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Some Properties of aqueous solutions of cetyl trimethyl ammonium bromide in the presence of substituted benzoic acid salts.

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SUMMARY

This work is chiefly concerned with the properties of aqueous solutions of cetyl trimethyl ammonium bromide (CTAB) in the presence of certain additives which are mainly derivatives of benzoic acid such as sodium salicylate or sodium p-chlorobenzoate.

In the first part of the work, the adsorption of CTAB from its aqueous solutions on to graphite, alumina, titanium dioxide and silica has been studied. In all cases, the CTAB appears to be adsorbed by an ion exchange process. A bimolecular layer is formed. In the first layer, the ionic head of the CTA^+ is held to the surface by chemical forces while the paraffin chain is oriented away from the surface and in the second layer, the reverse orientation occurs. The effect of seven benzoic acid salts on the amount of CTA^+ adsorbed on alumina has been found to be qualitatively related to their effects on the viscosity of CTAB solutions. The sodium salicylate - CTAB system has been examined in more detail and an adsorbed film containing equimolecular amounts of salicylate and CTA^+ has been found to form on alumina. The salicylate - CTA^+ complex covers a greater part of the surface than the CTA^+ alone and consequently gives a better measure of the surface area of the powder.

The sedimentation volume of titanium dioxide in CTAB solutions has also been investigated and the effect of sodium salicylate, sodium p-chlorobenzoate and sodium p-hydroxybenzoate on this sedimentation volume has been related to their effects on the viscosity of CTAB solutions.

In the second part of the work, the approximate activity coefficient of Br' in CTAB solutions was measured using electrolytically prepared silver-silver bromide electrodes. The critical micelle concentrations of CTAB (in .002M KBr) and of dodecyl trimethyl ammonium bromide were determined by this method and found to agree with the values obtained by other workers. The activity coefficient of Br' was also measured in solutions containing CTAB and salts similar to those used in the adsorption and sedimentation work. Changes in the activity coefficient of Br' on addition of these salts were again found to be related to their effects of the viscoity of CTAB solutions.

Finally, a preliminary attempt was made to investigate the elastic properties of the visco-elastic solutions. These solutions were contained in the gap between two vertical co-axial glass cylinders which were caused to oscillate harmonically. The response of the liquid was observed by focussing a microscope on a very small bead which had been suspended in the liquid.

The results again showed that the salicylate -CTA^+ complex acquires some stability when the salicylate and the CTA^+ are present in equimolecular amounts. The structure of the solutions, particularly the p-chlorobenzoate - CTA^+ solutions, seems to be altered on shearing.

An effort has been made to interpret the results of different types of experiments in terms of long threadlike aggregates formed by interaction of the CTA^+ with the organic salt.

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GENERAL INTRODUCTION

Aqueous Solutions of Paraffin Chain Salts.

Aqueous solutions of paraffin chain salts owe their most remarkable properties to the possession of two widely differing characteristics by the one ion. G. S. Hartley[1] has coined the term 'amphipathy' - both feelings - to describe this property of paraffin chain salts since the presence of a hydrophilic, ionic group gives the salt a sympathy for water, while, at the same time, the hydrophobic hydrocarbon chain gives an antipathy for water. While not all paraffin chain salts show unusual properties, the term 'amphipathic substance' is perhaps more restrictive than others, such as soaps, detergents, or colloidal electrolytes, which are often used instead.

Prior to 1908, it was generally believed that soaps were ordinary colloids. However, in that year, McBain and his collaborators[2,3,4,5] began a series of investigations which revealed properties very different from other colloids. It had been known previously that the conductivity of soaps was rather high for a colloid, but this had been ascribed to hydrolysis. McBain[4], however, showed that the alkali produced by hydrolysis could only explain a small fraction of conductivity. Nevertheless, the osmotic activity of soap solutions was extremely low, for example McBain and Salmon[6] found that the concentration of osmotically active particles in potassium stearate solution was considerably less than it would be if the soap were dissolved as an undissociated salt. McBain was thus led to postulate an ionic micelle which would have low osmotic activity but considerable conductivity. Now the equivalent conductivity of soap solutions falls with increasing concentration, at low concentrations, reaches a minimum and then slowly rises to an approximately constant value[7]. This latter rise in conductivity was considered by McBain to be a consequence of the formation of a small polyvalent, ionic micelle, since, according to Stokes' Law, the resistance to motion of a sphere through a liquid is proportional to its radius, so that if m soap ions aggregate to form a micelle of charge m, the mobility and hence the conductivity of the micelle will be $m^{2/3}$ that of m single ions. The initial fall in conductivity was due to the formation of undissociated molecules and later neutral colloid, for McBain believed soaps to be essentially rather weak electrolytes.

The sudden change in a number of properties of paraffin chain salts in a limited range of concentration was considered by Jones and Bury[8] in 1927, to be a consequence of the law of mass action as applied to the association of single molecules to form complexes containing a large number of molecules. If the concentration of single molecules is C_1 and of aggregates

C_m and K is the equilibrium constant, then for the equilibrium

$$\text{micelle} \rightleftharpoons m \text{ single molecules}$$

$$K = \frac{(C_i)^m}{C_m}$$

As Grindley and Bury[9] pointed out, only when C_i is comparable with $K^{1/m}$, will the concentration of micelles become appreciable. When C_i is greater than $K^{1/m}$, the concentration of micelles will increase rapidly with increasing total concentration. The rate of this change will increase as m increases. The concentration at which micelles begin to form was termed the critical micelle concentration (C.M.C.) by Davies and Bury[10], in the course of their work on the partial specific volume of potassium n-octoate in its aqueous solutions.

The work on the partial specific volume of paraffin chain salts[9,10] had revealed changes in this property which were explainable in terms of the considerations given above. Lottermoser and Püschel[11] found that the equivalent conductivity of various alkyl sodium sulphates fell only slowly at very low concentration until, at a fairly definite concentration, it dropped with an abruptness which depended on the length of the hydrocarbon chain. In a somewhat similar investigation, Hartley and Malsch[12] suggested that the sudden fall in conductivity indicated the formation of micelles.

In 1935, Murray and Hartley[13] applied the law of mass action to a micelle consisting of a large number of ions but with an appreciable part of its charge neutralised by adherent gegenions. By representing the micelle as Na_pA_m where $m > p$, they obtained

$$K = \frac{(C - C_m.{}^{p}/_{m})^{p}.(C - C_m)^{m}}{C_m}$$

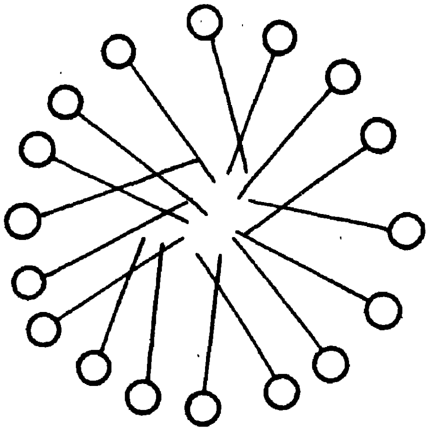
where C is the total concentration. It was shown by this equation that the formation of micelles is more abrupt if the association of gegenions with the micelle is considered.

In 1936, Hartley, Collie and Samis[14] investigated the conductivity and transport numbers of some quaternary ammonium salts. They found that, in the region where the equivalent conductivity was falling rapidly, the transport number of the paraffin chain ion rose sharply and eventually reached values greater than unity, indicating that some of the gegenions were so strongly attached to the micelle that they travelled in the opposite direction to that in which free gegenions would travel. It was then possible to explain all the known facts about aqueous solutions of paraffin chain salts on the basis of a spherical micelle (originally suggested by Reychler[15] in 1913) containing, for a salt with sixteen carbon atoms per chain, about fifty paraffin chain ions aggregated together with the paraffin chains directed towards the interior and the ionised, hydrophilic heads on the exterior, and having some 25-40 gegenions attached to the surface (fig. I).

According to Hartley, the fall in equivalent conductivity was due to the effect of the gegenions attached to the micelle since they both reduced the mobility of the paraffin chain aggregate and, in part, ceased to carry current themselves, these effects overcoming the increase in conductivity of the paraffin chain aggregate to be expected from Stokes' law and, indeed, shown by the transport number measurements. At high field strengths, the paraffin chain aggregate tends to be torn away from its atmosphere of adherent gegenions, so that the "Stokes' law increase" in the mobility of the micelle becomes more important and the equivalent conductivity actually rises above the infinite dilution value.[12]

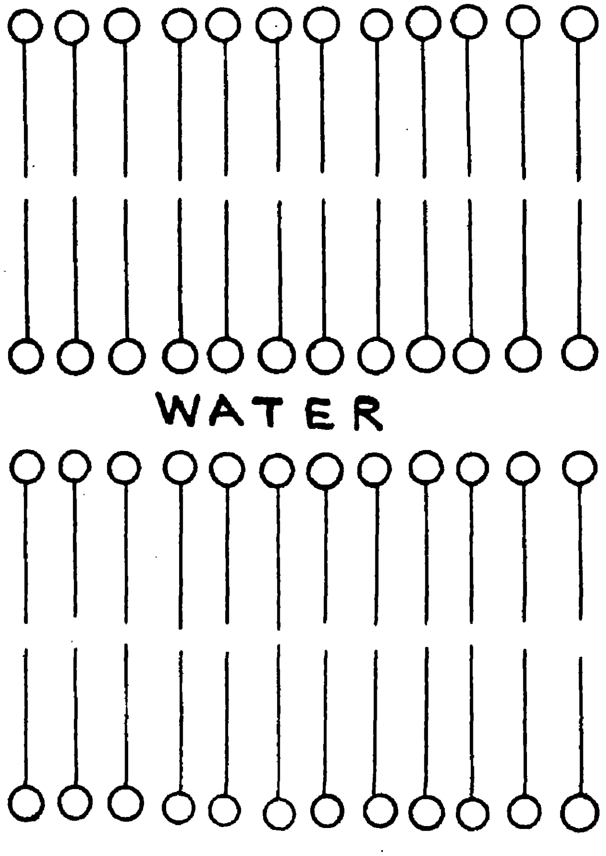
Hartley[1] also suggested that the formation of micelles was due, not so much to any actual repulsion between the water and the paraffin chain, as to the strong cohesion between the water molecules. The cohesion between water molecules falls off rapidly as their separation is increased so that to introduce, into water, a large aggregate of paraffin chains may not require much more energy than to introduce one paraffin chain. The strong cohesion between water molecules means that single paraffin chains are under a considerable compressive force.

FIG. 1



SPHERICAL MICELLE

(HARTLEY)



LAMELLAR MICELLE

(Mc BAIN)

On aggregation the compressive force per paraffin chain is decreased and the chains tend to expand, while the water molecules tend to contract. This is clearly shown by the work of Bury *et al.*[9,10] on the partial specific volumes of paraffin chain salts and of water, in these solutions.

One of the main phenomena which Hartley had not explained before 1936, was the rise in conductivity in such soaps as potassium laurate, palmitate etc. McBain had believed that his ionic micelle predominated over the 'neutral' colloid in this region of concentration and so produced a rise in conductivity. This implied 'retrograde dissociation' i.e. dissociation of already associated neutral colloid with increasing concentration. While Hartley accepted 'retrograde dissociation' of his spherical micelle as a possibility at higher concentrations, he believed that an increase in the mobility of the gegenions was also possible. In 1939, he considered that the latter explanation was the most probable[16] since in concentrated solutions, the ionic atmospheres of the micelles will tend to encroach on one another so that increase in concentration should increase the amount of free gegenions relative to those more tightly bound.

In 1937, Hess and Gundermann[17] discovered that soap solutions gave more definite X-ray diffraction patterns than normal solutions. Later other workers using X-ray methods e.g. Hess, Kiessig, et al.[18,19] Dervichian and Lachampt[20], Stauff[21], Harkins et al.[22] tended to adopt the lamellar only slightly ionised micelle of McBain since it was believed that the micelles must possess some regular structure to produce the diffraction effects.

At first, two X-ray bands were observed, one - the short (S) spacing - having a value of about 4.6 Å, is independent of the length of the hydrocarbon chain and of the concentration, and it was thought to be due to a parallel arrangement of hydrocarbon chains in the micelle. The second band - the (I) band - varies with concentration and was believed to give the intermicellar distance. McBain[23] considered that X-ray bands proved the existence of lamellar micelles even though they did not appear over the whole range of concentration in which he believed colloid to be present.

In 1947, Harkins and his collaborators discovered a third (M) band[24,25] somewhat weaker than the other two and independent of concentration. This was identified as the distance between the polar heads of the micelle, its value being approximately twice the length of the hydrocarbon chain. While Harkins believed, as did Hartley, that there was only one type of micelle in dilute soap solutions, he pictured it as a short cylinder containing anything from 30 to 170 soap molecules, rather than as a sphere.

Bernal[26] pointed out that to explain the X-ray data by a lamellar micelle meant omitting a considerable fraction of the water present, as the micelle would have to be separated by a greater depth of water, laterally, than that held between the ionic faces. Hartley[27] suggested that in fairly concentrated solutions, repulsive effects between spherical micelles could give rise to a regular structure in solution which would give X-ray diffraction bands. He was able to find reasonable values for the size of his spherical micelle by using the long (I) X-ray spacing as the distance between the centres of the micelles. Furthermore the spherical micelle was capable of explaining this X-ray band without omitting a large fraction of the water present.

Corrin[28], originally a supporter of the McBain theory, was also able to account for the X-ray data on the basis of a spherical micelle and he concluded that this type of measurement would not allow a decision between lamellar and spherical micelles.

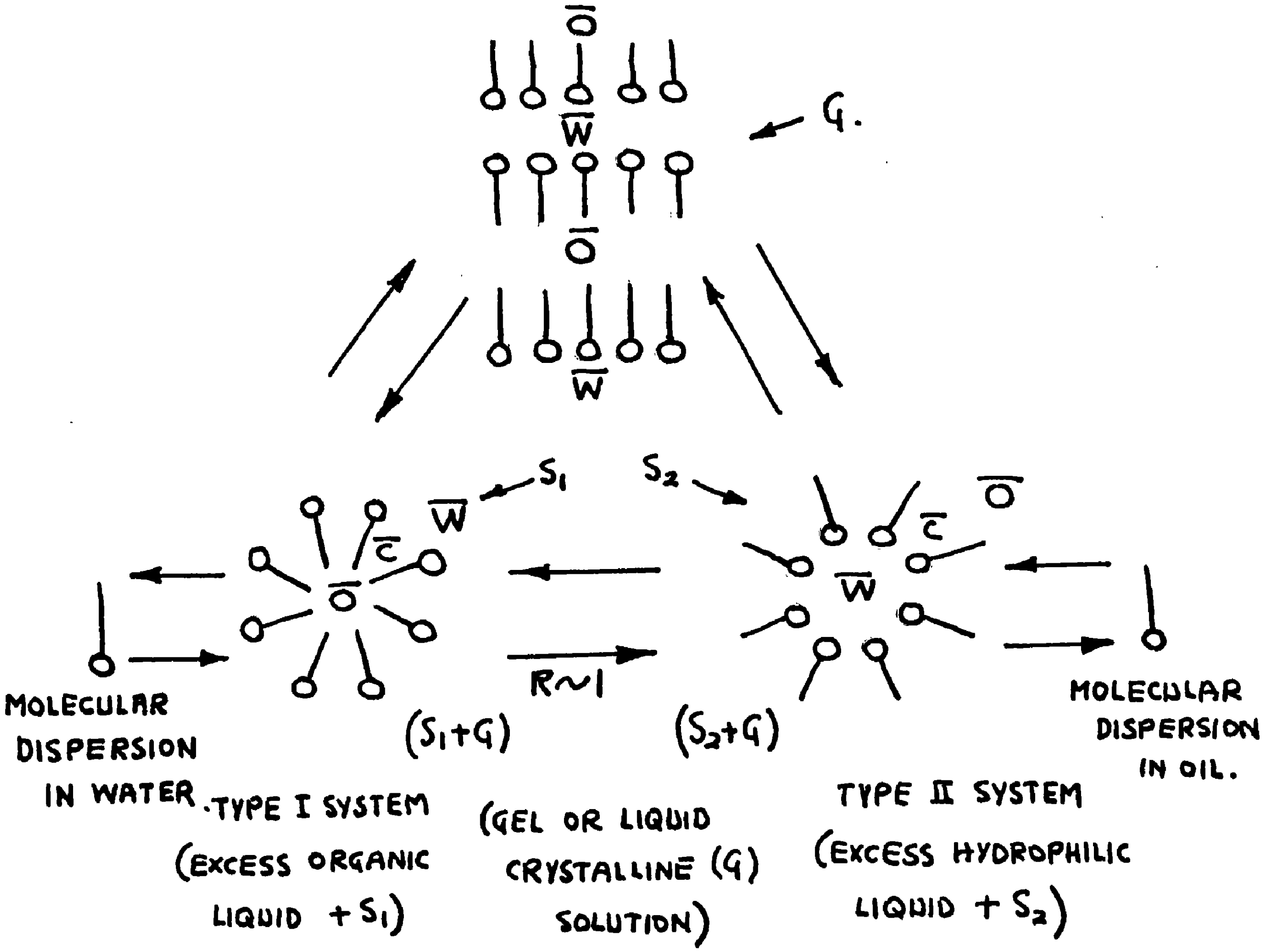
There are thus two main theories concerning the nature of the micelles in soap solutions. McBain postulates at least two types of micelle, the first, a small polyvalent, ionic micelle containing not more than ten paraffin chain ions and retaining its charge, while the second is the larger, almost neutral lamellar micelle with the paraffin chains aligned parallel to one another (fig. I). The ionic micelle is believed to be formed before the concentration generally known as the C.M.C., is reached. While some investigations have shown a rise in conductivity before the C.M.C.[29,30] others have not confirmed this[31]. McBain[32] has pointed out that Hartley's spherical micelle agrees none too well with the dimensions of soap molecules. He has described all published diagrams as a 'travesty of well known atomic and molecular dimensions, since, even if these short thick rods could be close packed radially, as Ward[33] calculates, over 70% of the micellar surface would be occupied by hydrocarbon'. In general McBain believes the properties of soap solutions to be too complicated to be explained by one type of micelle i.e. 'if there is any way in which ions or ion pairs can come together or associate with any reduction in free energy... then that complex must exist, however slight, in soap solutions'.

On the other hand, Hartley[1] has pointed out that McBain's postulate of an abrupt decrease in the simple dissociation of paraffin chain salts, is open to two serious objections. First 'there is no probable mechanism for this decrease as long as the paraffin chain ions remain separate from one another', and second, 'the decrease is supposed to cease at just the concentration where, in the formation of aggregates of paraffin chain ions, a very probable mechanism for its commencement comes into being'.

Other workers have tended to adopt views similar to either Hartley's or McBain's theories. Thus Lawrence[34] proposed a type of spherical micelle in which the paraffin chains were arranged alongside one another. He also believed that 'secondary' micelles were formed by cohesion of the polar end groups of the spherical micelles[35]. Klevens[36] has suggested an oblate spheroid. Harkins[37], who at one time proposed a cylindrical micelle, has more recently considered a quasi-oblate spheroid with the characteristics of both the cylindrical micelle and the oblate spheroid.

Winsor[38,39] has developed a very general theory which is particularly suitable for dealing with some solubilisation phenomena.

This is shown diagrammatically below:



$\overline{W}$ is the hydrophilic section of the micelle

$\overline{C}$ is the amphiphilic section of the micelle

$\overline{O}$ is the lipophilic section of the micelle

R is the ratio of the dispersing tendencies of lipophilic and hydrophilic faces of $\overline{C}$ respectively.

There are thus three types of micelles visualised. Winsor believes that they exist together in equilibrium with one another, the amount of each depending on the temperature and composition of the system.

Paraffin Chain Salts in the Presence of Additives.

Solubilisation.

McBain[32] has defined solubilisation as 'the spontaneous passage of molecules of a substance, insoluble in water, into a dilute aqueous solution of a detergent, to form a thermodynamically stable solution'. It has been suggested by Lawrence[40] that solubilisation may be divided into two types depending on the polarity of the additive or solubilisate. First there is incorporation into the hydrocarbon interior of the micelle, for non-polar solubilisates, and second, incorporation into the palisade layer of the micelle with the polar solubilisate oriented in approximately the same manner as the soap molecule.

(i) Incorporation into the Hydrocarbon Centre of the Micelle.

Hartley[41] found the solubility of trans-azobenzene in aqueous solutions of cetyl pyridinium chloride to be roughly the same as its solubility in an equivalent amount of liquid hexadecane, suggesting a liquid paraffinic interior in the micelles. Extensive X-ray work by Krishnamurti[42], Hess *et al*.[17,19,21] Hughes, Sawyer and Vinograd[43] and Harkins, Mattoon and colleagues[44,25] has given more direct evidence that the non-polar hydrocarbons penetrate into the interior of the micelle, e.g. the weak (M) X-ray band has been shown to increase as hydrocarbon is added to the solution, reaching a maximum when the limit of solubilisation is reached[25].

Cationic detergents generally solubilise several times more hydrocarbon than do anionic detergents of similar chain length[45]. The ~~rate of increase of~~ solubilisation of hydrocarbons increases with soap concentration, any excess hydrocarbon being present as a separate phase. Increase in the chain length of the solubilisate decreases solubilisation while cyclisation has the opposite effect[46,47]. Addition of a polar compound, e.g. a long chain alcohol, greatly enhances the solubilisation of a hydrocarbon while the presence of a hydrocarbon increases the solubilisation of a polar compound[48]. This has been explained on the grounds that solubilisation of both polar and non-polar additives increases the size of the micelles and so allows them to take up more non-polar or polar additives respectively.

(ii) Penetration into the Palisade Layer of the Micelle.

The solubilisation of polar additives, e.g. long chain alcohols, amines etc., is usually markedly different from that of non-polar additives. For instance, there is no increase in the 'M' X-ray spacing and the ~~rate of~~ solubilisation decreases with increasing concentration ‸ of soap / although the amount actually solubilised is greater than for comparable hydrocarbon additives. Studies of the effect of changes in the nature of the soap and the additive e.g. chain length, polarity, charge, chain branching, etc., tend to confirm the difference in mechanism mentioned above between the solubilisation of polar and non-polar additives[49].

While the solubilisation of long chain alcohols increases as the chain length of the solubiliser is increased, it tends to level off eventually. The transition which occurs here has been discussed by Klevens[50] on the basis of the relative amphiphilic properties of the long chain alcohols and by Winsor[51] who suggests that the relatively hydrophilic additives tend to form his type II systems (i.e. S_2 micelles plus excess aqueous liquid) while the more lipophilic additives give type I systems (i.e. S_1 micelles plus excess organic liquid).

More recently, Lawrence et al.[52] have indicated that the solubilisation of polar additives, containing more than about 5 carbon atoms per chain, by soaps such as teepol, C.T.A.B., etc., follows a general behaviour. Initial additions of additive are solubilised to a clear isotropic solution with a large increase in viscosity. At a certain concentration a liquid crystalline phase begins to separate. The volume of this phase increases to a maximum on further additions but then decreases until another isotropic solution is obtained. Further additions cause separation into two phases. The viscosity of these solutions reaches a maximum which coincides with the separation of the liquid crystalline phase. Subsequently another, much greater maximum is reached at roughly equimolecular amounts of soap and additive for the longer chain alcohols, but the ratio (alcohol to soap) increases as the chain length of the alcohol is reduced. If the additive chain contains less than 5 carbon atoms, the liquid crystalline phase does not appear. The nature of the liquid crystalline phase depends on the composition of the system but in the region of high viscosity it has a silky, striated texture.

The lower alcohols e.g. methyl or ethyl, are considered to be associated with the soap by attraction of polar groups while the higher alcohols are packed in between the hydrocarbon soap chains. The resulting micelle is not regarded as a 'complex' nor is the interaction between the soap and additive attributed to hydrogen bonding.

Lawrence also found that whereas aniline, benzyl alcohol and phenyl ethyl alcohol give liquid crystalline phases, phenol and cresol give systems too soluble for the liquid crystalline phase to appear. Previously, in a somewhat similar investigation, Angelescu and his colleagues[53,54] had studied the effect of additions of phenol, cresol and other phenolic compounds, on the viscosity and conductivity of various anionic soap solutions. At suitable concentrations, the viscosity rose to a maximum, then fell to a minimum and finally rose again almost linearly. They also found (as did Lawrence) that the conductivity was at a minimum when the viscosity was at a maximum and vice versa. The polar molecules were believed both to attach themselves to the soap ions on the exterior of the micelle and to penetrate into the micelle. Angelescu also claimed to have found some evidence for compound formation.

The Effect of Electrolytes on Soap Solutions.

The effect of simple electrolytes on the C.M.C. of soap solutions has been studied by a number of workers. Hartley[41] measured the C.M.C. of cetyl pyridinium chloride by the solubilisation of trans-azobenzene. Initial additions of sodium chloride greatly decreased the C.M.C. e.g. .01 N NaCl reduced the C.M.C. from 9×10^{-4} M to 1.5×10^{-4} M, but subsequent additions had much less effect. Other work by Tartar, Cadle, Wright and others[55,56] has confirmed the reduction in the C.M.C. of soap solutions on addition of simple electrolytes. Corrin and Harkins[57] have shown that, for anionic soaps, the reduction in the C.M.C. is practically independent of the anion of the added electrolyte while, for cationic soaps, it is independent of the cation of the added electrolyte. Simple electrolytes are generally considered to 'screen' the repulsion of the charged ionic heads of the soap ions and, by so reducing the principle force preventing micelle formation, to stabilise the micelles with a consequent reduction in the C.M.C.

Debye[58,59], using light scattering techniques, believed that there was an increase in the size of micelles on addition of electrolyte but the interpretation of such results has recently been criticised by Hutchinson[60] who suggests that light scattering measurements give information about the charge rather than the size of micelles.

Kolthoff and Johnson[61] claim to have shown 'solubilisation by exchange of counter ion', by measuring the solubility of the slightly soluble dodecyl ammonium thiosulphate in the soluble dodecyl ammonium bromide. The solubility is first decreased due to the mass action effect but when the C.M.C. of the bromide has been reached, micelles are formed with anions as counter ions. Anions adsorbed on the micelle then exchange with anions in solution. Thus anions of the slightly soluble compound are withdrawn from solution and the solubility increases above the C.M.C.

The effect of amphiphilic electrolytes on soap solutions depends on the nature of the charged head of the electrolyte and on the hydrophobic character of the electrolyte ion. Where the electrolyte ion has the same charge as the soap ion and is of similar chain length (i.e. where the electrolyte is a soap ion) solubilisation occurs, the less soluble soap being considered to be solubilised by the more soluble one[62]. Where the amphiphilic electrolyte ion is of opposite charge to the soap ion, precipitation occurs provided both ions have chains containing more than about twelve carbon atoms. This has been utilised as a means of estimating either cationic or anionic detergents. Where the amphiphilic ion is of opposite charge to the soap ion but has little hydrophobic character, it is simply adsorbed onto the surface of the micelle. Between the last two extreme cases, transition effects occur. Scott, Tartar and Lingafelter[63] have shown that although sodium octane sulphonate and octyl trimethyl ammonium bromide only show evidence of micelles at high concentrations, octyl trimethyl ammonium octane sulphonate is quite colloidal with a C.M.C. of about .02M. The micelles which are formed in this solution carry only a slight charge (between one and two). With longer chains, the solutions become more opalescent and Anacker[64] has identified dilute solutions of decyl trimethyl ammonium decyl sulphonate as emulsions.

Winsor[65] has studied systems formed by the addition of cyclo-hexyl ammonium chloride to solutions of sodium undecane--3-sulphate. A water-clear isotropic solution S_1 is formed at first. Subsequent additions produce, in turn, an (S_1 + G) biphasic system, a liquid crystalline solution, a (G + S_2) system appearing isotropic at first but later settling into two phases and finally a type II system. This type II system became clear on gentle stirring but separated into two phases again when at rest. The clear, apparently isotropic single phase solutions which show streaming birefringence are regarded as stable (S + G) emulsions. Where separation occurs, the difference between the refractive indices and densities of the two phases is very slight. The possibility of two equilibrium phases existing together with zero interfacial tension is suggested.

The Viscosity of Soap Solutions

The viscosity of soap solutions both alone and in the prescence of additives is often anomalous i.e. it is not constant as the shear force causing flow is altered. According to Newton's viscosity law

$$S = \eta \frac{d\sigma}{dt}$$

where S is the shearing force

η, a constant, is the viscosity coefficient

and $\frac{d\sigma}{dt}$ is the rate of shear.

Fluids which do not obey this equation over a normal range of shearing force are sometimes called non-Newtonian or else said to possess structural viscosity. This latter term derives from the work of Ostwald[66] on the viscosity of emulsoids and it is intended to describe the effect of an ordered structure on the viscosity of a solution.

An example of a viscous soap solution is a concentrated sodium oleate solution which has been studied by Philipoff and Hess[67]. At high pressure and concentration (e.g. about 35%), the solutions showed a well defined structural viscosity expressed by a falling viscosity coefficient. Philipoff[68] also studied the effect of m-cresol on sodium oleate solutions and found that the maximum non-Newtonian behaviour was observed in those solutions which produced a maximum viscosity on the viscosity-concentration curve.

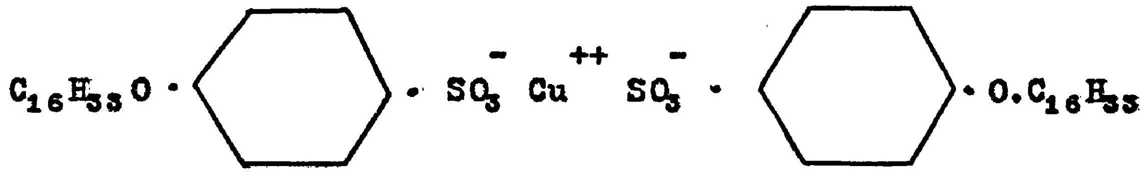
Ostwald[69] has suggested that structural viscosity may be due to the overlapping of the solvent envelopes which surround most colloidal particles while McBain[70] considers that the viscosity of colloidal solutions will depend on the ability of individual particles to aggregate into a reticular porous structure which can retain a large volume of solvent.

Visco-Elastic Soap Solutions.

While soap solutions which possess high viscosity are comparatively common, there are not so many soap solutions, which show pronounced elastic behaviour. Perhaps the best known example is ammonium oleate. When a beaker containing ammonium oleate solution (about .005N) is rotated, and then stopped, the solution will at first continue to rotate under its own momentum for a short time but then rotate in the reverse direction showing a kind of elastic quality (elastic recoil). Such solutions are often much more dilute than those which are viscous gels.

Hatschek and Jane[71] studied ammonium oleate solutions in a Couette viscometer. When the outer cylinder was rotated at constant speed, the torque on the inner one, after a short normal period, increased to an irregularly fluctuating value many times greater. After a period of rest, this behaviour could be repeated. It seemed that a gelatinous structure was actually built up by the process of shear and dissipated again at rest.

Later Andrade and Lewis[72] showed that the anomalous increase in torque was associated with the onset of turbulence. In 1938, Hartley[73] remarked that the turbulence itself, also anomalous and of abnormal appearance, was another result of the structure built up, rather than the direct cause of the increased torque. Hartley also described a remarkable example of visco-elastic behaviour in dilute solution shown by a .02% solution of the copper salt of p-hexadecoxy benzene sulphonic



acid at 80-90°C. If this solution is undisturbed, a stream of air bubbles will rise through it in a manner similar to that in which they would rise through water and also in a similar time. If the solution is gently stirred, however, the upward course of the bubbles takes much longer and is extremely irregular. The bubbles frequently collect in small clusters and whether single or in clusters they are seen to halt at, or be diverted round, invisible barriers. About a minute after stirring is stopped, the normal behaviour is completely restored. Hartley calls this 'negative thixotropic behaviour'.

More recently Bungenberg de Jong and others[74,75] have studied the viscous and elastic properties of aqueous sodium oleate in the presence of various additives (electrolytes or polar organic compounds), while Pilpel[76] has shown that a typical visco-elastic soap solution appears to show much the same mechanical behaviour as other types of visco-elastic solutions e.g. polymethyl methacrylate in toluene.

Winsor[65] has discussed the nature of visco-elastic soap solutions and has attempted to explain some their properties by means of his theory of micellar equilibrium, He considers these 'solutions' to be, in fact, intimate emulsions of (S + G) phases. On stirring such a solution as ammonium oleate, he believes that a finely dispersed emulsion is formed and that this emulsion reverts, on standing, to a coarse, possibly multiple, dispersion. The marked hysteresis in mechanical properties derives, he argues, from the progress of the dispersion of the (S + G) emulsions when the 'solutions' are under shear and of their partial coagulation when at rest.

Visco-Elastic Solutions formed by the Addition of Certain Organic Electrolytes to Aqueous Cetyl Trimethyl Ammonium Bromide (CTAB).

In the course of some work in this laboratory on the viscosity of CTAB/phenol/water/electrolyte systems, Dr. W. Good and Mr. E. Walker[77] were led to examine the system CTAB-sodium salicylate-water. This solution had a viscosity, as measured by the time of flow through an Ostwald viscometer, which was vastly greater than anything hitherto encountered. It was also noticeable, however, that most of the solutions were extremely elastic and that they showed properties which are typical of visco-elastic soap solutions. For example, on streaming they become birefringent while, when sheared between vertical coaxial cylinders they 'climb' the inner wall (the Weissenberg effect).

Subsequently the viscosity of a large number of C.T.A.B. solutions containing different types of electrolytes was measured by use of the Ostwald viscometer. The viscosity-concentration curves were generally similar in that the viscosity first rises to a maximum as the electrolyte is added to a fixed amount of C.T.A.B. and then falls again almost as sharply. The principal results were obtained using a .027 M concentration of C.T.A.B and they are shown in tabular form below. The figures refer to the time in seconds for the solution of maximum viscosity to run through a No.2 B.S.S. viscometer, while the numbers in brackets are the molarities of the salts $X10^2$ in these solutions. The zeroes in the table indicate that the isomer in question has no effect on the viscosity of .027M C.T.A.B. solution.

TABLE I

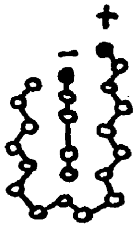
Salt	Para	Meta	Ortho
Chlorobenzoate	27,800 (5.4)	12,000 (5.7)	0
Toluate	5,600 (16.8)	140 (7.7)	0
Toluenesulphonate	1,275 (4.3)	-	314 (4.3)
Cresylate	1,120 (7.2)	156 (10.8)	31 (7.8)
Nitrobenzoate	32 (3.3)	0	0
Benzenedicarboxylate	0	0	1,420 (5.0)
Aminobenzoate	0	0	61 (6.6)
Hydroxybenzoate (salicylate)	0	1,880 (8.8)	212,900 (1.7) 65,000 (8.0) (two maxima)
Benzoate	28 (10.0)		

While the precise significance of the time of flow of these solutions, especially the more visco-elastic ones, through a viscometer, is not clearly understood, the above figures do give an indication of the size of the aggregates producing viscous behaviour, in these solutions. The mechanical behaviour of the more elastic solutions is so susceptible to changes in shearing force that the term 'viscosity' is rather misleading and has only been used in connection with them because a whole range of solutions from those of Newtonian viscosity to those possessing highly complex elastic structures, is encountered in this work.

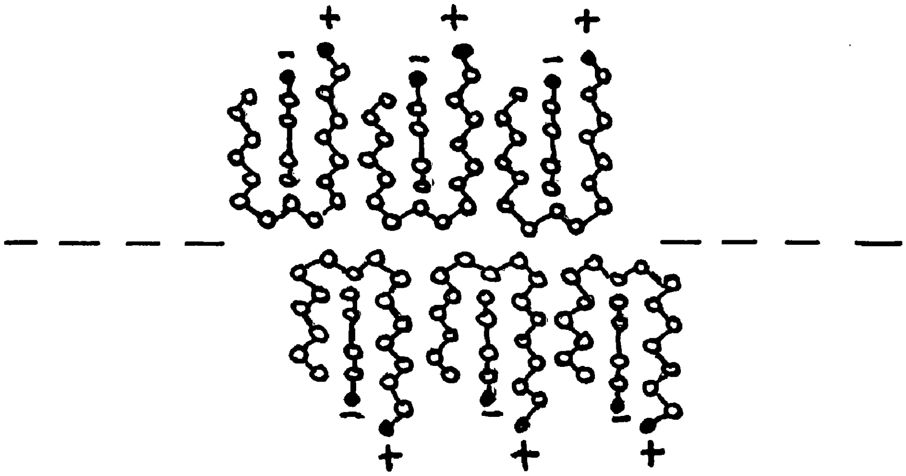
Among the salts shown above, two are outstanding in their effect on the viscosity of C.T.A.B. solutions. One is sodium salicylate and the other, sodium p-chlorobenzoate. The former is unusual in that the viscosity-concentration curve has two maxima, the first a very sharp one, the second much broader. Viscosity effects begin to appear in CTA$^+$-salicylate solutions at concentrations at which the viscosity of the solutions containing the other additives is still normal i.e. the same as water.

A number of other more complex salts have been examined. The introduction of a hydroxy group in the '4' position of the salicylate ion to give 2:4-dihydroxy benzoate almost completely destroys the visco-elastic effect. On the other hand, the 2:6-dihydroxy benzoate shows two maxima of magnitude comparable to the salicylate but occurring over a very much reduced range of concentration and in a region of salt concentration even lower than that in which the salicylate shows its greatest viscosity effect. The p-chlorobenzoate ion is less sensitive to the introduction of more chlorine atoms, the 2:4 and the 3:4-dichlorobenzoates both giving quite viscous solutions with the C.T.A.B., though not as viscous as the p-chlorobenzoate -C.T.A.B. solution itself.

On the basis of the evidence available and by a study of suitable molecular models, Dr. Good considers that the hydrocarbon chain of the C.T.A.$^+$ ion tends to be hooked round the hydrophobic part of the organic electrolyte i.e.



this unit being associated with the other of similar structure to give a large threadlike (or possibly lamellar) aggregate such as.



Other evidence favouring this view is that the length of the cationic chain seems to be critical. When dodecyl trimethyl ammonium bromide or octadecyl trimethyl ammonium bromide are used in place of C.T.A.B., the visco-elastic effects are greatly reduced. Furthermore the introduction of the bulky phenyl grouping into the salicylate ion to give 3-phenyl salicylate, leads to a much less viscous solution than that obtained with salicylate.

Good and Walker have also shown that sodium salicylate and sodium p-chlorobenzoate both appear to have an unusual effect on the C.M.C. of C.T.A.B. solutions. As the salt is added to the C.T.A.B., the C.M.C. is reduced (as with an ordinary electrolyte), but this effect is soon reversed and the C.M.C. increases to a value considerably in excess of the C.M.C. of C.T.A.B. alone.

PART I.

The Adsorption of CTAB from aqueous solutions on graphite, alumina, titanium dioxide and silica.

INTRODUCTION

The adsorption (Γ) of a substance is classically defined for the interface or boundary between two phases by the equation

$$\Gamma = \int_0^\infty [c(x) - c(\infty)]dx$$

where c is the concentration of the substance, x is the distance from the 'interfacial plane' and $c(\infty)$ is the concentration in the bulk phase outside the interfacial region. The 'interfacial plane' was defined by J. W. Gibbs[78] as an origin, placed somewhat arbitrarily in the interfacial region. Defined in this way, the adsorption of a substance implies no mechanism.

The most studied interfaces between two phases are the solid-gas, the vapour-liquid and the solid-liquid interfaces. The first two, although not strictly concerned with this investigation, may be mentioned briefly as some of their characteristics are analogous to those of the solid-liquid interface.

The adsorption of a gas at the surface of a solid has been interpreted mainly by the theories of Langmuir[79] and Brunauer, Emmett, Teller, Deming (L.S.) and Deming (W.E.)[80,81]. The Langmuir equation was derived for the equilibrium between gas molecules adhering to a homogeneous surface due to short range forces, and those which tended to rebound into the gaseous phase. The adsorbed film was considered to be unimolecular. Brunauer *et al.* generalised the Langmuir equation in order to account for multilayer adsorption and they were able to eventually explain the five types of isotherms obtained in the physical adsorption of gases on solids.

The gas-liquid interface is of interest here in connection with the adsorption of long chain amphiphilic compounds, such as palmitic acid, on the surface of water to form unimolecular films. When subjected to a suitable pressure, such substances become oriented with the polar group in the aqueous phase and the hydrocarbon chains aligned parallel to one another but directed away from the aqueous phase. Studies of this phenomena have revealed valuable information about the dimensions of certain molecules.

When the amphiphilic compound is soluble in the aqueous phase, there is a rapid reduction in the surface tension of the solution at low concentrations of the additive. Subsequently a minimum is found but this seems to be due to small amounts of surface active impurities which are solubilised once the C.M.C. has been reached[82]. The surface tension eventually becomes constant since all further added solute dissolves as micelles.

For a number of reasons, adsorption at the solution-solid interface is, in general, more complicated than at the gas-solid or the gas-liquid interfaces. First, competition for the surface between the solvent and the solute molecules must be taken into account at higher concentrations. Fortunately, the most interesting changes in the adsorption of surface active agents occur at low concentrations, so that any error involved in neglecting the adsorption of solvent is generally less than that of the usual experimental methods[83]. Second, even if the surface of the solid is homogeneous, there are usually large numbers of corners, faces and edges, which give rise to adsorption sites of different energies since their residual attractive forces are different[84]. Third, many solid surfaces are heterogeneous and contain functional groups scattered at random over the surface. These many give rise to 'active sites' where special types of adsorptions may occur. This is particularly the case where the surface has been chemically or physically pretreated. For instance, by using different temperatures and gases, Bartell and Lloyd[85] showed that the surface of charcoal could be made to appear either polar or non-polar.

Solid adsorbents are usually divided into two classes i.e. polar and non-polar. The former type tend to adsorb by specific ionic forces, the latter by physical or Van Der Waals forces.

Examples of polar adsorbents are alumina, titanium dioxide, silica gel, glass, barium sulphate and of non-polar adsorbents, graphite, paraffin and some charcoals. Polar adsorbents usually adsorb electrolytes by ion exchange, one ion being more strongly adsorbed than the other.

The technique of adsorption measurements for dilute solutions is usually comparatively simple and involves shaking a certain volume of solution with a weighed amount of adsorbent until equilibrium is reached, removing the solution by filtration, centrifugation or decantation and then measuring the concentration of the resulting solution by any suitable method. Where the solute is an electrolyte, it is best to analyse for both ions.

In the absence of a general theory, the results are usually fitted to the Langmuir equation or the empirical Freundlich equation[86]. The latter is $a/m = kc^n$ where a is the amount adsorbed in suitable units (usually mols~~/gm. of adsorbent~~), c is the equilibrium concentration, m is the weight of adsorbent used, and k and n are constants. A modified B.E.T. equation has been applied to the adsorption of dyes from aqueous solution onto pigments[87].

The adsorption of aqueous solutions of paraffin chain salts on solids has been the subject of only a few investigations. Held and Samochwalov[88] measured the adsorption of the laurate ion from sodium laurate solutions on barium sulphate powder. They pointed out the well known fact that soap solutions tended to 'float' or coagulate powders at low concentrations, but at higher concentrations, to disperse them. This was believed to be related to a layer of soap ions being at first chemisorbed with the polar groups attached to the surface and the hydrocarbon chains tending to be oriented into the solution, hence the reason for the coagulation of the powder. When the first layer was saturated, the soap ions would then be adsorbed in the reverse sense in order to eliminate the hydrocarbon-water interface. The experimental evidence for this view was first, that the area of the powder determined by adsorption of the soap from aqueous solution was approximately twice that determined by adsorption of lauric acid from benzene and by means of the microscope, due to a double layer of soap ions in the aqueous system, second, that there was a maximum in the flotation of the powder and third, that sulphate ions appeared in solution after adsorption, due to ion exchange.

Similar measurements were made by Held and Khainsky[89] on the adsorption of sodium oleate and sodium nonylate on cinnabar powder. The adsorption of the soap was found to be accompanied by hydrolysis, the solution being more alkaline after adsorption than before.

The effect of CTAB on aqueous suspensions of Prussian Blue was studied by Tomlinson[90]. He showed that, as CTAB was added to the system, the sedimentation volume of the powder increased (showing an increasing degree of flocculation), reached a maximum and then fell again. A highly deflocculated suspension was eventually obtained in which complete sedimentation did not occur. Independent adsorption measurements showed that the CTAB was quantitatively completely adsorbed until a concentration corresponding to the maximum sedimentation volume was reached. Subsequently the adsorption was much less powerful. The initial adsorption was irreversible while the subsequent adsorbate could be washed off. Furthermore the maximum sedimentation volume in water corresponded to the minimum sedimentation volume in benzene and to the maximum ease of transfer from aqueous to non-aqueous media. It was thus concluded that up to this point the CTAB was chemisorbed as a unimolecular layer with the hydrocarbon chains oriented towards the water, but once the surface was saturated, a second unilayer was formed on top of the first due to amphipathic (or non-specific) adsorption. The polar, ionised groups are then oriented towards the water, reversing the effect of the first adsorbed layer.

This type of adsorption has been termed 'adsorption with reversed orientation' by Moilliet[91], who, noting that it occurs more with cationic detergents, suggests that it is due either to the surface active cation being attracted by the negative charge which most solids assume in water, or to specific salt linkages between the paraffin chain cations and ionogenic groups in the surface of the solid.

The adsorption of aqueous solutions of sodium dodecyl sulphate and of sodium myristate on graphite and polystyrene of known surface area, was investigated by Corrin, Harkins etal.[83]. This work is an example of amphipathic adsorption, both solids being essentially hydrophobic and free from surface impurities. The adsorption isotherms had two unusual features i.e. a discontinuity when the equilibrium concentration was close to the C.M.C. and a maximum at a somewhat higher concentration. The area occupied by one molecule of the paraffin chain ion was found to be rather higher than that for a compressed film on an aqueous subphase, and this was attributed to repulsive forces between the ionic heads of the adsorbed long chain ions.

In a similar investigation on the adsorption of sodium alkyl aryl sulphonates on cotton, Meader and Fries[92] also found a maximum and a discontinuity at the CMC. Ewing and Rhoda[93] obtained the relative surface areas of zinc oxide pigments by adsorption of Daxad11 , a wetting agent containing various molecular species of unknown composition. Fischer and Harkins[94] have shown that the adsorbed film between a hydrocarbon oil and sodium oleate solutions, is monomolecular, with the ionic group oriented towards the water and the paraffin chain towards the oil.

Since it was believed that sodium salicylate and sodium *p*-chlorobenzoate were able, in effect, to 'bind' together CTA^+ micelles in solution to form enormous aggregates, it was decided to examine whether these salts had a comparable effect on CTA^+ which had been adsorbed at a solid surface. The following results are chiefly concerned with this problem.

EXPERIMENTAL

Preparation of CTAB.

222 gms. of 30% (w/w) alcoholic trimethylamine were added to 273 gms. of pure cetyl bromide contained in a stoppered flask, and the mixture was left standing for 24 hours. The alcohol was then removed, in part, by vacuum distillation at 60°C. The crude product was broken up and recrystallised twice from a mixture of ethyl alcohol and ethyl acetate. The purity of the CTAB, as determined by titration of the bromine with silver nitrate and ammonium thiocyanate, and by precipitation as CTA dichromate, was 98.5% i.e. a 1% aqueous solution is .0270 M.

Estimation of CTA^+

(i) By titration with sodium dodecyl sulphate.

The CTA^+ solution was titrated against a mixture of 10 c.c. of .005M sodium dodecyl sulphate, 25 c.c. of a solution containing .003% methylene blue, 1.2% sulphuric acid, 5% sodium sulphate and 15 c.c. chloroform, all contained in a 250 c.c. stoppered reagent bottle. The CTA^+ solution was added a c.c., or less, at a time, until the two layers were indistinguishable (as viewed in reflected light). This is according to the method of Epton[95]. This estimation was used to study adsorption of the CTAB alone. It was found to be unreliable in the presence of organic salts.

(ii) As Cetyl trimethyl ammonium dichromate.

An excess of standard potassium dichromate solution was run into the CTA^+ solution. The precipitate, initially colloidal, became coagulated in the presence of excess dichromate. In the presence of organic salts the precipitate remained colloidal and it was necessary to add sufficient dilute hydrochloric acid to produce coagulation. After filtration, the excess dichromate was estimated with iodine and thiosulphate.

Estimation of Bromide.

The bromide was precipitated as silver bromide by standard silver nitrate solution, the excess silver nitrate being estimated by titration with ammonium thiocyanate in the presence of ferric alum and dilute nitric acid.

Adsorption Method.

The CTAB solution-powder mixtures were shaken overnight in an air cabinet thermostated at $(25 \pm .1)^\circ C$. The powder was than separated either by filtration through fine filter paper in the case of the alumina or through a No.4 sintered glass funnel under vacuum in the case of the silica and titanium dioxide powders. Bromine estimations were made on the filtered solution. The CTA^+ was estimated by the dye method except when organic salts were present, the solutions being either diluted or else made up with CTAB solution, to an approximate concentration of .005M.

Adsorption of CTAB on Graphite.

It was hoped that a study of the physical adsorption of CTAB on a hydrophobic surface could be made, both on account of the simpler structure of the adsorbed layer and also because chemisorption involves specific surface interactions whose nature are not clearly understood.

Since paraffin chain salts had been found to be amphipathically adsorbed on graphite by Corrin, Harkins etc.,[83] efforts were made to secure a pure specimen of this material. The best graphite obtainable was a special suspension in water supplied by the General Electric Company. It had an ash content of about 1%. The adsorption isotherm obtained for Br′ with this suspension, which contained 49.4% by weight of graphite, is given in fig. 2. Its shape is quite different from that found by Corrin and Harkins (fig. 3), but it is similar to isotherms for the adsorption of Br′ from CTAB solutions on alumina, silica and titanium dioxide. These isotherms are given later and are shown to indicate that the CTA^+ is being chemisorbed. It appeared that the surface of this graphite sample must contain a great deal of impurity.

An animal charcoal sample of the type used for decolourising solutions, was also used as an adsorbent and the adsorption of Br′ from aqueous CTAB on it, is shown in fig.4. It is probable that the CTA^+ is both chemically and physically adsorbed on

FIG. 3.

ADSORPTION OF LONG-CHAIN ELECTROLYTE FROM AQUEOUS SOLUTIONS ON GRAPHITE.

[FROM CORRIN, LIND, ROGINSKY AND HARKINS
J. COLLOID SCI., 4, 485 (1949)]

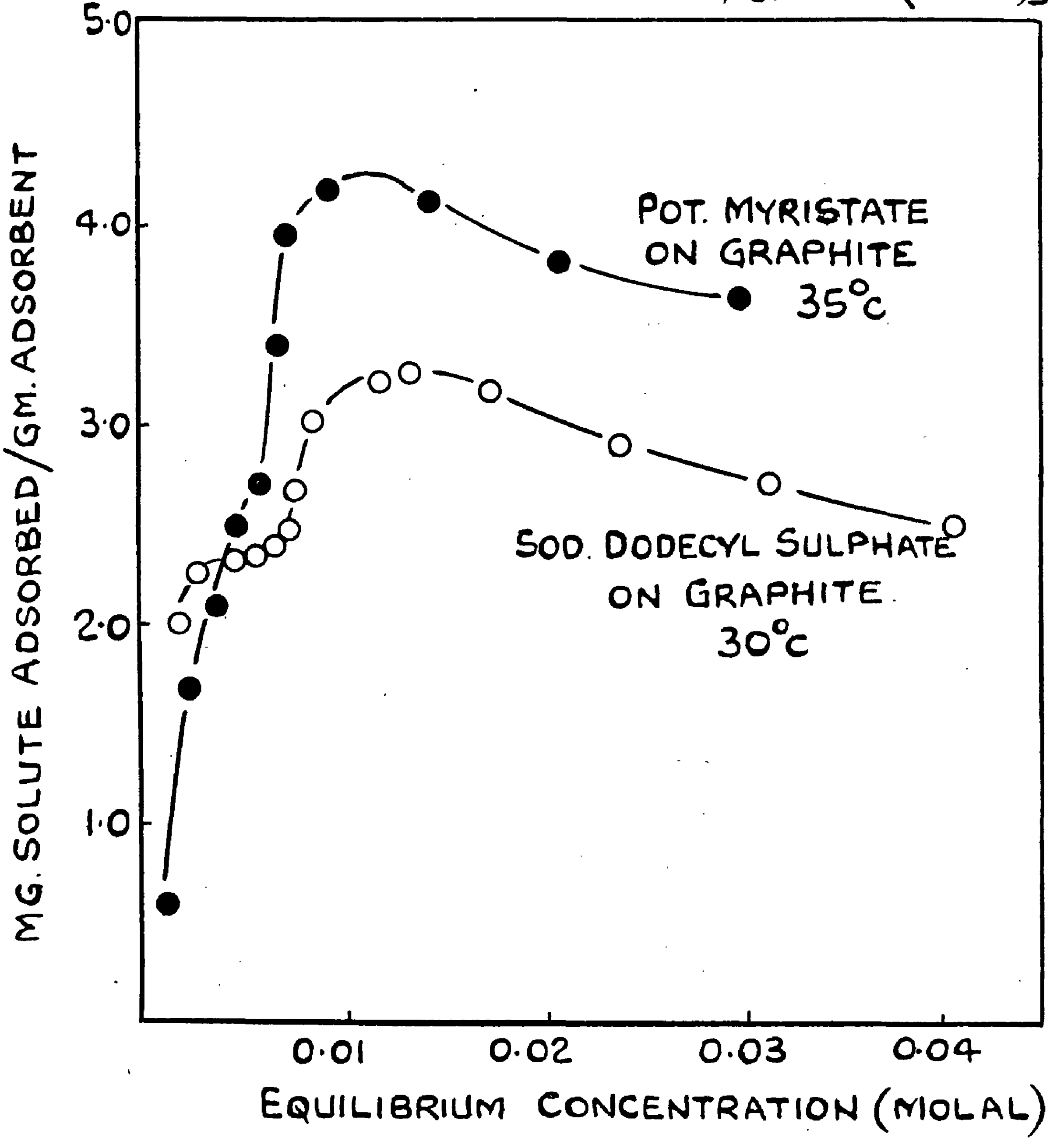
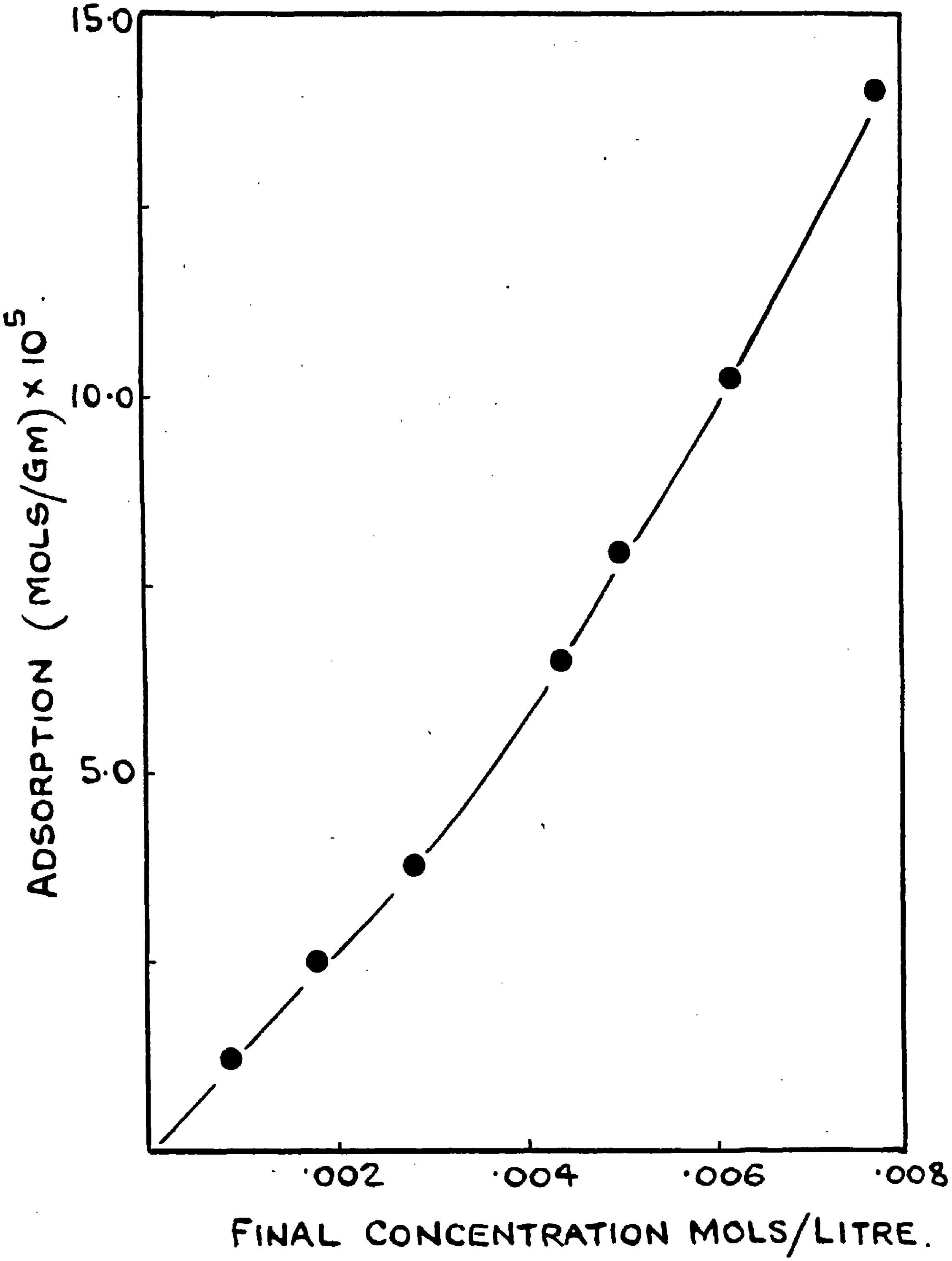


FIG. 4.

ADSORPTION OF C.T.A.B. ON CHARCOAL

6·5 GMS: IN 50 CCS.

Br′ ANALYSED.



the surface of this powder. The difficulty in obtaining a pure specimen of a hydrophobic powder led to the investigation being confined to hydrophilic powders.

Adsorption of CTAB on Alumina.

Chromatographic alumina, standardised according to Brockmann,[96] was used for all adsorption experiments. Its surface area, as determined by nitrogen adsorption at -183°C was 69.6 m^2/g (see Appendix).

An equilibrium curve, for 10 gm. alumina in 50 c.c. .0270M CTAB, is shown in fig.5. The time taken to reach equilibrium was between three and four hours. This is rather longer than that required for all the other adsorbents studied, and is presumably due to the porous nature of the alumina surface.

Adsorption isotherms for 2.5 gm. alumina in 50 c.c. solution are shown in fig.6. In this case both CTA^+ and Br' ions were analysed.

The principle features of these isotherms are:

(i) The initial rate of adsorption of CTA^+, with respect to concentration, is very high, while that of Br' is zero.

(ii) The maximum adsorption values of both ions are very different i.e. (1.60×10^{-4}) mol/gm. for the CTA^+ and (1.02×10^{-4}) mol./gm. for the Br', showing that ion exchange is involved in at least part of the adsorption process. The maximum adsorption values are reached at the same initial concentration of CTAB

FIG. 5.

EQUILIBRIUM CURVE FOR 10 GMS. ALUMINA.
IN 50 CCS. ·027 M CTAB.

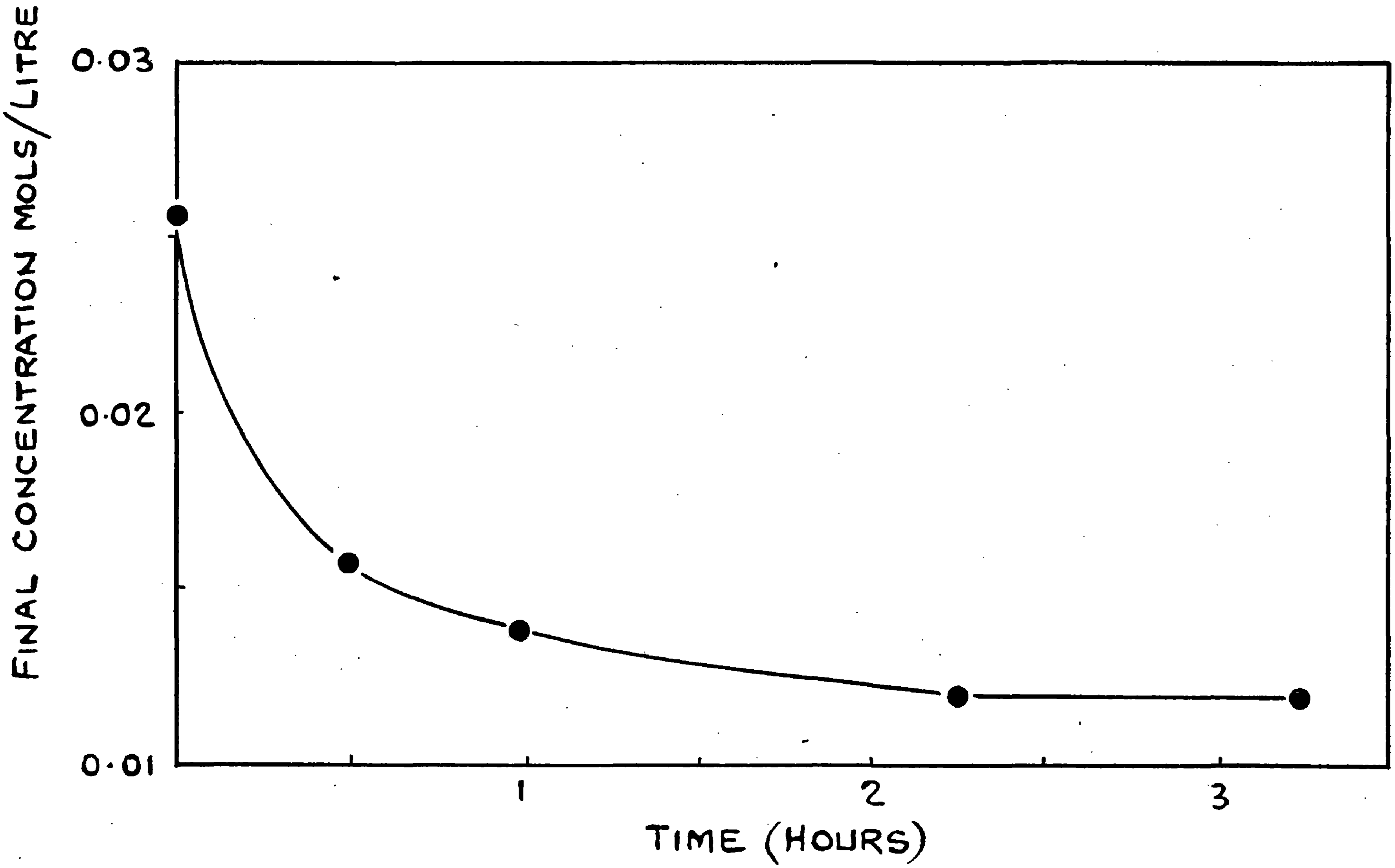
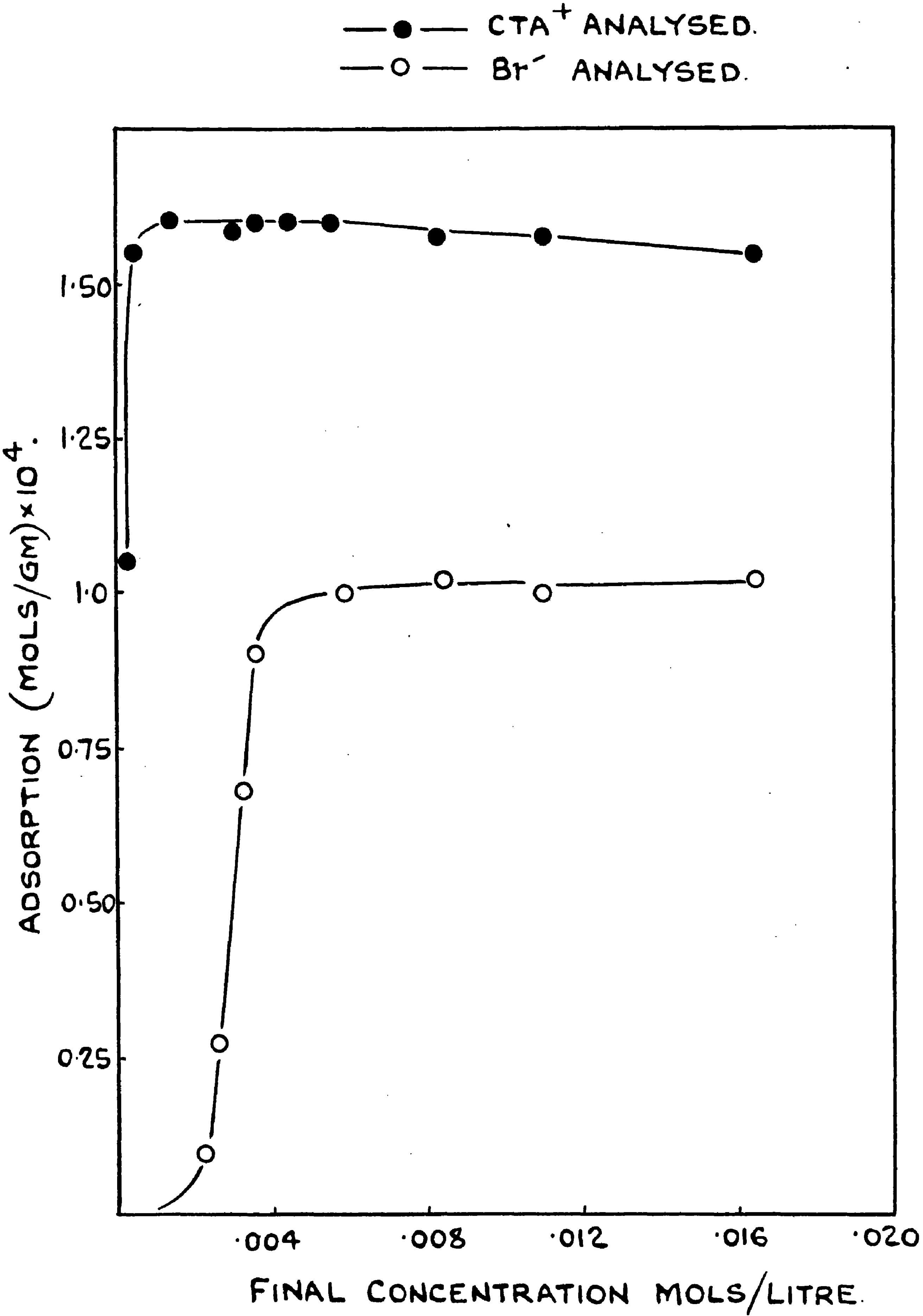


FIG. 6.

ADSORPTION OF C.T.A.B. ON ALUMINA.



These results are adequately explained by the mechanism given earlier for adsorption of a long chain paraffin salt with 'reversed orientation'[91]. Thus the first 'unilayer' of CTA^+ ions is formed by ion exchange with impurities on the surface of the alumina, the polar $N(CH_3)_3{}^+$ group holding the ion to the surface by powerful electrostatic attraction. As the initial concentration of CTAB is increased, the active surface available for chemisorption becomes smaller and the CTA^+ begins to be amphipathically (or physically) adsorbed. This part of the adsorption process is characterised by the Br' isotherm which is actually, for most of the adsorption process, a plot of the amount of CTA^+ amphipathically adsorbed (measured by the adsorption of Br') against the amount of CTA^+ chemisorbed (measured by the final concentration of Br'). This assumes, quite reasonably, that the Br' ion is only adsorbed in company with the CTA^+ ion (this will be discussed in more detail later).

The total amount of CTA^+ chemisorbed - a measure of the active surface area - can be found:-

1. From the difference between the total amount of CTA^+ adsorbed i.e. 1.60×10^{-4} mol./gm. and the total amount of physically adsorbed CTA^+ i.e. 1.02×10^{-4} mol./gm. This difference is equal to 0.58×10^{-4} mol/gm.

or 2. From the amount of Br' in solution after adsorption since this represents, within appropriate limits, the amount of chemisorbed CTA^+. The actual selection of a point on the Br' isotherm which represents the maximum amount of chemisorbed CTA^+ is rather difficult since Br' begins to accumulate in solution towards the end of the adsorption process, due to unadsorbed CTAB. If, however, one selects the point of inflexion of the graph, the value obtained for the total amount of chemisorbed CTA^+ is 0.64×10^{-4} mol/gm., which is in reasonable agreement with the previous result.

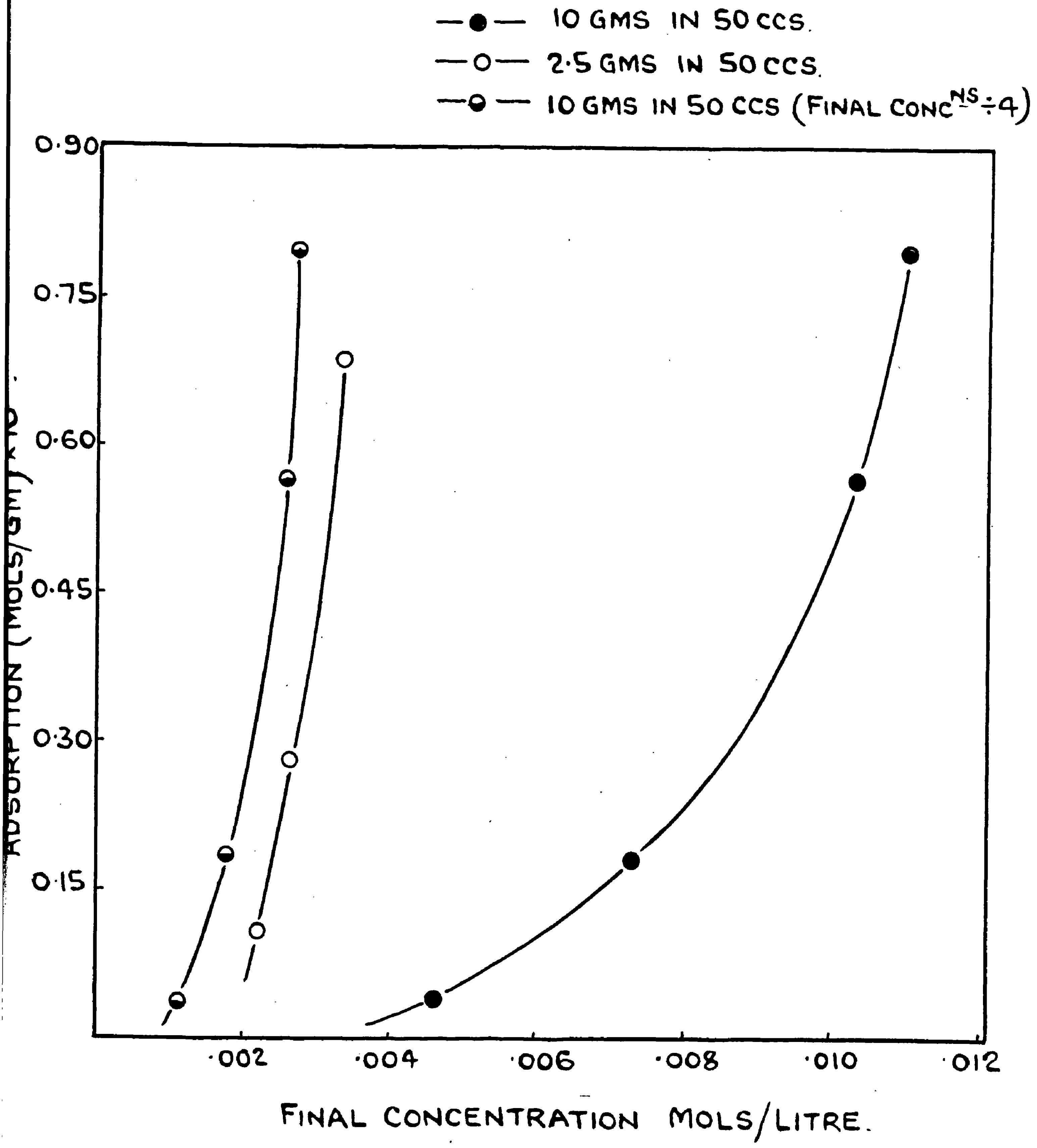
In order to confirm the shape of the Br' isotherm at low initial concentrations of CTAB, it is necessary to use a higher ratio of alumina to solution and fig.7 shows a Br' isotherm determined using 10 gm. of alumina in 50 c.c. solution. It can be seen that the initial slope is certainly very small and probably zero. This means that the CTA^+ is all chemisorbed at low initial concentrations of CTAB. Thus the alumina itself is not sufficiently hydrophobic to allow the paraffin chain ions to be adsorbed amphipathically at its surface.

If, for the system containing 10 gm. alumina in 50 c.c. solution, the final concentrations of Br' in fig.7 are divided by four, the same isotherm as was obtained for 2.5 gm. alumina should result. However, as also shown in fig.7, there is a significant difference between the two isotherms. It is not possible to say what is the precise explanation of this effect.

FIG. 7.

ADSORPTION OF CTAB ON ALUMINA.

Br' ANALYSED.



The Br′ isotherms in figs. 6 and 7 also show that the formation of the 2nd layer of CTA^+ ions (the physically adsorbed layer) occurs long before the 1st layer of CTA^+ ions (the chemisorbed layer) is complete, indeed the 1st layer is only saturated when the 2nd layer is almost half formed. This is in part due to the amphipathy of the CTA^+, which effect is able to compete with the specific electrostatic interactions which are the cause of the chemisorption. It may be that with a less surface active compound a clearer differentiation between the formation of the two layers would be possible.

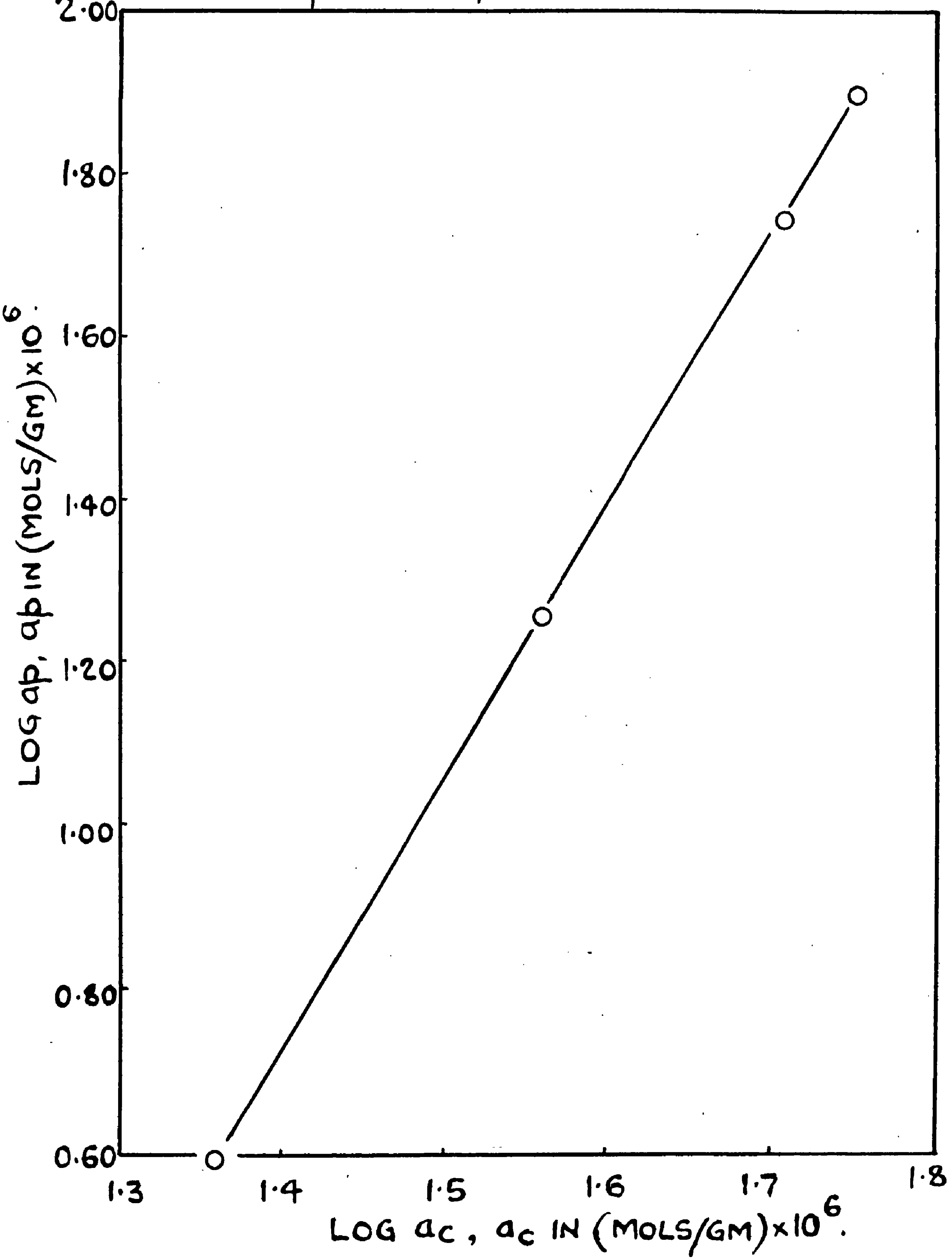
As mentioned previously, the Br′ isotherm, in for example fig.7, represents in effect a plot of the physically adsorbed CTA^+ against the chemisorbed CTA^+. If a_p represents the former while a_c represents the latter, then the plot of log a_p against log a_c is, for that part of the isotherm with which fig.7 is concerned, seen from fig.8 to be a straight line. The actual relation is $a_c = ka_p^n$ where $k = 15.1$ and $n = 0.30$, a_p and a_c being, in this case, in mol./gm. x 10^6. This adsorption equation[86] is of the same form as Freundlich's equation[86] which is known to represent for many simple adsorptions e.g. acetic acid on charcoal, the relation between a solute in an adsorbed layer and in solution. That this relation should hold for the adsorption of CTAB may be due to some similarity between the forces which cause CTA^+ to be distributed between the

FIG. 8.

ADSORPTION OF CTAB ON ALUMINA

10 GMS IN 50 CCS.

a_c IS MOLS/GM × 10^6 CTA^+ CHEMISORBED
a_p IS MOLS/GM × 10^6 CTA^+ PHYSICALLY ADSORBED



chemisorbed and physically adsorbed states and the forces which cause a solute such as acetic acid to be distributed between an adsorbed layer and a solution.

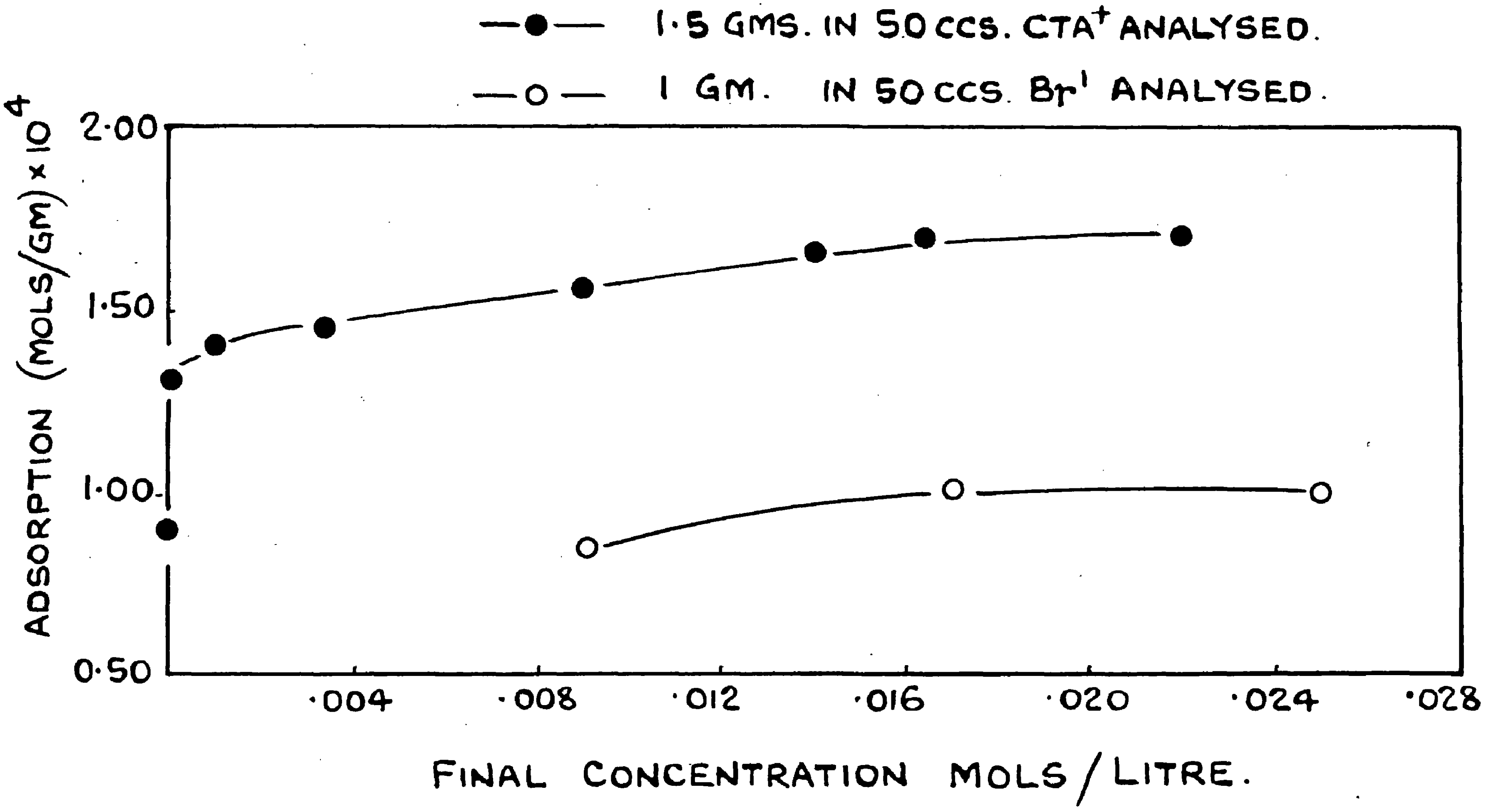
Finally, since the amount of adsorption at high ratios of alumina to solution was not quite proportional to the weight of alumina used (fig. 7), two more isotherms were determined, one for the adsorption of CTA^+ on 1.5 gm. alumina in 50 c.c. solution, the other for the adsorption of Br' on 1 gm. alumina in 50 c.c. solution (fig. 9). The amounts adsorbed are approximately the same as for 2.5 gm. alumina in 50 c.c. solution (see fig.6) indicating, at these lower ratios of adsorbent to solution, proportionality between the amount of adsorbent and the amount of adsorption.

Adsorption of Cetyl trimethyl ammonium nitrate on Alumina.

$CTANO_3$ was prepared by mixing CTAB and $AgNO_3$ in equimolecular amounts adding water, filtering off the precipitated AgBr using a No.4 sintered glass funnel, evaporating to dryness under vacuum and crystallising the product from ethyl acetate. A carbon analysis gave 66.5% as against the theoretical value of 65.8%. Since the same amount of CTA^+ was adsorbed from $CTANO_3$ solutions as from CTAB solutions at the same initial concentration, the two compounds were similarly adsorbed. The amount of Br' in the $CTANO_3$ solutions was negligible before adsorption and remained

FIG. 9.

ADSORPTION OF CTAB ON ALUMINA.



so after adsorption. It was thus shown that the impurity displaced from the surface by the CTA^+ had no effect on the Br' estimation.

'Purified' Alumina.

In an effort to confirm that the CTAB is adsorbed by ion exchange due to ionic impurities on the surface, the powder was neutralised with dilute hydrochloric acid and then washed by decantation at regular intervals for three weeks until the supernatant liquid showed no trace of chloride ion. While this treatment washed away most of the finer grains, the surface area of the adsorbent was practically unchanged as measured by nitrogen adsorption (see appendix). Nevertheless this material adsorbed neither CTA^+ nor Br' from CTAB solutions. This is in agreement with the work of Schwab and Jockers[97] who found that copper ions were preferentially adsorbed by commercial alumina from copper sulphate solutions and that the filtrate showed the reactions of sodium. It was found that even the purest commercial alumina contained sodium ions which could be replaced by copper ions.

It, therefore, seems that adsorption of the CTAB is essentially due to the active sites available on the surface for exchange, the alumina, itself, not being sufficiently hydrophobic to adsorb the CTAB amphipathically.

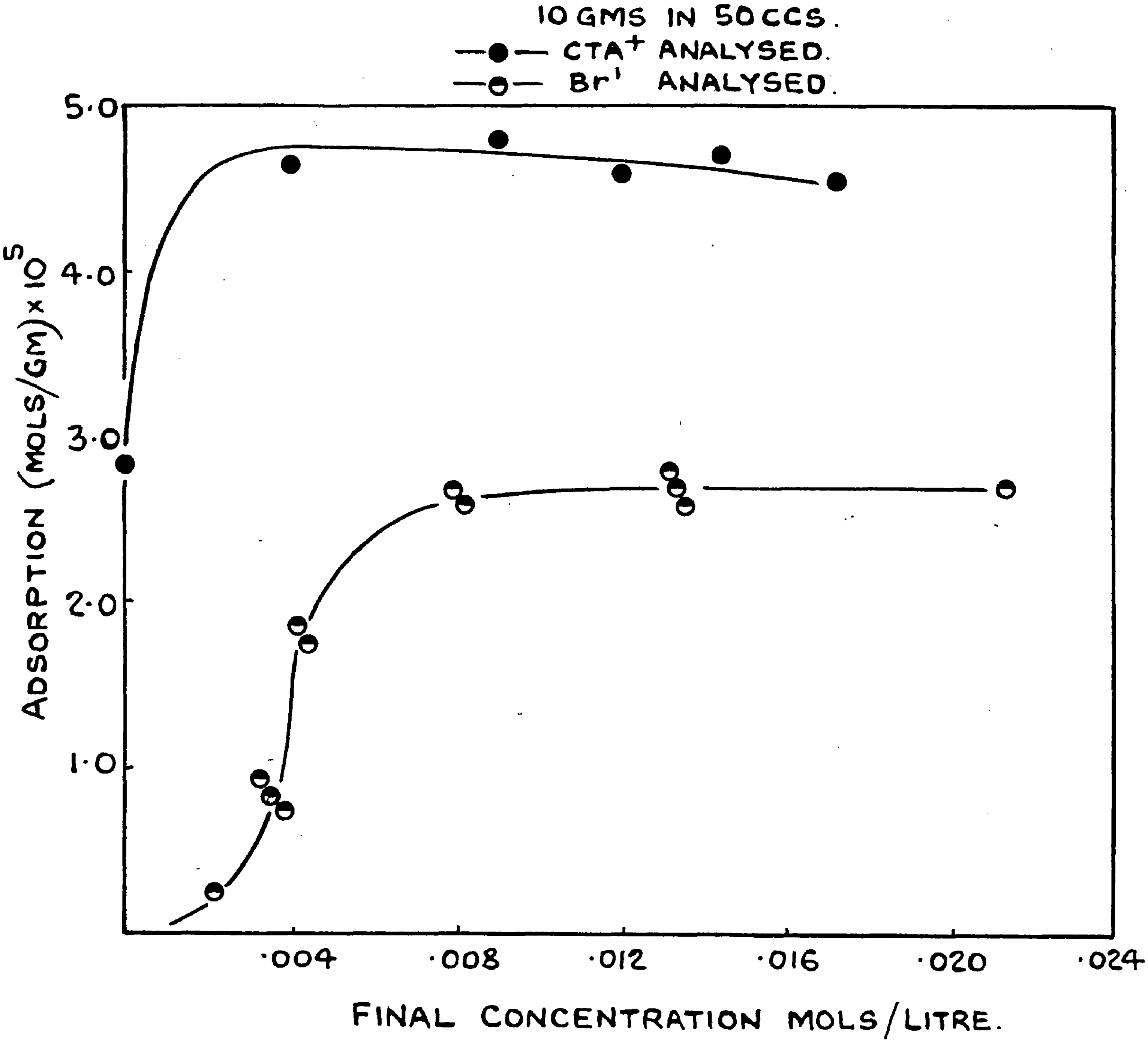
Adsorption of CTAB on Titanium Dioxide.

Four samples of titanium dioxide, supplied by British Titan Products, were tested for adsorption. Pure titanium dioxide, containing 94% of rutile, gave no adsorption. Two rutile samples, known as 'Rutiox CR' and 'Rutiox H.D.' gave only small adsorptions. The other sample, known as 'Anatase E,' gave sufficient adsorption to allow its use for further measurements. The chief difference between the Rutiox and Anatase powders, in regard to composition, was that the Rutiox contained appreciable amounts of zinc oxide and alumina of the order of 1%. The Anatase E contained .4% of soluble salts and the other two half as much. The surface area of the anatase E, by N_2 adsorption, was 7.6 m^2/g.

The adsorption curves obtained with 10 gm. anatase in 50 c.c. solution are shown in fig. 10. The shapes of the isotherms are essentially similar to those found for alumina. The amount of CTA^+ chemisorbed calculated from the difference between the total amount of CTA^+ adsorbed, 4.8×10^{-5} mol/gm., and the total amount of amphipathically adsorbed CTA^+, 2.7×10^{-5} mol/gm., is 2.1×10^{-5} mol/gm. This is in excellent agreement with the value found from the position of the point of inflexion of the Br' isotherm i.e. 2.2×10^{-5} mol/gm.

FIG. 10.

ADSORPTION OF CTAB ON 'ANATASE E'.



Adsorption of CTAB on Silica

The silica powder contained about 93% silica together with other oxides e.g. Fe_2O_3, Al_2O_3. It is non-porous, with a surface area of 8.0 m^2/g.

Isotherms for 5 gm. silica in 50 c.c. solution are shown in fig. 11. They are very similar to those found for alumina and titanium dioxide although, in this case, amphipathic adsorption commences more rapidly than before. This may indicate a more powerful chemisorption force than exists between the CTA^+ and the alumina or titanium dioxide. The amount of CTA^+ chemisorbed calculated from the difference between the total amount of CTA^+ adsorbed, 8.3×10^{-5} mol/gm., and the total amount of amphipathically adsorbed CTA^+, 4.9×10^{-5} mol/gm., is 3.4×10^{-5} mol/gm. while the value from the Br' isotherm is 3.5×10^{-5} mol/gm.

A Br' isotherm for 15 gm. silica in 50 c.c. solution is shown in fig. 12. When these results are compared with those obtained with 5 gm. silica in 50 c.c. solution, each final concentration being divided by three, there is seen to be a slight difference similar to that found for alumina.

FIG. 11.

ADSORPTION OF CTAB ON SILICA

5 GMS IN 50 CCS

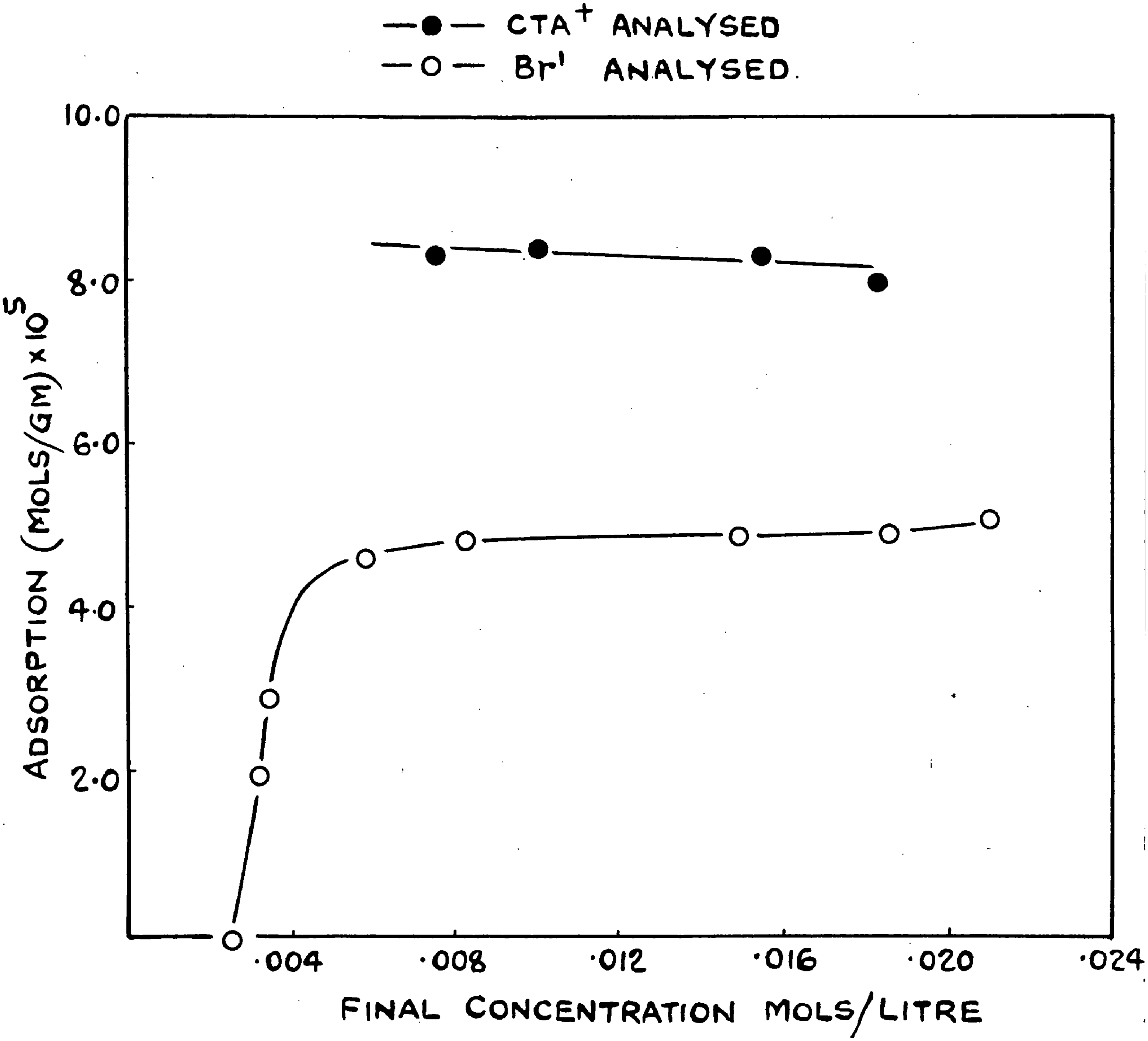
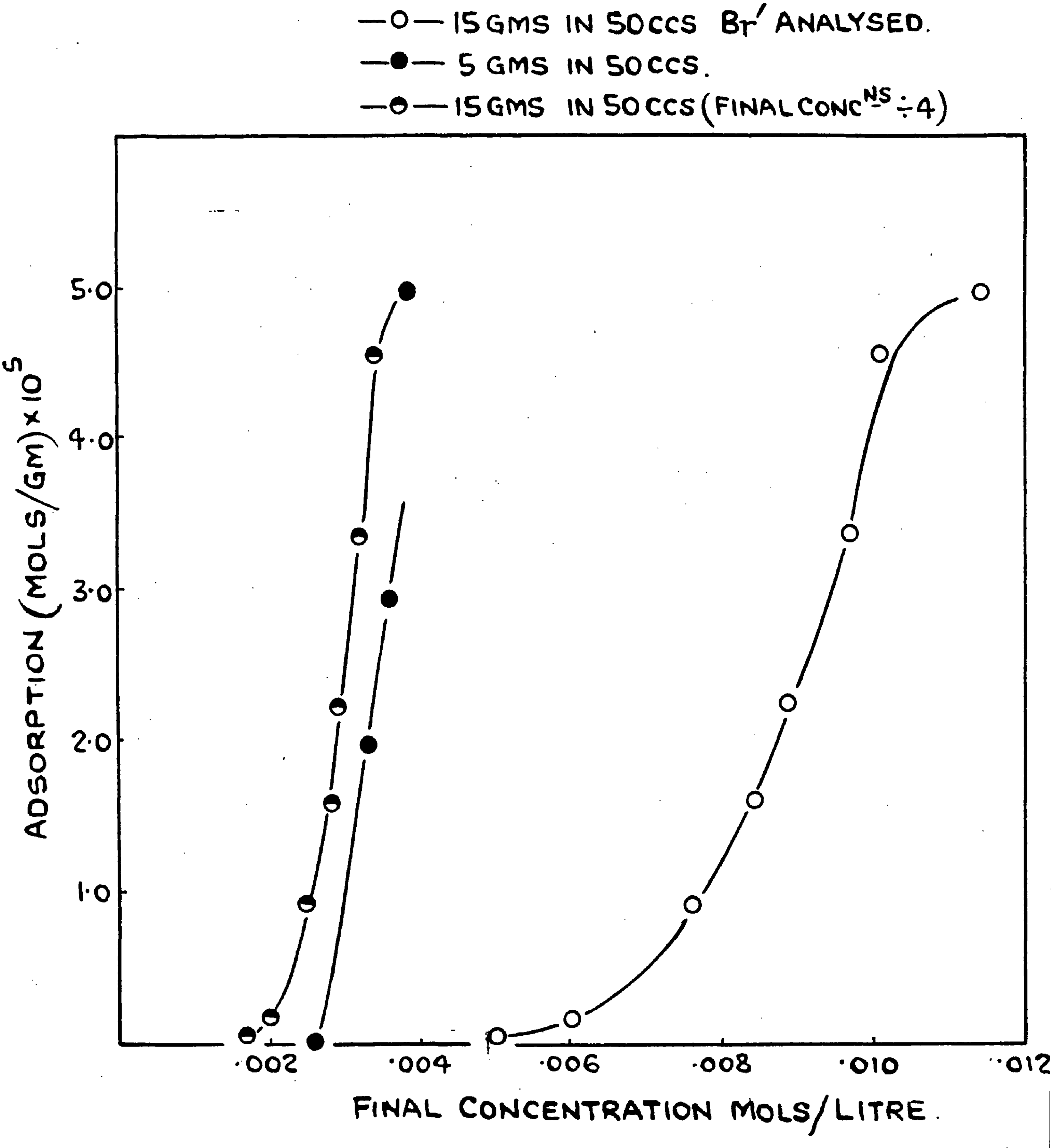


FIG. 12.

ADSORPTION OF CTAB ON SILICA.



Adsorption of Sodium Dodecyl Sulphate on Alumina.

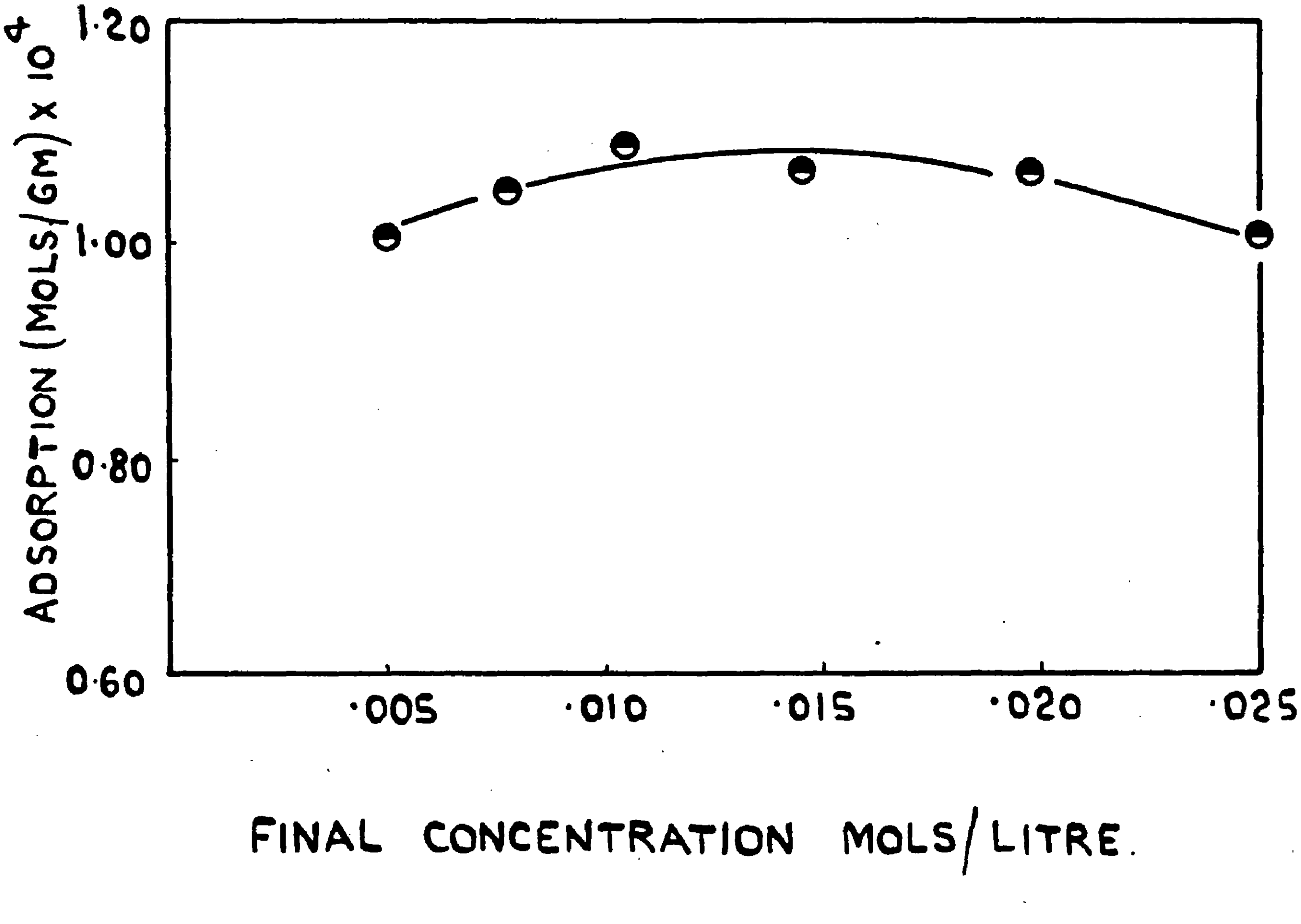
The sodium dodecyl sulphate (S.D.S.) used for these adsorption experiments was the B.D.H. material recrystallised twice from alcohol and ethyl acetate. It was estimated, using standard CTAB, by the dye method. Owing to the hydrolysis which aqueous solutions of S.D.S. underwent at low concentrations, the lowest concentration of S.D.S. used was .008 M where the degree of hydrolysis was believed to be negligible.

The isotherm found for 2.5 gm. alumina in 50 c.c. solution is shown in fig. 13. The broad maximum is more noticeable here than with CTAB adsorbed on alumina and it is probably similar to the maximum obtained by Corrin and Harkins for the adsorption of sodium dodecyl sulphate on graphite[83], indeed it occurs at approximately the same equilibrium concentration i.e. .014 mol/ litre. The adsorption is, however, likely to be with 'reversed orientation' i.e. the alumina seems capable of behaving as both a cation and an anion exchanger.

FIG. 13.

ADSORPTION OF SODIUM DODECYL SULPHATE ON ALUMINA.

2·5 GMS. IN 50 CCS.



Effect of Organic Salts on the Adsorption of CTA^+ on Alumina.

Alumina was chosen as adsorbent due to its availability in large quantities, its versatility as an adsorbent and the comparative ease with which it could be separated from the CTAB-salt mixtures, some of which are visco-elastic.

The following organic salts were used - sodium benzoate, p-nitrobenzoate, p-aminobenzoate, o-aminobenzoate, p-hydroxybenzoate, o-hydroxybenzoate, (sodium salicylate) and p-chlorobenzoate. The sodium salicylate was B.D.H., the others were prepared by neutralising the appropriate acid with sodium hydroxide and crystallising the sodium salt by cooling in ice. The initial concentration of CTAB was .0135M in each case. Initial concentrations of salts up to .025M were used.

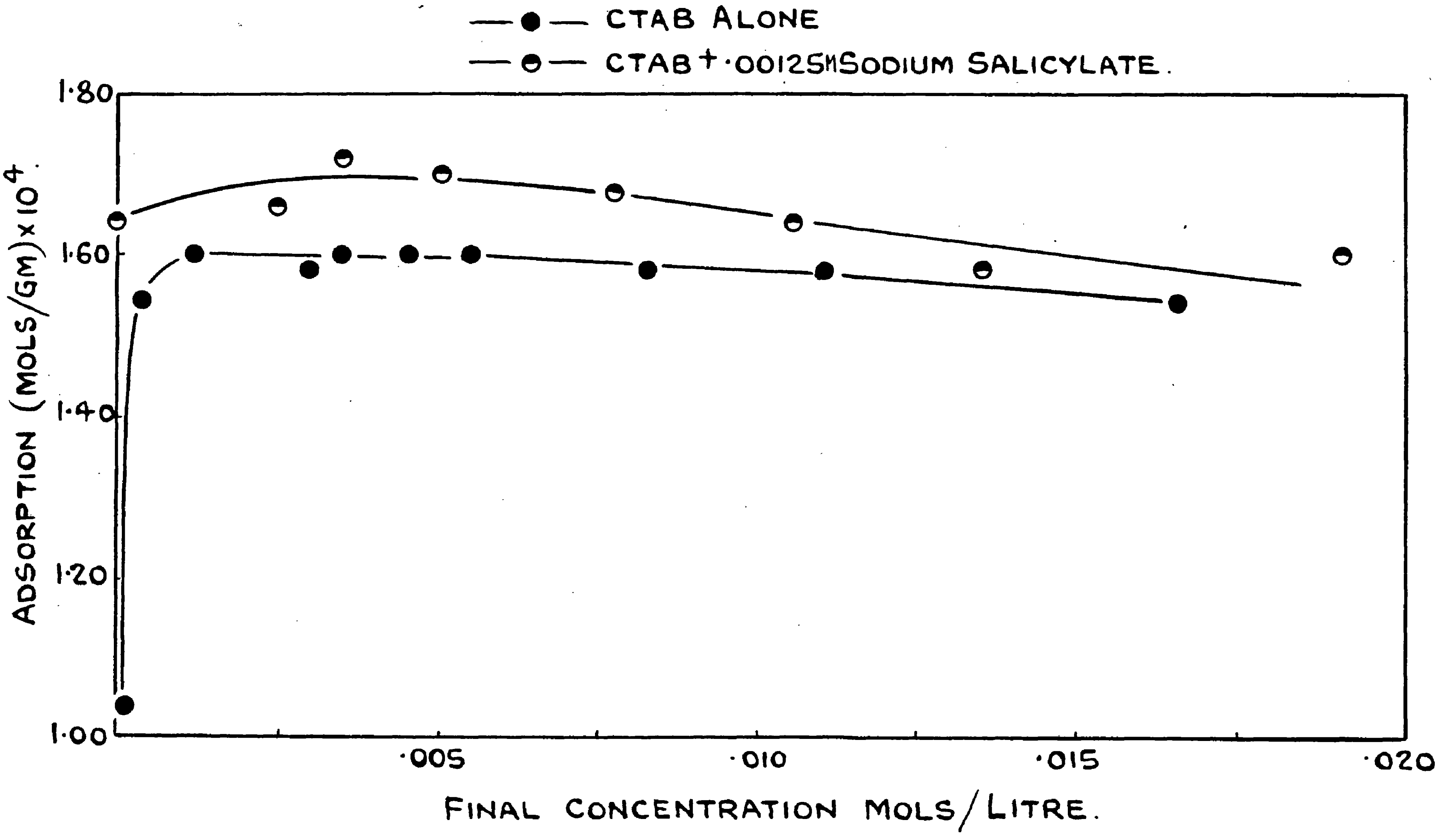
Results.

The first salt tried was sodium salicylate. Since this salt interfered with the estimation of the CTA^+ by the dye method, the results were obtained at very low salicylate concentrations where the estimation was reliable. The effect of a constant concentration of salicylate, .00125M, is shown in fig. 14. There is a small but definite increase in the amount of CTA^+ adsorbed.

In order to study higher concentrations of salts, the CTA^+ was estimated as insoluble cetyl trimethyl ammonium dichromate

FIG. 14.

EFFECT OF ·00125 M SODIUM SALICYLATE ON THE ADSORPTION OF CTA$^+$ ON 2·5 GMS ALUMINA.



by the method given previously. Blank experiments with each additive confirmed the reliability of the estimation.

With the visco-elastic solutions formed by the CTAB - sodium salicylate and the CTAB - sodium p-chlorobenzoate systems, it was found that the alumina tended to 'clump' together. This curious phenomenon is quite unlike the effect of a normal viscous solution e.g. glycerine-water mixtures or paraffin on alumina. In these solutions, the alumina particles are quite randomly scattered and have no tendency to aggregate, while in the visco-elastic solutions they tend to lump together in blobs or chains. While it is possible that this is an adsorption effect, a more likely explanation is that it is a purely mechanical effect due to the inhomogeneity of the visco-elastic solution (see page 23 for example) the alumina tending to accumulate in the regions between the visco-elastic aggregates. In spite of this effect, the results obtained with visco-elastic solutions were reproducible except for the most concentrated solutions studied at a later date.

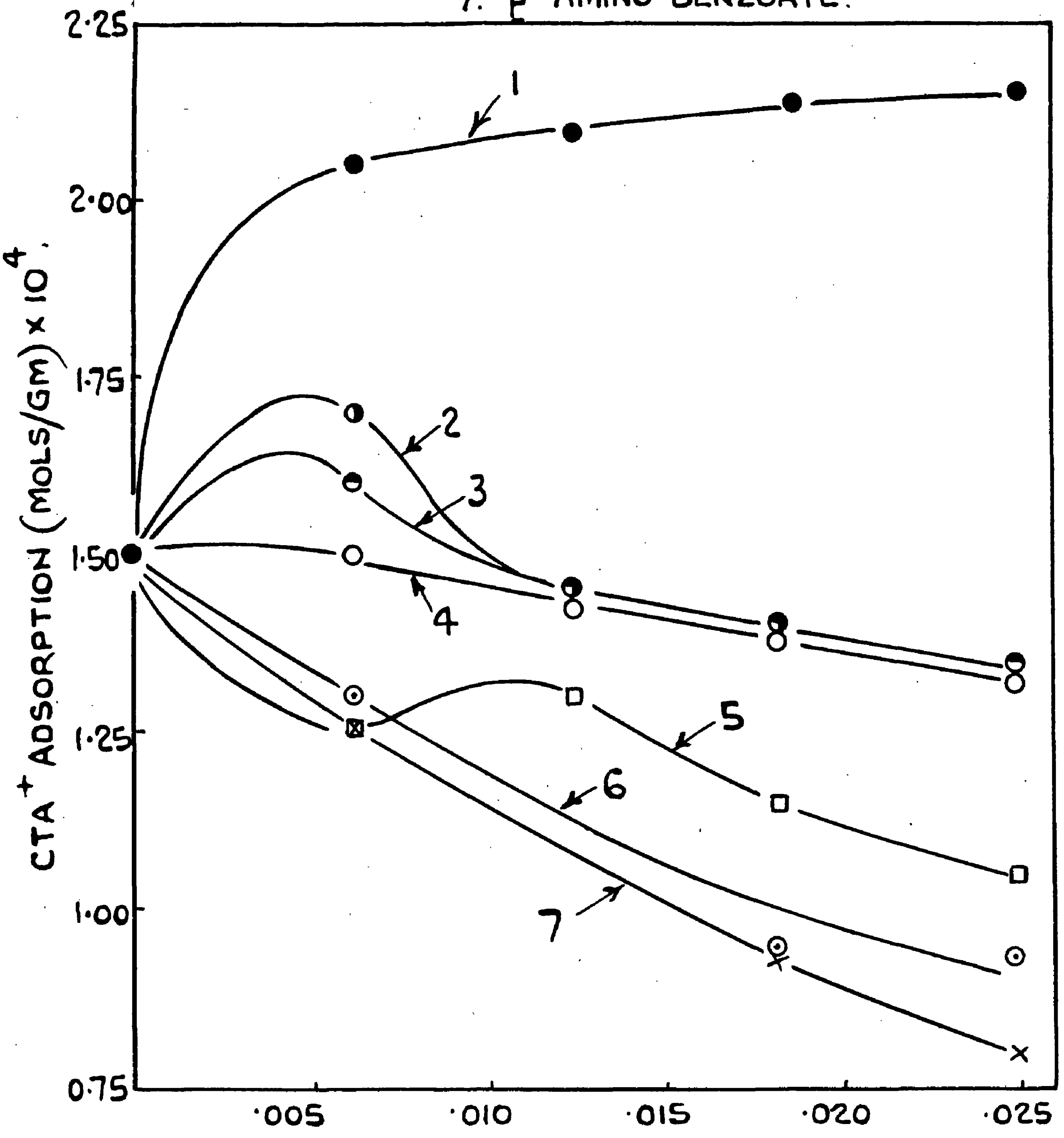
The effect of the salts is shown graphically in fig. 15. With the possible exception of sodium o-aminobenzoate, the salts fall into three classes in their effects.

1. Sodium p-hydroxy and p-amino benzoates decrease the amount of CTA^+ adsorbed, reducing it by about half at an initial concentration of .025M.

FIG. 15.

EFFECT OF SODIUM SALTS OF ORGANIC ACIDS ON CTA$^+$ ADSORBED ON 2·5 GMS ALUMINA. INITIAL CONC^N CTAB, ·0135M

1. SALICYLATE
2. p-CHLORO BENZOATE.
3. p-NITRO BENZOATE
4. BENZOATE.
5. o-AMINO BENZOATE
6. p-HYDROXY BENZOATE.
7. p-AMINO BENZOATE.



INITIAL CONCENTRATION OF ADDITIVE

MOLS / LITRE.

2. Sodium benzoate, p-chloro and p-nitro benzoates also decrease the CTA^+ adsorbed but to a much lesser extent. In addition, the latter two initially increase the adsorption of the CTA^+, although at higher concentrations of the salts they give the same effect as benzoate. These maxima have both been reproduced.

3. Sodium salicylate is unique among these salts in always increasing the CTA^+ adsorbed, although saturation is eventually reached.

It is fairly obvious that there is, at any rate, a qualitative relation between the effect of these salts on the viscosity of CTAB-salt mixtures and their effect on the adsorption of the CTA^+ on alumina. Thus sodium p-hydroxy and p-aminobenzoates, which have been classed together above, both show no effect on the viscosity of CTAB solutions[77]. Sodium p-nitrobenzoate and sodium benzoate both show slight viscosity maxima while sodium p-chlorobenzoate is second only to sodium salicylate in its effect on the viscosity. The sodium salicylate itself gives the greatest adsorption effect as also it does viscosity effect. It may therefore be said that, in general, an additive which tends to increase the viscosity of CTAB solutions, also tends to increase (or rather, not to decrease) the adsorption of CTA^+. The immediate object of the investigation - to show a relation between the effect of the organic salt on the structure of the CTA^+ micelles in solution and its effect, if any, on the adorbed CTA^+ - was thus achieved.

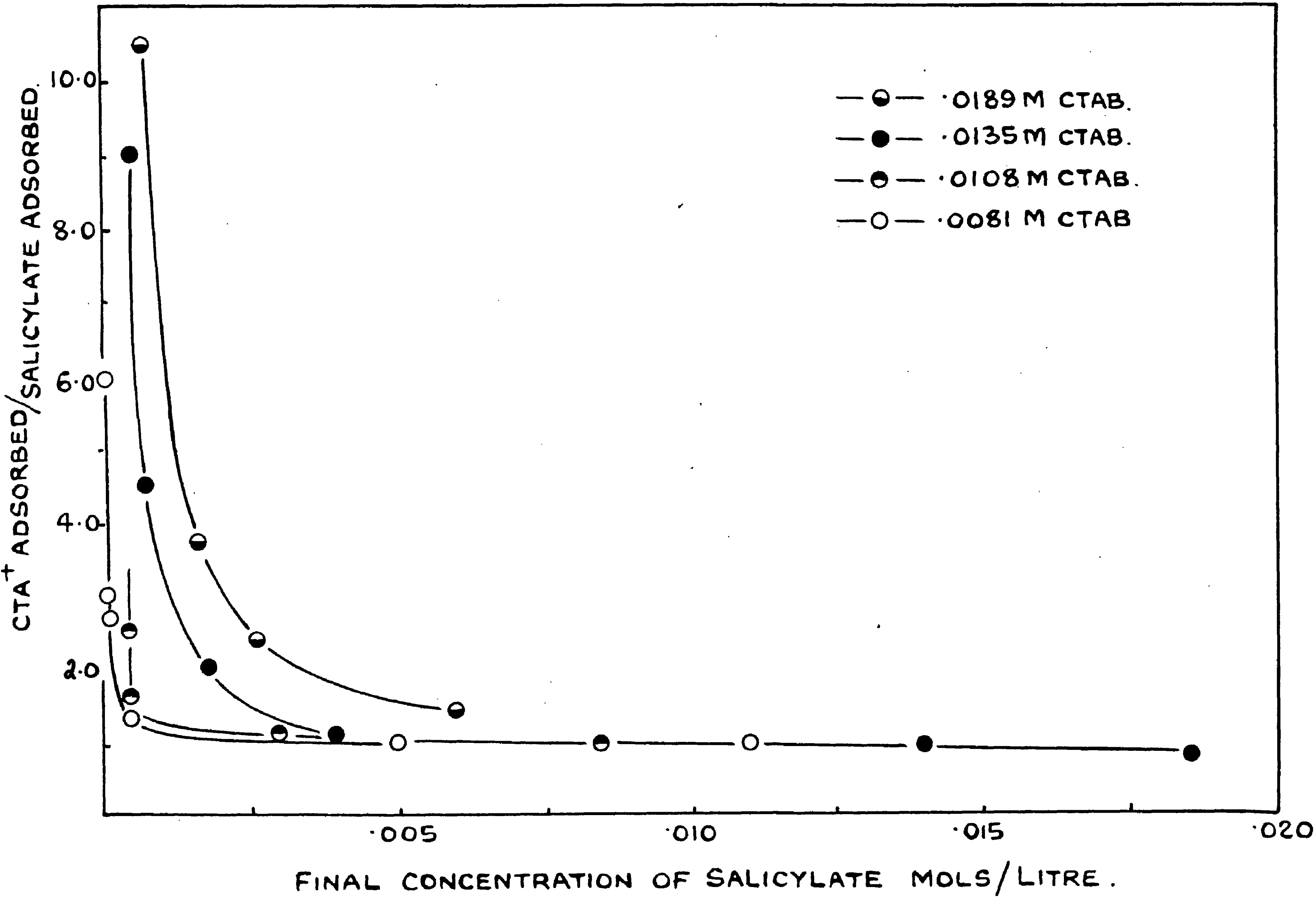
Adsorption of CTAB - sodium salicylate mixtures on Alumina.

Since ferric ions produce on intense violet colour with salicylate, it was possible to estimate, colorimetrically, the amount of salicylate in solution after adsorption by adding ferric chloride and acetic acid in appropriate amounts and measuring the optical density (at 520 mμ) of the resulting solution by means of a Spekker absorptiometer. The presence of CTAB reduces the intensity of this colour but it was found possible to allow for this effect by appropriate calibration with known quantities of CTAB.[98]

All experiments were carried out with 2.5 gm. alumina in 50 c.c. solution. The initial concentration of CTAB was kept constant at various values while the initial concentration of salicylate was varied. The visco-elasticity of the solutions gives rise to some difficulties in separating the alumina from the solution after adsorption. Where possible, the adsorption tubes were left for several days in a water thermostat at 25°C. In many cases the alumina settled in a mass at the bottom of the tube leaving a water-clear supernatant liquid. It is of some interest to note that with CTAB and alumina there was always a fine suspension left, even after several days in a thermostat. The clearing up of this slight turbidity by the addition of salicylate is probably connected with the tendency of the alumina

FIG. 16.

EFFECT OF SODIUM SALICYLATE ON ADSORPTION OF CTA^+ ON 2·5 GMS. ALUMINA AT VARIOUS CONC^{NS}. OF CTAB.



to 'lump' together in visco-elastic solutions. In cases where the supernatant liquid contained considerable amounts of alumina even after days of standing, it was necessary to filter the solution. This requires some care since the first few c.c.s of filtrate are much less viscous than the original solution, presumably because the large aggregates of CTA^+ - salicylate do not easily pass through the filter. This behaviour emphasises the inhomogeneity of the visco-elastic solution.

Results.

Fig. 16 shows the ratio of the CTA^+ adsorbed to the salicylate adsorbed plotted against final concentration of salicylate in solution. From this graph it can be seen that the CTA^+ and the salicylate are adsorbed in approximately equimolecular amounts except at concentrations of salicylate which are low relative to the initial CTAB concentration. There is, however, a certain tendency for the ratio of the CTA^+ adsorbed to the salicylate adsorbed to decrease at high concentrations of salicylate and this is reflected in fig. 17 in which the amount of salicylate adsorbed is plotted against the final concentration of salicylate. The plot of the amount of CTA^+ adsorbed against the final concentration of salicylate is almost horizontal at higher concentrations of salicylate (fig.18).

If, in fig.16, two systems containing different initial concentrations of CTAB but having the same final concentration of

FIG. 17.

ADSORPTION OF SALICYLATE FROM CTAB-SALICYLATE SOLUTIONS BY 2·5 GMS. ALUMINA.

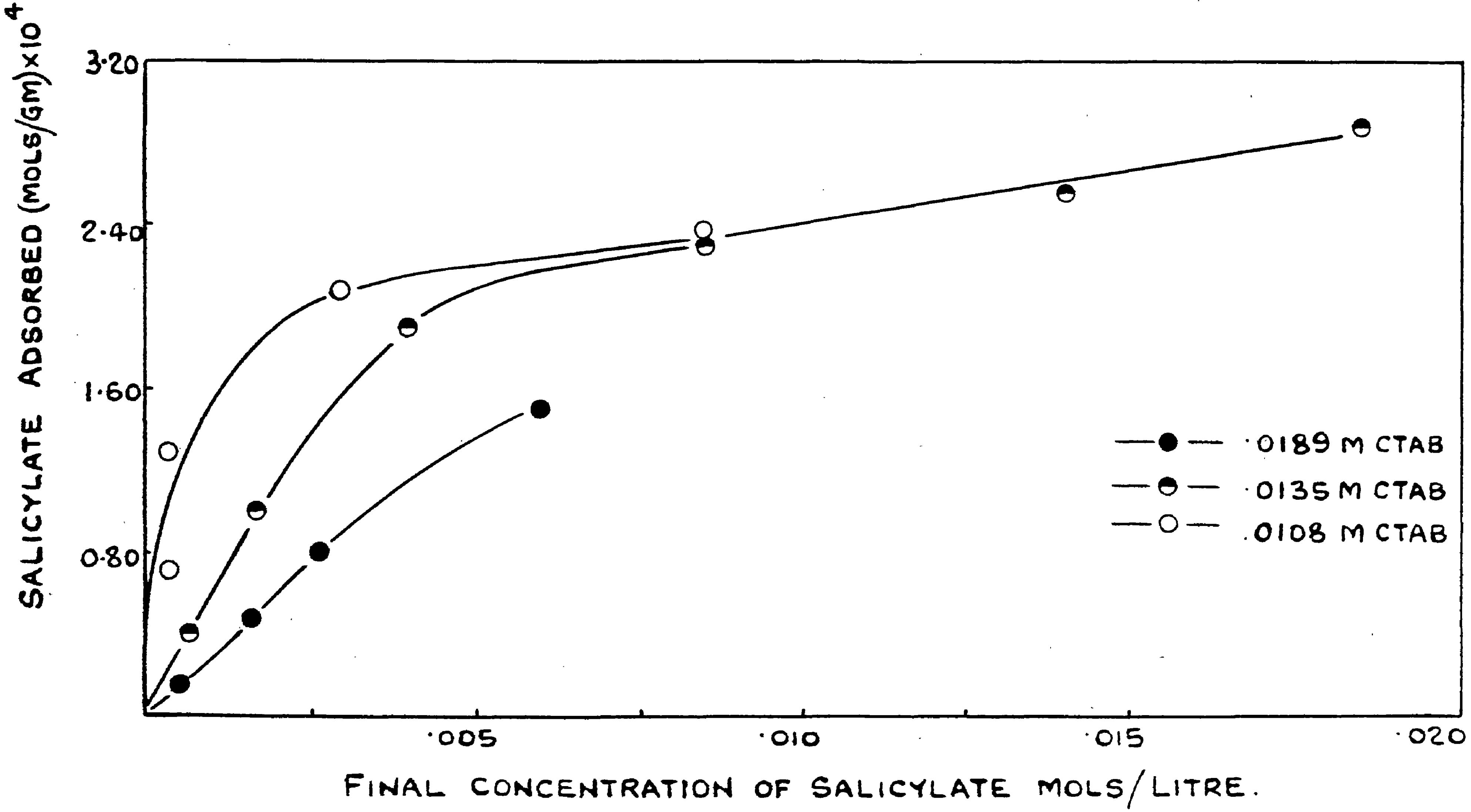
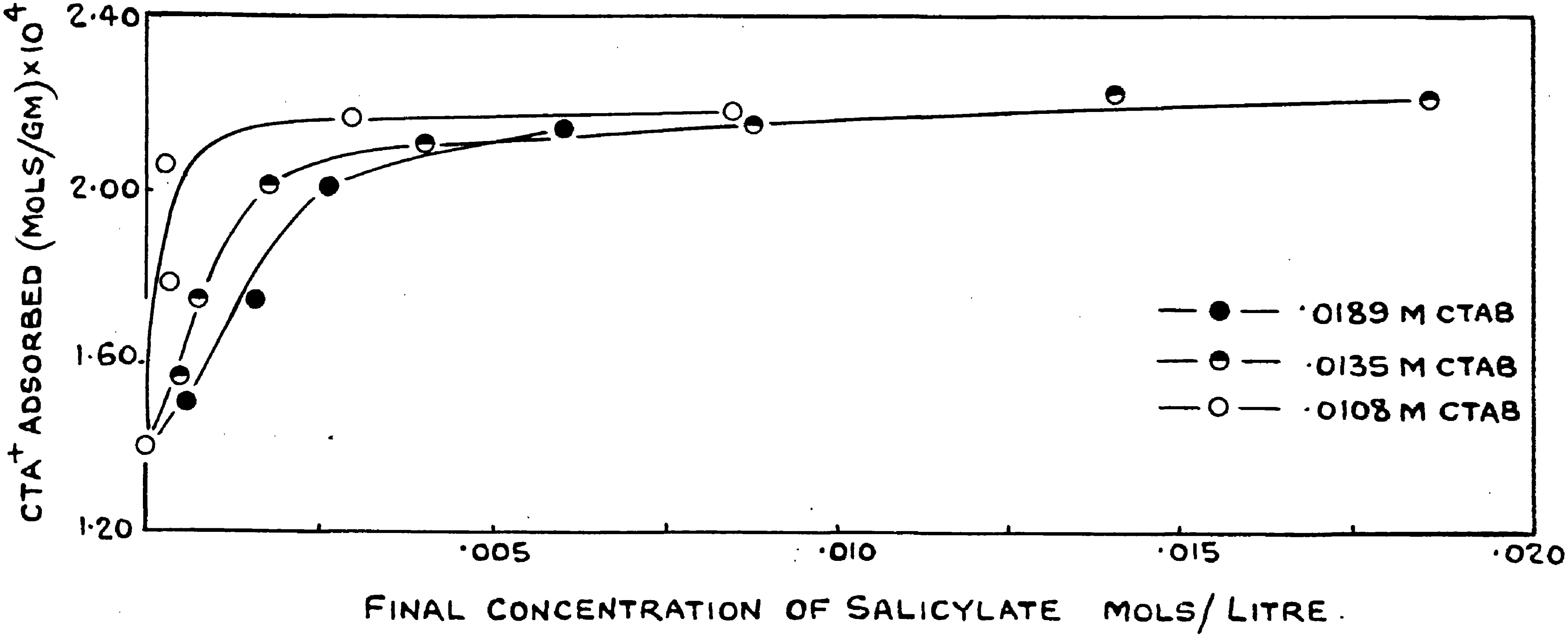


FIG. 18.

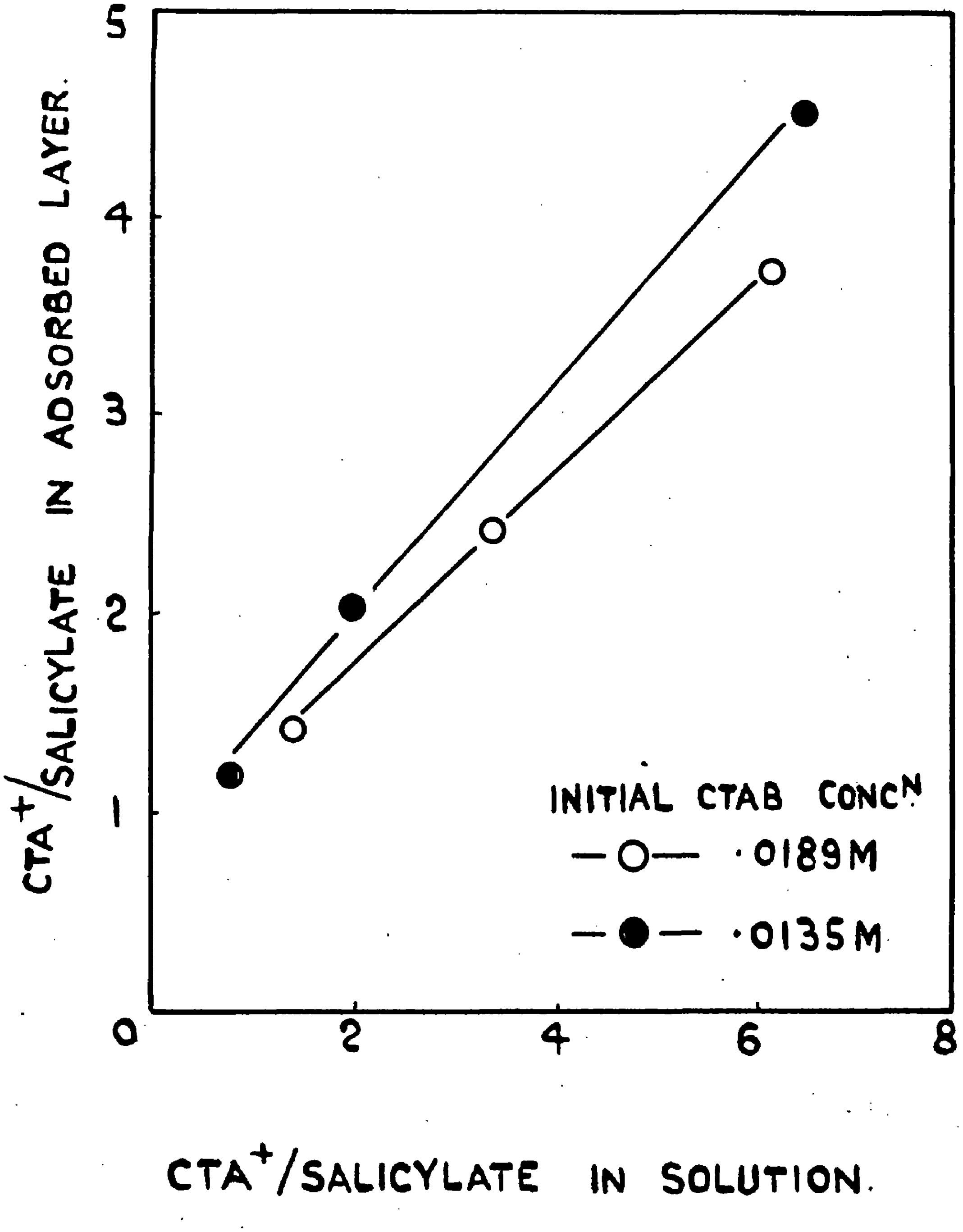
EFFECT OF SODIUM SALICYLATE ON ADSORPTION OF CTA$^+$ ON 2·5 GMS. ALUMINA AT VARIOUS CONC^{NS} OF CTAB.



salicylate, are examined, it can be seen that the ratio of CTA^+ adsorbed to salicylate adsorbed is greater in that system which contains the greater amount of CTA^+ provided the surface is not saturated. This is not because the amount of CTA^+ adsorbed is greater in the system containing the greater amount of CTA^+ (indeed as fig. 18 shows, it is slightly smaller) but because the salicylate adsorbed is much smaller i.e. before the surface is saturated with CTA^+ and salicylate, the amount of salicylate adsorbed is decreased as the concentration of CTA^+ in solution is increased. This is also shown by fig. 19 in which the ratio of the CTA^+ to the salicylate in the adsorbed layer is plotted against the same ratio in solution, for concentrations below the saturation values. Only two isotherms are shown here as in the other two the final concentration of salicylate is very low. The ratio of CTA^+ to salicylate in the adsorbed layer is approximately proportional to the same ratio in solution although the 'constant' of proportionality is dependent to some extent on the total amount of CTA^+ present. That straight lines are obtained in both cases suggests that the structures of the CTA^+ - salicylate adsorbed layer and the CTA^+ - salicylate complex in solution are similar i.e. the structure of the CTA^+ - salicylate complex in solution is essentially two-dimensional..

FIG. 19.

RELATION BETWEEN CTA+/SALICYLATE ADSORBED AND CTA+/SALICYLATE IN SOLUTION.



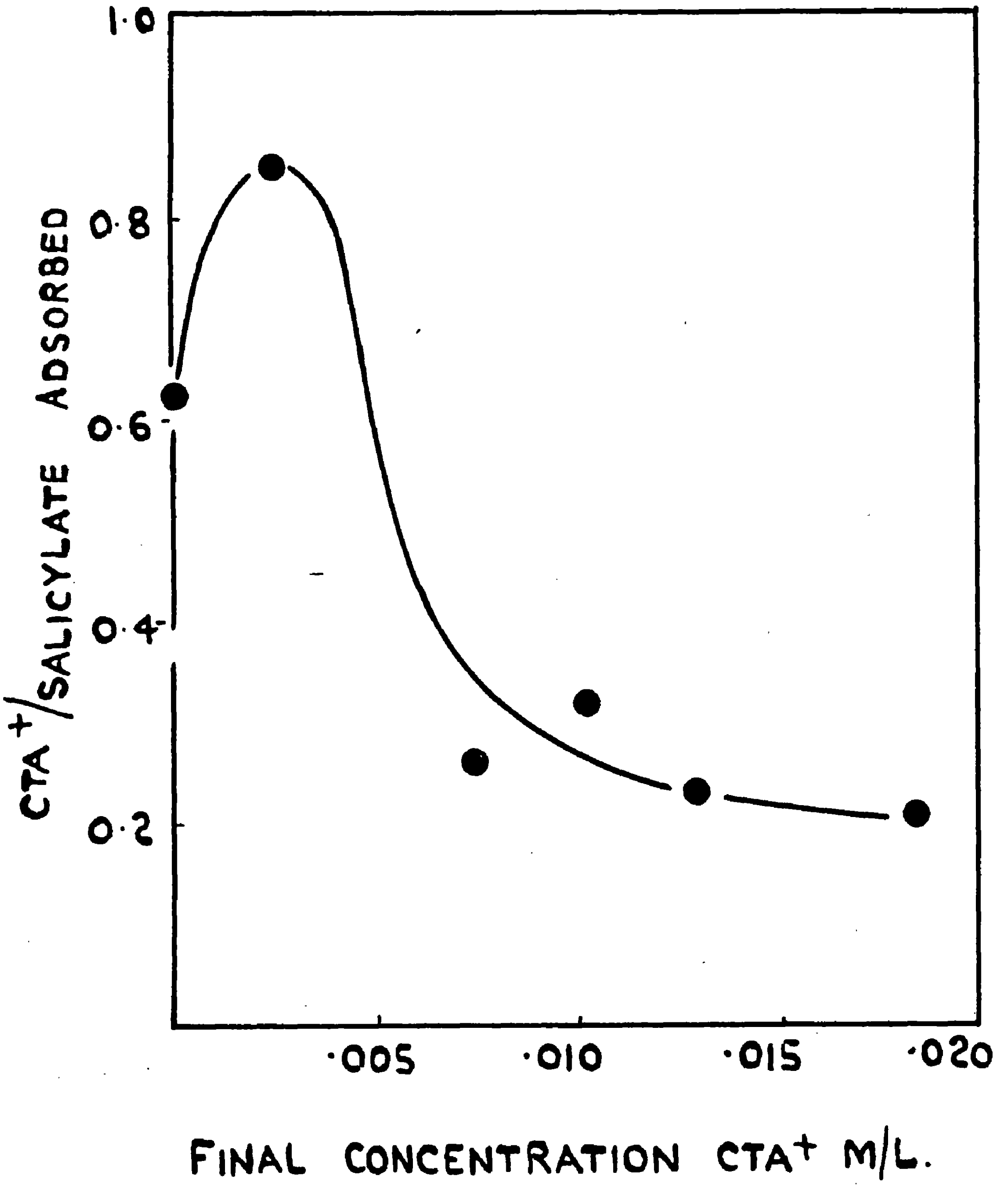
Adsorption of CTA^+- salicylate on 'Purified' Alumina.

While the purified alumina did not adsorb CTA^+, it was found that it did adsorb sodium salicylate, in fact about twice as much as did the commercial alumina. Although CTA^+ alone was not adsorbed by the purified alumina, it was found that it was adsorbed in the presence of salicylate, the ratio of the amount of CTA^+ to salicylate in the adsorbed layer being plotted against the final concentration of CTA^+ in Fig. 20. The CTA^+ and the salicylate do not appear to be adsorbed in equal amounts at any concentration. The actual amount of CTA^+ adsorbed is, even at its highest value, only about a quarter of that adsorbed from CTA^+ - salicylate solutions by commercial alumina. The unusual shape of the curve is rather difficult to account for.

FIG. 20

ADSORPTION OF CTAB - SOD. SALICYLATE ON TO 2·5 GMS. 'PURIFIED' ALUMINA.

INITIAL CONCN SALICYLATE IS ·0067M



Sedimentation Volume of Titanium Dioxide in CTAB Solutions.

Experimental.

Tubes 6" high and ½" internal diameter were used. They were made from specially selected tubing of accurate internal bore. The ends of the tubes were flat.

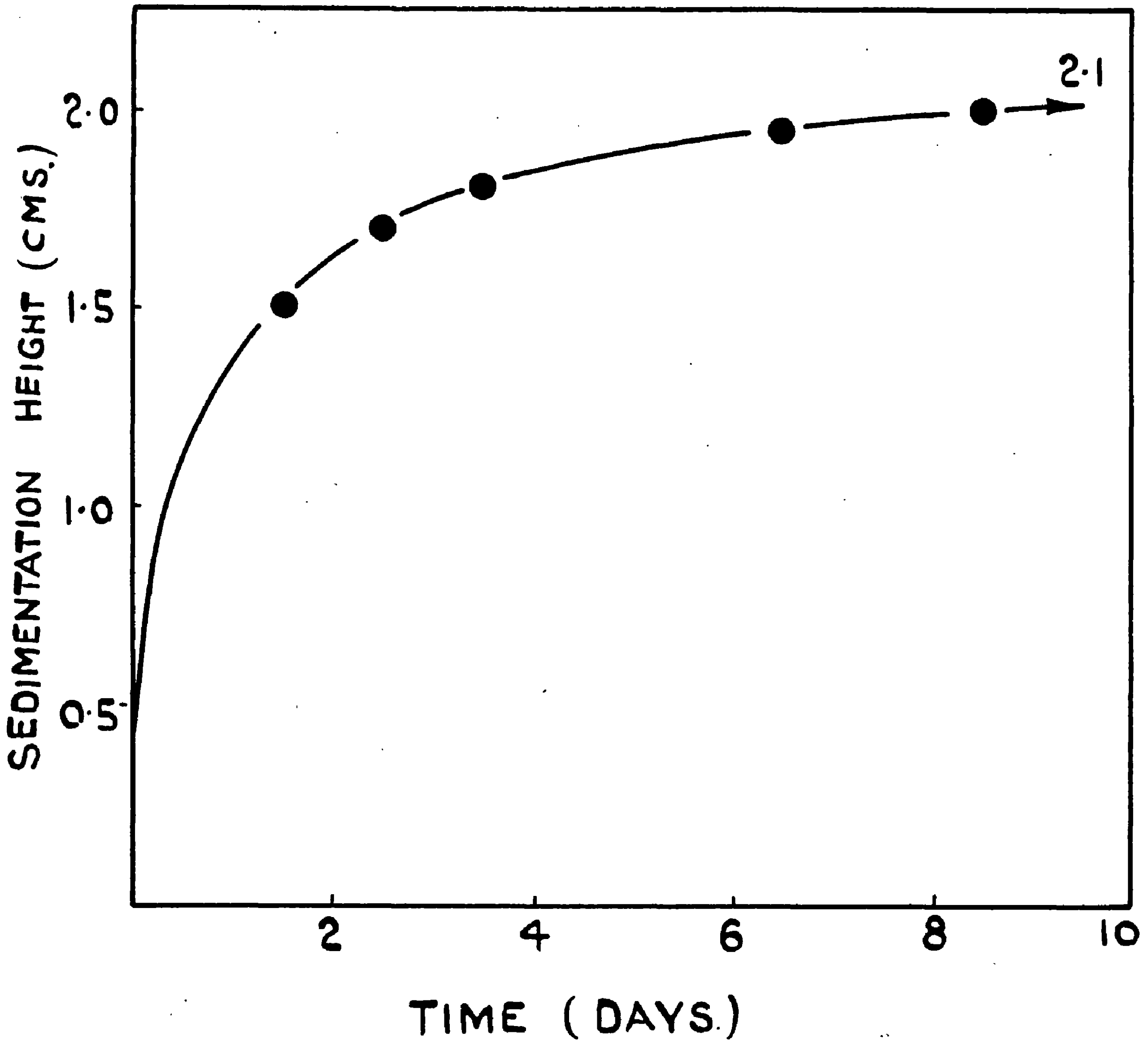
The CTAB solutions at 25°C were run into the titanium dioxide powder in a beaker which had previously been kept at 25°C in an air thermostat. The mixture was slowly rotated for about a minute, care being taken to avoid bubbling of the soap. The mixture was then rotated as vigorously as practicable to secure efficient mixing and then poured into the sedimentation tube which was returned to the air thermostat. In most cases the powder sedimentated rapidly and the height of the powder in the tube could be read off after an hour. Solutions which contained finely dispersed powder were left a sufficient time to become clear before readings were taken.

Results.

Most of the sedimentation heights reached equilibrium values fairly quickly, although in presence of relatively large amounts of CTAB and in the absence of CTAB, equilibrium was reached very slowly. Fig.21 shows the equilibrium curve for 5 gm. of 'anatase E' in 25 c.c. water. Fig.22 shows the graph of the sedimentation volume, as measured by the height of the

FIG. 21.

SEDIMENTATION OF 5 GMS. TITANIUM DIOXIDE IN 25 CCS. WATER.



titanium dioxide in the tube, against the concentration of CTAB. Its general shape is well known[90] i.e. a maximum sedimentation volume at a low concentration of CTAB, approximately 6.7×10^{-4} M and an even lower sedimentation volume in more concentrated (i.e. $>$ .008M) CTAB than in the water-titanium dioxide system.

If the formation of the unilayer of chemisorbed CTA^+ had been completed before amphipathic adsorption commenced, it would be expected that the concentration at which the sedimentation volume was a maximum would have been equal to the total concentration of chemisorbed CTA^+. Of course, as shown in the adsorption measurements, the CTA^+ is adsorbed amphipathically long before the completion of the chemisorbed layer but it is possible to calculate, from the adsorption measurements (fig.10) the initial concentration of CTAB at which a maximum area of hydrocarbon surface is exposed to the solution provided one assumes (a) that each physically adsorbed CTA^+ ion 'shields' one chemisorbed CTA^+ ion, and

(b) that the hydrocarbon chains are orientated normally to the surface.

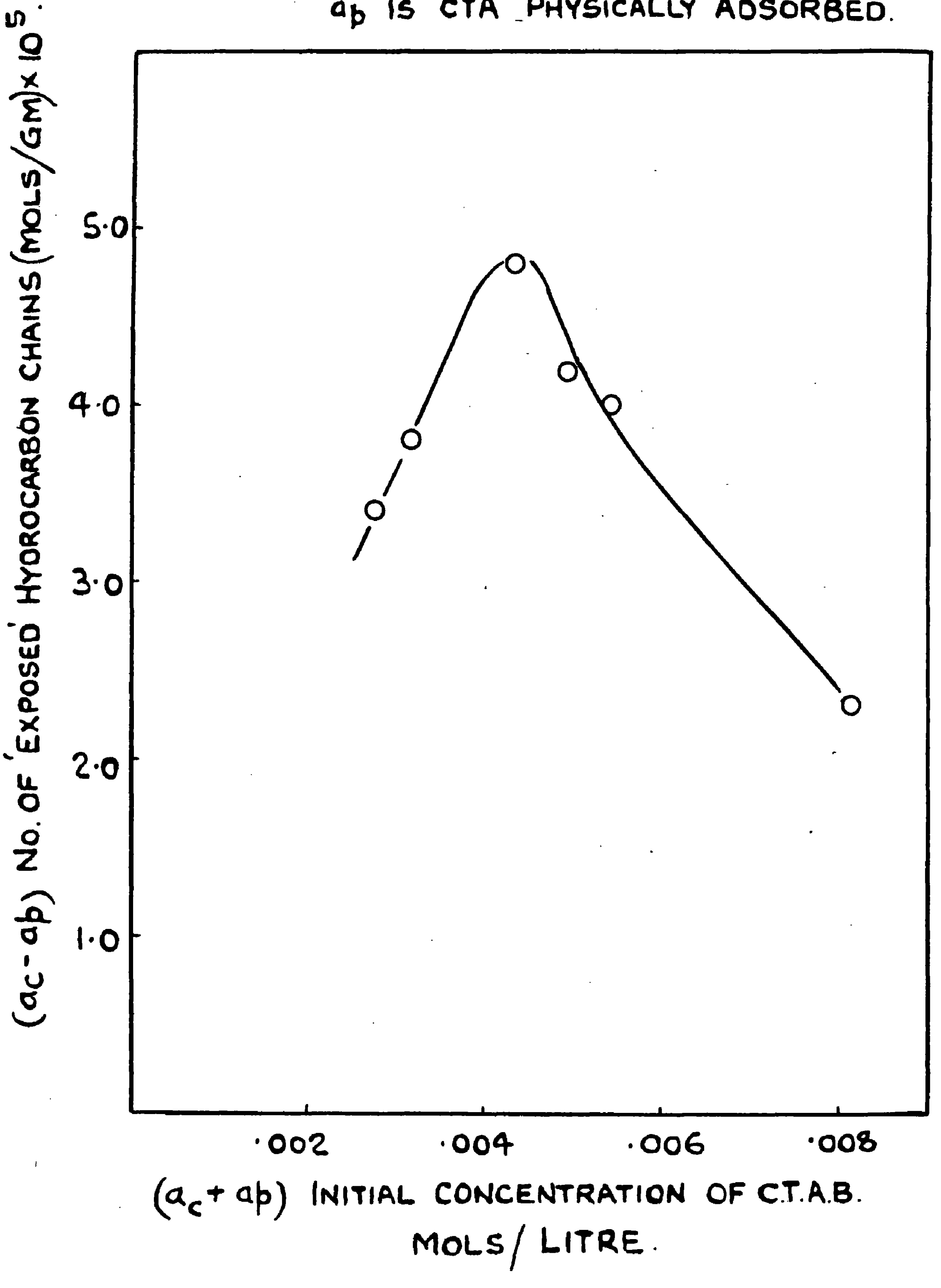
Thus fig.23 shows the hydrocarbon surface exposed to the solution, as measured by the difference between the amount of CTA^+ chemisorbed and the amount physically adsorbed, plotted against the initial concentration of CTAB. A maximum is reached at .0044 mol./litre. Now, although there is some

FIG. 23.

PLOT OF $(a_c - a_p)$ AGAINST $(a_c + a_p)$ FOR TiO_2

a_c IS CTA^+ CHEMISORBED.

a_p IS CTA^+ PHYSICALLY ADSORBED.



doubt as to the precise value of the maximum sedimentation volume, it certainly lies below .001 mol/litre, initial CTAB concentration. It therefore seems that the maximum sedimentation volume is not connected with the maximum area of hydrocarbon exposed to the solution. While the two assumptions made above could be in error, a more likely explanation of this discrepancy is that the addition of a small amount of physically adsorbed CTA^+ to the surface film has a vastly greater effect in decreasing the sedimentation volume than the addition of the same amount of chemisorbed CTA^+ has in increasing the sedimentation volume. In fact, it may well be that the maximum sedimentation volume occurs at a concentration at which physical adsorption has just commenced.

Effect of Sodium Salicylate - CTAB on the sedimentation volume of TiO_2.

Experimental.

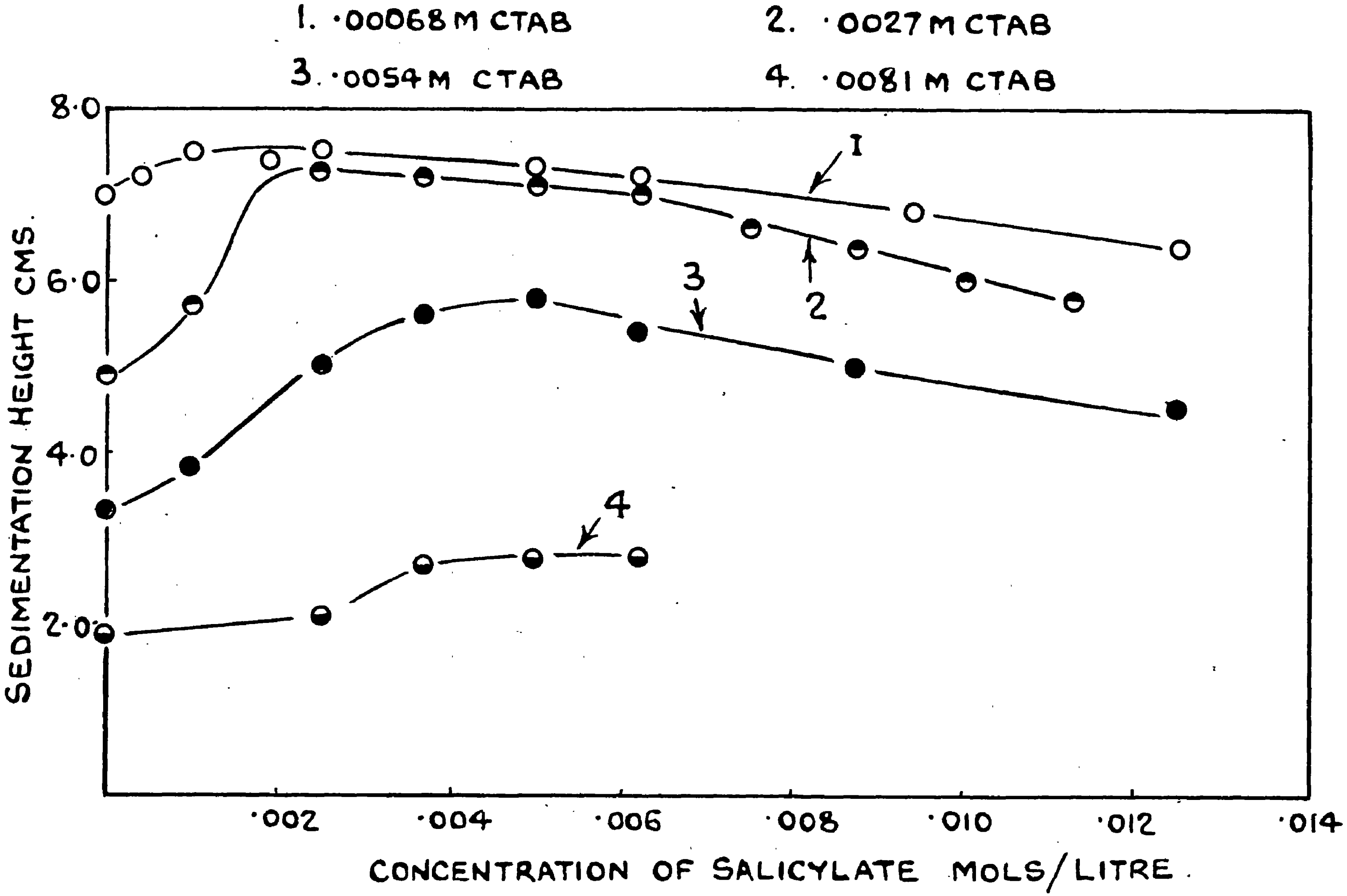
The experiments were carried out with various fixed concentrations of CTAB containing different amounts of sodium salicylate. Four different concentrations of CTAB were used i.e. .00068M, .0027M, .0054M and .0081M. Solutions which were visco-elastic were stirred into the powder. It was noticeable that the CTAB - salicylate solutions did not 'wet' the titanium dioxide as easily as water or CTAB did, a similar behaviour to that found with alumina. However, after stirring for about half a minute, the visco-elasticity disappeared, in most cases, due to the adsorption of the salts and the mixture appeared very similar to those found with CTAB alone.

Results.

The graph of the sedimentation volume against the initial concentration of salicylate is shown in fig.24 for the four concentrations of CTAB. The curves are similar chiefly in that there is an initial rise in the sedimentation volume to a maximum value, followed by a steady decrease. While the effect of the salicylate in increasing the sedimentation volume of .00068M CTAB TiO_2 is slight, it must be remembered that this is the concentration at which the sedimentation volume is at a maximum with CTAB alone. The most spectacular effect is found

FIG. 24.

EFFECT OF SODIUM SALICYLATE ON SEDIMENTATION HEIGHT IN DIFFERENT CONC$^{NS.}$ OF CTAB.



by the addition of .0025M salicylate to the .0027M CTAB-TiO_2 system since the sedimentation volume rises to almost the maximum value found with .00068M CTAB. That the CTAB and the salicylate are present in approximately equimolecular amounts suggests a close parallel between this system and the adsorption systems previously studied and discussed on pages.55-57. Confirmation that the maximum sedimentation volume is reached when the salicylate and the CTA^+ are present in equimolecular amounts, is shown by the maximum sedimentation volume which occurs on the addition of .005M salicylate to .0054M CTAB. (curve 3, fig.24).

This rise in the sedimentation volume with addition of salicylate is accompanied by a very marked change in the appearance of the supernatant liquid above the settled powder. For instance, with .0027M CTAB alone, there is a fine suspension above the powder which never really sedimentates. Addition of .0025M salicylate completely clears this away giving a water-clear liquid. This is particularly an effect of higher concentrations of salicylate i.e. about .0125M since the supernatant liquid is cleared without a corresponding increase in the sedimentation volume. The appearance of the settled powder at high concentrations of salicylate is also changed in a recognisable but almost indefinable way.

The Effect of Sodium p-hydroxybenzoate and Sodium p-chlorobenzoate on the sedimentation volume.

To compare the effects of these additives with that of sodium salicylate, an initial concentration of .0027M CTAB was used. The results are shown in fig.25 in which the graph for.0027M CTAB -sodium salicylate is also shown. The p-hydroxybenzoate has a slight effect in increasing the sedimentation volume but it is not really comparable with that of the sodium salicylate. On the other hand, the p-chlorobenzoate has a similar effect to sodium salicylate although the sedimentation volume is not so great. Furthermore the maximum sedimentation occurs at a rather high concentration of p-chlorobenzoate i.e. .0046 mol/litre. At this point the ratio of the p-chlorobenzoate to the CTA^+ in the adsorbed layer is $\frac{.0046}{.0027}$ or 1.7 assuming that all the p-chlorobenzoate is adsorbed. In fig.26 viscosity curves for the salicylate and the p-chlorobenzoate in .0135M CTAB are shown. The maximum viscosity in the salicylate - CTA^+ solution occurs in the region of equimolecularity but for the p-chlorobenzoate - CTA^+, it occurs at about .024M i.e. when the ratio of the p-chlorobenzoate to the CTA^+ in the solution is $\frac{.024}{.0135}$ or 1.8. This may indicate that the p-chlorobenzoate - CTA^+ system has its most 'interesting' properties when the ratio of the p-chlorobenzoate to the CTA^+ is about 1.7.

FIG. 25.

EFFECT OF SOME SODIUM SALTS OF ORGANIC ACIDS ON THE SEDIMENTATION HEIGHT OF TiO_2 IN ·0027M CTAB.

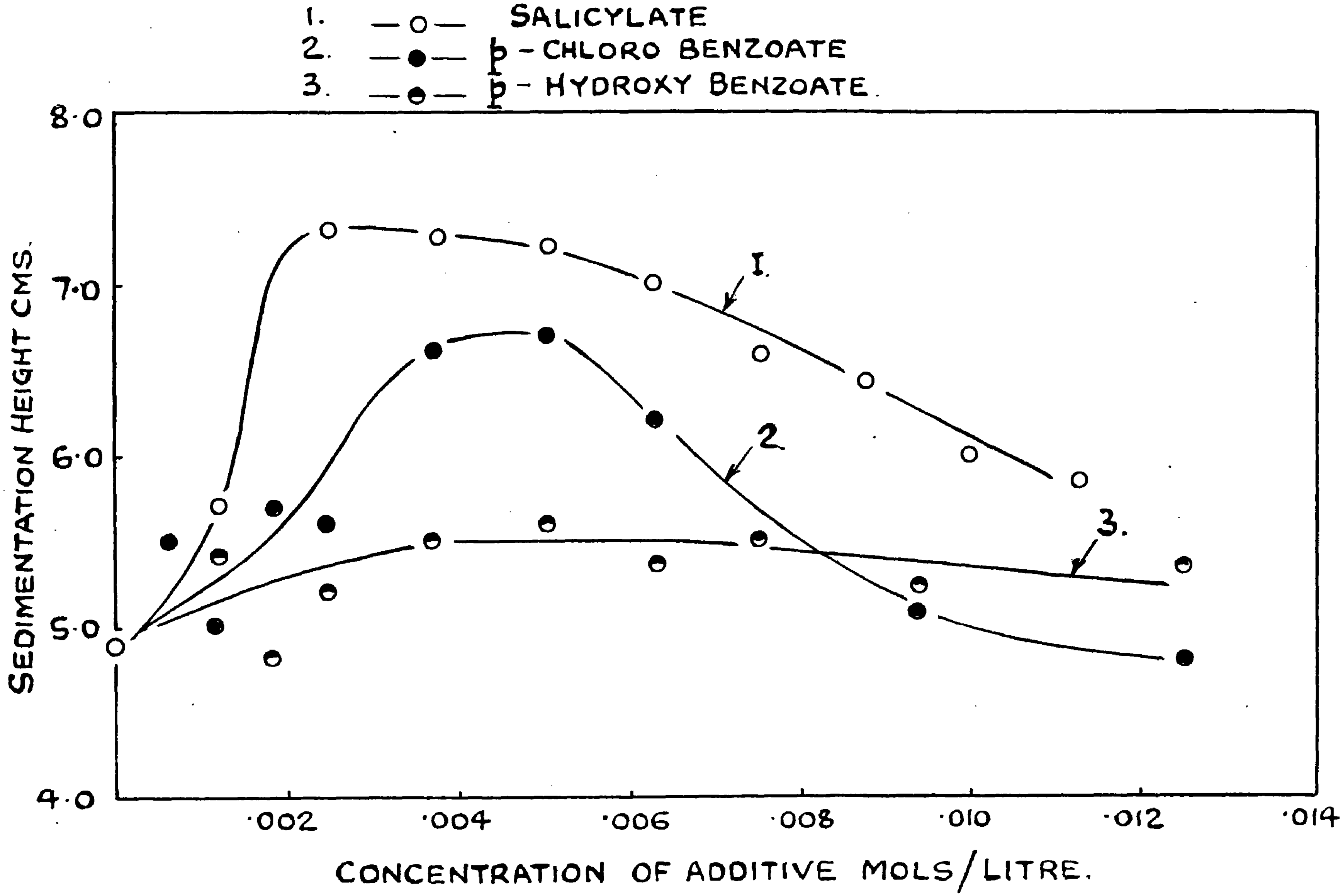
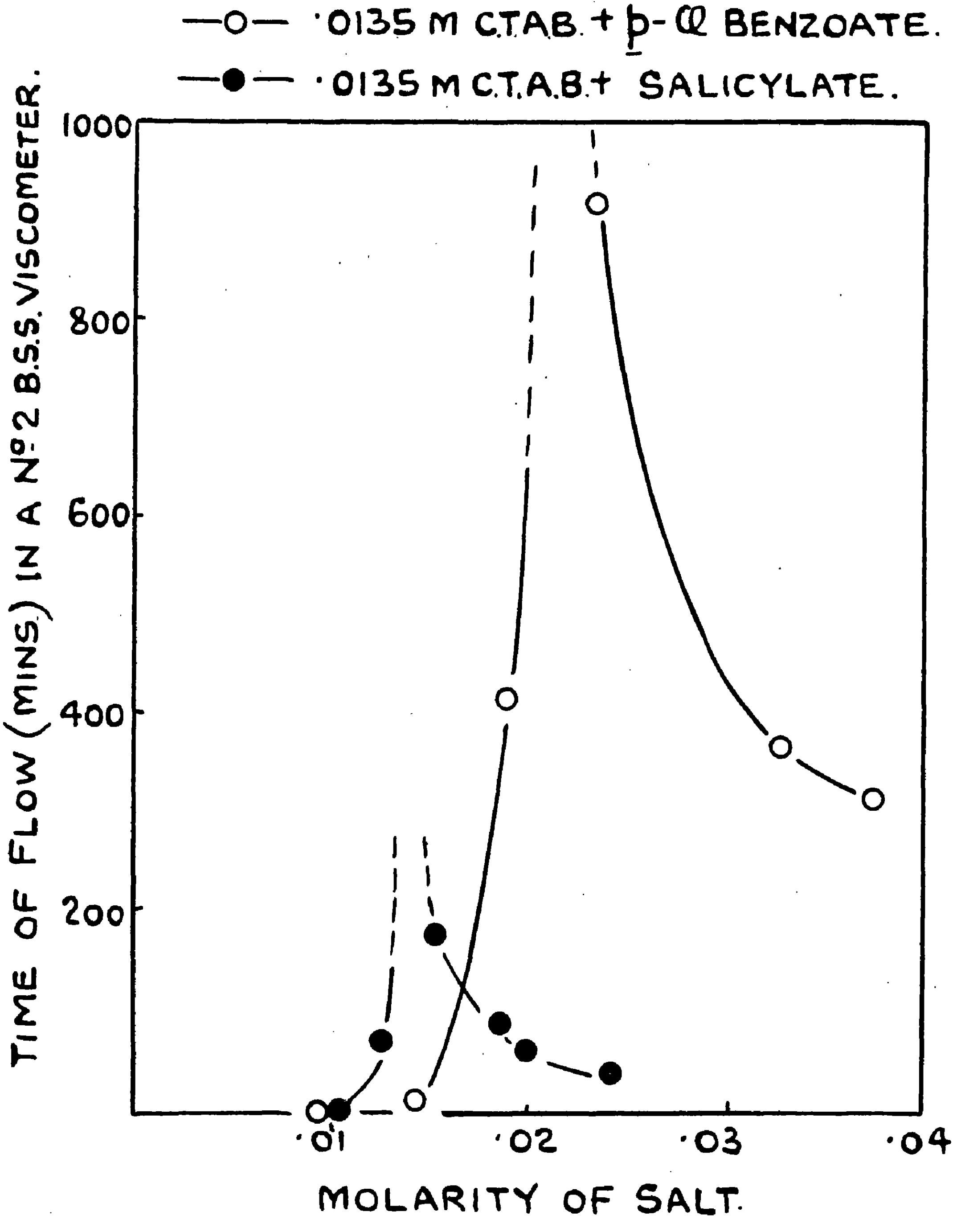


FIG. 26.

VISCOSITY OF C.T.A.B. - SOD. SALICYLATE AND OF C.T.A.B. - SOD. p - Cl BENZOATE SOLUTIONS AT 25°C



Discussion

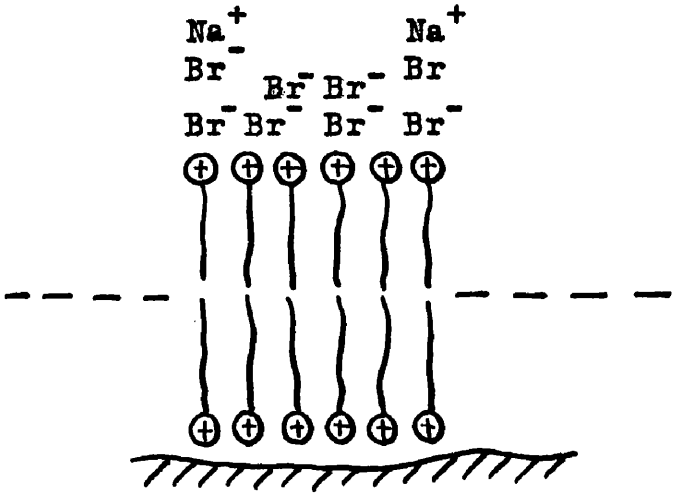
As indicated previously, the principal results may be explained on the basis of the 'adsorption with reversed orientation' theory given in the introduction to the adsorption work. It has been stated that the Br′isotherms represent a plot of the amount of CTA^+ amphipathically adsorbed against the amount of CTA^+ chemisorbed, until the region in which the adsorption begins to decrease. The justification for this is that it is just what would be anticipated to occur if a double layer of ions is formed, the first layer being chemisorbed by ion exchange, the second being physically adsorbed. The process of adsorption could be visualised as follows.

Initial additions of CTA^+ ions come into contact with the surface layer of the adsorbent. The precise mechanism by which the ions diffuse into the surface remains unknown but there must be a considerable reduction in the free energy of the system when the CTA^+ exchanges with a cation from the surface (probably sodium in the case of the alumina), because water tends to be expelled from the surface and hydrocarbon chains are interposed between the solid and the solution. The insoluble salt formed by the ion exchange remains attached to the surface while the soluble salt (NaBr with alumina) apparently diffuses away. This is shown by the almost zero slope of the Br′isotherm at low concentrations. After a certain amount of CTA^+ has been absorbed, amphipathic adsorption begins with the second layer formed so as to reduce the hydrocarbon - water interface. It has, however, been pointed out (page 45) that only something in the region of half the chemisorption sites which are ultimately filled, have been filled when the second layer begins to form.

There are at least three reasons for this. First the necessity to reduce the hydrocarbon - water interface, second, the chemisorption sites will be of different energy levels and third, chemisorption sites may actually be blocked by the bulky hydrocarbon chains. While the work of Tomlinson[90] reported in the introduction, had suggested that the maximum in the sedimentation volume coincided with the completion of the first adsorbed layer, it has been pointed out (page 61) that this maximum could, perhaps, be better regarded as the point at which amphipathic adsorption begins. Of course, these two views become more alike as the change from the chemisorbed CTA^+ layer to the physically adsorbed CTA^+ layer becomes more abrupt and this will depend on the nature of the adsorbent.

Once amphipathic adsorption begins (i.e. adsorption of Br' begins), a difficulty in the interpretation of the results is presented since it is not possible to say whether all the

Br' is adsorbed in company with an equivalent amount of CTA^+ ions. There seems no reason to believe that the Br' is adsorbed by anion exchange with the adsorbent since this would be expected to occur even at the lowest concentrations. However, it is possible that some of the soluble salt (say NaBr) produced by ion exchange is adsorbed by the second layer. The surface film might then be represented as



[It should be emphasised here that this sort of diagram is intended primarily for explanatory purposes, not for exactly representing the surface film, which will be much more chaotic than the ordered structure shown. This diagram does, however, contain the essential features of the adsorbed film].

While it is probable that salts are adsorbed to some extent by micelles in solution, it has not really been established to what extent. It is likely, however, that the amount of adsorption is comparitively slight (this is supported by some measurements on the activity coefficient of Br' in (CTAB + KBr) solutions presented in part II)

Furthermore the surface of the adsorbed film is likely to differ considerably from the surface of the micelles in solution in regard to its curvature. This adsorption may, however, explain a very slight discrepancy between the CTA^+ and Br' isotherms at concentrations above that required to produce saturation of the adsorbed film. Figs. 6, 10 and 11 show that the CTA^+ adsorption tends to decrease slightly at higher concentrations while the Br' adsorption does not, showing that Br' is being adsorbed in excess of that adsorbed in company with the CTA^+.

In general, however, the fact that it is possible to calculate (pages 43,48,49) the amount of CTA^+ adsorbed by measurement of the Br' adsorbed and in solution is strong evidence in favour of the identification of the Br' adsorbed with the CTA^+ amphipathically adsorbed and the Br' in solution with the CTA^+ chemisorbed.

These CTA^+ adsorption values may be used in at least two ways to give some information about the adsorption layer.

(1) If each CTA^+ ion is taken to occupy an area of $35\mathring{A}^2$, the 'active' surface area may be calculated from the product of this number, the amount of CTA^+ chemisorbed and Avogadro's number. The results so obtained are summarised in table II, together with those obtained independently by N_2 adsorption.

TABLE II

Powder	'Active' surface area m^2/g	Surface area by N_2 ads^n. m^2/g.	% Surface covered
Alumina	12.2	69.6	18
TiO_2	4.4	7.6	58
Silica	7.2	8.0	90

The porous nature of the alumina may contribute to the small fraction of the surface apparently available for CTA^+ adsorption, the CTA^+ ion being unable to penetrate the finer pores.

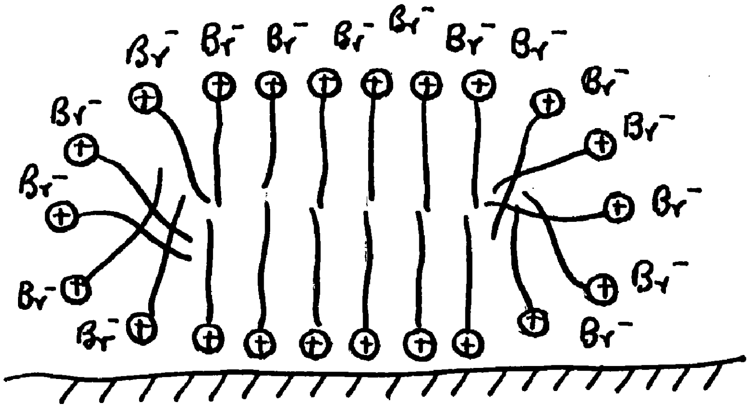
(2) If a double layer of CTA^+ ions were formed on a smooth surface it might be anticipated that the amount of amphipathically adsorbed CTA^+ (a_p) would be equal to the amount of chemisorbed CTA^+ (a_c) when saturation is reached. In the actual experimental case, however, this is far from being the case. The results are summarised in table III for convenience.

TABLE III

Powder	a_p at saturation mol./gm. x 10^5	a_c at saturation mol./gm. x 10^5	a_p/a_c
Alumina	10.2	5.8	1.8
TiO_2	2.7	2.1	1.3
Silica	4.9	3.4	1.4

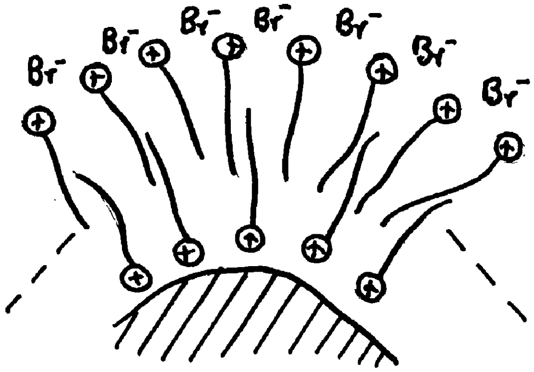
The ratio a_p/a_c is greater than unity in all three cases and this may be due to the adsorbed film tending to have one or all of the following three structures.

(a) Since only part of the surface contains active sites for adsorption, small 'surface' micelles, rather than one enormous micelle covering the surface, may be expected to be formed. This may be represented as



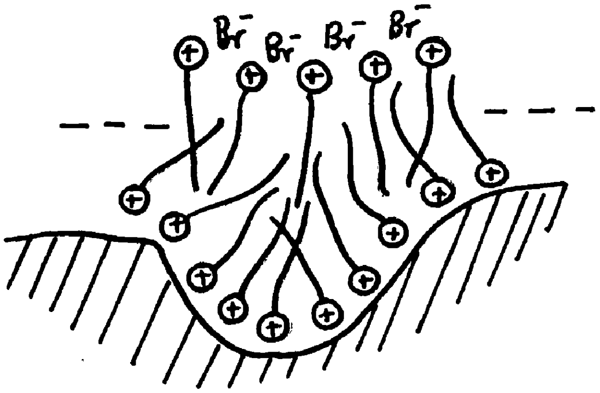
This will contribute to an increase in the ratio a_p/a_c .

(b) The convex nature of the surfaces of all powders will tend to produce a double layer like this



leading to an increase in the ratio a_p/a_c .

(c) Certain irregularities will give rise to such an arrangement as



giving a decrease in the ratio a_p/a_c .

Such is the complexity of the surface of a solid that this can be considered only as a crude outline of the nature of the adsorbed layer. There are many other complications about which little is known, which will influence this picture e.g. surface active sites may be expected to form on more exposed parts of the surface while the deformation of spherical, cylindrical or lamellar micelles, due to attachment to the surface, will affect the stability of the micelles.

Although it may be said that this ratio a_p/a_c is related to the nature of the surface and to the number and distribution of active sites thereon, more precise suggestions are necessarily tentative owing to the lack of data available. Thus while it is quite likely that the high a_p/a_c ratio for alumina is related to the low surface area actually covered by the adsorbate [due to (a)] there is also the possibility that the porous nature of the alumina, involving a rather rough surface, enables micelles of the type (b) to predominate. However, the crude picture outlined above does, at any rate, indicate the preponderance of the structures (a) and (b) for all the adsorbents studied.

The Effect of Organic Salts on the adsorption of CTA^+ on Alumina and on the Sedimentation Volume of TiO_2 in CTAB Solutions.

The principal facts which seem to have been established are

(1) Sodium salicylate has a unique effect, among additives studied in always increasing the amount of CTA^+ adsorbed on alumina, all the other salts having the opposite effect.

(2) In the presence of sufficient salicylate, the adsorbed layer contains CTA^+ and salicylate in approximately equimolecular amounts.

(3) Sodium salicylate and sodium _p_-chlorobenzoate both tend to produce considerable increases in the sedimentation volume of TiO_2 in certain CTA^+ solutions while sodium _p_-hydroxybenzoate has only a slight effect.

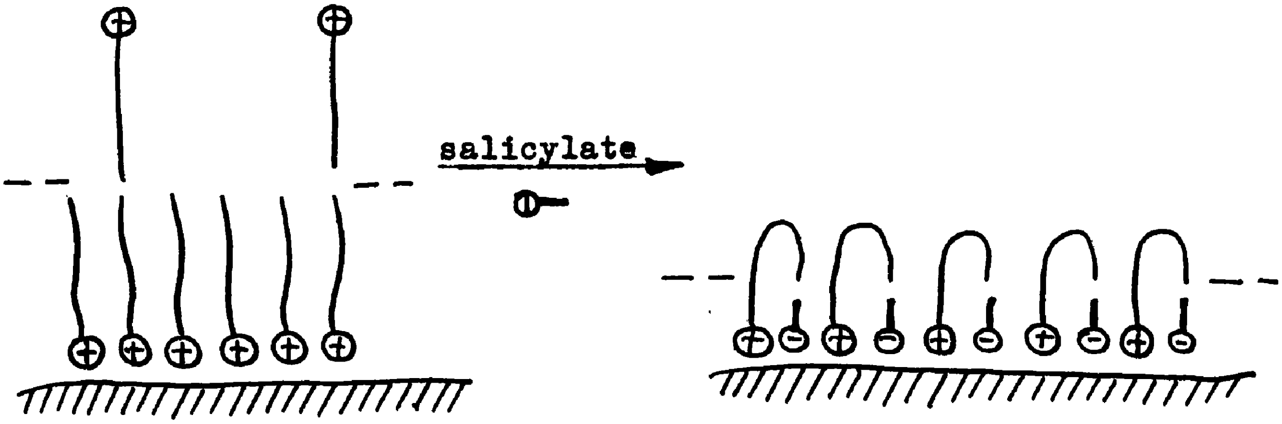
The Effect of Sodium Salicylate on the CTAB Adsorption Layer.

The principal sedimentation results with TiO_2 were obtained using two concentrations of CTAB i.e. .0027M and .0054M, and independent adsorption measurements show that all of this CTAB is adsorbed. In the first case about .0022 m/l. CTA^+ is chemisorbed and .005 m/l is physically adsorbed while in the second, .0037 m/l CTA^+ is chemisorbed while .0017 m/l is physically adsorbed. At both these concentrations the sedimentation volume has fallen below its highest value due, presumably, to the effect of the amphipathically adsorbed CTA^+.

Adsorption measurements (in fig. 16) on alumina with CTAB - sodium salicylate mixtures at .0081M, total CTAB concentration (when the surface layer is not saturated with CTA^+) have shown that practically all the salicylate is adsorbed i.e. until equimolecularity has been reached. It is therefore likely that in the TiO_2 systems, all the initially added salicylate is adsorbed.

The rise in the sedimentation volume in both .0027M and .0054M CTAB solutions on addition of salicylate is most probably due to the removal of all the amphipathically adsorbed CTA^+ in the first case (since the sedimentation volume rises to the highest recorded value) and in the second case, to the removal of part of the amphipathically adsorbed CTA^+. This CTA^+ presumably interacts with the salicylate in such a way that it either becomes oriented in the 'reverse' sense or else occupies a very much smaller portion of the surface layer. The TiO_2 particles will then tend to coalesce to a greater extent and a loose, porous, structure with a high sedimentation volume, will form. There is, however, no indication that the salicylate which is initially added, interacts only with an amount of CTA^+ equivalent to that physically adsorbed in the absence of salicylate, since the sedimentation volume only reaches a maximum when the CTA^+ and salicylate are present in equal amounts and the adsorption results also show the significance of equimolecularity.

Although these results only indicate a very close association between the CTA^+ and the salicylate, the type of micelle visualised by Good and Walker[77] and shown in the introduction accords quite well with steric considerations of the adsorbed layer. The increase in the sedimentation volume may be roughly represented by

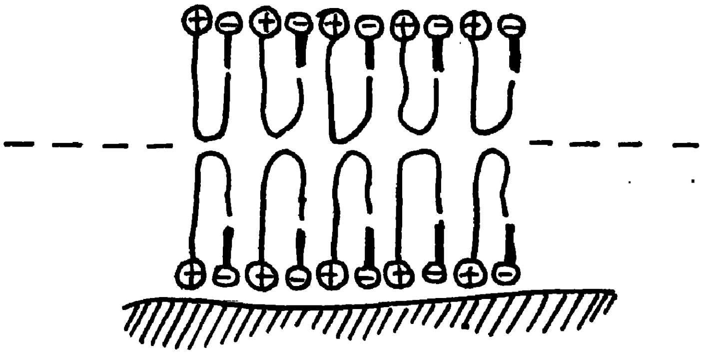


Some of the salicylate may be chemisorbed by anion sites thus enabling the CTA^+-salicylate complex to cover a larger part of the surface. It is also likely that this complex can cover parts of the surface where neither ion is actually chemisorbed i.e. the salicylate will 'bind' CTA^+ ions together to form a large aggregate on the surface in the same way as it 'binds' them together in solution.

The adsorption results generally tend to substantiate the views outlined above. When the surface is not saturated with CTA^+, all the salicylate is adsorbed until equimolecularity is reached although there does seem to be a tendency for the adsorption of salicylate to continue beyond this. This is probably due to the 'mass action' adsorption by ion exchange on surface of the second layer of the CTA^+-salicylate complex.

When the surface is not saturated with CTA^+, there is, at first, competition for the salicylate between the CTA^+ adsorbed and that in solution. The salicylate appears to be distributed between the adsorption layer and the solution in a somewhat similar way to that in which a substance is distributed between two phases i.e. the structure of the aggregates in the adsorbed layer and in solution appear to be rather similar. The adsorption layer could be regarded as consisting of polymeric aggregates attached to the surface at various points but these aggregates cannot extend into the solution to any great degree as the amount of CTA^+ adsorbed is remarkably constant during large variations in salicylate concentration.

The remarkable increase in CTA^+ adsorption in the presence of salicylate may be attributed to the ability of the CTA^+ - salicylate aggregate to cover most of the surface or to adsorption of salicylate or to a further layer or part of a layer formed on top of the bimolecular layer. If the first of these reasons is correct i.e. if the adsorption layer completely covers the surface e.g.



it should be possible to obtain the surface area from these adsorption measurements. Taking the area per CTA^+ ion as $35\,\mathring{A}^2$ and as $24\,\mathring{A}^2$ for the salicylate[99], the surface area should be

$$\tfrac{1}{2}.\ 2.16 \times 10^{-4}.\ 6.02 \times 10^{23}(35 \times 10^{-20} + 24 \times 10^{-20})\,m^2/g$$

$$\text{or } 38.5\ m^2/g.$$

The value obtained by N_2 adsorption was 69.6 m^2/g. Such is the porous nature of the surface of alumina that this result suggests the possibility of using the adsorption of CTAB - sodium salicylate from aqueous solutions onto powders in order to obtain, at any rate, a rough estimate of the surface area.

The Effect of Sodium p-hydroxy and p-amino benzoates on the CTAB Adsorption Layer.

The considerable reduction in the amount of CTA^+ adsorbed on alumina on addition of sodium p-hydroxy or p-amino benzoates (and to a lesser extent sodium o-aminobenzoate) is very interesting but rather difficult to account for since only one concentration of CTA^+ has been used.

It is possible that these salts increase the stability and number of the micelles in solution at the expense of those adsorbed on the surface but the amount of CTA^+ displaced from the surface is so great as to discredit this.

A more likely explanation is that the salts somehow separate the ionic groups of the adsorbed CTA^+ ions. Since the surface micelles are fixed in size, there will be a reduction in the amount of CTA^+ adsorbed simply due to the space occupied by the salt in the micelle. Actual penetration of such an ion as p-hydroxybenzoate into a CTA^+ micelle in a way similar to that suggested for the salicylate, has, however, two drawbacks. First, the energy required to remove the polar hydroxy group from the water will reduce the stability and therefore the amount of the resulting micelle. Second, there is no particular reason to suspect any other type of force which might allow the p-hydroxybenzoate to penetrate into the micelle since the viscosity of CTAB - sodium p-hydroxybenzoate solutions is the same as water.

The Effect of sodium benzoate and sodium p-nitro and p-chloro benzoates on the CTA^+ Adsorption Layer.

These salts appear to have effects intermediate between those of sodium salicylate on the one hand and sodium *p*-hydroxy and *p*-amino benzoates on the other. The adsorption layer in the presence of all three additives is thus likely to be a fusion of the different types of adsorption layers formed between salicylate and CTA^+ and between CTA^+ and *p*-hydroxy or *p*-amino benzoates. The *p*-chloro and *p*-nitro benzoates seem to behave more like salicylate at first in that they increase the adsorption of CTA^+, but the aggregating tendency of the surface micelles breaks down at higher concentrations of the additive.

The sedimentation effect with *p*-chlorobenzoate confirms that this salt has a similar, but not such a powerful, influence as salicylate on the CTA^+ adsorption layer. It may be that although the CTA^+-*p*-chlorobenzoate aggregate has a highly extensive structure in solution (as shown by the viscosity effects), this structure tend to break down when the aggregate is confined to two dimensions. It could therefore be that the cause of the visco-elasticity in *p*-chlorobenzoate - CTA^+ solutions is different from that in salicylate - CTA^+ solutions even though their mechanical behaviour is rather similar.

PART II.

The Approximate activity coefficient of Br′ in aqueous CTAB and CTAB-salt solutions.

INTRODUCTION

Although thermodynamics does not permit the evaluation of individual ionic activities, it is, nevertheless, convenient to use 'hypothetical' ionic activities, with the understanding that it is only ionic activity products or ratios which have any physical significance. In this work the activity of the bromine ion (referred to as $a_{Br'}$) has been obtained (for KBr solutions) from the mean activity of KBr in aqueous solutions by the assumption that $a_{Br'} = a_{K+}$

The measurement of the activities of ions in soap solutions has always involved a liquid junction potential whose value is doubtful but is assumed to be eliminated by means of a suitable salt bridge. It is for this reason that the term 'approximate activity coefficient' is used here. There have, nonetheless, been a number of investigations whose value chiefly resides in establishing changes in activity coefficients rather than in accurately measuring their values.

Lottermoser and Püschel[11] measured the silver ion activity coefficients of silver salts of some alkyl sulphuric acids and found an abrupt fall at the same concentration at which the conductivity also fell. The silver ion activity reached a minimum in approximately the same region as the conductivity.

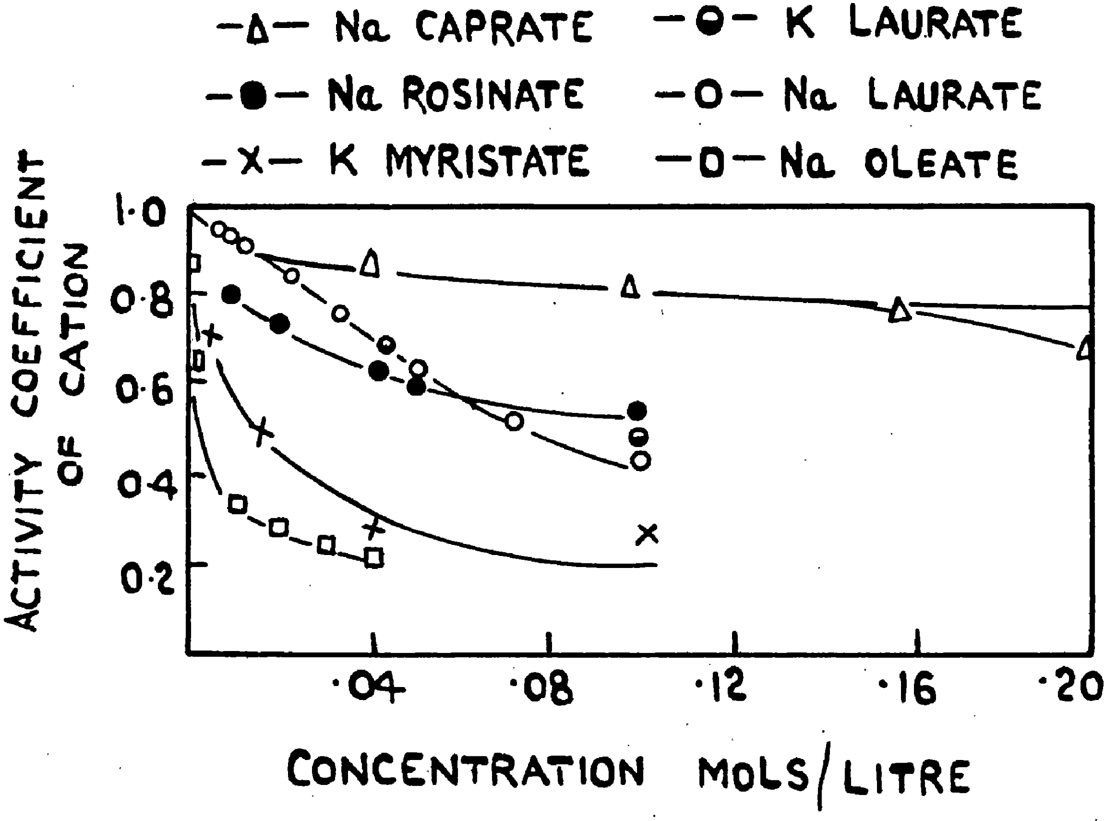
McBain and Williams[100] determined hydrogen ion activities in aqueous solutions of cetyl sulphonic acid at 90°C. The activity remained high even above the concentration regarded as the CMC. McBain and Betz[101], in similar work, found that the hydrogen ion activity in solutions of other paraffin chain sulphonic acids, fell along with the conductivity, but an abrupt change was not observed.

Carr, Johnson and Kolthoff[102] have measured cation activities in solutions of sodium caprate, laurate, oleate and rosinate and potassium laurate and myristate, by means of collodion membrane electrodes. A suitable collodion electrode behaves towards cations in much the same way as the glass electrode behaves towards hydrogen ions, but it is not specific for one ion and can thus only be used to determine activities when only one simple salt is present. Their results are shown in fig.27. The activity coefficient begins to decrease at a concentration which coincides with the CMC. and, at higher concentrations, it appears to approach a limiting value. The CMC of some of the longer chain salts is too low to be detected by this method. The activity of the sodium ion in sodium laurate solutions is practically the same as the activity of the potassium ion in pot. laurate solutions of the same concentration. In discussing this work later, Kolthoff and Johnson[103] point out that "the small

FIG. 27.

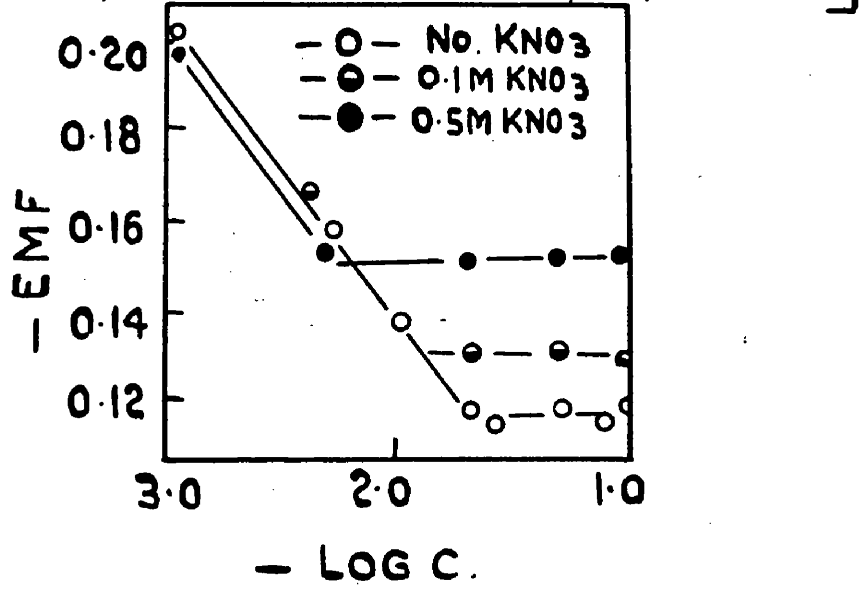
CATION ACTIVITY COEFFICIENTS IN VARIOUS SOAP SOLUTIONS

[FROM CARR, JOHNSON AND KOLTHOFF, J-PHYS. + COLLOID CHEM., 51, 636 (1947)]



C.M.C. OF POT. LAURATE – KNO3 SOLUTIONS

[FROM KOLTHOFF AND JOHNSON, J, PHYS. + COLLOID CHEM., 52, 22 (1948)]



activity coefficients of the sodium ions in solutions of micellised sodium salts of detergents,are not caused by the formation of 'undissociated' salt, but by the facts that the negative charges in the micelle are very close together and that these charges are in fixed positions". Kolthoff and Johnson[103] used the cell.

$Ag | Ag$ laurate(s) K laurate, $KNO_3 || KCl$ (saturated), $Hg_2Cl_2 | Hg$

to measure the anion activity in solutions of potassium laurate at 30°C. Their results are also shown in fig.27. The CMC is clearly shown as an abrupt break in the emf-concentration curve and it decreases with increasing amounts of potassium nitrate. The activity of the laurate ion becomes practically constant once the CMC has been reached, showing that laurate which is unmicellised below the CMC does not micellise above the CMC. It was believed that the liquid junction potential did not obscure the conclusions which were drawn from the results.

Experimental.

Preparation of the Electrodes.

(1) Thermal Ag-AgBr electrodes.

Silver oxide was prepared by adding the necessary amount of caustic soda to silver nitrate solution and washing the resulting precipitate thoroughly. Silver bromate was prepared in a similar way from potassium bromate and silver nitrate. A mixture of 90% silver oxide and 10% silver bromate was then made in a paste with water and coated onto a platinum wire spiral which had been sealed into low melting pyrex glass. The paste was decomposed in a furnace at 600°C for 10 minutes. When not in use the electrodes were kept in .01MKBr. This is the method of Keston[104].

(2) Electrolytic Ag-AgBr electrodes.

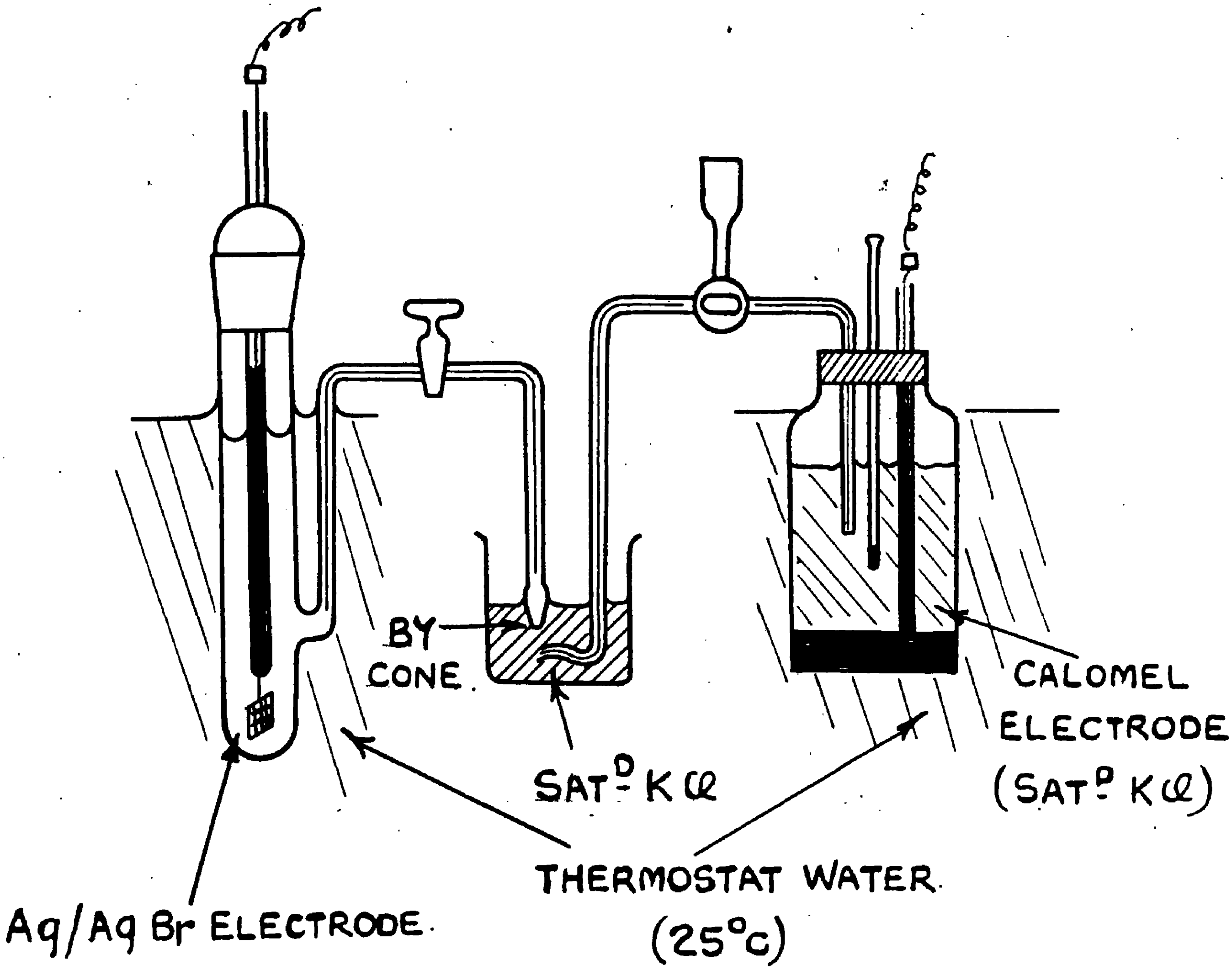
Platinum gauze 0.5 cm. x 1.0 cm was welded to platinum wire and then sealed into soda glass tubing. After these platinum bases had been cleaned by heating to brightness in a flame and then immersing them in boiling concentrated nitric acid, they were electroplated with silver at a current of 4mA per electrode for 24 hr. The silver plating bath was made up by dissolving 10 gm. recrystallised potassium silver cyanide in a litre of distilled water and adding enough dilute silver nitrate solution to produce a faint cloud of silver cyanide. When this had settled, the bath was ready for use.

After electroplating, the electrodes were washed for 10 days in frequent changes of distilled water to remove adsorbed contaminations. Finally they were bromidised electrolytically in $\overline{N}$HBr at 4mA per electrode for one hour.[105]

Apparatus.

Two calomel half cells, prepared by standard methods, were used. Their potentials differed by 0.1 mv. The Ag-AgBr electrode was connected to the calomel half-cell by means of a saturated solution of KCl as shown in fig.28. The Ag-AgBr electrode and the calomel half cell were both immersed in a water thermostat at (25 ± .1)°C while the salt bridge was kept outside. The emf of the cell was obtained by means of a Tinsley Potentiometer standardised from a Weston Cell. A Cambridge 'spot' galvanometer was found to be sufficiently sensitive.

FIG. 28.



EMF APPARATUS.

Results.

The Thermal Ag-AgBr Electrodes.

Some difficulty was encountered in preparing electrodes giving the same emf in KBr solutions. However eventually three electrodes were prepared which gave values agreeing to ± 0.2mv in .01, .02 and .04M KBr. The average values were .0487, .0658 and .0817v respectively for the emf of the cell.

The electrodes were then put into different CTAB solutions and the emf readings taken (equilibrium taking about 6 hr.). After washing in distilled water, the three electrodes were placed in .02M KBr. The emf's were .0706, .0714 and .0739v after equilibrium. Clearly the electrodes had been affected by the treatment with CTAB. They were washed in acetone but the emf readings remained at .0706, .0714 and .0739v on returning the electrodes to .02M KBr. It was suspected therefore that the CTA^+ had been chemisorbed by the electrodes and, since a dilute solution of alcoholic potash was known to remove CTA^+ chemisorbed on glass, the electrodes were treated with such a solution for about ten minutes followed by washing in distilled water for half an hour. On replacement in .02M KBr, the emf was .0663v ± .2mv which, although 0.5mv higher than for fresh electrodes, nevertheless showed that most of the adsorbed CTA^+ had been removed.

An example of the behaviour of two of these electrodes on identical treatment is shown below,

$$\text{electrode}\ \begin{matrix}1\\2\end{matrix}\Bigg\}\xrightarrow[\text{potash}]{\text{alcoholic}}\ \underset{\text{in .02M KBr}}{\begin{matrix}.0662\\.0664\end{matrix}}\Bigg\}\xrightarrow[\text{with water}]{\text{washed}}\ \underset{\text{in .027M CTAB}}{\begin{matrix}.0596\\.0544\end{matrix}}\Bigg\}\xrightarrow[\text{with water}]{\text{washed}}\ \underset{\text{in .0135M CTAB}}{\begin{matrix}.0416\\.0366\end{matrix}}$$

The drop in the emf on changing from .0270M CTAB to .0135M CTAB is approximately the same for both electrodes i.e. .0179v although the absolute values of the emf's are very different. Thus, while these electrodes give different emf's in the same CTAB solutions, they appear to respond to changes in the concentration of CTAB in approximately the same way i.e. they might be used to measure changes in Br activity in CTAB solutions, but not to measure the absolute value of the Br activity.

The unreliability of the thermal electrode in CTAB solutions is further shown by occasional random fluctuations in potential (as much as 0.5mv) over a period of some hours. This type of electrode is thus considered not suitable for work in CTAB solutions.

The Electrolytic Ag-AgBr Electrode.

This type of electrode was found to be easier to reproduce than the thermal electrode. Furthermore CTAB has no permanent effect on the electrode i.e. it appears to be perfectly reversible in all concentrations of CTAB.

The average emf's of four electrodes at various concentrations of KBr are shown in Table IV. The mean activity coefficients of KBr[106] are used to calculate the activity of the Br' at each concentration. Since the solutions are dilute and great accuracy is not required, the molarity and the molality have been assumed equal.

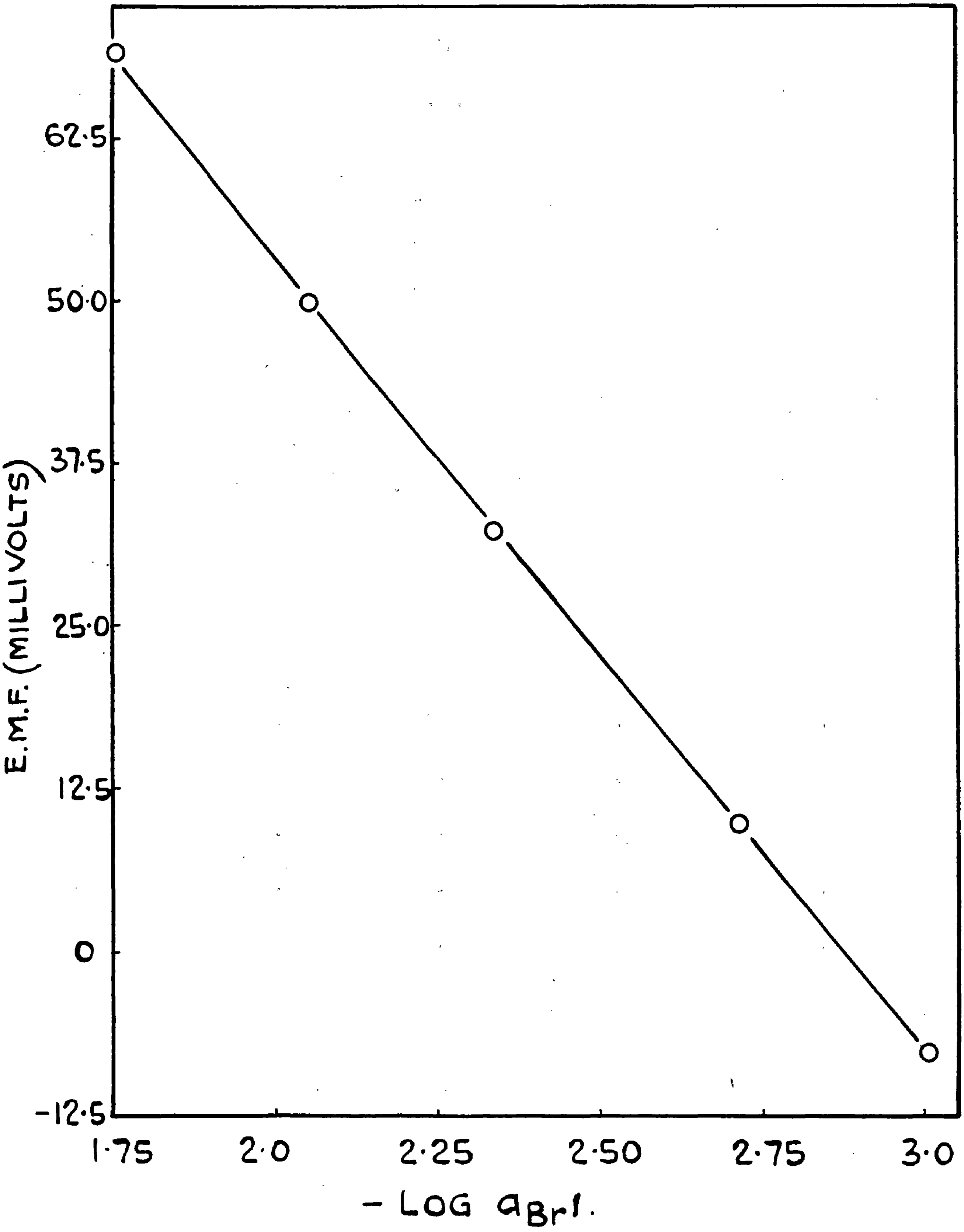
TABLE IV.

emf (e) Volts ± 0.1 mv	Molarity of KBr	$\gamma_{Br'}$	$a_{Br'}$	$-\log a_{Br'}$
.0657	.02	.87	.0174	1.760
.0492	.01	.90	.0090	2.045
.0325	.005	.93	.00464	2.334
.0100	.002	.95	.00190	2.721
-.0069	.001	.97	.00097	3.015

The emf is plotted against the $-\log a_{Br'}$ in fig.29. The equation of this straight line is

FIG. 29.

CALIBRATION OF THE E.M.F. OF THE CELL AGAINST LOG a_{Br^1}.



$$e = 0.168 + .05784 \log a_{Br} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Since the cell is

$$\overset{+}{Hg} \left| Hg_2Cl_2, \ KCl(s) \right\| KCl(s) \left\| KBr(m), \ AgBr \right| \overset{-}{Ag}$$

then $$e = e_{calomel} - e^{\circ}{}_{Ag} + \frac{RT}{nF} \ln a_{Br}$$

or at 25°C $$e = (e_{calomel} - e^{\circ}{}_{Ag}) + .05914 \log a_{Br}$$

The potential of the calomel half cell is +.2422, while that of the standard Ag-AgBr electrode is +.0713.[107]

Thus $$e = 0.171 + .05914 \log a_{Br} \qquad \ldots\ldots\ldots\ldots\ldots\ldots(2)$$

The difference in the emf's calculated from equations (1) and (2) is about 1 mv for a .02M KBr solution. This discrepancy is due, perhaps, to the existence of a liquid junction potential which may be approximately calculated for the boundary between KBr and saturated KCl from the equation.

$$E_j = \frac{RT}{F} \sum \int_{(a_i)_2}^{(a_i)_1} \frac{t_i}{Z_i} \cdot d(\ln a_i)$$

where E_j is the junction potential

t_i is the transport number of the ith ion.

Z_i is the valency of the ith ion

a_i is the activity of the ith ion

and the numerical subscripts refer to the solutions.

This gives $$E_j = -\frac{RT}{F} \left\{ (t_K - t_{Cl}) \ln a_{KCl} + (t_K - t_{Br}) \ln a_{KBr} \right\}$$

for this boundary.

Insertion of appropriate numerical values in this equation gives

$$E_j = -(.0005 + .002 \log a_{Br}) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

It therefore seems that the constant term in equation (1) is somewhat lower by about 2 mv than anticipated on the basis of equation (3). This may be due to some defect in the standard potential of the Ag-AgBr electrode and the calomel.

The CMC of Dodecyl Trimethyl Ammonium Bromide (DTAB) and of CTAB in .002MKBr

The emf's of the cell for various concentrations of DTAB are plotted against -log $C_{Br'}$ in fig.30. The change in slope of the line at a concentration of .0145M indicates a sharp alteration in the rate at which the activity coefficient is changing with respect to the concentration. This presumably is the CMC of DTAB and it agrees with the value of .014M found by Tartar[108] and by Corrin and Harkins.[109] The emf of the cell may be plotted against -log $a_{Br'}$, for concentrations below the CMC if it is assumed that the activity coefficient of the Br′ is the same in DTAB as in KBr. The straight line so obtained exactly obeys equation (1) indicating that this assumption is correct.

While it was not possible to measure the CMC of CTAB alone, because of the high resistance of the cell, the addition of .002M KBr to each CTAB concentration gave a measurable potential and in fig.31 the emf is plotted against - log $C_{Br'}$. Although the readings are somewhat more scattered than for DTAB because of the smaller emf differences between comparable concentrations, it is clear that there is, again, an alteration in the slope of the line at a concentration of 4.3×10^{-4}M.

FIG. 30.

DETERMINATION OF THE C.M.C. OF D.T.A.B. AT 25° C.

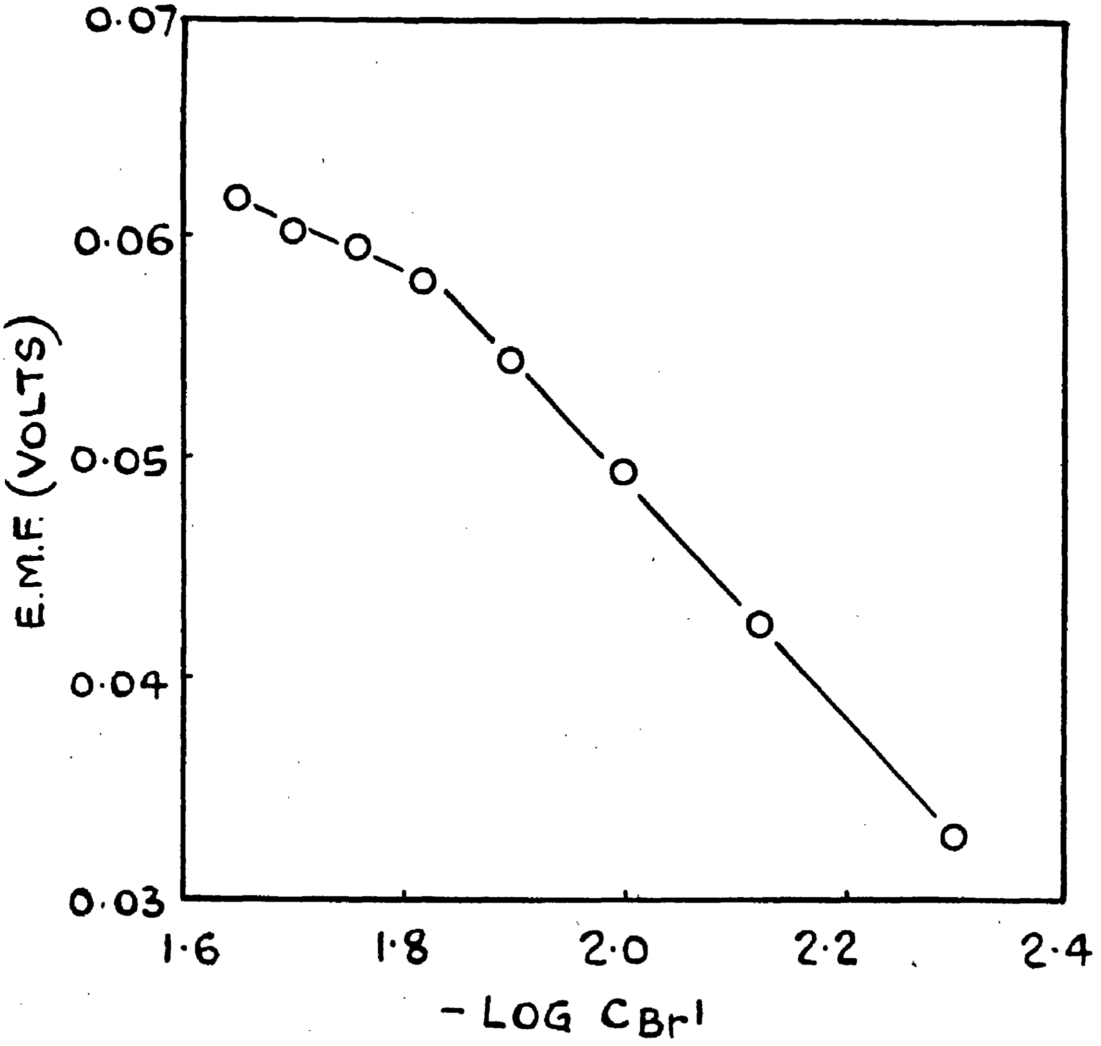
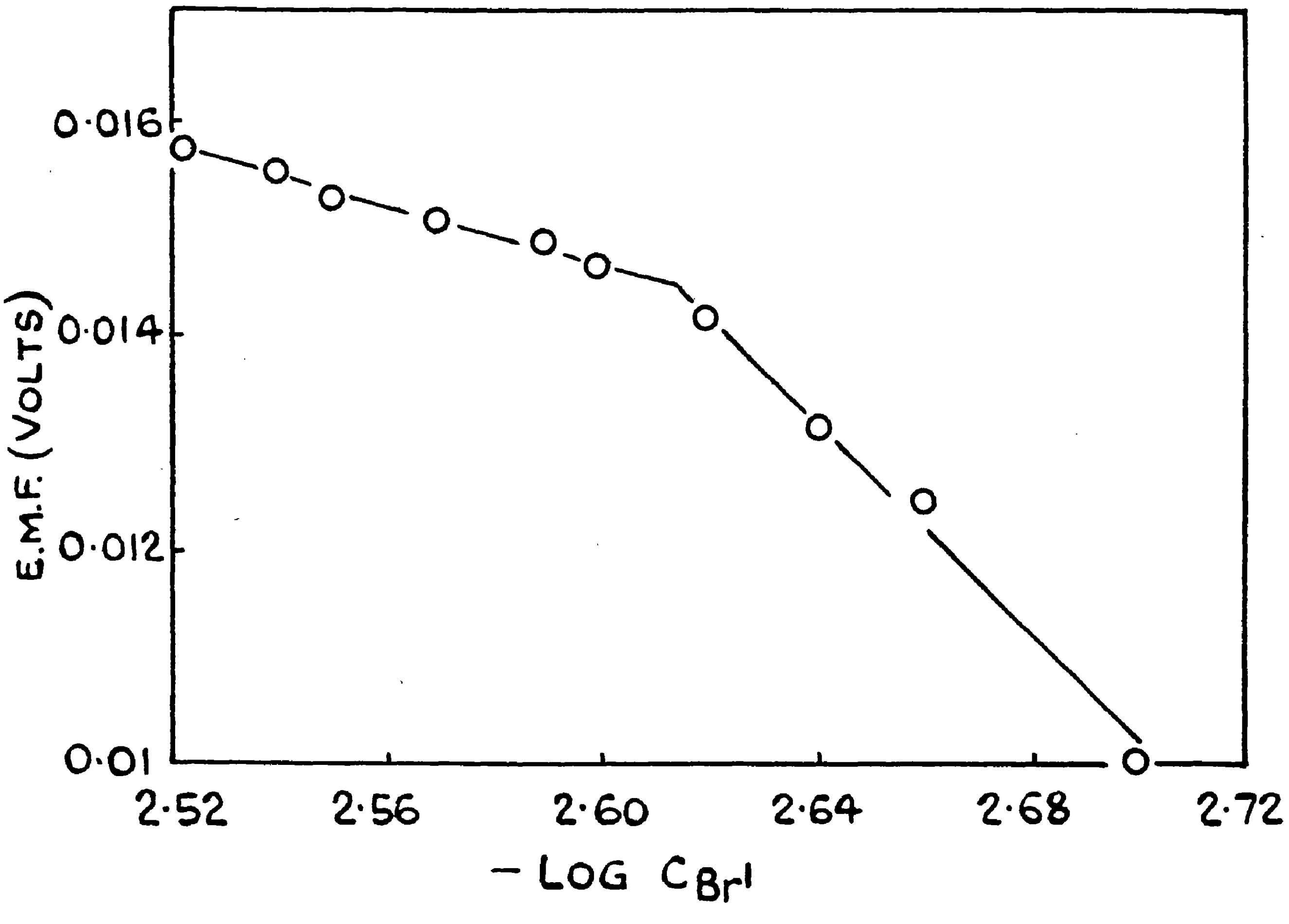


FIG. 31.

DETERMINATION OF THE C.M.C.
OF C.T.A.B. IN ·002M KBr AT 25°C.



This appears to be a reasonable value for the CMC since in a somewhat similar system (sodium chloride in cetyl pyridinium chloride) Hartley[41] obtains about 5.5×10^{-4} M as the CMC determined by the solubilisation of azobenzene.

The Approximate Activity Coefficient of Br' in DTAB and CTAB Solutions.

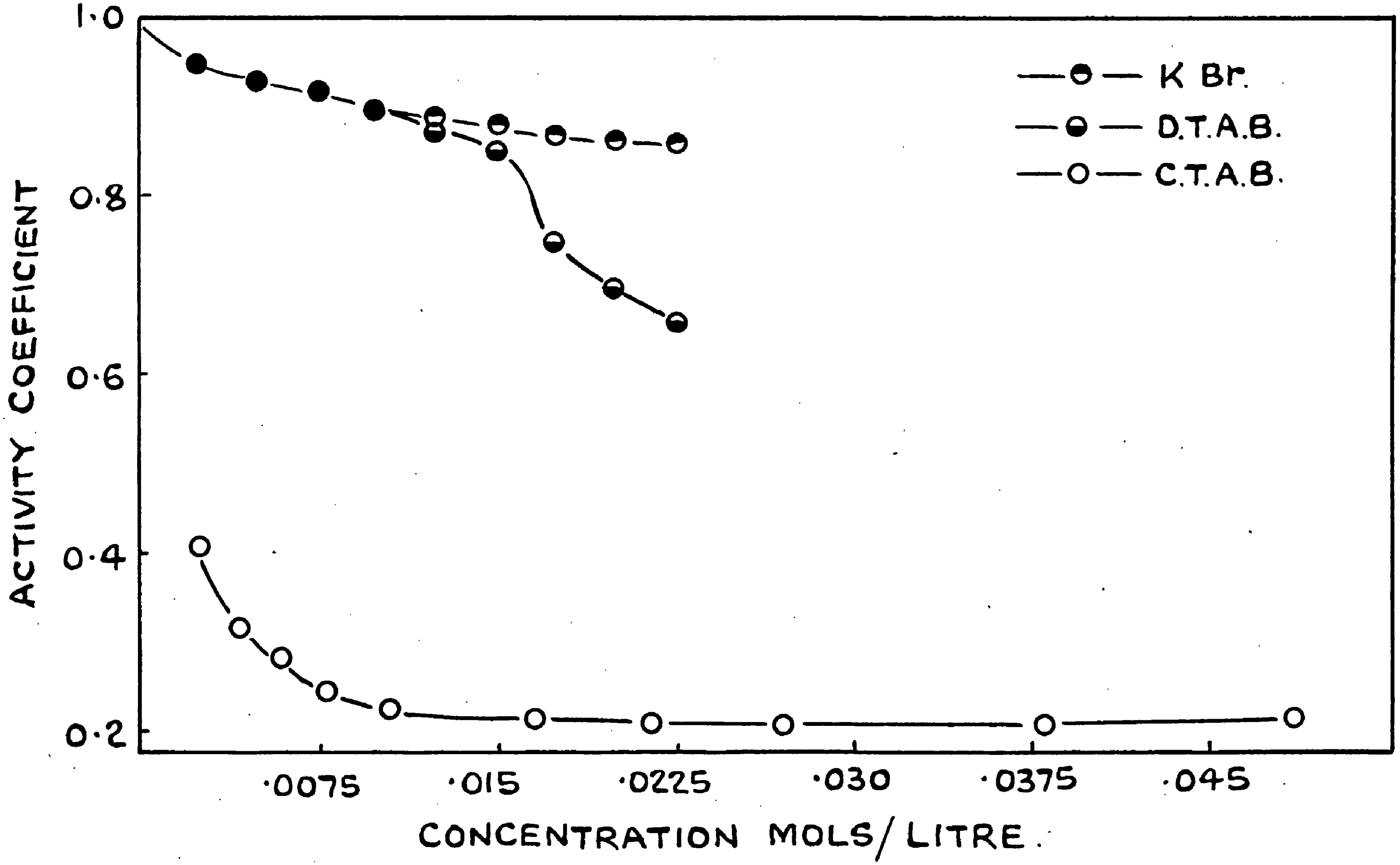
The emf's of the cell at various concentrations of DTAB and CTAB were measured and the activity coefficient of the Br' was determined by means of the calibration graph (fig.29). Fig. 32 shows these activity coefficients plotted against the concentration of the Br' and also, for comparison, the activity coefficients for KBr solutions.

The activity coefficient of the Br' in DTAB appears to be dropping more rapidly than the corresponding activity coefficient in KBr before the CMC is reached. This gives some support to the view that the CMC is better regarded as a narrow range of concentration than as one distinct concentration.

FIG. 32.

ACTIVITY COEFFICIENT OF Br' IN CTAB AND DTAB SOLUTIONS.

AT 25°C.



The Effect of Some Organic Salts on the Activity Coefficient of Br′ in CTAB.

In pursuance of the main object of this work, the effect of various salts - of the type which give viscosity effects with CTAB - on the activity coefficient of Br′ in CTAB was investigated by measuring the emf of the cell with appropriate concentrations of the additive in a fixed amount of CTAB (.0135M). By use of the calibration graph (fig.29), the activity coefficient of the Br′ may be obtained and this is plotted, in fig.33, against the concentration of the salt. There are three main features in this graph.

(1) Every salt increases the activity coefficient of the Br′. This is due to the Br′ ion, held to the CTA^+ micelle by electrostatic attraction, being replaced to some extent by the negative salt ion. This is in marked contrast to the decrease in the activity coefficient of Br′ in a normal electrolyte, e.g. KBr, on addition of a similar salt (see fig.36 later).

(2) There is a fairly abrupt change in the slope of the graphs on addition of sufficient additive. This is shown rather more clearly by fig.34 in which the activity coefficient is plotted against the logarithm of the salt concentration. The concentration of the salt at which the 'break' occurs lies near the concentration of the CTA^+ itself. Furthermore the abruptness of the change increases in the order $NaNO_3$, Na p-hydroxybenzoate,

FIG. 33.

EFFECT OF SOME SODIUM SALTS ON THE ACTIV
OF Br' IN ·0135 M CTAB.

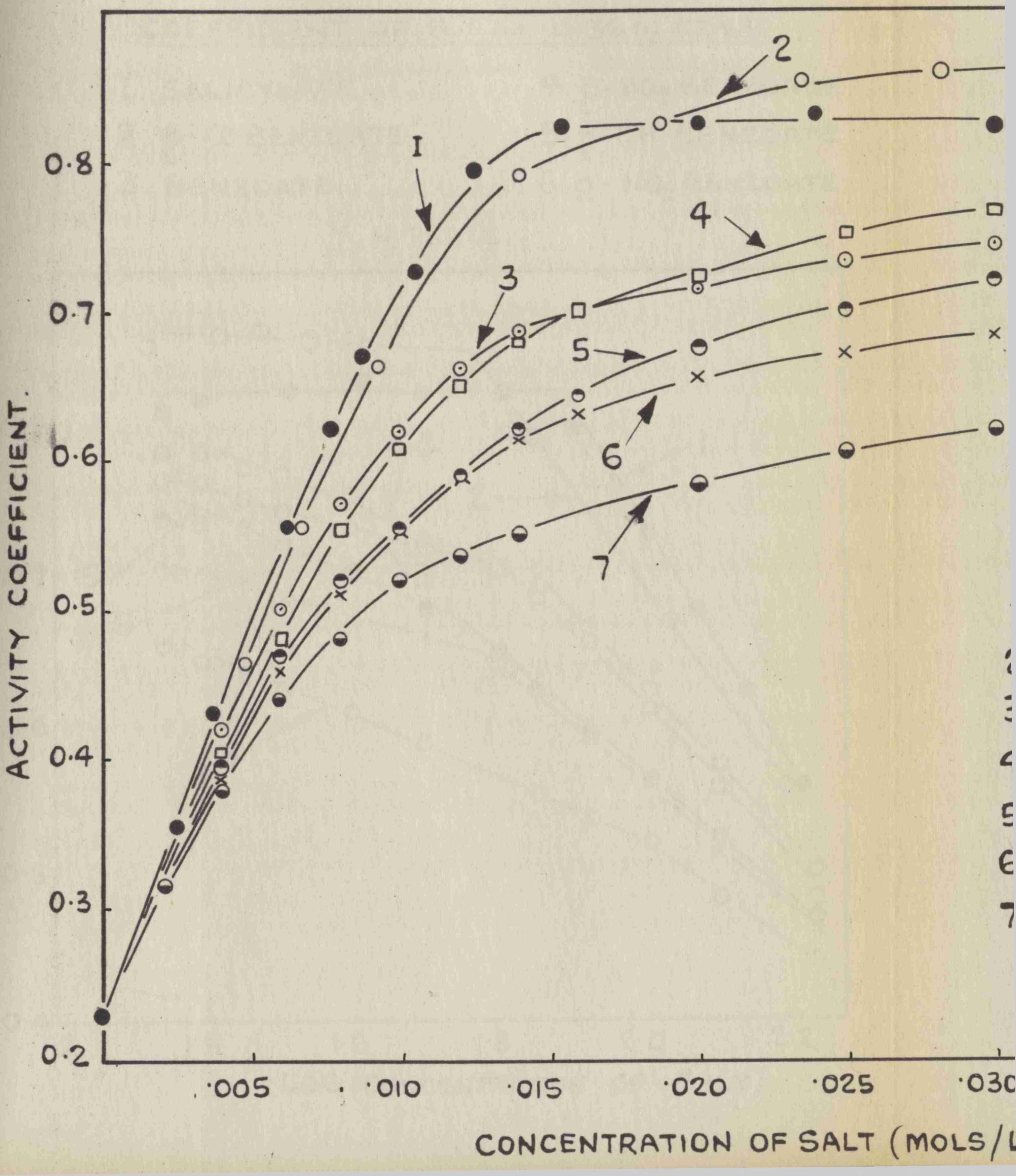
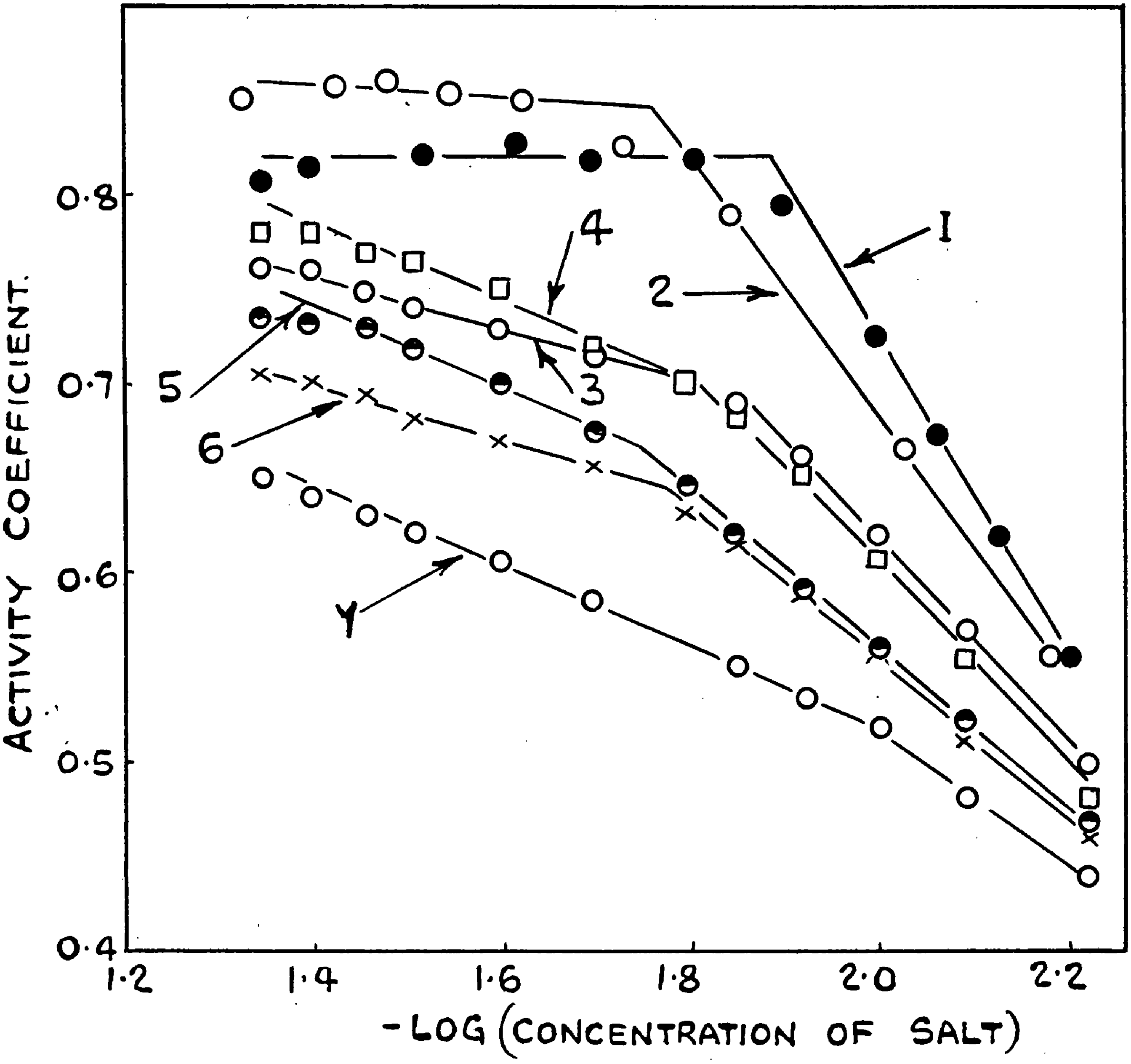


FIG. 34.

EFFECT OF SOME SODIUM SALTS ON THE ACTIVITY COEFFICIENT OF Br' IN ·0135 M C.T.A.B.

1. SALICYLATE
2. p-Cl BENZOATE
3. BENZOATE
4. p-NO$_2$ BENZOATE.
5. p-OH BENZOATE.
6. o-NO$_2$ BENZOATE.

Y. NITRATE.



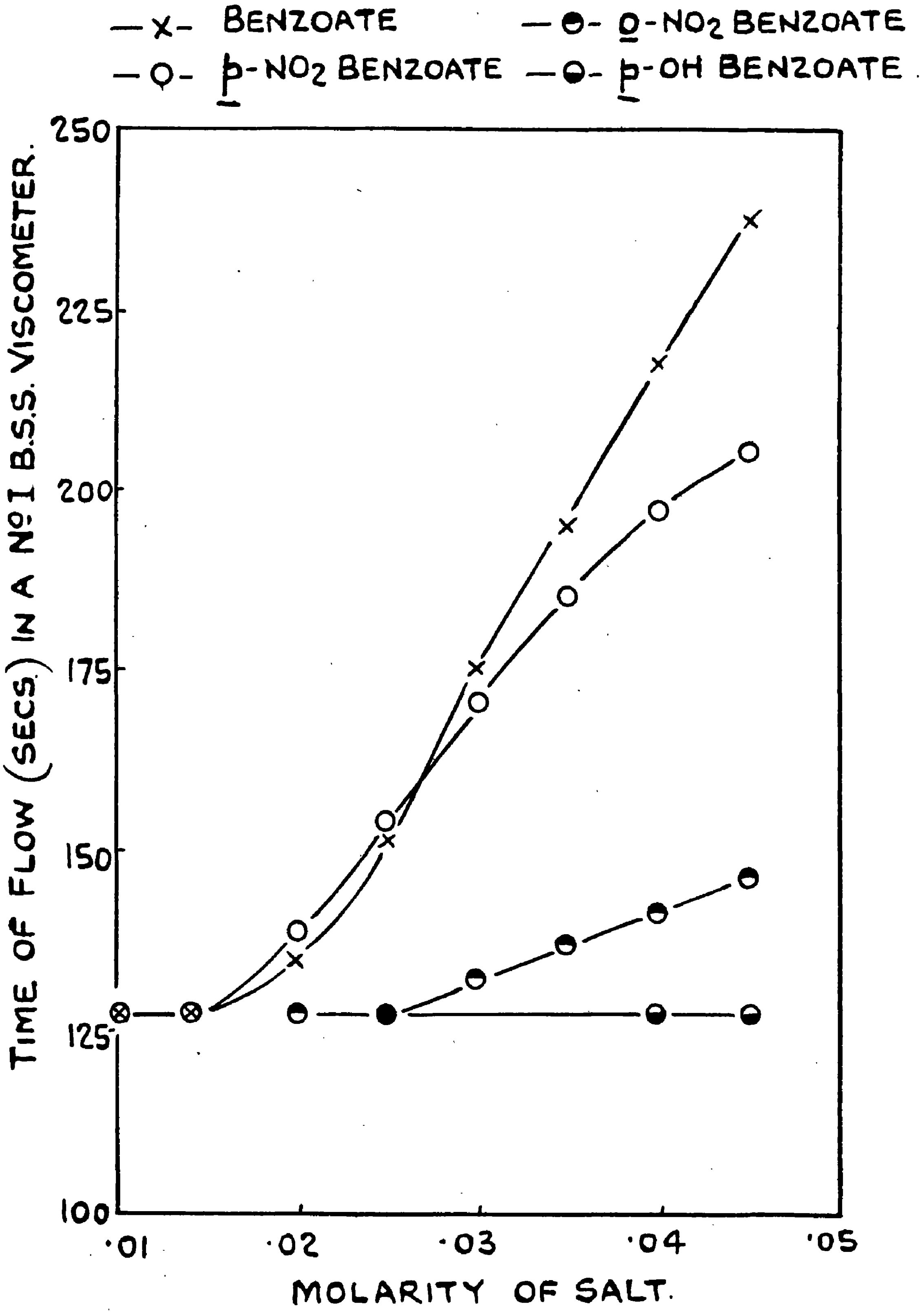
Na o-nitrobenzoate, Na p-nitrobenzoate, Na benzoate, Na p-chlorobenzoate, Na salicylate. There is also some indication that the concentration of additive at the 'break' decreased in the same order, although not every salt obeys this i.e. $NaNO_3$ or Na p-chlorobenzoate and, in any case, the effect is rather small.

(3) Just prior to the 'break' in the curves, the tendency of equimolecular amounts of the salts to increase the activity coefficient of the Br' decreases in the order given above i.e. the salts increase the activity of the Br' in the same order as they increase the viscosity of the solution. There is, however, no quantitative relation between these effects as figs. 26 and 35, in which viscosities at 25°C in No.2 and No.1 Ostwald viscometers respectively are plotted against concentrations, show. It is also worth noting that differences in the activity coefficient can be detected long before the solutions show viscosity effects.

FIG. 35.

VISCOSITY OF SOME C.T.A.B.-SALT MIXTURES AT 25°C

(MOLARITY OF C.T.A.B. IS ·0135 M IN EACH CASE)

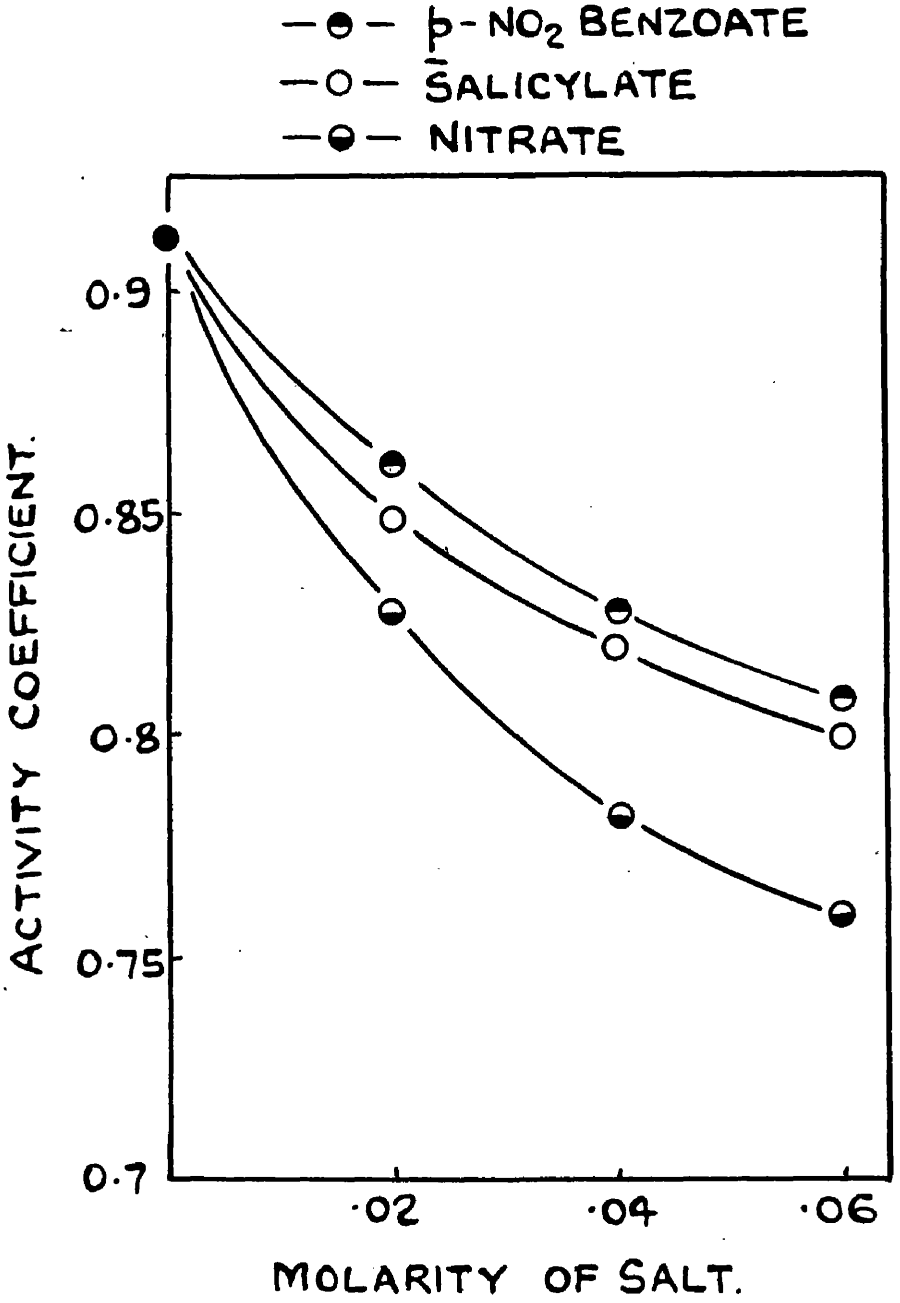


Effect of Na salicylate, Na p-nitrobenzoate and $NaNO_3$ on the Activity Coefficient of Br′ in KBr.

Fig. 36 shows the effect of additions of Na salicylate, Na *p*-nitrobenzoate and $NaNO_3$ on the activity coefficient of Br′ in .008M KBr. The decrease in the activity coefficient of the Br′ in these solutions contrasts with the increase in the activity coefficient of Br′ in CTAB solutions on addition of the same salts (fig.33).

FIG. 36.

EFFECT OF SOME SODIUM SALTS ON THE ACTIVITY COEFFICIENT OF Br' IN ·008 M KBr.

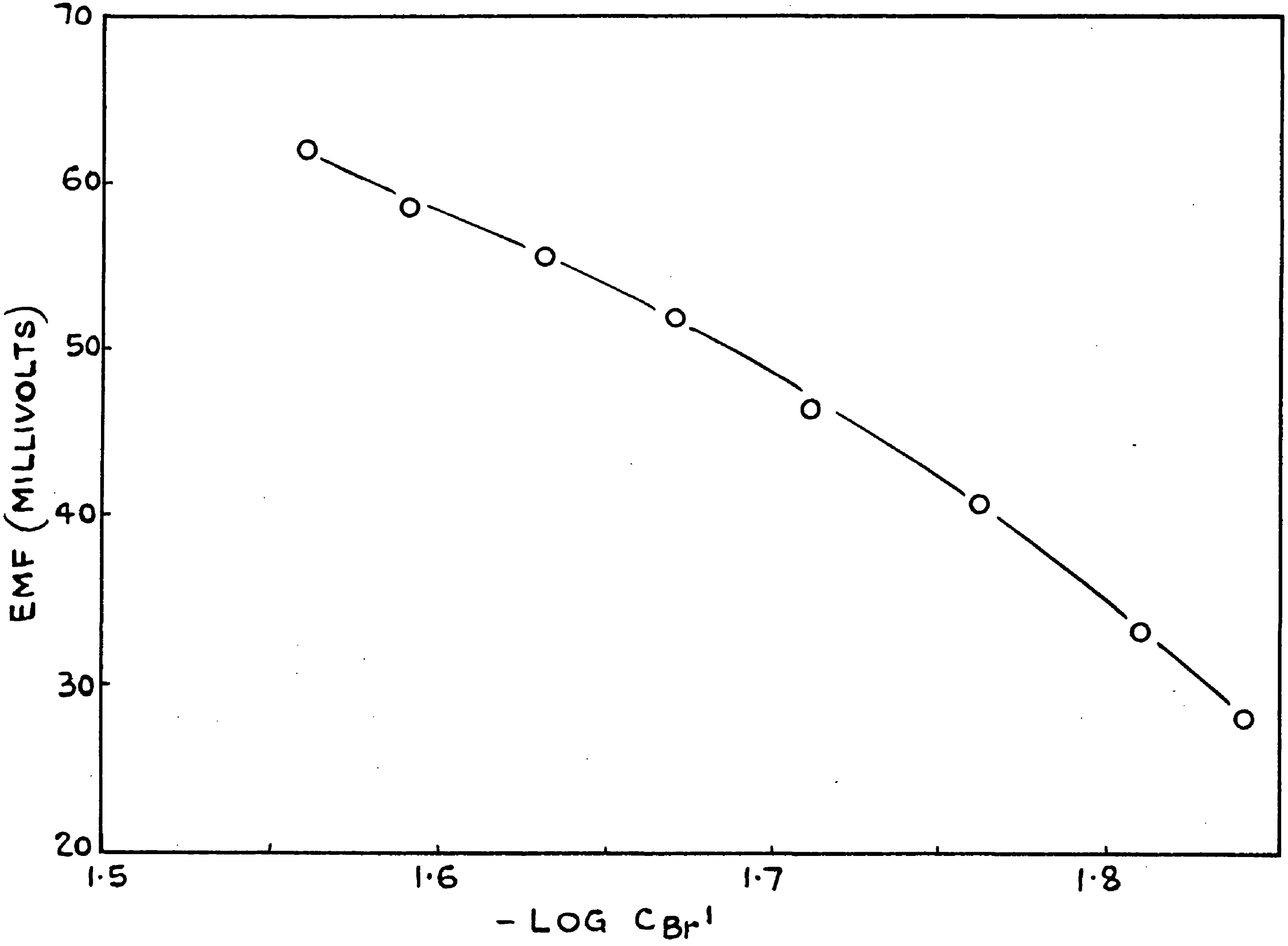


The Effect of KBr on .0135M CTAB Solution.

The emf's corresponding to a number of solutions containing different amounts of KBr in a constant amount of CTAB (.0135M), are plotted against - log $C_{Br'}$ (where $C_{Br'}$ is the total concentration of Br′ present) in fig.37.

If the CTAB behaved as a simple electrolyte a straight line would be anticipated. The slight curve which is actually obtained indicates that the rate at which the activity coefficient of Br′ decreases (with respect to concentration) in(CTAB + KBr) solutions is greater than the rate at which the activity coefficient of Br′ decreases in KBr solutions as the concentration of KBr is increased i.e. the CTAB micelle adsorbs a certain (though small) amount of KBr in (CTAB + KBr) solutions.

FIG. 37.



Discussion

The Validity of the Results.

The thermal Ag-AgBr electrode appears to adsorb CTA^+ and the adsorption affects the reversibility of the electrode. While the electrolytic Ag-AgBr electrode does not adsorb CTA^+ irreversibly, it is possible, although not particularly likely, that it might adsorb the CTA^+ reversibly i.e. amphipathically. While the activity coefficient of the Br' in CTAB (in the presence of .002M KBr) has been measured below the CMC of the CTAB, the results are rather unreliable owing to the small value of this CMC. It has, however, been established that DTAB behaves exactly as does KBr below its CMC and since the adsorption work of Corrin, Harkins _et al._[83] shows that a surface active agent adsorbs amphipathically below its CMC, it seems that, if the DTAB is amphipathically adsorbed on the electrode, the adsorption does not affect the electrode potential. We can thus be fairly certain that the electrode is responding only to changes in the bulk of the solution and not to changes, if any, in the surface layer of the electrode.

The more serious criticism of there being a liquid junction potential, large enough to affect the results, cannot strictly be refuted by the experimental results obtained. Where, however, comparison is possible with other work, as, for instance, the activity coefficient of Br' in CTAB solutions compared with the activity coefficient of sodium in sodium oleate[102], there is general agreement in the way the coefficient varies with concentration etc.

The Activity Coefficient of Br′ in CTAB-salt Solutions.

The effect of certain substituted benzoate salts on the activity coefficient of Br′ in CTAB solutions is, as has been pointed out on page 94, related to the effect of the same salts on the viscosity of CTAB solutions. It is therefore appropriate to inquire whether the first effect (referred to, for convenience, as the 'activity effect') throws any light on the second effect (the 'viscosity effect') or vice-versa.

The abrupt change in the rate at which the activity coefficient of the Br′ ion is altering with respect to concentration of salt (fig. 34) in a region near to the concentration of the CTA^+ itself, is a clear indication of a close association between the negative benzoate-type ion and the positive CTA^+. The more abrupt the change and the closer it lies to the concentration of the CTA^+, then the closer should be the association between the CTA^+ and the benzoate-type ion. While this could indicate either incorporation of the benzoate-type ion into the palisade layer of the micelle or strong external attachment to the CTA^+ on the surface of the micelle, it is the former view which will be adopted subsequently (particularly for salicylate and p-chlorobenzoate) as both viscosity work[77] and adsorption work

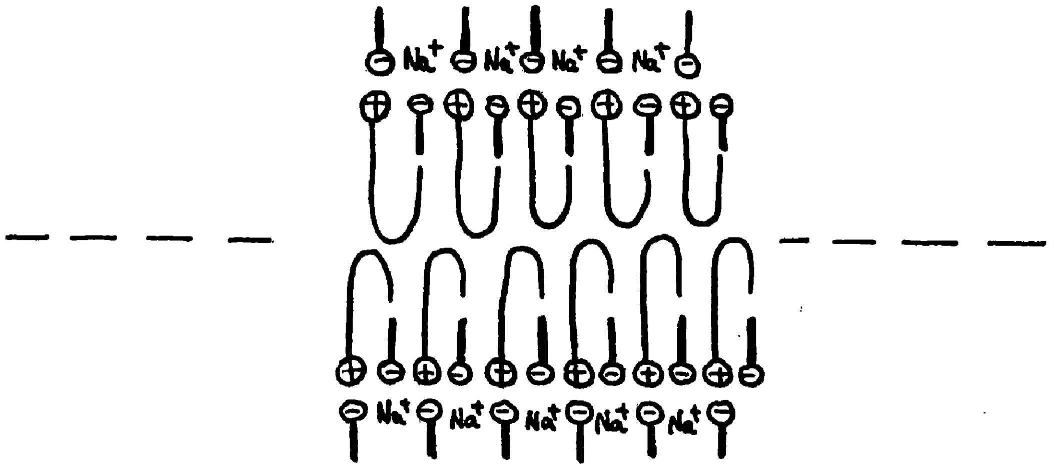
(Part I) have already indicated it. It is not suggested that p-hydroxybenzoate for example, which gives no viscosity effect, is incorporated into the micelle. It does, however, seem from fig.34 that the p-hydroxybenzoate ion is more strongly attached to the surface of the micelle than the nitrate ion.

Once this "solubilisation" of the salicylate or p-chlorobenzoate is accepted, the explanation of the activity effect is as follows. Examining first the system .0135M CTAB with additions of sodium salicylate, it can be seen from fig. 33 that at a concentration of salicylate of .002M (perhaps even less) the effect of this additive in increasing the activity coefficient is distinctly greater than that of the others e.g. nitrate or p-hydroxybenzoate. This indicates that the salicylate ion is already more powerfully solubilised than the other additives, presumably because of the peculiar interaction which it seems to be necessary to assume operates in the CTA^+-salicylate micelle[77]. Now since the 'break' in fig. 34 for salicylate occurs at about .0130M i.e. close to the concentration of CTA^+ present, it may be assumed that below this concentration, virtually all the salicylate is solubilised into the micelle. Thus at the concentration of.002M where where is only salicylate ion to about seven CTA^+ ions, the interaction which seems to be responsible for the formation of enormous CTA^+- salicylate aggregates, is already operating. The importance of this is that it seems to indicate that this interaction is, at least partly, between the CTA^+ and the salicylate. This tends to discredit any theory which suggests that the stability of the CTA^+- salicylate micelle is due to hydrogen bonds between salicylate ions.

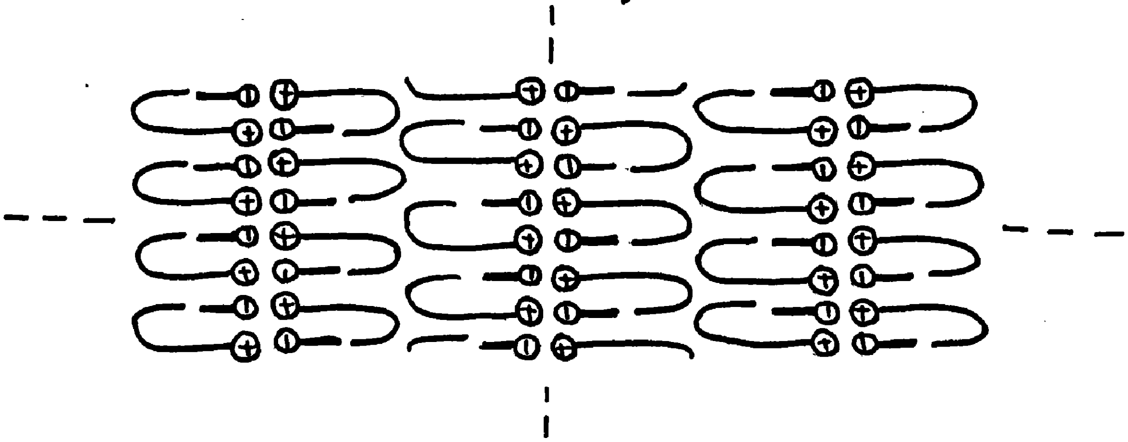
Once the amount of salicylate has reached approximately the concentration of CTA^+, the activity coefficient of the Br' is about 0.82. Since the activity coefficient of the Br' in .0135M NaBr is about 0.89, it would seem that the CTA^+ - salicylate complex behaves somewhat like a weakly dissociated salt. As the concentration of the salicylate is further increased to .045M, the activity coefficient of the Br' drops from 0.82 to only 0.81, while for a similar addition of sodium salicylate to NaBr it would be expected to drop from 0.89 to 0.83. This phenomenon will be discussed at greater length in the case of p-chlorobenzoate in CTAB which will be discussed next.

Sodium p-chlorobenzoate behaves somewhat similarly to sodium salicylate at concentrations up to about .010M. Thereafter the most significant difference is that the activity coefficient of the Br' reaches a rather higher value, 0.86 at a concentration of 0.033 M. Now the activity coefficient of Br' in .0135M NaBr plus .0195M sodium p-chlorobenzoate i.e. (.033-.0135) should be about 0.85 which means that a negative amount of Br' is attached to the CTA^+ - p-chlorobenzoate micelle - an impossibility.

The high activity coefficients of Br′ in these CTAB - sodium p-chlorobenzoate solutions (and to a lesser extent CTAB - sodium salicylate solutions) may be explained by two effects. First there must be a considerable amount of p-chlorobenzoate ion attached to the surface of the CTA$^+$ - p-chlorobenzoate micelle, represented diagrammatically thus,



and second, the CTA$^+$ - p-chlorobenzoate micelle may tend to behave as a neutral colloid thus,



The first of these possibilities might be expected to occur since it appears that these benzoate-type ions are more strongly attached to the surface of CTA$^+$ micelles than are the ions of a simple electrolyte e.g. NaBr (see page 100). If an 'ideal' micelle were formed, such as that shown, the free *p*-chlorobenzoate would be, for the concentration considered here, only .006M (i.e. .033 - 2 x .0135). The activity coefficient of Br' in .0135M NaBr plus .006M sodium *p*-chlorobenzoate would be about 0.89, so that a certain amount of Br' would be attached to the surface of the CTA^+- *p*-chlorobenzoate micelle, a condition which would be expected in such a system as is considered here.

The second possibility has been introduced here because it gives rise to a possible explanation of the cross-linkages which it would seem to be necessary to assume exist in such a visco-elastic solution as that formed between CTAB and sodium *p*-chlorobenzoate. The model shown above is clearly capable of extension in three dimensions. The first type of micelle would not be expected to give rise to visco-elastic solutions since the diffuse layer of ions on its surface would prevent any cohesion between separate aggregates.

Some supports for this second type of micelle are

(1) There is some reason for believing that the CTA^+ - *p*-chlorobenzoate system is more elastic than the CTA^+ - salicylate system. Thus the time of flow of these *p*-chlorobenzoate - CTAB solutions through a viscometer is very much greater than the time of flow for comparable salicylate - CTAB solutions (fig.26). Although the rheological properties of these visco-elastic solutions are

extremely complex, it is not at all improbable that the time of flow through a viscometer is closely connected with the length of the polymer chains and the amount of cross-linking in these solutions, particularly at low rates of shear. Furthermore, the p-chlorobenzoate - CTAB solutions give an impression of being more elastic than salicylate - CTAB solutions. Thus, after being gently disturbed, a p-chlorobenzoate-CTAB solution, in a half full 100 c.c. graduated flask, will oscillate some 15 times while a comparable salicylate - CTAB solution will only oscillate two or three times.

(2) The activity of the Br' in CTA^+ - p-chlorobenzoate solutions reaches its maximum value in the region of the maximum in the time of flow through the viscometer. This is also true for salicylate - CTAB solutions in the sense that a maximum time of flow seems to occur at the actual concentration of the CTA^+ itself i.e. .0135M while this is also the concentration of salicylate just necessary to raise the activity coefficient of the Br' to its maximum value. The maximum in the activity coefficient might thus be ascribed to almost neutral colloid being at its least ionised.

(3) Unless a certain amount of neutral colloid is postulated, there will be large areas of positive and negative changes, macroscopically neutral, but microscopically centres for the attraction of the excess salts in these visco-elastic solutions.

It is not easy to see why these localised charges should not attract considerable amounts of Br' leading to lower activity coefficients than are actually observed.

It is probable that an equilibrium exists between these two types of micelles (andpossibly others) in visco-elastic solutions of the type studied here.

The other additives lie between the p-chlorobenzoate and the salicylate on the one hand, and the nitrate on the other, in their activity effects as indeed they do in their viscosity effects. Their behaviour may be described by attributing two characteristics to them namely, strong attachment to the micelle surface and incorporation into the palisade layer of the micelle. Such salts as benzoate, p-nitrobenzoate and o-nitrobenzoate may be expected to show both these characteristics, the o-nitrobenzoate being incorporated into the micelle to a lesser extent than the other two. The p-hydroxybenzoate may be expected to only show strong attachment to the micelle surface.

PART III.

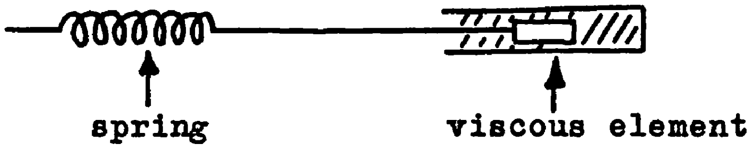
Some Visco-Elastic Properties of CTAB - Sodium Salicylate and CTAB - *p*-Chlorobenzoate Solutions,

INTRODUCTION

The classical treatment of visco-elasticity dates from the time of Maxwell who described a simple type of visco-elastic behaviour by means of the equation

$$\frac{dS}{dt} = n\frac{d\sigma}{dt} - \frac{S}{t_r}$$

where S is a component of stress, n is the coefficient of elasticity, σ is a component of strain and t_r is the relaxation time of the system. A mechanical model which obeys this equation is a spring and dashpot coupled in series thus



the elastic constant of the spring is n while the viscosity of the viscous element is nt_r. The behaviour of the visco-elastic material is thus divided up into a viscous and an elastic element. Most visco-elastic materials do not obey this equation and in order to obtain equations which do describe their mechanical properties it is necessary to use generalised models consisting of numerous spring and dashpot systems coupled in series or parallel. The properties of the generalised Maxwell model, in which the systems are arranged in parallel, are described by the equation

$$\frac{dS(t_r)}{dt} = n(t_r) \cdot \frac{d\sigma}{dt} - \frac{S(t_r)}{t_r}$$

$$S = \int_0^\infty S(t_r)dt_r$$

where $S(t_r)$ are partial stresses associated with the relaxation time t_r and $n(t_r)dt_r$ is the contribution to the modulus of the Maxwell elements whose relaxation times lie between t_r and $(t_r + dt_r)$.

By use of arbitrary values of $n(t_r)$, the distribution of relaxation times, it has been possible to describe certain types of visco-elastic behaviour[110,111]. Other models have been used to describe systems which show complex phenomena such as creep. The great disadvantage, however, in using these models to describe visco-elastic systems has been clearly summed up by Scott-Blair[112] - "it does not follow that because a complex material shows a simple exponential behaviour, such as would be predicted from a model of a few springs and viscous elements, that such a model in any way represents its structure".

Attempts have been made by Lodge, Tobolsky and others[113,114,115] to extend the kinetic theory of rubberlike elasticity to the more complicated problem of visco-elasticity. A true rubber is believed to contain flexible linear polymer chains linked together by chemical cross-bonds. While the crosslinkages must be sufficient to unite the polymer chains into a gigantic network, they must not be so extensive that there are not a sufficient number of flexible chains between the cross-links. Tobolsky then considers the visco-elastic liquid to consist of a network structure in which the cross-linkages are continually breaking and reforming.

Pilpel[76] has shown that the mechanical properties of a visco-elastic soap solution (potassium oleate, oleyl alcohol, potassium carbonate, water) are similar to those of polymethyl methacrylate dissolved in toluene and to aluminium laurate in petrol. He believes that the mechanical properties of such solutions may eventually be explained in terms of the molecular or micellar networks which they are generally believed to consist of and has shown[116] that when individual soap molecules aggregate into long threadlike micelles, there is a decrease in the free energy of the system.

Other work on the visco-elastic properties of soap solutions by Hatschek and Jane[71], Andrade and Lewis[72], Hartley[73], Bungenberg de Jong[74,75] and Winsor[65] has been noted in the general introduction.

The actual measurement of the elastic properties of visco-elastic materials generally involves the application of some kind of sinusoidal stress. Thus Freundlich and Seifriz[117] suspended a small nickel particle in the material being examined and deflected it by means of an electromagnet, Bingham and

Robertson[118] applied oscillating forces to the end of a capillary tube in which the liquid was contained and Ferry[119] set up vibrations in a gel by means of a vibrating glass plate.

A type of Couette viscometer is also used to measure elastic properties, the outer cylinder being caused to oscillate while the deflection of the inner one is recorded. Toms and Strawbridge[120] have used such an instrument to investigate the visco-elastic properties of polymethyl methacrylate in various organic solvents e.g. pyridine. The visco-elastic effect is divided into an elastic and a viscous effect. Two relaxation times are used, the first a stress relaxation time, the second a rate of strain relaxation time. An attempt is made to relate the relaxation times to solutions whose properties are attributed to the ever-changing 'entanglement - cohesions' of long chain molecules.

Experimental.

Visco-elastic Solutions in a Freely Oscillating Cylinder.

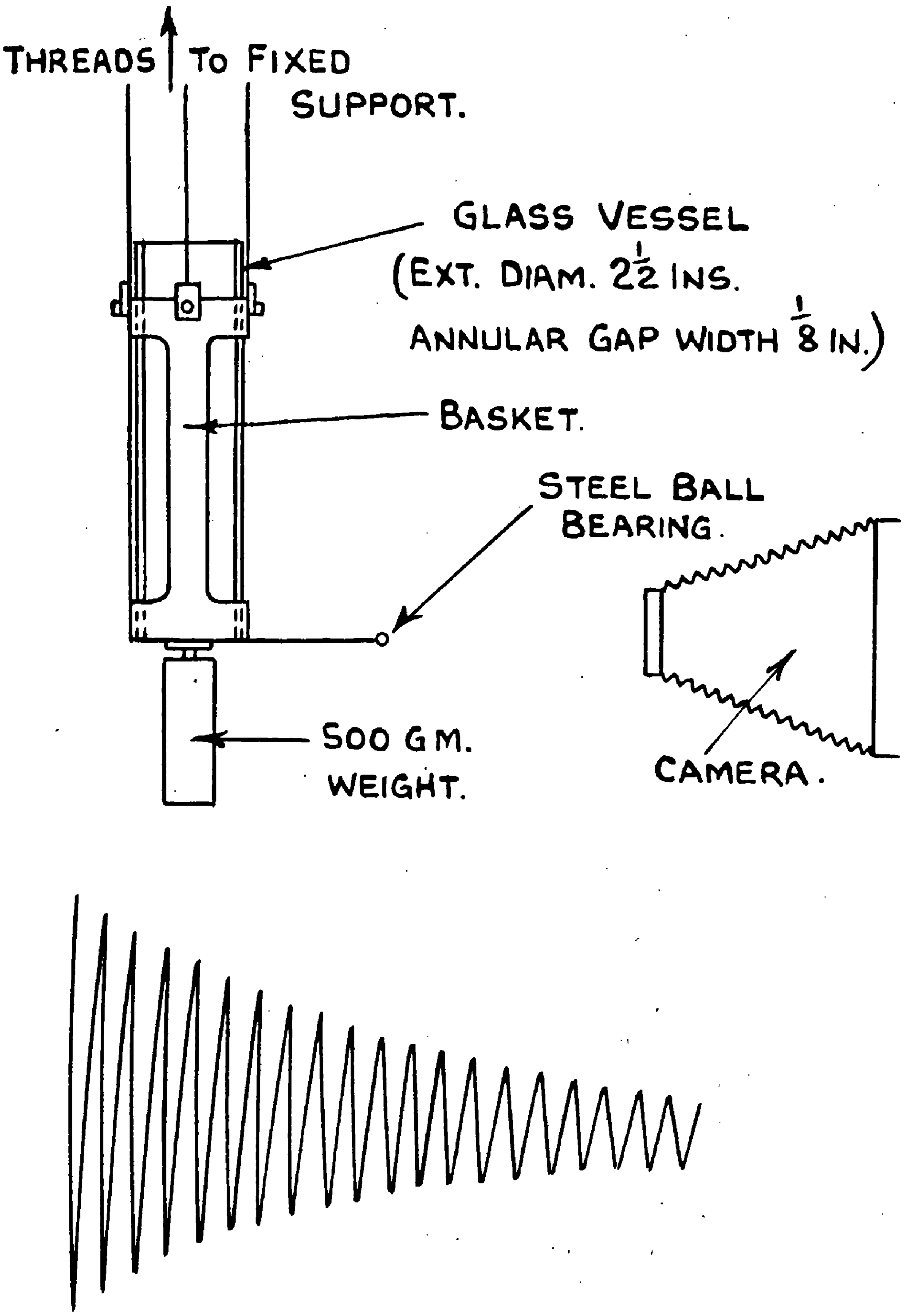
Apparatus (Fig.38)

A glass vessel, consisting of two cylinders of different diameters sealed at one end, contained the liquid to be investigated. This vessel had been taken from a Dewar flask and its annular gap made as uniform as possible by heating its sealed end until the glass was pliable. The glass vessel was contained in a brass basket which had been suspended by means of three vertical threads from a fixed support. The support could be momentarily twisted in order to set the apparatus oscillating. A series of seven brass weights, of the same weight but different shapes, could be screwed into the bottom of the brass basket to alter the period of its oscillation. The oscillation of a small steel ball, fixed at the end of a rod projecting from the bottom of the brass basket, was recorded by means of a camera with photographic paper rotating on a drum at constant speed.

Procedure

The glass vessel, filled to a mark with the liquid under examination, was placed in the brass basket. On twisting the support, oscillation began and the constant speed drum of the camera was started as soon after this as possible. The shutter of the camera was then opened for a measured period of time

FIG. 38.



A TYPICAL TRACE.

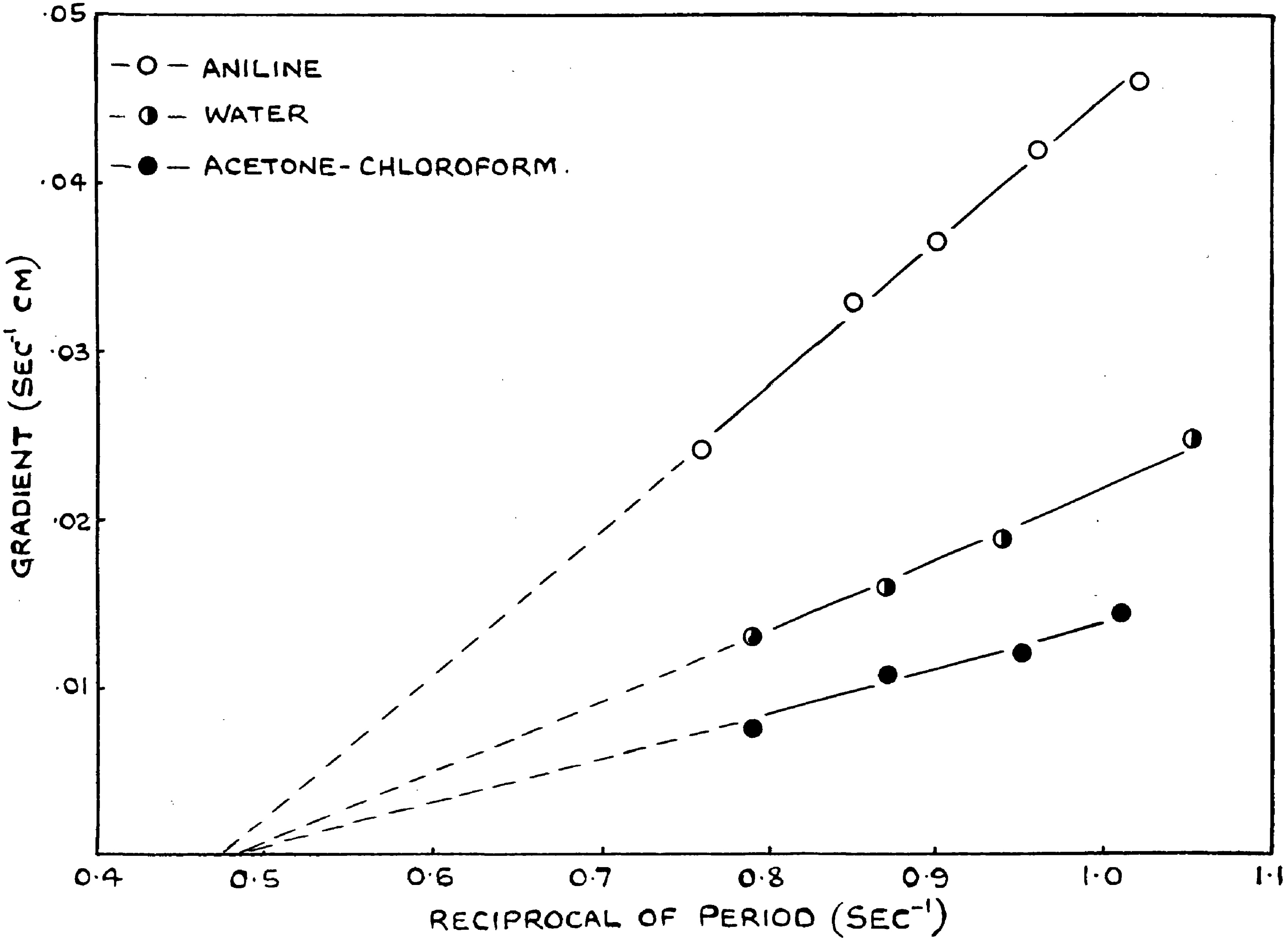
depending on how long the oscillations were taking to dampen to a small value. This procedure was repeated with the other weights. The camera was then taken into a dark room and the photographic roll of paper was removed, developed, fixed, washed and finally hung up to dry.

Results.

A typical trace is shown in fig.38. Since the time to obtain this trace had been measured and the total number of oscillations could be read off from it, the period of the oscillation could be found. Furthermore, it was found, for this type of trace, that the logarithm of the amplitude of the oscillation at a time t, after the beginning of the observation, was proportional to t. It was thus possible to obtain two constants, i.e. the gradient of the logarithm of the amplitude plotted against t, and the reciprocal of the period, for each weight.

In fig.39 these constants are plotted against one another, for different weights, for three Newtonian liquids of different viscosities - acetone-chloroform, water and aniline in order of increasing viscosity. Three apparently straight lines are obtained which, on extrapolation, intersect at the same point on the period axis. This suggests that there is a certain weight for which there is no damping when an ordinary Newtonian liquid is used. It was believed that if this weight could be

FIG. 39.

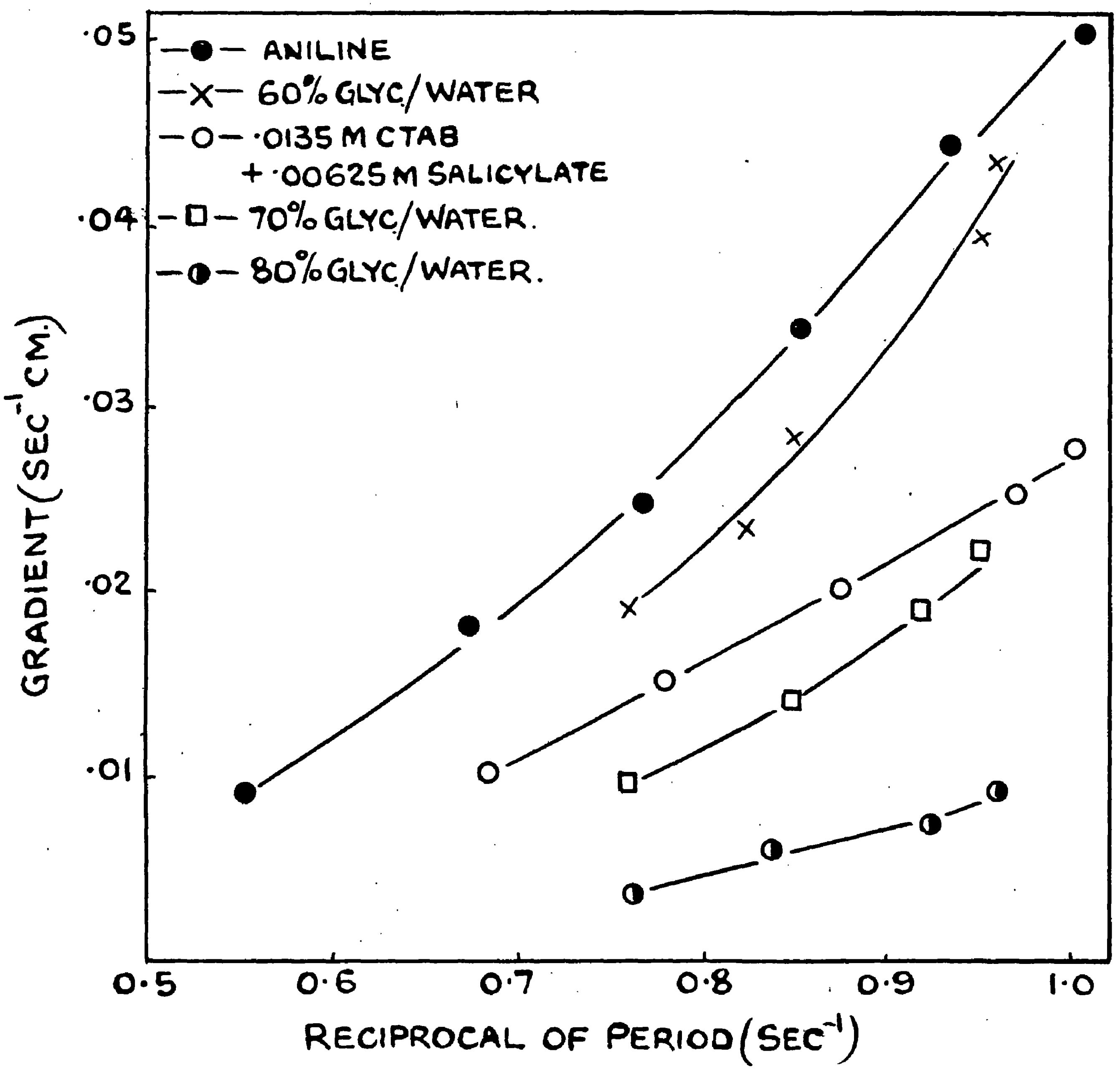


–○– ANILINE
–◑– WATER
–●– ACETONE-CHLOROFORM.
·05
·04
·03
·02
·01
GRADIENT (SEC⁻¹ CM)
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1·1
RECIPROCAL OF PERIOD (SEC⁻¹)

found, a visco-elastic liquid might give a damping effect where the Newtonian liquid would not and that this damping might be related to the elasticity of the visco-elastic liquid. Consequently two more weights were designed to give longer periods and fig.40 shows the results for aniline obtained by use of these weights as well as the others already in use. The 'straight' line now appears as a curve which may well approach the origin tangentially. This is, perhaps, more in line with theory, since the damping observed in practice is due to the decay of strain under finite stress in the viscous (Newtonian)liquid (or, in another way, to the inability of the viscous liquid to store potential energy under stress). The damping therefore will only disappear when the stress is zero i.e. when the cylinder is oscillating infinitely slowly. It is thus probable that the 'certain' weight mentioned above is a very thin disc of infinite diameter.

Also shown in fig.40 are other curves for various mixtures of glycerine and water - all more viscous than aniline - and a curve for .00625M sodium salicylate in .0135M CTAB - a visco-elastic solution. It is apparent that the damping effect goes through a maximum as the viscosity is increased. Measurements of the viscosity of the visco-elastic solution in an Ostwald viscometer showed that it lay between the viscosities of 60% and 70%

FIG. 40.



·05
·04
·03
·02
·01
0·5
0·6
0·7
0·8
0·9
1·0
GRADIENT (SEC⁻¹ CM.)
RECIPROCAL OF PERIOD (SEC⁻¹)
—●— ANILINE
—X— 60% GLYC/WATER
—O— ·0135 M CTAB + ·00625 M SALICYLATE
—□— 70% GLYC/WATER.
—◐— 80% GLYC/WATER.

glycerine-water mixtures, just as its damping effect lies between those for these two solutions,- owing to the very large variation in the viscosity readings, at 20°C, for this visco-elastic solution due to its inhomogeneity (see page 52), any more quantitative statement is unreliable. The damping curve for the visco-elastic solution is similar in shape to the other curves except for a slight difference at lower periods. There is thus no real indication of elasticity in this type of experiment and it became apparent that the period of oscillation was far too high to allow the elastic effects to come into play. Rather than attempt difficult and cumbersome modifications to the existing apparatus, it was decided to achieve higher frequencies by subjecting the visco-elastic liquid to a forced oscillation.

Visco-elastic Solutions Under Forced Oscillations.

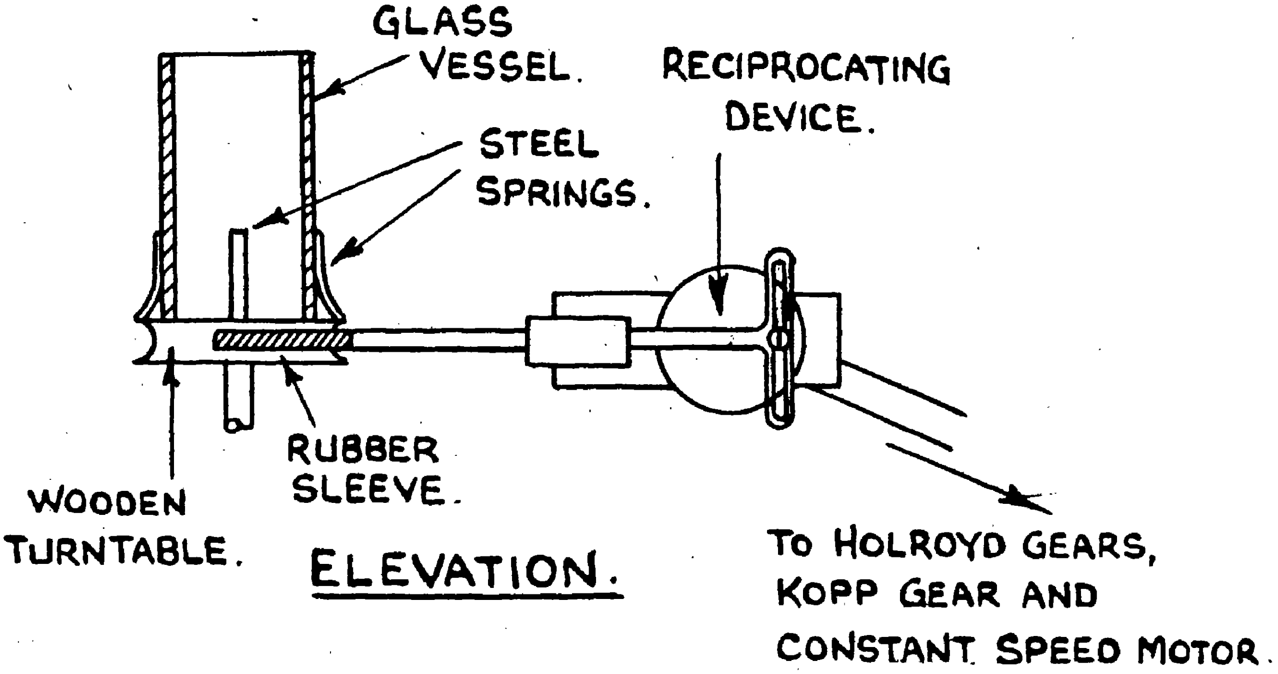
Apparatus (Fig.41)

A glass vessel, similar to that used previously (fig.38) save that it was 4 in. high, was fixed centrally onto a wooden disc by means of four steel springs. In order to observe the motion of the liquid in the annular gap, a small metal ball was suspended, from a hook at the top of the vessel, by means of a very fine thread. This ball was made by dipping fine platinum wire into molten solder and catching a very small piece of the solder on the tip of the wire. A gentle heating produced a small bright sphere of metal of diameter 0.6 mm. The platinum wire was cut off close to the ball leaving just enough wire to tie on the fine thread.

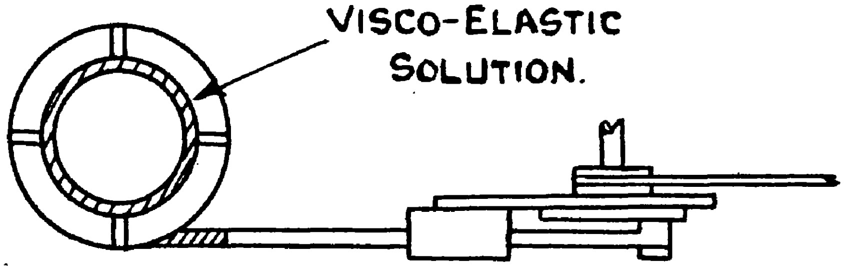
The wooden disc was oscillated by the friction drive of the piston of a reciprocating device which could be so altered as to give a range of six amplitudes. The reciprocating device was, in turn, driven by two Holyroyd reduction gears, used separately, a Kopp gear capable of a continuously variable, ninefold, change in speed and a constant speed induction motor.

The glass vessel and supports were contained in an air thermostat at (25 ± .2)°C. The motion of the metal ball was observed through a travelling microscope.

FIG. 41.



ELEVATION.



PLAN.

Procedure.

The solutions to be studied were kept in a water thermostat at 25°C until ready for use. Many of these visco-elastic solutions had been previously heated to 60°C to ensure as much homogeneity as possible. When the appropriate solution had been poured into the annular gap, the metal ball was lowered, or pushed into position depending on the visco-elasticity of the liquid. In many cases, the thread was not fully stretched, but this had no influence on the results, provided that the thread was prevented from clinging to the vertical glass walls.

The motor was then started and the Kopp gear adjusted to give a suitable oscillation. The amplitude of the ball was measured by observing it at the extremities of its oscillation by means of the travelling microscope. The frequency of the oscillation was obtained by counting the number of revolutions of the wheel of the reciprocating device in a measured time. The frequency of the oscillation was then increased and the amplitude and period of the bead measured. The results are then obtained for each solution as a graph of the ratio, ϕ, of the amplitude of the bead's oscillation to the amplitude of oscillation of the annular vessel, plotted against the frequency of the oscillation. The amplitude of oscillation of the annular vessel was the smallest the apparatus was capable of, its value being 0.28 radians.

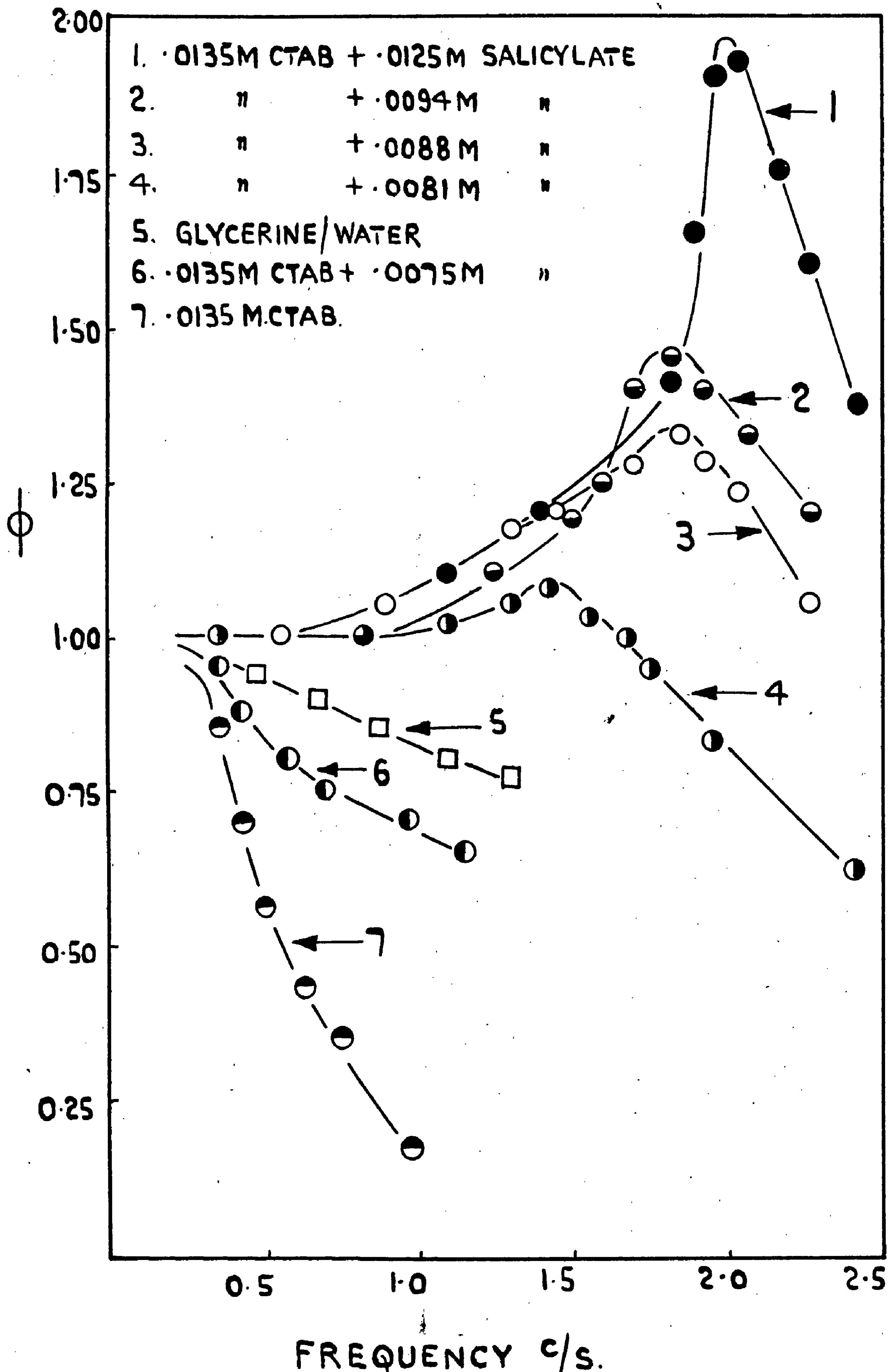
Results.

Sodium Salicylate -CTAB Solutions

All soap solutions studied in this work contained .0135M CTAB. The results obtained with solutions containing different amounts of salicylate are shown in figs.42, 43 and 44, it being necessary to separate these graphs due to the similarity of some of them. Fig.42 also shows the behaviour of two Newtonian liquids i.e. .0135M CTAB which has the same viscosity as water and a glycerine-water mixture some fifteen times more viscous than water. There is a steady decrease in the amplitude of the bead as the frequency of the oscillation is increased but this decrease is less as the viscosity of the liquid increases. A Newtonian liquid of very high viscosity would be expected to give an almost horizontal straight line.

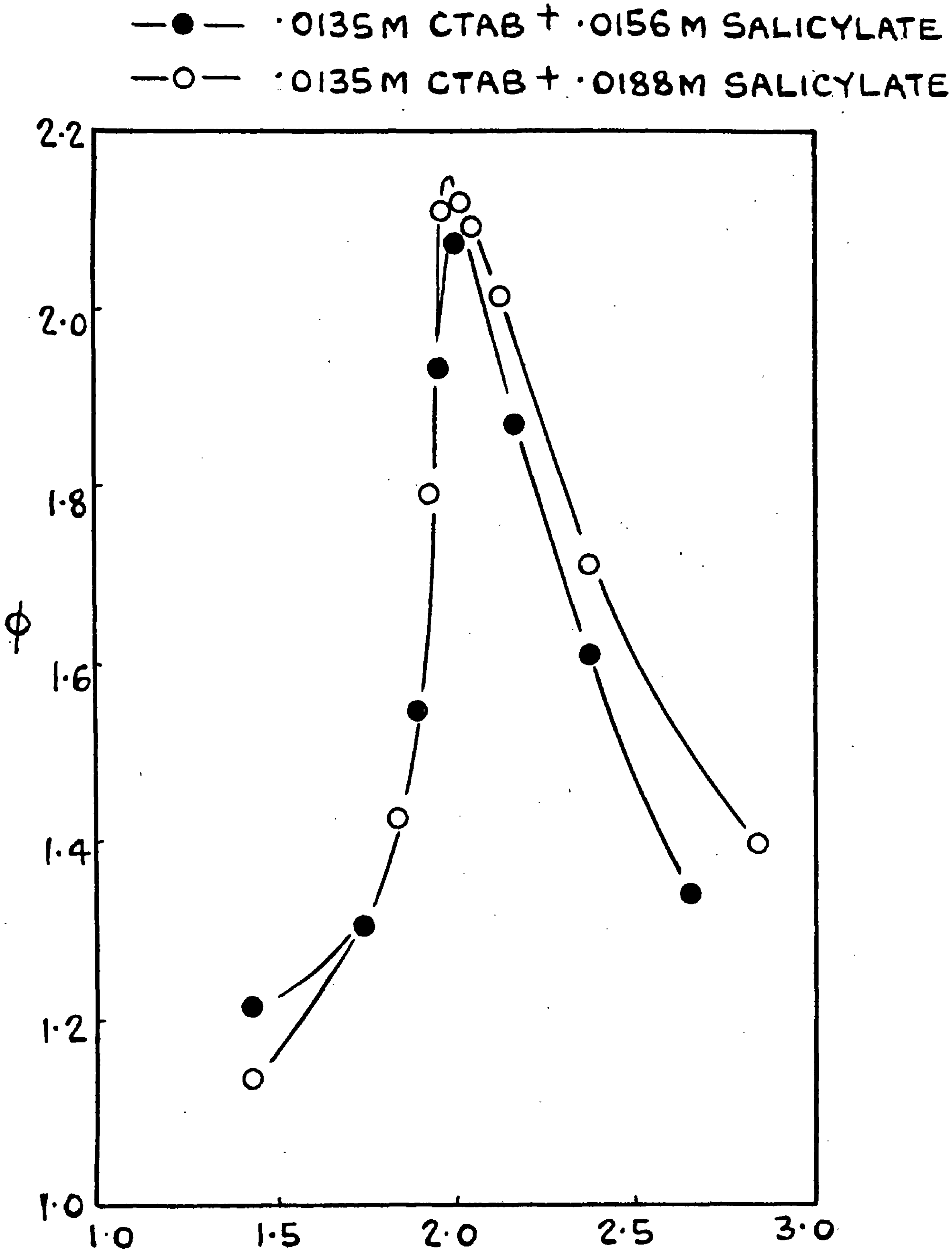
The .0135M CTAB, .0075M salicylate solution appears to behave in the same way as the glycerine-water mixture even although it possesses elastic properties easily detected by the 'elastic recoil' of bubbles. Indeed this recoil effect can be detected in solutions as dilute as .0135M CTAB, .0040 M salicylate. It thus seems that these visco-elastic solutions behave like viscous Newtonian liquids in this apparatus until a certain degree of elasticity has been attained although it is possible that a

FIG. 42.



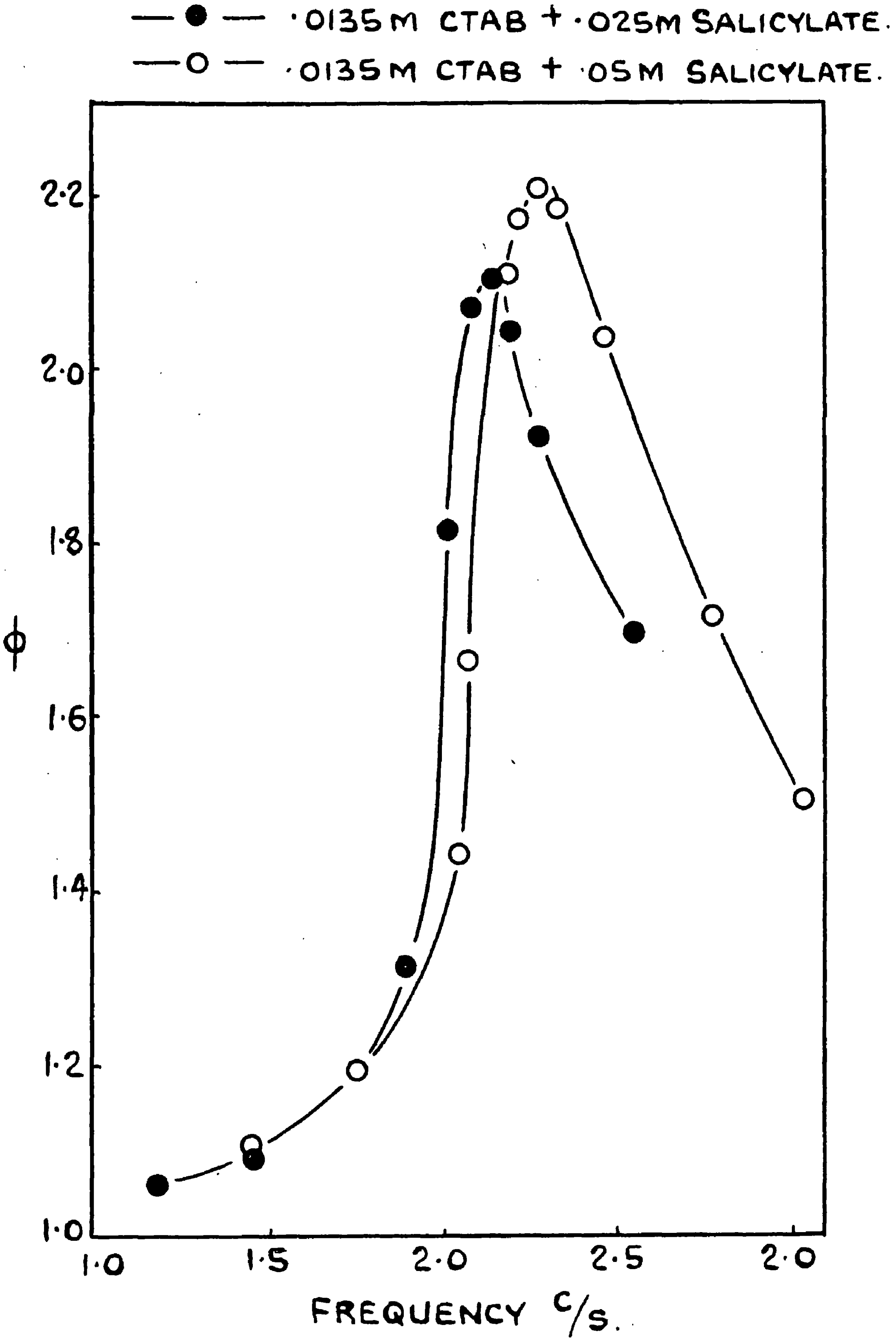
1. ·0135M CTAB + ·0125M SALICYLATE
2. " + ·0094M "
3. " + ·0088M "
4. " + ·0081M "
5. GLYCERINE/WATER
6. ·0135M CTAB + ·0075M "
7. ·0135 M.CTAB.
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
φ
0·5
1·0
1·5
2·0
2·5
FREQUENCY c/s.
1
2
3
4
5
6
7

FIG. 43.



—●— ·0135 M CTAB + ·0156 M SALICYLATE
—○— ·0135 M CTAB + ·0188 M SALICYLATE
φ
2·2
2·0
1·8
1·6
1·4
1·2
1·0
1·0
1·5
2·0
2·5
3·0
FREQUENCY C/S.

FIG. 44.



—●— ·0135M CTAB + ·025M SALICYLATE.
—○— ·0135M CTAB + ·05M SALICYLATE.
2·2
2·0
1·8
1·6
1·4
1·2
1·0
φ
1·0
1·5
2·0
2·5
2·0
FREQUENCY c/s.

more sensitive instrument could detect differences in behaviour before this. Once the elasticity becomes really established, pronounced maxima are obtained which are analogous to those observed when a model consisting of springs and dashpots, e.g. Maxwell's model, is subjected to a forced oscillation.

The two most significant features of these results are

(i) After a concentration of about .0125M salicylate has been reached, there is very little difference between the curves over a considerable change of salicylate concentration. This possibly indicates that the structure of the solution alters very little compared to the changes which occur before this concentration has been reached.

(ii) The asymmetric nature of the peaks of the curves for the more concentrated solutions. A likely explanation of this was found during the study of p-chlorobenzoate - CTAB solutions.

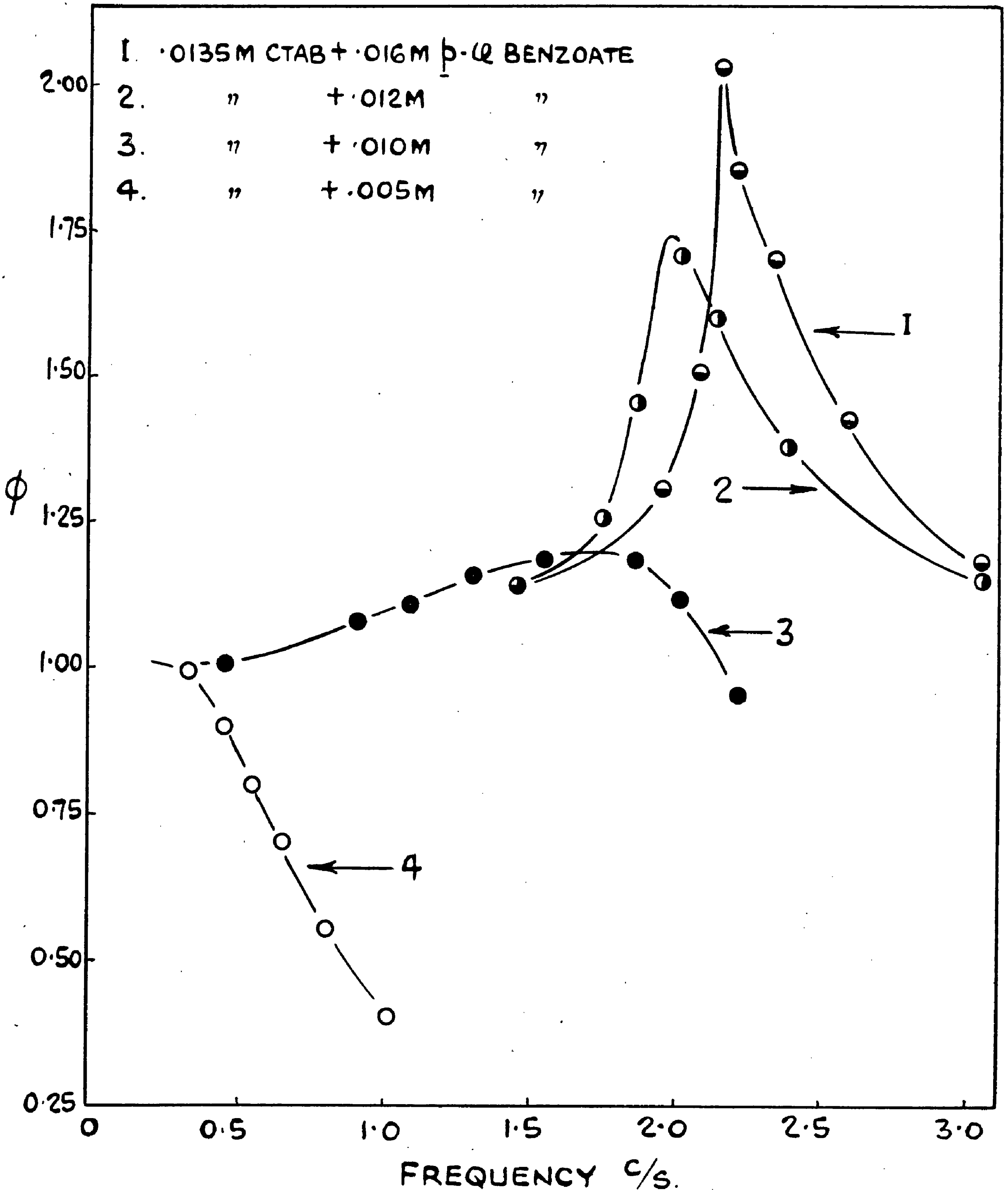
Sodium p-Chlorobenzoate - CTAB Solutions.

The results obtained with various concentrations of p-chlorobenzoate in .0135M CTAB are shown in figs. 45, 46 and 47.

These results are very similar to those found for salicylate-CTAB solutions save that the p-chlorobenzoate - CTAB solutions show maximum structural effects at concentrations which are noticeably higher than for salicylate - CTAB solutions - a result also shown, at any rate qualitatively, by viscosity measurements (fig.26).

The p-chlorobenzoate solutions, however, show a peculiar phenomenon which only appears to be shown in very slight degree by salicylate - CTAB solutions. As the frequency of the oscillation is increased there comes a point at which a slight increase in the frequency produces a very large increase in the amplitude of oscillation of the bead. This increase does not, however, entirely occur immediately the frequency of the oscillation is increased and, in fact, the amplitude of oscillation of the bead only reaches a constant value again, in many cases, one or two minutes after this increase in frequency is made. It may be that this effect is due to an alteration in the structure of the liquid as the frequency of the oscillation is changed. It is likely that the asymmetric shape of the peaks of all the curves for the more concentrated solutions, is connected with this phenomenon and, indeed, a comparison of

FIG 45.



I. ·0135M CTAB + ·016M p-Cl BENZOATE
2. " + ·012M "
3. " + ·010M "
4. " + ·005M "
2·00
1·75
1·50
1·25
1·00
0·75
0·50
0·25
φ
0
0·5
1·0
1·5
2·0
2·5
3·0
FREQUENCY c/s.
I
2
3
4

FIG. 46.

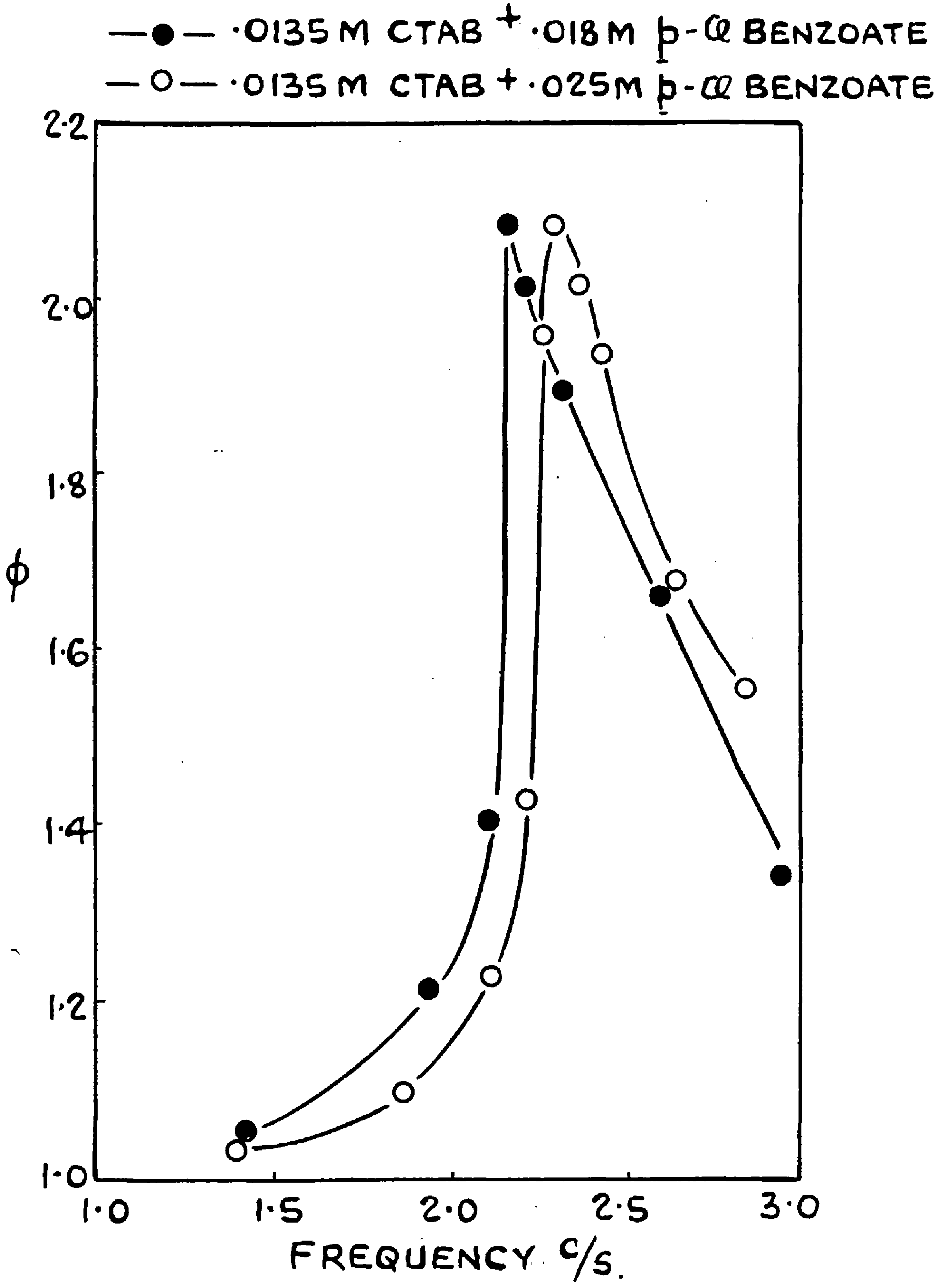
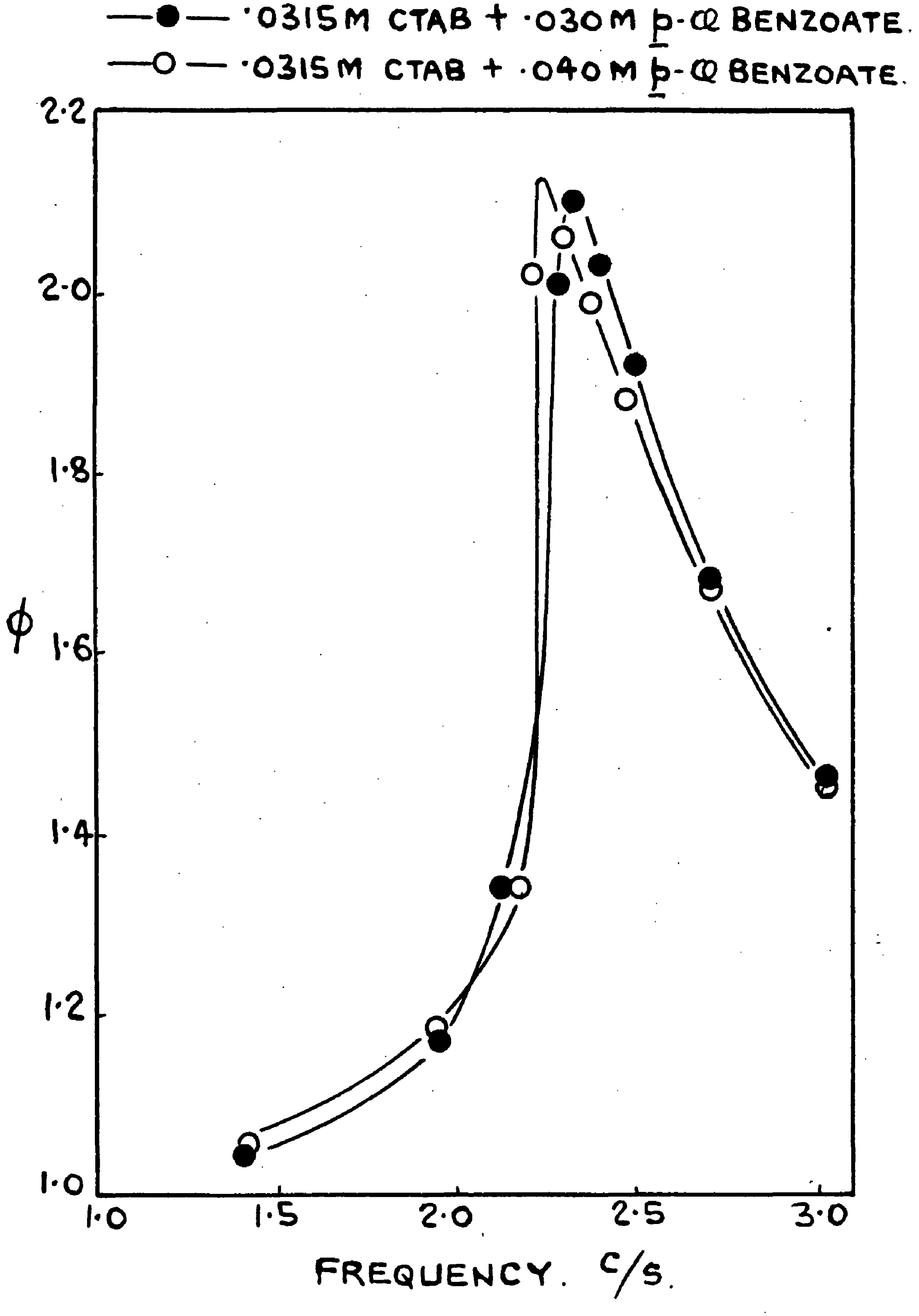

—●— ·0135 M CTAB + ·018 M p-Cl BENZOATE
—○— ·0135 M CTAB + ·025 M p-Cl BENZOATE
φ
2·2
2·0
1·8
1·6
1·4
1·2
1·0
1·0
1·5
2·0
2·5
3·0
FREQUENCY c/s.

FIG. 47.



—●— ·0315 M CTAB + ·030 M p-Cl BENZOATE.
—○— ·0315 M CTAB + ·040 M p-Cl BENZOATE.
2·2
2·0
1·8
ϕ
1·6
1·4
1·2
1·0
1·0
1·5
2·0
2·5
3·0
FREQUENCY. c/s.

curves obtained for *p*-chlorobenzoate - CTAB solutions with those obtained for salicylate - CTAB solutions shows that the shapes of the former are more asymmetric than those of the latter.

The gradual breakdown, when the stress is removed, of the structure formed when the applied frequency gives a maximum amplitude of oscillation of the liquid, can easily be demonstrated by suddenly reducing the frequency from this value to a very low value. The liquid continues to oscillate with a considerable amplitude but gradually this amplitude dies away until a steady value is reached. This is not an ordinary damping effect since it is not observed with CTA^+ - salicylate solutions.

When one of these visco-elastic solutions is poured from the glass vessel immediately after an oscillating experiment, it appears, to the eye, to behave in a different way from a solution poured from the same vessel but without any mechanical treatment. It is not easy to define just what the difference is but, loosely speaking, the solution which has been subjected to the oscillatory treatment appears tougher and more elastic i.e. work hardened. Yet the oscillatory experiments give no clear evidence of hysteresis in the mechanical behaviour of these solutions, there being little difference between curves obtained by increasing the frequency of the oscillation and those obtained by reducing it from a high value.

The Effect of Phenol on CTAB - Sodium Salicylate Solutions.

It had been observed by Walker[77] that small quantities of phenol appeared to destroy the elasticity of CTAB - salicylate solutions without greatly affecting the time taken for these solutions to flow through an Ostwald viscometer. To investigate whether the present type of experiment could clarify this observation, a number of solutions containing the same amounts of CTAB (.0135M) and phenol (.005M) but with different amounts of salicylate, were prepared. These salicylate concentrations were .0125M, .0156M, .0188M, and .025M.

It certainly appeared, by merely handling all these solutions, that the elasticity was greatly reduced, but when examined in the oscillating annular vessel, the curves obtained for the first two solutions (.0125M, .0156M) were practically the same as for similar solutions without any phenol. There was a slight difference with the .0188M solution and this is shown in fig.48. With the .025M solution, a greater effect was observed. This is shown in fig.49 together with curves for solutions containing .0135M CTAB and .025M salicylate and various other concentrations of phenol. There is no doubt that the elasticity of the solutions is destroyed eventually, but the amount of phenol required to do this cannot be described as small. Furthermore the time of flow through the Ostwald viscometer is greatly

FIG. 48.

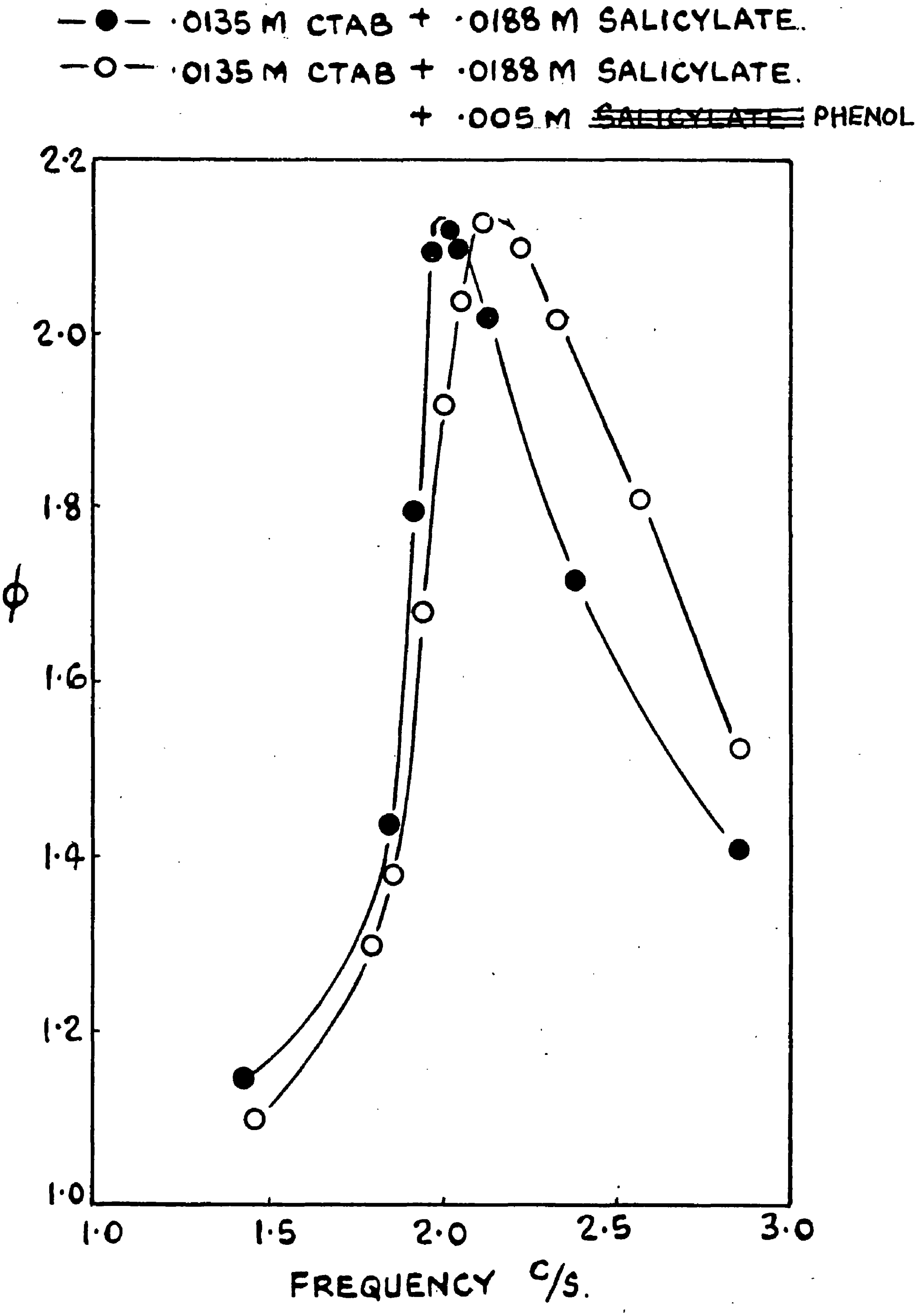
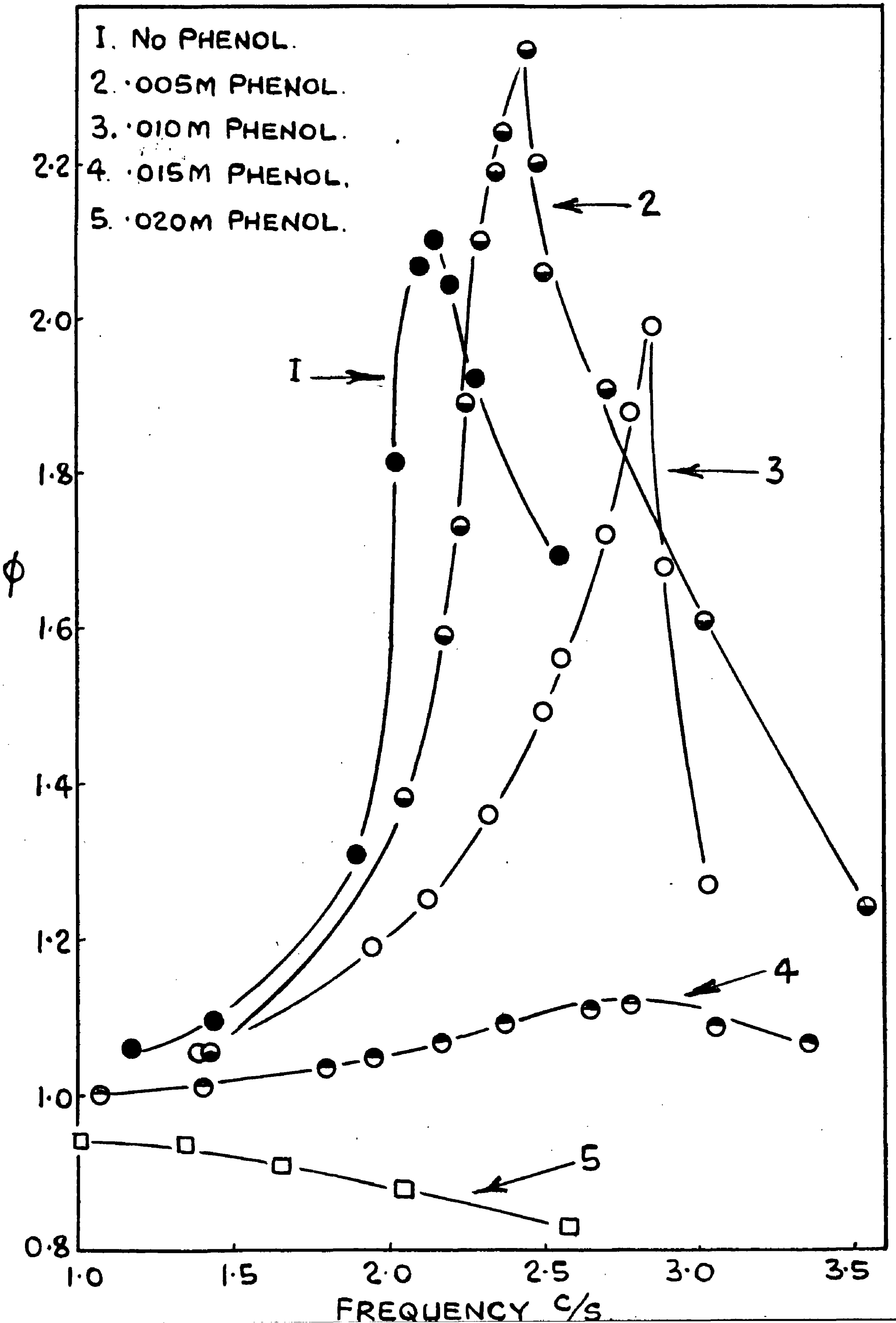

—●— ·0135 M CTAB + ·0188 M SALICYLATE.
—○— ·0135 M CTAB + ·0188 M SALICYLATE.
+ ·005 M ~~SALICYLATE~~ PHENOL
2·2
2·0
1·8
1·6
1·4
1·2
1·0
φ
1·0
1·5
2·0
2·5
3·0
FREQUENCY c/s.

FIG. 45.

ALL SOLUTIONS CONTAIN ·0135M CTAB + ·025M SALICYLATE.
+ VARIOUS AMOUNTS OF PHENOL.



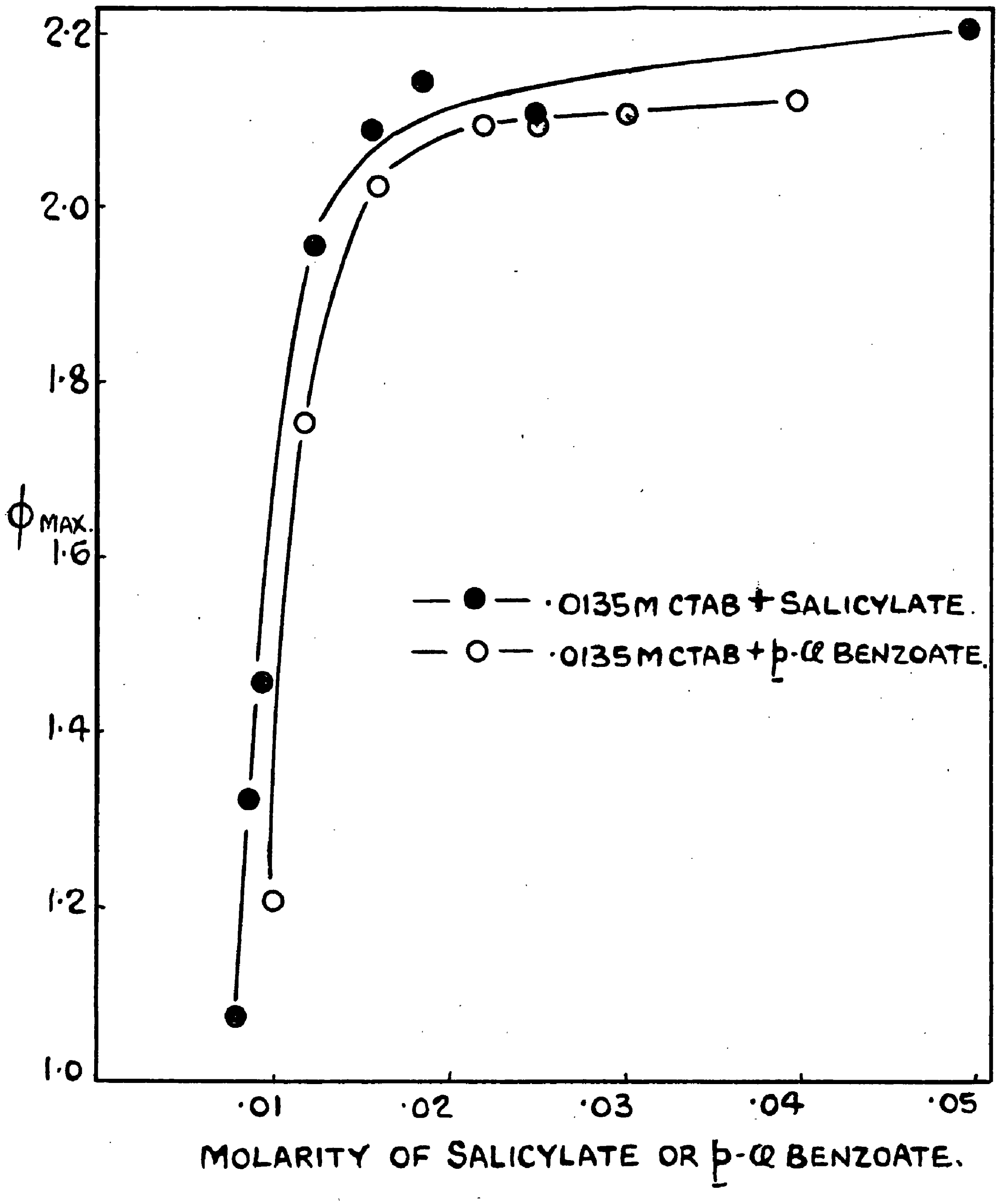
reduced in a way, roughly comparable, to that in which the maximum amplitude of oscillation of the liquid is reduced.

Discussion

While the interpretation of the results might be rendered more precise by applying to them a treatment which divides the visco-elastic effect into a viscous and an elastic effect (see for example Toms and Strawbridge[120]), it so happens that useful information can be obtained without using a procedure, the validity of which has not yet been definitely established.

The principal reason for this is that, with salicylate and p-chlorobenzoate solutions, there is very little difference between the curves once a certain concentration of the salt has been reached. This is clearly shown in fig.50 in which the ratio of the maximum amplitude of oscillation of each solution to the amplitude of oscillation of the glass vessel i.e. ϕ max, is plotted against the molarity of the salt for both CTA^+ - salicylate and CTA^+ - p-chlorobenzoate solutions. If the value of ϕ max. is taken as an approximate measure of the dimension of the elastic structure, then the structure of the salicylate - CTAB solutions build up to a maximum at a concentration approximately equivalent to that of the CTA^+ present, while the structure of p-chlorobenzoate - CTAB solutions reaches a maximum when the p-chlorobenzoate is present in amount slightly greater to that of the CTA^+. This is very similar to what is indicated by viscosity measurements but there is a difference. For, whereas the viscosity experiments indicated that the structure of the

FIG. 50.


2·2
2·0
1·8
1·6
1·4
1·2
1·0
φ MAX.
·01
·02
·03
·04
·05
MOLARITY OF SALICYLATE OR p-Cl BENZOATE.
—●— ·0135M CTAB + SALICYLATE.
—○— ·0135M CTAB + p-Cl BENZOATE.

aggregate in solution attained a maximum extension and then, on subsequent addition of more salicylate (say), disintegrated considerably, these oscillatory experiments indicate that, while a structure is built up by addition of salicylate to CTAB, this structure remains stable on the addition of more salicylate. This difference between viscosity and oscillatory experiments may be accounted for if the structure of the solution is dependent on the shearing force to which it is, and has been subjected. More direct evidence, by visual observation, that a structure is built up by suitable mechanical treatment has already been described on page118.

This mechanical property (i.e. change of structure on mechanical treatment) is very similar to the effects shown by ammonium oleate[71] and to the negative thixotropic behaviour described by Hartley[73], although it should be mentioned that at least the latter behaviour was concerned with solutions whose elastic properties would probably only give small maxima, if any at all, in a typical experiment of the type used here. The behaviour of dilute salicylate - CTAB solutions (e.g. .004M -.008M salicylate in .0135M CTAB) is similar to that described by Hartley, so that this negative thixotropic behaviour appears to be shown over the whole range of elastic behaviour.

p-chlorobenzoate - CTAB solutions also seem to show positive thixotropic behaviour. The ability of some such solutions to oscillate for ten-fifteen seconds has already been mentioned on page 104. If such a solution is given a violent rotation, the elastic recoil all but disappears but if the solution is then left standing for a few minutes, the elastic oscillations caused by mild rotary disturbance, can be shown again.

These visco-elastic solutions thus appear to show either positive or negative thixotropic behaviour depending on the shearing force to which they are, or have been, subjected to. It is possible that many other properties of these solutions change when the solutions are, or have been, mechanically treated.

While high concentrations of phenol undoubtably destroy the elasticity of salicylate - CTAB solutions, it is difficult to say just what happens at low concentrations. Certainly the frequency at which $\phi_{max.}$ occurs increases as the phenol concentration increases, but there is no particular reason to believe that this means that the elasticity is decreased; in fact, if anything, the opposite view is suggested. It will be seen again that observations made on these solutions under different mechanical conditions, differ.

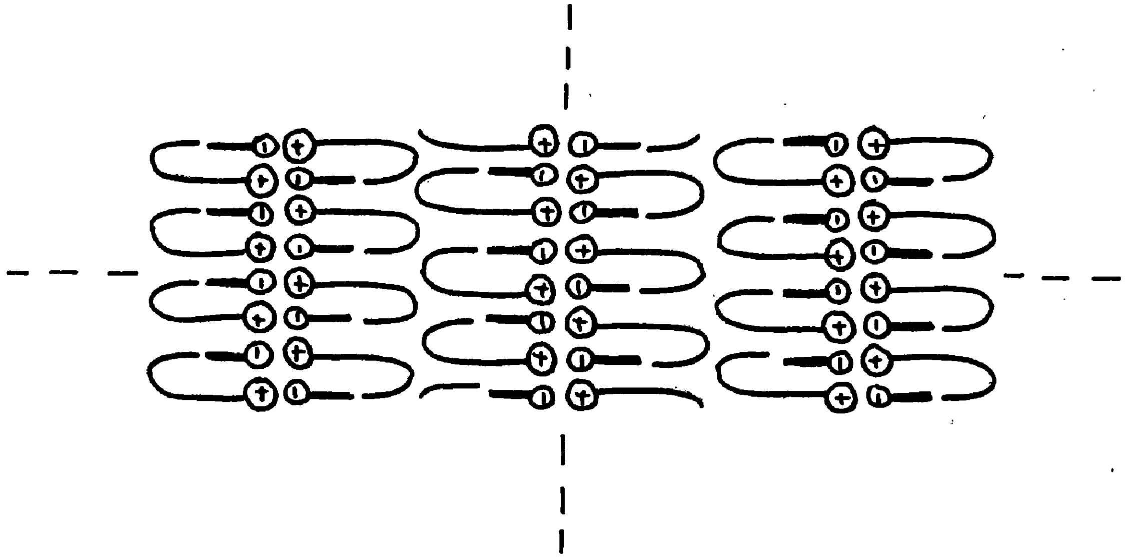
PART IV

General Discussion and Conclusions.

The principal result emerging from the present work has been the demonstration of the stability of the salicylate - CTA^+ micelle. Every measurement which has been made on viscosity, adsorption, sedimentation volume, activity coefficient and elasticity has shown that, as salicylate is added to CTAB, a structure gradually builds up whose stability is optimal when the salicylate and CTA^+ are present in roughly equimolecular amounts. Viscosity measurements suggest that, on further additions of salicylate, this structure gradually breaks down, while adsorption, activity coefficient and elasticity measurements suggest that it does not. Reconciliation of this contradiction may be afforded by the following considerations.

Salicylate - CTA^+ micelles are believed by us to consist essentially of long threadlike micelles, whose surface contains positive and negative charges arranged alternately (see diagram on page 28). The enormous length of these micelles would appear to arise from some factor which gives the micellar structure considerable stability in at least one dimension. In the case of the salicylate - CTA^+ micelle as with other benzoate ion derivatives[77] this factor is apparently some peculiar property of the benzene ring.

The long threadlike character of the micelles does not, however, by itself explain why these salicylate - CTA^+ solutions show elastic recoil effects since, although the precise explanation of visco-elasticity is not known, it is generally agreed that elastic effects require some cohesion between long molecular chains. In salicylate - CTA^+ solutions, the peculiar positive-negative surface may well be responsible for this cohesion, for, while the micelles of cationic or anionic soaps are repelled from one another by the ~~gegenions which are held~~ net charge on their surfaces, micelles which have a positive-negative array of surface charges will tend to interact with one another in a manner suggested by the diagram below, and this interaction will persist though less strongly even if the surface of the long micelles is hydrated.



If this large three-dimensional structure is regarded as being composed of units of long threadlike micelles, then it would have, with respect to these units, a low entropy which would not favour the formation of the structure to an unlimited extent. Therefore it might be supposed on these grounds that only at a very few parts of the surface of the long micelles, does ionic interaction occur to produce the structure. We have here what we consider to be the condition necessary for the production of elastic recoil effects i.e. long, threadlike micelles loosely attached at only a few points on their surfaces. The weakness of the large three-dimensional aggregate in the plane of the charged ions, due to both low entropy and to possible hydration of the surfaces of the individual units which make up the aggregate, would explain the occurrence of viscous or flow properties in these solutions. Strong interaction, on the other hand, in the plane of the charged ions would result in gelling of the system.

The visco-elastic properties of these salicylate - CTA^+ solutions are thus to be considered the result of the operation of two factors, first the interaction between the CTA^+ and the salicylate which causes long threadlike micelles to form, and second, the less powerful interaction between these micelles which causes the formation of a three-dimensional structure. Now the second of these interactions is likely to be more sensitive to the presence of excess salts than is the first interaction since the ionic or charged exterior of the micelle is involved. Furthermore, destruction of, or interference with this second interaction will chiefly affect properties dependent on the large average size of the three-dimensional aggregate, such as mechanical behaviour as shown for example in viscosity.

Properties depending on the existence of threadlike micelles, may be expected to be differently affected by changing physical conditions. Thus different physical measurements on these solutions may require different interpretations depending on whether the experiments are chiefly concerned with the threadlike micelles or with those formed by aggregation of the threadlike micelles.

We are now in a position to return to the question of why adsorption, activity coefficient and elasticity measurements should suggest that the CTA^+-salicylate aggregate is unaffected by excess salicylate while viscosity measurements suggest that the aggregate breaks down in the presence of excess salicylate. If the above discussion is correct, one set of measurements is concerned with the three-dimensional structure, the other with the threadlike unit out of which the larger structure is built.

The viscosity measurements, involving as they do a bulk property of the solution, will be principally concerned with the large three-dimensional aggregates. As has been pointed out, the three-dimensional aggregate is likely to be sensitive to the presence of excess salts, and this accords with the observation that the viscosity of the CTA^+ - salicylate solution falls in presence of excess salicylate. The adsorption measurements on the other hand will be concerned with the threadlike micelles rather than the three-dimensional ones since an adsorbed film is generally of two dimensional character. The threadlike micelles would appear therefore to be unaffected by excess salicylate.

Thus, in conclusion, we believe that the interaction between CTA^+ and salicylate in aqueous solutions leads to the formation of both long threadlike micelles and a larger three-dimensional aggregate composed of units of these.

The long, threadlike micelle is stable in the presence of excess salicylate while the three-dimensional micelle breaks down.

The behaviour of p-chlorobenzoate - CTA^+ solutions has proved to be more difficult to interpret. In adsorption it has been seen that the influence of p-chlorobenzoate is much the same as that of salts such as p-nitrobenzoate or benzoate, while in viscosity, activity coefficient and elasticity, its influence rather resembles that of salicylate. However, if the view that there exists micelles of different structures (two and three-dimensional) in salicylate - CTA^+ solutions, is correct, then the difference in behaviour between p-chlorobenzoate - CTA^+ solutions and salicylate -CTA^+ solutions must be due to the presence of micelles in the former solutions of somewhat different structure from those in the latter. That the salicylate - CTA^+ system is in some ways different from the *p*-chlorobenzoate - CTA^+ system may be connected with the undoubted existence of hydrogen bonding in the salicylate ion. But beyond this vague suggestion nothing further can be said at present.

APPENDIX

The Determination of the Surface Areas of Powders by the Adsorption of Nitrogen at -183°C.

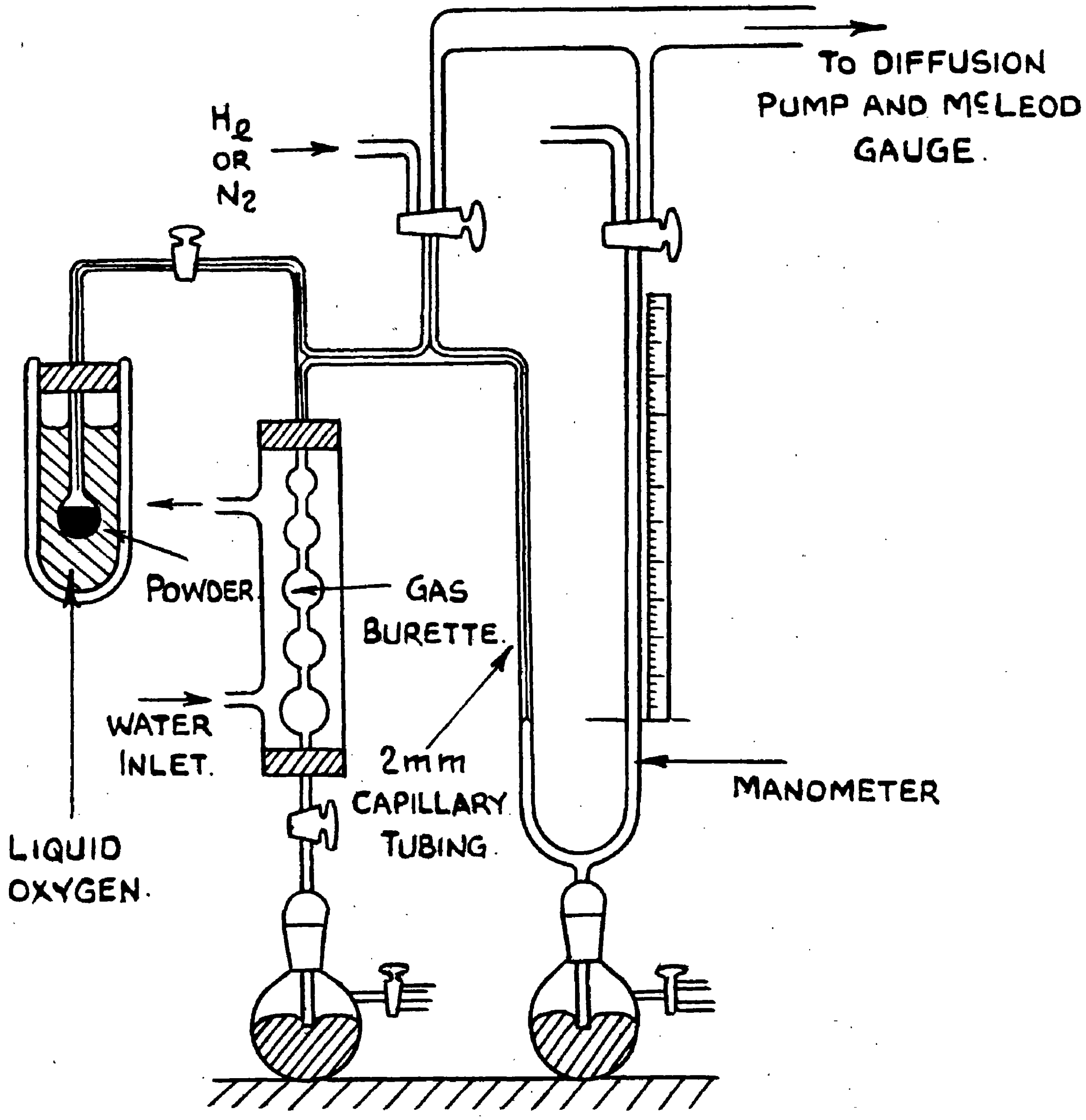
Procedure

This method for the determination of the surface areas of the powders used in the adsorption experiments (Part I) has been developed from the work of Brunauer, Emmett and Teller[80] and was chosen here chiefly because of its reliability. The procedure used was essentially that of Emmett[121].

'White spot' nitrogen, which contains .0015% oxygen, was used as the adsorbate, liquid oxygen and liquid nitrogen as the cold baths and spectographically pure Helium as a means of calibration. The powders were those which were mentioned in Part I. A diagram of the apparatus is shown in fig.51.

The powder, whose surface area was to be determined, was weighed into the adsorption bulb which was then sealed onto the apparatus. The adsorption bulb was evacuated at 110°C until the pressure above the powder was 10^{-6} mm Hg. Next, the appropriate cold bath was placed in position with the stopcock to the evacuated adsorbent closed and the 'dead space' in the adsorption bulb determined by allowing Helium to enter the gas burette. After measuring the volume and pressure of this Helium, the stopcock was opened and the system allowed to equilibrate. Then the stopcock was closed and the volume and pressure of the Helium left in the burette measured. Finally the whole system was evacuated to 10^{-6} mm Hg and the stopcock

FIG. 51.



GAS ADSORPTION APPARATUS.

to the adsorbent again closed.

The procedure for the adsorption of the nitrogen gas is exactly similar except that the system takes slightly longer to equilibrate. To measure the adsorption at various pressures, nitrogen is either added to the burette system or else the level of the mercury in the burette is raised. Desorption experiments always showed that there was no hysteresis at the pressures studied. All gas volumes were converted to S.T.P.

The volume of gas adsorbed at S.T.P. $V_a = V_t - V_h(1 + \alpha) - V_f$
where V_t is the total volume of nitrogen admitted to the system

V_h is the volume of nitrogen required to fill the 'dead space' to the pressure p of the experiment.

α is the correction factor to account for gas imperfection at the bath temperature.

and V_f is the volume of nitrogen left in the burette at the time of the measurement.

At the temperature of liquid oxygen, - 183°C, α is 2.87% for nitrogen at 760 mm. and varies linearly with pressure.

Results.

The results obtained using 'anatase E' powder as adsorbent are shown below in some detail while the final results obtained with other powders are shown at the end. In spite of decreased adsorption, liquid oxygen was preferred to liquid nitrogen since it maintained a constant temperature over longer periods.

Weight of 'anatase E' used = 12.0130 g.

'Dead space' determination.

Initial volume of Helium (S.T.P.) = 22.7 c.c.
Volume after opening stopcock to adsorbent (S.T.P.) = 14.4 c.c.
Pressure of Helium at equilibrium = 13.1 cm.
.. Volume of Helium at S.T.P. to fill dead space 13.1 cm. Hg. = 8.3 c.c.
and volume of Helium at S.T.P. to fill 'dead space' to 76 cm. Hg. = 48.2 c.c.

Nitrogen adsorption

TABLE V.

Vol.at S.T.P. initially c.c.	Vol.at S.T.P. finally c.c.	Equil.press p cm. Hg.	$(\alpha+1)$	V_h	$px10^3/p_o$	$\frac{px10^3}{V_A(p_o-p)}$	V_A (c.c.)
34.5	9.4	8.6	1.00	5.4	30.8	1.61	19.7
9.4	3.4	15.9	1.01	10.2	56.8	2.88	21.0
38.6	30.0	27.2	1.01	17.6	97.8	4.88	22.2
30.0	21.6	37.8	1.01	24.2	136	6.54	24.0
21.6	16.2	44.8	1.02	29.0	161	7.81	24.6
16.2	10.9	51.7	1.02	33.5	185	8.98	25.4
46.7	36.6	64.3	1.02	41.6	231	11.0	27.4
36.6	27.5	76.1	1.03	49.7	273	13.3	28.4

In the above Table V, p_o the liquefaction pressure of nitrogen at -183°C was calculated from the equation[122]

$$\log. p = A/T + B + CT + DT^2$$

where $A = -316.824$, $B = 4.47582$, $C = -.0071701$ and $D = 2.94 \times 10^{-5}$

p being in atmospheres and T in °K.

V_A is plotted against p/p_o in fig.52 for all the adsorbents used.

The B.E.T. equation is

$$\frac{p}{V_A(p_o - p)} = \frac{1}{Vmc} + \frac{(c-1)\,p}{Vmcp_o}$$

where $c = e^{-(E_1 - E_L)RT}$, E_n being the average heat of adsorption of the nth layer.

$p/V_A(p_o - p)$ is plotted against p/p_o in fig.53 for all the adsorbents used.

From this graph V_m, the volume of gas required to form a monolayer, is 20.9 c.c. at S.T.P. for the 'anatase E'.

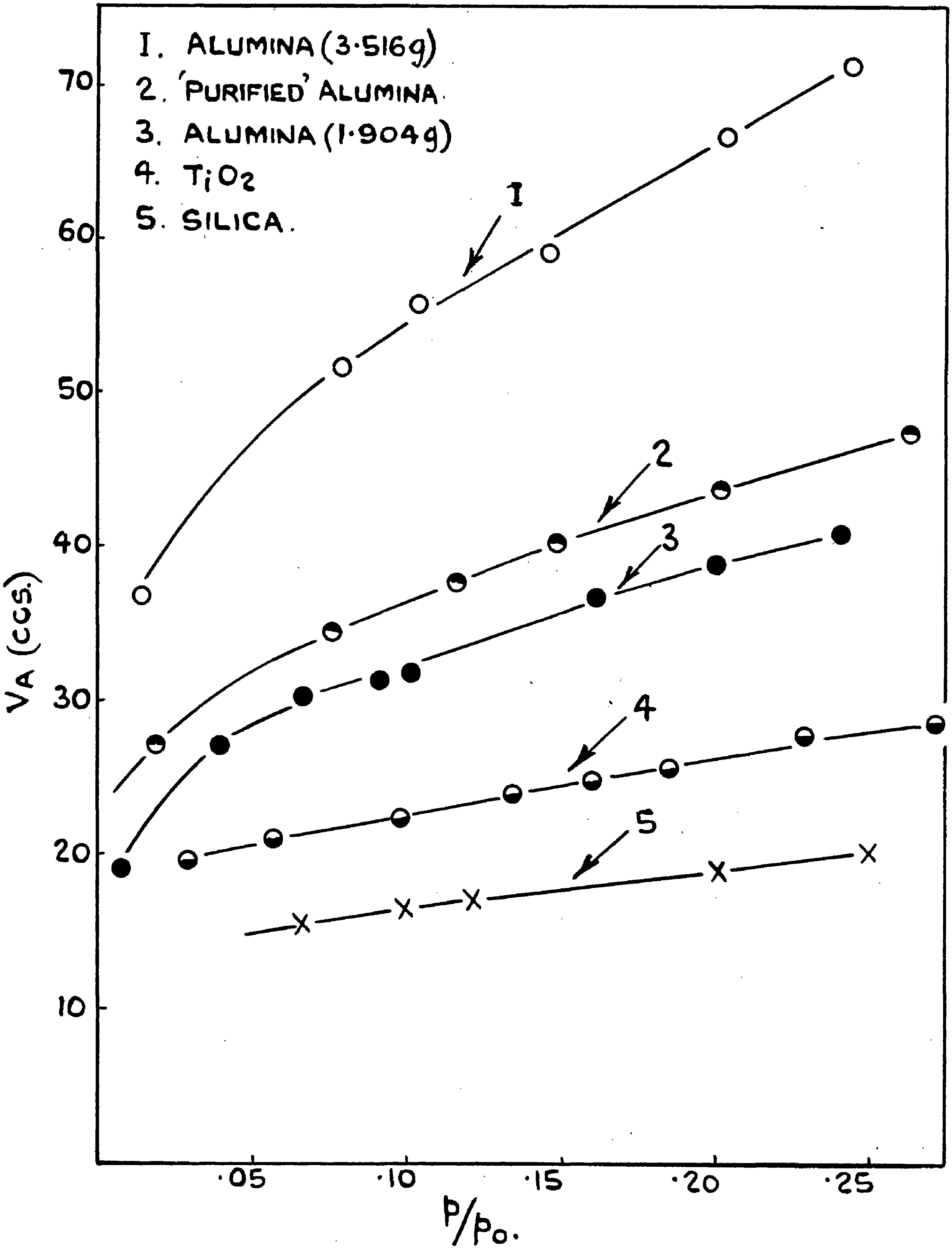
Taking the area occupied by one nitrogen molecule as 16.2Å^2, the surface area of the 'anatase E' powder is

$$= \frac{20.9 \times 6.02 \times 10^{23} \times 16.2 \times 10^{-20}}{2.24 \times 10^{4} \times 12.0130} \; m^2/g.$$

or $7.6\ m^2/g$.

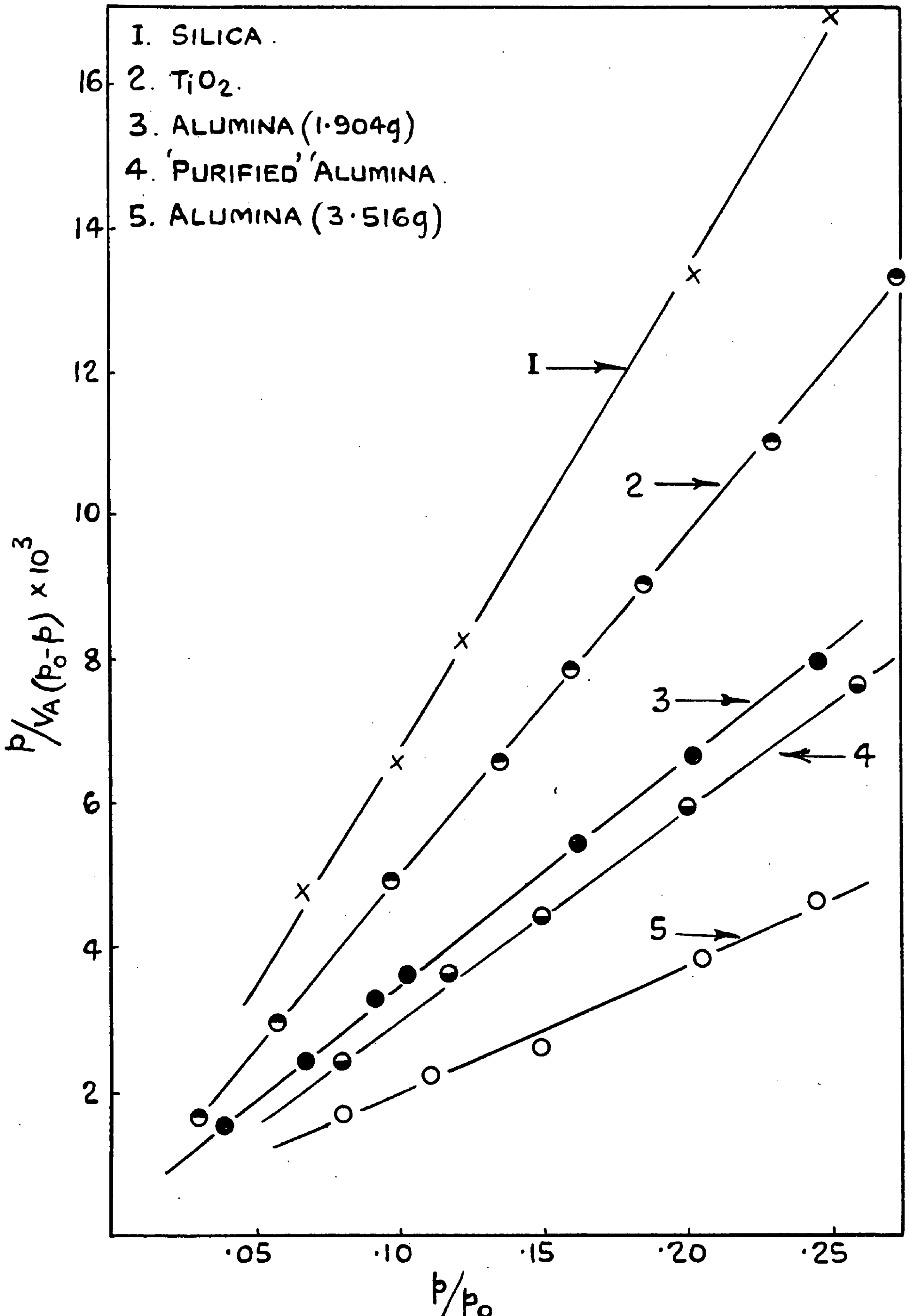
This lies within the range of values specified by British Titan Products and was thus considered to demonstrate the reliability of the apparatus.

FIG. 52.



I. ALUMINA (3·516g)
2. 'PURIFIED' ALUMINA
3. ALUMINA (1·904g)
4. TiO2
5. SILICA
I
2
3
4
5
70
60
50
40
30
20
10
VA (ccs.)
·05
·10
·15
·20
·25
P/Po.

FIG.



I. SILICA.
2. TiO$_2$.
3. ALUMINA (1·904g)
4. 'PURIFIED' ALUMINA.
5. ALUMINA (3·516g)
I
2
3
4
5
16
14
12
10
8
6
4
2
·05
·10
·15
·20
·25
$p/V_A(p_0-p) \times 10^3$
p/p_0

The results are summed up below

TABLE VI.

Powder	Surface Area m^2/g.
Anatase E	7.6
Silica	8.0
Alumina	69.6
'Purified' alumina	76.4

Duplicate determinations with the alumina powder agreed within 0.5%.

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