ADSORPTION AND ELECTROKINETIC STUDIES OF CARBON BLACKS

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by

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ABSTRACT

In the Introduction the importance of zeta-potential in colloidal chemistry is briefly explained. The problem of the small magnitude of the apparent electrokinetic charge density is outlined, and the theoretical treatments of the electrical double layer and of electrokinetic phenomena are summarized. The different systems used for calculating zeta potentials and the nominal charge density are reviewed and theories proposed for interpreting the results are considered. The object of the present work and method of treatment are formulated.

Adsorption of surfactants from aqueous solution on different carbon blacks has been studied primarily to provide an accurate measure of adsorption charge. Surface area relationships, adsorption maxima and the effect of graphitization, ash and tar content of the carbons on these maxima were incidental problems that were examined.

Zeta-potentials were calculated from electrophoretic mobilities of the three graphitized carbons of different particle size as a function of surface coverage, using Overbeek's equation. The most reliable results (those subject to small relaxation corrections) were used for calculating diffuse charge densities. The latter were found to be a variable fraction of the adsorption charge. Differentiation between the two main theories for this

deviation (namely, enhanced viscosity or Stern's specific adsorption of counterions) was achieved by measurement of negative adsorption of co-ions, an equilibrium property of the double layer which should be independent of viscosity. The combined results are in favour of Stern's structure for the double layer. Different counterions were used to test the theory.

Measurements of surface conductance were also made and the results were found consistent with the same theory.

Potentiometric titrations of the carbon-oxygen complexes and surface tension measurements for the surfactants used are recorded in Appendices.

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1. INTRODUCTION

Colloidal materials, natural or synthetic, are of wide use in every aspect of modern life. They vary greatly in their properties, preparation and application and include a wide range of materials such as clays, soils, silk, cotton and wool fibres, soaps, inks, paints, drugs, milk, butter and many others. While the art of preparing and processing colloidal materials goes back many thousands of years - in fact, as far back as civilization itself - no experiments which can properly be termed scientific are on record much before the beginning of the nineteenth century.

From experimental work on various colloidal materials such as sols of gold, silver halides, sulphur and proteins, it was found that stable hydrophobic sols lose their stability quite easily in presence of small quantities of electrolytes. Experiments with unsymmetrical electrolytes showed that polyvalent cations cause instability to some sols and not to the others, whereas polyvalent anions behave in the opposite sense. From such experiments it was concluded that colloidal particles have an electric charge of a certain sign. Stability is due to electrical repulsion forces between the charged particles. Only polyvalent ions of opposite sign to the particle charge are critical in causing coagulation. Their final effect is a reduction in the electrical repulsion forces with the result that the attraction forces between the particles which are always present predominate.

The concepts of an electrical double layer surrounding a particle and an electrokinetic (zeta - or, ζ) potential were thus established. The role of electrical effects was first clarified by Donnan in 1910, while Burton in 1906 suggested that a stable hydrophobic colloid loses stability when the ζ -potential of the dispersed phase is reduced below a certain critical value. Upon the magnitude of ζ depends the success of many technological problems such as flotation, detergency and soil fertility. Quantitative expressions for the stability of hydrophobic colloids have been given by Derjaguin and Landau (1941) and by Verwey and Overbeek (1948).

In the last three decades the determination of ζ -potentials from electrokinetic phenomena was the subject of many published papers. Many refinements were added to the classical theory, and it can be said that ζ can be determined now for most systems with confidence. But the question which still cannot be answered with the same confidence is the precise significance of ζ -potentials. Certainly it is not an exact measure of the 'surface potential' in most practical cases. ζ is always less than the theoretical thermodynamic surface potential and its magnitude depends to a greater extent on the environment than on the actual charge on the surface.

Several explanations have been given for the diminished value of ζ as compared with surface potential; for example, it may be ascribed to specific adsorption of counterions, surface roughness or viscous effects, or combinations of more than one of these effects.

At present, however, there is no clear understanding of the relation between surface charge densities calculated from ζ -potentials and the actual charge on the surface. Although this problem has been the subject of several investigations, most of the results cannot be considered conclusive as many of the systems studied were for ill-defined surfaces of uncertain chemical structure.

The aim of the present work was to determine, on well-characterized carbon surfaces, the magnitude of charge densities calculated from zeta potentials as compared with the actual charges on the surface as determined from accurate adsorption experiments. The different views given by other workers on the reasons for the deviation of these results will be discussed. Experiments necessary to support one view or the other were carried out; in particular, the negative adsorption of co-ions and the surface conductivity of the carbon particles were investigated.

A brief account of current ideas about the structure of and distribution of ions in the electrical double layer is presented first.

1.1 The electrical double layer

When a particle is immersed in a liquid its surface acquires an electric charge which is formed mainly by ionization of surface groupings, adsorption of potential determining ions, or loss of an ion of sufficiently high valency, e.g., in a crystal lattice (unbalanced charge) which is frequently found with clays.

As the system as a whole is electrically neutral an equal charge of opposite sign to that on the surface must be present in the intermicellar liquid. In consequence of the attraction between charges of opposite sign, charges and counter-charges remain in each other's neighbourhood, forming an electrical double layer surrounding the particle. Ions of the like charge to the surface are repelled.

In the earlier pictures of the double layer, Perrin (1904) assumed it to be built up by two 'mono-ionic' layers of opposite charges separated by a certain distance, the electrical potential declining linearly, as in the dielectric of a parallel plate condenser. This simple picture, which neglects the thermal agitation of the ions, is often ascribed to Helmholtz (1879). This picture may hold in the presence of high electrolyte concentrations, where the double layer is very thin, and also, theoretically, at the absolute zero of temperature.

In 1910 Gouy developed the model of a diffuse double layer as an equilibrium system in which the thermal motion of the ions tends to maintain homogeneous distribution of the charge while the electrical force retains the double layer. Accordingly the average number (n) of each kind of ion at any point in the double layer where the average potential is Ψ , is given by Boltzmann relation:

$$n_{\pm} = n_o \quad \exp(\mp\ ze\,\Psi/kT) \tag{1}$$

for symmetrical electrolytes where n_o = the number of ions/cm^3 far from the surface (where $\Psi = 0$), z = the valence of the ions, e the electronic charge, k the Boltzmann constant and T the absolute temperature.

The space charge density (ρ) is given by the algebraic sum of the ionic charges per unit volume.

$$\rho = ze\ (n_+ - n_-) \tag{2}$$

or $$\rho = -2ze\ n_o\ \sinh\ (ze\,\Psi/kT) \tag{2a}$$

The charge density is related to the potential Ψ by the Poisson's equation

$$\nabla\ \Psi = -\frac{4\pi\rho}{\varepsilon} \tag{3}$$

$$= \frac{8\pi n_o ze}{\varepsilon}\ \sinh(ze\,\Psi/kT) \tag{4}$$

where ε is the dielectric constant.

For small values of Ψ ($z\ \Psi < 25$ mV) equation (4) simplifies to

$$\nabla\,\Psi = \kappa^2\,\Psi \tag{4a}$$

where $\kappa = (8\pi n_o e^2 z^2/\varepsilon\, kT)^{1/2}$, the so-called inverse of the double layer 'thickness'.

The approximation (4a) has often been used as the starting point in colloid chemical problems because of the mathematical difficulties involved in the application of the complete equation (4), but there is no necessity for this approximation.

For an infinitely large plane interface, the change of potential ψ with distance x from the surface can be obtained by integration of equation (4). A first integration can be carried out after multiplying equation (4) by $2d\psi/dx$, and making use of the condition that for $x \rightarrow \infty$, $\psi \rightarrow 0$ and $d\psi/dx \rightarrow 0$.

$$\therefore \quad \frac{d\psi}{dx} = - \sqrt{8\pi n_0 kT/\varepsilon}\left[\exp(ze\psi/2kT) - \exp(-ze\psi/2kT)\right] \qquad (5)$$

The second integration of equation (5) leads to equation (6) for the conditions:

$$\psi = \psi_0 \text{ for } x = 0$$

$$\therefore \quad \varkappa x = \ln \frac{[\exp(ze\psi/2kT)+1][\exp(ze\psi_0/2kT) - 1]}{[\exp(ze\psi/2kT)-1][\exp(ze\psi_0/2kT)+1]} \qquad (6)$$

and for small potentials it reduces to

$$\varkappa x = \ln \psi_0/\psi \quad \text{or} \quad \psi = \psi_0 e^{-\varkappa x} \qquad (7)$$

Thus for given values of ψ_0 and $\varkappa$, the potential ψ can be calculated at any distance x from the surface. The potential falls off purely exponentially with distance for small surface potentials. The potential difference ψ_0 between two phases is not accessible, however, to direct experimental determination, but it can be estimated from a thermodynamic consideration of the phases involved (Parsons 1954).

For a spherical particle the electric potential is only a function of the distance from the centre of the particle (a + x) where a is the particle radius. Considering the Debye-Hüchel approximation for small potentials (eqn.4a), the potential ψ_x at a distance x from the particle surface is given by:

$$\psi_x = \psi_o \frac{a}{a+x} e^{-\chi x} \tag{7a}$$

which shows that the potential falls off more rapidly by the factor a/(a+x) than the purely exponential expression found for flat double layer. An exact analytical solution for a spherical double layer cannot be obtained, but accurate numerical solutions are available (Hoskin 1953 and Loeb, Overbeek and Wiersema 1961).

Surface charge density. The condition of electroneutrality of the total double layer requires that the surface charge (σ) is equal and opposite to the total space charge in the diffuse layer, or

$$\sigma = - \int_o^\infty \rho \, dx \tag{8}$$

Substituting for the value of ρ from equation (3), equation (8) can be integrated as follows:

$$\sigma = \int_0^\infty \frac{\varepsilon}{4\pi} \frac{d^2 \psi}{dx^2}\, dx = - \frac{\varepsilon}{4\pi} \left(\frac{d\psi}{dx}\right)_{x=0} \qquad (9)$$

Inserting the value for $d\psi/dx$ from equation (5) we find

$$\sigma = \left(\frac{\varepsilon n_0 kT}{2\pi}\right)^{1/2} \left[\exp(ze \psi_0/2kT) - \exp(-ze \psi_0/2kT)\right] \qquad (10)$$

This equation simplifies, for small potentials ($z \psi_0 < 25\mathrm{mV}$), to

$$\sigma = \frac{\varepsilon \varkappa}{4\pi} \psi_0 \qquad (10a)$$

Thus, for small double-layer potentials, σ is directly proportional to ψ_0. For large potentials σ increases more rapidly with the double layer potential ψ_0, the positive term in equation (10) being more important. The negative term in equation (10) corresponds to the repulsion (or 'negative adsorption') of ions of the same sign as the surface ('co-ions'). For a given value of ψ_0, σ is proportional to $\varkappa$ and therefore to $\sqrt{\mu}$ (μ, the ionic strength).

Stern's theory.

The Gouy theory introduced above, based on the assumption of neglecting the size of the ions, considering them as 'point-charges', has two serious defects. Firstly, when the solution is not very dilute and the surface potential is about 200mV, which is not an extremely high potential, an impossible value for counter-ions concentration could be expected near the surface. Neglecting the ionic size counter-ions can approach the surface without any limit.

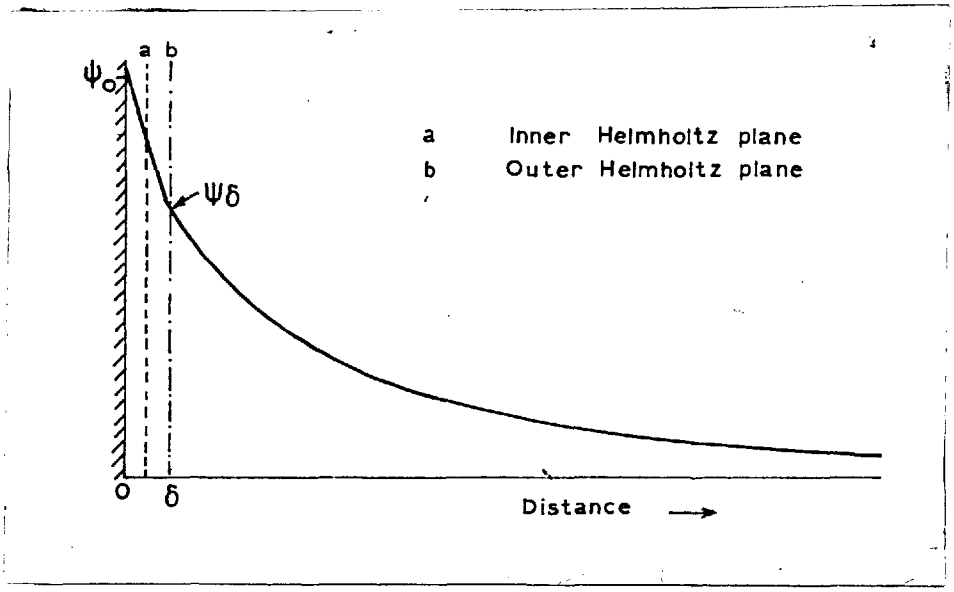


Fig. 1. Distribution of potential in the double layer according to Grahame.

Secondly, for counter-ions of the same valency the specificity of the ions disappears in a pure diffuse (Gouy) double layer which is contrary to practice.

Stern (1924) corrected for the finite dimensions of the ions especially for the first layer of ions in solution, which cannot approach the wall to a distance smaller than a few Å units, and forms something like a fixed layer of counter-ions at a distance δ from the surface. The rest of the double layer will be of the diffuse 'Gouy' type. Stern also considered the possibility of specific adsorption of counter-ions and assumed that these ions are also located in the plane δ. The specificity is introduced by allowing for the specific adsorption potentials of the ions. The total potential gradient ψ_o consists of a linear part in the 'Stern layer' or the 'molecular condenser', followed by the usual exponential decay in the diffuse part.

Further improvements to Stern's theory have been developed by several authors, notably Grahame (1947). Grahame distinguished two planes in the double layer parallel to the surface which he denoted as the inner and outer Helmholtz planes. The outer Helmholtz plane lies at the distance of closest approach to the surface for hydrated ions, still belonging to the diffuse double layer. The inner Helmholtz plane is the plane in which specifically adsorbed and presumably dehydrated ions are found.

As a consequence of the presence of the Stern layer, the highest potential in the diffuse part of the double layer will be in the experimentally determined range of 100-150mV. The Gouy equations are therefore applicable to the diffuse part and corrections of these equations to include the finite size of the ions and the dielectric constant change are not important in most practical cases (Levine and Bell 1960). The use of the term $ze\psi/kT$ in equation (1) instead of the work done in bringing an ion to the distance x, is justified when the number of surface charges are high and the concentration is not too high (Casimir 1944).

Specific adsorption can best be demonstrated for polyvalent inorganic and surface-active organic counter-ions which cause a sharp drop in the zeta-potential at very low concentrations and a charge reversal at higher concentrations (Rutgers and DeSmet 1945), Schenkel and Kitchener 1960).

1.2. Zeta-potential and the Electrokinetic phenomena

The electrokinetic or zeta-potential, ζ , though a rather ill-defined quantity is of great importance in the quantitative study of electrokinetic effects in colloid chemistry. It is considered to be the potential at the surface of shear or 'slipping plane', parallel to the actual phase boundary, but displaced somewhat to the side of the liquid. The liquid is assumed to be completely immobile between the phase boundary and the slipping plane, and to have its normal viscosity beyond this plane. The zeta-potential is apparently always less than ψ_0 but may be close to ψ_δ, the potential at the Stern layer, particularly for low ionic concentrations or low surface potentials or both.

The zeta-potential is determined indirectly from the electrokinetic phenomena, i.e. phenomena involving electricity and connected with a tangential movement of the two phases along each other. A relative mechanical motion occurs between the different phases when they are subjected to an external electric field, or when mechanical motion is brought about in either phases there results a transport of electricity.

To the first category belong the phenomena

1) Electro-osmosis. The movement of a liquid with respect to a stationary solid (capillary or a porous diaphragm) as a result of an applied electric field.
2) Electrophoresis. The movement of charged particles through a dispersion medium under the influence of a potential gradient. Electrophoresis is therefore the reverse phenomenon of electro-osmosis and is one of the most thoroughly investigated electrokinetic phenomenon.

To the second group belong the phenomena

3) Streaming potential. When a liquid is forced through a capillary or a porous plug, a potential difference is developed at the ends of the capillary or plug.
4) Sedimentation potential. By allowing particles to fall through a column of liquid (under gravitation or centrifugal field), a potential difference is set up across the column. It is also called migration potential or the Dorn effect (1880).
5) Electroviscous effects. In a laminar field of flow, the outer parts of the double layer are drawn away

from the particle, the original situation in the double layer tends to restore itself by conduction, and the dissipation of energy in this conduction may be seen as the cause of increased viscosity.

As the electrokinetic phenomena are all fundamentally of the same origin they should lead to the same value of ζ for a given system. However, many of the results given by different investigators for one and the same system differ too much from each other even when using the same method of measurement. This may be due partly to the fact that in the earlier investigations necessary corrections such as for example surface conductance and time-of-relaxation effect had not been fully distinguished and accounted for in the interpretation of electrokinetic results, and partly by the difficulties of getting really comparable surfaces for the different experiments.

There exist, however, in the literature cases where different electrokinetic measurements agree quite satisfactorily and demonstrate their equality; some of these results are quoted here briefly. Harrison and Elton (1959) found good agreement between the zeta-potentials of gold particles determined by micro-electrophoresis and the streaming potential results of Hurd and Hackerman (1956). Wijga (1946), using glass capillaries, found identical zeta-potentials from streaming and electro-osmosis experiments. The equality of electrophoretic and electro-osmotic zeta-potentials was demonstrated by Abramson et al. (1942) by covering both the particles and the wall of the microelectrophoresis cell with a layer of protein. Dulin and Elton (1952) compared their sedimentation velocities for fused silica spheres in potassium chloride solutions with the streaming potential results of Jones and Wood (1945). The results agree within 5°/o if the latter's results were corrected for release of silver from Ag/AgCl electrodes used. Parker and Wasik (1958) found reasonable agreement between the measured increase in viscosity for detergent solutions and those calculated from the electrophoretic mobility data given by Stigter and Mysels (1955) using the theoretical equations of Booth (1950a).

The viscosity and the dielectric constant in the electric double layer.

Although the electrokinetic phenomena are all equivalent and lead to the same value of ζ , there remains an uncertainty of the correct value of ζ in the electric double layer as the constancy of viscosity (η) and dielectric constant (ε) is doubtful. All electrokinetic equations are governed by the quantity $\int \frac{\varepsilon}{\eta} \, d\psi$ which simply reduces to $\frac{\varepsilon}{\eta} \zeta$ for constant ε and η.

The dielectric constant in the double layer tends to decrease mainly because of the ionic strength (concentration) effect and the electric field strength present near the surface (dielectric saturation). Second-order effects, mainly electric polarization near the interface and Coulomb interactions near the interface between the ions and the interface, tend to cancel each other (Sparnaay 1958). However, for the diffuse outer part of the electric double layer the decrease in ε is not important and can be neglected (Bolt 1955, Lyklema and Overbeek 1961).

The increase in viscosity is, however, more important as the influence of the electric field on viscosity is more pronounced than on the dielectric constant. From a theoretical consideration Lyklema and Overbeek (1961) estimated the visco-electric constant of water in the equation given by Andrade and Dodd (1951) relating viscosity to the electric field strength. From their calculations they concluded that the viscosity correction is very important specially for high surface potentials. Specific adsorption of counter-ions was not taken into consideration. The increase in viscosity with surface potential may lead to a constant value of ζ irrespective of ψ_o. However, this problem of enhanced viscosity will be discussed later in full detail in chapter 6.

1.3. The relation between ζ and ψ_o.

The problem of trying to understand the relation between nominal surface charge density calculated from ζ using the diffuse double layer equations and the 'actual' charge on the surface has attracted the attention of many investigators. In all cases ζ and ψ_0 are close to each other for very low ψ_0 potentials, but diverge at higher potentials; ζ is always less than ψ_0. Several reasons were given for this deviation. Various systems were investigated for these studies, but only three will be discussed - namely, silver halides, glass and oil interfaces.

Silver halides has been investigated extensively. ψ_0 can be readily calculated at any given salt concentration, from the analytically determined concentration of the potential determining ions (silver and/or halide) at that particular salt concentration and at the zero point of cha~~n~~rge. ζ is usually determined from electrophoretic mobilities. Verwey and Kruyt (1933), Basinski (1941), Lyklema and Overbeek (1961a) and many others, found that ζ and ψ_0 are fair~~b~~ly close to each other only round the zero point of cha~~n~~rge.

The determination of surface area for silver halides is not entirely satisfactory. Lyklema and Overbeek (1961a) found great variations in the estimated areas from dry and wet methods. The position of zero point of cha~~n~~rge is not at all constant for a given halide. Jonker (1943) found that during ageing of fresh silver bromide sols, the zero point is shifted to higher concentrations of silver ion. Julien (1933) found that large particles have a more negative potential than fine ones.

Glass interfaces have often been investigated as glass can be obtained practically in any form suitable for different electrokinetic measurements. From conductimetric measurements Benton and Elton (1953) obtained the number of ions adsorbed on the surface of silica glass. The zeta-potential values of Dulin and Elton (1953) were used to calculate the charge density in the diffuse double layer. The latter is approximately equal to the actual charge on the surface in very dilute concentrations ($\simeq$ 2 x 10^{-5}M HCl). At higher electrolyte concentrations they deviate greatly. Glass, however, suffers from the disadvantage of dissolution of the soluble surface layer, the extent of which differs from one type of glass to another and the way in which the glass was treated. Again the effect of hydrogen, hydroxyl, carbonate and other impurity ions is quite considerable and could lead to misleading results at these extremely low salt concentrations.

A better-defined surface for the study of the relation between ζ and ψ_o can be found at the oil/water interface in presence of adsorbed surface-active agents. ζ and ψ_o are obtained from mobility and interfacial tension measurements respectively. Haydon (1960) found that ζ and ψ_o

potentials converge towards low charge densities ($< 30{,}000$ e.s.u./cm^2) and diverge at higher charge densities. As Haydon pointed out, some discrepancies in the results are to be expected, at low surface charge densities, because of trace impurities and adsorption of inorganic salts at the interface.

In oil droplets there is the possibility of internal liquid circulation with the result of enhancing electrophoretic mobilities. In their calculations Anderson (1959) and Haydon (1960) considered the oil droplets as solid particles with no internal liquid circulation following the conclusions drawn by Linton and Sutherland (1957) and Nawab and Mason (1958). These authors suggest that the presence of an interfacial film formed by emulsifying agent tends to inhibit internal liquid circulation. This is certainly the case with microscopic droplets in the presence of surfactant.

From these experiments it is quite clear that ζ is always less than ψ_o. This could be due to the fact that ζ is a measure of the potential at a slipping plane at a distance d from the phase boundary. The distance d can be easily calculated from equation (6), from the experimentally determined ζ values and an estimate of ψ_o. Calculations by Eversole and Lahr (1941) and Eversole and Broadman (1941) for published electrokinetic potentials show that d varies from 8 - 63 Å for ceramics and glass interfaces in presence of alkali metal salt solutions. Anderson (1959) found values of 10-20 Å for the oil/water interface in presence of sodium dodecyl sulphate. The immobile layer would have to be rather thick in most cases which seems doubtful. Bikerman (1941) considers the existence of an immobile layer as simply due to roughness of all solid surfaces but this would not apply to emulsion droplets. Haydon and Taylor (1960) consider that at the oil-water interface the hydrophobic 'chains' are partly in the water phase and some of the counter-ions lie behind the head groups (between the chains).

In conclusion, it seems that two extreme factors could be considered as the main reason for the deviation of ζ from Ψ_0.

a) No specific adsorption of counter-ions. With increase of surface potential the increase in viscosity becomes more and more important. The actual value of viscosity and dielectric constant in the electric double layer should be used in the electrokinetic equations to have a correct estimate for the potential.

b) Specific adsorption of counter-ions. ζ is very close, if not equal, to Ψ_δ, the potential in the Stern layer. The dielectric constant correction is negligible. The viscosity increase, if any, can be accounted for by the approximate calculations of Lyklema and Overbeek (1961).

Both factors, however, lead to a reduced zeta-potential and for a clear distinction between case (a) or (b) some other properties of the electric double layer must be investigated. Haydon (1960a) has investigated 'surface potentials' at the oil-water interface, but their significance is equally open to doubt. The expulsion (negative adsorption) of ions of same sign as the surface (co-ions) is one property of the double layer potential that is, presumably, not influenced by the viscosity term.

1.4. Aim of this work

The aim of the present work is to check the validity of the theories mentioned above, for calculating surface charge densities from electrokinetic measurements by comparing these values with the actual charges on the surface. To avoid the uncertainties in earlier work, an experimental model has been chosen such that electrokinetic measurements may be carried out on particles with known surface charges. The system consists of strongly ionized surface-active agents adsorbed at the carbon black-water interface. Carbon blacks in the form of spherical particles were found to be suitable for this work, as they can be obtained in varying particle sizes, and clean, practically non-ionogenic surfaces can be obtained by heating the carbon to high temperatures (2700°C).

Adsorption isotherms of surface-active agents from water and salt solutions were determined on different carbons to find the most reliable system for the electrokinetic studies and to provide an accurate estimate of surface charge densities. Zeta-potentials determined from electrophoresis experiments were used in calculating charge densities on the basis of the diffuse double layer equations.

The possible reasons given for the deviation of ζ from ψ_o in this work were investigated by negative adsorption and surface conductance measurements.

2. ADSORPTION FROM SOLUTION

2.1. Introduction

Adsorption isotherms for organic solutes on solid surfaces are of various forms, which are sometimes indicative of the adsorption mechanism involved. The shape depends to a large extent on the nature of the substrate, the solute and the solvent used. In a recent survey, Giles et al. (1960) classified such adsorption isotherms according to the nature of the slope of the initial part of the isotherm into four main classes - i) 'S curves', found with systems where solvent molecules compete strongly for the available adsorption sites with solute molecules of moderate inter-molecular attraction adsorbed vertically on the surface, ii) 'L curves' or 'Langmuir isotherms', where there is not much competition from the solvent, and the solute molecules are adsorbed either flat or vertically oriented, iii) 'H curves' (high affinity), which is a special case of the L curves, where at low concentrations the solute is practically completely adsorbed, and in some systems ionic interaction is involved, iv) 'C curves' (constant partition), linear curves, sometimes followed by a plateau, given by solutes which penetrate into the solid more readily than does the solvent. Then, according to the shape of the parts of the curves farther from the origin and the significance of plateaux and changes of slope, Giles subdivided each main class to 3 - 5 sub-groups.

Adsorption from aqueous solution is, in some cases, limited to a monolayer. The isotherms are characterised, in these cases, by having a plateau sometimes covering a wide range of concentration. The Langmuir (1916) adsorption isotherm, originally derived for gas adsorption, has been very widely applied to adsorption from solution, the pressure terms being replaced by concentration terms. Langmuir's equation may be written as follows

$$x/m = abC/\left(1+bC\right) \qquad (11)$$

where x/m denotes the amount of adsorbate per unit amount of solid (e.g. equiv./g, g/g, etc.), $\underline{C}$ is the equilibrium concentration of adsorbate, $\underline{a}$ and $\underline{b}$ are constants for a given system the first is related to the area of the solid and the second to the heat of adsorption. The values of $\underline{a}$ and $\underline{b}$ can be readily calculated from a linear graph of the Langmuir equation

$$\left(\frac{1}{x/m}\right) = \frac{1}{ab}\left(\frac{1}{C}\right) + \frac{1}{a} \qquad (12)$$

Multilayer adsorption is sometimes observed, however, for adsorbates of limited solubility in water, generally with an inverse relationship between the extent of adsorption of a species and its solubility. Hansen and Craig (1954) found that the amounts of C_5 and C_7 n-aliphatic alcohols or acids adsorbed per gram of carbon black were superimposable on each other if plotted against their reduced concentration C/C_o. C_o denotes the solubility of the adsorbate in the solvent. The adsorption increased greatly as C/C_o approached unity in a manner similar to low -temperature gas adsorption. Similar results had been reported by Hansen et al. (1949, 1953).

Adsorption isotherms of surface-active agents from aqueous solution follow two main types - isotherms with a plateau covering a wide range of concentration and those with an adsorption maximum that occurs at concentrations higher than the critical micelle concentration (c.m.c.) of the surfactant. In some cases there is a minimum after the first maximum and the curve thereafter rises again. Occasionally still more complex curves with successive maxima occur (Meader and Fries, 1952).

Zettlemayer et al. (1957) found that the adsorption of sodium dodecylbenzene sulphonate on Graphon reached a practically constant value close to the c.m.c. The same is true for the adsorption of Aerosol OT on carbon blacks (Abram and Parfitt 1962), of cationic and anionic surface active agents on alumina (Tamamushi and Tamaki 1957), of cationic, anionic and non-ionic surfactants on carbon blacks (Rose et al. 1951) and non-ionic surfactants on silica (Bell 1959) and on calcium carbonate (Kuno and Abe 1961).

Maxima in the adsorption isotherms above the critical micelle concentration were observed in several systems.

It was reported by Aickin (1944) for the adsorption isotherms of alkyl sulphates on wool. Corrin, Lind, Roginsky and Harkins (1949) found a maximum in the adsorption isotherms of sodium dodecyl sulphate and potassium myristate from water on ash-free graphite. A discontinuity in the isotherms was observed at the c.m.c. and the maximum occurred at an equilibrium concentration of 2-3 times the c.m.c. Similar observations were reported for the adsorption isotherms of a number of anionic surfactants on cotton and wool cloth by Meader and Fries (1952); on cotton and nickel by Fava and Eyring (1956) and on cotton and carbon black by Vold and Phansalkar (1955). Sexsmith and White (1959) found adsorption maxima for the isotherms of cationic surfactant on a number of cellulosic materials.

In a study of the origin of adsorption maxima Vold and Sivaramakrishnan (1958) found that the amount of sodium dodecylbenzene sulphonate adsorbed depends on the ash-content of the carbon black. However, elimination of the ash by acid treatment did not entirely eliminate or shift the concentration of the maximum in the adsorption isotherm. More recently Razumikhina and Aleksandrova (1961) found that the adsorption isotherm of sodium di-n-butylnaphthalene sulphonate on ionogenic wood charcoal had two distinct steps. The first had a hydrolytic character (associated with an increase of pH) and the adsorption isotherm was steep; presumably this indicated adsorption with reversed orientation of the surfactant molecules, forming a monolayer on the surface with the hydrophobic part of the molecule directed outwards. The second part of the isotherm inclined less sharply (concave to the concentration axis) without any appreciable changes in the pH of the solution. The adsorption reached a maximum at an equilibrium concentration of about 8 times the c.m.c. Total adsorption at the second step was twice that of the first. A second layer was assumed to be formed on top of the first, the surfactant molecules being held by tail-to-tail adsorption.

For most of the systems mentioned above it was found that the peculiar break or discontinuity (close to the c.m.c.) and the maximum in the adsorption versus concentration curves arose from anomalous properties of the solutions rather than from pecularities of the adsorbate-surface properties.

Various reasons have been given to account for the appearance of a maximum in the adsorption isotherm and the decline in adsorption with increase in equilibrium concentration. Meader and Fries (1952) assumed that the sharp rise in the adsorption isotherm is due to adsorption of micelles from solution. It was suggested that at higher concentrations the adsorption of micelles begins to level off, while the adsorption of single ions may be expected to decrease somewhat; consequently the total amount adsorbed reaches a maximum. A decrease in the activity of the surfactant ions, and hence a decrease in adsorption, with increase of concentration was suggested by Corrin et al. (1949) based on a theoretical application of the mass action principle for the equilibrium between surfactant ions, counterions and micelles in solution.

Fava and Eyring (1956) were in favour of the idea of the possible existence in solution of a range of aggregates (specially close to the c.m.c.) and that only the smallest of these aggregates are capable of being adsorbed together with the single surfactant ions. To overcome the expected change in the specific rate of desorption according to the initial amount adsorbed on the surface, which was not observed experimentally, they assumed that once on the surface these small aggregates dissociate into single molecules, so that the final adsorbate is distributed over the surface in the same way whether the molecule arrived on the surface alone or as an aggregate. An explanation for the decline in adsorption was given by Vold and Sivaramakrishnan (1958) as due to aggregation of adsorbed ions into surface micelles at a certain solution concentration. Desorption of these surface micelles was thought to be a result of collision at the surface with micelles from the solution, and from kinetic considerations, they derived a set of equations which seems to provide a maximum in the adsorption isotherms. Sexsmith and White (1959) criticized Vold and Sivaramakrishnan (1958) derivations which appear to violate the principle of microscopic reversibility and, from statistical thermodynamic derivations using models similar to Vold's, produced no equations showing maxima for adsorption. Again Sexsmith and White (1959) considered the adsorption maxima as a result of the maximum in the activity of the surfactant ions.

At the present it appears, however, that a satisfactory explanation for the occurrence of a maximum in adsorption is not available. Most of the adsorbents used had heterogeneous surfaces and normal or reversed orientation of surfactant molecules were reported. Accurate surface areas were not known in several cases. Probably the most reliable results were those of Corrin et al. (1949) and Vold and Sivaramakrishnan (1958). From accurate values of surface area, determined by low -temperature gas adsorption, it was found that, even at the maximum point, the amount of surfactant adsorbed was not sufficient to form a close-packed monolayer over the whole surface. This is probably due to presence of oxygen complexes on most carbon surfaces, although Corrin et al. reported that their graphite was free of carbon-oxygen complexes.

Estimation of surface areas for polar and non-polar adsorbents by means of adsorption from solution have often been investigated. Although such methods are more rapid and require less elaborate apparatus than does gas adsorption, the dangers of obtaining misleading results are considerable. Limited solubility of adsorbates may lead to multilayer formation, or the adsorbed molecules fail to form a complete monolayer on the surface due mainly to the partial heterogeneity of the surfaces. In some cases the magnitude of adsorption was found to depend, to a large extent, upon the solvent used (Kipling and Wright, 1962).

In some instances, however, complete monolayers were obtained and surface areas were successfully calculated from adsorption results. The amount of solvent included in the monolayer is usually negligible in these systems. Harkins and Gans (1931) and Ewing (1939) found good agreement between the surface areas of metal oxides obtained from adsorption of aliphatic acids and esters from benzene solutions and those estimated from the partile size. Maron, Babalek and Fok (1956) determined the surface area for a number of carbon blacks from adsorption of laurate and myristate from aqueous solutions. The values were found to be identical with the nitrogen adsorption data up to a nitrogen area of 50 m^2/g. For the finer blacks adsorption results gave a lower estimate of the areas and this was attributed to surface roughness on a molecular scale. Surface areas of several systems have also been reported by Smith and Hurley (1949), Crisp (1956), Kipling et al. (1960, 1962) and Giles and Nakhwa (1962). The adsorption method gives, however, relative surface areas as, in most cases, an estimate of the cross-section of the adsorbate molecule is required. This is usually determined by either considering the geometry of the molecule or from the adsorption results on an adsorbent of known surface area.

In general it appears that solids behave differently according to their surface heterogeneity, which accounts for many of the anomalous results observed in adsorption experiments. Adsorption of surface-active agents from aqueous solutions is expected to follow one of two types, either physical adsorption (in which the surfactant molecules are more or less normally oriented with their hydrophobic part adsorbed to a hydrophobic site on the solid surface and the head group directed outwards) or the interaction between the functional group of the surfactant and an ionic or polar site on the surface (i.e., a reversed orientation). This type of orientation can lead to the appearance of a second layer with the functional group of the surfactant molecule directed outwards. Which of these mechanisms predomonates will depend upon the nature of the solid surface and the surfactant involved.

In this work the adsorption of surface-active agents on a number of carbon blacks has been investigated primarily with the object of finding a suitable experimental system for electrokinetic studies. Some consideration has been given to the surface chemistry of the carbons, the surface area relationships, and the existence of maxima in some of the isotherms; but these considerations were largely incidental to the main problem.

2.2. Experimental

i) Carbon Blacks

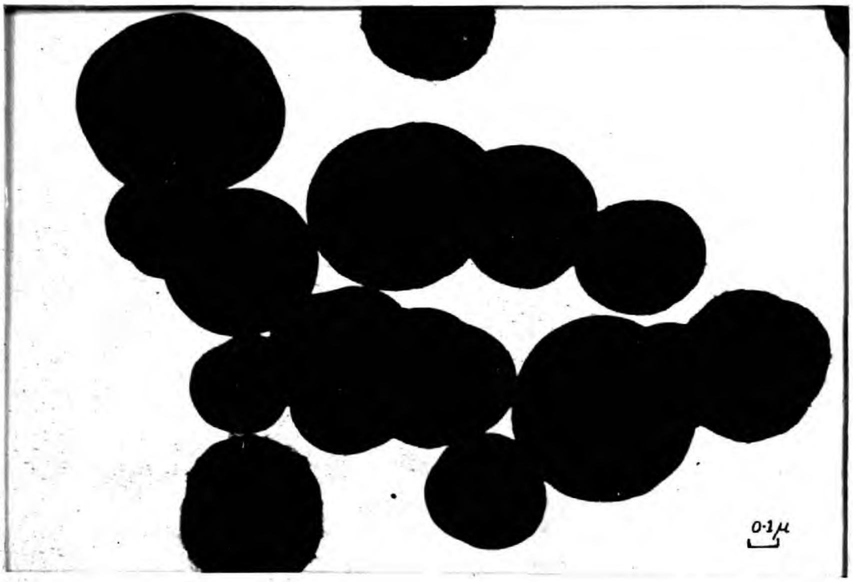
Carbon black is a particulate form of elementary carbon prepared by the partial combustion or thermal decomposition of gaseous or liquid hydrocarbons. According to the methods of manufacture carbon blacks are classified into three main groups, channel, furnace combustion and furnace thermal. They are produced in a wide variety of particle sizes ranging from 50 - 5000 Å. Blacks are composed of spherical particles which are essentially non-porous. This statement is based on the fact that, for most blacks, the surface area determined from nitrogen adsorption approximates to that estimated from particle size. Depending upon the process of manufacture they contain 95 to 99°/o carbon, the remainder consisting chiefly of combined oxygen and hydrogen.

The hyd~~d~~rogen present in carbon is residual hydrogen from the hydrocarbon raw material and is more or less evenly distributed throughout the particle (Anderson and Emmett, 1952).

The oxygen present in carbon black is chemisorbed on the particle surface in the form of carbon-oxygen complexes. The amount present has a considerable effect on the hydrophilic properties and the pH of an aqueous sludge of the carbon. The amount of chemisorbed oxygen is usually higher for channel than for thermal blacks. This is due to the fact that during the process of manufacture channel blacks are exposed at high temperature to excess oxygen and are partially oxidised. This does not occur with the thermal blacks which are made in a reducing atmosphere. The chemisorbed oxygen and hydrogen present on carbon blacks are collectively termed 'volatile matter'. When the blacks are heated in the absence of air to 1000°C, the hydrogen is evolved as molecular hydrogen and the oxygen as carbon monoxide and dioxide. The loss in weight resulting from such treatment is taken as the 'volatile content' of the black.

Ash of varying amounts is usually found after combustion of carbon blacks specially furnace blacks, and originates mainly from the hardness of the water used in manufacture. The manufacture of furnace blacks requires the use of substantial quantities of water for cooling the hot carbon-laden combustion gases prior to the collection of the black. It is expected, therefore, that the ash content will vary from one sample to another. Spectroscopic analysis by Vold and Sivaramakrishnan (1958) showed that calcium was the principal metallic constituent of the ash of their furnace black.

Heat-treatment of carbon blacks in an inert atmosphere at temperatures up to 2700°C results in a marked degree of graphitization and the formation of a practically inert surface. In the process of heat treatment, minute crystallites, forming the carbon particles, grow by a condensation process; the rate of crystallite growth is accelerated at temperatures over 2000°C. The final product consists of particles of predominantly doubly truncated polygonal bipyramids, as shown from the electron microscope pictures of Graham and Kay (1961). Plate 1 shows 'Sterling MT' before and after graphitization (the latter electron micrograph was kindly provided by Mr. H. I. Matthews of Imperial College). The uniformity and planarity of the surfaces increases with increase in particle size. In the process of graphitization a decrease in surface area



CARBON BLACK ("STERLING MT", CABOT CARBON CO.)

GRAPHITIZED CARBON ("STERLING MT")

ELECTRON MICROGRAPH BY MR.H.I.MATTHEWS

Plate 1.

is usually observed. This is due to decrease in surface roughness and an increase in density. The slight decrease in particle diameter is not sufficient to influence the final surface area.

The extent of heterogeneity of the graphitized carbon blacks was studied by adsorption of polar molecules. Young, Chessick, Healey and Zettlemoyer (1954) found that for 'Graphon' (graphitized 'Spheron 6') the vast majority of the surface sites are hydrophobic and only 1/1500 of the nitrogen surface area takes up water strongly. They supposed that these hydrophilic sites probably arise from traces of surface oxides that might be expected to form at the edge atoms of the graphite planes. Heterogeneity of the same order of magnitude had been reported by Graham (1957).

In this work three carbon blacks, together with their graphitized forms, were used. These are, Spheron 6, a medium-processing channel black and its graphitized form Graphon, a fine and a medium thermal black, Sterling FT and Sterling MT respectively. No particular names are given by the manufacture for the heat-treated Sterlings and they will be distinguished here by the term 'graphitized' instead of the term 'original' assigned to the untreated carbons. The carbon blacks were kindly provided by Dr. W. R. Smith of Cabot Inc., U.S.A. Table 1 shows some of the characteristics of these blacks taken from the manufacturer's data together with their nitrogen areas kindly determined by Dr. E. Redman (Morganite Research Ltd., London). The potentiometric titrations of the acidic and basic chemisorbed groups on the surface of the different blacks are given in Appendix 1.

TABLE 1. CARBON BLACKS

	Volatile Content (^{o}/o)	Ash (^{o}/o)	Average particle diameter (Å)	Surface Area (m^2/g)
Spheron 6	5	0.07	250	113.2
Graphon	0.08	0.01	-	94.2
Sterling FT (original)	0.5	0.07	2000	14.1
Sterling FT (graphitized)	0.06	0.02	-	13.3
Sterling MT (original)	< 1	0.07	4720	7.9
Sterling MT (graphitized)	0.04	0.04	-	6.9

ii) Surface-active agents

a) Cetyltrimethylammonium bromide ('Cetavlon')

$CH_3\ (CH_2)_{15}\ N(CH_3)_3\ Br$

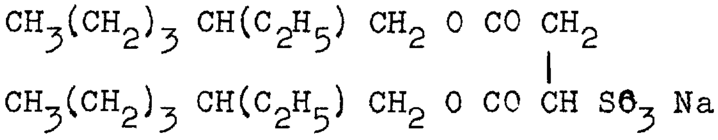
The B.D.H. sample was extracted twice with redistilled petrolum ether (b.p. 60 - 80^{o}C) to remove extractable non-ionic organic impurities. The extracted and dried sample was then recrystallized twice from hot acetone containing about 2^{o}/o water (Nash, 1958). The final product was evacuated at about 70^{o}C for three hours and then kept over phosphorous pentoxide in a desiccator.

The determination of the quaternary amine content by the formation of an insoluble salt with potassium dichromate (Renard, 1952) was carried out as follows. To 0.1706 g of dried Cetavlon dissolved in 5 ml of water and acidified with 3 drops of glacial acetic acid, a known excess of standard potassium dichromate solution (25 ml of 0.0964 N) was added. After 24 hours the yellow amine-dichromate precipitate was filtered through a small cotton plug and rinsed three times with 5 ml portions of water. The filtrate and washings were collected in a 50-ml volumetric flask, made up to the mark and analysed volumetrically by the thiosulphate method (Vogel 1951) for the uncombined dichromate. To run a control the Cetavlon-dichromate precipitate was redissolved by pouring 10 ml acetic acid and 15 ml of carbon tetrachloride through the cotton filter. To the collected solution a few crystals of potassium iodide and 2 drops of hydrochloric acid were added and the librated iodine titrated against a standardized solution of sodium thiosulphate until the carbon tetrachloride layer became colourless. The results of analyses showed that the combined dichromate (in the precipitate) was equivalent to a Cetavlon content of 0.1701 g whereas analysis of excess dichromate gave 0.1685 g Cetavlon. The mean of the two results gave a

99.3°/o quaternary amine content. This can be considered as an acceptable purity, if the limited accuracy of volumetric analysis (±1°/o) is taken into account

A further check for the purity of Cetavlon was obtained from the absence of a minimum in the surface tension-concentration curve (Appendix 2). The critical concentration for micelle formation (c.m.c.) was found to be at a concentration of 0.9 m.mole/l. Lawrence and Stenson (1957) reported a c.m.c. of 1 mM for Cetavlon from conductance and interfacial surface tension, and Nash (1958) found a value of 0.9 mM by the foam density method.

b) <u>Sodium di-2-ethylhexyl sulphosuccinate ('Aerosol OT')</u>



$$\begin{array}{l} \mathrm{CH_3(CH_2)_3\;CH(C_2H_5)\;CH_2\;O\;CO\;CH_2} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad | \\ \mathrm{CH_3(CH_2)_3\;CH(C_2H_5)\;CH_2\;O\;CO\;CH\;SO_3\;Na} \end{array}$$

The sample used was a B.D.H. product. It contained about 1°/o water and traces of inorganic salts and probably organic intermediates left behind during manufacture. Attempts to purify Aerosol OT by crystallization from methanol-water mixture, by the method given by Williams, Woodbery and Dixon (1957) for the normal homologue, were not successful. Variations in the ratio alcohol:water and temperature led in all cases to a very viscous product without any sign of crystal formation. The same was true for several other organic solvents and is thought to be a consequence of the branched chain.

Aerosol OT was, therefore, purified by treating the material (dried over P_2O_5) with dry redistilled acetone to remove inorganic salts and other insoluble impurities. From the clear filtrate, the Aerosol OT was recovered by evaporating the acetone under reduced pressure at room temperature. The extracted material was kept under vacuum over phosphorus pentoxide in a desiccator for several days before carrying out any measurements. The surface tension-concentration curve (Appendix 2) showed no minimum and gave a critical concentration for micelle formation at 2.5 mmole/l . This value of c.m.c. is identical with that given by Williams et al. (1957) for their highly purified Aerosol OT. Their ether extracted Aerosol OT was purified by adsorbing organic impurities (if any) from a dilute aqueous solution on to an activated charcoal of high purity (Da~~c~~rco G-60) having small pores that can accommodate impurities but not Aerosol OT molecules. It appears, therefore, that a simple acetone extraction is sufficient to obtain Aerosol OT of sufficient purity.

The methods of preparation of the lithium, caesium and the silver forms of Aerosol OT, by a cation-exchange resin (Zeo-Karb 225) are given in Appendix 2, together with their critical micelle concentration in presence of 0.01 N salt solutions. The divalent salts of Aerosol OT were not sufficiently soluble in water for accurate adsorption work, though Aerosol OT solutions in presence of 0.5 mM $MgCl_2$ were clear at low concentrations of the former. The ionic strength of the magnesium solutions were adjusted to the required values by adding sodium chloride.

iii) Inorganic salts

The following salts were used in some of the adsorption experiments.

Sodium chloride, analytical grade, recrystallized once: lithium chloride, (Williams and Hopkins G.P.R.) without further purification: caesium chloride, analytical grade: silver nitrate, analytical grade, recrystallized twice: magnesium chloride, analytical grade, without further purification.

In all cases approximate solutions (about 0.03 N) were prepared and their chloride or silver content analysed gravimetrically as silver chloride (Vogel, 1951).

iv) Experimental procedure in adsorption measurements

The 50-ml round-bottom flasks, fitted with B-24 stoppers, were first treated with chromic acid, washed carefully with distilled water and dried in an oven at 120°C. The requisite weight of carbon was introduced into the flask from a weighing-bottle and 20 ml of a standard solution of surface-active agent in water or salt solution added. The flask was then stoppered and shaken in an air thermostat (25°C ± 1°C) for not less than two hours. This time is sufficient for adsorption, which is usually complete in these systems in less than one hour. It was not possible, however, to determine the rate of adsorption as the carbons were easily dispersed upon addition of surfactant and it requires at least 30 minutes centrifugation to obtain a clear solution for analysis. From conductivity measurements Maron et al. (1956) found that several minutes were sufficient to attain equilibrium for the adsorption of surface-active agents from water on carbon blacks. Shaking for up to 6hr. did not show any change in the amount adsorbed. After shaking, the suspension was then centrifuged at 3000 r.p.m. (30 - 40 min.) and 10 ml of the clear solution analysed for change in surfactant concentration.

Dispersions of the fine carbons Spheron 6 and Graphon were somewhat difficult to clarify by centrifuging, especially at high surface coverages (> 70°/o). Membrane filters (grade AP, provided by OXO Ltd.) were found efficient in obtaining clear solutions for analysis. The filters were thin and did not retain any measurable quantities of the soluble components of the filtered solution. They were cut into small discs (2 cm in diam.) that fitted a small Hirsch funnel connected through a

B-19 cone to a 3-limb receiver adaptor. Two of the limbs were provided with 25-ml flasks while the third was stoppered. Filtration was carried out under slightly reduced pressure. The first few ml of the filtrate were usually discoloured and, therefore, collected separately in one of the two flasks. The receiver adaptor was then rotated, while the system under reduced pressure, and the following clear 11-12 ml collected for analysis.

The determination of surface-active agents was based on the dye-transfer method. It depends on the reaction of one type of surfactant with the oppositely charged surfactant in the presence of a dye and an immiscible organic solvent. The transfer of colour from one phase to the other serves to indicate the end-point.

Jones (1945) observed in his work with methylene blue that the presence of cationic surface-active agents interferes with the solvent solubility of the methylene blue-anionic surfactant salt, and that no coloured complex can be extracted at all if the cationic surfactant is present in stoichiometric excess. This led to Epton's procedure (1947, 1948) of titrating one surfactant type with the other in presence of methylene blue and an organic solvent.

In general, two main principles are involved in the dye-transfer method.

a) The solvent-soluble salt of a surfactant and a dye is destroyed by an oppositely charged surfactant and the dye released into the water phase.

b) The water-soluble mixture of a surfactant and a dye of like charge yields the dye to excess oppositely charged surfactant, forming a solvent-soluble salt.

More recently, Rosen and Goldsmith (1960) gave a review of the different systems involved in dye-transfer titrations. The pH, the ease of transfer and visibility of the colour are the main deciding factors in the choice of a given system for analysis. Two different methods depending on the second principle were, therefore, used for estimating the two surfactants used in this work.

Analysis of Cetavlon

As dye, a solution of 0.03 g methylene blue, 12 g conc. H_2SO_4 and 50 g Na_2SO_4 per litre was used. The method of analysis was that given by Weatherburn (1950) and Hillenbrand et al. (1951). To 10 ml Cetavlon solution in a 250-ml glass stoppered bottle 40 ml distilled water, 20 ml methylene blue solution and 20 ml chloroform were added. This was then titrated with a standard aqueous solution of Aerosol OT. The bottle was shaken vigorously after each addition; a stable emulsion was obtained at first with much foaming but by progressive neutralization of Cetavlon the emulsion became less stable and the foaming decreased. Close to the end-point the blue colour in the upper water layer began to migrate to the lower layer. The Aerosol OT solution was then added drop-wise until the end-point was reached, at which point the colour in both phases was equal when viewed by transmitted light.

Analysis of Aerosol OT

The dye solution consisted of 0.04°/o aqueous solution of bromophenol blue. The method given by Barr, Oliver and Stubbings (1948) was used. To 10 ml of Aerosol OT solution in a 400-ml glass stoppered bottle was added 90 ml distilled water, 2-3 drops of bromophenol blue, 2 drops of 1M sodium carbonate and 50 ml chloroform. The solution was titrated with a standard solution of Cetavlon. The aqueous layer was at first purple in colour with much foaming and changed to blue towards the end point with the phases easily separated. The end-point is that at which the blue colour shifts to the organic layer. For concentrated solutions of Aerosol OT (> 10 m.mole/l.) it was found that analysis of 10 ml gave a very turbid aqueous layer and phase separation was not sharp. These concentrated solutions were, therefore, analysed by titrating 4-6 g of solution instead of 10 ml as in all main experiments.

Inorganic salts in solution were found to have no effect on the titration of Aerosol OT. In case of silver nitrate a precipitate of hydrous silver oxide was obtained in these alkaline solutions and a few more drops of dye were needed, but the position of the end-point did not change, as checked by adding varying amounts of silver nitrate to solutions of Aerosol OT of known titre.

The titration was accurate to better than $\pm 1^{o}/o$ for the two surface-active agents over most of the range of concentration studied. However, for surfactant concentrations much less than o·1 m.mole/l . the titration method did not show the same accuracy mentioned above. This limitation in titration does not, however, influence the adsorption results greatly as the surfactant concentration left in solution was less than a few percent of the original concentration, and the equilibrium concentration of surfactant was not of great importance for the purposes of the present research. To check the magnitude of these low equilibrium concentrations, their surface tension was determined and their concentrations evaluated from a calibration curve (Table 9).

The accuracy of the adsorption results was found, however, to vary according to the relative change in surfactant concentration. In general the results were accurate to better than $\pm 2^{o}/o$ in the least favourable conditions.

2.3. RESULTS AND DISCUSSION

i) Adsorption of Aerosol OT from water

The adsorption results on the six carbons used in this work are given in tables 2 - 7 and shown in figures 2, 3, 6 and 7. All the adsorption isotherms have the general form of Langmuir adsorption isotherm with a well-defined plateau covering a wide range of concentration, without any indication of multilayer formation. Adsorption is always complete at equilibrium concentrations slightly higher than critical concentration for micelle formation, i.e., corresponding to a slight increase in activity above the c.m.c. A marked difference between the adsorption isotherms for the original and graphitized carbons (Fig. 2 and 3) is that the initial part of the isotherms for the former is always shifted to higher equilibrium concentration than for the latter. This suggests a change in nature of the surface, rather than a change in area.

Figure 4 is a graph of percentage surface coverage for the three graphitized blacks against equilibrium concentration, assuming that the saturation plateau is a complete monolayer. The experimental points, as shown in the graph, lie on one and the same curve. Most of the deviations observed are within the experimental error of the adsorption results. This graph demonstrates

TABLE 2. ADSORPTION OF AEROSOL OT FROM WATER ON TO GRAPHON

Initial concn. (m.mole/l.)	Wt. of carbon (g)	Equilm.concn. (m.mole/l.)	Amt.ads. (μ equiv./g)	Surf. coverage (%)
3.681	0.704	0.056	103.0	51.5
5.524	0.715	0.140	150.6	75.3
7.362	0.714	1.039	177.2	88.6
9.202	0.701	2.331	196.0	98.0
11.048	0.712	3.876	201.4	100.7
18.404	0.508	13.312	200.4	100.2

TABLE 3. ADSORPTION OF AEROSOL OT FROM WATER ON TO SPHERON 6

3.681	0.683	0.140	103.7
5.524	0.681	0.421	149.9
7.362	0.732	1.376	163.5
9.202	0.698	2.615	188.7
11.048	0.712	4.072	195.9
18.404	0.696	11.072	210.6

TABLE 4. ADSORPTION OF AEROSOL OT FROM WATER ON TO STERLING FT (ORIGINAL)

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt.ads. (µ equiv. /g)	1/eqm.concn. (l/mole)	1/amt.ads. (g/µ equiv.) x 10^2
0.810	0.977	0.169	13.1	5.92	7.63
1.473	1.014	0.534	18.5	1.87	5.41
2.209	1.006	1.011	23.8	0.99	4.20
2.761	0.999	1.433	26.6	0.70	3.76
3.681	1.008	2.162	30.1	0.46	3.32
5.524	1.022	3.959	30.6	0.25	3.27
7.361	0.986	5.755	32.6	0.17	3.07
11.050	0.989	9.436	32.7	0.11	3.06

TABLE 5. ADSORPTION OF AEROSOL OT FROM WATER ON TO STERLING FT (GRAPHITIZED)

				Surface coverage (°/o)
0.810	1.057	0.084	13.8	43.7
1.473	1.035	0.224	24.1	76.6
2.209	1.027	0.870	26.1	82.8
2.761	1.004	1.320	28.7	91.2
4.418	0.996	2.893	30.6	97.3
5.524	0.976	3.988	31.5	100.0
7.361	1.002	5.808	31.0	98.4
11.050	1.032	9.408	31.8	101.0

TABLE 6. ADSORPTION OF AEROSOL OT FROM WATER ON TO GRAPHITIZED STERLING MT

Initial concn. (m.mole/ l.)	Wt.of carbon (g)	Equilm.concn. (m.mole/l.)	Amt.ads. (μ equiv./g)	Surf. coverage (°/o)
0.886	1.602	0.085	10.0	61.7
1.772	1.672	0.676	13.1	80.9
2.253	1.510	1.154	14.6	90.1
3.097	1.510	1.943	15.3	94.4
4.626	1.603	3.379	15.6	96.3
6.891	1.514	5.687	15.9	98.1
9.843	1.521	8.615	16.2	100.0

TABLE 7. ADSORPTION OF AEROSOL OT FROM WATER ON TO STERLING MT (ORIGINAL)

0.886	1.521	0.140	9.8
1.772	1.550	0.704	13.8
2.953	1.550	1.689	16.3
4.521	1.600	3.209	16.4
6.891	1.471	5.658	16.8
9.843	1.549	8.502	17.3
Desorption experiments		0.676	15.6
		0.253	12.4
		0.141	10.5

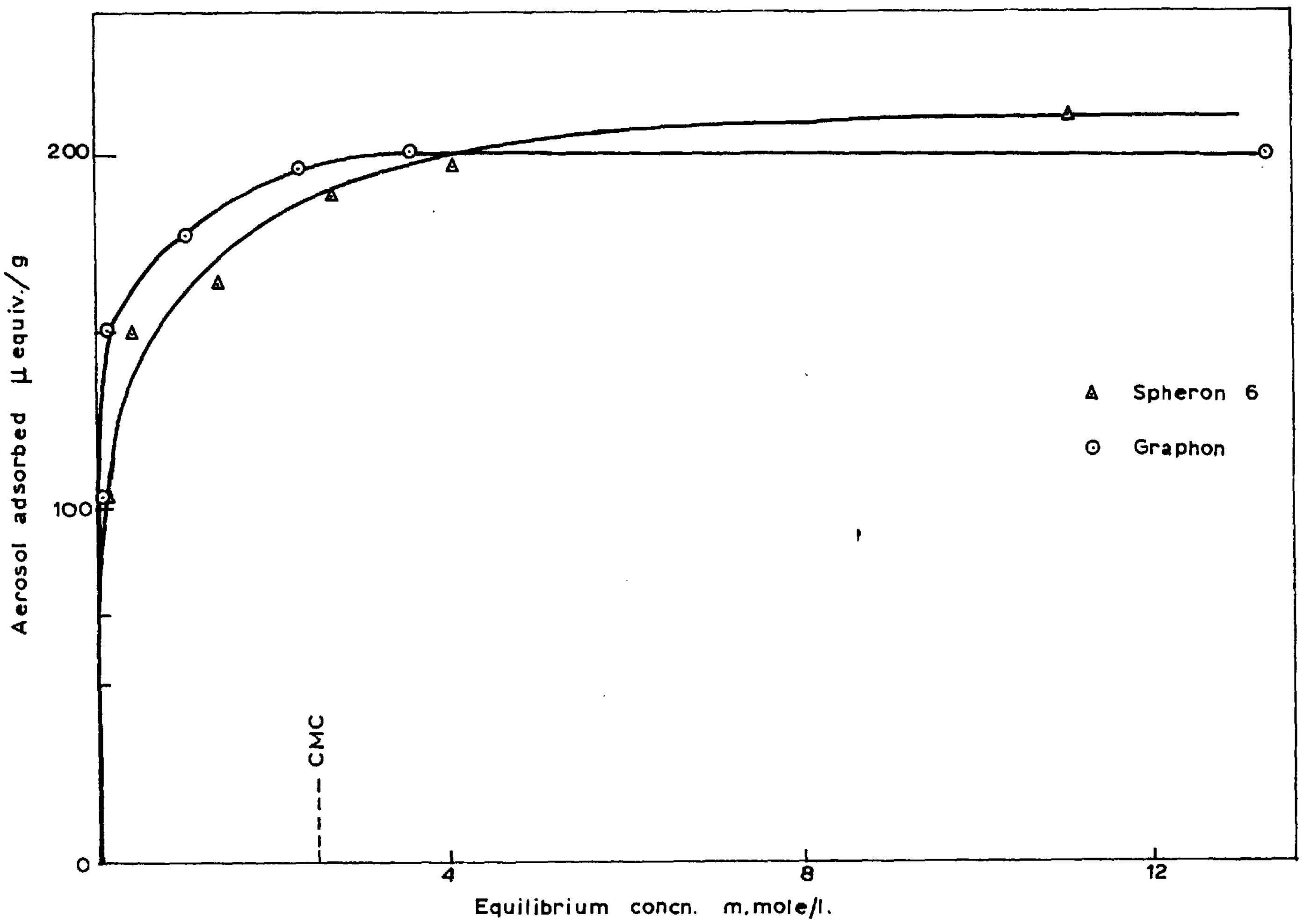


FIG.2 Adsorption isotherms for Aerosol OT on "Spheron 6" and "Graphon"

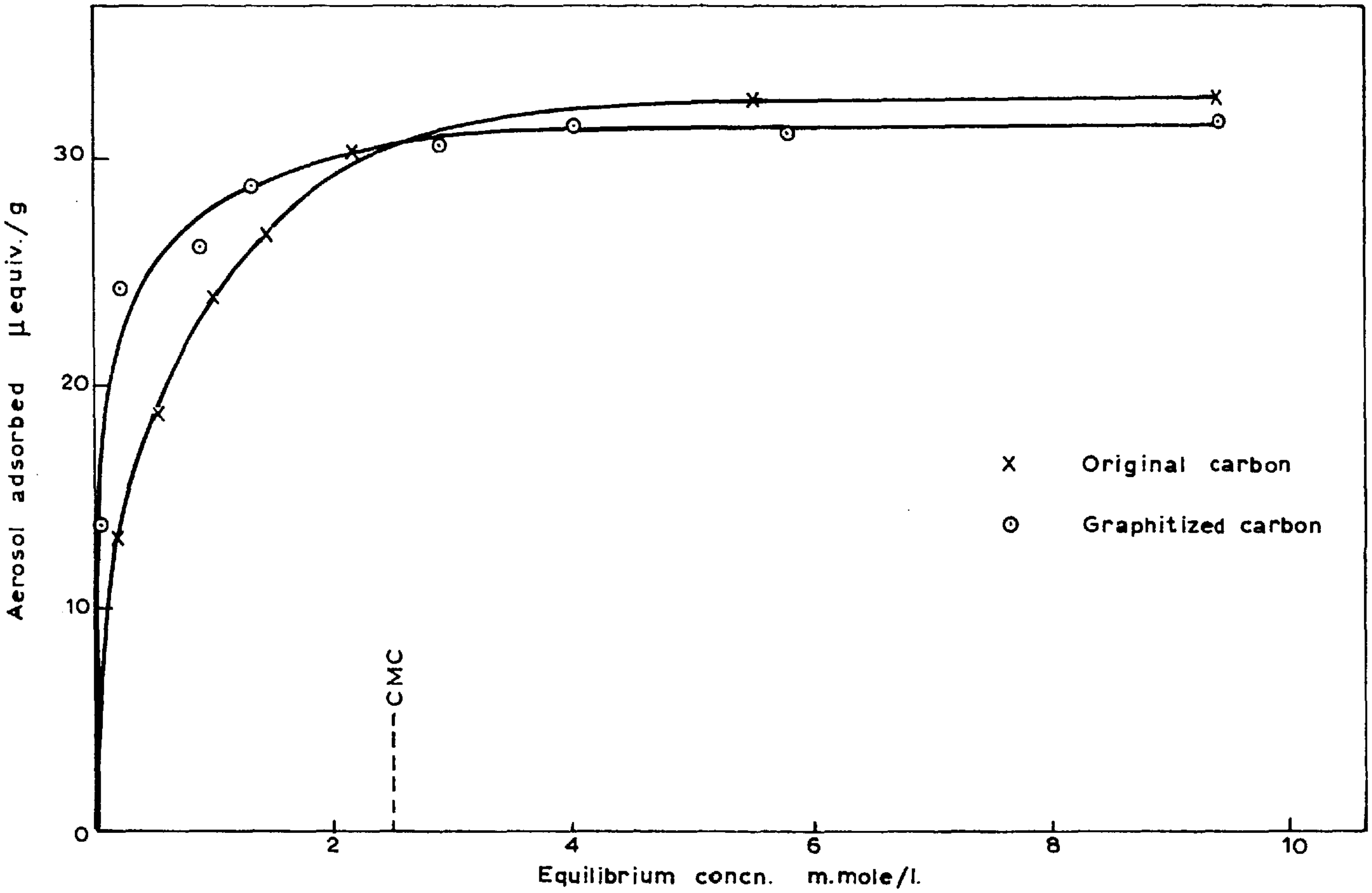


FIG. 3 Adsorption isotherms for Aerosol OT on "Sterling FT"

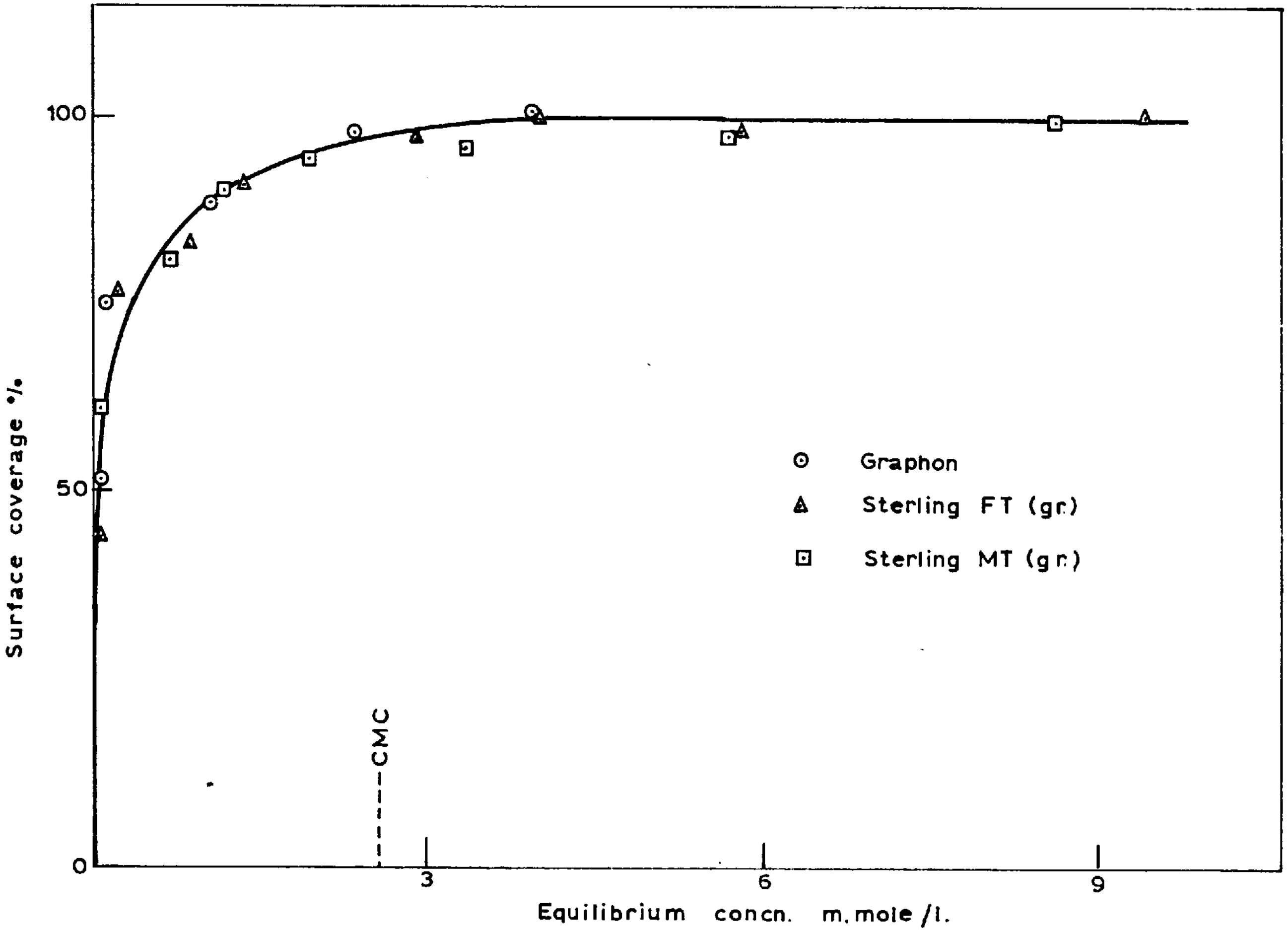


FIG. 4 Adsorption isotherm for Aerosol OT on graphitized carbon blocks

that the Aerosol OT molecules are adsorbed on surfaces having nearly the same surface properties. It is believed that the surface of these carbons consists essentially of homogeneous basal planes of graphite crystals formed during the process of graphitization at 2700°C (Kasatotchkine et al. 1960). The Aerosol OT molecules are expected, therefore, to be adsorbed physically on the surface; that is, the hydrophobic part of the surfactant molecule adsorbed to the hydrophobic graphitized surface while the head groups are directed towards the aqueous phase. The significance of figure 4 is that for any given equilibrium concentration all the graphitized blacks have the same percentage coverage and presumably the same surface charge density. Similar conclusions concerning the uniform behaviour of graphitized thermal blacks had been reached by Isirikyan and Kiselev (1961) from vapour adsorption results.

While graphitized carbon blacks possess a surface that is practically free from oxygen complexes the original carbon surfaces are partially covered with titratable acidic as well as basic groups in varying proportions (Appendix 1) and hence the orientation of adsorbed Aerosol OT molecules is somewhat complicated for these original carbons. Two ways of orientation of adsorbed surfactant molecules are possible; physical adsorption on hydrophobic sites or reversed orientation with the sulphonic groups interacting with ionic or polar sites on the surface. Which of these types of orientation predominates is not easy to prove. Therefore the pH changes that take place during adsorption, the zeta-potential and flotation tests were examined for Sterling MT (original) when its surface was about 85°/o covered with Aerosol OT. (This carbon was chosen for this study as most of the measurements in this work were carried out on it).

On shaking Sterling MT (original) with deaerated distilled water (prepared by passing a slow stream of H_2 for a long time through boiled distilled water, pH = 6.4 - 6.7) an increase in pH was observed. And on mixing 1.5g carbon suspended in 10 ml of water (pH = 7.9) with 10 ml of fresh solution of Aerosol OT (pH = 5.4) in the same treated water, a pH of 7.1 was obtained after stirring for 30 minutes in a stoppered flask previously washed several times with the treated water. The pH of the suspension remained constant for some hours after shaking. The original concentration of Aerosol OT was adjusted to give about 14 μ equiv./g carbon (≃ 85°/o coverage). From the measured values of pH, the calculated release of alkali due to possible salt-formation between the basic surface groups and the Aerosol OT anions was found to be negligible (< 0.1 μ equiv.). If there were a significant amount of salt-formation with basic groups on the surface and hence release of OH^- a much higher pH would be expected after adsorption of Aerosol OT: for example, a release of 1 μ equiv. of alkali in 20 ml solution would give a pH $\simeq 9.7$. It is, therefore, concluded that only a small proportion (perhaps few per cent) of the adsorbed Aerosol OT on Sterling MT (original) is chemisorbed in reversed orientation. It may be argued that as the carbon surface contains also acidic groups part of the released base neutralizes these groups and hence does not show an increase in pH. However, the titration experiments (Appendix 1) of acidic groups on Sterling MT (original) showed that for neutralizing 0.5 μ equiv./g carbon the pH must be greater than 10.

The zeta-potentials of dispersions of Sterling MT (original) in Aerosol OT were determined by the moving-boundary technique and found to vary from -60 to -98 mV for surface coverages between 70 and $100^{\circ}/o$. Observations on the amount of carbon carried by foam showed that little of it sticks to the bubbles: indeed, its flotation behaviour was exactly the same as that of graphitized Sterling MT whose surface had been rendered hydrophobic by adsorbing an equivalent amount ($\simeq 85^{\circ}/o$ coverage) of Aerosol OT from water solution. From all the above observations it seems that most of the adsorbed Aerosol

OT molecules on Sterling MT (original) are physical adsorption and oriented with their sulphonic groups towards the aqueous phase.

The reversibility of the process of adsorption of Aerosol OT on Sterling MT (original) was checked as follows. A weighed sample of the carbon in a centrifuge cup was equilibrated at room temperature (17°C) with a known solution of Aerosol OT in water. The suspension was then centrifuged, the equilibrium concentration determined and most of the equilibrium solution syphoned carefully and that left in association with the carbon determined by weighing. Water was then added (total solution 25 - 27 ml), the total weight recorded and the mixture stirred. After equilibration and centrifugation, the new equilibrium concentration was determined. From the original equilibrium concentration, the volume of this solution left after syphoning, the original amount of Aerosol OT adsorbed on the carbon surface and the volume and concentration of the new equilibrium solution, the new adsorption value of Aerosol OT on the surface can be readily calculated. Once this was done, the same process of desorption was repeated again on the same suspension of carbon. The results of these desorption experiments are given in table 7 and shown in figure 7. The points fall fairly well on the same adsorption isotherm, indicating that the process of adsorption of Aerosol OT on Sterling MT (original) is a reversible one.

Figure 5 shows a linear Langmuir plot for the adsorption of Aerosol OT on the original and graphitized forms of Sterling FT (surface coverages 60 - 100^{o}/o). For the original carbon the experimental results were used whereas for the graphitized carbon the points were taken from the isotherm in figure 4. The graph shows that for each form of the carbon the points lie approximately on a straight line. The different slopes observed for these curves indicate the change in nature of the surface induced during the graphitization process. Similar curves are shown by the other carbons. However, these plots have not much physical significance as the Langmuir isotherm is based on an ideal model which is not entirely applicable to this system. The fact that the adsorption of Aerosol OT varies with ionic strength (as will be seen later) is not in favour of a localized adsorption hypothesis. Again, in applying the Langmuir isotherm the pressure terms are replaced by equilibrium concentrations of surfactant and not activities where the latter is undoubtely far less than the former and changes but slightly at concentrations above the c.m.c.

The surface area occupied by the Aerosol OT molecule, at the limit of adsorption studied was calculated for the

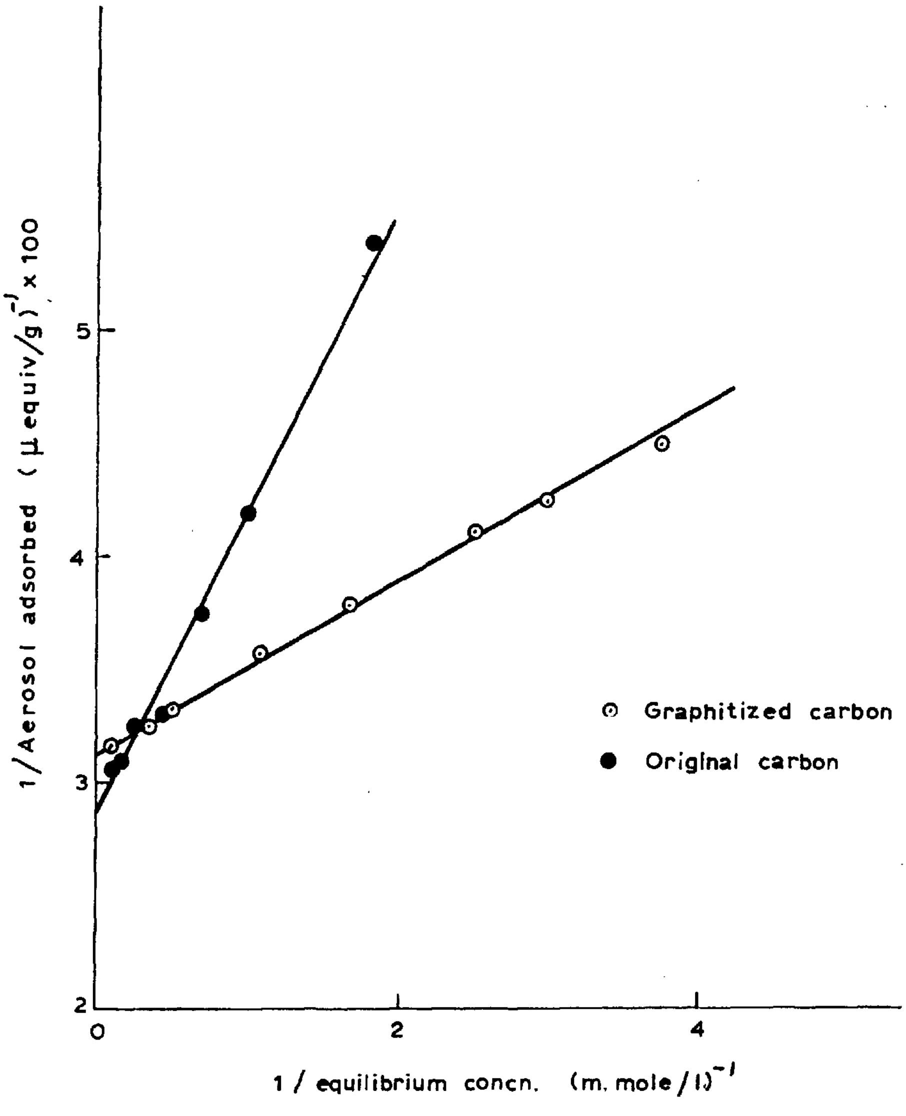


FIG. 5 Langmuir plot for the adsorption of Aerosol OT on "Sterling FT"

different carbons from the amount of surfactant adsorbed at the plateau of the isotherm and the nitrogen surface area of the carbons (table 1). For the graphitized carbons the amounts of Aerosol OT adsorbed were 200, 31.5 and 16.2 μ equiv./g for Graphon, Sterling FT and Sterling MT respectively. For the Sterlings FT and MT the calculated area was 70.1 and 70.7 Å^2/molecule respectively. A value of about 70 Å^2/Aerosol OT molecule has been reported by Abram (1960) from measurements on a scale molecular model, of the effective area of Aerosol OT in an unstrained configuration with the molecule adsorbed vertically. The calculated areas per molecule for the two Sterlings agree satisfactorily (within 1°/o) with Abram's figure, indicating that Aerosol OT forms a complete monolayer on their surface. It is concluded, therefore, that the surface area of graphitized Sterlings could be determined accurately (± 1°/o) from adsorption results of Aerosol OT from water assuming a cross-sectional area of 70 Å^2/molecule. For Graphon, however, the Aerosol OT adsorption gave an area of 84.3 m^2/g compared with the nitrogen area of 94.2 m^2/g. This shows a marked deviation between the two methods. The probable reason for this deviation is that the surface of Graphon is not as smooth as that of the graphitized Sterlings. Minute depressions in the surface will not be available to the same extent to the bulky Aerosol OT molecules as they are for the much smaller nitrogen molecules. Deviation in areas due to incomplete dispersion of the carbon or presence of surface oxides is not likely. All adsorption experiments were performed under the same conditions of shaking and similar deviations would be expected from the two graphitized Sterlings, although probably to a different extent. Again the relative increase in adsorption of Aerosol OT by adding inorganic salts was found to be approximately the same for Graphon and graphitized Sterling MT (amt. ads. from 0.01 N NaCl/amt. ads. from water = 1.05 and 1.068 for Graphon and Sterling MT respectively). Titration of surface oxides (Appendix 1) and the work of Young et al. (1954) showed that only minute amounts (< 0.1°/o of the surface) are present on the surface and cannot account for all this difference in surface area determinations.

In the process of graphitization the occluded hydrogen starts to come off as the temperature is raised to 950°C (Polley et al. 1953). This leaves a system of narrow pores which collapse on heating the samples to higher temperatures. From the electron microscope studies of Kuroda and Akamatu (1959) and Graham and Kay (1961) it was found that the degree of graphitization and hence surface planarity of carbon blacks increases with increase in particle size. It is, therefore, clear why significant deviation between Aerosol OT and nitrogen surface areas had not been observed for the graphitized Sterlings of large particle size (diam. > 2000 Å) whereas it was observed for the finer carbon Graphon (diam. 250 Å). Similar deviations had been reported by Maron et al. (1956) for the fine and not for the coarse carbon blacks. Therefore, an area of 84.3 m^2/g Graphon, available for the bulky Aerosol OT molecules to form a complete monolayer, represents the effective surface area of the carbon without dealing with the fine structures on the surface. Other bulky surface-active agent molecules would probably give similar results.

Adsorption of Aerosol OT on the original carbons did not form so compact a monolayer. The percentage surface coverages calculated from the amount of Aerosol OT adsorbed (area 70 $Å^2$/molecule) and the nitrogen surface areas were 80.8, 97.1 and 90.7 for Spheron 6, Sterling FT and Sterling MT respectively. This was expected as the original carbon surfaces are partially covered with oxygen complexes and not as smooth as the graphitized ones. More oxides were found on the surface of Sterling MT than on Sterling FT (Appendix 1). These surface coverages cannot be considered as a measure of the hydrophobic portion of the surface. Some of the Aerosol OT molecules may be adsorbed by reversed orientation and the rest by physical adsorption. Again the Aerosol OT molecules are bulky, carrying two ethyl side chains in the 2-position far from the hydrophobic end and bridges over hydrophilic surface sites can be formed by the main two chains of the Aerosol OT molecules. The packing of surfactant molecules is also influenced by ionic forces, as shown below.

ii) Adsorption of Aerosol OT from salt solutions on graphitized Sterling MT

The adsorption results for different salt forms of Aerosol OT from inorganic salt solutions of constant ionic strength (ca.0.01, the contribution from Aerosol OT not included) are shown in figure 6 and recorded in tables 8 - 12. On the same graph is plotted the adsorption isotherm of Aerosol OT from water for comparison. The adsorption isotherms in presence of monovalent cations follow a Langmuir form and show no sign of multilayer formation. Adsorption is usually complete at equilibrium concentrations somewhat higher than the critical micelle concentration. The latter is reduced by the addition of inorganic salts and the effect of counterions is quite pronounced (Appendix 2). The initial parts of the adsorption isotherms are quite steep and for a given coverage the equilibrium concentration is proportional to the c.m.c. As shown from the surface tension measurements (Table 9), the equilibrium concentration is greatly diminished with

TABLE 8. ADSORPTION OF Li-AEROSOL OT FROM 0.01 N LiCl ON TO GRAPHITIZED STERLING MT

Initial conc. (m.mole/l.)	Wt. of carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
0.898	1.496	0.056	11.6
2.059	1.492	0.929	15.2
3.222	1.513	2.041	15.6
5.113	1.504	3.942	15.7
7.004	1.511	5.799	15.9

TABLE 9. ADSORPTION OF AEROSOL OT FROM 0.01 N NaCl ON TO GRAPHITIZED STERLING MT

0.225	1.525	-	3.0	(a)
0.450	1.502	<0.001	6.0	(a)
0.675	1.514	0.001	8.9	(a)
0.900	1.504	0.006	11.9	(a)
1.253	1.500	0.211	13.9	
1.772	1.575	0.563	15.3	
2.953	1.622	1.661	15.9	
4.626	1.497	3.379	16.7	
6.891	1.926	5.264	16.9	
9.090	1.912	7.348	17.4	

(a) Equilibrium concentration determined by surface tension measurements.

TABLE 10. ADSORPTION OF Ag-AEROSOL OT FROM 0.01 N $AgNO_3$ ON TO GRAPHITIZED STERLING MT

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm concn. (m.mole/l.)	Amt. ads. (µ equiv./g)
1.025	1.502	0.056	12.9
1.845	1.528	0.648	15.7
2.665	1.516	1.408	16.6
4.100	1.516	2.815	17.0
5.534	1.502	4.223	17.4
7.175	1.502	5.911	16.8

TABLE 11

ADSORPTION OF Cs-AEROSOL OT FROM 0.0 1 N C_sCl ON TO GRAPHITIZED STERLING MT

0.937	1.478	0.030	12.3
1.757	1.490	0.530	16.5
2.570	1.515	1.255	17.4
4.207	1.518	2.795	18.6
5.855	1.521	4.440	18.6
7.028	1.494	5.615	18.9

TABLE 12. ADSORPTION OF AEROSOL OT FROM 0.5 mM $MgCl_2$ + 8.5 mM NaCl ON TO GRAPHITIZED STERLING MT

(a) 1.5 g carbon

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
1.029	1.515	0.022	13.3
1.543	1.506	0.338	16.0
2.229	1.497	0.958	17.0
3.430	1.504	2.027	18.7
5.143	1.515	3.575	20.7
5.968	1.497	4.363	21.4
6.861	1.500	5.011	24.7
7.717	1.506	5.968	23.2
8.573	1.513	6.869	22.5

(b) 1 g carbon

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
1.543	0.996	0.721	16.5
2.572	1.003	1.633	18.7
4.271	0.996	3.153	22.4
5.058	0.996	3.885	23.6
5.968	1.000	4.730	24.8
6.861	1.004	5.574	25.6
7.890	1.005	6.475	28.2
8.918	0.996	7.629	25.9

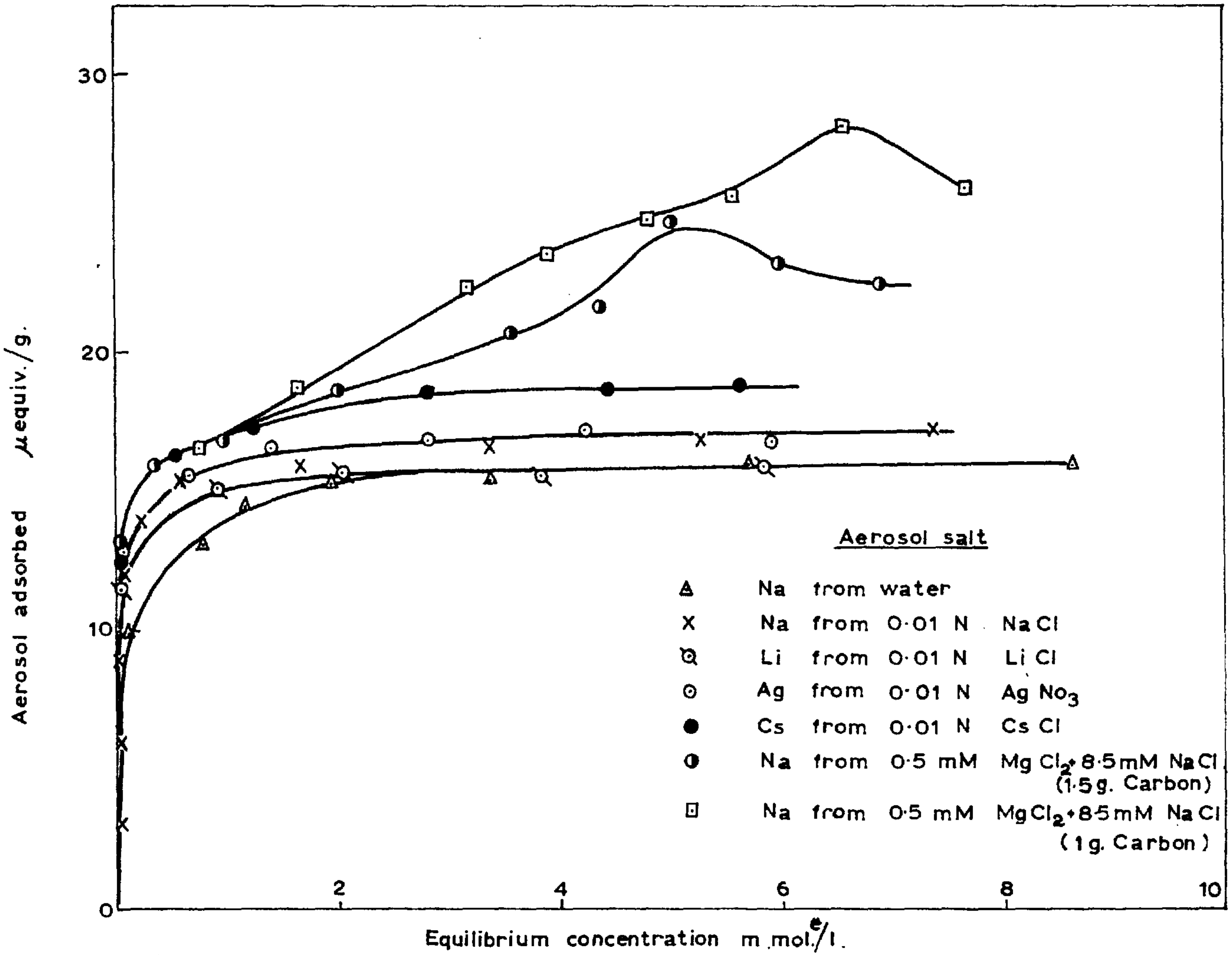


Fig. 6 Adsorption isotherms for different salts of Aerosol OT on Sterling MT (graphitized)

decreasing surface coverage.

The area occupied by an Aerosol OT molecule on the surface at complete adsorption is reduced by addition of salts of different cations and follows the order Cs < Ag $\simeq$ Na < Li. This difference in packing can be looked at as either due to close packing of cations between the surfactant ions or as a result of the equilibrium between the cohesive forces between the hydrocarbon chains tending to bring chains closer and concentrate away from the aqueous phase, and the electrical repulsive forces between the head groups tending to push molecules apart. For a given surfactant the cohesive energy contribution will be constant and ions of charge opposite to that of the long chain ions will have a marked effect on the degree of packing by reducing the repulsive forces between the head groups. From these two assumptions it is expected, therefore, that for monovalent cations the area occupied by an Aerosol OT molecule is related to the hydrated radius of the cations. The hydrated radii of the monovalent cations used in this work were calculated from their corresponding mobilities at infinite dilution (25^{o}C, Robinson and Stokes 1955) using the equation given by Ulich (1930, 1934). For an accurate comparison of the effect of univalent cations it would be more appropriate, however, to use the distance of closest approach rather than the hydrated ionic radius. In the absence of data on the activity coefficients of Aerosol OT solutions, the values of the distance of closest approach for the alkali metal halides calculated by Kressman and Kitchener (1949), for 0.1 N solutions, are given below for qualitative comparison

Cation	Area per Aerosol molecule (Å^2)	Hydrated radius (Å)	Distance of closest approach (Å)
Li^+	71.6	2.37	5.56
Na^+	66.2	1.83	4.49
Ag^+	66.2	1.48	-
Cs^+	61.0	1.18	2.96

An exception to the above expectation is that for the sodium and silver forms. The two salt forms gave practically the same adsorption isotherm. The change in area is probably within the experimental error of the adsorption results (± 2°/o).

The formation of more than a monolayer in the adsorption isotherm in presence of 0.5mM $MgCl_2$ + 8.5 mM NaCl is attributed to the tendency of Mg^{++} to form co-ordinate salts; thus the structure of the adsorbed films may be represented by a monolayer of Aerosol OT molecules adsorbed vertically on the carbon surface having their ionic heads outwards; then the Mg ions being divalent can hold a second layer of Aerosol OT ions. If this assumption is valid, the equivalent of Aerosol OT more than a monolayer ought to be (a) equal to or less than half the equivalent of magnesium in solution and (b) dependent on the ratio of carbon to magnesium in a given solution, i.e., should change according to the weight of carbon added to the 20 ml of the solution. The number of equivalents of magnesium in 20 ml of solution is 20 μ equiv., and for a monolayer of 18.8 μ equiv./g (taken from Cs curve, both having the same initial part): the equivalent of Aerosol OT in excess of a monolayer at the maximum (24.6 μ equiv./g) in the isotherm for 1.5 g carbon is 8.7 μ equiv. To prove the second assumption the isotherm was repeated using 1 g of carbon; in that case the adsorption per unit area at the maximum ought to be higher and actually it approximates to 9.3 μ equiv./g carbon in excess of a monolayer.

The decreasing sorption with increasing equilibrium concentration beyond the maximum is due in this case to competition of the Aerosol OT molecules on the surface and in solution for the limited supply of magnesium ions. The concentration of Na-Aerosol OT being here above the critical micelle concentration, Mg-Aerosol OT may be solubilized by the Na-micelles.

iii) Adsorption of Aerosol OT from salt solutions on to Sterling MT (original)

The adsorption results of different salt forms of Aerosol OT from salt solution on to Sterling MT (original) are given in tables 13 - 17 and shown in figure 7. For all the experiments the ionic strength was kept constant at 0.01 (contribution from Aerosol OT not included) except the isotherm in presence of 0.5 mM $MgCl_2$ + 7 mM NaCl where the ionic strength was 0.0085. The adsorption isotherm of Aerosol OT from water is also plotted on the same graph for comparison.

In presence of added inorganic salts, all the adsorption isotherms showed two distinct, and approximately equal, steps and a maximum in adsorption with the exception of that in presence of lithium chloride. The position of the adsorption maximum for the different salt forms had no direct relation to the critical micelle concentration. The maxima occurred at equilibrium concentration higher than the c.m.c., the ratio of the former to the latter varied from about 2.5 times for the silver-form to about 7 times for the sodium-form.

The effect of counterions (cations) is quite clear from the graph; whereas no maximum can be obtained in the presence of 0.01 N LiCl in the concentration range studied, a maximum was obtained for the sodium form at

TABLE 13. ADSORPTION OF Li-AEROSOL OT FROM 0.01 N LiCl ON TO STERLING MT (ORIGINAL)

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
1.144	1.516	0.140	13.2
2.002	1.546	0.732	16.4
2.860	1.463	1.599	17.2
5.005	1.497	3.659	18.0
9.296	1.472	7.961	18.1

TABLE 14. ADSORPTION OF AEROSOL OT FROM 0.01 N NaCl ON TO STERLING MT (ORIGINAL)

0.886	1.541	0.056	10.8
1.772	1.511	0.535	16.4
2.953	1.666	1.407	18.6
4.626	1.554	3.152	19.0
5.405	1.486	3.800	21.6
6.167	1.487	4.420	23.5
6.892	1.518	5.011	24.8
6.892	1.484	5.067	24.6
7.725	1.514	5.658	27.3
8.694	1.486	6.588	28.3
10.265	1.518	7.792	32.6
11.971	1.482	9.256	36.7
13.615	1.511	10.934	35.5
15.286	1.538	12.894	31.1

TABLE 15. ADSORPTION OF Ag-AEROSOL OT FROM 0.01 N AgNO$_3$ ON TO STERLING MT (ORIGINAL)

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
1.014	1.557	0.056	12.3
1.521	1.493	0.168	18.1
2.028	1.479	0.477	21.0
2.535	1.571	0.777	22.4
3.042	1.504	1.180	24.8
4.056	1.515	1.800	29.7
5.070	1.481	2.614	33.2
6.084	1.565	3.541	32.5
7.098	1.894	4.217	30.4
7.906	1.512	5.347	26.9

TABLE 16. ADSORPTION OF AEROSOL OT FROM 0.5 mM MgCl$_2$ + 7.0 mM NaCl ON TO STERLING MT (ORIGINAL)

1.018	1.496	0.050	12.9
1.527	1.496	0.281	16.7
2.035	1.522	0.675	17.9
3.053	1.508	1.436	21.4
4.580	1.494	2.500	27.9
6.106	1.499	3.744	31.5
7.633	1.490	5.433	29.5

TABLE 17. ADSORPTION OF Cs-AEROSOL OT FROM 0.01 N CsCl ON TO STERLING MT (ORIGINAL)

a) Untreated Sterling MT

Initial concn. (m.mole/l.)	Wt. of Carbon (g)	Equilm. concn. (m.mole/l.)	Amt.ads. (μ equiv./g
0.919	1.572	0.035	11.2
1.757	1.500	0.395	18.2
2.621	1.513	1.070	20.5
3.521	1.510	1.633	25.1
4.171	1.510	2.045	28.2
5.039	1.497	2.534	33.5
6.047	1.490	3.322	36.6

b) Ash-treated Sterling MT

2.621	1.513	1.126	19.8
3.527	1.503	1.689	24.5
5.039	1.503	2.506	33.7
6.047	1.500	3.463	34.5

c) Tar-treated Sterling MT

4.171	1.495	2.055	28.3
6.047	1.501	3.322	36.3

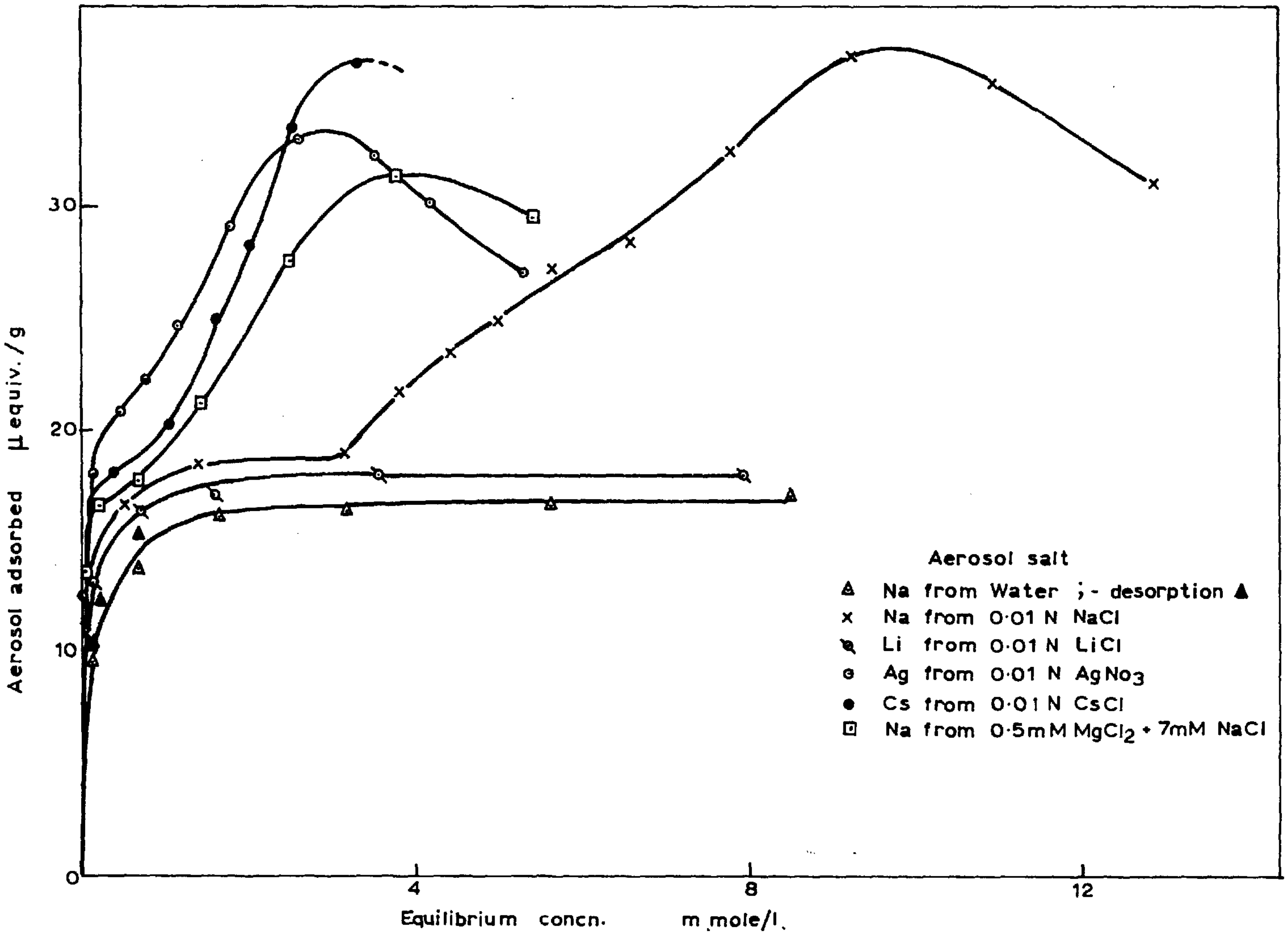


FIG. 7 Adsorption isotherms for different salts of Aerosol OT on "Sterling MT" (original)

high equilibrium concentrations, and the equilibrium concentration at the maximum adsorption is reduced from Na to Ag in the following order Na > Mg > Cs > Ag. This, in a manner, follows an inverse order of the affinity of sulphonic groups in ion-exchange resins for cations, being Na < Cs < Ag < Mg for a given concentration (Kitchener 1959). Therefore, it is clear that the higher the affinity of the sulphonic group to the counterion the easier will be the formation of the adsorption maximum at low surfactant concentration.

All solutions around the adsorption maximum tended to exhibit a bluish tint due to colloidal Aerosol OT which does not settle. Solutions of Li-Aerosol OT in 0.01 N LiCl were quite clear at all concentrations and no maximum was obtained in the concentration range studied The percent of light transmitted through solutions of Na-Aerosol OT in 0.01 N NaCl and Ag-Aerosol OT in 0.01 N Ag NO_3 was measured as a function of Aerosol OT concentration, an E.E.L. absorptiometer (Model B) with a blue filter (No.602) being used. The two salt forms started to be turbid as shown by the sudden change in light transmission at concentrations of 9.2 mM and 2.0 mM for the sodium and silver forms respectively. The corresponding adsorption maximum occurred at equilibrium concentration of 10.0 ± 0.5 mM and 2.8 ± 0.2 mM respectively. It appears, therefore, that a sharp rise in adsorption leading to a maximum is associated with adsorption from a supersaturated surfactant solution.

That the maximum in the adsorption isotherms is due to true adsorption and not surface precipitation is shown by the results of adsorption on graphitized Sterling MT (figure 6), where the same solutions at the same concentration range were used, without showing any sign of a second layer. Also, the descending part of the isotherms make it clear that at still higher concentrations the amount of surfactant adsorbed on the surface decreases whereas it would be expected to increase if the process were a precipitation.

From the results of adsorption on original and graphitized Sterling MT the formation of a maximum in the adsorption isotherms seems to depend on two main factors, (a) the presence of surface oxygen complexes and (b) the Aerosol OT solution close to its saturation limit. As shown previously, the graphitized carbons have practically non-ionogenic surfaces whereas the original ones are partially covered with surface oxide complexes. Another difference between the graphitized and the original carbons is that the latter contain a higher proportion of ash and some extractable tarry material left behind during manufacture. During graphitization (at 2700°C) the tarry material decomposes while most of the ash volatilizes. Therefore, before concluding that the oxygen complexes are the only difference between the two forms of carbon and responsible for the maximum in adsorption, an experiment was carried out in which the ash and tar were removed and further adsorption determinations made.

The ash content of Sterling MT (original) was determined by slow burning about 3 g of the carbon in a platinum crucible: it was found to be 0.07°/o. About 20 g of the carbon was then treated with 50 ml of 4 N HCl, prepared from the constant-boiling acid. The mixture was heated on a water-bath for 5h with occasional stirring and finally washed with distilled water until free of chloride and dried at 130°C for 6h. The ash content was found to be reduced to less than 0.01°/o by this simple acid treatment. The adsorption results of Cs-Aerosol OT from 0.01 N CsCl are shown in figure 8 and table 17. The graph shows that the ash-treated carbon gave approximately the same results, with the exception that the point near the maximum gave a somewhat lower value. The difference ($\simeq$ 5°/o) is not great and not far from the experimental error. The ash is, therefore, considered to have little, if any, effect on the position and magnitude of the maximum. The significant effect of ash on adsorption, reported by Vold and Sivaramakrishnan (1958),

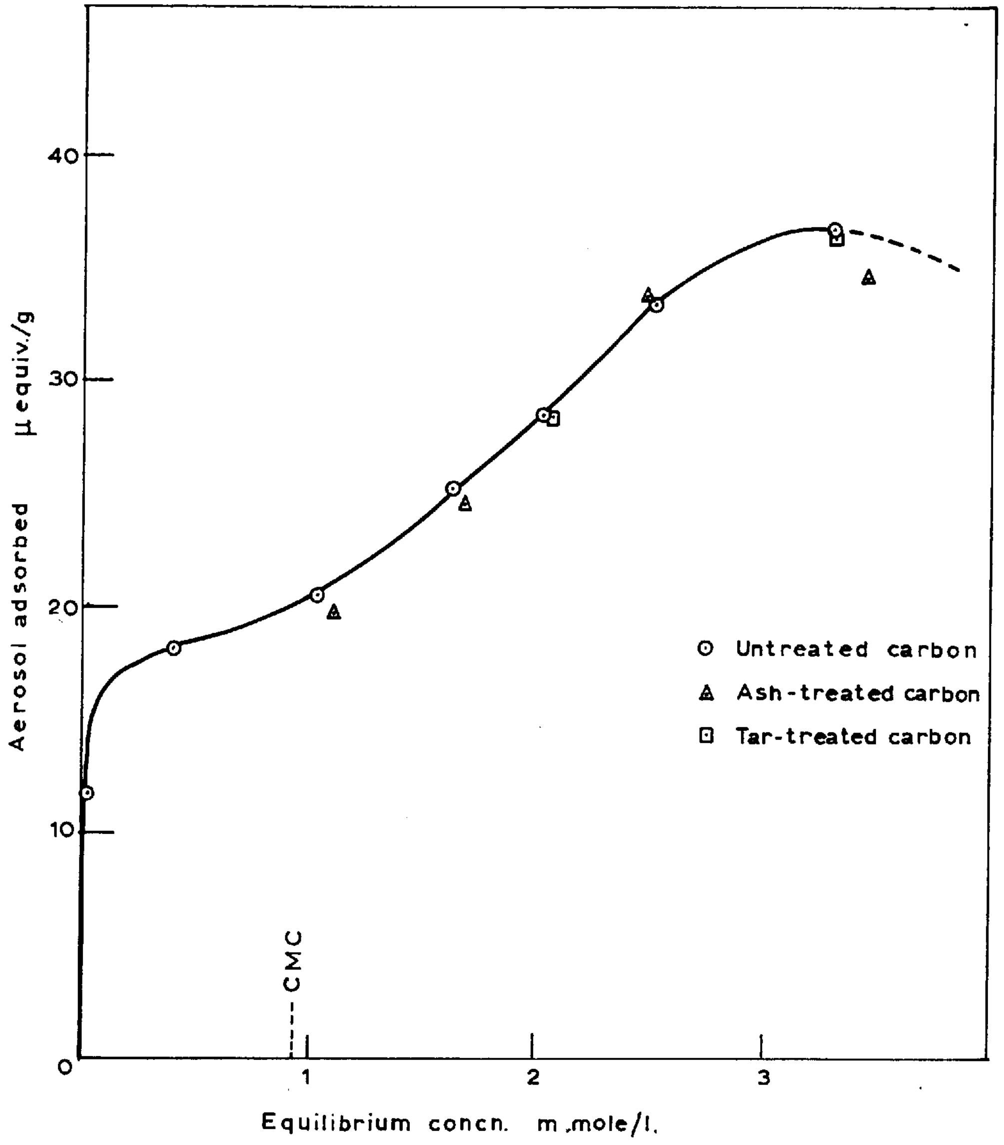


FIG. 8 Adsorption isotherm for Cs-Aerosol OT from 0·01 Cs Cl on "Sterling MT" (original)

was due to the fact that their carbon contained 0.45°/o ash.

The tarry material was removed by benzene extraction in a sohxlet until the extract was colourless (originally yellow). This was followed by washing with redistilled acetone and finally dried at 120°C. The adsorption results of Cs-Aerosol OT from 0.01 N CsCl (figure 8, table 17) show that the tar has no effect on the adsorption behaviour of the carbon.

In view of the nitrogen surface area of the original Sterling MT (7.9 m^2/g) the adsorbed Aerosol OT at the maximum seems to be arranged in two layers. The area occupied by the Aerosol OT molecule in each layer (assuming two equal layers) was 70, 78, 72 and 84 Å^2 for the cations Na, Ag, Cs and Mg-Na respectively. These values are not far from the area occupied by the Aerosol OT molecule in a complete monolayer.

The more probable arrangement of the adsorbed Aerosol OT molecules in these supposed two layers is a reversed orientation in the first layer leaving the hydrophobic part of the molecules outwards which can hold a second layer by tail-to-tail adsorption - sometimes called the 'bimolecular leaflet'. This type of arrangement is indicated by the fact that the carbon surface at equilibrium concentrations round the maximum in adsorption is hydrophilic in flotation tests and also by the magnitude of the measured zeta-potentials. For equilibrium concentrations close to the maximum zeta-potentials of -89 and -85 mV were found for the sodium and silver forms respectively, which are comparable with those found for the graphitized Sterling MT (Chapter 6) under the same conditions of salt content, where only monolayer physical adsorption occurs. Similarly these zeta-potentials figures are close to -91 mV found for the lithium form at full coverage where multilayer formation was not observed.

From figure 7 it is observed that reversed orientation is easier (shifted to low equilibrium concentrations) the greater the affinity of the counterion for the sulphonic group. As the adsorption is not associated with a significant increase in pH ($< 0.3\ \mu$ equiv. OH^-/g carbon) the Aerosol OT molecules in the first layer are probably partly reacting with basic groups on the surface and partly held by surface polar sites. This type of orientation is helped by the presence of added inorganic salt (0.01 N) which have the effect of reducing the thickness of the ionic atmosphere and hence the repulsive forces. However, the actual cause for this particular type of adsorption and the decline in the amount of surfactant adsorbed with increase in equilibrium concentration cannot be satisfactorily explained without a careful study of the properties of this system and in particular the phase relations for these surfactant solutions. Abnormal behaviour had always been found with similar turbid solutions. Kolthoff and Stricks (1949) found that turbid surfactant solutions gave higher solubilization results than expected from non-turbid ones of the same concentration. Debye and Anacker (1951), from light-scattering results of turbid surfactant solutions, showed that the originally spherical micelles changed to rod-shaped ones with a sharp increase in micellar weight.

The nature of the adsorption maximum found in this particular system, is different from that reported by Corrin et al. (1949) and Vold and Sivaramakrishnan (1958) in that with their carbons only a monolayer was found. Again the maximum in their isotherms was found for surfactants adsorbed from water. None of the isotherms determined in this work in the absence of added salts showed any sign of maximum formation whether the carbons used were original or graphitized. A maximum in the activity of the surfactant with increase in concentration as suggested by Corrin et al. (1949) or adsorption of micelles (Meader and Fries 1952) would be expected to show approximately the same result for graphitized and original carbons which is not the case for this system.

These adsorption results are also different from the multilayer adsorption results reported by Hansen et al. (1953) where their original and graphitized carbon gave practically the same adsorption isotherms without any maximum in adsorption. The adsorption isotherms found by Razumikhina and Aleksandrova (1961) are very similar to those reported here but nothing was mentioned about the purity of their dibutylnaphthalene sulphonate (inorganic salt content) or whether adsorption was carried out from water or salt solutions.

iv) Adsorption of Cetavlon from water

The adsorption results of Cetavlon on to Spheron 6, Graphon and Sterling FT are shown in figures 9 and 10, and given in tables 18 - 21. The isotherms are of the Langmuir type with a well-defined plateau covering a wide range of concentration and without any sign of multilayer formation. Adsorption is always complete at equilibrium concentrations equal to or slightly higher than the critical micelle concentration. The amount of Cetavlon adsorbed by the graphitized carbons is higher than that for the corresponding original ones of higher surface areas, indicating that the latter are not fully covered. The area occupied by Cetavlon molecule, calculated from the amount adsorbed (plateau) and the nitrogen

TABLE 18. ADSORPTION OF CETAVLON FROM WATER ON TO GRAPHON

Initial concn. (m.mole/l.)	Wt. of carbon (g)	Equilm.concn. (m.mole/l.)	amt. ads. μ equiv./g
3.620	0.694	-	104.3
5.429	0.706	0.140	149.8
9.050	0.711	0.463	241.5
13.804	0.980	0.619	269.0
12.700	0.736	1.427	306.4
13.804	0.688	2.585	326.0
23.100	0.708	11.280	333.9

TABLE 19. ADSORPTION OF CETAVLON FROM WATER ON TO SPHERON 6

3.620	0.689	0.010	104.7
5.429	0.708	0.113	150.2
9.050	0.709	0.323	246.1
11.550	0.718	0.754	300.7
12.700	0.680	2.155	310.0
13.804	0.699	3.231	302.6
23.100	0.701	11.960	317.8
23.100	0.635	13.040	316.8 (a)

(a) carbon shaken for 6 hours

TABLE 20. ADSORPTION OF CETAVLON FROM WATER ON TO GRAPHITIZED STERLING FT

Initial concn. (m.mole/l.)	Wt. of carbon (g)	Equilm. concn. (m.mole/l.)	Amt. ads. (μ equiv./g)
1.810	0.995	0.232	31.7
2.534	1.011	0.447	41.3
2.895	0.979	0.619	46.5
3.302	1.027	0.727	50.2
3.620	0.992	0.808	56.7
4.253	1.003	1.352	57.8
5.429	1.018	2.477	58.0

TABLE 21. ADSORPTION OF CETAVLON FROM WATER ON TO STERLING FT (ORIGINAL)

1.810	1.134	0.167	28.9
2.534	1.109	0.342	39.6
2.895	1.054	0.463	43.4
3.302	0.976	0.819	50.8
3.620	1.054	0.926	51.0
5.429	1.082	2.693	50.5
5.429	1.053	2.827	49.3 (a)

(a) carbon shaken for 25 minutes

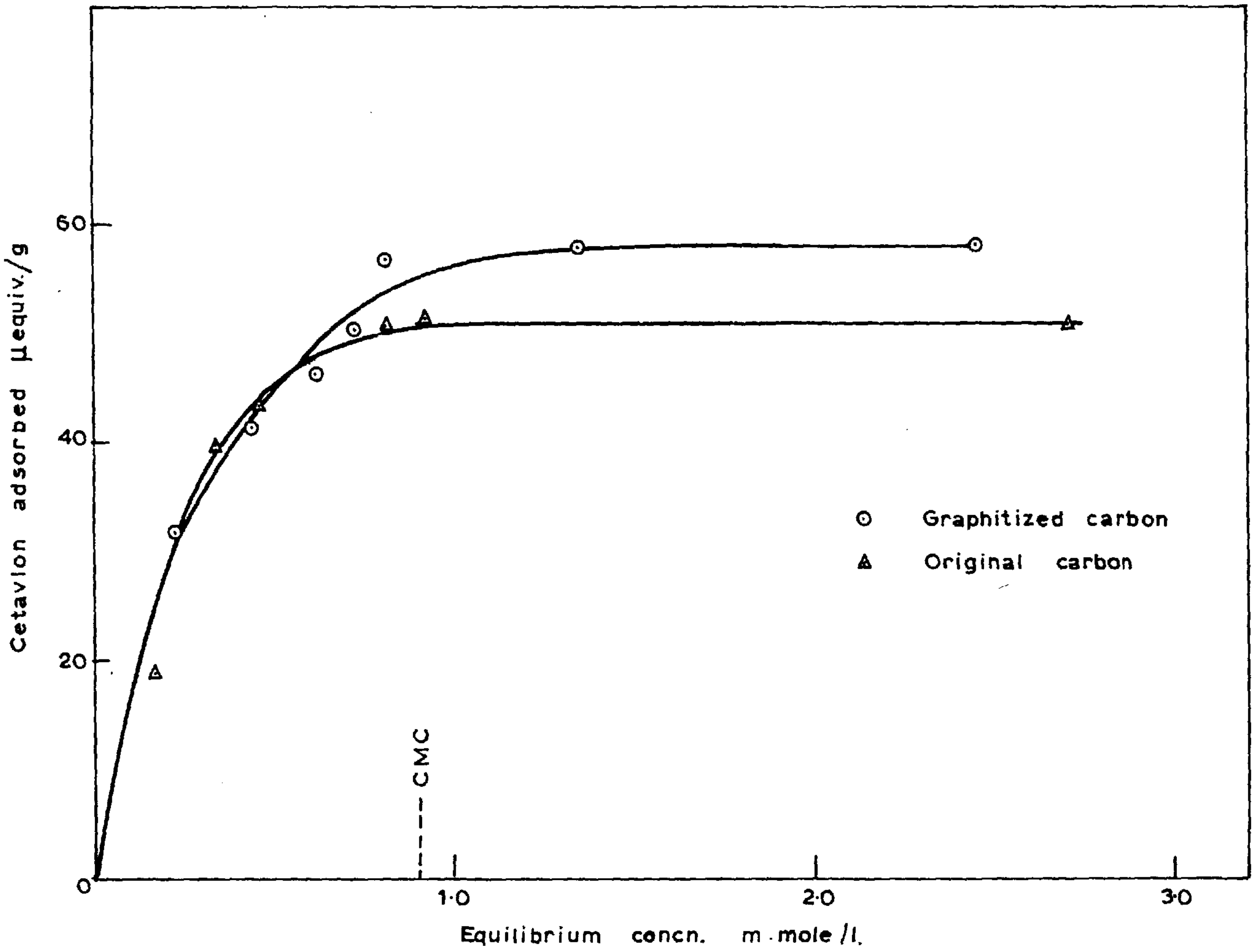


FIG. 9 Adsorption isotherms for Cetavlon on "Sterling FT"

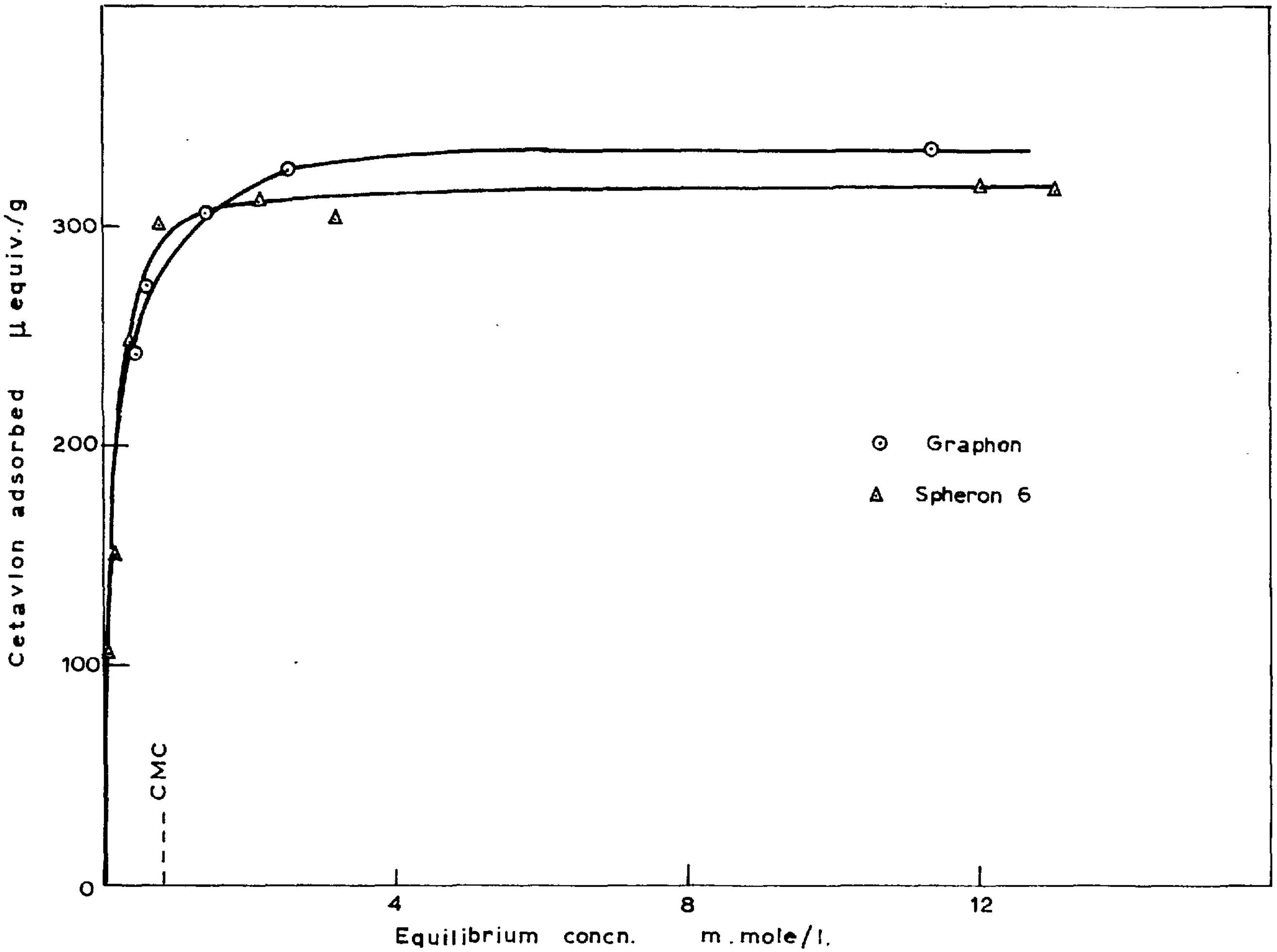


Fig 10 Adsorption isotherms for Cetavlon on "Spheron 6" and "Graphon"

surface area was 38.1 and 41.9 Å^2 in case of graphitized Sterling FT (13.3 m^2/g) and Graphon (84.3 m^2/g) respectively. One of the disadvantages of Cetavlon in adsorption work is that the cross-section of the molecule is governed mainly by the comparatively short, bulky quarternary amine head group and not by the normal paraffin chain (n - C_{16}). Any slight change in the level of the head groups could lead to a variation in the area occupied by the molecules.

The surface coverages of the original carbon blacks were calculated from the amount of Cetavlon adsorbed (40 Å^2/molecule) and the nitrogen surface areas, and were found to be 67.4^0/o and 85.4^0/o for spheron 6 and original Sterling FT. These coverages are, however, less than the corresponding values obtained from adsorption of Aerosol OT. It seems that Cetavlon is not as effective in covering heterogeneous surfaces as Aerosol OT, as bridges cannot be formed by Cetavlon molecules.

Several conclusions can be drawn from the studies of adsorption from solution.

1. Graphitized carbon blacks, with homogeneous surfaces, behave in a uniform way towards surface-active agents which are adsorbed physically on their surface. Surface charge densities can be easily evaluated from a knowledge of equilibrium concentration. These carbons are reliable substrates for other surface measurements.

2. Surface areas of the graphitized Sterlings can be calculated satisfactorily (± 1°/o) from adsorption of Aerosol OT from water assuming an area of 70 Å^2/molecule. Less satisfactorily area was obtained for the finer carbon Graphon and thought to be due to surface roughness. Areas determined from Cetavlon adsorption had a higher error (± 5°/o).

3. Surface area of original carbon blacks cannot be determined from adsorption results as the surfaces are not completely covered. Some of the adsorbed Aerosol OT molecules are reversed in orientation and therefore these systems cannot be used quantitatively for electrokinetic measurements.

4. None of the adsorption isotherms, determined for the adsorption of the two surfactants from water on the six carbon blacks, showed any sign of multilayer formation; only a monolayer was observed, and the isotherms characterised by a well-defined plateau.

5. Multilayer adsorption with a maximum in the adsorption isotherms was observed with the original carbon, Sterling MT, for the adsorption of Aerosol OT from super-saturated solutions caused by adding inorganic salts. The corresponding graphitized carbon gave normal adsorption isotherms from the same solutions.

6. The ash and tarry material on Sterling MT (original)

has insignificant effects on the position and magnitude of the adsorption maximum.

3. ELECTROPHORESIS

3.1. Theoretical

The evaluation of zeta-potentials from electrophoretic velocities was presented in 1879 by Helmholtz as a part of his theory of electrokinetic phenomena. Later Smoluchowski (1918) improved and extended these relations without, however, altering the final results. For stream-line flow and from a consideration of the electrical and frictional forces, the electrophoretic velocity (v) of a particle was obtained as:

$$v = \frac{\varepsilon \, E \, \zeta}{4 \, \pi \, \eta} \qquad (13)$$

The velocity is entirely a function of the ζ-potential (not the charge), and the applied electric field strength E and independent of particle shape.

Equation (13) was based on the following assumptions:

a) The extension of the double layer is small compared with the radius of curvature at any point on the particle surface.

b) The particle is non-conducting.

c) The viscosity and dielectric constant have the same value in the electric double layer as in the bulk of the liquid.

d) The applied field is simply superimposed on the field due to the electrical double layer.

In 1924 Huckel applied to colloidal particles the method of calculations used in the theory of conductance of strong electrolytes (Debye and Huckel 1923) and arrived at the following equation for the electrophoretic velocity

$$v = \frac{\varepsilon \zeta}{6 \pi \eta} E \qquad (14)$$

It is equivalent to Smoluckowski's equation except the term 1/4 is equal to 1/6 in Huckel's equation.

The confusion that arose over the question of which of these equations (13) and (14) was applicable to a given system was resolved by Henry (1931). Henry showed that the difference between the two treatments is whether the deformation of the applied field by the presence of the particles in the liquid is accounted for or not. Huckel's equation is applicable only either, if the conductivity of the particle is exactly the same as that of the liquid or if the dimensions of the particles are small compared with the thickness of the double layer. The electrophoretic velocity is in all cases given by:

$$v = \frac{\varepsilon \zeta E}{6 \pi \eta} f_1 (\varkappa a) \qquad (15)$$

where $f_1(\varkappa a)$, the so-called Henry's function, depends upon the magnitude of $\varkappa a$, the product of the inverse of the double layer thickness and the particle radius. $f_1(\varkappa a)$ varies from 1 - 1.5 and can be easily calculated for any value of $\varkappa a$ from Henry's equation (15a), which for non-conducting spheres reads:

$$v = \frac{\varepsilon \zeta E}{6\pi \eta} \left[1 + \frac{(\varkappa a)^2}{16} - \frac{5(\varkappa a)^3}{48} - \frac{(\varkappa a)^4}{96} + \frac{(\varkappa a)^5}{96} \dots \right] \tag{15a}$$

For $\varkappa a >> 1$; $f_1(\varkappa a) = 1.5$ and eqn.(15) reduces to Smoluckowski's equation (13)

For $\varkappa a << 1$, $f_1(\varkappa a) = 1$ and eqn.(15) reduces to Huckel's equation (14).

Conducting particles usually behave as insulators in electrophoresis because of surface polarization which in most practical cases is large enough to stop any further current to pass through the particle.

Overbeek (1943) corrected Henry's equation (15) for the influence of the relaxation effect on the particle velocity, and an equivalent treatment was given by Booth (1950). The relaxation effect arises from the fact that when a particle in suspension is subjected to an electric field the outer part of the double layer moves in a direction opposite to that of the particle, thus deforming the original symmetry of the double layer. By electric conduction and diffusion the double layer tends to restore its symmetry, a short time, the relaxation time, is required. The double layer lags somewhat behind the particle giving rise to an extra electric field, oppositely directed to the applied field, which tends to slow down the movement of the particle. Overbeek's simplified electrophoretic equations are:

a) For symmetrical electrolytes

$$v = \frac{\varepsilon \zeta E}{6\pi \eta} \left[f_1(\kappa a) - z^2 \left(\frac{e\zeta}{kT}\right)^2 f_3(\kappa a) - \frac{(\rho_+ + \rho_-)}{2e} \cdot \frac{\varepsilon kT}{6\pi \eta e} \cdot \left(\frac{e\zeta}{kT}\right)^2 \cdot f_4(\kappa a) \right] \quad (16)$$

b) For non-symmetrical electrolytes

$$v = \frac{\varepsilon \zeta E}{6\pi} \left[f_1(\kappa a) - (z_- - z_+) \frac{e\zeta}{kT} \cdot f_2(\kappa a) - \frac{z_+ \rho_+ + z_- \rho_-}{(z_+ + z_-)e} \cdot \frac{\varepsilon kT}{6\pi \eta e} \cdot \left(\frac{e\zeta}{kT}\right)^2 \cdot f_4(\kappa a) \right] \quad (17)$$

where $f_1(\kappa a)$ is Henry's function; the values of the functions $f_2(\kappa a)$, $f_3(\kappa a)$ and $f_4(\kappa a)$ were presented in tables by Overbeek (1943), and ρ_+ and ρ_- are the friction constants for the cation and anion of the electrolyte respectively.

Figure 11 shows the influence of the relaxation effect on the mobility in 1-1 valent electrolytes and different surface potentials. From the graph the following conclusions are drawn for the application of Overbeek's equations.

1) The relaxation correction is not important over the whole range of κa for small potentials ($\zeta < 25$ mV).

2) For very small and very large values of κa, the relaxation correction may be neglected.

3) For intermediate values of κa, the relaxation effect is an important correction factor, specially if ζ is not small.

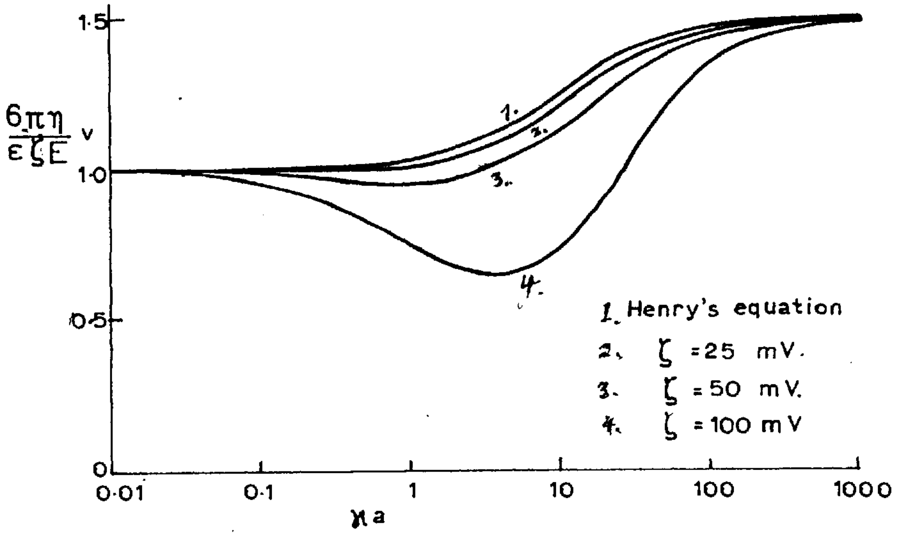


Fig. 11. The influence of relaxation for different potentials and 1 - 1 valent electrolytes

Although the Overbeek's equations were derived for small potentials ($z\zeta < 25$ mV), they are often used for much higher zeta-potentials. Their quantitative validity is doubtful, at least, for intermediate values of κa where the corrections are very large. Watanabe (1960) concluded that these equations are reliable for high zeta-potentials. But if really reliable data are required, it is necessary to choose a κa-range beyond the area for maximum relaxation effects.

Figure 12 illustrates for two hypothetical zeta potentials (50 and 100 mV) the theoretical variation of mobility with particle size for the three carbons used

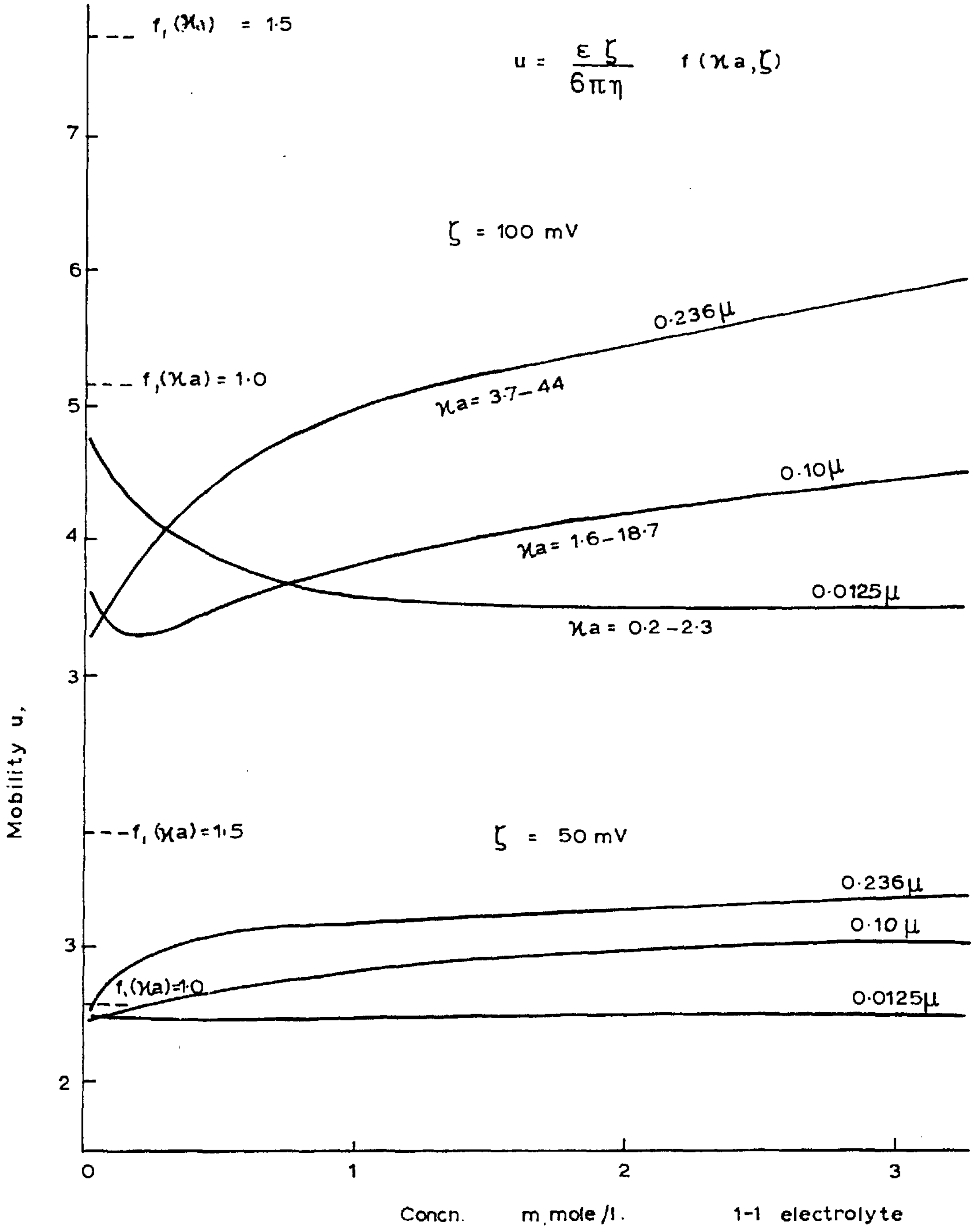


FIG. 12 Theoretical influence of particle size on mobility for assumed (constant) potentials of 50 and 100 mV.

in this work. For the smaller potential the mobility changes practically according to Henry's factor. The relaxation effect is small and tends to lower the mobility. For 100 mV, the mobility increases for Sterling MT, decreases for Graphon and passes through a minimum for Sterling FT with increase in concentration. This change in mobility can be easily understood by considering the magnitude of κa for the different carbons and where it lies with respect to the relaxation maximum as shown in figure 11. At high concentrations the mobility increases with increase in particle size. The necessity for the corrections is obvious.

Mooney (1924, 1931) has observed a variation of mobility with size of droplets of various liquids suspended in water and aqueous solutions. The mobility increases with increase in droplet size and finally reaches a constant value.

The surface conductivity effect. Booth (1948) and Henry (1948) independently extended Henry's equation (eqn.15) by including a correcting factor to take into account the surface conductivity effect. The surface conductivity is due to the fact that the electrical double layer contains a higher concentration of ions than the bulk of the solution (Chapter 5). For large κa and non-conducting spheres the corrected electrophoretic velocity is given by

$$v = \frac{\varepsilon \zeta E}{4 \pi \eta} \cdot \left(\frac{a\,\sigma_o}{a\,\sigma_o + \sigma_s} \right) \qquad (18)$$

where σ_o and σ_s are the specific bulk and surface conductivity respectively. The correction is, however, small for large particles if the correct value of σ_s is used. For example, using the experimentally determined σ_s for graphitized Sterling MT in Aerosol OT and 0.01 N NaCl (table 25) the factor $\left(a\,\sigma_o/a\,\sigma_o+\sigma_s\right)$ is equal to 0.966. A ~~small correction factor~~. However, both Overbeek (1943) and Booth (1950) allowed for the diffuse double layer conductivity in their corrections for the relaxation effects, so no separate correction is needed.

3.2. Apparatus for Electrophoresis

Of the several methods used for measuring electrophoretic velocity of particles two were adopted in this study - the moving boundary method (in which a suspension of particles are measured in the same time), and the microscopic method (where single, individual particles, are observed). The two methods ought to give the same result. But owing to the fact that moving boundary has the advantage of accurate temperature control which is not easy for the micro-electrophoresis cell used, the latter was only used when it was found difficult to prepare accurately the suspension for the moving boundary technique. This was the case only for low surface coverages of the carbons, i.e. when the suspensions were unstable.

The moving boundary apparatus

A modified Burton (1906) U-tube, shown in figure 13, was used. The main U-tube, a Pyrex tubing of 1 cm in diameter, was fitted with two vacuum stop-cocks of the same bore as the main tube (Ghosh and Ghosh 1957). It carries near the top two side arms of sufficient length to prevent ions released from the working electrodes from migrating into the main tube (Price and Lewis 1933). Any change in ionic concentrations and consequent changes in resistance are, therefore, confined to the side arms. The working electrodes are two carbon rods dipped in saturated potassium chloride solution and connected to the side arms through agar gel links. The potential electrodes are small platinum wires adjusted to be just below the connections to the side arms and kept in position with stoppers that fit at the top of the main tube. The effective distance between the two electrodes is determined from conductivity measurements (Burton 1906).

To determine the potential gradient across the main tube a known potential from a dry battery was put across the platinum electrodes and the potential in the tube was adjusted to be equal to this by varying the voltage between the carbon electrodes. A balance method was employed to

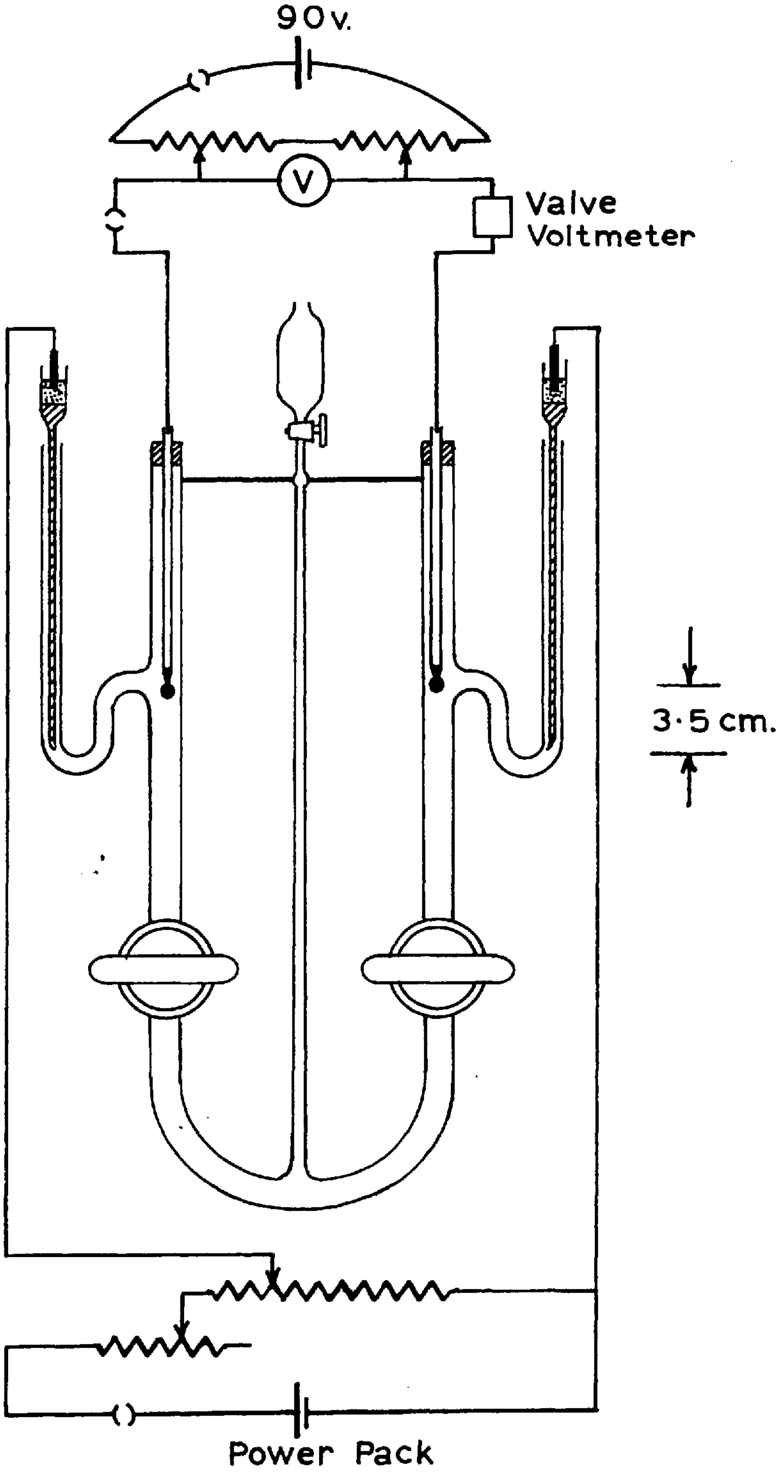


Fig. 13 Moving boundary electrophoresis cell

match the potentials, the null point being found with the aid of a valve-voltmeter (Taylor Electrical Instruments Limited, Model 500) sensitive to 0.1 V.

In order to keep the potential gradient across the main tube constant, the potential across the side arms had to be adjusted at three-minute intervals throughout the run. The arrangement used to effect his adjustment is shown diagrammatically in figure 13.

The micro-electrophoresis cell

Two main types of cells are in use, the cylindrical cell (Mattson 1928, 1933), and the flat or rectangular ones (Abramson et al. 1942). They can be used as vertical or horizontal, open or closed cells. In all cases electro-osmosis along the cell wall occurs. Although in rectangular cells the optical conditions are good, the liquid flow is complicated. The stationary layer depends on the ratio of breadth to depth of the cell; again they are expensive and difficult to construct.

To overcome the optical difficulties in cylindrical cells, the bent cylindrical capillary tube cell developed by Schenkel and Kitchener(1958) was used in this work. The cell is constructed from a precision-bore Hysil glass capillary (1.5 mm diam.) bent into an arc of radius 2.5 cm. A tiny elliptical hole is obtained by grinding the convex part of the cell wall. The hole is then covered with a piece of microscopic cover-glass which is sealed in place by a Canada balsam solution.

The cell is fitted with a pair of stop-cocks, a funnel on one side for filling and a pair of electrodes (platinised-platinum coils) which are suitable for the salt concentrations used here without causing any gassing. The cell was firmly mounted horizontally on a special microscope mechanical stage that could be moved sideways as well as forward and backward.

A Leitz microscope was used, but the top lens of the sub-stage condenser was removed to give a broad beam of light on the cell and a heat filter was inserted at the bottom of the condenser. A x 20 objective and a x 10 ocular, fitted with a grid which had been calibrated with a stage micrometer, were used. The draw-tube of the microscope was fixed at 17 cm giving a magnification of approximately 210 times. The working distance of the x 20 objective was just sufficient focussing from top to bottom. The microscope's fine adjustment micrometer could be read to 6 μ and focussed with a reproducibility of $\pm$ 9 μ.

Determination of the stationary level

In a closed cylindrical cell, where the net flow of liquid is zero, the electroösmotic flow of liquid along the walls is counterbalanced by a flow in the opposite direction along its centre. The stationary level is that at which the electro-osmotic and return flows just cancel, and only at such levels can true electrophoretic movements be observed. At any other level, the observed movement of a particle is determined by the algebraic summation of the electrophoretic and electro-osmotic effects. For a cylindrical cell of radius a the stationary level can be easily calculated from the velocity distribution of the liquid in the cell and found to be at a distance 0.293 a from the wall (Mattson 1933). During a run the top and bottom of the cell were first located in the microscope and their readings on the microscope's fine adjustment micrometer recorded. The position of the top and bottom stationary levels can be easily calculated from the cell's depth recorded.

The potential was supplied by a 0-120 volt variable voltage dry battery. A multirange microammeter in series with the cell provided a measure of the current flowing through the cell. A reversing switch in the circuit permitted a convenient reversal of polarity.

3.3. EXPERIMENTAL

1. Preparation of carbon dispersions

As the main object of this study was to compare the charge densities calculated from mobility experiments with the actual surface charge as determined from adsorption experiments for different surface coverages, great care had to be taken in preparing very dilute dispersions of known surface coverages.

From the adsorption experiments presented in chapter 2, a satisfactory measurable equilibrium concentration can be found for surface coverages higher than 70 - 80°/o. Below these coverages the adsorption isotherms are so steep and slight change in equilibrium concentration could lead to misleading surface coverages. Therefore, two methods were adopted for the preparation of dispersions of accurately known surface charge.

For the higher region of surface charges the moving boundary method was used and the dispersions prepared as follows: To about 40 ml of surfactant solution of prearranged concentration in a 50-ml flask fitted with a B-24 stopper, about 4 mg of the appropriate carbon was added carefully on one side of the mouth of the flask. The carbon was wetted with the surfactant solution. and finally ground gently by inserting the stopper and rotating it for a short time. Later in the work an ultrasonic dispersing apparatus was available and used for preparing dispersions. Both methods led to the same results but the latter is more efficient at low surface coverages. The surfactant adsorbed by the carbon is very small (less than 0.5°/o) compared with the total surfactant content in the solution; the supernatant solution in all cases had the same composition as that used for preparing the dispersions. The actual surface charge was calculated from the appropriate adsorption isotherm (chapter 2) for any given equilibrium concentration.

For low surface coverages (< 70°/o) the micro-electrophoresis cell was used and the dispersions prepared as follows:

To a known weight of carbon (about 1 g) in a 50-ml flask was added 40 ml of surfactant solution of prearranged concentration. The flask was then stoppered and shaken for two hours. The mixture was finally centrifuged and the clear equilibrium solution transferred to another flask. To the latter, a little of the sedimented carbon (about 1 mg) was added and dispersed by exposure to ultrasonic waves. In this way practically all the surfactant added was adsorbed on the carbon surface and very little if any was left in solution (Table 9). From the weight of the carbon and the initial concentration of the surfactant the surface adsorption density can be easily calculated.

2. Measurements of Mobilities

Moving boundary: Surfactant solutions of prearranged concentrations were prepared in 100-ml measuring flasks with and without added inorganic electrolytes. The clean dry moving boundary cell was rinsed twice with portions of the solution. The dispersion, prepared as outlined above, was introduced to the cell through the central delivery tube. The lower part of the U-tube as well as the bores of the stop-cocks were filled with the dispersion, and the stop-cocks were then closed. The portion above the stop-cocks was then filled with the rest of the surfactant solution, the level of solution in the two limbs was made always the same by filling to certain marks. The platinum electrodes and the two agar gel links with their carbon electrodes were placed in their positions. The electrophoresis cell was then transferred to a water thermostat maintained at $25^{\circ}C \pm 0.05^{\circ}C$.

After about 30 min. the two stop-cocks were cautiously opened, the one on the observation side was opened first to keep the boundary sharp. The tap in the delivery tube was carefully opened to allow the boundary to rise in the vertical limb to a level about 2 cm above the stop-cocks, when the desired level was reached, it was closed. The sharpness of the boundary depended, to a great extent, on the rate of delivery which had to be very slow. The boundary was usually left for 5 minutes to level up, if not so, before applying the current. A potential of about 80 V was applied across the carbon electrodes from a 0-220 volt variable voltage d.c. power pack. The upward distance traversed by the boundary was recorded every 5 minutes by means of a cathetometer readable to 0.02 mm. A time of 20 to 30 minutes was sufficient for the boundary to traverse a distance of about 1 cm. The velocity was obtained from the linear plot of time versus distance moved. The boundary was illuminated by a 6-volt lamp and observed against a white background.

The potential across the main platinum electrodes (50 - 60 V) was recorded from the sensitive voltmeter put across the dry battery, and kept constant by adjusting the potential across the side arms at 3-minute intervals throughout the run. The balance method was used to prevent polarization at the electrodes during measurements.

The boundaries were quite sharp and stable. Convection in the cell was practically eliminated. The electro-osmosis due to the charged wall is negligible in tubes of 1 cm diameter (Currie 1931), and the suspension and the clear supernatant solution have practically the same density. The current passing through the cell was always less than 1.5 mA, and the heat generated from this current (0.003 W/cm^3) is far less than the maximum permissible figure (0.15 W/cm^3) for this cell (Longsworth 1959).

Results from moving boundary are accurate to ± 1^o/o. Upward and downward velocities, measured for the same suspension by reversing the current, agreed well within the experimental error.

Micro-electrophoresis. The cell was rinsed with chromic-nitric acid cleaning mixture and then washed several times with distilled water. The water was then displaced with an 0.01 N NaCl solution and finally with the suspension. The latter was allowed to stand for several minutes and replaced at least twice before starting the measurements. The taps were closed and the top and bottom of the cell were located in the microscope and their readings on the microscope's fine adjustment micrometer noted. The microscope was at first focussed on the top stationary level. The time for a particle in focus to transverse the grid (95 μ) was recorded. The polarity of the cell was then reversed and the measurement repeated. In all ten particles were timed as they went back and forth on reversal of current. The same was repeated at the bottom stationary level of the cell. The cell was then refilled with the same suspension and the measurements repeated and the average velocity was determined. To reduce the tendency of gassing in the cell during a run the potential was applied only when a

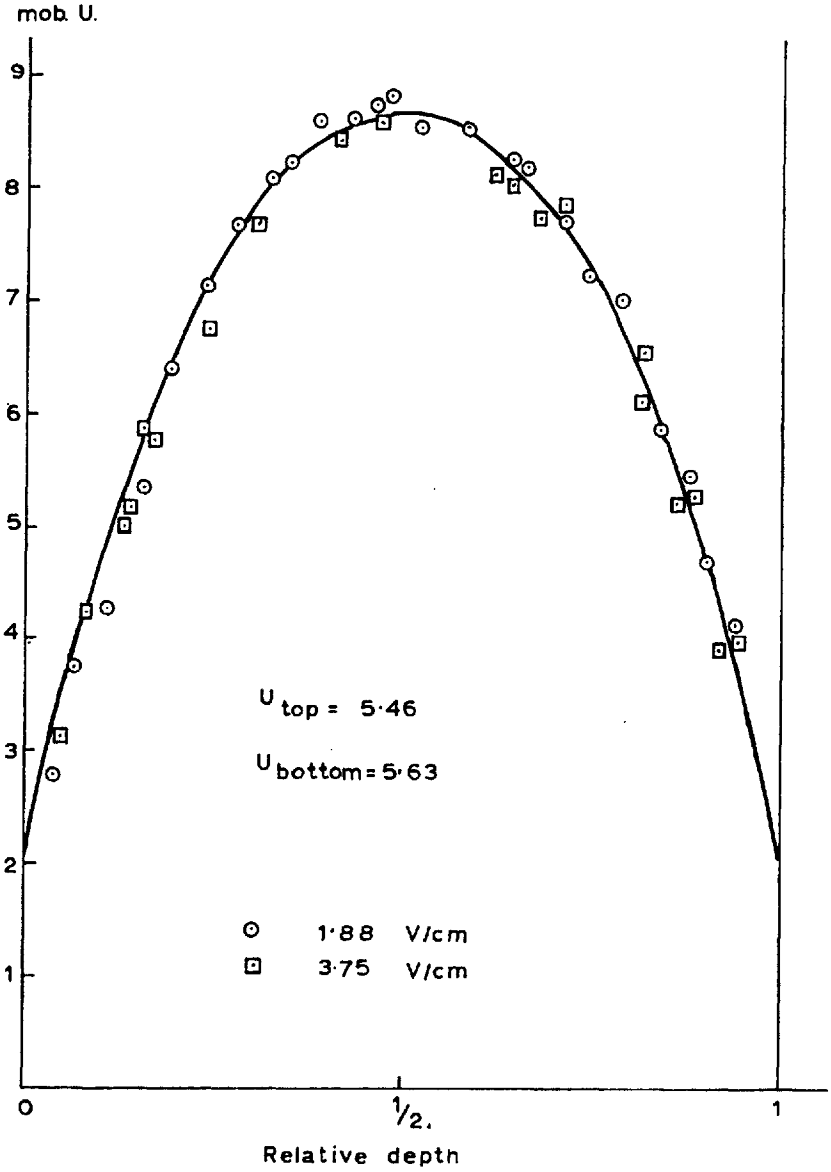


FIG.14 Mobility for different field strengths

particle had to be timed. The current flowing through the cell and the room temperature were recorded in the same time of measurement.

The potential gradient (E) in the capillary was determined from Ohm's law

$$E = \frac{I}{B\,K_s} \tag{19}$$

I, the current flowing through the cell, B the cross-section area of the capillary at the point of observation was determined by means of a mercury thread and K_s the specific conductance of the suspension.

To check the form of the velocity-depth curve and the influence of applied field on the mobility of particles, the complete parabola for two different potential gradients is shown in figure 14 for graphitized Sterling MT at full coverage. The figure shows that the mobility is independent of the applied potential gradient and the parabola is symmetrical; the mobilities read off the graph at a distance 0.147 units from each end of the relative depth differ by about 3°/o. Their mean differs by about 1°/o from the average mobility determined only at the two stationary levels. It is concluded, therefore, that measurements at the stationary levels are satisfactory. The results are reproducible to ± 2°/o for intermediate coverages and to about ± 3°/o for the lowest mobilities measured.

4. NEGATIVE ADSORPTION OF 'CO-IONS'

4.1. Introduction

As was pointed out in the main introduction (chapter 1), the presence of a charge at the solid-liquid interface, causes a redistribution of ions in the vicinity of the particle surface. Counterions are attracted and concentrated near the interface while co-ions are repelled, i.e., there is a deficit of charges of same sign in the electrical double layer. The phenomenon of negative adsorption can be explained by the assumption that a certain volume of liquid surrounding the particle is inaccessible for co-ions due to electrostatic repulsions. These ions will appear as an increase in the concentration of the dispersion phase. Figure 15 shows a schematic representation of concentration distribution of counterions and co-ions for a flat electrical double layer.

The Donnan (1911, 1924) equilibrium equations have frequently been used to study the equilibrium distribution of ions between an ion-exchange resin phase and an aqueous electrolyte. Kitchener (1959) however, in a comprehensive review of this work, had shown that abnormally low values of ionic activities in the resin phase were obtained from the Donnan equation for low external electrolyte concentrations, and Overbeek (1952, 1956) suggested that the Donnan theory cannot be used to describe the distribution of ions

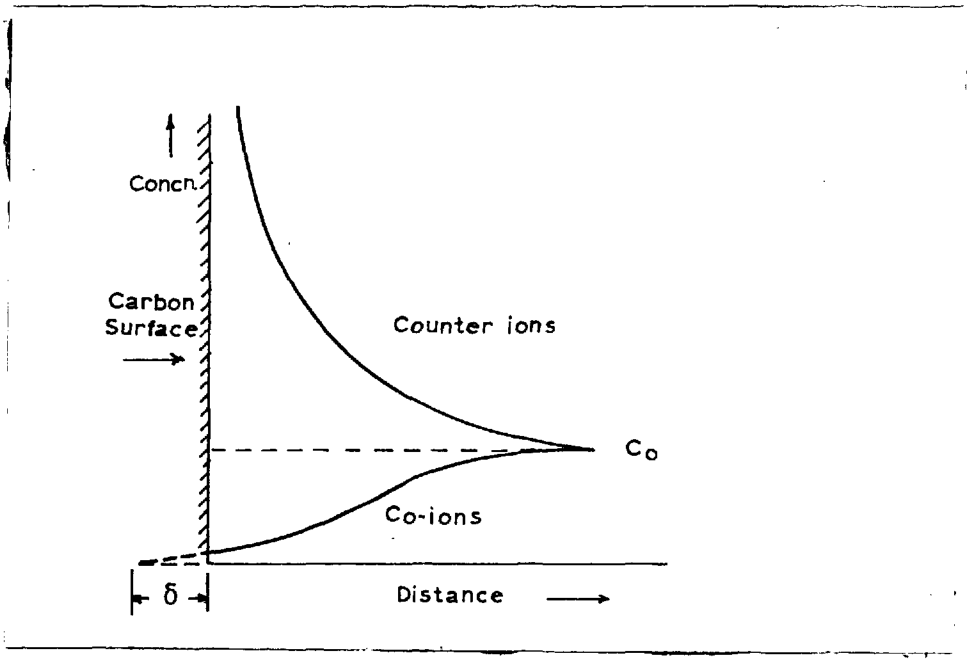


Fig. 15. Concn. of ions in the flat double layer $\zeta > 25$ mV.

in colloidal systems in which the electrical potential, and hence the concentration, varies within the colloid phase.

Schofield (1947), making use of the Gouy theory of the diffuse double layer, related the negative adsorption of co-ions to the surface charge density by the approximate equation

$$\frac{\Gamma^-}{C_o} = \frac{2}{(\beta\ C_o)^{1/2}} - \delta \qquad (20)$$

$$\simeq \frac{2}{(\beta\ C_o)^{1/2}} - \frac{4}{\beta\Gamma} \qquad (20a)$$

for uni-univalent electrolytes, where Γ is the surface charge density in the diffuse double layer in mequiv./cm^2, Γ^- is that part of Γ due to the deficit of the repelled ions, $\underline{C_o}$ the normality of the external solution and β stands for $8 \pi e^2 N/1000 \varepsilon kT$. The three terms in eqn. (20) have the dimension of distance (cm). The first term on the right hand side of the equation is a function of concentration and not charge and is in fact equal to twice the Debye-Huckel ionic atmosphere thickness ($1/\varkappa$). The second term $\delta \simeq 4/\beta\Gamma$ indicates the distance from the charged surface at which the extrapolated concentration-distance function (Fig. 15) of the co-ions would reach zero (i.e. potential approaching infinity), it is therefore a function of the distance between charges on the surface and hence the surface charge density.

Equation (20) was developed for flat surfaces and uniformly distributed surface charges. The distance between opposing surfaces should be large compared with the double layer thickness for there to be no appreciable overlapping of double layers. For highly charged surfaces the approximation was made that the distance δ can be expressed by $4/\beta\Gamma$. The full derivation of Schofield's equation, for symmetrical and non-symmetrical electrolytes where the extent of double layers overlapping is small, has been given more recently by Shone (1962). Schofield (1947) and Schofield and Talibuddin (1948) applied equation (20) for the study of negative adsorption of anions by bentonite and jute fibres at different salt concentrations and considered it to be a good approximation, irrespective of particle size and shape, provided the first term is several times the second one. But with decreasing electrolyte concentration when the two terms are of the same order of magnitude equation (20) cannot be applied quantitatively as the extent of overlapping of the double layers is not small in such cases.

The derivation of a general approximate equation for negative adsorption for symmetrical electrolytes to cover a wide range of concentration, was given by Bolt and Warkentin (1958) in the form

$$\Gamma-/C_o = 2/K_c - \delta \qquad (21)$$

where $$K_c = (\beta C_o\ (U_c + 1/U_c)/2)^{1/2} \qquad (22)$$

for flat surfaces, where $U_c = C/C_o$ represents the ratio of the concentration C at the mid-point between two opposing surfaces with overlapping double layers and C_o the concentration far away from the surface (potential → 0). The value of U_c can be calculated from a knowledge of the potential at the mid-point between the opposing charged surfaces by applying equation (1). For negligible double-layer overlapping equation (21) reduces to Schofield's equation (20).

Klaarenbeek (1946) was the first to treat the problem of negative adsorption accurately by taking into account the variation of the electrical potential in the different parts of the electrical double layer. The local concentrations were related to the local potentials and then the sum taken. Instead of describing the distribution of ions by the ratio of the concentrations in the two phases (Donnan equations), it was expressed as the fraction of the charge of the colloid that is compensated by an excess of counterions or by a deficit of co-ions respectively. This excess and deficit can be found by integrating the local concentrations over the available volume and subtracting the bulk concentration taken over the same volume. The total charge is found as the sum of deficit and excess. For a flat negatively charged surface and a uni-univalent electrolyte the fraction of the particle charge (α-) compensated by a deficit of co-ions (anions) is given by

$$\alpha_{-} = \frac{\exp(e\,\psi_o/2kT) - 1}{\exp(e\,\psi_o/2kT) - \exp(-e\,\psi_o/2kT)} \qquad (23)$$

α_{-} is, however, equivalent to Γ^{-}/Γ in equation (20) with any units to express their values, but for simplicity, the same units of mequiv./cm^2 will be used in equation (24) also.

Equation (23) which is equivalent to Schofield's equation (20) provided the limitations in the latter are fulfilled, shows that α_- increases with decrease in surface potential and approaches the value of 0.5 when $\psi_o \rightarrow 0$. Klaarenbeek (1946) considered also the problem of overlapping of opposing double layers at low electrolyte concentration or high colloid concentration or both. The overlapping obviously makes the absolute value of the potential higher and cuts off the low potential tail of the double layer. This leads to a decrease in the estimated value of α_- compared with expected if overlapping is not in play. Klaarenbeek derived a number of equations to account for overlapping but they involve considerable numerical computation and require a knowledge of the potential at the mid-point between the opposing surfaces. By applying these equations to gum arabic sols, Klaarenbeek found good agreement between the experimentally determined α_- and that calculated for overlapping double layers at constant salt content and varying concentration of gum arabic. Some of these results were reported by Overbeek (1952, 1956).

In the literature a limited number of investigations deal with the problem of negative adsorption by colloids. Negative adsorption of anions was studied for clay suspensions by Mattson (1929), Rutgers, and Hendrickx (1958), Chaussidon (1958) and Bolt and Warkentin (1958), for gum arabic sols by Klaarenbeek (1946) and for jute fibres by Schofield and Talibuddin (1948). In the field of ion-exchange resins, Shone (1962) found that equation (20) fits the results better than the Donnan equation for low electrolyte concentrations. Most of the reported work was for substances where either the surface area or the surface charge or both are not known accurately. The main object of the work was either to test the validity of the theoretical equations over a given concentration range or to determine surface areas and hence Γ , from values of negative adsorption per unit weight at different electrolyte concentration. No attempts have been made to correlate the experimentally calculated Γ with the actual charge on the surface, or to find out if Γ is of the same order of magnitude as the surface charge calculated from zeta-potentials.

The present work is, therefore, directed to calculating surface charge densities from negative adsorption results of co-ions for carbon black systems of known surface adsorption. As the magnitude of negative adsorption per unit area is small, the graphitized carbon black Graphon was used as it has a high surface area per unit weight. Its surface was charged to different prearranged values by adsorption of Aerosol OT. The ionic strength of the system was kept constant by working in 0.01 N or 0.001 N sodium chloride solutions. Negative adsorption of co-ions, if it could be determined satisfactorily, would provide useful information about the structure of the electrical double layer. It is a direct consequence of charge distribution and hence potential in the double layer and, being an equilibrium property, should not be influenced by the viscosity of the solution. Although the Gouy theory neglects the specific properties of the diffuse ions (apart from valency) it is likely that this omission will be less serious in considerations of the distribution of the repelled ions since the latter will largely occupy a spatial region in the double layer for which the basic assumptions of the Gouy model should be valid.

4.2. Experimental

i) Determination of negative adsorption of chloride

As the change in concentration in negative adsorption experiments is expected to be small, accurate estimation of chloride concentration is essential. For work with 0.01 N NaCl the differential potentiometric titration of chloride ion against silver nitrate solution was used, whereas for the negative adsorption experiments from 0.001 N NaCl, where the potentiometric titration would be less accurate, radio-active chlorine was used and its

β- activity determined. The methods of analysis and their accuracy are given below.

Potentiometric determination of chloride ion. The differential method of titration first suggested by Cox (1925) and later developed by MacInnes (1939) was used. The principle involves the use of two electrodes of the same type; one of the electrodes is left free in contact with solution, while the other is placed in a small glass tube dipped in the solution, connection between the solution surrounding the electrode and the main solution being through a fine capillary at the bottom of the glass tube to minimize mixing. The addition of a small volume (ΔV) of the titrating solution produces a small concentration difference between the main solution and its enclosed part and a measurable potential difference (ΔE) is set up between the two electrodes. Once this potential has been measured, the two solutions are mixed by applying pressure to force the solution out the glass tube through the capillary and fresh solution is allowed in. The process is repeated several times to ensure complete mixing and this can be checked by the zero potential measured between the two electrodes. Further additions of solution are made and the corresponding potential measured. The end-point is obtained as the maximum in the graph of ΔE against ΔV.

The differential method has the advantages of eliminating contamination of the titrated solutions by materials from liquid junctions and also no material is lost by diffusion into the latter. Although uncertainty due to liquid junction potentials is not entirely eliminated it is negligible since in the differential method the two solutions giving rise to a difference of potential ΔE are in all cases of very nearly the same concentration. The error involved in the observed end-point by holding out a small portion of the solution while each increment of titrating solution is added, is negligible (MacInnes 1939). In this work this error was always less than 0.1°/o.

Two silver electrodes were used in this work. Two platinum gauzes, about 1 sq. in. each, were rolled to form a tube, about 5 mm diam., and heavily coated with silver by electrodeposition from a solution of recrystallized potassium argentocyanide (MacInnes and Parker 1915). About 2g of 0.01 N sodium chloride in a total volume of 15 ml of 0.5 N ammonium nitrate were titrated against approximately 0.005 N silver nitrate. Small equal additions of titrant were made consecutively from a motorized piston micro-burette (Metrohm Ltd., Switzerland), and potentials measured to ±0.1 mV on a precision potentiometer (Tinsley Potentiometer, Type 4025). Aerosol OT was found to have no effect on the course of titration as proved by adding known amounts of it to sodium chloride solutions of known titre. Some of the results of titration in presence and absence of Aerosol OT are given here.

Wt. of 0.01 N NaCl (g)	Vol. of $AgNO_3$ (ml)	Vol. of $AgNO_3$/g 0.01 N NaCl (ml/g)
2.044	4.210	2.060
1.982	4.095	2.064
1.984	4.080	2.058
1.983 + 10 μ equiv. Aerosol OT	4.080	2.058

As shown from the last column the maximum difference on replicates was less than 0.3°/o and the differential potentiometric titration can be considered satisfactory for such low chloride concentration (about 0.001 N after dilution).

<u>Determination of chloride ion by radiotracer</u>. Radioactive chlorine was provided in the form of ≃ 4 N HCl^{36} by the Radiochemical Centre, Amersham (specific activity = 232 $\mu c/gCl^-$, (c = curie), half life period = 3×10^5 year, β-emissions of maximum energy = 0.7 MeV). A stock solution of 0.0225 N $NaCl^{36}$ was prepared by pipetting about 0.14 ml of the acid solution into a 25-ml measuring

flask and neutralizing to methyl orange with a standardized solution of 0.06 N sodium hydroxide. The flask was then made up to the mark. The total activity of the solution was about 4.5 μc. Solutions of 0.001 N $NaCl^{36}$ were prepared by diluting 4.45 g of the stock solution to 100 ml.

The β-radiation from 1 g of solution (0.001 N), dried on standard planchets, was determined by a windowless scintillation counter. The counter was a product of Isotope Developments Ltd., Aldermaston, and incorporates the following parts, a scalar type 1800, an amplifier - selector type 1830, a high voltage supply type 1820 and a scintillation counter type 663 A, fitted with a plastic phosphor (2 mm thick) and was inverted in position over a lead shielding drawer unit type 723. The samples were introduced to the counting position by means of a light-tight drawer, which holds the planchets in a lowered position for loading and raises them under the phosphor. Plots for the background count-rate and the net sample count-rate against the voltage (E.H.T.) applied to the photomultiplier at different input discriminator voltages and various amplification factors, were determined to find the best condition for counting. This condition for Cl^{36} was found, for a full channel width, to be at an E.H.T. = 0.61 kV, an input discriminator voltage of 15 V and amplification of x200. These setting figures satisfy the two conditions, firstly the sample count rate showed a minimum variation with variation with E.H.T. (corresponding to a point on the 'plateau' of the curve) and secondly the background count-rate was minimal compared with the sample count rate (Francis et al. 1959).

The counter was usually switched on one day before counting to insure stability. Sample and background counts were recorded for 3 1-hour or 6 half-hour intervals and the mean net count per minute used in the calculations. Samples for the original radio-active solution were prepared by transferring about 1 g of the solution (0.001 N $NaCl^{36}$) to a clean circular planchet (35 mm diam.) and 1 ml of 0.2 N sodium chloride solution was added to it to have the same solid weight on the planchet as in the case of experiments of negative adsorption. To prevent creeping of solution on the wall of the planchet and to have a firm deposit, 0.5 ml of gelatin solution (2 g/l.) was added. The solution was then evaporated slowly to dryness by an infra-red lamp. It was found sometimes that a low count was obtained if the solid was not uniformly distributed over the planchet. To overcome this possible error in results, samples were always redissolved by adding a little water, dried and then counted again. Consistent counts were taken as a confirmation of uniform distribution of solid on the planchet.

The weight of dired samples was the same in all experiments and equal to about 13 mg. The sample thickness was therefore about 1.3 mg/cm^2 and self-absorption is negligible and constant. The small resolving time (275 μ sec) of the scintillation counter (highest sample count = 120 c.p.s.) and long half-life period of Cl^{36}, make any corrections for the rate of counting negligibly small. The results of counting were accurate to better than ± 1^{o}/o.

ii) Determination of negative adsorption

To avoid direct determination of the slight increase in chloride concentration in the equilibrium solution due to negative adsorption (a few per cent, depending upon area of solid and volume and concentration of solutions) and possible contamination by ions leached from the carbon, the following method, depending on measuring the decrease in chloride ion in the electric double layer, was used to determine the negative adsorption. It is given in detail for experiments from 0.01 N NaCl solutions and slight modifications for isotopic work will be given later.

To a known weight of Graphon (about 2 g) in a 50-ml centrifuge cup was added 30 ml of an Aerosol OT solution in 0.01 N NaCl. The suspension was stirred for two hours at room temperature (17^{o}C ± 2^{o}C), centrifuged, if necessary, and the clear solution analyzed for equilibrium Aerosol OT. The carbon residue was then washed thrice with 20 ml portions of a fresh solution of Aerosol OT (of the same concentration as in equilibrium) in 0.01 N NaCl. Solutions were equilibrated for 30 minutes. After the last washing about 2 g of equilibrium solution were pipetted for determination of original concentration of chloride ion. The rest of the solution was finally syphoned carefully, and the weight of solution left in association with the carbon recorded. Its chloride content was then extracted in about 20 ml of 0.5 N ammonium nitrate (analytical grade, with no chloride reaction). The total weight of solution was recorded and after 30 minutes of continuous stirring a known weight of the clear solution (about 15 g) was analyzed for its chloride content. From the reduction in chloride concentration (compared with that expected for the weight of solution analyzed) and the surface area of the carbon the negative adsorption was calculated. To give a clear picture of this procedure, one experimental result is given here.

Wt. of Graphon = 1.997 g

Aerosol OT soln.: 30 ml of 4.353 mM Aerosol OT in 0.01 N NaCl

Wt. of Aerosol ads. = 0.[illegible]574 g

Wt. of 0.01 N NaCl for analysis (original concn.) = 2.028 g ≡ 4.15 ml Ag NO_3

Wt. of soln. associated with carbon = 4.052 g

Wt. of soln. associated with carbon + NH_4NO_3 soln.
= 20.494 g

Wt. of NH_4NO_3 soln. for analysis of Cl^- = 14.990 g

$\equiv$ 5.05 ml $AgNO_3$

= 2.468 g 0.01 N NaCl.

∴ weight of 0.01 N NaCl soln. in association with the carbon = 3.372 g

and weight of water free from chloride = 4.052 - 3.372

= 0.68 g

∴ negative adsorption of chloride ion = 3.4 μ equiv./g Graphon

= 4.06×10^{-9} μ equiv/cm^2

In experiments with isotopic chlorine 1 g Graphon and 15 ml Aerosol OT solution in 0.001 N $NaCl^{36}$ were used. After the last washing 1 g of equilibrium solution was transferred for counting and the rest of the solution syphoned. The isotopic chloride in the solution associated with the carbon was extracted by adding an equal volume of tracer-free 0.2 N NaCl (about 2 ml). The total weight of the solution was recorded and 2 g transferred and counted for their reduced Cl^{36} concentration. The room temperature was 20°C ± 2°C.

Loss in weight due to evaporation, especially in the last step of washing, was minimized by covering the centrifuge cup by tin foil. Solutions for counting were delivered directly to the planchets from a short 3-ml pipette, fitted with a rubber bulb, that could be hung from the tin cover on the centrifuge cup with its tip just below the surface of the solution. The weight of solution transferred to the planchet was recorded from the weight of the centrifuge cup and its contents before and after delivery.

The experiments were done in duplicate and to have different surface coverages the concentration of Aerosol OT was adjusted according to prearranged values. The difference between duplicates was between about 1 and 5°/o for the two series of experiments (0.01 and 0.001 N NaCl). The highest difference (5°/o) was found for the experiment with the lowest surface coverage in 0.01 N NaCl (table 22), probably because of the relatively small change in chloride concentration due to negative adsorption. For most experiments the difference was about 2-3°/o. This is a reasonable deviation in face of the number of steps taken in determining negative adsorption, the limited accuracy of analysis and the relatively small change in chloride concentration (10 - 30°/o). For all the experiments except that for the highest coverage in 0.001 N NaCl, the Aerosol OT concentration in equilibrium was small (< 2°/o) compared with the total chloride concentration in solution and therefore, no corrections were applied to account for the negative adsorption of Aerosol OT anions. For the highest coverage experiment in 0.001 N NaCl[36], the concentration of Aerosol OT in equilibrium was 5°/o that of chloride ion. The experimentally determined results for negative adsorption of chloride ion were therefore increased by 5°/o to correct for Aerosol OT anions in solution, assuming no preferential exclusion of anions from the electrical double layer. The density of 0.01 N and 0.001 N NaCl solutions was considered unity, the error involved in this approximation being far less than the experimental error. The double layer in presence of added salts in the step of extraction of chloride ion, is very thin and hence negative adsorption of anions in this case is of minor importance and will not influence the final results.

4.3. Results and discussion

Table 22 shows the results of negative adsorption of chloride ions by the negatively charged surface of Graphon. The ionic strength of the solutions was kept constant at 0.01 for the first set of results whereas in the second set it was 0.001. In each set the surface of Graphon was charged to 4 different values by adjusting the original concentration of Aerosol OT. The surface coverages given in the table were referred to full coverages by Aerosol OT (plateau of the adsorption isotherm) in the two salt solutions (210 and 200 μ equiv./g Graphon from 0.01 and 0.001 N NaCl respectively). Although, for the two salt solutions, two equal surface coverages have slightly different surface charge densities, they are used here for convenience in the discussion of results. The highest surface coverages studied were limited to 84 and 75°/o for the two sets of experiments respectively, as for higher coverages the concentration of Aerosol OT in equilibrium will be appreciable and its anions negatively adsorbed from the diffuse double layer thus causing a decrease in the experimentally measured change in chloride concentration and hence less accuracy in the results. (Also, at full coverages centrifugation was not efficient and filtration requires transfer of solid and hence the possible loss in material).

The results show that for the highest surface coverages (30°/o and higher) the negative adsorption of chloride ions changes little over this range. This indicates that the structure and distribution of ions in the diffuse part of the electrical double layer is, in each set of experiments, approximately the same irrespective of changes in the surfactant adsorption density on the surface. For the lowest surface coverage studied (10°/o) the negative adsorption dropped quite sharply for the experiment in 0.01 N NaCl but less sharply in the 0.001 N solution.

For calculation of surface charge density, Γ , from

TABLE 22. NEGATIVE ADSORPTION OF CHLORIDE IONS

a) From 0.01 N NaCl

Expt.No.	Wt.of Graphon (g)	Aerosol OT ads. (μ equiv./g)	Surf. coverage (%)	Chloride desorbed (μ equiv./g)
1	1.845	175.7	83.7	3.51 ± 0.07
2	2.114	113.3	54.0	3.66 ± 0.05
3	1.997	64.5	30.7	3.42 ± 0.02
4	1.869	20.2	9.6	1.44 ± 0.04

b) From 0.001 N NaCl[36]

1	1.000	150.7	75.3	0.685 ± 0.015
2	1.000	112.8	56.4	0.643 ± 0.006
3	1.000	65.2	32.6	0.635 ± 0.01
4	1.000	20.4	10.2	0.470 ± 0.01

any of the equations given above two main points have to be clarified, firstly the magnitude of 'overlapping' of opposing double layers in these systems (as the analytical data apply to sedimented carbon suspensions), and, secondly, the applicability of equations (20-23), derived for flat surfaces, to curved surfaces, as is the case here. For convenience the results of negative adsorption from 0.01 N NaCl will be discussed first.

i) <u>Negative adsorption of chloride ions from 0.01 N NaCl Overlapping of opposing double layers</u>. An approximate check of the extent of 'overlapping' can be obtained by considering the volume of the carbon sediment and calculating the thickness of the water film surrounding the particles. In 0.01 N NaCl solution the 2g of Graphon used (about 1 ml) occupy a sediment volume of about 4.5 ml; thus the volume of liquid in the sediment is about 3.5 ml. The packing density is about 22°/o i.e., an open packing. For separate Graphon particles of radius 125 Å the calculated spherical shell of water surrounding each particle amounts to 80 Å thick. A second and more probable configuration of carbon in the sediments is that the spherical particles form chains imbedded in a cylinder of water. The radius of this hypothetical cylinder was calculated and found to be about 215 Å. For a particle radius of 125 Å it is clear, therefore, that the least thickness of the water layer (film) is 90 Å. For 0.01 N NaCl the Debye-Huckel equivalent thickness of the double layer is 30 Å and, therefore, in all cases there is enough room for the double layer to extend without great overlapping with those of the opposite surfaces.

As Schofield (1947) had pointed out, overlapping is not significant if the thickness of the ionic atmosphere is less than half the distance between opposing surfaces.

A rough estimate of the magnitude of the latter can also be obtained by considering the experimentally determined nominal thickness of water layer completely free of anions (co-ions) that surrounds the solid surface. For coverages of 30°/o and higher the mean negative adsorption was 3.53 μ equiv./g Graphon, i.e., corresponding to 0.353 ml of 'water completely free' of chloride ions and for a carbon of surface area 84.3 m^2/g, this volume of water corresponds to a layer of water 42 Å thick (calculated for a flat surface). This last figure suggests that half the distance between opposing surfaces is more than 42 Å and hence greater than the thickness of the ionic atmosphere and, therefore, overlapping is not important here.

Calculation of theoretical negative adsorption from spherical double layers. Theoretical equations for negative adsorption are available only for flat double layers. For experiments from 0.01 N NaCl, with Graphon particles of radius a = 125 Å and $1/\varkappa = 30$ Å, $\varkappa a \simeq 4$ and therefore the surface can no longer be considered as a flat one and a comparison of the magnitude of negative adsorption for spherical and flat double layer is necessary. For spherical double layers the negative adsorption can be evaluated approximately by dividing the double layer into small shells of equal thickness and calculating the negative adsorption in each shell and finally summing up over the entire double layer thickness. The potential (ψ_x) at any point at a distance x from a curved surface is related to the surface potential ψ_o by the equation

$$\psi_x = \psi_o \frac{a}{R} \exp(-\chi x)\, C_{(r)} \qquad (24)$$

based on the numerical solution of the Poisson-Baltzmann equation by Hoskin (1953), where R = a + x and $C_{(r)}$ is a function of χR for a given value of surface potential and χa and given in tables by Hoskin.

The concentration of co-ions at a point x from the surface is related to ψ_x by the Boltzmann relation

$$C_- = C_o \exp(e\,\psi_x/kT) \qquad (25)$$

and the quantity (equivalents) of co-ions in shell of thickness dR is

$$= C_- (4\pi R^2)\, dR \qquad (26)$$

The negative adsorption in shell = $(C_o - C_-)\, 4\pi R^2\, dR$ (27)

$$\text{Total negative adsorption} = 4\pi \int_{R=a}^{R=\infty} (C_o - C_-) R^2 dR \qquad (28)$$

Substituting for the value of C_- from equation (25), the approximate negative adsorption is given by

Approximate negative adsorption =

$$= 4\pi C_o \sum_{1}^{n} \left[1 - \exp(e\,\psi x/kT)\right] R^2 \Delta R \qquad (29)$$

per particle of radius (a). For negative adsorption per unit area, the resultant value from equation (29) was divided by the area/particle.

Equation (29) was used to calculate the theoretical negative adsorption for two surface potentials (ψ_o) of 100 and 50 mV. The function $C_{(r)}$ (eqn.24) was obtained from Hoskin's tables for a value of $\varkappa a = 3$. The summation was carried out to cover a liquid film surrounding the particle from the particle surface to a distance of $\varkappa x = 4$ (i.e. x = 120 Å). At this distance the potential ψ_x is reduced to a negligible value (< 1 mV). The thickness ΔR of each shell was taken equal to 7.5 Å, i.e. n = 17. The area under the curve for the negative adsorption as a function of distance (eqn.29) was obtained by applying Simpson's rule to the calculated values. If y is put equal to $\left[1-\exp(e\,\psi x/kT)R^2 \right]$ then for 17 values Simpson's rule gives the value of the summation in equation (29) as equal to

$$\Sigma = {}^1/3\ \Delta R \Big[(y_1+y_{17}) + 2(y_3+y_5+\dots+y_{15}) + 4(y_2+y_4+\dots+y_{16}) \Big] \qquad (30)$$

For each surface potential (50 and 100 mV) the corresponding surface charge density Γ (or σ) was calculated from the numerical tables for spherical double layers ($\varkappa a = 3$) given by Lyklema and Overbeek (1959). For flat surfaces, the theoretical negative adsorption was calculated from Klaarenbeek's equation (23) for the same surface potentials (50 and 100 mV.), and the corresponding surface charge densities from the full equation for high potentials (eqn.10). The results of these calculations are shown in table 23.

TABLE 23. THEORETICAL NEGATIVE ADSORPTION FOR FLAT AND SPHERICAL DOUBLE LAYERS

a) ψ_o = 100 mV.

Double layer	Neg.ads. Γ^- (m.equiv./cm^2)x10^9	Surf.charge density (m.equiv./cm^2)x10^8	Γ^-/Γ (°/o)
Flat	5.22	4.17	12.52
Spherical	7.00	5.05	13.86

b) ψ_o = 50 mV.

Double layer	Neg.ads. Γ^- (m.equiv./cm^2)x10^9	Surf.charge density (m.equiv./cm^2)x10^8	Γ^-/Γ (°/o)
Flat	3.79	1.38	27.46
Spherical	4.80	1.81	26.52

Thus from the last column in table 23 it is clear that, for spherical double layers, the fraction of surface charge that appears as negative adsorption is about 10°/o higher than for that of a flat double layer for the higher potential of 100 mV., but slightly less ($\simeq$ 4°/o) for the lower potential of 50 mV. These figures may be slightly altered by a few per cent (increase in Γ^- for spherical double layer) if the summation were carried out to still increasing values of distance from the surface (for flat surfaces the integration is carried to infinity). However, the effect of extending the summation is not large and it may be concluded that for a given surface charge density the negative adsorption is not much altered by the curvature of the surface in that particular system. As the experimental results for negative adsorption (in 0.01 N NaCl) apply to a system intermediate between those calculated for ψ_o = 100 and 50 mV, the error involved in using flat double layer equations (20 - 23) is not serious and not more than 5°/o.

Another approach to the problem of overlapping of opposing double layers can be made by calculating for the above two potentials the theoretical negative adsorption in the spherical liquid film surrounding the particle up to a distance of $\varkappa x = 3$ i.e., to a distance of 90 Å from the surface (assuming no change in potential distribution due to double layers overlapping). The calculations showed that the net effect of overlapping is a reduction in the magnitude of negative adsorption and amounts to about 10°/o for ψ_o = 100 mV and about 6°/o for the lower potential of 50 mV. Therefore, the effects on negative adsorption results due to surface curvature and overlapping of opposing double layers are of opposite sign and probability partly cancel in these 0.01 N sodium chloride solutions.

Table 24a shows the values of the diffuse charge densities (Γ) calculated from the experimentally determined negative adsorption of chloride from 0.01 N NaCl using Schofield's equation (20). In the same table are included the actual surfactant surface charge ($\Gamma_{ads.}$) obtained from the amount of Aerosol OT adsorbed from solution, and the term δ for checking the applicability of equation (20). For the first three points (coverages 30 - 85°/o) the value of δ is always less than 1/3 of $(1/\beta\ C_o)^{1/2}$ and therefore equation (20) can be applied to the results of negative adsorption (Schofield 1947). For the lowest coverage studied (10°/o) the experimental negative adsorption gave a value of δ which is comparable with ($\simeq$ 2/3) the first term and, therefore, a quantitative application of equation (20) is not permissible. As the number of charges on the surface are greatly reduced, in the last case, the assumption that δ can be approximated by $4/\beta\Gamma$ is not valid as it is only the case for a highly uniformally charged surface. Bolt's equation (21) cannot be applied for this case of low surface coverage as the equation deals with overlapping of opposing double layers, which is not much in 0.01 N solutions, rather than corrections for the term δ. It can be concluded, therefore, that the calculated values of (Γ) given in table 24a are a measure of the charge density in the diffuse double layer for coverages

TABLE 24. SURFACE CHARGE DENSITIES FROM NEGATIVE ADSORPTION OF CHLORIDE IONS

a) From 0.01 N NaCl ; $2/(\beta Co)^{1/2} = 6 \times 10^{-7}$ cm.

Surf.coverage ($^{o}/o$)	Γ^- (m. equiv./cm^2) x 10^9	δ (cm)x10^7	Γ (m.equiv./cm^2) x 10^8	$\Gamma_{ads.}$ (m.equiv./cm^2) x 10^7	$\frac{\Gamma}{\Gamma_{ads.}}$ ($^{o}/o$)
83.7	4.16	1.84	1.96	2.08	9.4
54.0	4.34	1.66	2.17	1.34	16.2
30.7	4.06	1.94	1.86	0.77	24.1
9.6	1.71	4.29	0.84	0.24	(35.0)

b) From 0.001 N $NaCl^{36}$; $2/(\beta Co)^{1/2} = 1.9 \times 10^{-6}$ cm.

Surf.coverage ($^{o}/o$)	Γ^- (m. equiv./cm^2) x 10^9	δ (cm)x10^7	Γ (m.equiv./cm^2) x 10^8	$\Gamma_{ads.}$ (m.equiv./cm^2) x 10^7	$\frac{\Gamma}{\Gamma_{ads.}}$ ($^{o}/o$)
75.3	0.81	10.9	0.33	1.79	(1.8)
56.4	0.76	11.4	0.32	1.34	(2.4)
32.6	0.75	11.5	0.31	0.77	(4.1)
10.2	0.56	13.4	0.27	0.24	(11.2)

of 30°/o and higher and only for the 10°/o coverage that the listed value of (Γ) is uncertain.

From table 24(a) it is clear that the charge density Γ of the diffuse part of the electrical double layer, calculated from equation (20), is a fraction of the actual surfactant adsorption charge on the surface of Graphon ($\Gamma_{ads.}$). It is equal to 9.4°/o of the surfactant charge for the higher coverage of 84°/o, but with decrease in surface charge a higher proportion of the total charge appears as a diffuse double layer and reaches a value of 24°/o for the 31°/o surface coverage and a still higher proportion (probably more than 35°/o) is expected for the lowest surface coverage of 10°/o. The reasons for the diminished charge in the Gouy's diffuse part of the electrical double layer will be discussed in chapter (6) with the general discussion of electrokinetic results.

ii) <u>Negative adsorption of chloride ions from 0.001 N NaCl</u>[36]. Comparison of these results with theory presents certain problems. In 0.001 N NaCl solution the electric double layer extends further than in 0.01 N NaCl solution and $1/\varkappa$ reaches 95 Å (at 20°C), and therefore the value of $\varkappa a$ is smaller ($\simeq$ 1.3). The packing of the carbon in the seddiment is not much different from that in 0.01 N NaCl and therefore overlapping of opposing double layers is more serious as half the distance between opposing surfaces is comparable with $1/\kappa$. This is clear from table 24b where the value of the second term δ (eqn. 20) is always larger than half the first term at all the surface coverages studied. This makes a check for the application of flat double layer equations for the negative adsorption results from these curved surfaces unnecessary as qualitative rather than quantitative use of the negative adsorption results is appropriate. Application of Bolt's equation (21) to allow for the opposing double layers overlapping requires a knowledge of the potential at the mid-point between the opposing surfaces. In this particular system for negative adsorption the half distance between the opposing surfaces is not accurately known and the same is true for the potential at that point. But for a qualitative application of Bolt's equation, to show the effect of overlapping, this distance can be assumed equal to 90 Å (as in 0.01 N solution and a chain of Graphon particles) and then the potential at the 'mid-point' between the surface can be calculated. Another approximation required for these calculations is the use of the experimental zeta-potential as a measure of surface potential and assumption that there is no change in potential distribution due to overlapping of double layers. Only one result (for

56°/o coverage) will be checked to show the influence of Bolt correction on the magnitude of Γ.

For $\Psi_o = \zeta = -83$ mV, the corresponding potential at a distance 90 Å from the surface is equal to -27 mV (calculated from eqn.(6) for high potential and flat double layer). The value of $U_c = C/C_o$ in equation (22) can be calculated from equation (1) and is equal to 2.94 and hence $K_c = 1.347 \times 10^6$ cm^{-1}. The value of $2/K_c$ is equal to 1.48×10^{-6} cm compared with 1.90×10^{-6} cm for $2/(\beta C_o)^{1/2}$. The values of δ, Γ and $\Gamma / \Gamma_{ads.}$ for Bolt's equation are 7.2×10^{-7} cm, 5.02×10^{-9} m.equiv./cm^2 and 3.7°/o respectively, while the corresponding values from Schofield's equation are 11.4×10^{-7} cm, 3.2×10^{-9} m.equiv./cm^2 and 2.4°/o respectively. This approximate correction for overlapping shows an increase in the corrected values of Γ and $\Gamma / \Gamma_{ads.}$. A quantitative correction for overlapping could only be determined if the exact potential and hence U_c in Bolt's equation at the point mid-distance between opposing surfaces were accurately known, but these are not available in this system of negative adsorption measurements.

Table 24(b) shows the values of δ, Γ and $\Gamma / \Gamma_{ads.}$ calculated from the experimental values of negative adsorption of chloride ion using Schofield's equation (20) without any corrections. They are listed only to show their magnitude and not as a quantitative measure of charge in the diffuse electric double layer. Qualitatively the results show a marked increase in the proportion of the surfactant adsorption charge that appears in the diffuse part of the electric double layer with decrease in surface charge density. In spite of the lack of quantitative significance of the negative adsorption results from 0.001 N sodium chloride solutions, the results show that the general picture of the double layer is not altered much by working at two different ionic strengths. The two sets of results show that the negative adsorption of co-ions and hence the electric potential in the diffuse double layer changes slightly over a wide range of surface ion densities ($\simeq$ 23,000 - 60,000 e.s.u./cm^2 or $\simeq$ 0.8 - 2.0 x 10^{-7} m.equiv./cm^2), and a decrease in negative adsorption is obtained for the two sets of results at the lowest surface coverage studied (10°/o).

It would be ideal, of course, to measure negative adsorption of co-ions from solutions of 0.1 N NaCl to avoid double layers overlapping, but this would require the use of a surface of an even higher area than Graphon to obtain measurable changes in electrolyte concentration.

Application of Klaarenbeek's formula (eqn.23) to negative adsorption results necessitates the use of one of two quantities, the charge or the potential in the electrical double layer. As the calculated charge in the Gouy's diffuse double layer is always different from the surface charge the latter cannot be used in equation (23) to calculate the electrical potential. A more appropriate test for the negative adsorption results and hence the structure of the double layer would be, however, to use the determined zeta-potentials and hence its diffuse charge densities to calculate the theoretical values of negative adsorption, comparing them with the experimentally determined values of negative adsorption. This test suffers, however, from the uncertainty of the measured zeta-potential, due to use of bulk solution viscosity and not the actual value of viscosity in the electrical double layer. Alternatively, comparison between experimental negative adsorption and that calculated from conventional zeta-potentials could be regarded as a test of the assumption that the viscosity in the diffuse double layer is, or is not, normal. Application of equation (23) to negative adsorption will, therefore, be discussed in chapter (6) after considering the significance of the measured zeta-potentials and the effect of the viscosity term.

5. SURFACE CONDUCTANCE

5.1. Introduction

It had been observed, as early as 1893 by Reinhold and Rucher, that the conductivity of black soap films is several times the conductivity of the bulk solution and that the difference between the two conductivities is greatly diminished by addition of inorganic salts. Fricke and Curtis (1936) were able to prepare suspensions that had twice the conductivity of the suspending fluid. The increased conductance in such cases is due to the ions associated with the interface and is called 'surface conductance'. The surface conductance originates from the fact that the electrical double layer surrounding a particle , for example, contains a higher number of ions per unit volume than the liquid in bulk. On application of an electric field, ions in the double layer that still possess free movement will contribute to surface conductance. It is expected, however, that although the primary charges on the surface are responsible for the presence of the electrical double layer, they do not contribute to surface conductance; nevertheless, they contribute to bulk conductance of suspensions by the movement of the whole particle (electrophoretic mobility, Henry 1948). The mobile ions in the diffuse double layer are, therefore, the ones responsible for surface conductance.

Its magnitude depends, for a given system, on the mobility and number of ions in the diffuse double layer in excess of those normally present in bulk solution.

Another factor in surface conductance is the electro-osmotic movement of the liquid film surrounding the particles: this modifies the mobility of the ions in the electric double layer. Electro-osmosis occurs because the diffuse part of the double layer carries a charge opposite to that on the surface. The ions in the charged liquid layer move, therefore, relatively to the solid with a mobility which is the sum or difference of the electro-osmotic mobility and the ordinary ionic mobility.

The theory of surface conductance was worked out by several authors - notably Bikerman (1933, 1935) and Urban, White and Strassner (1935). The theoretical surface conductance (σ_s) due to excess ions in the Gouy diffuse double layer is given by the following expression, for uni-univalent electrolytes and a negative surface.

$$\sigma_s = \left(\frac{\varepsilon kTc}{2\pi Ne^2}\right)^{1/2} \left[(e^{e\zeta/2kT} - 1)\left(\lambda_+ + \frac{\varepsilon RT}{2\pi\eta}\right) + (e^{-e\zeta/2kT} - 1)\left(\lambda_- + \frac{\varepsilon RT}{2\pi\eta}\right)\right] \qquad (31)$$

where λ_+ and λ_- are the ionic conductances of the cation and anion in bulk solution respectively. The term $\varepsilon RT/2\pi\eta$ represents the contribution of electro-osmosis to conductance.

It was suggested by Bikerman (1933) that as the electro-osmosis term involves the movement of the whole liquid it would disappear with alternating currents of frequencies much lower than those required for the Debye-Falkenhagen effect (1928) with ordinary conductivities (10^7 cycles/sec.). On the other hand Rosenhead and Miller (1937), from a theoretical analysis, concluded that the 'dispersion' of electro-osmosis is not in evidence even at frequencies as high as 10^5 cycles/sec. and that electro-osmosis is expected to disperse at frequencies comparable with those that produce the ordinary Debye-Falkenhagen effect. Experimentally, Fricke and Curtis (1936) found that surface conductances are practically independent of the frequency between 500 and 10^5 cycles/sec., and Urban, Feldman and White (1935) did not observe much difference between the surface conductance for direct current and 1000 cycles alternating current.

Urban, White and Strassner (1935) modified equation (31) to include additional terms to account for the contribution to surface conductance by the ions in the Stern layer. Although their modified equation was based on a number of approximations regarding the number of ions in the Stern layer, it showed a better agreement with their measured surface conductances than equation (31). However, it seems unlikely that ions in the Stern layer would have sufficient mobility to contribute significantly to surface conductance.

Several methods and equations have been developed for estimating surface conductance of different systems, such as capillary tubes (Rutgers and de Smet, 1947), insoluble monolayers (McBain and Peaker 1929) and suspensions of different particle forms (Fricke and Curtis (1936), and Street, 1956, 1960).

For suspensions of spherical particles Fricke and Curtis (1936) developed an equation for determining surface conductance, based on an expression deduced by Maxwell (1892). For non-conducting spheres of radius (a) the surface conductance (σ_s) per unit area is given by

$$\sigma_s = \frac{K_1 a \left[(K/K_1 - 1) + \rho/2(K/K_1 + 2)\right]}{\rho(K/K_1 + 2) - (K/K_1 - 1)} \qquad (32)$$

where K and K_1 are the specific conductivities of the suspension and suspending medium respectively and ρ the volume concentration of the solid in suspension. Depending on the particle radius, salt content (conductivity) and the magnitude of surface conductance, K in equation (32) can be equal to, less than or greater than K_1. Equation (32) is based on the assumption that the thickness (t) of the region from which the surface conductance is derived, is small compared with the radius of the suspended particle so that $(a+t)^3$ can be approximated to $a^3 + 3ta^2$.

Henry (1948) stressed that for fine particles (< 1 μ) the measured suspension conductivity should be corrected for the conductivity (K_p) caused by the movement of the charged particles in the electric field. Henry showed that K_p is equal to

$$K_p = \frac{3\rho}{a} \cdot U \sigma \tag{33}$$

where U is the mobility of the particles and σ its specific charge density. K in equation (32) is therefore equal to $K_{susp.} - K_p$ where $K_{susp.}$ is the measured suspension conductivity.

The problem of measuring surface conductance and comparing it with the theoretical values obtained from equations (31) using the zeta-potential, has been considered by several workers; glass interfaces have been most studied. Overbeek (1952) and Davies and Rideal (1961) tabulated some of the published surface conductances. From the tables it can be seen that for the same system great deviations (up to a 100 times) were found. These deviations are probably mainly due to the unreliable surfaces used and the various ways in which measurements and calculations were used. Bikerman (1942) pointed out that, for glass surfaces, there is the possible swelling of the walls of the glass pores which could lead to anomalously high surface conductance if ions can pass along the swollen region.

The agreement or disagreement between measured and calculated values of surface conductance is, therefore, subject to the choice of a suitable interface for work. Reasonable agreement was found, for example, for clay suspensions in different salts by Street (1956, 1960). Among those who found disagreement between the theoretical and experimental values of surface conductance are Mossman and Mason (1959) for cylindrical pads of different fibrous materials and van Olphen (1957) for bentonites in different cation forms. In all cases the experimental surface conductance was always several times the theoretical one, calculated from the zeta-potential of the system involved.

In this work it was, therefore, planned to measure the surface conductance of graphitized carbon blacks with their surfaces covered with a monolayer of Aerosol OT, and to compare these values with the theoretical surface conductances calculated from the zeta-potentials of these carbons under the same conditions. From these measurements it is possible, in principle, to obtain some additional information about the structure and distribution of ions in the electric double layer. The experimental values can be also used to check the magnitude of surface conductance in retarding the electrophoretic mobility of particles.

5.2. Experimental

The surface conductance measurements were made by adding a known weight of graphitized carbon black to a known volume of Aerosol OT (about 100 ml) in water or in 0.01 N NaCl. In all cases the original concentration of Aerosol OT was sufficiently high so that after adsorption by the carbon (a few percent) the equilibrium concentration ranged between 2 and 3 times the c.m.c. The suspension, in a 100-ml flask fitted with a B-24 stopper, was stirred all the time with a magnetic stirrer. Dispersion of the carbon was achieved by exposing the suspension to ultrasonic waves for 5 minute periods 3 or 4 times in the course of about 4 hours. This treatment was found enough for dispersing the carbon as shown by the constancy of the suspension conductivity, and the fact that the resistance of the suspension became independent of rate of stirring. Also, only a small capacitance (< 0.001 μF) was then required to balance the bridge. To make stirring possible during the run, the 100-ml flask was enclosed in a small glass vessel and water from a thermostat ($25 \pm 0.05^{\circ}C$) was circulated by a pump round the flask at the rate of 4 - 5 l./min.

After attainment of equilibrium, the conductivity of the suspension was recorded, the carbon removed by centrifugation and the conductivity of the clear suspending medium measured. A dipping-type conductivity cell (Mullard) was used after fitting it with a B-24 cone to fit the flask. In all cases the level of the solution to be measured was about 2 cm above the top holes of the conductivity cell.

The conductivity was determined by a conventional bridge consisting of ratio arms of resistances up to 10,000 ohm (± 0.05°/o), adjusted to 1000 ohm each, a decade resistance up to 111,111 ohm across which was put a moving-vane air condenser of capacity 0.001 μF and finally the unknown resistance of the cell to be measured. An Advance oscillator (type H-1) was used at 1000 cycles/sec frequency, of sinesoidal wave form; the voltage output could be varied from 0 - 20 V. A transformer was placed between the oscillator and the conductivity bridge. The balance in the latter was detected by means of a cathode ray oscilloscope (Q - Scan, Marconi Instruments Ltd.). Two opposite points of the bridge were connected, through a transistor amplifier to the Y-plates of the oscilloscope. The X-plates of the latter were fed directly from the oscillator. All the leads were screened and the screening as well as the water-thermostat were earthed at a common point.

When the amplifier input to the cathode ray oscilloscope (c.$\overset{r}{\gamma}$.O) was zero a horizontal line appeared on its screen the length of which depended on the voltage input from the oscillator. The latter was adjusted, in conjunction with the sensitivity and attenuater switches for the x-plates of the c.r.o., until an oscillator output of about 1 - 1.5 volts gave a straight line extending over about 5/6 of the screen. If the bridge was not balanced and the amplifier input on, the straight line did not remain horizontal and also tended to become ellipsoidal, if the capacitances were not balanced. The balance in the bridge was obtained by adjusting the decade resistance together with the air condenser until a straight horizontal line is obtained on the screen of the c.r.o.

The conductance bridge was sensitive to ± 0.4 ohm in 1000 ohm. The small capacitance (< 0.001 μF) across the decade resistance did not necessitate correction for the resistance of the conductivity cell (Vigoureaux and Webb 1936).

The cell constant of the conductivity cell was determined by measuring its resistance with a standard solution of recrystallized potassium chloride. The chloride content of the solution was determined gravimetrically as silver chloride and the solution conductance was calculated from the empirical equation given by Shedlovsky (1934). The cell constant was found to be 1.40 ± 0.004 cm^{-1}.

The volume concentration of the carbon in suspension was calculated from the weight of the carbon used and the total volume of suspension. For this case the density of the graphitized Sterlings MT and FT was determined by displacement of purified benzene in a 50-ml specific gravity bottle at 25°C, and found to be 2.15 ± 0.01 g/c.c.

5.3. Results and discussion

The surface conductance was determined for graphitized Sterling MT and Sterling FT with their surfaces fully covered with Aerosol OT from water solutions for the former carbon and from 0.01 N NaCl for the two carbons. These systems were chosen so that κa should be always greater than 34 and hence the approximation in the equation of Fricke and Curtis (eqn. 32) is valid. The conductivity of the suspension was corrected for the contribution by the mobility of the charged particles (K_p, Henry's correction). In all cases it was found that the suspension conductivity was less than that of the suspending liquid, as the contribution from surface conductance to the total conductivity of the suspension was small compared with the effect of the volume of the particles. Isolated particles of carbon of size $< 0.5\mu$ are expected to behave as insulators in suspension due to surface polarization: the reduced total conductance proves that this is so.

Table 25 shows the measured surface conductances for the three systems studied at different volume concentrations of carbon. The results show a random variation of surface conductance with volume concentration. The large error observed in some results is due to the small change in the conductivities K and K_1 (< $4^{o}/o$) because in calculating surface conductance (eqn. 32) differences are involved. However, the means of the results for the two carbons in 0.01 N NaCl solution show reasonable agreement. For both cases the surfaces had the same adsorption density and as the ionic strength was the same, the structure of the double layer should, indeed, be comparable. The results for Sterling MT in absence of added sodium chloride (Table 25c) show a high value of σ_s at the highest volume concentration measured. It is about 4 times the mean of the first three points ($\sigma_s = 0.78 \pm 0.21$) where the volume concentration is small and only slightly different from each other. Similar discrepancies in results were found by Street (1956) and van Olphen (1957).

Attempts to measure surface conductance as a function of surface coverage for these systems were not successful. To have a ~~reasonabl~~y measurable change in σ_s, the surface coverage ought to be reduced considerably; but it was found that, for coverages below $80^{o}/o$, although the carbon can be easily dispersed by ultrasonic waves, the suspension showed within a few minutes of this treatment a marked increase in capacitance and conductance which was dependent

TABLE 25. SURFACE CONDUCTANCE RESULTS FOR GRAPHITIZED CARBON BLACKS

Vol.concn. ρ	$K_{susp.}$ (ohm^{-1} cm^{-1}) x 10^3	K_1 (ohm^{-1} cm^{-1}) x 10^3	K_p (ohm^{-1} cm^{-1}) x 10^6	σ_s (ohm^{-1}) x 10^9 Expt.	Calc.
	a) Sterling MT - Aerosol OT - 0.01 N NaCl				
0.0218	1.523	1.566	4.71	1.46	
0.0255	1.483	1.531	5.52	0.92	
0.0306	1.509	1.565	6.62	1.39	
			mean	1.26±0.29	1.60
	b) Sterling FT - Aerosol OT - 0.01 N NaCl				
0.0167	1.529	1.551	7.07	1.34	
0.0189	1.520	1.545	8.00	1.42	
0.0237	1.503	1.534	10.00	1.32	
				1.36±0.05	1.55
	c) Sterling MT - Aerosol OT - water				
0.00465	0.5005	0.5030	0.490	0.514	
0.00484	0.5019	0.5043	0.520	0.81	
0.00535	0.4997	0.5021	0.576	~~0~~1.01	
0.01766	0.4823	0.4850	1.90	3.13	
				1.36±1.21	1.04

on the rate of stirring. This effect was undoubtedly due to aggregation, and consequently the system could no longer be treated as a monodisperse suspension.

The theoretical surface conductance due to ions in the diffuse double layer was calculated from equation (31) using the estimated values of zeta-potential and the ionic conductances of the ions concerned. The zeta-potentials were -81.7, -87.7 and -80.7 mV for Sterling MT in 0.01 N NaCl and in water and for Sterling FT in 0.01 N NaCl solution respectively (all for full coverage with Aerosol OT). The ionic conductances for sodium and chloride ions at infinite dilution (25°C) were taken from Robinson and Stokes (1955) and their corresponding values at the experimental concentration (c.m.c. of Aerosol OT and sodium chloride if added) were calculated from the empirical equations given by Bockris (1959). For Aerosol OT anion the equivalent conductivity (25°C) was taken from the data of Brady and Salley (1948). In presence of added sodium chloride, where chloride as well as Aerosol OT anions are present, the mean conductance of the anions (averaged according to their proportions in solution - 100 parts Cl^- and 13 parts Aerosol OT), was used in equation (31). The ionic conductances used in calculations were:

λ_{Na^+} (no NaCl) = 48.1 ohm^{-1} cm^2 equiv.$^{-1}$
λ_{Na^+} (added NaCl) = 46.2
λ_{anion} (mean) = 65.9
$\lambda_{Aerosol}$ (no NaCl) = 21.0

Table 25 shows that the theoretical values of surface conductance, calculated for a Gouy diffuse electrical double layer, are in agreement with the measured values for the three systems studied to within the rather large limits of experimental error. This result is in favour of the hypothesis that the zeta-potential is a measure of the potential in a part of the double layer where the ions are present in a medium of normal viscosity and normal ionic mobilities.

Although surface conductance data are consistent with the measured zeta-potential, they cannot give conclusive evidence as to the diminished value of zeta compared with the theoretical surface potential. The two possible reasons for this deviation namely, viscosity effects or Stern adsorption of counterions, would have the same effect on the measured surface conductance. A sharp increase in viscosity of the liquid close to the interface due to the high electric field would reduce the ionic mobilities in this region and their contribution to surface conductance might be negligible. On the other hand specifically adsorbed counterions in a Stern layer can hardly have sufficient mobility to show in surface conductance.

Urban, White and Strassner (1935) argued that ions in the Stern layer should contribute to surface conductance and derived expressions based on Stern's theory; approximate values for available adsorption sites on the surface, and increased viscosity in the Stern layer were assigned. Although the additional conductance showed a better agreement with their experimental results - which was taken as evidence of the correctness of their assumptions - the added corrections were in some cases insignificant while their measured surface conductances are rather higher than those reported by many workers. For example, Urban et al. reported, for glass particles, values of σ_s equal to 37.2 and 7.39 x 10^{-9} ohm^{-1} for 10^{-2} and 10^{-3} N KCl solutions respectively whereas Fricke and Curtis (1936) found 1.8 and 0.58 x 10^{-9} ohm^{-1} for the same systems.

At the present time it can be said that the measured surface conductance represents the extra conductance associated with excess ions in a diffuse double layer whose potential is represented by the zeta-potential estimated from electrophoretic mobility. Also, the small magnitude of the measured surface conductance for these systems suggests that its retarding effect on electrophoretic mobilities of the particles is not large. The effect is allowed for in Overbeek's theory of electrophoresis.

6. ELECTROPHORESIS RESULTS AND DISCUSSION

Electrophoretic mobilities were determined for dispersions of graphitized carbon blacks with their surface charged to different values by adsorption from solution of Aerosol OT or Cetavlon. The surface adsorption charge was adjusted as required by controlling the original surfactant content in solution as outlined in the experimental part of this work (Chapter 3). Some mobility measurements were made with pure surfactant solutions in water and others in presence of 0.01 N inorganic salts. With the three graphitized carbons, Graphon, Sterling FT and Sterling MT of different particle size, these mobility measurements cover a wide range of κa from about 1 - 82; and can serve as an experimental test of the theories (Henry 1931 and Overbeek 1943) correcting for particle size and relaxation effects and in particular to Overbeek's relaxation corrections in the region of maximum relaxation (κa 1 - 10, Fig. 11) for surfaces of high potential.

The zeta-potentials (ζ) were calculated from electrophoretic mobilities by solving Overbeek's equation for symmetrical electrolytes, eqn.(16) and not the approximate equation, as rearranged by Hunter (1962); the friction constants (ρ) of the ions, required by the equation, were calculated from the corresponding ionic conductances (λ)

at infinite dilution (25°C) by the relation $\rho = e^2N/\lambda$. The ionic conductances were taken for inorganic ions from the tables given by Robinson and Stokes (1955), for Aerosol OT anion (22 ohm^{-1} cm^2 equiv.^{-1}) from Brady and Salley (1948) and for Cetavlon cation (19 ohm^{-1} cm^2 equiv.^{-1}) from the results of Scott and Tartar (1943). For experiments where inorganic salts were added to Aerosol OT solutions the value of ρ_{anion} was taken equal to the mean of the friction constant of the two anions in accordance with their relative proportions in solution. In practice, the relaxation corrections were small in presence of added inorganic salts. The values of κa required for calculating the different functions in equation (16) were obtained from the radius of the carbon particles (table 1) and $1/\kappa$ calculated on the basis that the maximum contribution of surfactants to the total ionic strength of the solution corresponds to their c.m.c. In some cases the zeta-potential given by Henry's equation (ζ_{Henry}, eqn. (15)) correcting Smoluchowski's equation for the effect of particle size but not relaxation effects, were calculated to compare with Overbeek's relaxation corrections.

Zeta-potentials were negative for all carbon dispersions in Aerosol OT and positive for those in presence of Cetavlon. Unless otherwise stated mobilities were obtained by the moving boundary technique (25°C).

Figure 16 shows the variation of mobility for the three graphitized blacks with the concentration of Aerosol OT in water solutions. The results for surface coverages of 60 - 100°/o show that in all cases the mobility decreases with decrease in surfactant concentration - that is, with decrease in specific adsorption charge density. The effect of particle size on mobility is quite clear at high concentration of Aerosol OT where the mobility increases with the particle size under comparable experimental conditions. However, with decrease in concentration where the values of $\varkappa a$ decrease and lie around the region of maximum relaxation corrections, the mobility curves start to cross each other. This crossing had been anticipated from the theoretical mobility curves calculated for the three carbons for two hypothetical potentials 50 and 100 mV. (Fig. 12, assuming $\rho_+ = \rho_-$ for $\lambda = 70$ ohm^{-1} cm^2 equiv.$^{-1}$). Therefore, the measured mobilities for particles of different sizes are in qualitative agreement with theory.

From adsorption experiments (Fig. 4) it was shown that for a given equilibrium concentration of Aerosol OT, the three graphitized carbon blacks have the same percentage surface coverage and presumably, therefore, the same specific adsorption charge density. It is to be expected, therefore, that the three carbons ought to give approximately

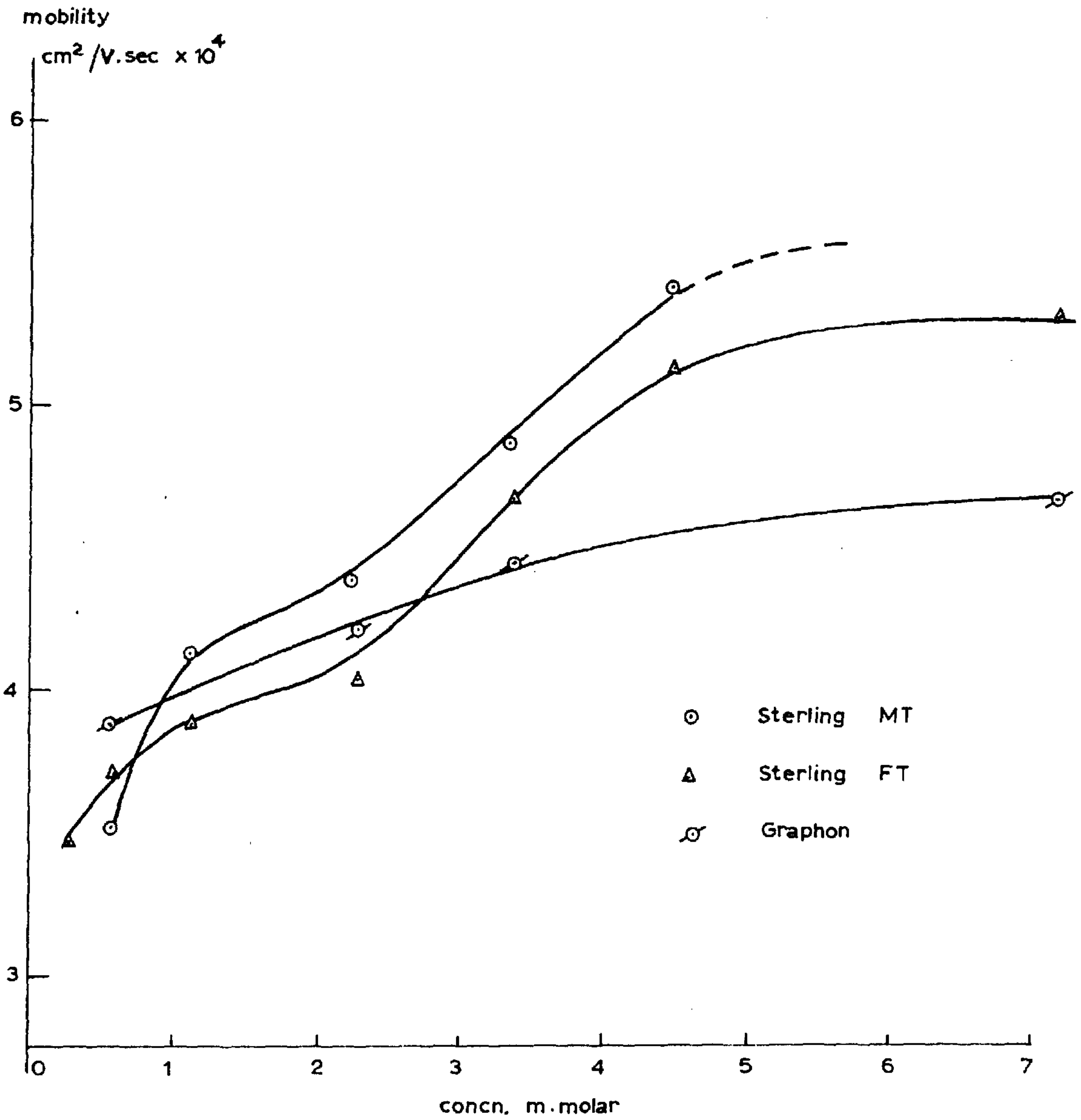


FIG. 16 Electrophoretic mobilities in Aerosol OT

the same zeta-potential (not exact potentials as the distribution of the latter is dependent on surface curvature) at a given equilibrium concentration if Overbeek's corrections for the relaxation effects are quantitatively applicable to the mobility data at this region of κa.

Table 26 shows that for Sterling MT (κa 18 - 39) the relaxation corrections given by Overbeek's theory are always less than 20^{o}/o and decrease with decrease of zeta-potential, i.e. with decrease in surface charge density and mobility. However, for Sterling FT under the same conditions of concentration and charge but smaller values of κa (6 - 16), the relaxation corrections are excessively high and the measured mobilities gave zeta-potentials up to -190 mV. These calculated potentials, and comparable figures for Graphon, are more than double those calculated for Sterling MT of κa values outside the region of maximum relaxation corrections. Experimentally, the mobilities of Sterling FT and Graphon particles in Aerosol OT solutions in water are higher than those predicted by the theory (Fig. 12) for potentials between 50 and 100 mV (potentials found for Sterling MT under the same experimental conditions). These results show the great error that could be involved in misusing Overbeek's equation, which was derived for small potentials, for systems of high potentials (> 50 mV) in this intermediate

TABLE 26. MOBILITY OF GRAPHITIZED CARBON BLACKS IN AEROSOL OT SOLUTIONS IN WATER

a) Sterling MT (graphitized)

Concn. of Aerosol m.molar	κa	Mobility (cm^2/V.sec) x 10^4	ζ (Henry) (mV)	ζ (Overbeek) (mV)
4.50	38.8	5.41	74.2	87.7
3.38	38.8	4.86	66.6	75.1
2.25	36.8	4.39	60.1	66.2
1.12	26.0	4.14	58.3	66.5
0.56	18.4	3.53	51.3	58.6
b) Sterling FT (graphitized)				
7.16	16.3	5.30	77.1	190
4.50	16.3	5.13	74.7	189
3.38	16.3	4.69	68.2	187
2.28	15.7	4.04	59.6	182
1.14	11.1	3.89	59.6	168
0.56	7.8	3.72	59.1	159
0.28	5.5	3.48	57.4	154

TABLE 26 (cont.)

c) Graphon

Concn. of Aerosol m.molar	κa	Mobility (cm^2/V.sec.)x10^4
7.16	2.0	4.66
3.45	2.0	4.45
2.30	2.0	4.22
0.56	1.0	3.87

TABLE 27. MOBILITY OF GRAPHITIZED STERLING FT IN CETAVLON SOLUTIONS IN WATER

Concn. of Cetavlon m.molar	κa	Mobility (cm^2/V.sec.)x10^4	ζ (Overbeek) (mV)
2.74	10.3	4.59	167
1.37	10.3	3.87	164
0.68	8.6	3.71	161
0.34	6.1	3.66	156
0.17	4.3	2.87	150

region of κa. Abnormally high potentials obtained by correcting mobilities for relaxation effects have been reported e.g. by Watanabe (1960) for silver iodide sols in surfactant solutions ($\kappa a = 1.2$, zeta-potentials up to 200 mV) and by Ottewill and Rastogi (1960) for similar systems. No valid conclusions can be drawn for systems falling in this region.

Mobility measurements for carbon dispersions in Cetavlon solutions in water are somewhat less favourable than those for Aerosol, as the c.m.c. of Cetavlon is lower than that of Aerosol and this results in decreasing the values of κa and hence more uncertainties in the relaxation corrections. Table 27 shows the mobility results for graphitized Sterling FT at different concentrations of Cetavlon ($\kappa a = 4 - 10$). Again the relaxation corrections are high and indicate the unreliable values of zeta-potentials given by misusing Overbeek's equation for these particular systems of intermediate values of κa.

To minimize relaxation effects so as to have reliable zeta-potentials it is necessary either to reduce the potential of the system or to increase κa. The second case and partly the first can be achieved, in the present system, by working with the larger carbon particles (Sterlin MT) in presence of inorganic salt solutions (0.01 N).

Electrokinetic measurements on Sterling MT from solutions of constant inorganic salt content offer two main advantages - a) the ionic strength of the system is only slightly changed ($\simeq 10^{o}/o$) over the entire range of surfactant concentration as the contribution from the latter is small; this keeps $1/\varkappa$, and hence the potential distribution in the electric double layer, approximately the same over the whole surface coverage range: b) by increasing $\varkappa$ and making $\varkappa a$ almost constant (for Sterling MT $\varkappa a$ varies between 80 - 82 for all concentrations of Aerosol OT in 0.01 N NaCl) the flat double layer equation can be used, for all the surface coverages, to calculate diffuse charge densities from zeta-potentials.

Table 28 shows the zeta-potential values calculated, by the Overbeek and Henry equations, from the mobilities of Sterling MT (graphitized) covered to different degrees ($10-100^{o}/o$) by adsorption of Aerosol OT from 0.01 N NaCl solutions. The first part of the table is for mobilities determined by the moving boundary apparatus where an accurately measurable equilibrium surfactant concentration was found. The second part of the table is for micro-electrophoretic mobilities at the low surface coverage region. The two methods of measurements gave comparable results, as shown by the values of zeta at full surface coverage; that from micro-electrophoresis being only slightly higher ($\simeq 3^{o}/o$) which is not far from the experimental error and may arise from the difficulty in estimating the cross-section area of the capillary tube at the point of observation. The table shows that corrections due to relaxation effects are small - always less than about 6°/o for all the measurements. This small correction indicates, therefore, that Overbeek's equation is being used in a region of $\varkappa a$ where it can be reliably applied to calculate zeta-potentials from mobility results. Also, for this system Henry's corrections to Smoluchowski's electrophoretic equation for particle size effect is small, as $f_1(\varkappa a)$ is equal to about 1.45 compared with 1.5 required by Smoluchowski's equation. It may be concluded, therefore, that the calculated zeta-potentials for this particular system can be considered reliable for calculating diffuse charge densities and other properties of the electric double layer.

However, in such calculations it is assumed that the viscosity and dielectric constant in the electric double layer are equal to those in the bulk solution, which is a questionable approximation. As the zeta-potential is usually considered as representing the potential at the slipping plane between the moving (diffuse) and the stationary phases when the liquid far away from the interface is considered to be of zero potential, the problem can be limited at the moment to the outer diffuse part

TABLE 28. ELECTROPHORESIS RESULTS FOR STERLING MT(GRAPHITIZED) IN AEROSOL OT AND 0.01 N NaCl

Equil. concn. mM	Ads. charge $\sigma_{ads.}$ (e.s.u./cm²)	Surf. coverage (°/o)	Mobility (cm²/V.sec) x 10^4	ζ Henry (mV)	ζ Overbeek (mV)	σ (e.s.u./cm²)	$\sigma/\sigma_{ads.}$ (°/o)	ψ_0 (mV)	d Å	ϕ (kT)
4.5	72510	100.0	5.80	77.3	81.7	8790	12.1	191	11.0	7.3
2.25	70410	96.1	5.64	75.2	79.2	8340	11.8	190	11.4	7.4
1.12	68330	93.4	5.49	73.2	76.8	7850	11.5	188	12.0	7.6
0.56	63710	88.2	5.37	71.6	75.0	7360	11.6	185	12.5	7.7
0.17	58340	76.3	5.18	69.1	72.2	6800	12.4	177	13.1	7.9
			Micro-electrophoresis							
Temp. (°C)										
20	72510	100.0	5.49	80.0	84.1	9350	12.9	191	10.4	7.1
22	47370	65.3	4.99	70.3	73.7	7080	14.9	170	12.3	7.5
20	37730	52.0	4.82	70.1	73.5	7120	18.9	158	11.9	7.2
20	22640	31.2	4.81	70.0	73.3	7090	31.3	132	10.0	6.5
22	15090	20.8	4.36	61.3	63.5	5620	37.2	111	12.4	6.7
21	7130	9.8	4.09	58.3	60.5	5280	74.0	75	4.9	5.2

of the double layer as this is responsible for the electrophoretic mobility of the particles. In a recent theoretical paper Lyklema and Overbeek (1961) discussed the effect of changes in dielectric constant (ε) and viscosity (η) in the diffuse electric double layer on calculating zeta-potentials from electrophoretic mobilities. It was concluded that for measurements from 0.01 N salt solutions it is justifiable to use the bulk value of ε in calculation of ζ ; an error of only 2°/o (decrease in ε) is incurred for $\zeta \geq 94$ mV. on the basis of Booth (1951) formula for the dielectric saturation of water. The viscosity of water was considered, however, to increase significantly with the strength (E) of the electric field. The relative increase in viscosity is related to E according to Andrade and Dodd (1951) by the equation

$$\frac{d\eta}{\eta} = fE^2 \qquad (34)$$

where f is the so-called 'viscoelectric constant'. For water this constant has not been determined but, from theoretical considerations, Lyklema and Overbeek put f equal to 1.02×10^{-11} V^{-2} cm^2 at 25°C which is about 5 times that for chloroform or chlorobenzene. Assuming the viscoelectric contant to be independent of concentration, Lyklema and Overbeek concluded that corrections due to enhanced viscosity in the diffuse double layer may reach 20°/o for systems measured in medium salt content

(> 0.01 M). Higher zeta-potentials are, therefore, expected if the correct mean viscosity is substituted in Smoluchowski's equation. These corrections to ζ are, however, subject to the highly uncertain value of the viscoelectric constant (f) of water and on the assumption that it does not depend on the nature and concentration of electrolytes. In the absence of an experimental measure of (f) for the system involved in this work it seems that application of any such 'corrections' to viscosity in the diffuse double layer is unjustified at present, though any values of zeta-potential calculated from mobilities assuming normal viscosity are obviously liable to be somewhat smaller than the actual potential at the 'slipping plane'.

The concept of a 'slipping plane' is an alternative simplified model. If it is assumed that the zeta-potential as calculated above represents the potential at the slip plane in the electric double layer, the distance (d) from the surface at which the slip occurs can be roughly calculated from the values of ζ at different surface coverages and the corresponding theoretical surface potential (ψ_o) using equation (6) (for flat double layers). The assumption was made, in these calculations, that there is no specific interaction between the ions in the electric double layer i.e., a completely diffuse double layer.

ψ_o can be estimated from equation (10) where the values of σ are taken equal to the specific adsorption charge density ($\sigma_{ads.}$ taken from adsorption isotherms).

Table 28 shows that for electrokinetic results on Sterling MT at different surface coverages in 0.01 N NaCl solutions, the hypothetical slip plane is situated for all coverages except the lowest ones (10°/o) at a distance between 10 and 13 Å from the surface with no indication of any regular trend. For 10°/o surface coverage where the surface potential is greatly reduced the slip occurs at a smaller distance d = 5 Å from the surface and indicates the small effect of surface potential on shifting the position of the slip plane. The calculated values of d, on the above assumptions indicate that an appreciably thick liquid layer close to the surface would have to be immobile. Values for d found on this hypothesis are of the same order of magnitude as those reported by Stigter and Mysels (1955) for surfactant micelles and by Anderson (1959) for the oil/water interface using the same assumption of no interactions between charges of opposite sign. Table 28 also shows that zeta is always a fraction of ψ_o that increases with decrease in the magnitude of the latter. This is in accord with what is usually observed for other systems (chapter 1); at low surface charges ζ is close to ψ_o, whereas the two diverge at higher charge densities.

6.1. Diffuse charge density and zeta-potential

An alternative hypothesis to that used above is to postulate that part of the adsorption charge is neutralized by counterions located in the Stern layer, the remainder of the counterions forming a diffuse double layer with normal electrokinetic properties. Table 28 shows the values of the diffuse charge density (σ) as calculated from equation (10) using the corresponding zeta-potentials for Sterling MT (graphitized). On comparing these calculated charges at different surface coverages with the adsorption charge density ($\sigma_{ads.}$) found from the adsorption results of Aerosol OT on the carbon, it is clear from table 28 and figure 17 that σ is always a variable fraction of the adsorption charge. At full surface coverage with the surfactant the calculated diffuse charge is only about 12°/o of the adsorption charge on the surface, but with decreasing the latter the diffuse charge (σ) increases gradually and reaches a value of about 74°/o of $\sigma_{ads.}$ for the lowest surface coverage studied (10°/o).

It is obvious, therefore, that either of the above theories or a combination of them would lead to the same result of reducing the apparent charge density (zeta-potential) in the diffuse part of the double layer. However, differentiation between their effects can be achieved by comparing electrokinetic results with those of negative adsorption. Negative adsorption of co-ions from the double layer is solely governed by the potential and not by the viscosity in the electric double layer because even if the viscosity is abnormally high close to the surface this will not prevent co-ions from being expelled from this region. (It is accepted that the dielectric constant is not greatly affected by the field).

Figure 17 shows a plot for the fraction of the adsorption surface charge that appears as a diffuse electric double layer, as shown by the zeta-potential and negative adsorption results, as a function of surface adsorption charge. Both results are for experiments from 0.01 N NaCl solution and Aerosol OT of varying amounts adsorbed on the surface. Although two different graphitized carbons were used in this graph, Sterling MT (for mobility) and Graphon (for negative adsorption), the adsorption results had shown that with their practically homogeneous surfaces their adsorption behaviour is the same. The choice here is only for practical reasons; Graphon with a high surface area per unit weight for a reasonable measure of negative adsorption of co-ions, and Sterling MT with large $\varkappa a$ to minimize

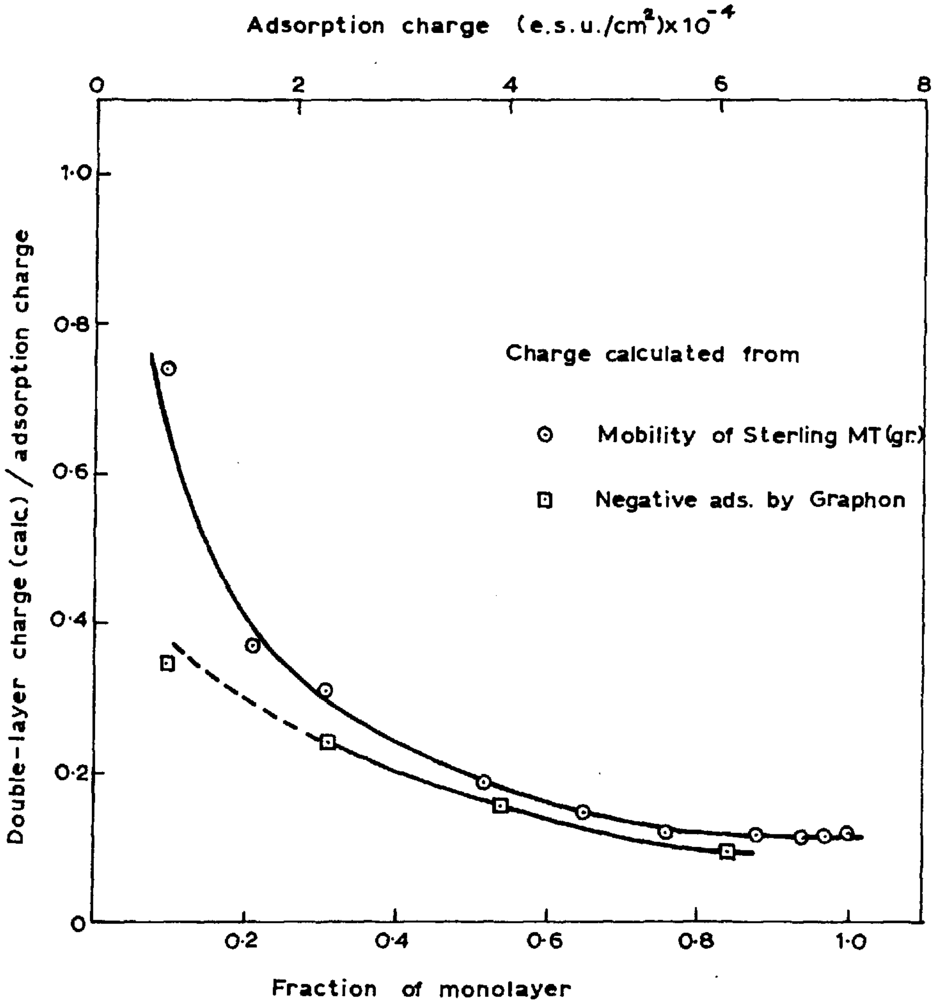


FIG.17 Double-layer charge calculated from mobility and negative adsorption results

the relaxation effects. The adsorption charge ($\sigma_{ods.}$) in figure 17 was calculated from the amount of Aerosol OT adsorbed on the surface and are accurate to better than ± $2^{o}/o$; the fraction of monolayer for each system is referred to a monolayer represented by the plateau of the corresponding adsorption isotherm (chapter 2). The point for negative adsorption at $10^{o}/o$ coverage (represented by a broken curve in figure 17) is, as shown before, of uncertain magnitude as it lies in a region of surface coverage where negative adsorption equations cannot be applied reliably.

The reasonable agreement between the zeta-potential and negative adsorption results as observed in figure 17 for surface coverages of $30^{o}/o$ and higher is in favour of the idea of specific adsorption of counterions in a Stern layer as the main factor responsible for showing a relatively small potential in the double layer (compared with the theoretical potential due to adsorbed ions on the surface). Specific adsorption of counterions, although greatly reducing the potential in the double layer, would not entirely eliminate the enhancement in viscosity in the double layer. However, the agreement shown in figure 17 suggests that its effect may be negligible in these systems and probably of the same order of the uncertainties involved in calculating charge densities from negative adsorption results and zeta-potentials from mobilities. This leads to the conclusion that the zeta-potentials, as calculated from electrophoretic mobilities, represent the potential at the plane of slip between the Stern layer and the diffuse parts of the electric double layer. Comparison between experimental and theoretical negative adsorption of co-ions can be shown by calculating the latter from zeta-potentials and their corresponding diffuse charge densities by applying Klaarenbeek's equation (eqn. 23). As shown from table 28 for surface coverages of about 30 - 80 °/o, where the negative adsorption results are reliable, the change in zeta-potential is small and the corresponding theoretical negative adsorption is almost the same in this region of surface coverage. Taking the intermediate coverage of 52°/o the corresponding theoretical negative adsorption is 4.66×10^{-9} m.equiv./cm^2 (for $\zeta = 73.5$ mV). Actually the measured negative adsorption at this coverage was 4.34×10^{-9} m.equiv./cm^2. The difference ($\simeq$ 7°/o) is not great and within the uncertainties involved in determining negative adsorption, as discussed in chapter 4.

Electrokinetic measurements for this particular system of graphitized carbon black show that at low adsorption charge densities ($\simeq$ 7000 e.s.u./cm^2, 10°/o surface coverage) most of the sodium counterions ($\simeq$ 74°/o) form a diffuse electric layer while only a small fraction is specifically adsorbed in a Stern layer. With gradual increase in surfactant charge, a large proportion of the added surfactant counterions goes to build up the Stern layer. The process of charging continues until at approximately full surface coverage with Aerosol OT only about 11 - 12°/o of the total surfactant charge appears as a diffuse layer.

Stern (1924) treated the specific adsorption of counterions in a manner analogous to the Langmuir localized adsorption model and derived equations to calculate the specific binding energies of counterions. Unfortunately the equations cannot be tested in a proper way as they require a knowledge of the potential in the Stern layer ψ_δ and hence its corresponding charge density, which is not subject to direct measurement. Grahame (1947) calculated these quantities from electrocapillary curves but his assumptions were criticized by Parsons (1954). An approximate test of Stern's theory is to use the assumptions that the estimated zeta-potential is equal to ψ_δ and to take the number of available sites on the surface for specific adsorption of counterions as equal to the number of adsorbed Aerosol OT molecules per unit area as it is more appropriate for a sodium ion to adsorb near a sulphonic group than on a bare graphitized surface (if any is available). Under these conditions the Stern equation for the specific adsorption of counterions (neglecting contributions from co-ions as they are greatly excluded from this region of the double layer) has the form

$$\frac{\sigma}{\sigma_{ads.}} = \frac{1}{1 + (Mn/N)\ \exp(-W/kT)} \qquad (35)$$

where the σ terms have the same significance as before, n is the number of ions/cm^3 in the bulk solution, N Avogadro's number and M the molecular weight of water. The value of N/M was assumed by Stern to represent the number of available positions for ions in the solution. W is the work of adsorption of the ion into the Stern layer and can be divided into electrostatic and chemical contributions, or

$$W = ze\zeta + \phi \qquad (36)$$

where ϕ is the specific chemical adsorption energy of the ion.

Table 28 shows that the calculated values of ϕ for the sodium counterions vary between 5.2 and 7.9 kT for the entire surface coverage range. In general ϕ is smaller for low surface coverages (< 50°/o) with the lowest value of 5.2 kT at 10°/o surface coverage but, on the whole there is no regular increase of ϕ with surface coverage. The calculated values of ϕ are of the same order of magnitude as those reported by Anderson (1959) from his work and others. However, there is no independent method of obtaining ϕ, and there is no reason to expect it to remain absolutely constant with varying surface coverage. For example, Levine et al. (1962) showed, from a theoretical consideration of the effect of the discreteness-of-charge in the inner Helmholtz plane, that ϕ is expected to increase with surface charge.

A partial test for the Stern theory would be to carry out electrokinetic measurements (mobilities) with mono- and polyvalent counterions of different affinities to examine the specificity of the theory. However, work with divalent cations is complicated in this system as the pure divalent salts of Aerosol OT are only slightly soluble in water, and use of mixed cations (e.g., Na and Mg as in adsorption experiments) cannot lead to a quantitative interpretation of the results as multilayer adsorption is possible (chapter 2) and also the proportion of divalent to monovalent cations in the double layer is different from that in the bulk solution. For example, van Voorst Vader (1960) found, for surfactant films, that the Ca^{++}/Na^{+} ratio at the interface may be more than 100 times higher than their concentration ratio in the solution. In the present work, therefore, experiments were confined to the monovalent cations of Aerosol OT, namely the Li, Cs and Ag in addition to Na. Mobility measurements were made for graphitized Sterling MT at full surface coverage with the appropriate salt form of Aerosol OT. The ionic strength of the solutions was kept almost constant by working from 0.01 N chloride or nitrate solutions of these monovalent cations. From electrophoretic mobilities ζ , σ, $\sigma/\sigma_{ads.}$ and ϕ were calculated and are shown in table 29.

TABLE 29. ELECTROPHORESIS RESULTS FOR STERLING MT (GRAPHITIZED) IN AEROSOL OT OF DIFFERENT CATIONS AND 0.01 N SALT SOLUTIONS

Cation form of Aerosol OT	Mobility $(cm^2/V.sec)$ $\times 10^4$	ζ mV	σ e.s.u./cm^2	$\sigma_{ads.}$ e.s.u./cm^2	$\sigma/\sigma_{ads.}$ $(^{o}/o)$	ϕ (kT)
Li	6.30	90.5	10610	67060	15.8	6.6
Na	5.80	81.7	8790	72510	12.1	7.3
Cs	6.19	87.8	9810	81310	12.1	7.1
Ag	5.64	79.2	8260	72510	11.4	7.5

From ion-exchange studies on sulphonic resins, it was found that the affinity of these monovalent cations towards the sulphonic groups are Ag > Cs > Na > Li, under comparable conditions (Kitchener 1959). According to the Stern theory, the lithium ion with its least affinity to the sulphonic group (because of its large hydrated radius) will not be adsorbed in the Stern layer to the same extent as the silver ion on the other end of this affinity series. This means that for the Li-form of Aerosol OT a higher proportion of the total counterions will appear in a diffuse double layer and hence show a higher zeta-potential compared with what is expected from the Ag-form. The sodium and caesium forms being, intermediate in the affinity series, would show values in between those of the lithium and silver.

Table 29 shows that the experimental data for the lithium and silver forms are in line with expectations; zeta is higher for the Li than for the Ag-form, $\phi_{Ag} > \phi_{Li}$ and the fraction of the total charge that appears as a diffuse double layer is greater for the lithium (15.8°/o) than for the silver form (11.4°/o). But, on examining the whole series there is overlapping between the results for the sodium and caesium form and although the results for Na and Cs forms fall in between those for the Li and Ag forms the ϕ and $\sigma/\sigma_{ads.}$ values for Na, Cs and Ag forms are close to each other, so that a firm conclusion about specificity is questionable.

However, two main factors partly contribute to the confused results observed in this set of measurements: first, on preparing the Caesium-Aerosol OT by the ion-exchange method (Appendix 2) it was found, by flame photometry, that only 75°/o of the sodium ions were exchanged for caesium and although the Na/Cs ratio was reduced to about 7°/o by working in 0.01 N CsCl it still constituted a reasonable fraction of the total cation content; secondly, although the electrophoretic mobilities for different monovalent counterions were determined from solutions of the same inorganic salt content (0.01 N) and hence the extension of the double layer is almost the same, the surfactant surface charge densities were not equal. As shown from the adsorption results (Fig. 6) the degree of packing of the adsorbed Aerosol OT molecules at full surface coverage, depends on the nature of the counterion, being closest for Cs and least close for Li form, with Ag and Na forms almost the same with an intermediate packing. With different charge densities, interactions between ions are expected to be different and would influence the measured values.

It would be more appropriate, therefore, to determine the mobility of Sterling MT (graphitized) when its surface is covered by exactly the same number of Aerosol OT molecules of different counterions. The latter can be adjusted accurately at low surface coverages (< 70°/o) where the equilibrium concentration is negligible and nearly all the added surfactant adsorbed on the surface. Unfortunately, this test suffers from the fact that only the micro-electrophoresis cell can be used in this range of coverage; this is less accurate and with its lack of temperature control, makes the measurement of the expected small differences unreliable. An important reason in favour of measuring electrophoretic mobilities at full surface coverage is that in this region the adsorption is not sensitive to the equilibrium concentration as is the case for the intermediate region of the adsorption isotherm; in the latter case uncertainties arise in evaluating adsorption charge densities.

In spite of the fact that electrokinetic experiments with different monovalent counterions did not entirely satisfy the required test for the Stern's theory, these experiments confirm the previous findings that the calculated charge in the diffuse double layer is only a fraction of the total Aerosol OT adsorption charge density whether the counterion was Li, Na, Cs or Ag.

The problem of accepting the idea of specific adsorption of counterions to form a Stern layer is, however, open to much argument, in particular when monovalent ions (e.g. sodium or chloride ions) are involved. Anderson (1959) and many others, in order to explain the observed divergence between calculated and adsorbed charge densities, considered the specific adsorption of monovalent counterions as the main factor responsible for this disagreement. Applying the Stern's equations for his results and a number of published electrokinetic data, Anderson (1959) calculated the specific adsorption potential of the alkali metal cations at negative interfaces and found ϕ values in the range of about 3 - 10 kT. On the other hand, Haydon and Taylor (1960, 1962) and Haydon (1960) excluded the idea of specific adsorption of monovalent inorganic counterions at the oil/water interface in presence of a number of surface-active agents and regarded these ions as having no tendency for specific binding. These authors assume a completely diffuse double layer and attributed the observed small electrophoretic zeta-potential as compared with the estimated surface potential to the neglect of important corrections in calculating zeta-potentials, in particular the increase in viscosity and the decrease in dielectric constant in the electric double layer. (Haydon and Taylor (1960) also considered the possible effect of penetration of counterions between the chains above the level of the surfactant head groups in their system of oil droplets.) In this sytem, at full surface coverage with Aerosol OT, there is no possible penetration of counterions between the chains as the latter are bulky and occupy most of the space; but, the counterions can fit in between the sulphonic head groups (i.e., on the same level). In a hexagonal close packed array with an area of 66.2 Å^2/ Aerosol molecule the distance between the centres of the counterions and the sulphonic group is 5.05 Å. For a sulphonic group of area of cross-section 24 Å^2 (van Voorst Vader, 1960a, from atomic models) the free space between the head groups can accommodate counterions of radii up to 2.29 Å which is greater than that of sodium (page 72). The same conclusions were arrived at for the caesium, silver and lithium forms of Aerosol at close packing.

Although the need for various modifications to the Gouy theory is indisputable, allowance for the specific properties of the ions (Stern modification) is also needed to explain ion-exchange affinity series and many of the observed electrokinetic results. Davies (1960), after investigating a large number of published electrokinetic results, in particular the effect on concentration on charge reversal arrived at the conclusion that in order to explain these results the introduction of ionic specificity is necessary. For alkali metal cations, Davies considered their specific binding energy to be only a few kT and ascribed the high values calculated by Anderson (1959) to the approximations involved in Stern's equations.

In the present work it has been shown that the negative adsorption results for these graphitized carbon systems are in favour of Stern's hypothesis of specific adsorption of counterions rather than an enhancement in viscosity as the main factor responsible for the relatively small zeta-potential (compared with that expected from the adsorption charge density).

7. SUMMARY OF CONCLUSIONS

1. Adsorption of Aerosol

Adsorption experiments showed that graphitized carbon blacks, because of their practically inert surfaces, are suitable substrates for surface studies; the isotherms provide an accurate measure of adsorption charge at any given equilibrium concentration. The compactness of the physically adsorbed monolayer of Aerosol OT molecules on these carbon surfaces changed with the ionic strength of the solution and the nature of the counterion. The partially heterogeneous original black surfaces are not ideal surfaces for providing accurate adsorption charges as incomplete monolayers and reversed adsorption is possible together with the physical adsorption. From supersaturated solutions of Aerosol adsorption maxima were observed with Sterling MT (original). These are not dependent on the ash and tar content of the carbon. Surface areas for graphitized Sterlings can be determined reliably from adsorption experiments; for Graphon the nitrogen area is greater by about 10°/o than the Aerosol area.

2. Negative adsorption of chloride

Results for negative adsorption of co-ions (chloride ions) by the Graphon-Aerosol OT - NaCl system indicated that the structure and distribution of ions in the electric double layer varies little over a wide range of surface coverage (30 - 80°/o), whether it is for systems in 0.01 or 0.001 N NaCl. Charge densities calculated from negative adsorption results in 0.01 N NaCl showed that the diffuse double-layer charge is a variable fraction of the adsorption charge.

3. Electrophoretic mobilities

Electrophoretic mobility of graphitized carbon black particles in Aerosol solution was found to vary with particle size in qualitative agreement with theory (Henry 1931, Overbeek 1943). Abnormally high zeta potentials are obtained by misuse of the Overbeek equation for systems of combined high mobility and intermediate $\varkappa a$. Reliable zeta potentials were obtained for Sterling MT (graphitized) in 0.01 N salt solutions (small relaxation corrections) and used in calculating diffuse charge densities. The latter was found to be in agreement with, within experimental error, those calculated from negative adsorption results.

4. The diffuse double-layer

The combined results, for this particular system, suggest that a Stern model with specifically adsorbed counterions is the appropriate structure of the double layer. The alternative view that an appreciable increase in viscosity in the double layer is responsible for small zeta-potentials is not consistent with the negative adsorption results which should not be influenced by the viscosity.

5. Specific adsorption of counterions

The electrophoretic zeta-potential is close to if not equal to Ψ_δ. The specific adsorption energy of counterions (Na) was estimated from Stern's theory and found to vary between 5.2 and 7.9 kT for the entire surface coverage range. Experiments with other monovalent counterions showed similar results, the order of ion binding being Ag > Cs $\approx$ Na > Li.

6. Surface conductance

The surface conductance experiments showed agreement between the theoretical (calculated from the zeta-potentials) and the experimental values of surface conductance, supporting the conclusion that zeta is a measure of the potential in a part of the double layer where the ions are present in a medium of normal viscosity and have normal ionic mobility.

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APPENDIX I

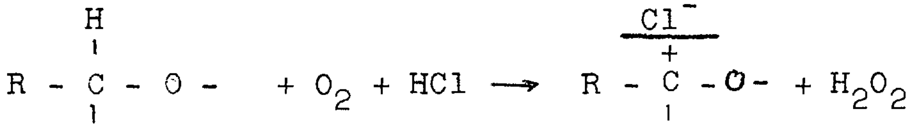
Potentiometric titration of surface oxides on carbon blacks

Carbon blacks generally carry some surface carbon-oxygen compounds in varying amounts, the properties and amounts of which depend greatly on the temperature treatment. Carbons activated in air at low temperatures (between 400 - 500°C) adsorb alkali while those activated at 800°C adsorb acid but little or no alkali; more alkali is adsorbed if the carbon is reoxidized in air at a lower temperature (Kruyt and deKadt 1929). Heat-treatment at temperatures higher than 1000°C virtually leaves no surface oxides (Smith 1959). The acidic and basic behaviour of carbons are the subject of a voluminous literature which is partly summarised by Steenberg (1944) and Garten and Weiss (1957). It is generally accepted that alkali adsorption is partly due to acidic carbon-oxygen complexes but the presence of basic carbon oxides is doubted by some authors (e.g. Steenberg).

The formulae proposed for the structure of the acidic surface oxides (Garten and Weiss 1957) were based on two main practical observations: a) the shape of the titration curves (Villars 1947, and Garten and Weiss 1955) that show no inflection point and suggest that the titrated groups are much weaker than carboxylic groups -

indeed, they resemble the titration curves of phenols:
b) the number and properties of methoxyl groups that can be introduced to the carbon surface by methylation with diazomethane. Three main surface acidic groups were considered to exist in varying amounts, namely: (1) phenolic hydroxyl groups that react with alkali and form a methoxyl derivative non-hydrolysable with dilute acid, (2) 'f-lactones', similar to those in the fluorescein and phthalein dyestuffs, that react with alkali and give a hydrolysable methoxyl derivative, and (3) normal lactone ('n-lactone') probably δ-lactone that reacts with alkali but not diazomethane.

The existence and structure of basic groups on carbons is open to doubt due to the lack of precise experimental evidence. In some instances it was proposed that acid adsorption is physical (e.g. Steenberg 1944), as suggested by the results of desorption in presence of non-electrolytes and that acid adsorption increases with salt content. On the other hand, it was found (e.g. Frumkin et al. 1931) that there is a relation between the amount of acid adsorbed on an out-gassed carbon ('H-carbon') and the oxygen pressure and part of the chemically adsorbed acid appears as hydrogen peroxide in solution. Garten and Weiss (1957) were in favour of combined chemical and physical acid adsorption (specially at high acid concentration which increases physical adsorption) and put forward a theory for the structure of basic carbon oxides based on a benzopyran-benzopyrylium (carbonium) redox system, which can be simply represented by the formula



$$R - \overset{\overset{\displaystyle H}{|}}{\underset{|}{C}} - O - \quad + O_2 + HCl \longrightarrow R - \overset{\overline{Cl^-}}{\overset{+}{\underset{|}{C}}} - O - \; + H_2O_2 \qquad (37)$$

The carbonium ion is stabilized by resonance, the +ve charge resonating between the carbon and oxygen atoms in the ring. Acid adsorption is, however, complicated as most of the carbons used contain an appreciable amount of ash and its influence on adsorption is not usually considered by many investigators.

Suspensions of carbon blacks in aqueous solutions are acidic in the case of channel blacks and alkaline for the furnace and graphitized blacks. The acidity or basicity of these suspensions is usually believed to be due to partial ionization of surface groups; the hydrogen or hydroxyl ions forming a diffuse layer are partly exchanged by ions in solution and the exchanged ions show the pH changes in solution. It is noteworthy, however, that some of the principal proponents of this view (e.g., Garten and Weiss) did not examine the influence of extraction on the carbons.

This appendix reports a short investigation (subsidiary to the main thesis) of the uptake of acid (HCl) and alkali (Na OH) by the several carbon blacks to find the magnitude of their surface complexes (if any) and the probable influence of such compounds on other surface measurements. Precision titrations were carried out. Two hydrogen electrodes (platinum foils covered with platinum black by electrodeposition from chloroplatinic acid containing a little lead acetate) and a Ag/AgCl electrode (platinum mesh base) were used to follow the course of titration. All titrations were determined for carbon dispersions in 0.01 N NaCl (and also 0.1 N NaCl for Graphon). The e.m.f. of the cell $H_2 | HCl | AgCl/Ag$ was measured by a Tinsley potentiometer (Model 4025, sensitive to ± 0.1 mV). A known weight of the carbon (about 0.6 - 1g) was introduced to a titrating vessel and wetted with 0.5 ml of redistilled alcohol; sodium chloride solution were then introduced slowly till complete wetting was attained and addition continued to a total volume of 70 ml. The electrodes as well as the tube for bubbling hydrogen were inserted in position and the vessel was made gas-tight except for a fine hole at the top round the capillary tube from which the titrant is delivered. Hydrogen gas, from a cylinder, was allowed to pass through a pre-saturator (filled with 0.01 N NaCl) before bubbling through the suspension; the bubbles were directed to stir the carbon in the same time. After saturation with hydrogen (constant e.m.f. in about 45 min.), the titrant was added in small portions from either a 0.5 ml micro-syringe or a motorized piston micro-burette and the e.m.f. recorded after equilibrium was reached (about 5 min.). The recorded potential of the two hydrogen electrodes did not usually differ by more than 0.2 mV, and was reproducible to ± 0.3 mV. Blank experiments were determined under the same conditions and all potentiometric titrations were carried out in a water-thermostat at 25 ± 0.05°C. The number of micro-equivalents of acid or base consumed was calculated from the difference between the blank and the carbon titration cruves for equal e.m.f. values.

Figure 18 shows a typical titration result for 0.61g Spheron 6 against 0.1 N NaOH. The carbon curve is smooth and shows no sign of an inflection point, thus indicating the weakly acidic character of the surface oxides. Complete adsorption of alkali (top curve in Fig. 18) was always reached only at a pH above 11. Experiments with 0.1 N HCl gave curves of the same general form and complete acid adsorption was found at pH values lower than 3 (original Sterling FT). Table 30 gives the acidic and basic titratable capacity of the different carbon blacks used in this work. It was found, however, difficult to

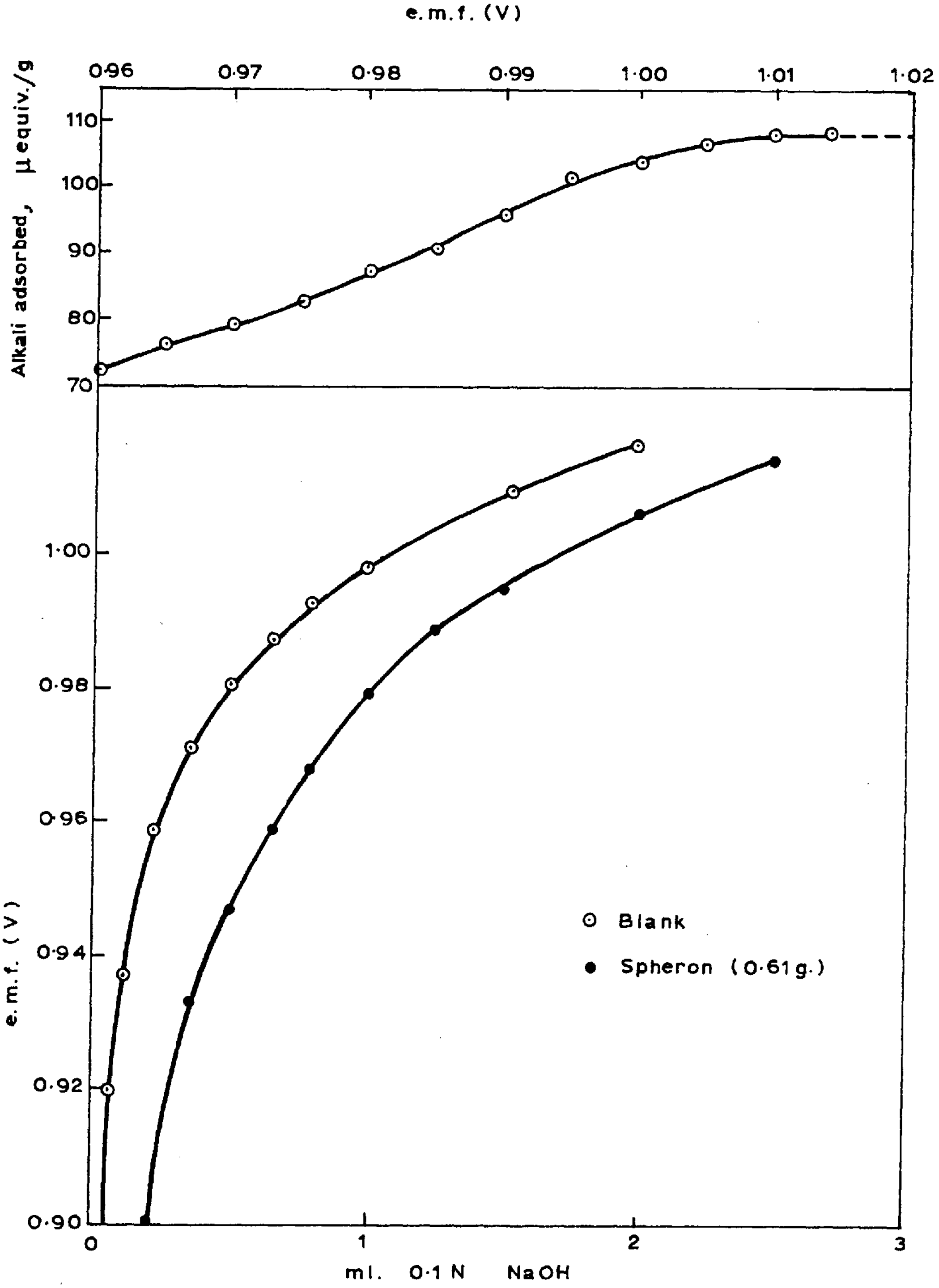


FIG. 18 Potentiometric titration of "Spheron 6" with alkali

determine small acid or base adsorption (about 5 μ equiv./g) by continuing the titration to either low or high pH values respectively (> 1 mM) as the e.m.f. of the blank and the carbon curves were very close (differing by < 1 mV) and are, therefore, close to the experimental error of the potentiometric titration. The values given in table 30 are equivalent to the highest adsorption calculated from the curves at intermediate pH values. The alkali adsorption figure given for Sterling MT (original) was obtained from pH measurements (PYE, pH-meter), under the same conditions, as it was found that at high pH values the AgCl is readily leached from the Ag/AgCl electrode and abnormally low e.m.f.'s were recorded. Similar effects were not observed with Spheron 6 or Sterling FT and pH measurement, although less accurate, gave comparable results with those found by e.m.f.; for example, an alkali adsorption of 100 μ equiv./g Spheron 6 was obtained from pH measurements.

These titration results indicate that all the original carbons adsorb both acid and base in varying amounts, whereas the graphitized carbons show insignificant adsorption values (only minute amounts with Graphon of higher surface area) and thus confirm the inert surface character of these heat-treated carbons.

Interpretation of acid adsorption by the different carbons is complicated, however, in this system as all the carbons contain some ash and whether acid adsorption is due to simple neutralization of basic surface oxides or interaction with metallic ash carbonates is difficult to decide. Physical adsorption of HCl by this system is not likely as the acid content was always less than 3 mM and little acid adsorption was observed by any of the carbons (e.g. by Spheron 6) in relation to their available surface area. In an experiment with Graphon it was found that on back-titration with 0.1 N NaOH part of the adsorbed HCl was not regenerated: this lends some support to the assumption of interaction of acid with ash but the small quantities measured make a firm conclusion impossible. (A better result might be obtained with Sterling FT (original) of a higher ash content (0.073^{o}/o).)

TABLE 30. ACID AND ALKALI ADSORPTION BY CARBON BLACKS

Carbon	NaOH ads. (μ equiv./g)	HCl ads. (μ equiv./g)
Spheron 6	107	17
Graphon	5	4
Sterling FT (original)	6	13.8
Sterling FT (graphitized)	-	-
Sterling MT (original)	7	5.4
Sterling MT (graphitized)	-	-

At the present time it may be said that these titration results show that graphitized carbons possess practically clean surfaces and are reliable for other surface-chemical studies, while the original carbons contain significant quantities of oxygen complexes and uncertainty would be involved in using them for electrokinetic work.

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APPENDIX 2

Surface-active agents

The methods of preparation of monovalent salt-forms of Aerosol OT are given in this appendix together with the surface tension measurements for solutions of the two surfactants, Aerosol OT and Cetavlon, determined to check the purity of these materials.

a) Preparation of monovalent salt-forms of Aerosol OT

The lithium, caesium and silver salts were prepared from the Na-form of Aerosol by a cation-exchange resin, Zeo-Karb 225 (a sulphonated cross-linked polystyrene resin with an exchange capacity of about 5 m.equiv./dry gram). The H-form of the resin was purified by converting it to the Na-form by treatment with dilute sodium hydroxide solution (3°/o solution) followed by regeneration with 2N HCl. This cycle was repeated once more and the fine resin fragments removed by a 'back wash' of distilled water. The resin was finally washed with water until free from chloride ion.

The silver-form of the resin was prepared in a dark room by slowly passing silver nitrate solution until the elute showed no sign of acidity (methyl orange). The resin was then left overnight in contact with excess silver nitrate and finally washed until free of silver ions. The caesium and lithium forms were prepared by adding caesium or lithium carbonate respectively to the hydrogen form until evolu~~a~~tion of carbon dioxide ceased. The resin was then left overnight with excess of the corresponding carbonate for complete diffusion of cations through the resin network and finally washed carefully until free of carbonate.

The different salt-forms of Aerosol OT were obtained by passing Aerosol OT (about 10 mM) through the appropriate resin form and after rejecting the first 50 ml, a volume of 500 - 800 ml was usually collected in about 12 hr. A resin weight with an exchange capacity of about 12 times the exchanged sodium was used for preparing the lithium and silver forms but only about 7 times for the caesium form. The silver content of the Ag-Aerosol OT (96 ± 1°/o) was determined gravimetrically as silver chloride, while the caesium content of Cs-Aerosol OT (about 75°/o) was estimated by flame photometry. The percentage of unexchanged sodium in the inorganic residue of 5 ml of Cs-Aerosol OT was determined by means of an E.E.L. flame photometer and a sodium filter (kindly determined by Mr. A. J. Thompson of Imperial College).

b) Surface tension measurements

The surface tension of surfactant solutions at different concentrations in water and a number of inorganic salt solutions was determined by the Wilhelmy (1863) plate method. The plate, a very thin platinum foil (1.87 cm wide), was suspended from a light beam carried on a horizontal torsion wire to which is fixed an angular scale vernier (readable to $\pm 0.5^{\circ}$). To one end of the beam (near the plate) was fixed a very fine capillary tube that could be observed with a travelling microscope to record the level of the plate. The constant of the torsion wire (number of degrees/g) was obtained from the linear calibration curve determined by adding known weights and recording the corresponding difference in the scale readings when the plate was restored to its original level. The apparatus was enclosed in a glass box to avoid air draughts.

Surface tensions of solutions were determined by first locating the position of the plate in the microscope and recording the scale reading. Surfactant solutions (20 - 30 ml) in a circular disk (6 cm diam) were then raised cautiously by means of a special screw until its surface just touched the platinum plate, the latter being pulled into the solution. The scale was then turned until the plate was raised to its original level and the difference in the scale readings recorded. By this procedure buoyancy effects, which are small for thin plates, is entirely eliminated. To ensure complete wetting and hence zero angle of contact, the platinum plate was always freshly ignited. The surface tension (γ) was calculated from the equation

$$\gamma = \frac{xg}{2bc} \qquad (38)$$

where x is the recorded scale difference (in degree); c the constant of the torsion wire (degree/g); g, the gravitational acceleration and b the width of the platinum foil.

All measurements were carried out at room temperature and equilibrium was usually reached in a few minutes. The apparatus was checked by measuring the surface tension of redistilled thiophene-free benzene which gave a value of 28.6 ± 0.1 dyne/cm at 22°C in agreement with 28.74 dyne/cm reported by Sudgen (1924) at 21°C.

Figures 19 and 20 show the surface tension-concentration curves for Cetavlon in water and the different salt forms of Aerosol OT in water and inorganic salt solutions (corresponding to those used for adsorption by Sterling MT (original), chapter 2). In all cases, except those for the Ag-Aerosol, minima in the surface tension-concentration curves were not observed. This indicates, as observed by Miles and Shedlovsky (1944), the absence of any more surface-active impurity species in these surfactant solutions. The methods used for purifying Cetavlon and Aerosol OT (chapter 2) are therefore, sufficient to give acceptably pure materials for this work.

The surface tension results also show the significant effect of ionic strength and nature of counterion (cf. Fig. 20) upon the critical micelle concentration. The c.m.c. of Aerosol OT is reduced by addition of inorganic salts and is lowest in presence of the divalent magnesium ions. These results are in line with the assumption of an equilibrium between the repulsive forces between the ionic head groups and the attraction (cohesive) forces between the hydrophobic part of the surfactant molecules, as discussed for the adsorption results (chapter 2). Figure 20 shows also the influence of counterions on reducing the surface tension of surfactant solutions at comparable ionic strength (Aickin 1944).

Table 31 gives the surface tension values of Aerosol OT solutions in water and 0.01 N NaCl, and in table 32 the c.m.c. of the different surfactants are listed.

The silver form of Aerosol OT was found to show a minimum in the surface tension-concentration curves from water and 0.01 N Ag NO_3 at concentrations below the c.m.c. From the work of Miles and Shedlovsky (1944), which is supported by others, it is generally assumed that a minimum is usually associated with the presence of impurities of a higher surface-activity which adsorb strongly at the air/water interface, and that with increasing total surfactant concentration their relative

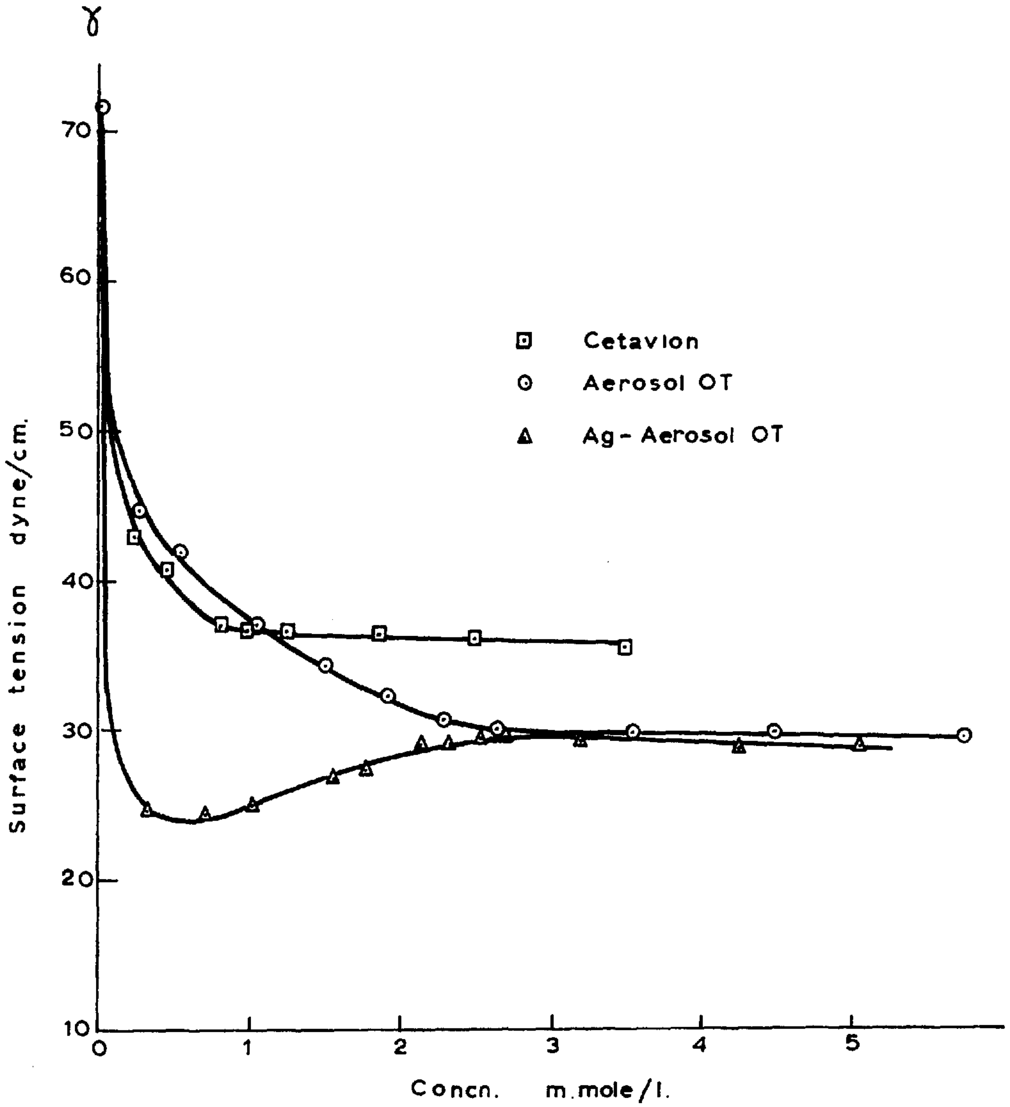

FIG. 19 Surface tension of surfactant solutions in water

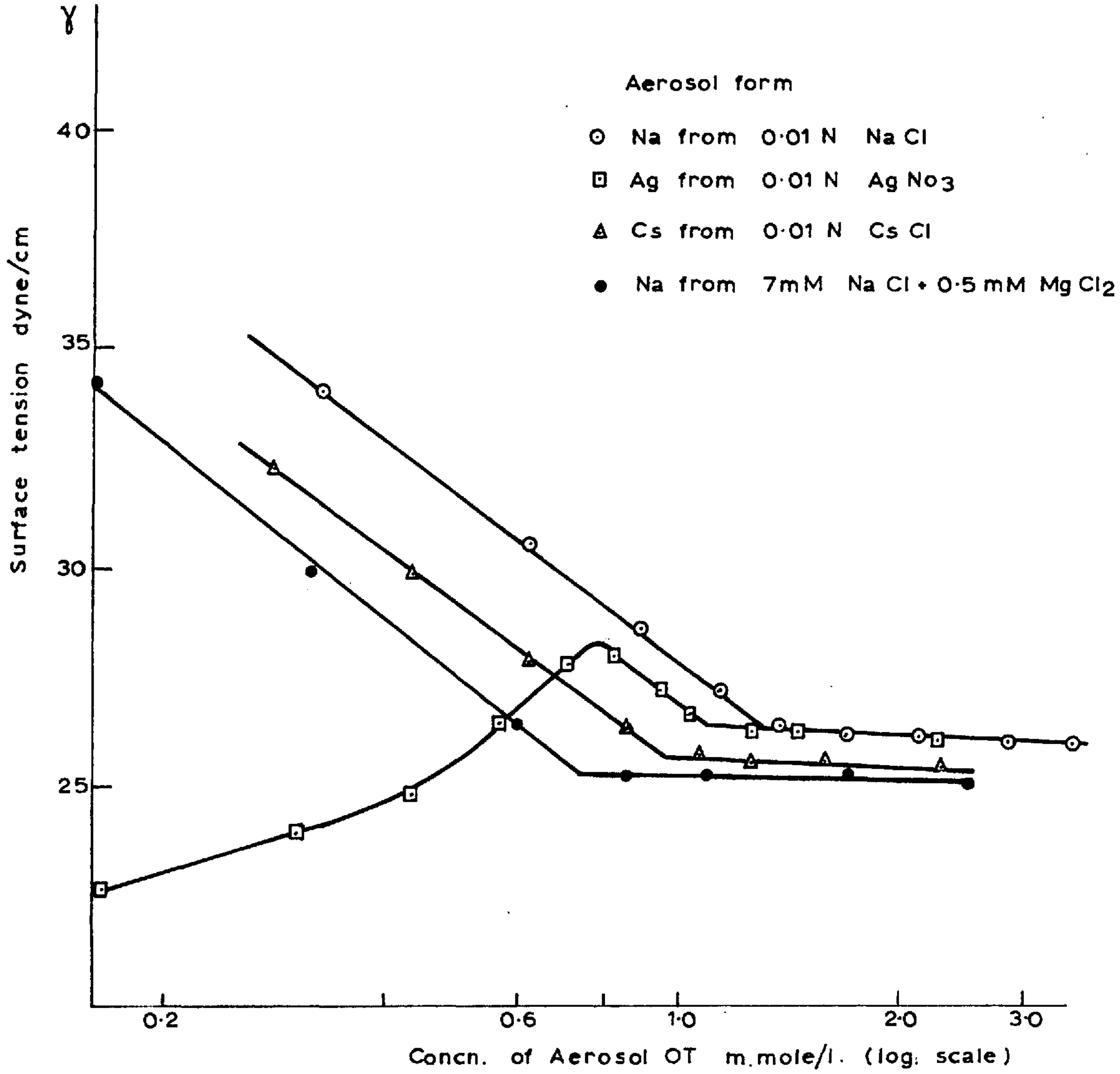

FIG. 20 Surface tension – concn. curves for different salt forms of Aerosol OT

proportion in the interface decreases and normal surface tension is then measured. It was at first thought that this minimum might be due to impurities accumulated during the preparation of Ag-Aerosol OT by the ion-exchange resin, but this is not entirely true as it was found that while the surface tension/concentration curve for Aerosol OT in 0.01 N Na NO_3 showed no minimum the same curve but from 0.0096 N Na NO_3 + 0.0004 N $AgNO_3$ (A.R. grade, recrystallized twice) showed a minimum, though a somewhat more shallow one than that observed in figure 19. (No special precautions were taken, however, to pro~~ets~~tect the solutions from daylight during the surface tension measurements.)

Figure 20 shows that in presence of added inorganic salts saturation adsorption (van Voorst Vader 1960) of surfactant at the interface had been reached in the surfactant concentration range from about 0.3 times the c.m.c. up to the c.m.c. From these straight lines the area per Aerosol OT molecule at the interface can be calculated by applying the Gibbs equation (as modified by Pethica 1954) for these surfactant solutions in presence of excess inorganic salt. The approximate equation reads

$$d\gamma = -RT\,\Gamma\, d\ln C \qquad (39)$$

where Γ is the surface excess of the surfactant at the interface (m.moles/cm^2). The concentration (C) was

TABLE 31. SURFACE TENSION OF AEROSOL OT SOLUTION

a) Aerosol in water (19°C)		b) Aerosol in 0.01 N NaCl(22°C)	
Concn. (mM)	γ (dyne/cm)	Concn. (mM)	γ (dyne/cm)
0.28	44.9	0.18	37.0
0.55	42.0	0.33	34.1
1.05	37.1	0.63	30.5
1.50	34.5	0.93	28.6
1.92	32.4	1.15	27.2
2.30	30.7	1.38	26.4
2.65	30.1	1.69	26.2
3.57	29.9	2.14	26.1
4.53	29.6	2.84	26.0
5.75	29.5	3.45	26.0

TABLE 32. CRITICAL MICELLE CONCENTRATION OF SURFACTANTS

Surfactant	c.m.c.(mM)	Temp.
Cetavlon	0.9	20
Na-Aerosol in water	2.5	20
Na-Aerosol in 0.01 N NaCl	1.3	23
Ag-Aerosol in 0.01 N Ag NO_3	1.1	20
Cs-Aerosol in 0.01 N Cs Cl	0.9	18
Aerosol in 7 mM NaCl + 0.5 mM $MgCl_2$	0.7	23

used instead of activity as the change in the activity coefficient is small over this limited surfactant concentration range in presence of high inorganic salt concentrations. The calculated area/molecule at the interface for the different salt forms of Aerosol OT were, 75 (23°C), 71(18°C) and 71 (23°C) Å^2 for the sodium, caesium and sodium-magnesium forms of Aerosol OT respectively. These values also show the effect of counterions on the packing of Aerosol molecules at the air/water interface and are in relative agreement with those found from adsorption experiments on graphitized carbon surfaces.

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