyes by the apparatus.

The cross-sectional areas of all the dye molecules were calculated using Catalin-Stuart models, in their most probable orientation according to the isotherm theory[59].

The spectral absorption curves of Safranine T were determined at several temperatures using the special cell heating device described by Grant *et al.*[103]. The cell was made from 3 mm. glass tubing and was heated by a constant voltage rectifier (Farnell Transistorised Power Supply, Type P.S.O.) set at a predetermined voltage and current.

RESULTS AND DISCUSSION.

Basic dyes are not normally adsorbed by acidified alumina due to the repulsion of the positive dye ions by the positive surface or in some few cases they are adsorbed to only a very small extent[99]. The adsorption of basic dyes by negatively charged chromatographic alumina is shown to be due to ion exchange rather than covalent bonding by the fact that the dyes without potential hydrogen bonding groups are completely desorbed from the alumina surface by rinsing with water (Fig. 14b,c) or by the preferential adsorption of a positively charged surface active agent (Lissolamine A, ICI). They can even be desorbed by another basic dye (as found by Michaelis[104] for /...

for the adsorption of basic dyes on tissue).

The dyes which have large, relatively flat, positively charged ions may be adsorbed by a solid in one of three ways. The ions could be adsorbed singly standing edge-on or lying flat on the surface or they could associate (like detergent ions) into large positively charged micelles which would be adsorbed strongly by the negative surface. It is seen from Table IV that all the dyes with the exception of Rhodamine B, 3B and 6GB are adsorbed at 20°C. in excess of the amount required for a true monolayer of molecules oriented flat to the surface suggesting that micelles and not single ions are being adsorbed. This is confirmed by a study of the isotherm shapes obtained. All dyes giving adsorption in excess of a monolayer have either an L or H isotherm according to the classification of solution isotherms[59]. As stated previously the L isotherm is indicative of either a monolayer of single molecules lying flat or the aggregation of molecules at the surface. An H isotherm denotes the adsorption of aggregates, thus since the amount of dye adsorbed in a flat orientation is more than that required for a monolayer, then the dyes are adsorbed as aggregates.

L isotherms are obtained for dyes, such as Methylene Blue, which are adsorbed only a little in excess of a monolayer, i.e. which have a low degree of aggregation, but dyes such as Ethyl Violet and Victoria Pure Blue BO which are adsorbed /...

adsorbed much in excess of a monolayer, i.e. which have a high degree of aggregation give H isotherms.

Rhodamine B has a free carboxyl group and so will be oriented in such a way that the negative, ionised carboxyl group is as far as possible from the negative surface. A suggested orientation on a negatively charged surface is shown in Fig. 17, in which the molecule is standing on end, one positive nitrogen atom bonded by ion-exchange to the negative ions on the surface. The other nitrogen atom can form either hydrogen bonds with the free carboxyl group or the nitrogen, which may be charged by resonance, can form ionic links with the ionised carboxyl group as shown, and so stabilise the adsorbed layer. The amount of Rhodamine B adsorbed can be considered approximately equivalent to a monolayer of monodisperse ions, assuming the proposed orientation (Table IV) and so Rhodamine B (Fig. 12) unlike the other basic dyes is not adsorbed in the form of micelles. Such an arrangement is confirmed by the S-shaped isotherm (Fig. 16c), which, according to the classification denotes end-on orientation of single ions to form a monolayer. The fact that bonding is through the positive charge by ion-exchange is thought to be correct since, in a qualitative test, Rhodamine B was completely desorbed by water showing that no covalent bonds had been formed.

The adsorption of Rhodamine B has been studied on several other /...

other substrates of different chemical properties from alumina. The author's colleague, R. B. McKay, has studied the adsorption of Rhodamine B on formalin fixed yeast cells. Rhodamine B on yeast gives an S isotherm and the amount adsorbed again corresponds to a monolayer of monodisperse ions adsorbed with the previously suggested orientation. L-isotherms are observed for the adsorption of Rhodamine B on graphite and on silk or wool (R. B. McKay, A. H. Tolia, private communications). In each case the amount adsorbed corresponds to a monolayer of monodisperse ions lying flat on the surface. Graphite which consists of condensed ring aromatic systems and proteins (silk and wool) which have a high proportion of hydrocarbon residues will have little attraction for the ionic groups of Rhodamine B. There will, however, be strong van der Waals forces between the aromatic nucleus of the dye and the non-polar surfaces causing the Rhodamine B molecule to lie flat on the surface.

It has been stated by Giles[30] that solutes adsorbed by covalent bonding cannot be fully desorbed by rinsing with water. p-Nitrophenol is adsorbed by alumina, partly by physical forces and partly by covalent bonds, since Fig. 14a shows that it is only partially desorbed by water. The covalently bound portion is not removed by rinsing. It is possible that a few molecules of p-nitrophenol are adsorbed first by covalent bonding or hydrogen bonding causing the molecule /...

molecule to be oriented in a vertical position to the surface. Further molecules can be adsorbed by physical forces and are held by those already present.

The molecule of Rhodamine 6GB (Fig. 13), a dye similar in structure to Rhodamine B (Fig. 12), has a carboxy ethyl ester group in place of the free carboxyl group, and it also has two free hydrogen atoms, both on the same side of the molecule. These hydrogen atoms are capable of forming hydrogen bonds with the hydroxyl groups at the alumina surface, so causing the molecule to orient itself edge-on to the surface. This suggested vertical orientation, as with Rhodamine B, is confirmed by the amount of Rhodamine 6GB adsorbed, which corresponds to a monolayer (Table IV) of vertically oriented molecules and the isotherm obtained (Fig. 16e) is again S in shape. This vertical orientation could still be caused by the attraction of the positively charged nitrogen atoms for the negative surface as in the case of Rhodamine B, but if this were true then adsorption would be by ion exchange. A desorption isotherm (Fig. 14d) shows, however, that at least part of the adsorbed Rhodamine 6GB cannot be desorbed by water, confirming adsorption by hydrogen bonding.

A few of the adsorption isotherms, instead of showing a flat plateau, display a maximum, e.g. Fig. 16b,c,d,h. This type of isotherm is common in the study of detergent solutions in which it occurs above the Critical Micellar Concentration (CMC) /...

(CMC), and it seems to be due to the presence of aggregates or micelles in solution. Thus it is possible that the direct adsorption of preformed micelles will take place at room temperature.

Adsorption has been shown to be an exothermic reaction and so the amount adsorbed should decrease with increased temperature. Ion-exchange adsorption reactions, however, which have a very low heat of adsorption, since no chemical bonds are formed, have hitherto shown no change in the amount adsorbed at two temperatures. Recently several anomalous adsorption results have been reported in which ion-exchange adsorption was shown to increase with increase in temperature[55,56]. The suggested explanation was that this anomalous effect was given by solutes which formed large aggregates. At higher temperature the aggregates in solution are thought to break down[105] giving a large percentage of monomeric dye which then builds up into larger aggregates on or immediately after adsorption. Since the adsorbed micelle is larger in hot than cold adsorption the association at high temperature must occur at the surface. The mechanism of association must differ at the substrate surface and in solution. This is understandable because in solution micelles are formed under the influence of solvation forces from all directions, but at the solid/liquid interface they are formed under the influence of strong forces mainly from one direction and therefore the structure /...

structure of the resultant aggregates will very probably differ in the two cases. Little is known, however, of the structure of micelles in solution and nothing of that of adsorbed micelles.

All the dyes used, with the exception of Crystal Violet (which is anyway similar in structure and behaviour to Ethyl Violet, Fig. 11), were studied at high temperature. The results obtained are illustrated in Fig. 16. With the exception of Methylene Blue, Safranine and the three Rhodamine dyes the amounts adsorbed increase with increased temperature. According to the theory of Giles et al.[55] this supports the hypothesis that the dyes are in the form of large aggregates. Methylene Blue, which appears to be only slightly aggregated - it is adsorbed only a little in excess of a monolayer (Table IV) - seems to behave as a normal ion exchange solute, since the amount adsorbed is independent of temperature. Rhodamine B, which is adsorbed by ion exchange to the extent of a monolayer is also temperature independent (Fig. 16c). Thus the dyes which exhibit the anomalous adsorption characteristics are only the triphenylmethane dyes, e.g. Ethyl Violet, Victoria Pure Blue BO and Magenta (Figs. 11,12). There seems to be some doubt, however, whether the aggregates at room temperature are adsorbed preformed or whether the monomer is first adsorbed and subsequently aggregated at the surface. At room temperature there will be a large percentage of /...

of associated dye molecules present in solution and according to McBain[106] and others[107-110], who have studied surface active agents, hydrocarbons and certain dyes, the aggregates in dilute solution, which have a relatively large charge for their size will move more rapidly than the monomer through the solution. They will therefore arrive at the surface first and will probably be preferentially adsorbed. In fact, this has been illustrated by Allingham et al.[19] by a comparison of the spectral absorption curves of Methylene Blue before and immediately after adsorption on silica. It is clear that the aggregate is adsorbed in preference to the monomer since the peak corresponding to the aggregate decreases after adsorption. If a series of basic dyes are studied at the same temperature (say 20°C.) then for each particular dye the percentage of associated ions will be approximately the same for solutions of the same strength and age. Therefore, if the aggregated dye is preferentially adsorbed the amount adsorbed will depend on the degree of aggregation of the dye at the particular temperature and will be independent of oppositely charged surfaces. If the monomer is preferentially adsorbed it will be able to arrange itself according to the nature of the surface, and if possible it will form a stable monolayer of monodisperse ions. At elevated temperature the percentage aggregate present has diminished considerably[105] giving a large excess of monomer. According to Giles et al.[55] this monomer /...

monomer can build up at the surface into even larger aggregates, possibly with a different structure, as discussed above.

Giles et al.[56] have suggested a possible energy level diagram to represent the endothermic adsorption of aggregated dye on a substrate. The author has extended this (Fig. 18) in an attempt to account for the disaggregation of the preformed aggregates in solution. Heat A is the heat required to break down aggregates formed in solution. Heat B is the heat evolved in reforming aggregates at the surface. X_1, X_2 and X_3 represent three possible energy levels giving endothermic, temperature independent, and exothermic adsorption respectively. The actual heat of adsorption, before re-aggregation, is small and will therefore not be important in determining the final energy levels. Since the adsorption of large aggregated molecules gives an endothermic adsorption the final energy level must be represented by X_1. Thus heat A must be greater than heat B, which supports the fact that the structures of the aggregates in solution and on the surface are different. For dyes with small aggregates, such as Methylene Blue, the adsorption is temperature independent or similar to normal ion-exchange and the energy level is represented by X_2 although both A and B will be small. In the next part of this work the adsorption of alizarin on alumina is discussed. This gives exothermic adsorption of large /...

large micelles and is represented by X_3. Thus from the diagram it can be seen that although the total adsorption of micelles can be endothermic, temperature independent or exothermic, depending on the formation of the aggregates, the actual adsorption step is exothermic in accordance with thermodynamic principles and the anomalies are only caused by aggregation. Since the structure of the aggregates in solution and at the surface is unknown no numerical values can be given for heats A or B but the amount by which the adsorption is endothermic or exothermic (over all) can be assessed from a comparison of two isotherms at two temperatures.

At 60°C. the shape of the adsorption isotherm of Safranine T has changed from L to S (Fig. 16g). The amount of dye adsorbed at the plateau of the high temperature isotherm corresponds closely both with adsorption of a monolayer of monodisperse Safranine molecules oriented edge-on to the surface (Table IV), and with the shape of the isotherm. At high temperature the Safranine molecule (Fig. 11) must carry a positive charge partly on the unsubstituted nitrogen atom which will bond with the negative surface. At an intermediate temperature (40.5°C.) the isotherm shape is again L and the amount adsorbed, although less than at 20°C, is still in excess of a monolayer of molecules oriented flat at the surface (Fig. 16g, Table IV). Although adsorption decreases /...

decreases with increase in temperature, between 20°C. and 40.5°C., which is in aggreement with thermodynamic principles, the fact that the orientation changes at high temperature suggests that adsorption is in fact being affected by changes in aggregation of the dye at different temperatures. At room temperature the aggregates are adsorbed, independent of the surface, but at high temperature when the amount of aggregate is small compared with the monomer the monodisperse ions will orientate themselves vertically at the surface and consequently instead of forming aggregates, as do the other basic dyes, the molecules form a stable monolayer of monodisperse ions. At 40.5°C. an intermediate situation is encountered in the aggregation of the dye molecules at the surface. In this case the aggregates are smaller than at 20°C. and yet they do not represent a monolayer of monodisperse molecules. The presence of preformed aggregates must hinder the formation of a monolayer of monodisperse ions. Safranine on alumina is completely desorbed by water, so that apparently no hydrogen bonds with the surface are formed by the amino groups even at 60°C. Hence the adsorbed species is altered by the temperature of adsorption apparently by the progressive disaggregation of the dye molecules.

Since the dye was adsorbed at 60°C. in the monodisperse form it was thought that it would be entirely dissociated in solution and so the disaggregation of Safranine was studied at several /...

several temperatures by measuring the y/x ratios of the two peaks of the absorption spectral curves according to the method of Giles, Rahman and Smith[111]. The dye solution under observation was heated using the apparatus designed by Grant et al.[103] and the absorption spectral curves drawn at several temperatures (Fig. 19). The y/x ratios were plotted against the logarithm of the corresponding temperatures and the linear relationship obtained (Fig. 20) showed that the dye disaggregated progressively with increased temperature up to 100°C. The y/x ratio of an ethanolic solution of the dye, at room temperature, was plotted (ignoring the solvatochromic shift) on the extrapolation of this experimental line (the intersection of the two broken lines). It is seen directly from the graph that in order to obtain a degree of disaggregation (y/x ratio) of the dye in aqueous solution similar to that in ethanol, the solution would require to be heated to 210°C. Grant et al.[103] have used their heating unit up to temperatures of about 270°C. without difficulty and so the spectral curve of an aqueous solution of Safranine was obtained at approximately 210°C. under pressure (Fig. 19a). The y/x ratio is similar to that at 100°C. (Fig. 20) showing that apparently no further disaggregation of a water solution takes place above about 100°C., although the low extinction coefficient suggests that some of the dye had dissociated at high temperature. It would appear, however, that ethanol is a /...

a stronger disaggregating agent for certain dyes than is hot water. Further work would be required, using different dyes and disaggregating solvents such as pyridene at high temperatures to elucidate this point.

It has been suggested above that Rhodamine 6GB is adsorbed by hydrogen bonding through the free hydrogen atoms in its molecule (Fig. 13). This is supported by the fact that Rhodamine 6GB is not completely desorbed by water (Fig. 14d) showing that the adsorption is not by simple ion exchange. A study of the adsorption isotherms of Rhodamine 6GB at two temperatures[112] shows that with increase in temperature adsorption decreases (Fig. 16e). Unlike Safranine there is no change in orientation and so Rhodamine 6GB is behaving as a normal adsorbate giving exothermic adsorption. This further supports the fact that hydrogen bonding and not ion-exchange is causing Rhodamine 6GB to be adsorbed.

Rhodamine 3B (Fig. 12), which has an esterified carboxyl group like Rhodamine 6GB but, like Rhodamine B has no free hydrogen atoms cannot be adsorbed by hydrogen bonds. The esterified carboxyl group cannot ionise to form cross links with the other adsorbed molecules as in the case of Rhodamine B (Fig. 17). Thus the carboxy ethyl ester will not be repelled from the surface and so the Rhodamine 3B can lie flat on the surface. This is supported by the L isotherm (Fig. 16d) although the molecules do not seem to aggregate since the amount /...

amount adsorbed corresponds to about a monolayer (Table IV).

It has been shown above that some dyes at room temperature have a higher degree of aggregation than others, e.g. Ethyl Violet is more aggregated than Methylene Blue, and that the dyes with a high degree of aggregation are adsorbed more in excess of a monolayer than are the dyes with small degrees of aggregation. From previous papers[12,19] a term "coverage factor" was introduced in an attempt to determine some relationship between the dye and the amount adsorbed. If the apparent surface area of a powder is calculated from the first plateau or maximum (if there is one e.g. Fig. 16b,c,d,h) of an adsorption isotherm, measuring the cross-sectional area of the molecule in its most probable orientation, and then divided by the true surface area measured by the adsorption of nitrogen or e.g. p-nitrophenol, the ratio obtained is known as the coverage factor. McKay[56] pointed out that using a series of basic dyes the coverage factor on yeast increased with increasing molecular weight of the dye. The author has studied the same series of basic dyes on negatively charged alumina and confirmed that the coverage factor increases with increasing molecular weight. A plot of the logarithm of coverage factor against the logarithm of cationic weight (molecular weight of the dye less the weight of the anion) of the dye is linear. When the author's results were compared with those of McKay and the results from a previous paper for

the /...

the adsorption of the same series of basic dyes on graphite[12] it was found that the three lines obtained were coincident (Fig. 21). The isotherms for the two dyes on graphite marked "?" had poorly defined plateaux in the original paper[12], but the author's colleague, C. C. Patel, has since repeated the isotherms using a similar sample of graphite and he found that the points do in fact lie on the coverage factor line.

When the adsorption results for the same basic dyes on MSC silica (a fine silica dust)[19] were studied in the same way, a straight line was again obtained. In this case, however, the line was parallel to those already mentioned but was not coincident with them. The explanation is that the surface area given for the MSC powder is in error due to an ageing effect and when a suitable correction is made the line is in fact coincident with that already shown. This will be discussed more fully in the next part of this work. The coverage factor, therefore, appears to be independent of the surface (if the charge of the dye and substrate are opposed). At room temperature, when Safranine is aggregated, the coverage factor on both yeast and alumina are similar whereas at high temperature Safranine behaves differently on yeast and alumina. On yeast Safranine is adsorbed to a greater extent at high temperature than at low[56], whereas on alumina at high temperature it forms a monolayer of vertically oriented molecules. This seems to suggest that at high temperature, when /...

when the dye is disaggregated, the substrate plays some part in the reaggregation at the surface. This supports the fact that in the cold it is probably the preformed aggregate which is being preferentially adsorbed

It was shown by McKay that Malachite Green, a typical basic dye, gives a coverage factor much less than that corresponding to its cationic weight[56]. The explanation given was that Malachite Green was unsymmetrically substituted. Possibly a better explanation would be that the effective cationic weight for coverage factor work is only about half of the total weight. The dye which is formed, like many green dyes, by joining a yellow and blue chromophore* with a conjugate blocking group, gives a coverage factor corresponding to its ~~blue~~ larger chromophore cationic weight. The complete molecular area will be effective in measuring the apparent surface area of the powder but the size of the micelle will only be governed by one of the two chromophores. A similar effect has been shown by the author's colleague N. B. Shah who found that the coverage factor of Solphenyl Brilliant Green 5GL on graphite was low compared with its full molecular weight. This dye is formed by joining a blue and yellow chromophore by means of a conjugate block. Again the coverage factor corresponds to the molecular weight of the ~~blue~~ larger chromophore.

A mixture of three of the basic dyes, when chromatographed /...

* As evident in the visible spectra

graphed from water on an alumina column, and eluted with water, separated in order of their coverage factors; Victoria Pure Blue BO (c.f. 11) was held most strongly, Safranine T (c.f. 2.4) less so and Methylene Blue BP (c.f. 1.95) least firmly.

CONCLUSIONS.

Basic dyes, with the exception of Rhodamine B, Rhodamine 6GB and Rhodamine 3B, are adsorbed by negatively charged alumina by ion exchange as cationic micelles. It is thought that at room temperature the aggregated dye is preferentially adsorbed, whereas at high temperature the monodisperse ions in solution are adsorbed to form larger aggregates at the surface, probably with a different structure from those formed in solution.

Because of their structures Rhodamine B and 6GB do not form aggregates but are adsorbed as monodisperse ions with a vertical orientation. Rhodamine 3B is adsorbed as a monolayer of ions with a flat orientation.

Dyes adsorbed by ion-exchange can be completely desorbed by rinsing with water but dyes which have a potential hydrogen-bonding group are not completely desorbed.

The triphenylmethane dyes Magenta, Ethyl Violet and Victoria /...

Victoria Pure Blue BO show anomalous endothermic adsorption and an energy diagram is given to explain this by the break down of dye aggregates with increase in temperature.

At high temperature Safranine T appears to re-orientate to give a monolayer of monodisperse ions adsorbed end-on to the surface. There appears to be no further disaggregation of the dye in aqueous solution above 100°C. although ethanolic solutions show a higher degree of disaggregation. This may be due to ethanol being a stronger disaggregating agent than hot water.

With the exception of the Rhodamines all the dyes, at room temperature, give the same coverage factors on chemically different substrates suggesting that adsorption is independent of substrate.

PART II.

SOME MISCELLANEOUS SOLUTION ADSORPTION SYSTEMS.

INTRODUCTION.

In this part several unrelated adsorption systems have been studied to discover whether the general principles governing the relation of adsorption mechanism to isotherm shape apply to all systems. From a consideration of the isotherm shapes obtained and the use of the classification of solution isotherms[59] the orientation of the adsorbed molecules and in some cases the type of bonding may be determined. For example, from a knowledge of the surface area of the substrate it is immediately apparent whether a solute is being adsorbed, not as single ions, but in the form of ionic micelles.

EXPERIMENTAL.

Solutes.

The phenol used was taken from an "AnalaR" sample and was not recrystallised. For some tests it was intensively dried over phosphorous pentoxide in a vacuum dessicator for two days. This dry phenol was dissolved in anhydrous *iso*-octane obtained "pure for spectroscopy". Other phenol solutions were prepared in de-ionised water.

The dye, C.I. 62055, was prepared by recrystallising a commercial sample of Solway Ultra Blue B (ICI, Ltd.) four times /...

times from an ethanol-water mixture (50:50, v/v) and then drying at 102°C.

p-Nitrophenol was recrystallised from water.

Alizarine Red AS was purified by "salting out" with sodium acetate, as described by Giles and Greczek[113]. Solutions were prepared in 1% (v/v) acetic acid and also in de-ionised water.

Alizarin (unsulphonated) was purified by sublimation and solutions were prepared in 50% (v/v) ethanol

All solutes were estimated spectrophotometrically - phenol at 270mμ and p-nitrophenol at 400mμ, after buffering with alkali[97].

Substrates.

The same chitin which had been used previously[15] was intensively dried in three different ways:-

(a) It was heated in an oven at 106-108°C. for seven hours and cooled in a dessicator.

(b) It was heated at 100°C. and 28"mercury in a vacuum dessicator for seven hours and cooled in a dessicator.

(c) It was dried over phosphorous pentoxide for two days.

In all cases no more than about 7% labile water was removed (Table V) and so the oven dried chitin was used in the experiments.

MSO silica was obtained from Messrs. Colin Stewart Ltd., and / ...

and a sample was intensively dried by heating at 130°C. for 24 hours and then by storing over Hi-Drite (Hi-Drite Ltd., London) for 24 hours. Some of this dried powder was exposed to a damp atmosphere for 24 hours.

The alumina was taken from the same sample used in Part I. A portion of it was acidified with hydrochloric acid (2N acid) according to the method of Giles et al.[20] and rinsed with de-ionised water and then dried at 130°C. in the oven.

Commercial red rubber tubing was cut in pieces about 0.1 inches cube, scoured with detergent, thoroughly rinsed with water and dried to room humidity. Synthetic rubber was cut in small pieces, soaked in warm water and dried to room humidity.

The adsorption procedure was exactly the same as described elsewhere[20] and in each test 0.1 or 0.2 g. samples of substrate were tumbled[102] with 10 ml. solution.

RESULTS AND DISCUSSION.

The Adsorption of Phenol on Chitin.

Giles and Hassan[15] have studied the adsorption of methanol from benzene and phenol from iso-octane on normally dried chitin. In both cases S isotherms were obtained.

Giles /...

Giles et al.[59] then studied the adsorption of methanol from benzene on intensively dried cellulose and obtained an L-isotherm. The small percentage of water remaining bound to the cellulose after normal drying was in this case probably competing with the methanol for the available sites - resulting in an S-isotherm[59]. When this water was removed by intensive drying there was no competition and thus an L-isotherm was obtained.

Chitin, which is an aminoacetyl derivative of cellulose, was shown by Giles et al.[114] to contain about 5% strongly bound water in its highly crystalline regions. This water was thought to be competing for the adsorption sites during the adsorption of phenol from iso-octane, resulting in an S-isotherm. The author attempted to remove this firmly bound water by several methods of intensive drying shown in Table V. In all cases only the surface labile water was removed.

After intensive drying of phenol over phosphorous pentoxide in a vacuum dessicator for two days a solution was made up in dry iso-octane. With this careful drying of the solution an L-isotherm was obtained on oven-dried chitin (Fig. 22) but the amount adsorbed is much less than that measured by Giles and Hassan[15] in the presence of traces of water. This reduction in adsorption in the absence of water is in agreement with Hirst and Lancaster's results[115]; they found that a trace of water in solution helped cuprous oxide to /...

to extract much more stearic acid from benzene solution than if the solution was perfectly dry.

The author's colleague A. H. Tolia found that the amount of phenol adsorbed from n-heptane by nylon was much reduced if the solution was perfectly dry. He also found that the shape of the isotherm changed from S to L (private communication). The fact that the isotherm shape changes when water is removed was also shown by Harkins and Gans[116] who found that only 1 part water in 100,000 parts solution produced a noticeable effect on the isotherm shape in the adsorption of stearic acid from benzene on titania.

Thus the 5% firmly bound water in chitin does not compete for the adsorption sites in the adsorption of phenol from iso-octane. The competition seems to come from labile water and traces of water in solution. Although the traces of water alter the shape of the isotherm they also appear to increase the amount adsorbed; probably this is a catalytic effect.

The Ageing of MSC Silica.

Allingham *et al.*[19] measured the surface area of MSC silica by air permeability and found it to be about 1 m^2/g. Several years later Giles and Nakhwa[97] quoted the area of the same powder as 5 m^2/g. by the adsorption of nitrogen, and obtained the same value by the adsorption of p-nitrophenol from a non-polar solvent and the adsorption of C. I. 62055 from water. They suggested that the previous value was low

due /...

due to the inaccuracies of the method used. The author measured the surface area, by the adsorption of C.I. 62055 (Fig. 23) on the same powder after it had been stored in a paper bag for approximately one year. The value calculated was 3.6 m^2/g., i.e. less than the value found by Giles and Nakhwa. Thus the surface area of this particular silica powder appears to decrease with age. If the original powder used by Allingham et al.[19] had a surface area of about 12 m^2/g. (which could well reduce to 5 m^2/g. on long exposure to the atmosphere and then to 3.6 m^2/g after further exposure) then the coverage factor values, based on Allingham's results (not shown) which at present are too high, would be coincident with the yeast, alumina and graphite values (Fig. 21) as discussed in the previous part.

The author heated a sample of the powder (of area 3.6m^2/g.) to 130°C. for several hours. The area of this dried powder, measured from the isotherm (Fig. 23), was then found to be 6.7 m^2/g., i.e. higher than the value of Giles and Nakhwa[97]. When the same dried powder was placed in a damp atmosphere for one day the amount adsorbed (Fig. 23) had decreased only slightly to a value corresponding to 6.5 m^2/g. showing that ageing has more effect than simple moisture adsorption on the surface area of the powder.

Since the surface area of the powder can alter it is assumed that the values quoted for the coverage factors by Allingham /...

Allingham *et al.*[19] are in error and when a suitable correction is made the coverage factor values approximate to those shown in Fig. 21.

The Rate of Adsorption of p-Nitrophenol on MSC Silica.

Nakhwa[99] has shown that the equilibrium adsorption of *p*-nitrophenol (PNP) on zinc gives an S-isotherm denoting a vertical orientation on the surface. When the rate curve was measured, however, two distinct plateaux were obtained[99]. These correspond to PNP in a flat orientation on the surface during the first few hours followed by a final vertical orientation at equilibrium.

The same S-shaped isotherm is found for PNP on alumina[99] but in this case adsorption is rapid and the various stages are not detectable in the rate curve. The author has studied the adsorption of PNP on MSC silica. Because of the repulsion between the negative ions of PNP and the negative surface the rate of adsorption is slow and several hours are required to reach equilibrium. The equilibrium isotherm is S-shaped, denoting a vertical orientation. The rate curve obtained (Fig. 24) shows that, as with zinc, the PNP molecule was initially lying flat on the surface and after several hours it assumed a vertical orientation.

From a comparison of the heights of the two plateaux with the corresponding cross-sectional areas of the molecule it is plain that in the final vertical orientation the PNP does /...

does not completely cover the surface. This is in agreement with the equilibrium measurements which show that because of the repulsion of PNP by the surface and the strong competition of the solvent (water) for the polar surface PNP does not completely cover the surface.

Thus molecules such as PNP which display an end-on orientation in an equilibrium isotherm may have passed through the initial flat orientation stage, although in many cases when the rate is high this re-orientation will be impossible to detect.

The Adsorption of Alizarin on Chromatographic Alumina.

The red metal-complex formed by the chelation of the alizarin molecule with aluminium in alumina was thought[24] to be the result of direct covalent combination of two molecules of alizarin with each aluminium atom at the surface of the oxide film. In fact Stewart[117] found that the ratio of alizarin to aluminium was 2:1 (after correction had been made for the use of potash alum instead of aluminium sulphate). The amount of alizarin adsorbed by the chromic acid film on aluminium corresponds approximately to a monolayer of molecules stacked edge-on to the surface.[100] Kiel and Heertjes[118], however, have shown that the alizarin-aluminium complex is planar in structure and so it would be sterically impossible for alizarin to bond to the aluminium in the surface in an edge-on orientation. If the metal complex is planar then the amount of alizarin adsorbed /...

adsorbed flat on the surface should not exceed a monolayer. In fact when the amount adsorbed is calculated assuming a flat orientation the coverage factor (see Part I) is about 3.0, suggesting that alizarin is adsorbed in excess[100]. Alizarin bonded directly to an aluminium atom in the surface would be under severe strain to maintain a planar complex. Datye and Giles[28] have recently put forward a new hypothesis for the chelation of alizarin with aluminium. They suggest that the aluminium atom is initially attached to one alizarin molecule. This attachment then weakens the Al-O bond to the surface and the 1:1 complex can break free into solution. The 1:1-alizarin-aluminium complex in solution can then form the planar negatively charged 2:1-metal complex, detected by Kiel and Heertjes[118]. Since the surface of the oxide film alumina[24] and acidified alumina powder[20] are positively charged the large 2:1-complex will form anionic micelles and be adsorbed much in excess of a monolayer.

The author has carried out a series of adsorption tests on acidified alumina powder, which is chemically similar to the anodic film, and is non-porous. The dye is not adsorbed by alkaline alumina and from the graphs (Fig. 25) it is obvious that the amount adsorbed increases as the pH of the surface decreases. The amount adsorbed in all cases is much in excess of a monolayer (shown by the horizontal broken line) supporting the hypothesis that the preformed lake is being adsorbed /...

adsorbed as anionic micelles.

According to the hypothesis referred to in the previous part a substance adsorbed as micelles can be removed either by washing with solvent or by the preferential adsorption of another similarly charged ion. Kiel and Heertjes found that the calcium complex which they prepared was only slightly soluble in hot dimethylformamide (DMF). When the dyed alumina powder is (Soxhlet) extracted with boiling DMF the dye is increasingly stripped. One feature not mentioned by Kiel and Heertjes[118] is that the hot solution of the alizarin complex changes reversibly from yellow to red in the cold; a possible explanation is that the red colour represents the alizarin complex in the form of a micelle but on heating the micelle breaks down to give the monomeric complex which may be yellow, or perhaps the yellow solution contains free alizarin and the 1:1 complex. If the dyed powder is heated with a strong solution of anionic detergent (Lissapol C, ICI) then the colour is progressively stripped from the powder, which suggests that the detergent is being preferentially adsorbed. In fact when the powder is initially treated with a strong solution of detergent followed by alizarin the dyeing reaction of alizarin is partly inhibited. These facts support the hypothesis that the alizarin is adsorbed as the preformed complex.

The amount of Alizarine Red (a monosulphonated water soluble /...

soluble derivative of alizarin) adsorbed at higher temperature was less than at room temperature, both in the presence of acetic acid and on hydrochloric acidified alumina (Fig. 25b,d). This phenomenon does not appear at first sight to agree with the hypothesis of endothermic adsorption of large micelles suggested by Giles et al.[55]. If, however, the heat taken in to break up the metal-complex aggregate in solution is less than the combined heats given out in adsorption and reformation of the aggregates at the surface, then the overall adsorption would be exothermic and would be represented by X_3 in Fig. 18, as discussed in the previous part. The whole adsorption process appears to have many complex stages which will probably interfere with a straightforward ion-exchange mechanism. More work should be carried out using other chelating dyes and metals to further clarify the matter.

Ethanol is known to be a strong disaggregating agent and so the amount of preformed aggregate in ethanolic solution will be less than in aqueous solution. It has been shown[19] that the aggregate is preferentially adsorbed in the cold and since less of it is present in ethanol than in water the amount adsorbed will be less (Fig. 25a).

Thus it may be suggested that alizarin is adsorbed not merely by covalent bonding directly with the surface of alumina but that it forms a 1:1-complex with aluminium, at the surface, which then breaks away and finally forms the 2:1-complex /...

2:1-complex in solution. This 2:1 complex being negatively charged[118] is readsorbed in the form of anionic micelles by the positive surface of the alumina.

The Adsorption of Phenol by Rubber.

The adsorption of phenol and phenolic derivatives by rubber is a source of concern in the food industry and can cause difficulties when rubber sealed pharmaceutical bottles are used for multidose purposes[119-123]. No actual relationship between adsorption and the filler content or the rubber content of various rubber mixtures was found by Wing[121-123], who has made a number of investigations of these systems. Silicone-filled rubber adsorbed phenol least[121], but this material is not self-sealing and after repeated sterilisation it gives off toxic substances[121], so that it is unsuitable for pharmaceutical use.

The author studied the adsorption of phenol from water on commercial red rubber and on synthetic rubber. The isotherms obtained are shown in Fig. 26, (Wing's data do not include isotherms). Natural rubber is largely hydrocarbon[124], and will have little attraction for water, although it might have a weak attraction for the aromatic nucleus of phenol; if so the adsorption would be by "solid solution" and the isotherm would be linear (C-type[59], Fig. 4d). In fact the isotherm on commercial rubber (Fig. 26) is L-type[59] denoting adsorption with a flat orientation at the surface. The phenol is /...

is probably being adsorbed by the 25% calcium carbonate present in commercial red rubber (India Tyre Company, private communication), perhaps by weak hydrogen bonds which are not sufficiently strong to hold the phenol molecule in an upright position. The fact that an L-isotherm and not a C-isotherm is obtained suggests that there is also penetration of water into the amorphous rubber matrix. This is supported by the results of Veith[125] who has shown that commercial rubber containing high proportions of fillers, e.g. whiting, clay, etc., does adsorb water and the adsorption is represented by the equation:-

$$n = Kt^{0.5}$$

where n is the quantity adsorbed per unit volume, t is time and K is a constant.

The maximum amount of phenol adsorbed on commercial rubber, (Fig. 26) is about 5 mg/g. and agrees well with the values obtained by Herd from his analyses of rubber washers[119].

The adsorption of phenol on synthetic, unfilled rubber (Fig. 26) gives an S-isotherm denoting an end-on orientation of the phenol molecule at the rubber surface[59]. In a qualitative test synthetic rubber was found to adsorb water which will penetrate at least some of its amorphous matrix. Since the phenol molecule is oriented end-on to the surface it is possible that the end of the aromatic nucleus furthest from /...

from the hydroxyl group is attached to the hydrocarbon while the hydrophilic hydroxyl group is attached to the film of water. The specific surface area (3.8 $m^2/g.$) calculated from the plateau, assuming an end-on orientation of the phenol molecule, is very low compared with wool or other fibrous materials, suggesting that only a fraction of the surface is available for the adsorption of phenol.

Thus phenol is adsorbed by filled rubber and by synthetic rubber by different mechanisms. In the case of filled rubber it is probably the polar fillers which adsorb phenol although more work is required to elucidate this point. Synthetic rubber, in the presence of a film of water probably has a weak attraction for the aromatic nucleus of the phenol molecule. At low concentrations of phenol (found in contaminated aerated water[119] and certain pharmaceutical preparations[121]) filled rubber has a much higher affinity for phenol than does synthetic rubber and so perhaps synthetic rubber derivatives could be used to advantage for certain bottle closures.

Table I. Statistical examination of atmospheric pollution data.

The following are the data:-

Source of variance	Degree of freedom	Sum of Squares	Mean Square
Summer			
Due to regression	1	2965.90	2965.90
About regression	101	7185.94	71.15
Total	102	10151.84	

$F=41.69$, with $N_1 = 1$ and $N_2 = 101$; therefore the straight line is highly significant and accounts for 29% of the regression.

Source of variance	Degree of freedom	Sum of Squares	Mean Square
Winter			
Due to regression	1	21833.97	21833.97
About regression	101	23464.79	232.32
Total	102	45298.76	

$F = 93.98$, with $N_1 = 1$, $N_2 = 101$; therefore the straight line is highly significant and accounts for 48% of the regression.

If t, calculated from the expression:-

$$t = \frac{b_W - b_s}{S\sqrt{\frac{1}{\sum_w (x-\bar{x})^2} + \frac{1}{\sum_s (x-\bar{x})}}}$$

Table I. contd.

with ($\phi_W + \phi_O$) degrees of freedom is significant, then the difference in regression coefficients will also be significant.

$$S^2 = \frac{\phi_W S_W^2 + \phi_S S_S^2}{\phi_W + \phi_S}$$

S_W^2 = variance about b_W with ϕ_W degrees of freedom.
S_s^2 = variance about b_s with ϕ_s degrees of freedom.
S^2 = combined variance about the two regressions.

$\therefore \quad S^2 = 151.735$

and t = 1.609 with 202 degrees of freedom.

This shows that the regression coefficients are different at the 10% level of significance.

Table II. Cationic dyes used.

Name.	C.I. Number.	Constitution.
Crystal Violet	42555	Fig. 11
Ethyl Violet	42600	Fig. 11
Magenta P	42510	Fig. 11
Malachite Green*	42000	Fig. 11
Methylene Blue BP	52015	Fig. 11
Rhodamine B	45170	Fig. 12
Rhodamine 3B	45175	Fig. 12
Rhodamine 6GB	45160	Fig. 13
Safranine T	50240	Fig. 11
Victoria Blue BN*	44045	Fig. 12
Victoria Pure Blue BO	42595	Fig. 12

* These dyes precipitated in the presence of alkaline alumina and could not be studied further.

Table III. Dye Analyses.

C.I. 42510. Found: C, 61.8; H, 6.4; (Na, 0.08). $C_{20}H_{20}N_3Cl$, $3H_2O$ requires C, 61.5; H, 6.65%. $C_{20}H_{20}N_3Cl$, $2H_2O$, 0.5 HCl requires C, 61.5; H, 6.3%.

C.I. 42555. Found: C, 66.4; H, 7.6; (Na, 0.24). $C_{25}H_{30}N_3Cl$, 1.5 H_2O, 0.5 HCl requires C, 66.3; H, 7.4; corresponding to 89.8% purity; $TiCl_3$ analysis gave purity of 88% corresponding to 3.05 H_2O.

C.I. 42595. Found: C, 72.4; H, 7.3; N, 7.8; (Na, 0.31). $C_{33}H_{40}N_3Cl$, HCl requires C, 72.2; H, 7.5; N, 7.7%.

C.I. 42600. Found: C, 69.4; H, 7.9; N, 7.8; $C_{31}H_{42}N_3Cl$,1.1HCl requires C, 69.6; H, 8.1; N, 7.9%.

C.I. 45170. Found: C, 67.0; H, 6.1; N, 5.5; Cl, 8.1; Na, nil. $C_{28}H_{31}O_3N_2Cl$, H_2O, 0.1 HCl requires C, 67.0; H, 6.6; N, 5.6; Cl, 7.8%.

C.I. 45175. Found: C, 65.9; H, 6.6; N, 5.0. $C_{30}H_{35}O_3N_2Cl$,HCl requires C, 66.5; H, 6.6; N, 5.2%.

C.I. 50240. Found: C, 59.3; H, 6.5; N, 14.2; (Na, 0.21). $C_{20}H_{19}N_4Cl$, $3H_2O$ requires C, 59.4; H, 6.2; N, 13.9%.

C.I. 52015. Found: C, 51.1; H, 7.2; Cl, 13.4; (Na, 0.12). $C_{18}H_{22}N_3SCl$, 3.3 H_2O, 0,58 HCl requires C, 50.5; H, 7.0; Cl, 13.4%.

Table IV. Adsorption data for basic dyes on alumina.

C.I. Number	Temp. °C.	Maximum* Adsorption. (mmole/kg.)	Molecular Area. (A^2)	c.f.**	Cationic Weight.	Isotherm Class.	Apparent Heat of Adsn.
42510	20	9.0	170	1.9	302	L2	pos.
	60	25.0		5.3		Lmx	
52015	20	13.0	120	1.95	310†	Lmx	zero
	60	13.0		1.95		Lmx	
50240	20	13.0	150	2.4	315	L2	neg.
	40.5	10.0		1.9		L2	
	60	9.0	90	1.0		S2	
42555	20	21.5	225	6.0	372	L2	
42600	20	20.5	270	6.9	456	L3	pos.
	60	42.0		14.2		H2	
42595	20	33.0	270	11.0	478	Hmx	neg.at low conc. pos. at high conc.
	60	48.0		16.2		L2	
45175	20	2.7	220	0.7	471	Lmx	zero
	60	2.7		0.7		Lmx	
45170	20	3.9	124	0.65	443	Smx	zero
	60	3.9		0.65		Smx	
45160	20	6.2	125	1.0	471	S3	neg.
	40.5	4.5		0.7		S3	

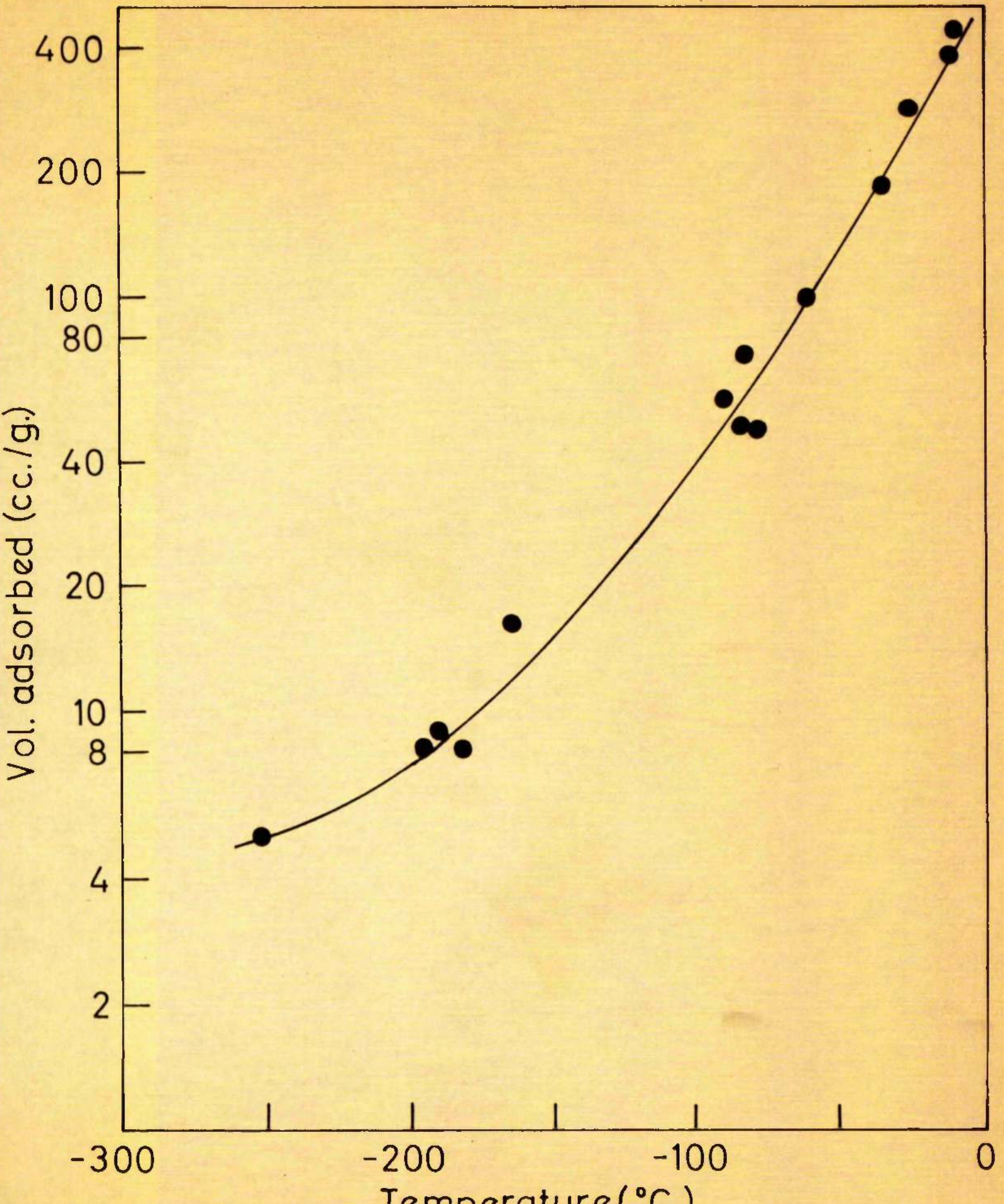
* Corrected for purity of dye.

** c.f. coverage factor (see page 78).

† Assuming the molecule has an additional C_2H_4 group (see Experimental)

Table V. Data for the drying of chitin.

Method of Drying.	Wt. of sample (g.).	Wt. of dry sample (g.).	Water, %.
Air Oven (106-108°C.)	2.0666	1.9202	7
Vac. Oven (100°C., 28"Hg.)	2.0713	1.9472	6
Vac. Dessicator (P_2O_5)	0.8620	0.8147	5



<u>Fig. 1</u>. The relation between the boiling point of a gas and the amount adsorbed by charcoal. (after Hene[46]

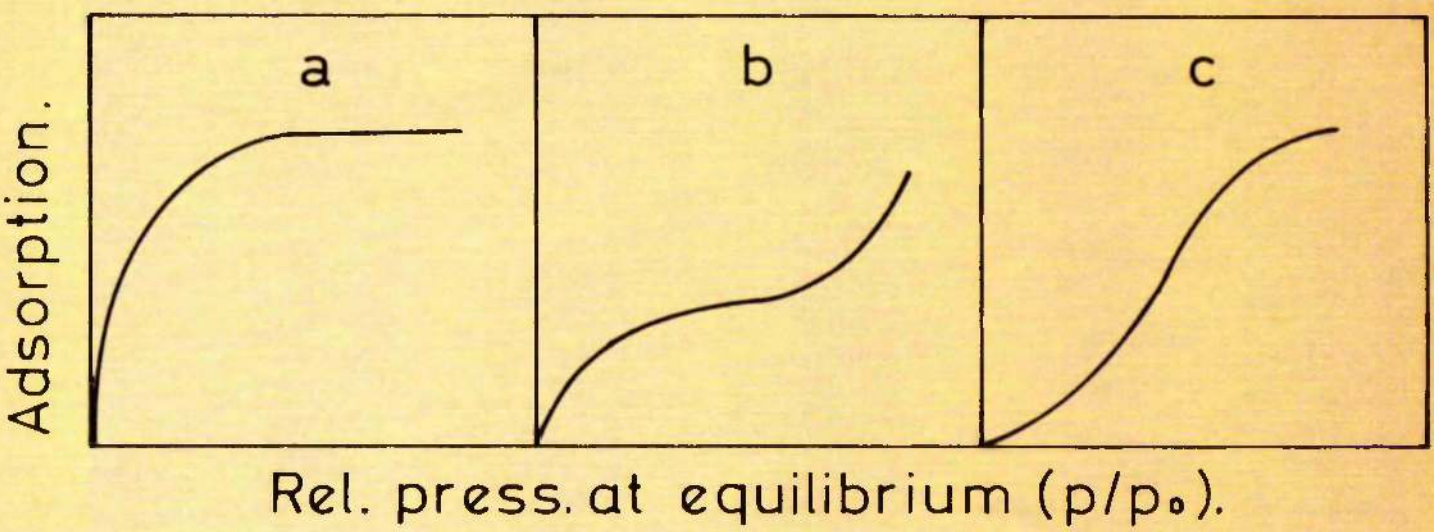


Fig. 2. Three vapour adsorption isotherms from the Brunauer classification[57].

a, type I; b, type II; c, type V.

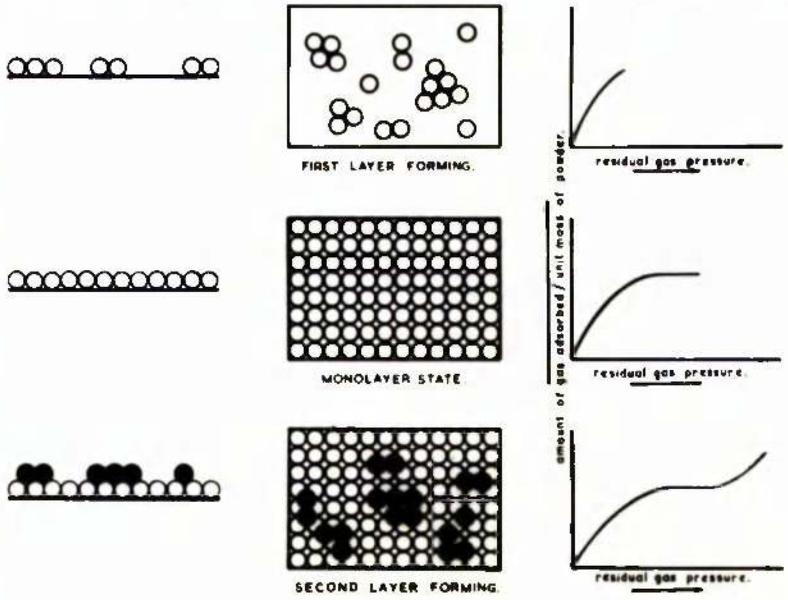


Fig. 3. Simple representation of the relationship between vapour adsorption and the shape of the adsorption isotherm.

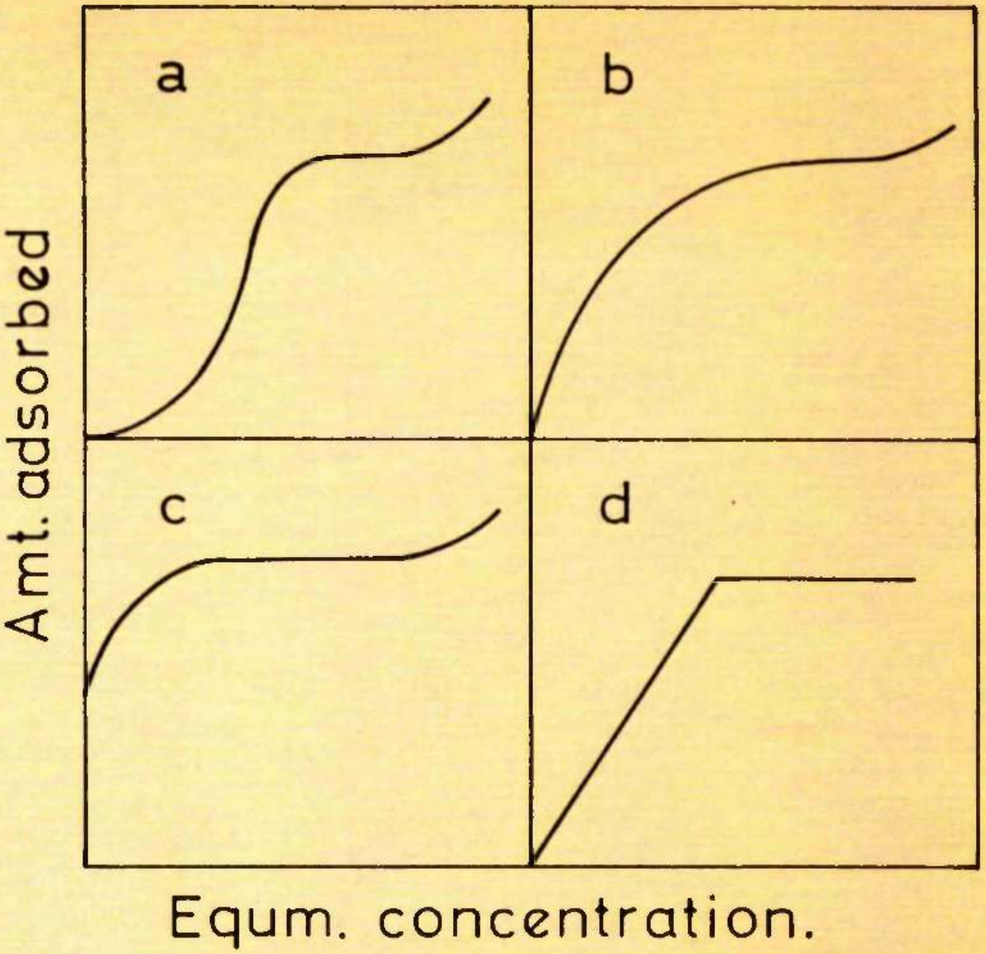


Fig. 4. Simple classification of solution adsorption isotherms[59].

a, S3; b, L3; c, H3; d, C2.

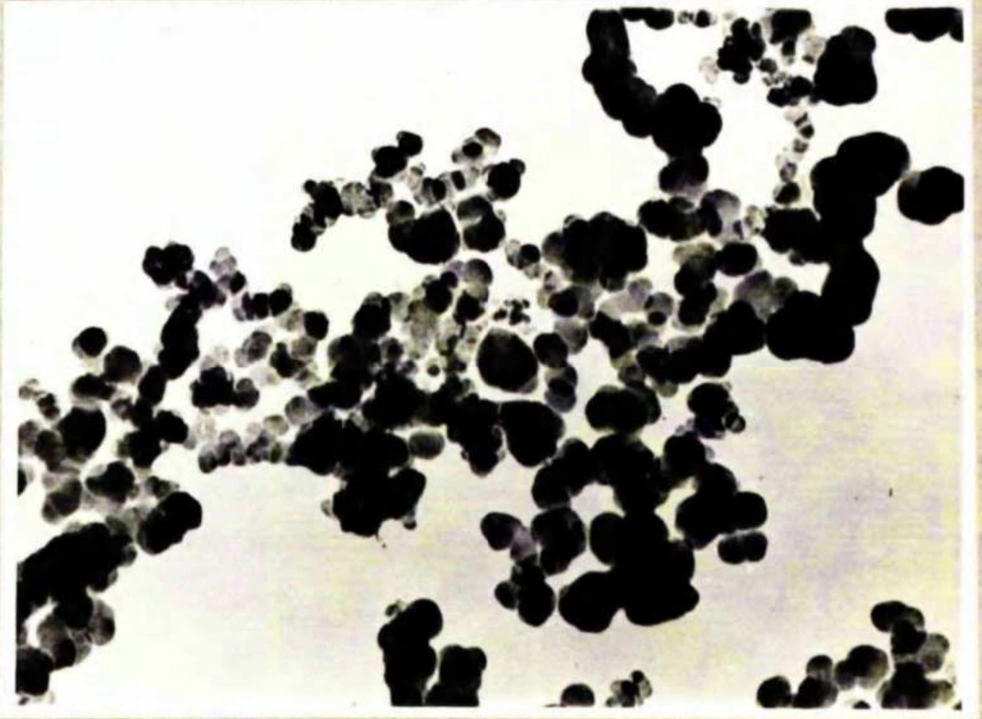


Fig. 5. Electron micrograph of low temperature carbon black. (Sterling MT, 35,000X).

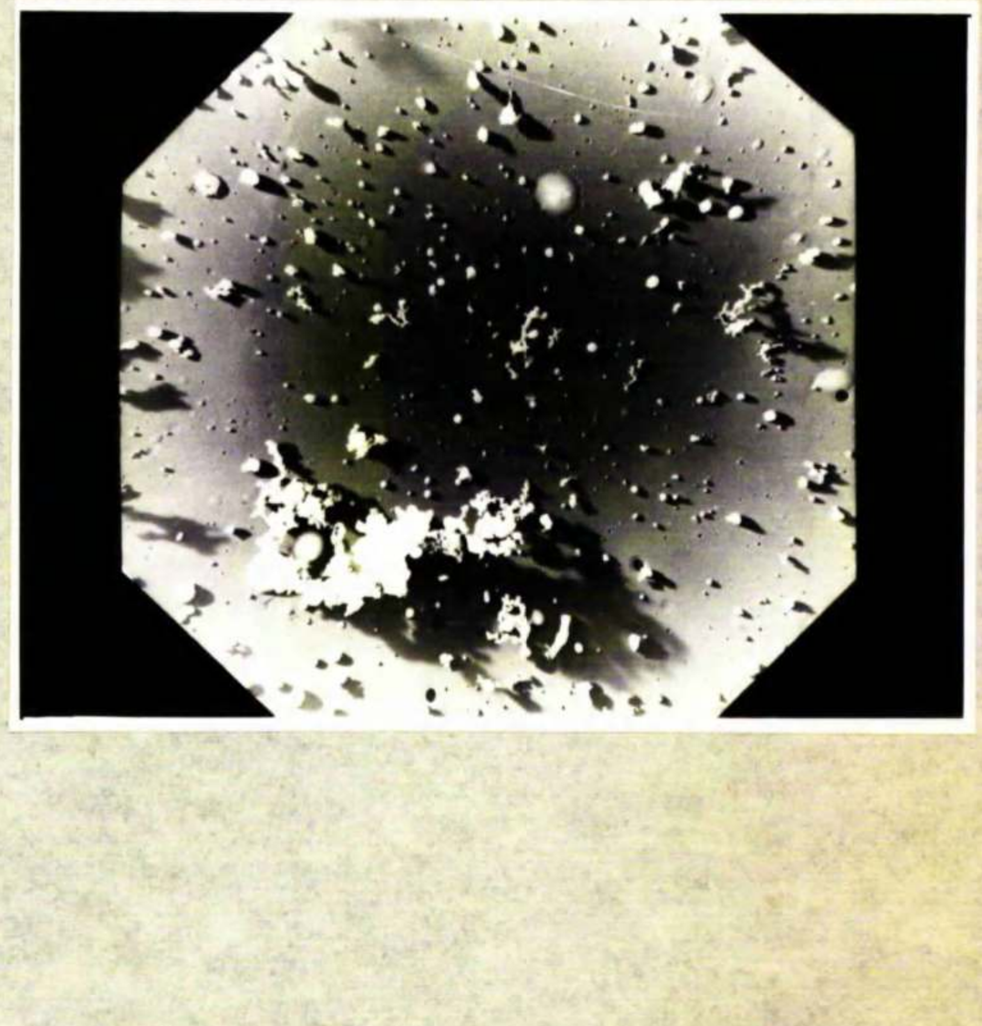


Fig. 6. Electron micrograph of solids from a Glasgow fog. (3000X).

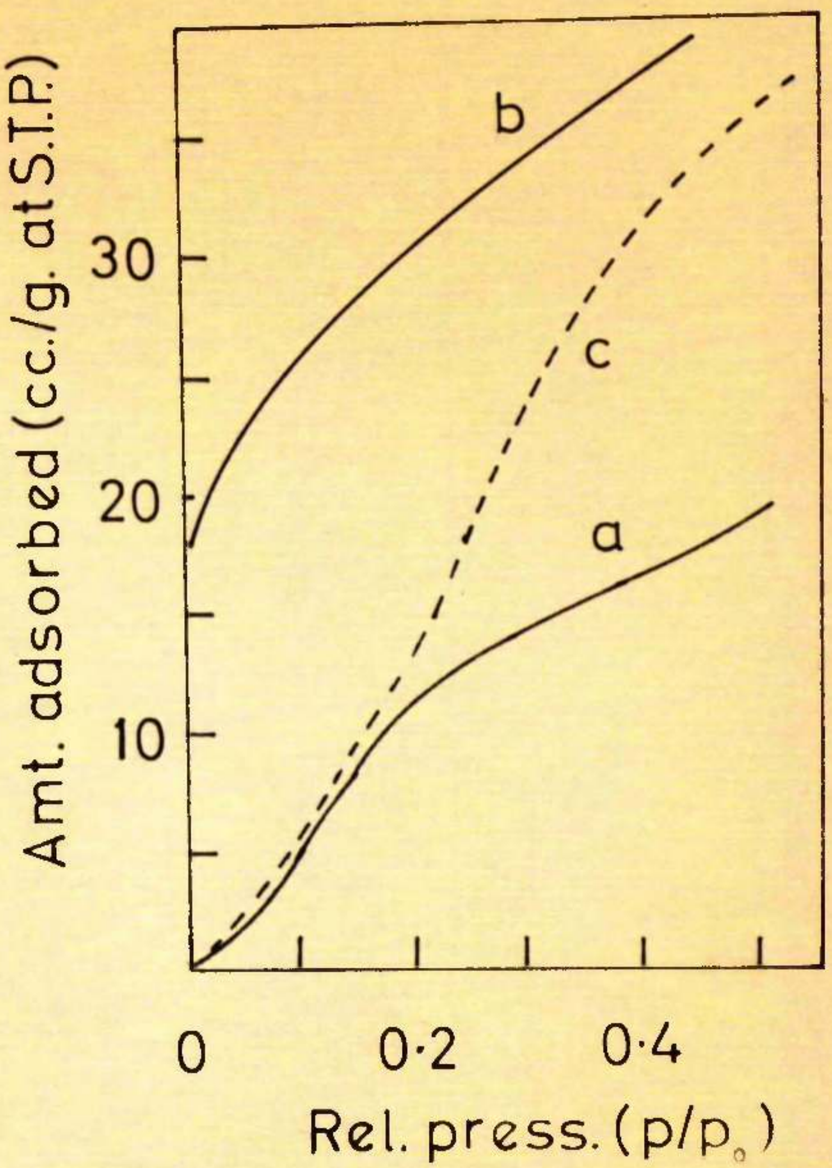


Fig. 7. Adsorption isotherms for sulphur dioxide gas[73] at 0°C. and for water vapour[76] at 25°C. on carbon. (full lines: sulphur dioxide)

a, high temperature carbon (Spheron 6, 2700).

b, low temperature carbon (Spheron 6).

c, water vapour on low temperature carbon (Spheron 6).

Fig. 8. Atmospheric pollution, summer and winter data[75], for Great Britain, except London, smoke concentration vs. sulphur dioxide concentration.

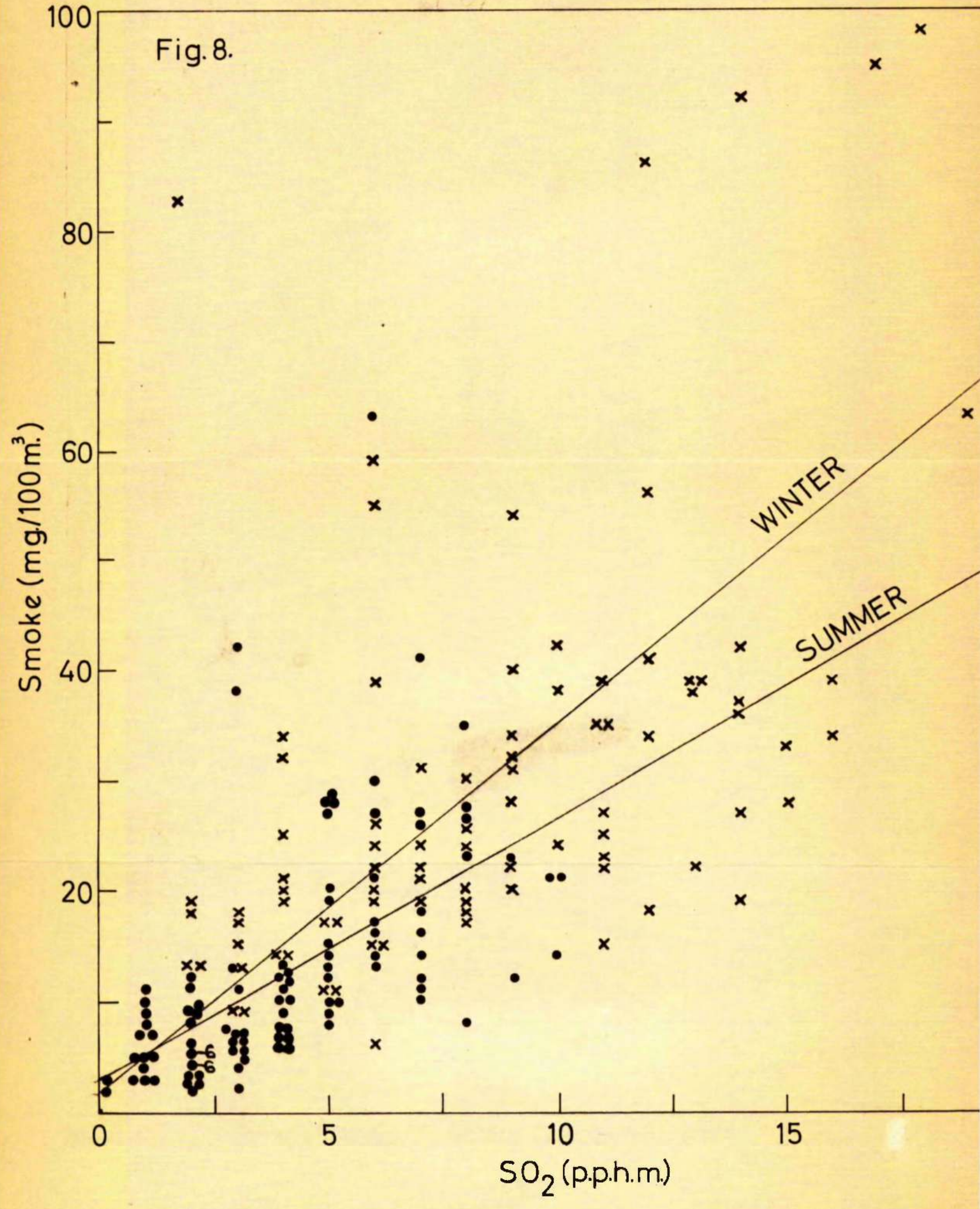
Winter data - crosses.

Summer data - circles.

Note two circles each representing six coincident points. The regression lines shown were calculated by the least squares method.

TOP

Fig. 8.



100
80
60
40
20
0
5
10
15
Smoke (mg./100 m.³)
SO₂ (p.p.h.m.)
WINTER
SUMMER
6
6

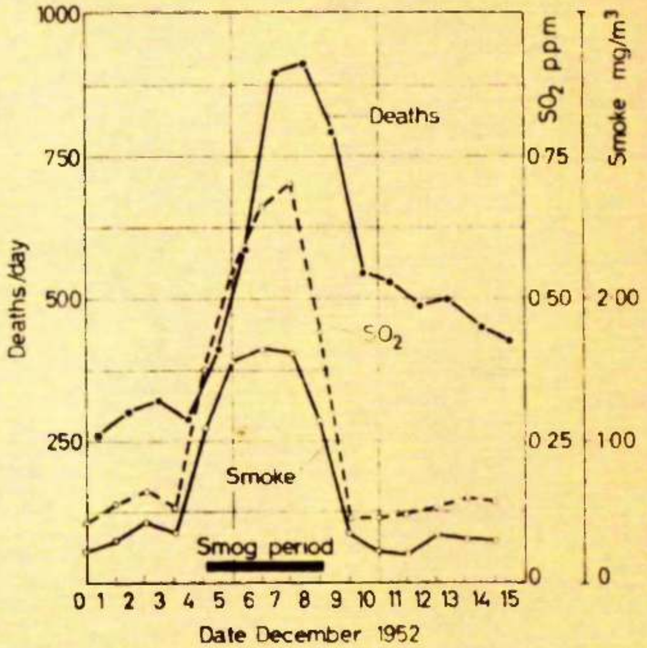
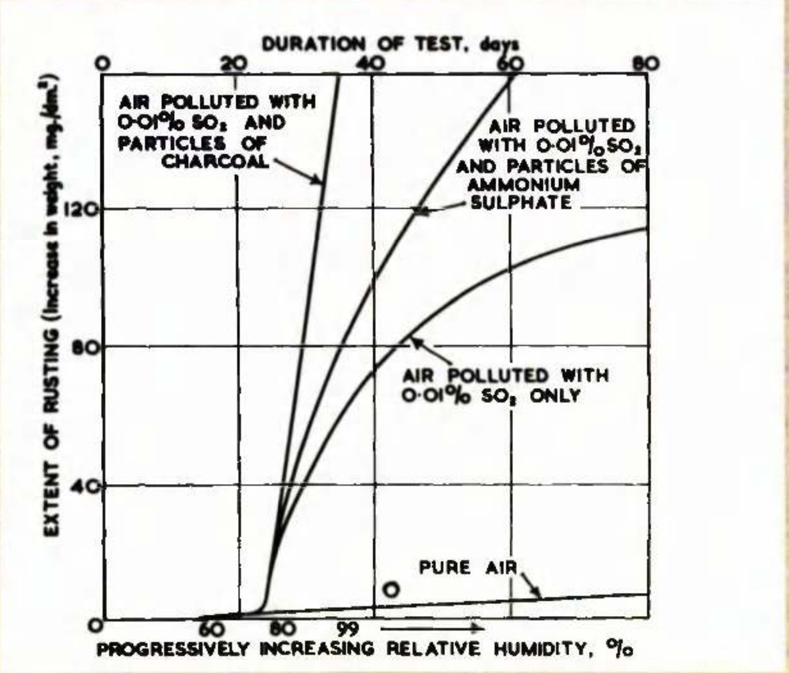


Figure 4—Daily air pollution and deaths. (Crown copyright reserved)

<u>Fig. 9</u>. Daily air pollution and deaths during the London fog of December 1952. (from ref. 64).



<u>Fig. 10</u>. The influence of solid particles and sulphur dioxide upon the rate of rusting of iron in damp air[87].

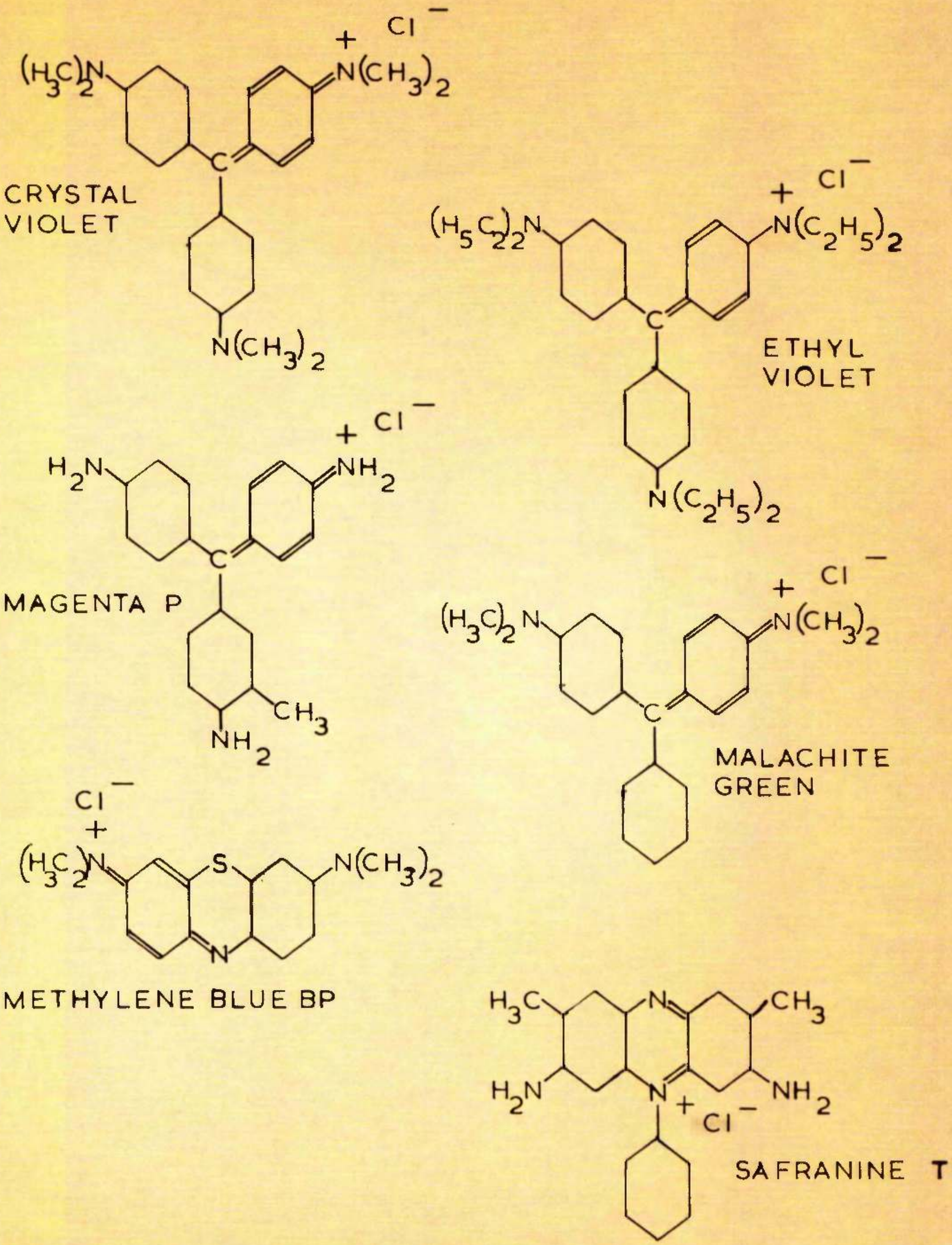


Fig. 11. Structural formulae for the cationic dyes used.

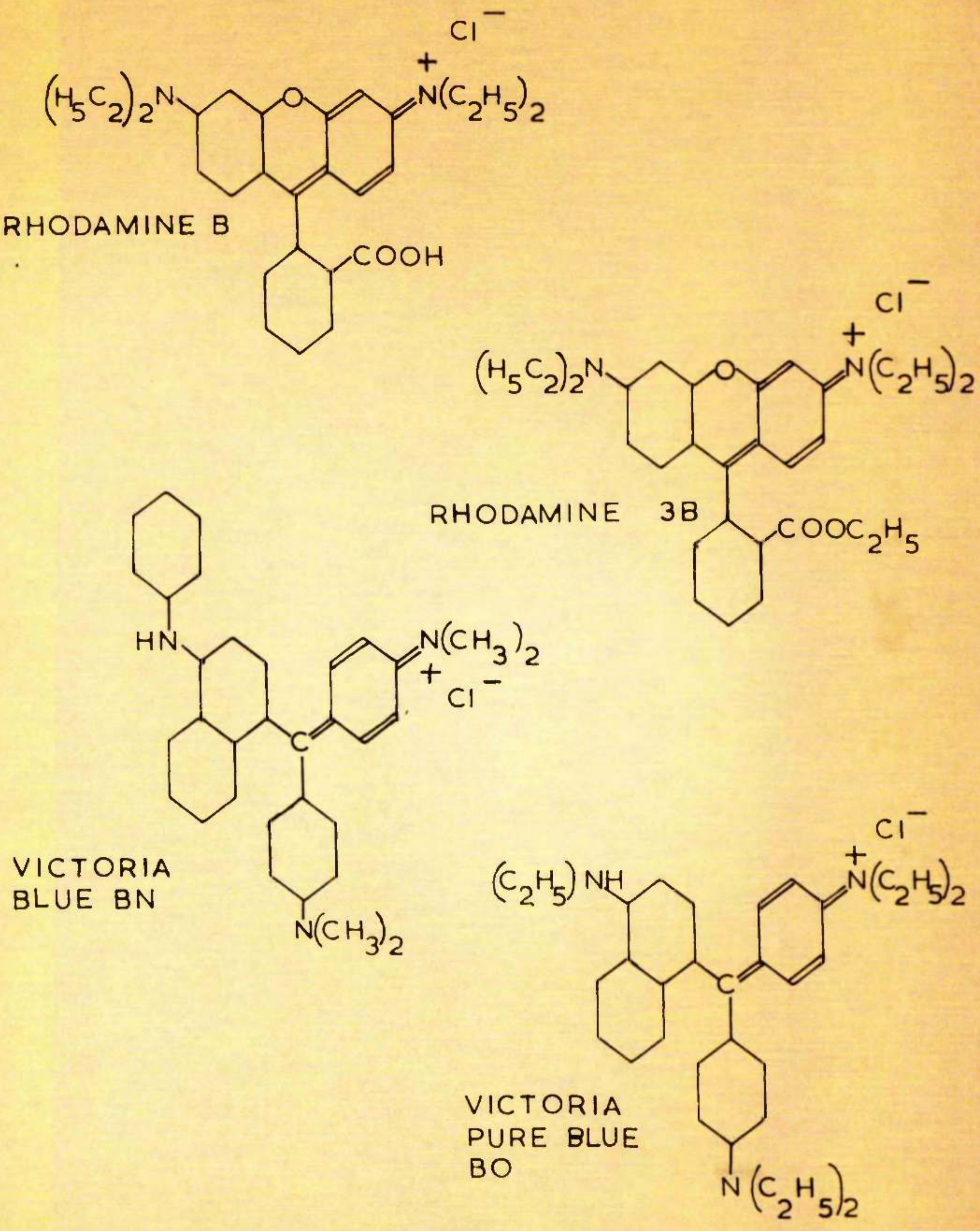
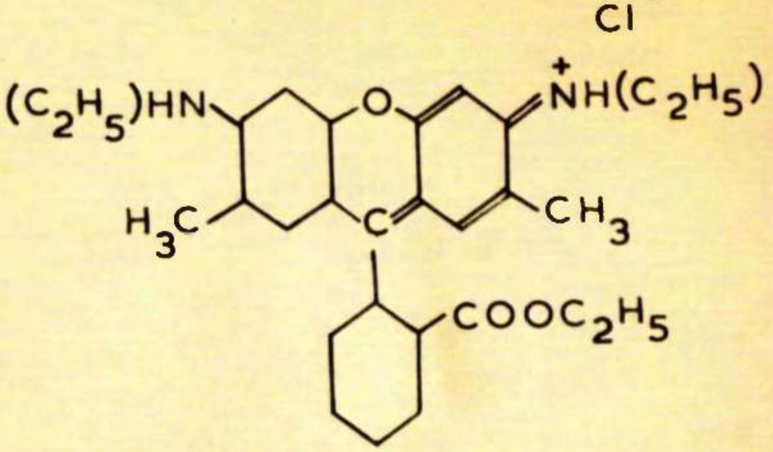


Fig. 12. Structural formulae for the cationic dyes used.



RHODAMINE 6GB

Fig. 13. Structural formulae for the cationic dyes used.

Fig. 14. Desorption isotherms of cationic dyes and p-nitrophenol. ○, adsorption; ●, desorption a, p-nitrophenol; b,c, C.I. 52015; d, C.I. 45160.

In b the desorption curve cannot follow the adsorption curve since the amount adsorbed at the starting point is less than at the maximum. When the desorption is commenced with a sample representing the maximum in the curve the adsorption and desorption curves, shown in c are coincident. The results together show that all the adsorbed dye is desorbable.

In d the adsorption and desorption tests were made with different samples of alumina but it is clear that some dye is not desorbable.

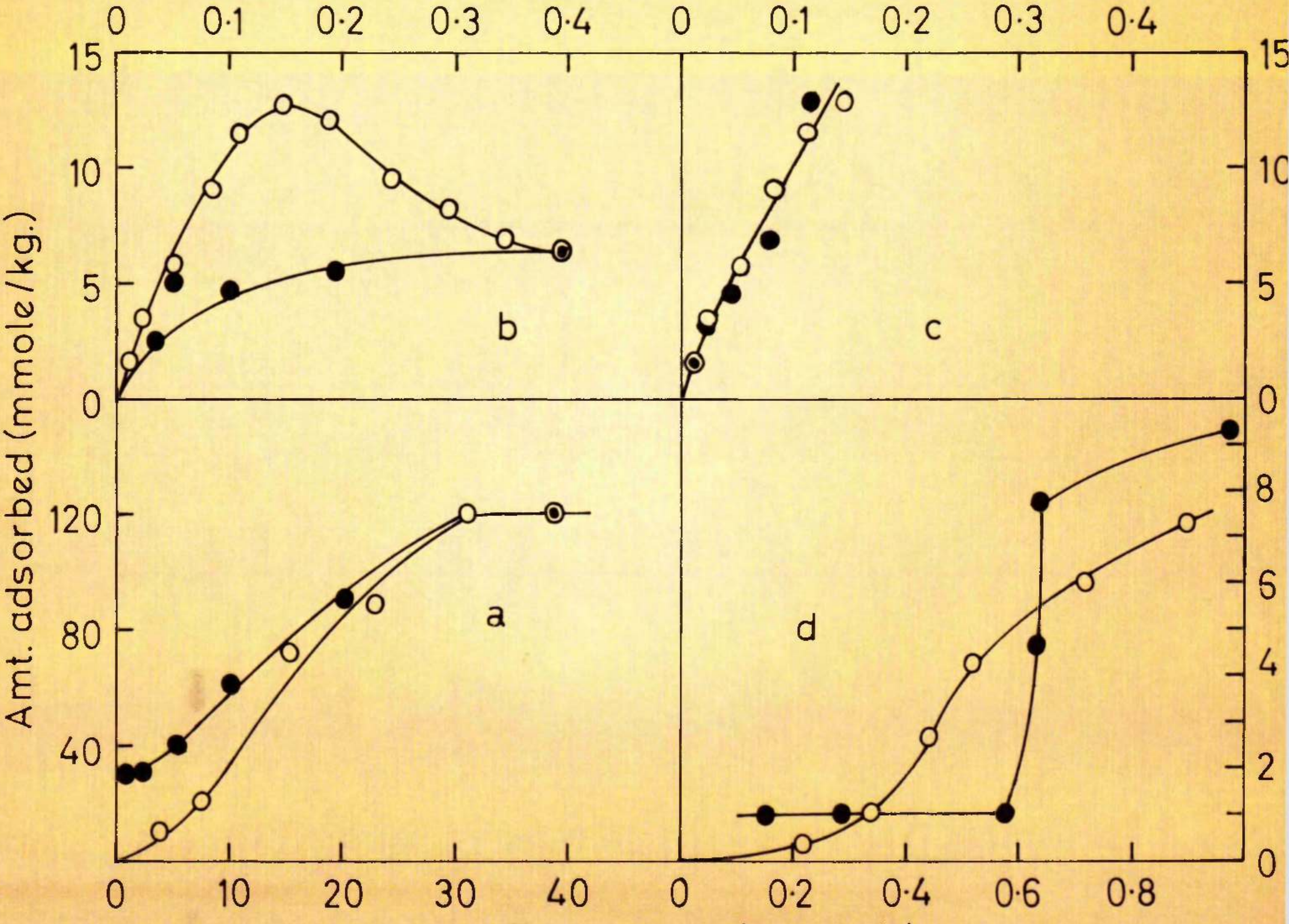

Amt. adsorbed (mmole/kg.)
Equm. conc. (mmole/l.)
0
0·1
0·2
0·3
0·4
0
0·1
0·2
0·3
0·4
15
10
5
0
120
80
40
0
10
20
30
40
0
0·2
0·4
0·6
0·8
15
10
5
0
8
6
4
2
0
a
b
c
d

Fig. 14.

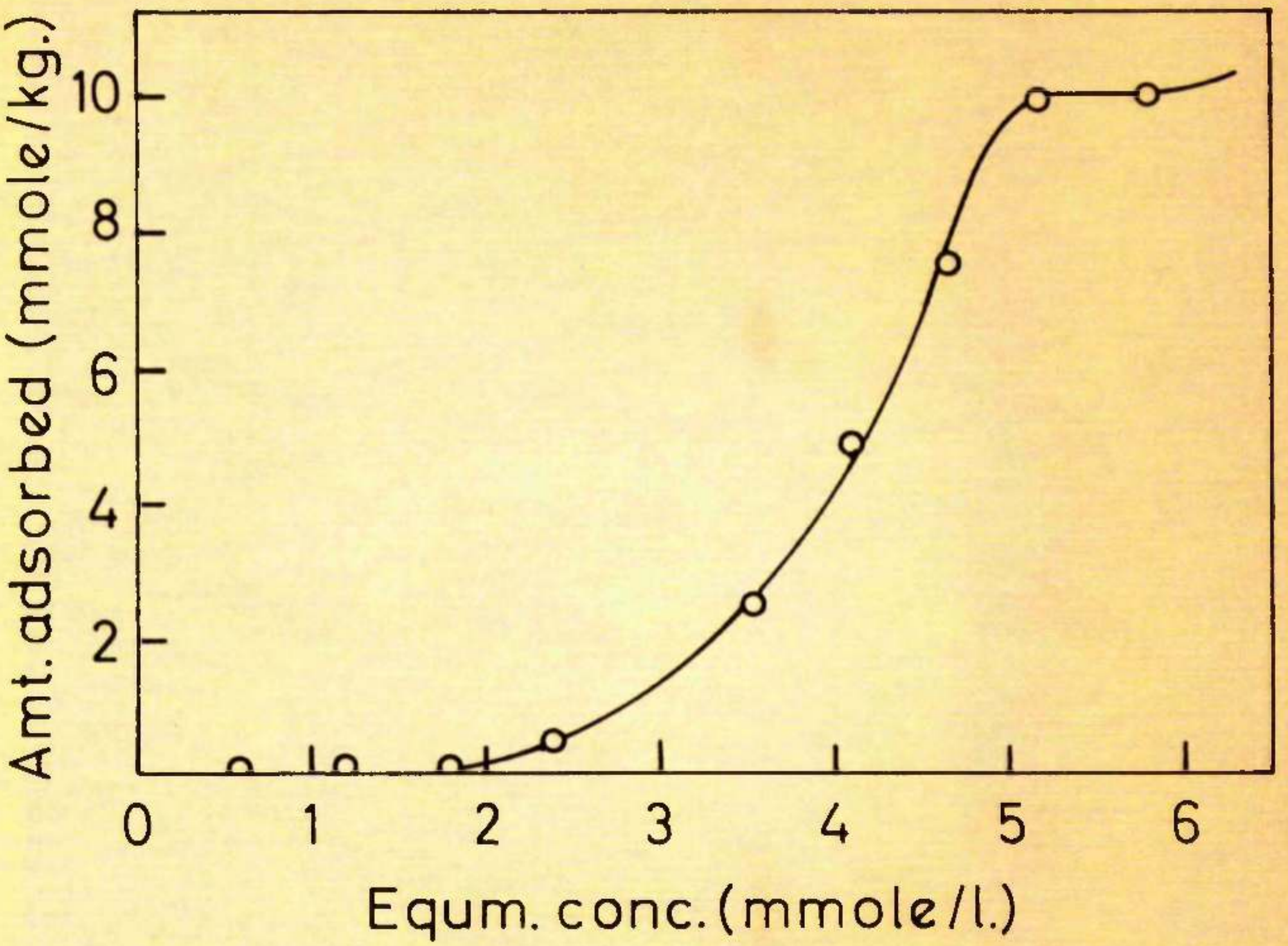


Fig. 15. Adsorption isotherm for C.I. 62055 on alumina.

Fig. 16. Adsorption isotherms for basic dyes on alkaline alumina. ○, 20°*C*. ◐, 40.5°*C*. ●, 60°*C*.

a, C.I. 42600; b, C.I. 42555,(lowest curve); C.I. 42595,(upper curves); c, C.I. 45170; d, C.I. 45175; e, C.I. 45160; f, C.I. 42510; g, C.I. 50240; h, C.I. 52015.

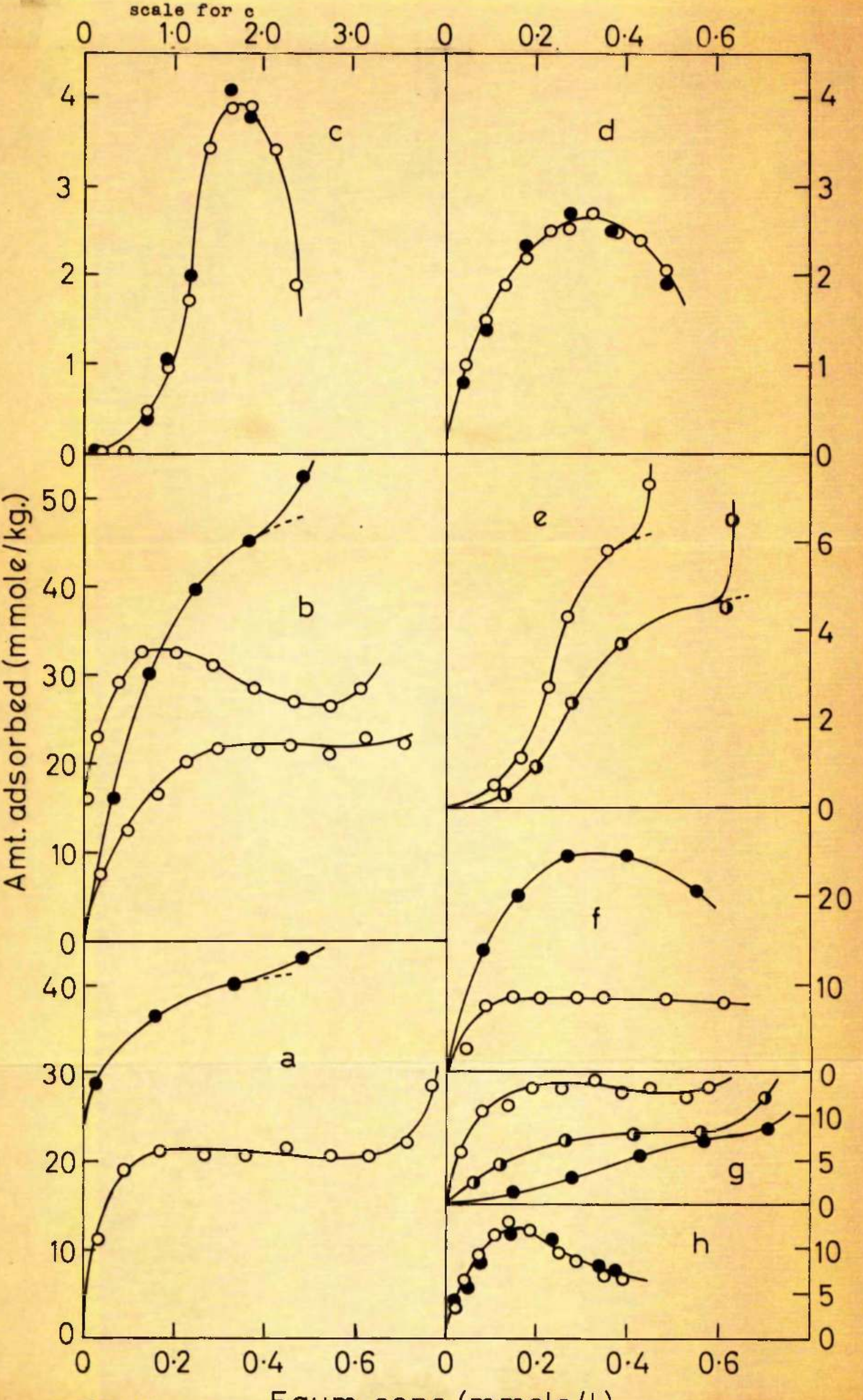
scale for c
0
1·0
2·0
3·0
0
0·2
0·4
0·6
c
d
b
e
a
f
g
h
Amt. adsorbed (mmole/kg.)
0
1
2
3
4
10
20
30
40
50
0
2
4
6
0
10
20
0
5
10
0
0·2
0·4
0·6
Equm. conc. (mmole/l.)

Fig. 16.

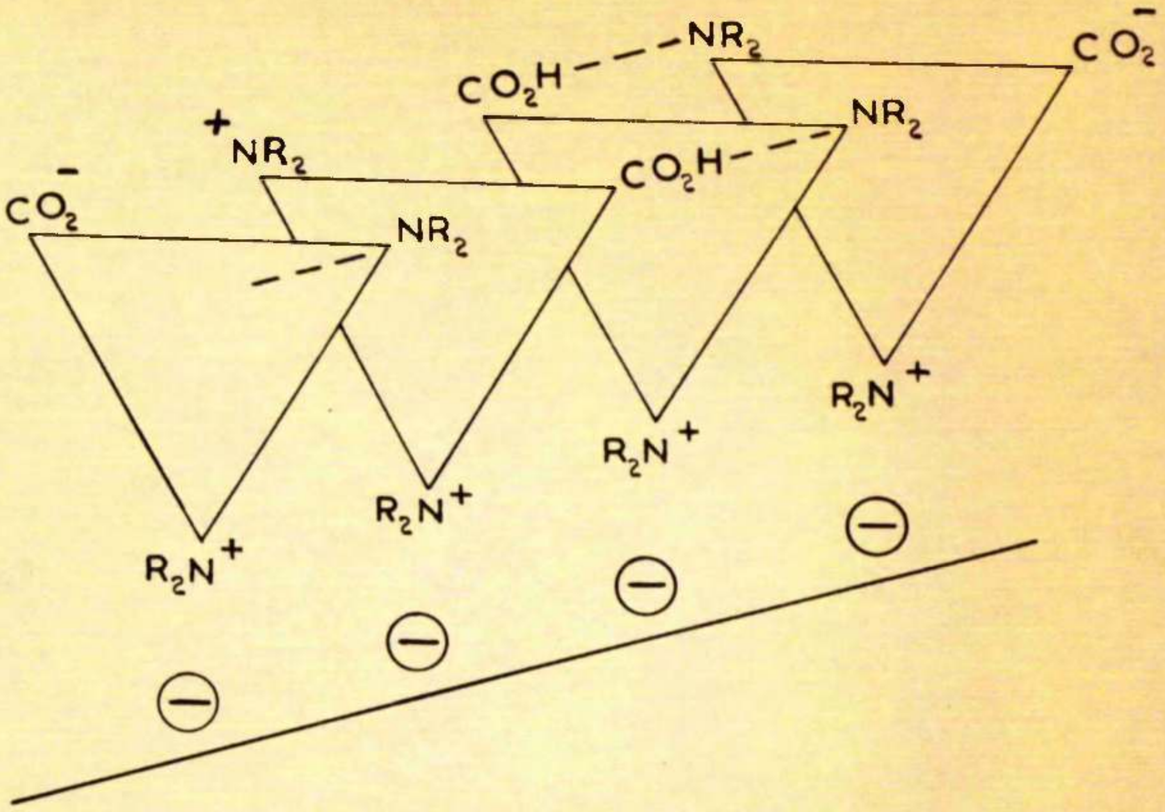


Fig. 17. Suggested orientation of Rhodamine B cations at a negative surface.

Fig. 18. Energy level of dye.

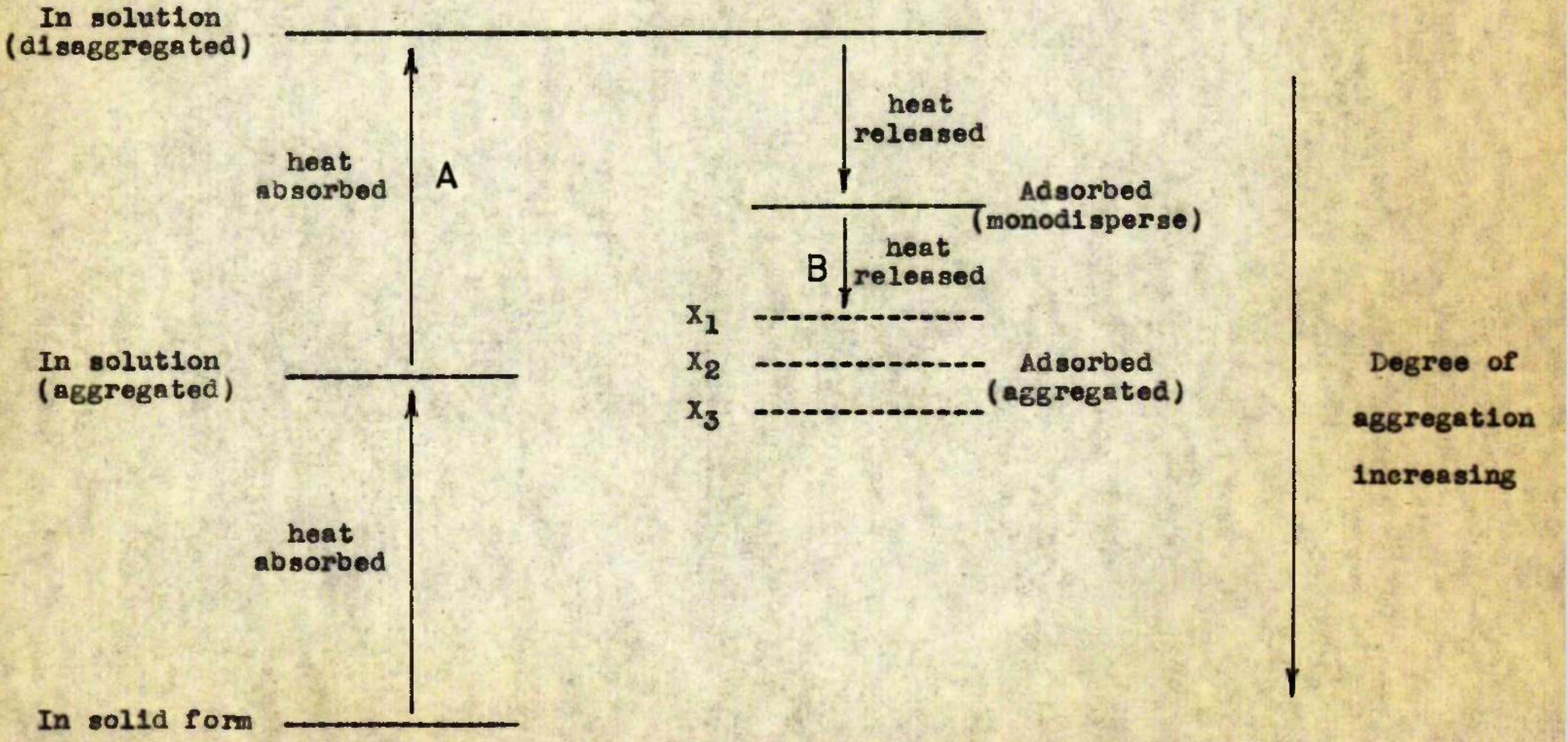
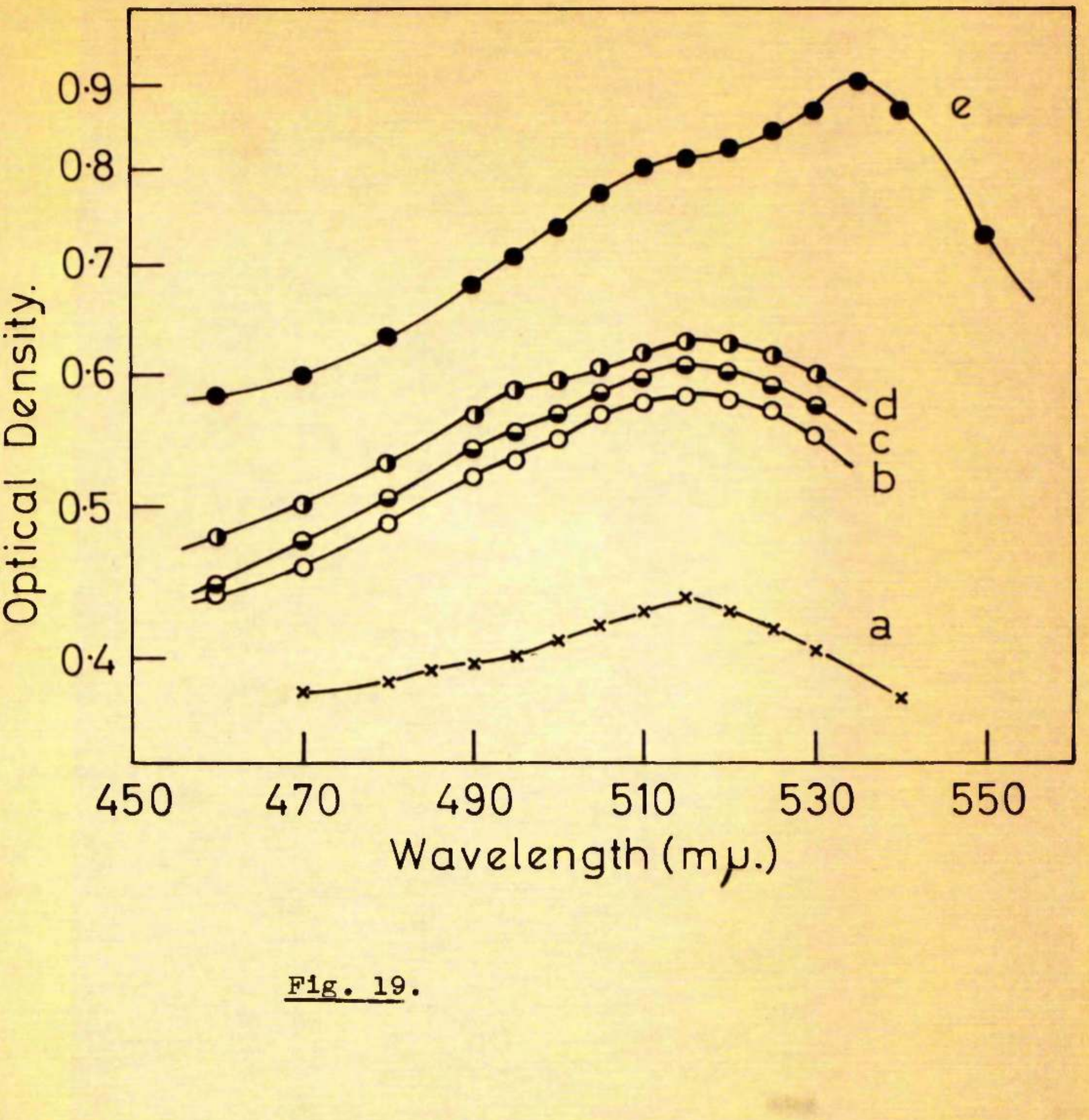


Fig. 19. Spectral absorption curves of Safranine T.
a-d, in water; a, 210°C; b, 65°C; c, 100°C; d, 20°C.
e, in ethanol at 20°C.

The solutions were all 3×10^{-5}M and were measured in 3 mm. bore glass tube cells. The small differences between b,c and d, are probably due to differences in the bore of the tubes used as cells. The low value of a is probably due to dye decomposition, which accounts also for the increased absorption throughout the shortwave region.



0·9
0·8
0·7
0·6
0·5
0·4
Optical Density.
450
470
490
510
530
550
Wavelength (mμ.)
e
d
c
b
a

Fig. 19.

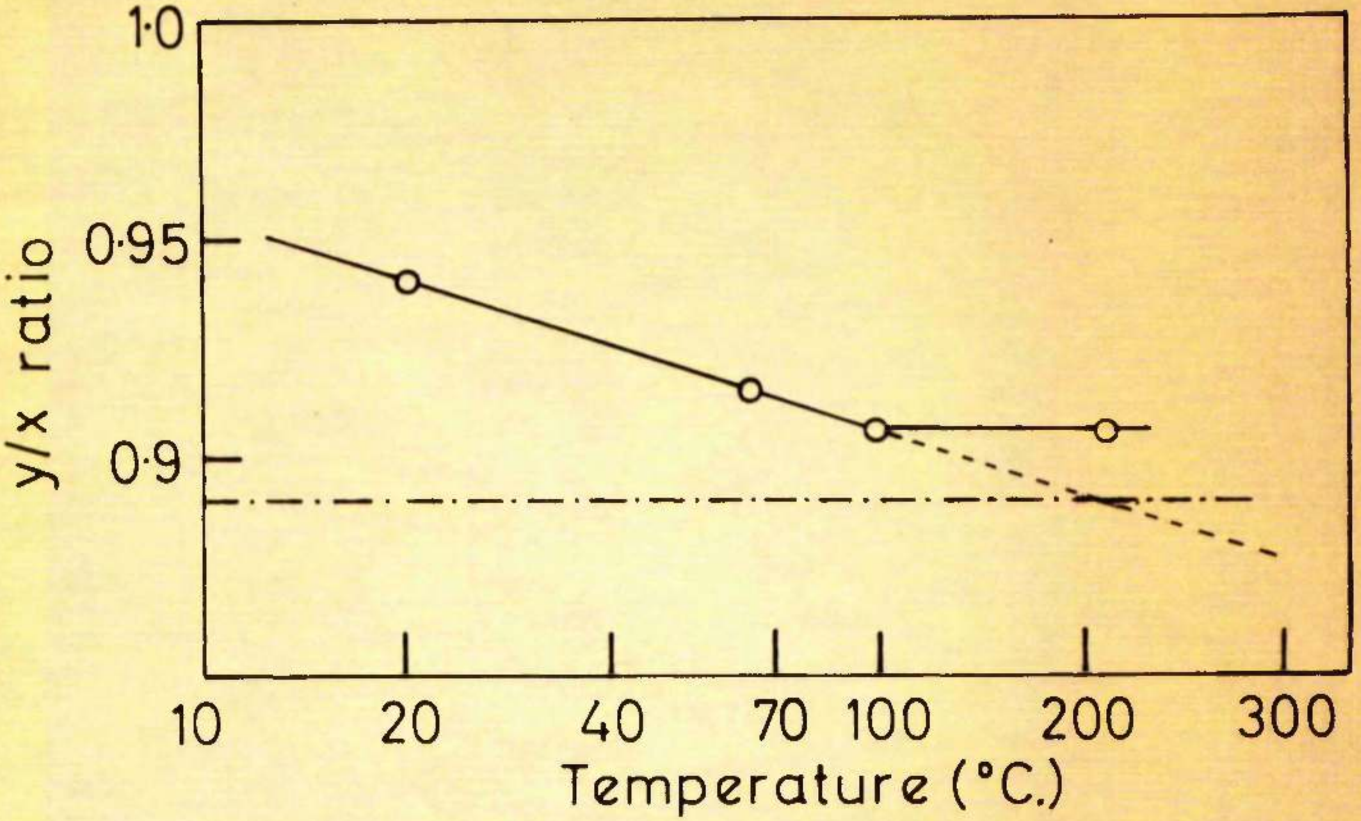


Fig. 20. The relation between the y/x ratio of Safranine T and the logarithm of the temperature.
The circles represent aqueous solutions.
The horizontal broken line represents the y/x ratio of the dye in ethanol at 20°C.

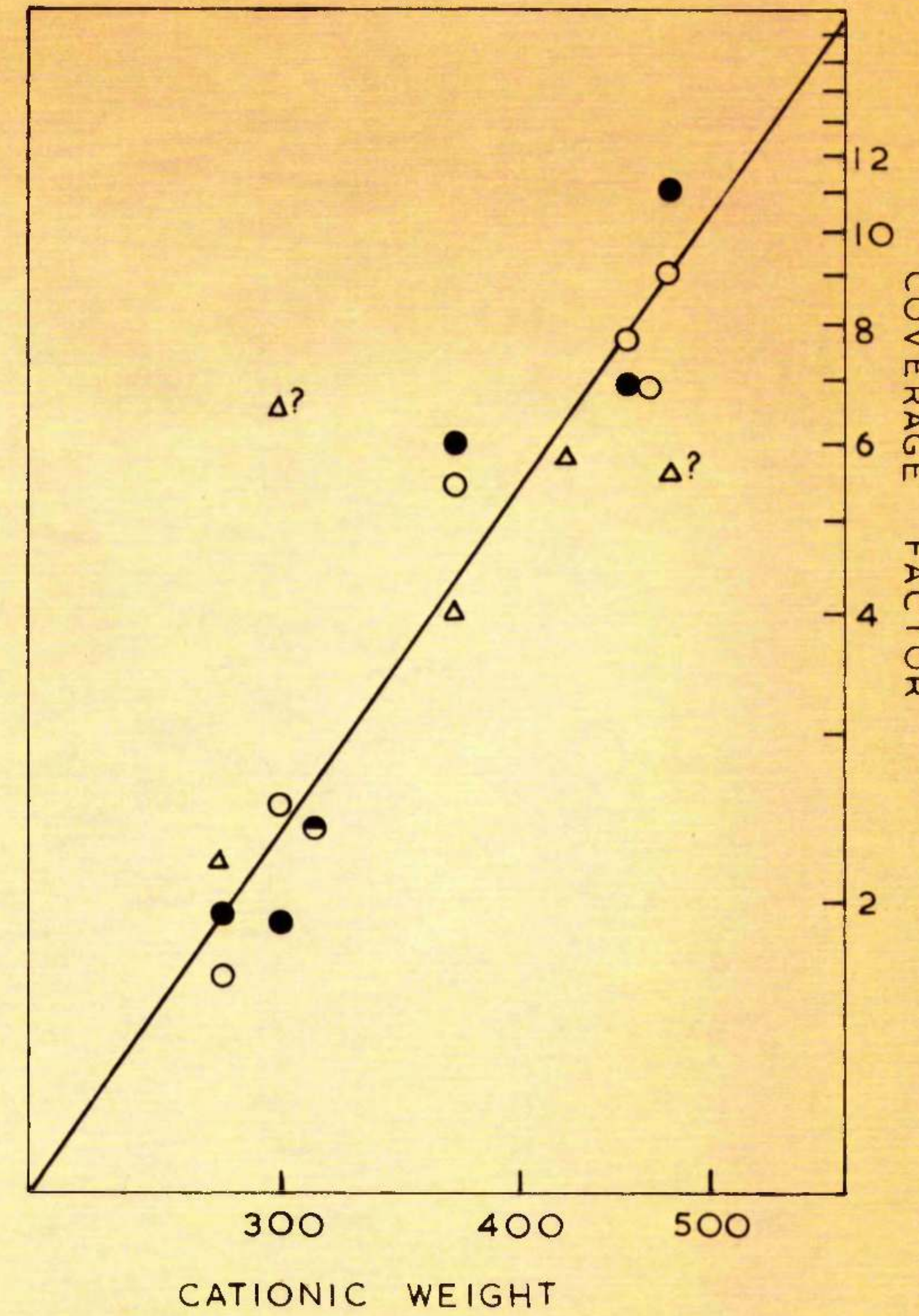


Fig. 21. Linear relationship between log. coverage factor and log. cationic weight of dyes adsorbed on three chemically distinct substrates. ○ Yeast; ● Chromatographic Alumina; △ Graphite.

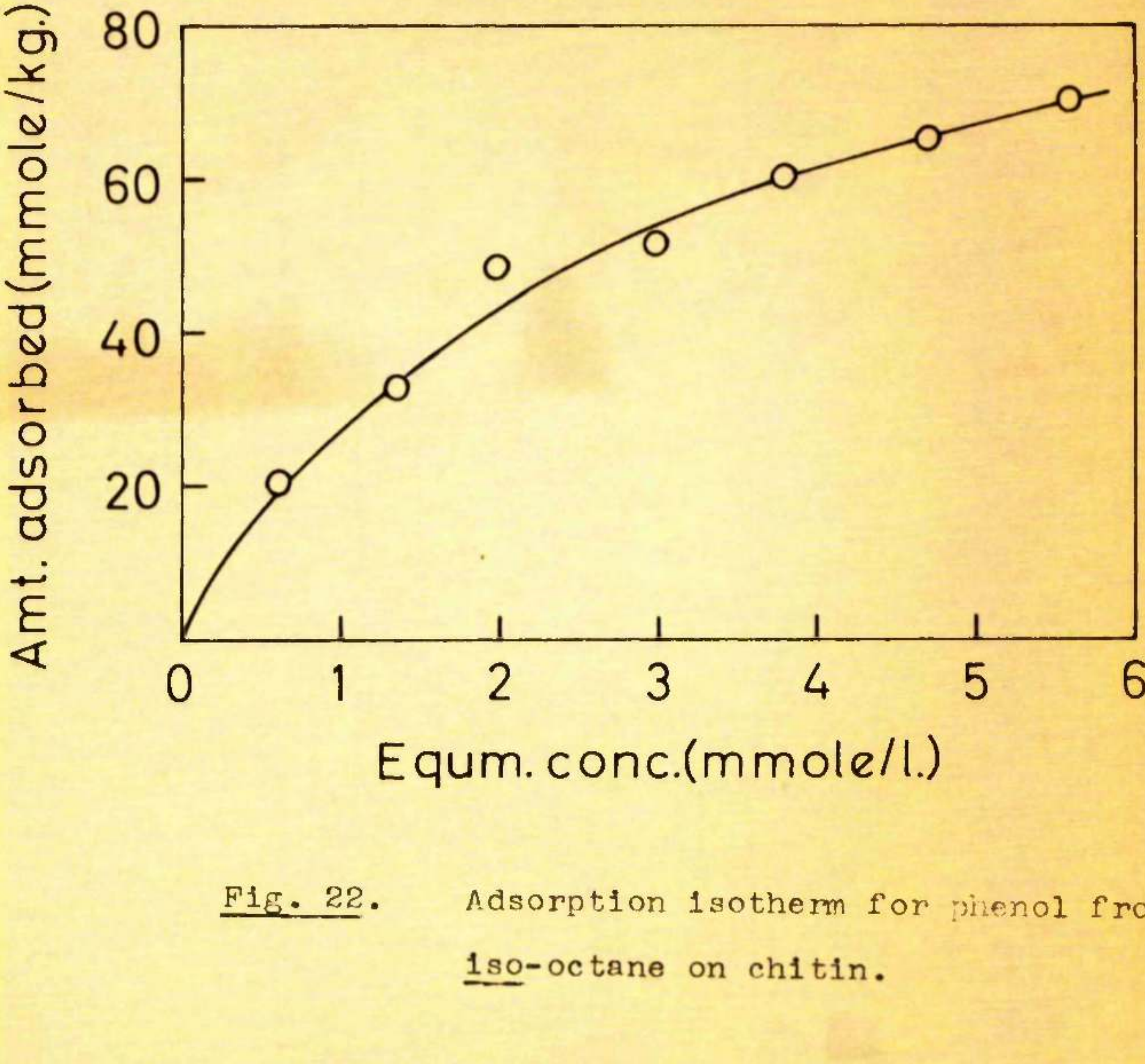
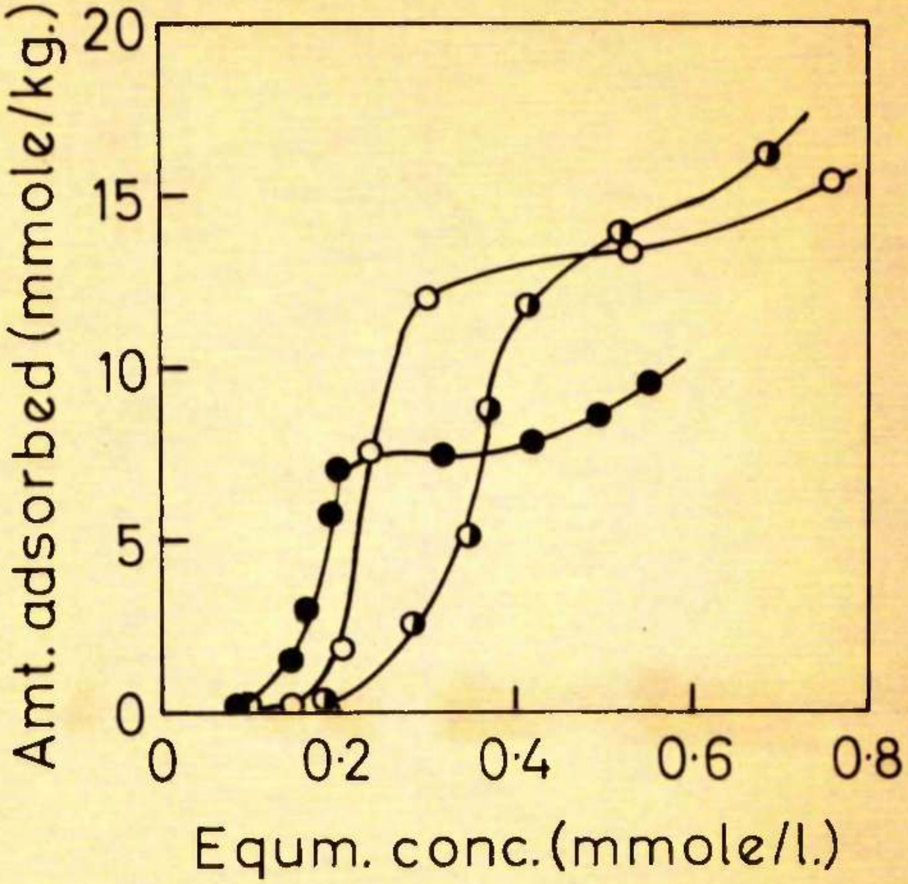


Fig. 22. Adsorption isotherm for phenol from *iso*-octane on chitin.



<u>Fig. 23.</u> Adsorption isotherms for C.I. 62055 on MSC silica.

● aged for one year in paper bag.
◐ intensively dried by heating to 130°C.
○ exposed to damp atmosphere for 24 hours.

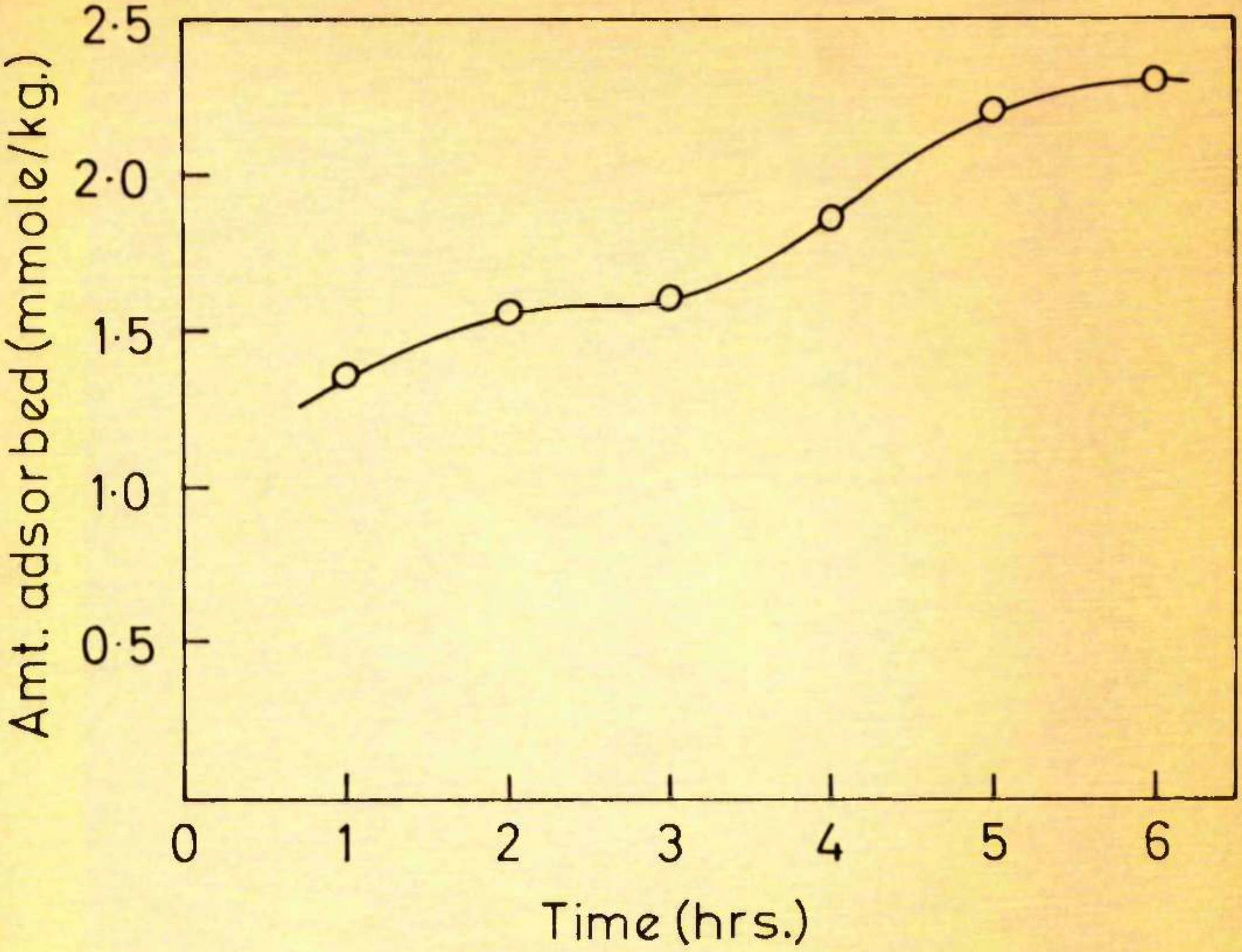


Fig. 24. Rate curve for the adsorption of p-nitrophenol on MSC silica.

Fig. 25. Adsorption isotherms of alizarin on chromatographic alumina powder.

a: Alizarin in 50% (v/v) ethanol-water at 26°*C*.

b,c: Alizarine Red S (monosulphonated alizarin) at 45° and 26°*C*. on chromatographic alumina powder in *ca*. 1% (v/v) acetic acid.

d,e: Alizarine Red S at 35° and 26°*C*. on powder previously treated with hydrochloric acid[20].

The horizontal broken line shows the approximate level of maximum adsorption of both dyes which would correspond to a monolayer of flatwise oriented dye molecules on the surface of this non-porous alumina.

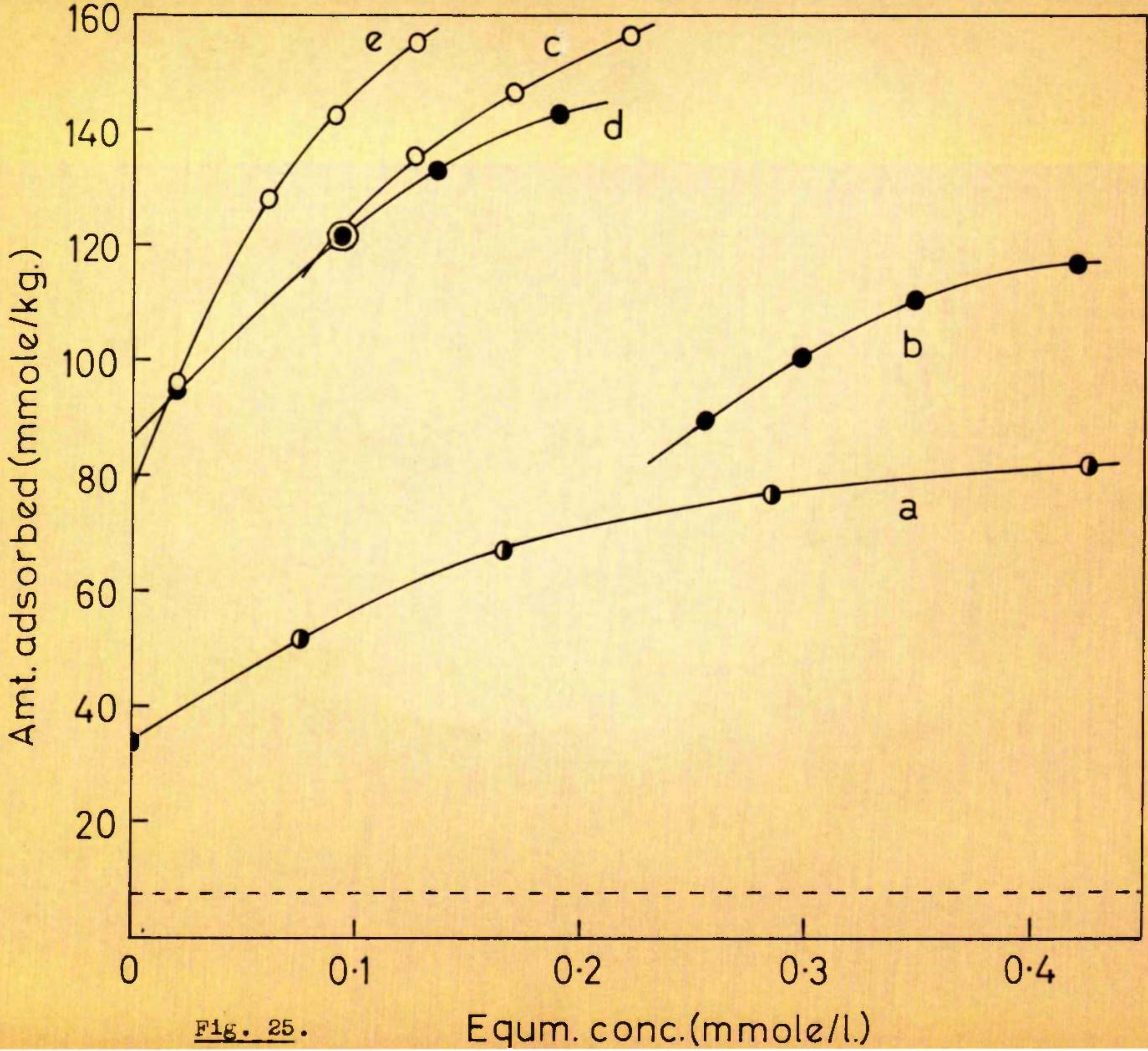
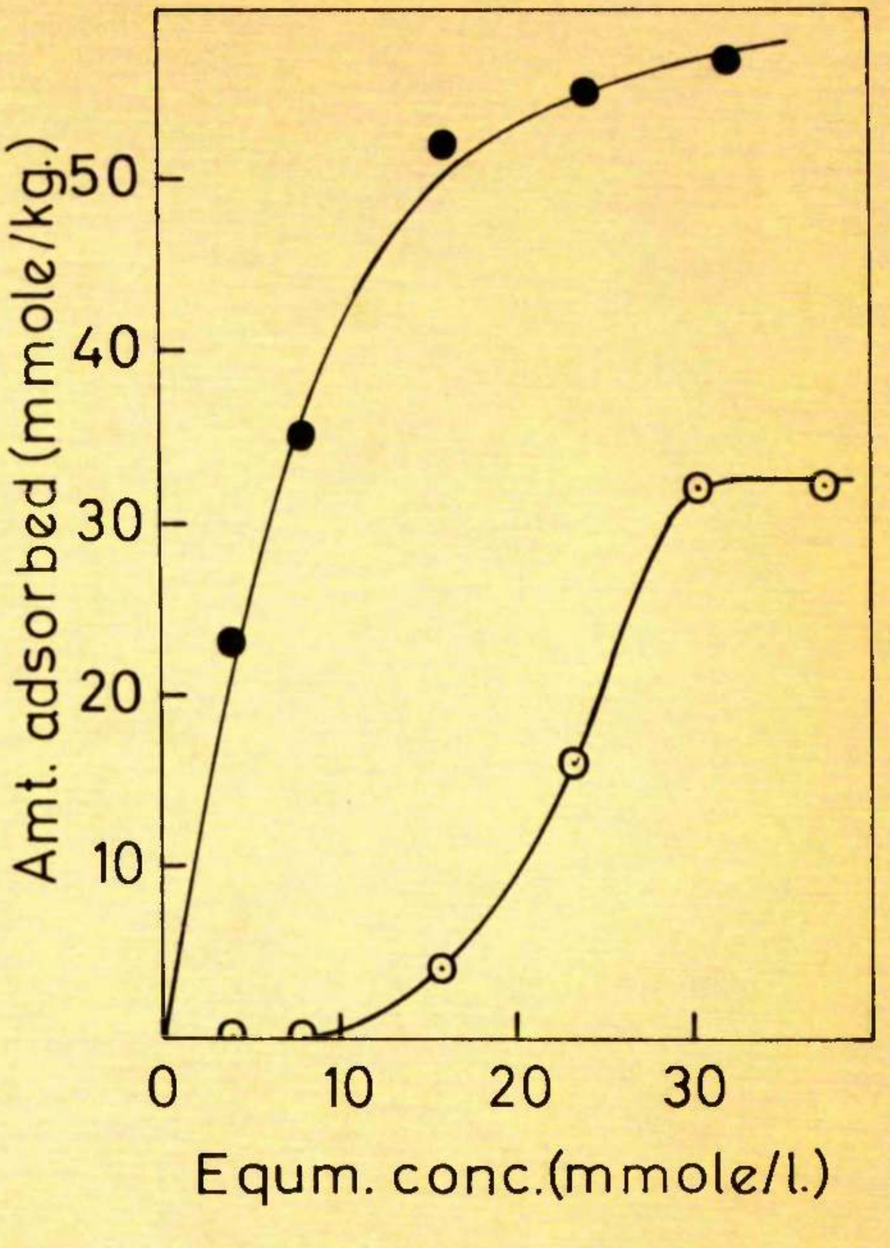

Amt. adsorbed (mmole/kg.)
160
140
120
100
80
60
40
20
0
0·1
0·2
0·3
0·4
Equm. conc.(mmole/l.)
a
b
c
d
e

Fig. 25.



<u>Fig. 26</u>. Adsorption isotherms for phenol on rubber

● , commercial red rubber.

⊙ , synthetic rubber.

REFERENCES.

1. Brunauer, "The Adsorption of Gases and Vapours", Oxford Univ. Press, London, 1944.
2. Osipow, "Surface Chemistry", Reinhold Publishing Corporation, New York; Chapman and Hall, Ltd., London, 1962.
3. Historical survey given in Deitz, "Bibliography of Solid Adsorbents", United States Cane Sugar Refiners and Bone Char Manufacturers and the National Bureau of Standards, 1944; and in ref. 1, chap. 1.
4. The Book of Judges, Chap. VI, vv. 36-40.
5. Brunt, Proc. Royal Institution, London, 1947, 34, 57; Ann. Rep. East Malling Research Station, Kent, England for 1958, 1959, 41.
6. Giles, J. Chem. Ed., 1962, 39, 584.
7. Adam, "The Physics and Chemistry of Surfaces", Oxford Univ. Press, London, 3rd Edition, 1941, Chaps. I and V.
8. Gregg, "The Surface Chemistry of Solids", Chapman and Hall, Ltd., London, 2nd Edition, 1961.
9. Verwey, Rec. Trav. Chim., 1946, 65, 521.
10. London, Z. Phys., 1930, 63, 245; Z. Phys. Chem., 1930, 11B, 222.
11. Polanyi and London, Naturwiss., 1930, 18, 1099.

12. Galbraith, Giles, Halliday, Hassan, McAllister, Macaulay and Macmillan, J. Appl. Chem., 1958, 8, 416.

13. Vickerstaff, "The Physical Chemistry of Dyeing", Chap. VI, Oliver and Boyd, London, 1954.

14. Giles, Jain and Hassan, Chem. and Ind., 1955, 629.

15. Giles and Hassan, J. Soc. Dyers Colourists, 1958, 74, 846.

16. Giles, Compte. rendu., 27e cong. international de chim. ind., Brussels, 1954.

17. Hodgson, J. Soc. Dyers Colourists, 1933, 49, 213.

18. Stated by Adamson, "Physical Chemistry of Surfaces", Chap. 13, Interscience Publishers, Inc., New York; Interscience Publishers Ltd., London, 1960.

19. Allingham, Cullen, Giles, Jain and Woods, J. Appl. Chem., 1958, 8, 108.

20. Cummings, Garven, Giles, Rahman, Sneddon and Stewart, J. Chem. Soc., 1959, 535.

21. O'Connor and Buchanan, Trans. Faraday Soc., 1956, 52, 397.

22. Schwab and Jockers, Naturwiss., 1937, 25, 44.

23. O'Connor, Johansen and Buchanan, Trans. Faraday Soc., 1956, 52, 229.

24. Giles, Mehta, Stewart and Subramanian, J. Chem. Soc., 1954, 4360.

25. Arshid, Desai, Duff, Giles, Jain and Macneal, J. Soc. Dyers Colourists, 1954, 70, 392.

26. Chipalkatti, Giles and Vallance, *J. Chem. Soc.*, 1954, 4375.

27. Giles, *Compte. rendu.*, 31e cong. international de chim. ind., 1958.

28. Datye and Giles, *Trans. Inst. Metal Finishing*, in press.

29. Vickerstaff, *J. Soc. Dyers Colourists*, 1957, *73*, 237; Rattee, *Research*, 1959, *12*, 15.

30. Giles, in "Chromatography", ed. Heftmann, Reinhold Publishing Corporation, New York, 1961.

31. Palmer, *Proc. Roy. Soc.*, 1920, *A98*, 13.

32. Constable, *Proc. Roy. Soc.*, 1925, *110*, 283.

33. Taylor, *Proc. Roy. Soc.*, 1925, *A108*, 105.

34. Kipling, *Quart. Revs. Chem. Soc.*, 1956, *10*, 1.

35. Gasser and Kipling, "Proceedings of the Fourth Confce. on Carbon", page 55, Pergamon Press, London, 1960.

36. Gaubert, *Compt. rendu.*, 1906, *143*, 936.

37. Butchart and Whetstone, *Discuss. Faraday Soc.*, 1949, *5*, 254.

38. Whetstone, *Discuss. Faraday Soc.*, 1949, *5*, 261.

39. Bunn, *Proc. Roy. Soc.*, 1933, *A141*, 567.

40. Traube, *Ann.*, 1891, *265*, 27.

41. Bruns, *Kolloid-Z.*, 1931, *54*, 33.

42. Arnold, *J. Amer. Chem. Soc.*, 1939, *61*, 1611.

43. Karrer and Nielson, *Ber. Ges. Physiol. Exptl. Pharmakol.*, 1935, *86*, 529.

44. Cook, <u>J. Chem. Soc</u>., 1938, 876.
45. de Saussure, <u>Gilbert's Ann. der Physik</u>, 1814, <u>47</u>, 113; <u>Ann. Phil</u>., 1815, <u>6</u>, 241, 331.
46. Hene, Dissertation, University of Hamburg, 1927, in ref. 1, chap. 1.
47. Arrhenius, "Theories of Solutions", p. 68.
48. Schmidt, <u>Z. phys. Chem</u>., 1928, <u>133</u>, 263.
49. Cassidy, <u>J. Amer. Chem. Soc</u>., 1940, <u>62</u>, 3073.
50. Bartell and Fu, <u>J. Phys. Chem</u>., 1929, <u>33</u>, 678.
51. Bartell and Miller, <u>J. Amer. Chem. Soc</u>., 1922, <u>44</u>, 1866; 1923, <u>45</u>, 1106.
52. Broda and Mark, <u>Z. phys. Chem</u>., 1937, <u>A180</u>, 392.
53. Baum and Broda, <u>Trans. Faraday Soc</u>., 1938, <u>34</u>, 797.
54. McBain and Bakr, <u>J. Amer. Chem. Soc</u>., 1924, <u>46</u>, 2718.
55. Giles, Greczek and Nakhwa, <u>J. Chem. Soc</u>., 1961, 93.
56. McKay, Ph.D. thesis, Glasgow, 1962.
57. Brunauer, Deming, Deming and Teller, <u>J. Amer. Chem. Soc</u>., 1940, <u>62</u>, 1723.
58. Langmuir, <u>J. Amer. Chem. Soc</u>., 1918, <u>40</u>, 1361.
59. Giles, MacEwan, Nakhwa and Smith, <u>J. Chem. Soc</u>., 1960, 3973.
60. Regan, <u>Chem. and Ind</u>., 1953, 1238.
61. Meetham, "Atmospheric Pollution, its origins and prevention", Pergamon Press, London and New York, 2nd edition, 1956.
62. Cohen and Ruston, "Smoke, a study of town air", Edward Arnold and Co., London, 1925.

63. "Air Pollution", Proc. U.S. Tech. Confce. on Air Pollution, McGraw-Hill Book Co., New York, 1952.

64. Thring, (ed.), "Air Pollution", Butterworths Scientific Publications, London, 1957.

65. Marsh, (ed.), Proc. 1959 Intern. Clean Air Confce., National Society for Clean Air, London, 1960.

66. Stern, (ed.), "Air Pollution", Vol. I, Academic Press, New York and London, 1962.

67. Stern, (ed.), "Air Pollution", Vol. II, Academic Press, New York and London, 1962.

68. Jacobson, in ref. 67, chap. 25.

69. Evelyn, "Fumifugium, or The Inconvenience of the Aer and Smoake of London Dissipated", 1661, new edn, 1772, G. Bedel and T. Collins, London.

70. In ref. 66, chap. X.

71. In ref. 61, chap. IX.

72. Meetham, Quart. J. Roy. Met. Soc., 1950, 76, 359.

73. Beebe and Dell, J. Phys. Chem., 1955, 59, 746.

74. Details of Standard Tests are given in refs. 60, 61 and 62.

75. D.S.I.R., "The Investigation of Atmospheric Pollution", 31st report, 1960, London, H.M.S.O.

76. Anderson and Emmett, J. Phys. Chem., 1952, 56, 756.

77. Firket, Trans. Faraday Soc., 1937, 32, 1192.

78. Roholm, J. Industr. Hyg., 1937, 19, 126.

79. Pattle and Cullumbine, *Brit. Med. J.*, 1956, *2*, 913.

80. Meetham, *Quart. J. Roy. Met. Soc.*, 1954, *80*, 96.

81. Cartwright, Nagelschmidt and Skidmore, *Quart. J. Roy. Met. Soc.*, 1956, *82*, 82.

82. Sim and Pattle, *J. Amer. Med. Asson.*, 1957, *165*, 1908.

83. Clifton, Kerridge, Pemberton, Moulds and Donoghue, in ref. 65, paper 61.

84. In ref. 64.

85. Anon., *J. Roy. Inst. Chem.*, 1963, *87*, 183.

86. Kelly, *J. Roy. Inst. Chem.*, 1963, *87*, 223.

87. Vernon, *Trans. Faraday Soc.*, 1927, *23*, 115; 1935, *31*, 1668.

88. Leighton, "Photochemistry of Air Pollution", chap. 9, Academic Press, New York and London, 1961.

89. Commins, reported in *J. Roy. Inst. Chem.*, 1963, *87*, 179.

90. Prati, "Rapports Presentes au Congres International de l'Aluminium", 1955, Vol. II, 39.

91. Baines, from part of a speech given at the Smoke Abatement Conference in Manchester, Nov. 1924, quoted in ref. 62.

92. In ref. 62, page 50.

93. Everett, *Trans. Faraday Soc.*, 1961, *57*, 1541.

94. In ref. 61, chap. 13.

95. Crowther and Ruston, *J. Agric. Science*, 1911, *4*, 25.

96. Kipling and Wright, *J. Chem. Soc.*, 1962, 855.

97. Giles and Nakhwa, J. Appl. Chem., 1962, 12, 266.

98. Orr and Dallavalle, "Fine Particle Measurement", chap. 8, The MacMillan Co., New York, 1959.

99. Nakhwa, Ph.D. thesis, Glasgow, 1961.

100. Giles, Mehta, Rahman and Stewart, J. Appl. Chem., 1959, 9, 457.

101. Brockmann and Schodder, Ber., 1941, 74B, 73; Brockmann, Discuss. Faraday Soc., 1949, 7, 58.

102. Clunie and Giles, Chem. and Ind., 1957, 481.

103. Grant, Glanville and Strachan, Spectrochim Acta., 1958, 12, 109.

104. Michaelis, "Cold Spring Harbor Symposium on Qualitative Biology", XII, 131, 1947.

105. Valko, J. Soc. Dyers Colourists, 1939, 55, 173; in ref. 13, chap. 3.

106. McBain, Trans. Faraday Soc., 1913, 9, 99.

107. Robinson and Moilliet, Proc. Roy. Soc., 1934, A143, 630.

108. Robinson, Trans. Faraday Soc., 1935, 31, 245.

109. Hartley, Collie and Samis, Trans. Faraday Soc., 1936, 32, 795.

110. Robinson and Garrett, Trans. Faraday Soc., 1939, 35, 771.

111. Giles, Rahman and Smith, J. Chem. Soc., 1961, 1209.

112. Easton, B.Sc. thesis, Glasgow, 1961

113. Giles and Greczek, Text. Res. J., 1962, 32, 506.

114. Giles, Hassan, Laidlaw and Subramanian, J. Soc. Dyers Colourists, 1958, 74, 647.

115. Hirst and Lancaster, Trans. Faraday Soc., 1951, 47, 315.

116. Harkins and Gans, J. Amer. Chem. Soc., 1931, 53, 2804.

117. Stewart, Ph.D. thesis, Glasgow, 1957.

118. Kiel and Heertjes, J. Soc. Dyers Colourists, 1963, 79, 21.

119. Herd, Pharm. J., 1955, 175, 187.

120. Anon., Pharm. J., 1955, 175, 145.

121. Wing, Pharm. J., 1955, 175, 180.

122. Wing, J. Pharm. and Pharmacol., 1956, 8, 734.

123. Wing, J. Pharm. and Pharmacol., 1956, 8, 738.

124. Stern, "Rubber, natural and synthetic", chap. 3, MacLaren and Sons, Ltd., London, 1954.

125. Veith, Kolloid-Z., 1942, 98, 52.