Some Physical Properties of
Aqueous Solutions of Cetyl
Trimethyl Ammonium Bromide.

A THESIS

submitted to

THE UNIVERSITY OF GLASGOW

in fulfilment of the
requirements for the

DEGREE OF DOCTOR OF PHILOSOPHY

by

STEWART A. McKELLAR

February, 1963.

ACKNOWLEDGEMENT

The author would like to express his sincerest gratitude to Dr. William Good for his advice and encouragement during the course of this work.

SUMMARY

This work is chiefly concerned with the viscous properties produced when certain phenolic compounds are added to an aqueous solution of cetyl trimethyl ammonium bromide (C.T.A.B.).

In the first part of this work the variation in the viscosity of an aqueous 1% C.T.A.B. system caused by the addition of certain phenolic compounds was studied. It was found that the addition of each phenolic compound caused the viscosity to increase to a maximum and thereafter, further additions produced a decrease.

The value of the viscosity maximum appeared to be dependent on the molecular shape and nature of the phenolic additive. It was found that, of the cresol isomers and of the ethyl phenol compounds added, the para isomer in each case produced the most viscous system. The results appeared to show that if the additive possessed a molecular form which facilitated the solubilisation of the phenolic compound molecules into the micelle so that they penetrated between neighbouring C.T.A. cations with their hydroxyl groups on the micelle surface, then it produced, with a 1% C.T.A.B. system, a viscosity maximum which had very pronounced viscous properties.

The shape of the curves of viscosity against concentration of phenolic additive, i.e. the sharp increase to a maximum followed by a decrease, is explained in terms of an intermicellar equilibrium in which C.T.A.B. spheroidal micelles, by progressive interaction with phenolic molecules, are transformed into lamellar or threadlike micelles which, with further addition of the phenolic compound,

re-arrange themselves in such a manner that they eventually revert to a spheroidal form. It is considered that the initial increase in viscous properties is due to the formation of these lamellar or threadlike micelles and that their subsequent re-arrangement causes the decrease.

During the study of the viscous properties of these systems of C.T.A.B. + phenolic additive, it was found that they possessed negative thixotropic properties, i.e. the system became more viscous when subjected to a shearing influence. Consequently, a study of this shearing effect using systems of 1% C.T.A.B. + phenol and of 0.05% C.T.A.B. + Sodium Salicylate was carried out. It was found that their viscous properties appeared to increase with speed of shearing to a limiting value. However, this increase was only temporary because each system reverted to its original viscosity when the shearing was stopped. The systems which gave maxima in viscosity were influenced to the greatest extent by shearing. There was no evidence that the viscosity of C.T.A.B. systems without any phenolic additive was affected by shearing.

It is suggested that the shearing causes the C.T.A.B. + phenolic additive micelles to aggregate into larger elongated micellar structures which are unstable when the system is at rest and consequently, when shearing ceases, these micellar structures gradually revert to their original form.

Also, various systems of 1% C.T.A.B. + phenol and of 0.05% C.T.A.B. + sodium salicylate were spread on a substrate of 80%

sodium nitrate solution and the molecular areas in the monomolecular surface films, which were formed, were determined. The measurements showed that the concentration of phenolic additive varied the molecular areas in the surface films in a similar manner to which it varied the viscosities.

Such determinations confirmed the view that the C.T.A. cation and phenolic additive molecule are most closely associated in systems which possess maximum viscous properties.

It was observed in Part IV, that while the addition of electrolytes to 1% C.T.A.B. had little effect on its viscous properties, their addition to 1% C.T.A.B. + 0.5% phenol (i.e. the system which gives the viscosity maximum) caused the viscosity to increase to a maximum and then to decrease. The effect of the addition of a number of electrolytes to a 1% C.T.A.B. + 0.5% phenol system suggested that the increase in viscous properties was primarily caused by the electrolyte anion. Also, it was found that, if the electrolyte anion was inorganic, the increase in viscous properties was a function of the size of the electrolyte anion, but if the anion was from the salt of an aliphatic acid then the increase in viscous properties was greatly influenced by the size of its hydrophobic group.

CONTENTS

HISTORICAL REVIEW

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AQUEOUS SOLUTION OF PARAFFIN - CHAIN SALTS

Hartley (1) has suggested that soaps may be regarded as belonging to a class of compounds appropriately designated as PARAFFIN - CHAIN SALTS. Such salts possess paraffinic chains with ionisable heads. In solution, the heads dissociate, or ionise, to give cationic or anionic long chain ions. The term "chain" cannot be defined rigidly but it usually implies any grouping containing eight or more carbon atoms. The most important property of a paraffin-chain salt is its behaviour in water.

Aqueous solutions of paraffin-chain salts display remarkable properties owing to the paraffinic ion possessing distinct regions of lipophilic (paraffin chain) and of hydrophilic (ionic head) character. Substances which possess such a dualistic character (lipophilic, hydrophilic) have been termed by Hartley (1) AMPHIPATHIC to indicate that they contain, within the one species, a grouping which has an affinity for water and one which is antipathetic to water. Now, Hartley (1) considered that there was no repulsion between lipophilic and hydrophilic regions and for this reason, Winsor (2) has suggested that the term AMPHIPHILIC may be more accurate than the term "amphipathic" which suggests some form of repulsion, and he defines amphiphilic compounds as those which possess, in the same molecule, distinct regions of lipophilic and of hydrophilic character.

Prior to 1910, measurements of the colligative properties of soap solutions had led to the idea that soaps were just ordinary colloids but, in that year McBain began a series of investigations (3) (4) (5) (6) which revealed that soaps possessed very different properties from other colloids.

It had been found that soap solutions possessed a higher conductivity than other colloids. The first explanation given for this phenomenon was that the conductivity was caused by alkali being produced due to a hydrolysis of the soap. This explanation appeared to be unsatisfactory when firstly, Goldsmidt and Weismann (7) observed that an ammonium soap, which is only slightly alkaline, has a conductivity almost equal to that of the corresponding potassium soap and secondly, when Reychler (8) noted that cetane sulphonic acid has a similar conductivity to cetyl triethyl ammonium iodide. Hydrolysis, as an explanation of the conductivity of soaps, was finally ruled out when McBain (5) showed that alkali produced by hydrolysis could only explain a small fraction of the conductivity. Thus the conductivity of soap solutions must be due to some process other than hydrolysis.

While the conductivity of soaps and other paraffin-chain salts is not so great as that of simple electrolytes - and in moderately concentrated solutions it is considerably less - it is greater than would be expected from their osmotic activity. McBain and Salmon (9), from the determination of the dewpoint of the vapour over a potassium stearate solution, found that the concentration of the osmotically active particles in solution was lower than it would be if the soap dissolved as an undissociated salt.

These results forced McBain to postulate the existence within soap solutions of ionic aggregates (ionic micelles) which would exhibit a low osmotic activity but a high conductivity.

Compounds which showed a higher conductivity than their osmotic activities implied were named by McBain COLLOIDAL ELECTROLYTES. He defined colloidal electrolytes as salts in which an ion has been replaced by a heavily hydrated polyvalent micelle which conducts electrically, as well as, or even better than, the simple ion it replaced.

Later, Hartley (1) introduced the term paraffin-chain salts for soaps and similarly behaving compounds in order to distinguish them from other colloidal electrolytes such as dyes, gums and proteins.

Investigations into conductivity of soap solutions (4) (10) showed that with increase in concentration, the equivalent conductivity fell, reached a minimum, and then slowly rose to an approximately steady value. McBain (11), in interpreting these results, considered that the initial fall in equivalent conductivity, was due to a decrease in electrolytic dissociation and that the subsequent increase in equivalent conductivity was the consequence of the formation of a small polyvalent ionic micelle.

$$nX^- \rightleftharpoons (X_n)^{n-}$$

X^- being the amphiphilic anion, n being the number of ions in the micelle.

Micelle formation in this manner would produce an aggregate having charge and volume n times that of the single amphiphilic ions.

Now, according to Stokes's Law the viscous resistance to this aggregate's movement, in a given electric field, would be only $1/n^{\frac{1}{3}}$ that exerted on n single ions and therefore the conductivity is $n^{\frac{2}{3}}$ times that of n single ions.

In 1927, Bury and Jones (12) were able to show, by applying the law of mass action to the equilibrium between single ions and micelles, that the transition from single ions to micelles would be fairly abrupt.

If, the concentration of single ions $= C_i$
the concentration of aggregates $= C_n$
and K is equilibrium constant
for the equilibrium of
n single ions $\rightleftharpoons$ micelle
$n\,X^- \rightleftharpoons (X_n)^{n-}$

where X^- is the amphiphilic ion, then, $K^{-1} = \frac{(Ci)^n}{C_n}$

Bury pointed out that, only when C_i is comparable with

$K^{-1/n}$, will the concentration of micelles become appreciable. When C_i is greater than $K^{-1/n}$, then the concentration of micelles will increase rapidly with increasing total concentration.

Thus, the concentration of salt at which micelles are formed would seem to be fairly specific. Bury (13) and (14) was able to produce experimental evidence to support this view when he showed that the partial specific volumes of certain paraffin-chain salts changed abruptly at a given concentration which he and his co-workers called the CRITICAL MICELLE CONCENTRATION (C.M.C.).

This concentration was smaller than that which produced the minimum in equivalent conductivity vs concentration of salt curve. Hence McBain's concept that homoionic aggregation caused the rise in equivalent conductivity beyond the minimum could no longer be accepted although the general principle that homoionic aggregation increased equivalent conductivity remained valid.

Lottermoser and Püschel (15), on measuring the conductivity of solutions of the higher alkyl sulphates, found that, in very dilute solutions, as the concentration rose the equivalent conductivity fell only very slowly and then, at a well defined concentration, an abrupt fall occurred. In 1934, Hartley and Malesch (16) suggested that the sudden fall, rather than a slow fall, was indicative of micelle formation. In subsequent years, similar results to those of Lottermoser and Püschel were obtained by Wright et.al. (17), Ralston (18) and Ekwall (19) when measuring the equivalent conductivity in very dilute solution of long chain sulphonates, long chain amine salts and salts of aliphatic acids respectively. These results suggested that the curve of equivalent conductivity against concentration of paraffin-chain salt for dilute solutions has, in general, a constant shape, all showing the sudden fall in equivalent conductivity at a well defined concentration of salt.

The curves showing the variation with concentration of many other physical properties, e.g. freezing point depression (20), density (21), surface tension (22), viscosity (23) and transport number (24), of aqueous solutions of paraffin-chain salts have fairly sharp breaks at a certain concentration which, for a given salt, is approximately the same for each property. This break in the curve of property against concentration of salt is taken as marking the commencement of the formation of aggregates, or micelles, and therefore the concentration of salt, at which this break in the curve takes place, is the C.M.C. of the paraffin-chain salt.

At very low concentrations of paraffin-chain salt (amphiphilic electrolyte), the curve of equivalent conductivity against concentration of salt lies close to the Onsager slope for a uni-univalent strong electrolyte. This is interpreted as showing that, at very low concentration, below the C.M.C., the paraffin-chain salt behaves as a strong electrolyte being completely dissociated into single ions (25).

The formation of micelles from single ions is thought to result from an increased number of encounters of amphiphilic ions brought about by increasing the concentration of paraffin-chain salt. The duration of a particular encounter depends on the mutual orientation of the colliding ions. The encounters in which the hydrocarbon chains of the amphiphilic ions are brought together are the most stable, and so create favourable conditions for the formation of aggregates or micelles.

Most investigators regard micelles as being in dynamic equilibrium with single ions and/or with smaller groupings of amphiphilic ions. The concentration of single ions in equilibrium being regarded as the C.M.C., but the size, the shape, the concentration and even the existence of groupings of amphiphilic ions, intermediate in size, between the single ions and micelles, are still a matter of considerable controversy (26) to (30).

Although it is generally agreed that micelles are formed at a certain concentration of paraffin-chain salt there are various interpretations as to the geometric characteristics of the micelles. Of the several interpretations put forward, most are variations of those suggested by Hartley (1) and by

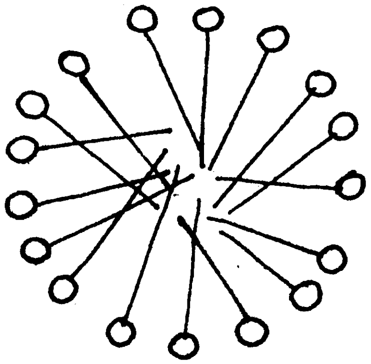
McBain (31) and (26).

Hartley (1) and (32) envisaged the micelle as consisting of paraffin chains, from the amphiphilic ions, aggregated together with their ionic heads penetrating into the surrounding water. He considers that the micelle is spherical in form - although it may be modified locally by the thermal motion of the molecules - and fluid in character. The fluid character is produced by a liquid interior of hydrocarbon tails which are in irregular juxtaposition with each molecule at least 4-5 Å apart (33). An idealised diagram of Hartley's micelle is shown in figure 1.

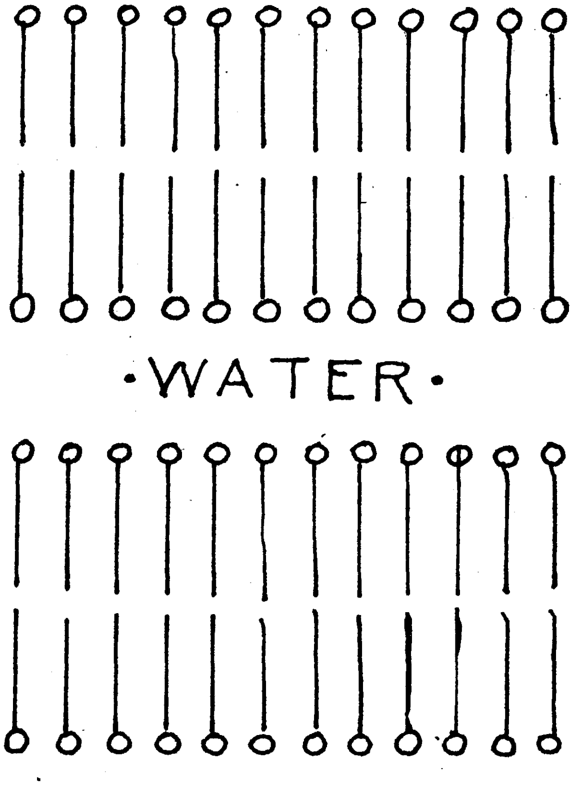
Hartley pointed out that the formation of micelles is not due to any very strong attraction of paraffin chains for one another nor to any repulsion between water molecules and the paraffin chains but to a very strong attraction of water molecules to one another. The cohesion of water molecules falls off rapidly as their separation is increased. Thus, once one or two paraffin-chain ions have been introduced between water molecules, the cohesion between these water molecules is so reduced that it requires little more energy for an aggregate of paraffin-chain ions to be subsequently formed.

Bury and his co-workers (12) and (13) have found that, on aggregation, the partial specific volume of the paraffin chains increased while that of the water decreased. This implies that strong cohesion between water molecules causes

·· FIG. 1 ··



·· SPHERICAL MICELLE ··
(HARTLEY)



·· LAMELLAR MICELLE ··
(Mc BAIN)

single paraffin chains to be under a compressive force but, when aggregation takes place, the compressive force per chain decreases.

Hartley has suggested that the completely developed paraffin-chain salt micelle has a diameter of approximately twice the length of the chain, because if it were any larger, the polar head would be drawn into the hydrocarbon interior and, if it were smaller, the maximum degree of segregation of regions of lipophilic and of hydrophilic character would not have taken place. From these considerations, Hartley has been able to estimate that there would be 50 amphiphilic ions in a fully developed micelle of a paraffin-chain salt containing 16 C atoms per chain.

Hartley realised that such a micelle as he was portraying, consisting solely of paraffin-chain ions, would possess a high charge and would therefore attract to its surface a large number of ions which are opposite in sign. These ions were termed by him GEGENIONS, or COUNTER IONS, and he suggested that their number for a C_{16} micelle would be from 25 to 40.

Clear evidence for the association of gegenions in the micelle has been obtained from the measurements of the transport numbers of several paraffin-chain salts (24) (34) (35). It has been found that, in the region where the equivalent conductivity was falling rapidly, the transport number of the amphiphilic 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.

In 1935, Murray and Hartley (36) were able to show that the formation of micelles would be more abrupt if the gegenions were associated to the micelle.

They considered a micelle $(R_nX_p)^{(n-p)\pm}$ where <u>R</u> is the amphiphilic ion, <u>X</u> is the gegenion, n and p the number of amphiphilic ions and gegenions in the micelle respectively, with the valence on the micelle $(n-p)\pm$ according to whether <u>R</u> is cationic or anionic.

If the concentration of paraffin-chain salt = C, the concentration in micellar form = C_n, and <u>K</u> is the equilibrium constant for the equilibrium of,

$$\underset{\text{ions}}{nR^{\pm}} + \underset{\text{ions}}{pX^{\pm}} \rightleftharpoons \underset{\text{micelles}}{R_nX_p^{(n-p)\pm}}$$

then by applying the law of mass action,

$$K^{-1} = \frac{(C - C_n\frac{p}{n})^p \ (C - C_n)^n}{C_n}$$

Using this equation, they demonstrated that dc_n/dc (the increase in concentration of micellar species due to a small increase in concentration of paraffin-chain salt), showed a very abrupt increase at a specific concentration. This abrupt increase was greater than the corresponding increase obtained by applying the law of mass action to a micelle where no gegenions are associated with it.

Hartley (36) has pointed out that the inclusion in the micelle of a considerable number of ions, of sign opposite to that of the amphiphilic ion, must effectively neutralise an equivalent charge on the micelle and also cause a number of free ions to be withdrawn from the conduction process. These two effects tend to lead to a reduction in equivalent conductivity and Hartley suggests that the result of these effects is illustrated by a sudden drop in equivalent conductivity immediately the concentration of salt increased above the C.M.C.

Now, according to Stokes's Law, homoionic aggregation (11) or aggregation containing ions of opposite signs (37), provided they show a sufficient excess of charge, would tend to enhance the conductivity with the result that an increase in equivalent conductivity would be expected as the concentration of salt becomes greater than the C.M.C.

There are several salts, e.g. quaternary ammonium bromates (38), octadecane -1 pyridinium iodate (39) and dialkyl-ammonium chlorides (40), which show this increase in equivalent conductivity and there are other paraffin-chain salts e.g. octadecane -1 pyridinium chloride (41) and dodecane -1 ammonium chloride (42), which in aqueous solution, show a decrease in equivalent conductivity as the concentration becomes slightly greater than the C.M.C. but, in the presence of methanol or ethanol, there is an increase in equivalent conductivity. Now these salts, which show an increase in equivalent conductivity in aqueous solutions, possess a low C.M.C. with the result that the adherence of the gegenions to the micelle is reduced and therefore the effect on the conductivity would be that of homoionic aggregation. The increase in equivalent conductivity which was found with aqueous alcoholic solutions of certain amphiphilic salts but which did not take place in aqueous solutions is due to the alcoholic additive reducing the degree of attachment of the gegenions to the micelle.

Therefore, it appears, according to Hartley's micellor theories, that at concentrations of salt slightly greater than the C.M.C. the equivalent conductivity decreases or increases according to the degree to which gegenions are attached to the micelles.

McBain (43) has pointed out that Hartley's 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." Also he noted that the paraffinic chains in the Hartley spherical micelle cannot be arranged radially although their length has been taken as the radius of a sphere, because the density throughout must remain that of a hydrocarbon.

Also, Ward (44) considers that a micelle constructed according to Hartley's manner seems improbable as it requires a large area of contact between paraffin and water.

For example, he has pointed out that a Hartley micelle constructed of dodecane -1 sodium sulphate would only have enough polar heads to cover a quarter of the micellar surface.

McBain (45) considered that Hartley's picture of micelle development leading to a single type of micelle structure was too simple to account for the various properties of soap solutions. He believed that more than one type of micelle must be present and stated (45) that, "If there is any way in which ions or ion pairs can come together or associate with any reduction in free energy, as by reducing interfacial energy or by more uninterrupted hydrogen bonding of water, then that complex must exist to some extent, however slight, in soap solutions. Each size, shape and arrangement will form in proportion to the reduction in free energy that it offers under each condition of concentration, temperature and presence of other salts and materials."

McBain (26) has postulated that, as a minimum, two forms of micelle must exist.

1. A micelle which is NEUTRAL, or slightly ionised and is lamellar in form consisting of a double leaflet of soap molecules placed end to end and side by side. His description of this Neutral Micelle in 1925 to the Royal Institution of Great Britain was as follows, "Each particle is like a pair of military hair brushes in which the bristles represent the hydrocarbon chains of the molecules arranged

parallel to each other in sheets, two such layers being put together hydrocarbon to hydrocarbon. The two backs of the brushes on the outside represent the hydrated layer and un-ionized electric double layer. A general survey of the facts with regard to the electric double layer has shown that only a minute fraction of such surfaces can ionize - hence the name 'NEUTRAL' micelle." An idealised diagram of such a neutral micelle is shown in figure 1. McBain considered that the formation of this neutral micelle was responsible for the falling off in conductivity above the C.M.C.

2. The other micellar form postulated by McBain was ionic and spherical and consisted of approximately ten amphiphilic ions. Such an aggregate has the same electrical driving force per ion per charge in an electrical field as each individual ion, but according to Stokes's Law, homoionic aggregation would cause the aggregate to have greater mobility than the individual ions.

According to McBain's theory, the existence and proportion of these micellar forms and probably intermediary forms are responsible for the properties of aqueous solutions of paraffin-chain salts.

An important feature of aqueous solutions of paraffin-chain salts is that, with increasing concentration of salt, the material transport number of the amphiphilic ion rises to a maximum and then falls off rather steeply (24) (35), (36) and (46). McBain (26) suggests that this is evidence that there is a change in the kind of average micelle in these systems, confirming that more than one kind of micelle must exist.

McBain's theory that there may exist, within the same solution, two distinct types of micelles such as:

(1) the Neutral Micelle, being crystalline and, in effect, non-ionised in character,

(2) the Spherical Ionic Micelle, being liquid and completely ionised,

was not accepted by Hartley et al.(47).

Thus, it can be seen that on the question of the nature of the colloidal micelle the two main schools of thought are substantially different.

Other investigators into the properties of aqueous solutions of paraffin-chain salts have suggested various forms for the micelle.

(1) Lawrence (48) has suggested that the micelles are spherical and that they are capable of forming "secondary" micelles by cohesion of the polar end groups (49)

(2) Klevens (50) has proposed that the micelle should be represented as an oblate spheroid.

(3) Harkins (51) firstly, postulated that the micelle was the shape of a "biscuit" (polar groups in the plane surface of the biscuit) but later, he suggested that the shape was a quasi-oblate spheroid (oblate spheroid tending to change into a cylindrical form).

Although many such micellar forms have been proposed, objections to each form have been raised. For example, Winsor (47) has stated that the existence of micelles in the form of ellipsoids and cylinders in isotropic solutions of paraffin-chain salts at rest, seems absurd because it implies that the paraffin-chain ions would spontaneously arrange themselves so that the mean distribution of neighbouring ions about the axis of symmetry of a given ion would not be symmetrical.

One most important property of aqueous solutions of paraffin-chain salts is their ability to enhance the solubility of substances which are feebly soluble in water. Thus any form of the micelle must be able to account for this behaviour.

SOLUBILISATION:

Solubilisation has been defined by McBain (43) as the spontaneous passage of solute molecules of a substance insoluble in water into an aqueous solution of a soap, or a detergent, in which a thermodynamically stable solution is formed. The formation of such a stable solution involved a decrease in the free energy, (which indicates its stability) and the diffusion of the added solute molecules from the bulk phase into soap micelles.

The subject of solubilisation has been reviewed by Klevens (52).

The solvent in the solubilisation process (i.e. paraffin-chain salt) is termed the SOLUBILIZER and the solute is termed the SOLUBILIZATE.

There are two generally accepted forms of solubilisation.

(1) Incorporation of the solute into the hydrocarbon centre of the amphiphilic micelle.

(2) Penetration by the solute of the palisade layer of the amphiphilic micelle.

INCORPORATION INTO HYDROCARBON CENTRE OF THE MICELLE

This is the type of solubilisation which non-polar compounds, such as hydrocarbons undergo. The solubilizate molecules are not oriented with respect to the water but are dissolved in the hydrocarbon interior of the micelle.

Hartley (53) found that the solubility of trans-azobenzene in aqueous solutions of cetyl pyridinium chloride was roughly the same as its solubility in an equivalent amount of liquid hexadecane. This suggested that the trans-azobenzene had dissolved in a paraffinic region and thus, as the paraffinic interior of the micelles was the only one existing in the aqueous solution of a paraffin-chain salt, the solubilisation must have been in this region. Other evidence supporting the view that solubilisation of non-polar substances is in the interior of the micelle has come from the X-ray work of Krishmurti (54) Hess et al (55-57), Stauff (58), Hughes and Vinograd (59) and Harkins and co-workers (60) and (61). They have shown that X-ray patterns are affected by the solubilisation of non-polar substances, e.g. the M-band, which is taken as corresponding to the diameter of the micelle, is increased by solubilisation of hydrocarbon. Also it has been shown by Klevens (62) that the solubilisation of hydrocarbons increased with increase in concentration of paraffin-chain salt.

PENETRATION INTO THE PALISADE LAYER OF THE MICELLE.

Solubilisation of polar compounds such as alcohols, amines, long-chain fatty acids, insoluble soaps, etc; occurs with penetration into the palisade layer rather than into the interior of the micelle. The polar molecules of the solubilizate appear to be oriented with respect to the water, and the solubilisation involves the hydrocarbon chains of the polar molecules penetrating between the soap ions to form a mixed micelle.

Schulman and Hughes (63) have shown that mixed films of alcohol and soap are possible. This type of evidence coupled with X-ray studies in which it has been shown by Harkins (64) and (65) and McBain (66) that the addition of polar additive gave X-ray measurements, (e.g. no increase in the M-band spacing) which indicate that the polar additive was not solubilised in the centre of the micelle.

Solubilisation depends on:-

(1) The chain length of the solubilizer.
(2) The charge on the solubilizer.
(3) The structure of the solubilizate.
(4) The temperature.
(5) The presence of various additives.

It has been found that increasing the chain length of the solubilizer causes an increase in the amount of hydrocarbon solubilized. The weight of D.M.A.B. (dimethylazobenzene) solubilised by salts of aliphatic acids having 12, 14, 16 and18 carbon atoms was found to increase linearly with the number of carbon atoms. In 1938, Samis and Hartley (67) were able to show, from mobility measurements, that the solvent powers of the micelles increased in the same order as do their micellar radii (which are a function of the chain length of the solubilizer).

It has been observed (52) that cationic paraffin-chain salts are more powerful solubilizers than anionic paraffin-chain salts of an equal chain length.

The structure of the solubilizate has a considerable effect on the nature and degree of solubilisation. From several publications (62), (68) and (69), it has been reported that, with increase in the length of the paraffin chain of the hydrocarbons, there is a decrease in the amount of hydrocarbon solubilised. Also, it has been noted that cyclic and unsaturated solubilizates are more soluble in aqueous paraffin-chain salt solutions than their corresponding saturated paraffinic hydrocarbons.

When the solubilizate is polar, its degree of polarity, or hydrogen bonding capacity, determines the position which the polar compound takes up in the palisade layer and thus controls the volume in the micelle available for solubilisation. From the data published by Harkins and Oppenheimer (70) on the solubilisation of polar compounds, it has been found that there was a general increase in solubility of the polar compound as the chain length of the solubilizer increased. The solubility of polar compounds in aqueous paraffin-chain salt solutions decreased with increase in length of the paraffinic chain of the polar solubilizate.

An increase in temperature normally results in an increase in the solubilisation of hydrocarbons in aqueous solutions of paraffin-chain salts. Also it has been noted (52) that the addition of electrolyte enhanced the solubilisation of hydrocarbons but decreased the amount of polar compounds solubilised in the micelles.

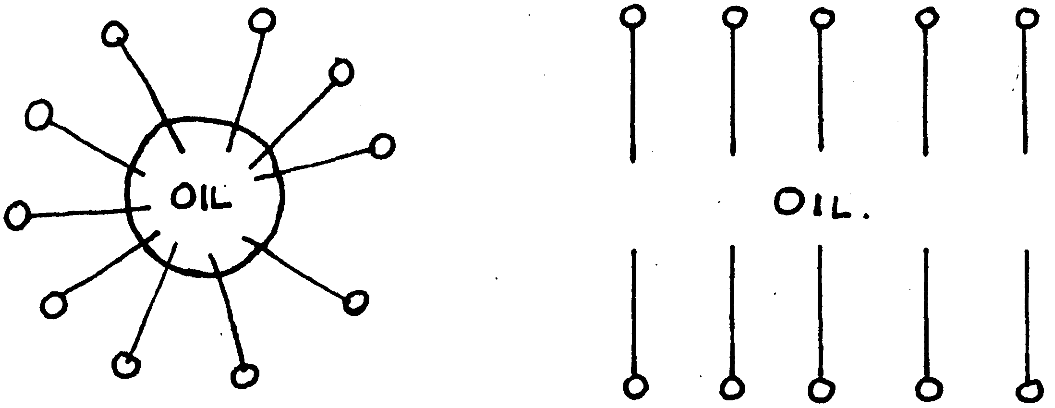
The view that there are two loci of solubilisation in the micelle has been confirmed experimentally by the work of Klevens (71). He found that the addition of hydrocarbons to aqueous solutions of paraffin-chain salts caused a larger amount of polar compounds to be solubilised. Also, he noted that addition of long-chain alcohols to aqueous solutions of paraffin-chain salts increased the solubility of hydrocarbons in the solutions.

Klevens has suggested that these results show that hydrocarbons are solubilised in the centre of the micelle and therefore increase the size of the micelle with the result that there is more available space in the palisade layer for the solubilisation of polar compounds. The penetration into the palisade layer by long-chain alcohols (polar solubilisation) increases the total energy of attraction in the micelle without a corresponding increase in the forces of repulsion (the mutual repulsion between the ionic heads of the solubilizer) with the resultant effect being the production of a micelle with a lower degree of order and hence a larger volume capable for solubilising hydrocarbons.

Adsorption on the exterior of the micelle has been suggested as a third form of solubilisation and was introduced (72) to explain the solubilisation of substances like dimethyl phthalate which is insoluble in water and in hydrocarbons. But Klevens (52) has pointed out that all compounds which are claimed to be adsorbed on the micelle are all semi-polar in nature and therefore has suggested that if sorption by the micelles occurs then it probably involves a slight penetration into the palisade layer of the micelle and consequently this type of solubilisation may be classed as a form of polar solubilisation.

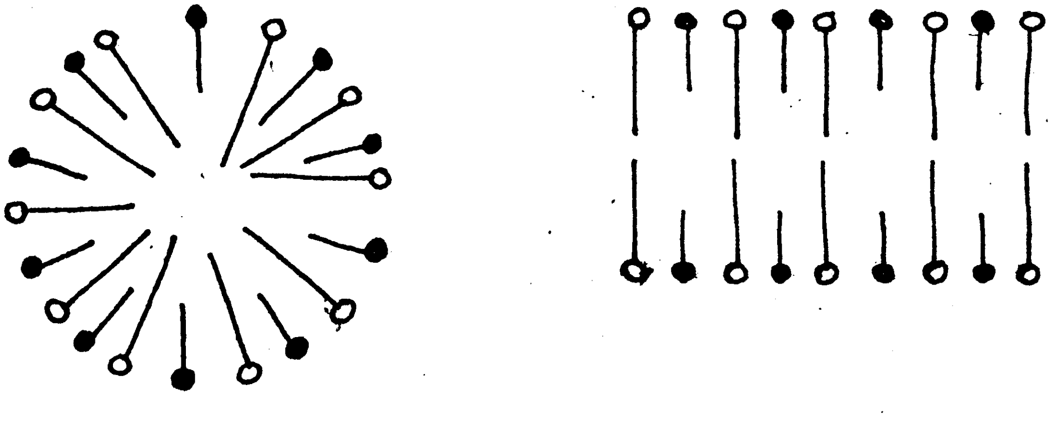
Figure 2 illustrates the two main types of solubilisation diagramatically. (Very idealised).

·· FIG. 2 ··



SOLUBILISATION OF NON-POLAR COMPOUND IN INTERIOR OF SPHERICAL MICELLE.

SOLUBILISATION OF NON-POLAR COMPOUND IN INTERIOR OF LAMELLAR MICELLE.



SOLUBILISATION OF POLAR COMPOUND IN PALISADE LAYER OF SPHERICAL MICELLE.

SOLUBILISATION OF POLAR COMPOUND IN PALISADE LAYER OF LAMELLAR MICELLE.

——○ = SOLUBILISER.

——● = SOLUBILISATE.

WINSOR'S INTERMICELLAR EQUILIBRIUM THEORY.

In a series of papers (73-79), Winsor has developed a very general theory to explain qualitatively the solubilisation of organic compounds in amphiphilic electrolytes and has shown that this general theory may be used to give an explanation on a micellar basis of the properties of aqueous solutions of paraffin-chain salts.

Winsor considers a system consisting of a paraffin-chain salt, water and a water-immiscible organic compound and he denotes the amphiphilic region by $\bar{C}$, the hydrophilic region (possibly containing inorganic ions etc.;) by $\bar{W}$ and the lipophilic region by $\bar{O}$.

He suggests that in this system the following molecular interactions take place. The molecular interactions promoting miscibility of $\bar{C}$ and $\bar{O}$ are,

$$A_{\bar{c}\bar{o}} = (A_{L\bar{c}\bar{o}} + A_{H\bar{c}\bar{o}})$$

where $A_{\bar{c}\bar{o}}$ is the affinity of $\bar{C}$ for $\bar{O}$. $A_{L\bar{c}\bar{o}}$ represents the interaction between the non-polar portions of the molecules (electrokinetic). The attractive force between the non-polar portions of the molecules is due to the movement of the electrons within the molecules because in neighbouring molecules these movements tend to become in phase with each other and therefore produce a mutual attraction. $A_{H\bar{c}\bar{o}}$ represents the interaction arising from the forces of polar character, between ions or dipoles, especially those due to hydrogen bonding. Similarly, the molecular interactions promoting miscibility between $\overline{C}$ and $\overline{W}$ are,

$$A_{\overline{c}\,\overline{w}} = (A_{H\,\overline{c}\,\overline{w}} + A_{L\,\overline{c}\,\overline{w}}).$$

Now, the molecular interactions opposing miscibility are $A_{\overline{o}\,\overline{o}}$, $A_{\overline{w}\,\overline{w}}$ and $A_{\overline{c}\,\overline{c}}$ which all promote segregation of the components either as separate phases or as regions of higher local concentration of these respective components (e.g. micelles) within their single phase solution.

For effective solubilisation, $\overline{C}$ must show a high co-solvency for $\overline{O}$ and $\overline{W}$. The greater $A_{\overline{c}\,\overline{o}}$ and $A_{\overline{c}\,\overline{w}}$ are, and the more equal they are, the higher will be the co-solvent effect of $\overline{C}$.

If $A_{\overline{c}\,\overline{o}} \ll A_{\overline{c}\,\overline{w}}$, then $\overline{W}$ will contain most of $\overline{C}$, and if $A_{\overline{c}\,\overline{w}} \ll A_{\overline{c}\,\overline{o}}$ then $\overline{O}$ will contain most of $\overline{C}$. Thus, $A_{\overline{c}\,\overline{w}}$ and $A_{\overline{c}\,\overline{o}}$ are respectively the tendencies for $\overline{C}$ to spread out into $\overline{W}$ (i.e. $\overline{C}$ becomes convex towards $\overline{W}$) and for $\overline{C}$ to spread into $\overline{O}$ (i.e. $\overline{C}$ becomes convex towards $\overline{O}$).

Therefore, the distribution of $\overline{C}$ in the system depends on the ratio of the tendency for $\overline{C}$ to spread into $\overline{O}$ to the tendency for $\overline{C}$ to spread into $\overline{W}$. Winsor has defined this ratio as being equal to R,

$$\text{i.e.} \quad R = \frac{\text{tendency of } \overline{C} \text{ to spread into } \overline{O}}{\text{tendency of } \overline{C} \text{ to spread into } \overline{W}}$$

$$\text{and he suggests that } R = \frac{A_{\overline{c}\,\overline{o}}}{A_{\overline{c}\,\overline{w}}} = \frac{A_{H\,\overline{c}\,\overline{o}} + A_{L\,\overline{c}\,\overline{o}}}{A_{H\,\overline{c}\,\overline{w}} + A_{L\,\overline{c}\,\overline{w}}}$$

and although Hartley (80) subsequently has pointed out that a more correct measure would be,

$$R = \frac{A_{\bar{C}\bar{O}} - A_{\bar{C}\bar{O}}}{A_{\bar{C}\bar{W}} - A_{\bar{W}\bar{W}}} = \frac{A_{H\bar{C}\bar{O}} + A_{L\bar{C}\bar{O}} - A_{H\bar{O}\bar{O}} - A_{L\bar{O}\bar{O}}}{A_{H\bar{C}\bar{W}} + A_{L\bar{C}\bar{W}} - A_{H\bar{W}\bar{W}} - A_{L\bar{W}\bar{W}}},$$

it has been found that, for a given $\bar{O}$ and $\bar{W}$, Winsor's formula and Hartley's formula give similar results and therefore, for normal use, Winsor's expression is usually employed.

Now, if the various molecular species within the system were arranged so that $A_{\bar{C}\bar{O}}$ and $A_{\bar{C}\bar{W}}$ were equal, then Winsor's ratio would be equal to unity, (i.e. $R = 1$) and $\bar{C}$ (amphiphilic region) would be neither convex towards $\bar{W}$ (hydrophilic region) nor towards $\bar{O}$ (lipophilic region). If $R < 1$, then $\bar{C}$ will become convex towards $\bar{W}$ while, if $R > 1$, then $\bar{C}$ will become convex towards $\bar{O}$.

In these systems, R is not regarded by Winsor as having one value throughout but that its value is changing from point to point and from time to time with thermal fluctuations in concentration due to the motions of the molecules. Thus $\bar{C}$ will be varying constantly in form due to these fluctuations with its convexity towards $\bar{O}$ or $\bar{W}$ depending on the mean value of R being greater or less than unity.

Winsor suggests that the micellar form existing in the system, where $R = 1$, would be laminar, consisting of alternate layers of water and bimolecular paraffin chain leaflets, with the centre of the micelle like a n-paraffin. The thickness of the leaflet would be equal to twice the extended length of the paraffin chain of the amphiphilic salt and the thickness of the water layer would depend on the concentration of water present. This type of micellar configuration has been termed by him the G phase.

When the mean value of R is moderately low (less than unity) the mean micellar form envisaged by Winsor is that of a spherical micelle S_1 corresponding to Hartley's spherical micelle while, at moderately high mean values of R (greater than unity), the micellar form is considered to be spherical S_2 with $\bar{C}$ being convex towards $\bar{O}$, corresponding to Schulman's lipophilic hydromicelle. (81)

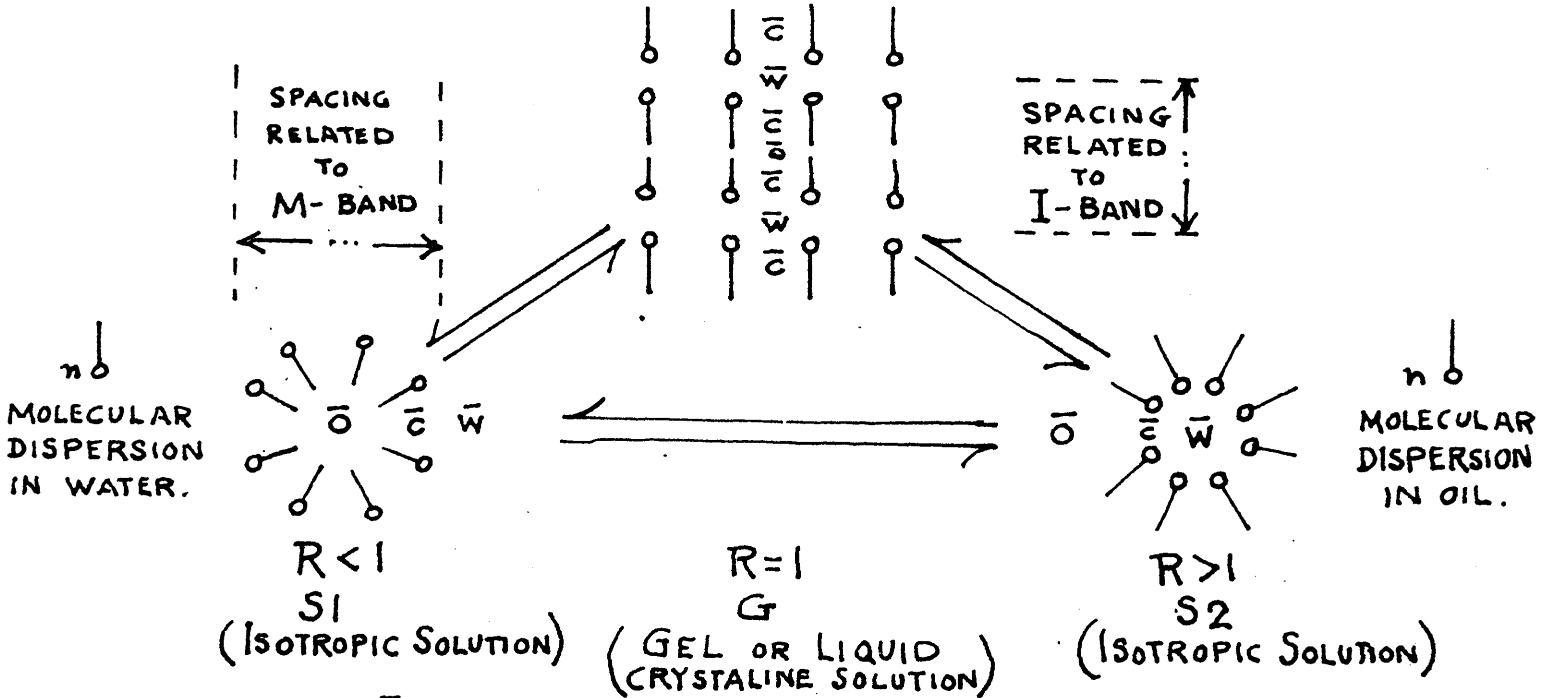
This intermicellar equilibrium is shown diagramatically in figure 3.

Winsor's intermicellar equilibrium may be used to explain the micellar form in systems of paraffin-chain salt and water by considering the ratio, R, varying as $A_{L\bar{c}\bar{o}} / A_{\bar{c}\bar{w}}$, where $\bar{C}$ is the paraffin-chain salt region and $\bar{W}$ is the hydrophilic region.

·· FIG. 3 ··

·· A DIAGRAMATIC REPRESENTATION OF WINSOR'S INTERMICELLAR EQUILIBRIUM. ··

SHOWING WINSOR'S SUGGESTED CORRELATION OF X-RAY DIFFRACTION BANDS.



$\bar{W}$ = HYDROPHILIC SECTION OF MICELLE.

$\bar{C}$ = AMPHIPHILIC SECTION OF MICELLE.

$\bar{O}$ = LIPOPHILIC SECTION OF MICELLE.

R = RATIO OF DISPERSING TENDENCIES ON LIPOPHILIC AND HYDROPHILIC SURFACES OF $\bar{C}$ RESPECTIVELY.

X-RAY MEASUREMENTS ON AQUEOUS SOLUTIONS OF PARAFFIN-CHAIN SALTS.

X-ray patterns in aqueous solutions of paraffin-chain salts will be produced by any regularly repeating distance between two regions in the solutions having electron densities which differ considerably from the average electron density. This distance may be, intramolecular (atoms within molecules), intramicellar (molecules or group of molecules within the micelles) or intermicellar (micelles within the solution).

There are three distinct characteristic bands in the X-ray diffraction of these solutions which are:

(1) S-band.
(2) M-band.
(3) I-band.

The S-band, or short spacing band, has been observed in many paraffin-chain salt solutions (82) and it was originally thought that this band related to the inter-hydrocarbon chain distance in a regularly constructed lamellar or "biscuit" micelle. But, as the S-band has also been detected in liquid n-primary alcohols, in liquid fatty acids and in n-paraffins (83), it is now generally agreed that the S-band is characteristic of normal liquid paraffin chains.

The M-band at first was identified by Harkins (61) and (82) with the thickness of the Harkins' "biscuit" micelle (i.e. twice the length of the paraffin chain) but, now it is considered that the M-band can be correlated with the diameter of the spherical micelle. In dilute solutions of aqueous paraffin-chain salts, solubilisation of hydrocarbon causes an expansion in the M-band. This is interpreted as showing that the solubilisation of hydrocarbon is in the centre of the micelle and causes an increase in its diameter. From the X-ray work of Harkins (82), Winsor has observed that, at a high concentration of amphiphilic salt, the solubilisation of hydrocarbon causes the expansion of the M-band to decrease and he has suggested that this is experimental proof of his intermicellar equilibrium theory. According to Winsor's theory, an increase in concentration of paraffin-chain salt displaces the intermicellar equilibrium to the right with the formation of the G phase. Now, hydrocarbon will dissolve preferentially in the G micelle with a smaller proportion dissolved in the S_1 micelle. Therefore, as the M-band measures the diameter of the S_1 micelle, the expansion of the M-band, owing to the solubilisation of hydrocarbon, would be greater in the lower, than in the higher, concentrations of amphiphilic salt.

The I-band spacing of aqueous solutions of paraffin-chain salts is found to increase on solubilisation of hydrocarbon and on dilution with water. Both these effects were interpreted by Hess et al (55-58) as being consistent with the view that the micelles in an aqueous solution of a paraffin-chain salt were lamellar. However, it was found that, although the expansion of the I-band caused by the solubilisation of benzene in potassium oleate solution corresponded with that calculated for a lamellar micelle, the expansion with other hydrocarbons and other amphiphilic salts could not be correlated with this micellar form.

In 1946, Bernal (84) pointed out that the expansion of the I-band spacing by water was smaller than would be expected if all the water entered between the double-layers in the lamellar micelle and therefore he suggested that the micelle would have to be separated by a greater lateral depth of water than that which it held between its ionic faces.

Due to these criticisms the interpretation of the I-band in terms of a double-layer spacing in the lamellar micelle was discarded by many investigators. Another explanation of the I-band was put forward by Hartley (85) who considered that in fairly concentrated solutions, the repulsive effects between spherical micelles would give rise to an almost regular structure which would produce the I-band.

The interpretation of the I-band on the basis of the inter-double-layer spacing in a lamellar micelle was maintained by McBain as he considered the objections to be due to variations in the distribution of the components between his two micellar forms (ionic and lamellar).

Winsor (47) has postulated that the I-band is related to the mean inter-double-layer distance in his G micelles, which he regards as being in equilibrium with either or both

S_1 and S_2 micellar forms.

A great deal of valuable information about aqueous solutions of paraffin-chain salts has been obtained from X-ray measurements but owing to the difficulty of interpreting the results it is not possible to obtain a complete understanding of the micellar forms existing in these solutions from X-ray studies alone.

LIGHT SCATTERING MEASUREMENTS ON AQUEOUS SOLUTIONS OF PARAFFIN-CHAIN SALTS.

The light scattering effect in colloidal solutions depends mainly on the interference effect originating at the suspended particles. If the particles are small compared with the wavelength of the incident light, each acts as a point source and the scattering depends largely on the microscopic heterogeneity of the solution.

Debye (86) has made use of this fact and has attempted to estimate the micellar weight of several cationic paraffin-chain salts by measuring the light scattered. The micellar weights obtained by Debye were not consistent with an invariable spherical micelle but could be interpreted in terms of a cylindrical micelle. As his measurements were carried out in the presence of inorganic salts, it is possible that cylindrical micelles may have been produced by the inorganic ions.

In 1951, Debye and Anacker (87) attempted to obtain information on the micellar shape by measurement of the dissymmetry in the intensity of the scattered light. In order to do this, it was necessary for them to use long chain paraffin-chain salts and to add large quantities of inorganic salts and thus the full significance of the results was difficult to appreciate.

Tartar (88) and (89) using light scattering techniques, measured the micellar weight of several cationic paraffin-chain salts and he found that his results were consistent with a spherical micelle which had an interior of radius equal to the maximum length of the hydrocarbon portion of the paraffin-chain salt. His data on alkyl pyridinium bromide indicated that the radius of the spherical micelle is equal to the alkyl chain length. This suggested that the benzene ring must be situated on the surface of the micelle. Also, Tartar observed that the area of the polar head at the surface of the hydrocarbon interior is approximately 66 sq.Å which shows that in micellar systems there is a considerable interface between hydrocarbon and water.

During the last decade many light scattering measurements have been carried out on aqueous solutions of paraffin-chain salts and, although considerable information has been obtained, as yet, no complete picture of the micellar system has evolved.

VISCO-ELASTIC SOLUTIONS OF AQUEOUS PARAFFIN-CHAIN SALTS.

There are many solutions of paraffin-chain salts which possess a very high viscosity, but there are few which display a pronounced elastic behaviour. Perhaps the best known example is an aqueous solution of ammonium oleate. It was found that, if an aqueous solution of ammonium oleate of about 0.005M was caused to rotate and the rotating force stopped the solution would, at first, continue to rotate under its own momentum for a short time and then rotate in the reverse direction. This showed a kind of elastic recoil.

Hatschek and Jane (90) studied these ammonium oleate solutions in a Couette viscometer and found that, when the outer cylinder was rotated at a constant angular velocity, the torque on the inner one, after a short period increased to an irregularly fluctuating value. After a period of rest, this experiment was repeated and similar results observed. It seemed that a gelatinous structure was actually built up by the process of shear and dissipated again at rest. Later, in 1926, Andrade and Lewis (91) showed that the anomalous increase of torque with a solution of ammonium oleate was associated with the onset of turbulence. But in 1938, Hartley pointed out that the turbulence itself was anomalous, was of abnormal appearance, and was the result of the structure built up, rather than the direct cause of the increased torque.

Hartley (92) has observed a similar visco-elastic behaviour in a o.02% solution of copper salt p-hexa decoxybenzene sulphonic acid at 80-90 °C and he suggested that this system possessed the property of NEGATIVE THIXOTROPY.

Aqueous solutions of several paraffin-chain salts showed visco-elasticity in the presence of sufficient inorganic salt and Pilpel (93) has suggested that the visco-elasticity is caused by the formation of linear micelles. Also, he (94) has shown that a typical visco-elastic solution of paraffin-chain salt appears to show much the same mechanical behaviour as other types of visco-elastic solutions such as polymethyl methacrylate in toluene.

Several research workers (95-102) have observed that the addition of certain benzene derivatives to aqueous solutions of paraffin-chain salts produced visco-elastic systems.

Winsor (47) has discussed the nature of these visco-elastic aqueous paraffin-chain salt solutions and has attempted to explain their properties by means of his theory of intermicellar equilibrium. He considers the reason these systems display visco-elastic properties is that they consist of intimate emulsions of (S + G) phases which, when stirred, form a finely dispersed emulsion and which revert to a coarse dispersion when stirring stops.

Lawrence (49) suggested that the visco-elastic properties of paraffin-chain salt solutions are due to the production of 'SECONDARY MICELLES' or aggregates of Hartley micelles, which are created by the formation of a crystal type lattice between the polar groups on the surface of adjacent micelles.

GENERAL INTRODUCTION.

GENERAL INTRODUCTION

THE VISCO-ELASTIC SOLUTIONS FORMED BY THE ADDITION OF ORGANIC COMPOUNDS TO AQUEOUS SOLUTIONS OF CETYL TRIMETHYL AMMONIUM BROMIDE.

It was observed in these laboratories (100) that, on adding phenol to an aqueous solution of cetyl trimethyl ammonium bromide (C.T.A.B.), the viscosity rose to a maximum and then fell to a minimum before finally showing an almost linear rise. This led Walker (100) to examine the system of C.T.A.B. and sodium salicylate in water. This solution had a viscosity, measured by the "time of flow" through an ostwald viscometer which was vastly greater than anything hitherto encountered. It was noticeable that this system displayed elastic properties.

Subsequently the viscosity of a large number of C.T.A.B. solutions containing different types of benzoate derivatives were measured with an ostwald viscometer. The curves of viscosity vs. concentration of benzoate derivatives were similar, in that, with increase in concentration of organic electrolyte to a fixed amount of C.T.A.B., the viscosity first rose to a maximum and then showed a steep decline.

The principal results were obtained using a 2.7×10^{-2}M concentration of C.T.A.B. in water and all the additives were sodium salts. It was found that the concentration of additive and the value of the viscosity at the maximum were characteristic of each organic electrolyte. Also, it was observed that even isomers of the same organic electrolyte gave maxima of different viscosities and that some isomers produced no observable maxima. For example, when using chlorobenzoate, the para isomer produced a large maximum and the meta only about half that of the para compound, while the ortho isomer gave no observable maximum. Similar results were observed with the isomers of toluate. The ortho isomers of benzene dicarboxylate and of aminobenzoate were the only isomers of these compounds to give a maximum while, in the case of nitrobenzoate, it was only the para isomer that produced a maximum.

Walker found that sodium salicylate had an outstanding effect on the viscous behaviour of aqueous 1% C.T.A.B. (2.7×10^{-2}M). The curve of viscosity vs concentration of additive had two maxima, the one at lower concentration, was over a small range and had a very high viscosity while the other, at higher concentration, was over a large range and gave a viscosity of lower value.

The spectacular curve of viscosity vs concentration of sodium salicylate induced Walker to determine the curves for sodium 2.4 and 2.6 dihydroxy benzoates (a hydroxy group in the '4' or '6' position of the salicylate ion). He discovered the curve produced by 2.4 dihydroxy benzoate had one small viscosity maximum, but that the 2.6 dihydroxy benzoate produced two viscosity maxima. These were comparable in viscosity value with those produced by sodium salicylate but occurred at a lower concentration of additive. Also, it was observed that sodium 2.4 dichlorobenzoate gave only one maximum in the curve of viscosity vs concentration of additive, while 3.4 dichlorobenzoate gave two maxima.

All additives which Walker found capable of producing maxima in the curves of viscosity vs concentration of additive to 1% C.T.A.B. were benzene derivatives. This prompted him to investigate additives containing no benzene ring. As valerate is an anion whose length is approximately equal to that of the benzoate anion, sodium valerate was added, but it failed to produce any effect. This seemed to indicate that the presence of the benzene ring is essential to the production of this viscous behaviour. Also, it had been noted that all additives producing maxima in viscosity, besides possessing a benzene ring had polar groups attached directly to the ring. Thus phenyl acetate was added to discover if this position for the polar group was essential to produce a viscosity maximum. Phenyl acetate on being added to aqueous solutions of 1% C.T.A.B. produced no maximum. So it appeared from Walker's work that the additive to 1% C.T.A.B. must possess a polar group attached directly to a benzene ring in order to give a viscosity maximum.

Measurements, other than viscosity, have been made on these systems of C.T.A.B. + organic additive in water.

Good and Milloy (99) have shown that the partial pressure of phenol above a system of C.T.A.B. + phenol in water deviated from ideal behaviour over the same concentration range of phenol in which the rapid increase and decrease in viscosity occurred. Also, Walker (100) found that the addition of phenol caused a decrease in the C.M.C. of C.T.A.B. and that there was a marked point of inflexion at the phenol concentration which produced with 1% C.T.A.B. the viscosity maximum. But, he observed that the addition of sodium salicylate caused the C.M.C. of C.T.A.B. to decrease to a minimum and then to increase to a value much higher than the initial value.

Ferguson (101) has studied the effect of seven benzoic acid salts on the amount of the C.T.A. cation adsorbed on alumina and he found qualitatively, that the order in which these salts increased the viscosity of C.T.A.B. solutions was respectively maintained by each salt in increasing the adsorption of the C.T.A. cation on alumina.

Besides adsorption measurements, Ferguson has measured the activity coefficient of the bromide ion in aqueous C.T.A.B. solutions containing six benzoic acid salts and he found that the salts increased the activity of the bromide ion in the same order as they produced large values of viscosity maxima. A study of the elasticity of aqueous solutions of C.T.A.B. (1.35×10^{-2}M) containing sodium salicylate showed that the concentration of sodium salicylate which produced a maximum in viscosity also produced a maximum in elasticity but while an increase in concentration of sodium salicylate caused a decrease in viscosity, the elasticity remained approximately constant.

Ferguson considered that his results showed that there is an interaction between the C.T.A. cation and the salicylate ion in aqueous solution which leads to the formation of threadlike micelles and to larger three dimensional aggregates composed of units of threadlike micelles. He envisaged that the threadlike micelles are responsible for the elasticity and that the three dimensional aggregates produce the viscous properties.

Nash (98) and (102) has observed that visco-elastic systems were produced by the addition of naphthols (α, β or dihydroxy) to aqueous solutions of C.T.A.B. He found that at 18°C the most visco-elastic system consisted of equimolar quantities of naphthol and C.T.A.B. Nash noted that these systems possessed variable viscosity which increased as the shearing force decreased. Also, he found that the systems appeared to "thicken" on the addition of various inorganic anions and that the addition of aliphatic alcohols destroyed completely the visco-elasticity in the system.

Nash has suggested that the visco-elastic properties may be due to the existence of positively charged micellar filaments within these systems.

To obtain a better understanding of these systems of aqueous solutions of C.T.A.B. containing benzene derivatives which have polar groups attached to the benzene nucleus, it was decided to investigate the effect on the viscous properties of 1% C.T.A.B. (2.7×10^{-2}M) due to the addition of phenolic compounds.

The first part of this work is devoted to this investigation.

PART I

THE EFFECT ON THE VISCOUS PROPERTIES OF 1% C.T.A.B. DUE TO THE ADDITION OF PHENOLIC COMPOUNDS

INTRODUCTION

Definition of Viscosity.

The viscosity of a liquid system can be defined as the force per unit area necessary to maintain a unit velocity gradient between two parallel planes which are kept a unit distance apart,

$$\text{i.e.} \qquad z = T/\left(\frac{dv}{dx}\right)$$

where T = force per unit area acting parallel to the planes = shearing force, dv/dx = velocity gradient perpendicular to the planes, z = viscosity coefficient of the liquid system.

The above equation was postulated by Newton and therefore any liquid system which obeys this law (i.e. shearing force proportional to velocity gradient) is known as a Newtonian system while any system which does not obey the law is described as being non-Newtonian, or said to possess Structural Viscosity.

This latter term was derived from the work of Ostwald (103) on the viscosity of "emulsoids" and it was intended to account for the effect on viscosity of an ordered structure existing within a liquid system. He suggested that structural viscosity may be due to the overlapping of the solvent envelopes which surround most colloidal particles.

EFFECT ON VISCOSITY OF THE ADDITION OF PHENOLS TO AQUEOUS SOLUTIONS OF PARAFFIN-CHAIN SALTS.

The viscosity of aqueous solutions of paraffin-chain salts in the presence of phenols was first investigated by Bourlet and Thomas (104) who claimed that, while the addition of phenol to potassium paraffin-chain salts caused the viscosity to rise, it produced a fall with sodium paraffin-chain salts. Repetition of these experiments by Angelescu and Popescu (105), using pure potassium and sodium paraffin-chain salts, disclosed that there existed scarcely any difference in the behaviour of the palmitate salts although there was a big difference with the oleate salts. In the same paper, Angelescu and Popescu describe the effect of adding increasing amounts of phenol or cresol to each of the following salts, sodium, potassium, lithium and ammonium salts of palmitic, stearic and oleic acids. In general, they found that the addition of cresol to all sodium oleate solutions, above a certain concentration, caused the viscosity to rise to a maximum and then to fall to a minimum before finally showing an almost linear rise. With increase in oleate concentration the maximum became more pronounced, but below a certain concentration of soap, the viscosity showed no observable maximum, as there was a continuous rise in viscosity with cresol concentration. The palmitate soap was found to exhibit a similar behaviour but the concentration of palmitate at which the occurrence of maximum was first observed, was considerably higher than that for oleate.

Angelescu and Popescu have suggested that the almost linear change in viscosity, in higher cresol concentration ranges, may indicate that these systems contain no "colloidal" particles, while over the concentration range, in which there is first an increase and then a decrease in viscosity, the systems are of a colloidal character. These authors considered the possibility that cresol may act as an acid, liberating the fatty acid from the soap and, that this fatty acid may then combine with the unchanged soap to form an acid soap whose colloidal character will cause the viscosity to rise. This explanation could not be accepted by them because it failed to explain the subsequent fall in viscosity accompanying further addition of cresol, or why all acids could not produce a pronounced increase in viscosity and why the maximum in viscosity disappeared as the concentration of soap decreased. Thus, the explanation of the viscosity as being due to acidic properties of cresol was discarded.

This led Angelescu and Popescu to suggest that cresol may have a dispersive action on aggregates and therefore the explanation of the viscosity maximum may be found in Ostwald's hypothesis (103) that the viscosity is greatest when the dispersoid attains a mean dispersion.

After studying the effect of other phenolic compounds on the viscosity of soap solutions, Angelescu and Manolescu (97) attributed the shape of the curve of viscosity against concentration of additive for these systems of soap + phenolic compound + water to be the combined result of:-

(a) "Outer Solvation" in which the polar molecules attach themselves to the soap ions forming an aggregate which orientates itself in accordance with the electric field.

(b) "Inner Solvation" where the dipolar molecules penetrate into the interior of the micelle and produce a pronounced swelling.

They pointed out that the controlling facter in (a) is the dipole moment of the "solvating liquid" (water + phenolic compound) while for (b) the solubility of the "solvating liquid" in the paraffinic interior of the micelle is the active factor.

In general, Angelescu and his collaborators failed to find any direct parallel between dipole moment and the effect on the viscosity but they found that the isomer with the highest dipole moment invariably produced the highest viscosity maximum. This they assumed, confirmed the "outer solvation" as a factor influencing the viscosity.

In 1941, Philipoff (106) observed that the addition of meta-cresol to a 0.435N sodium oleate solution produced a maximum in relative viscosity at a concentration of 3% meta-cresol and he also noted that, at this concentration, the system showed marked structural viscosity.

Determination of Viscosity.

A convenient method of determining the viscosity of a liquid system is to measure its rate of flow through a capillary tube.

If it is assumed that;

(1) every particle of the liquid system moves parallel to the axis (i.e. flow is streamlined),

(2) pressure is constant ovdr any cross-section (i.e. no radial flow),

(3) liquid in contact with the wall of the tube is at rest,

(4) the viscous resistance is proportional to the velocity of the liquid,

then, for steady flow, the force tending to retard the flow of the liquid system is balanced by the force causing it to flow.

$$\begin{aligned} \text{i.e.}\quad -z\,du/dr\ (\text{area}) \quad &= \pi\, r^2 P \\ (\text{retarding force}) \quad &= (\text{force causing motion}) \\ -z\,du/dr.\ 2\pi r l \quad &= \pi\, r^2 P \end{aligned}$$

where z = viscosity coefficient, u = velocity of the liquid at a distance r from the axis, l = length of the tube and P = the pressure difference.

$$\therefore \quad du/dr = -r.P/2.z.l.$$

Now, if the radius of the capillary tube is a, then at the wall of the tube r = a and u = o (because it has been assumed that the liquid at the tube wall is stationary).

$$\therefore u = \frac{P}{4zl}(a^2 - r^2).$$

Now, the volume of liquid flowing per unit time between r and r + dr is given by $2\pi r u . dr$, hence the total volume of liquid flowing through the tube per second (Q)

$$Q = \int_0^a 2\pi r u . dr$$

then substituting for u it can be shown that

$$Q = \frac{\pi . P . a^4}{8 . z . l} .$$

Thus for a certain apparatus, the slope of the curve of Q vs. P is a measure of the viscosity of the liquid system. If the apparatus is so designed that a constant volume of liquid flows through the capillary under the influence of a constant change in head of liquid, then the product of the time of flow (i.e. the time a constant volume of liquid takes to flow completely through the tube) and the density is proportional to the viscosity of the system.

$$z = k . d . t.$$

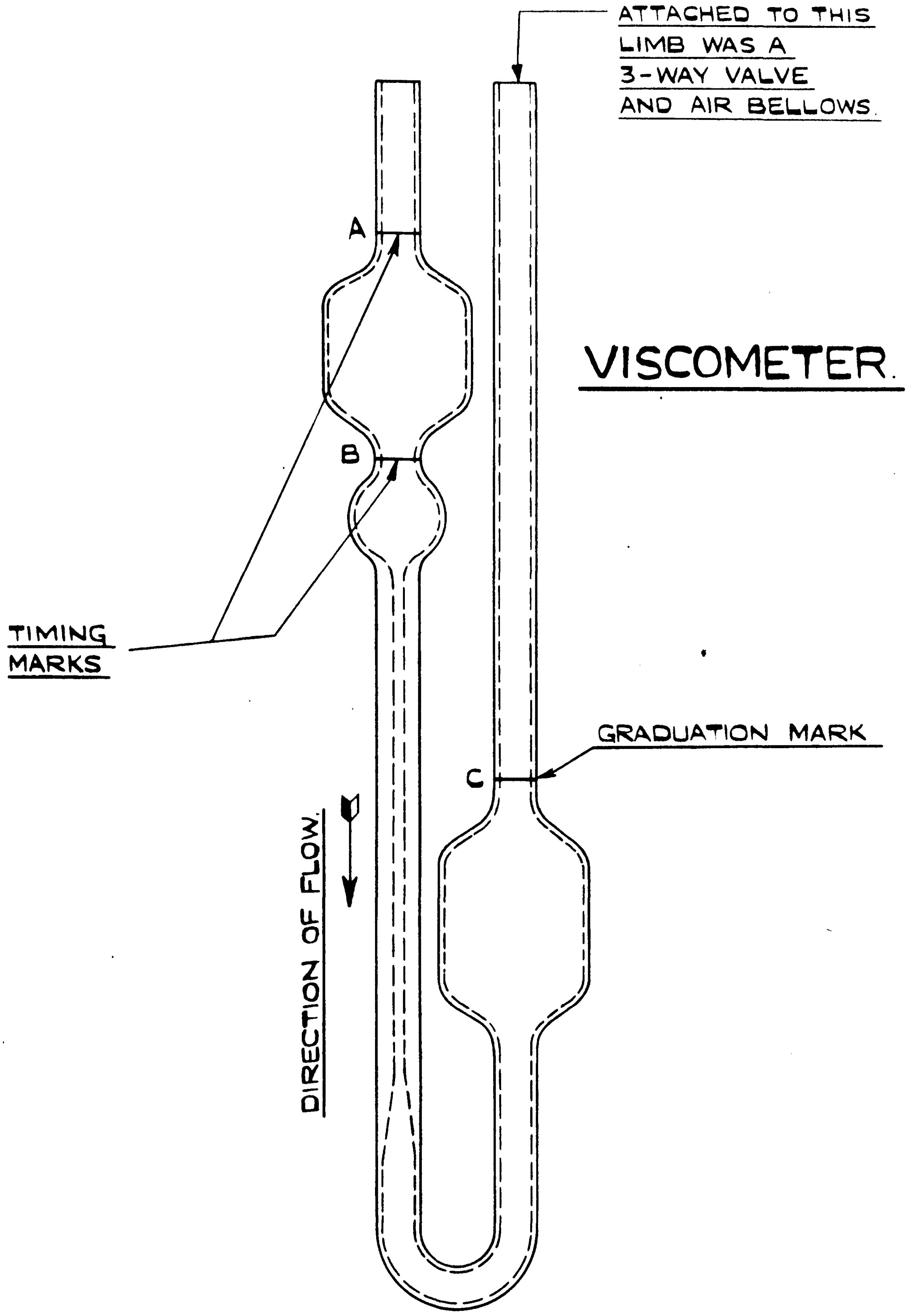
where d = density, t = time of flow and k = a constant for apparatus. Such an apparatus is an Ostwald Viscometer.

SECTION A

Section A of this work is devoted to a study of the changes in viscous properties due to the addition of phenolic compounds to aqueous solutions of 1% C.T.A.B. These changes are measured in an Ostwald Viscometer.

Apparatus Used.

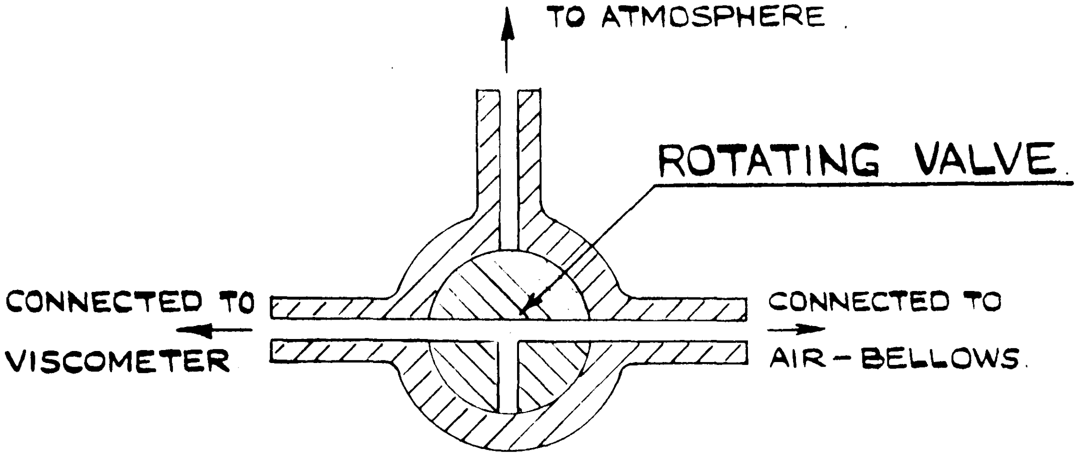
Two ostwald-type viscometers were used as measuring instruments. These viscometers were designated I (smaller diameter of capillary bore) and II (larger diameter of capillary bore). A diagram of an ostwald-type viscometer is shown in figure 4. The left-hand limb of the U-tube is essentially a pipette with two timing marks (A and B) between which the flow of liquid is timed. The time of flow of liquid is influenced by the resistance due to the size of the bore of the capillary in the left-hand limb. A constant volume of solution was used for each measurement by filling the viscometer to the graduation mark, C, on the right-hand limb. When setting up the viscometer it was fastened in a vertical position, in a glass-sided water bath so that its liquid level always remained below the bath water level. The water in the bath was kept constantly stirred by an electric stirrer and was thermostatically controlled to within ± 0.1 °C at 25°C. A three way valve, see figure 5, was attached to right-hand limb of the viscometer for the purpose of controlling the air pressure in it.



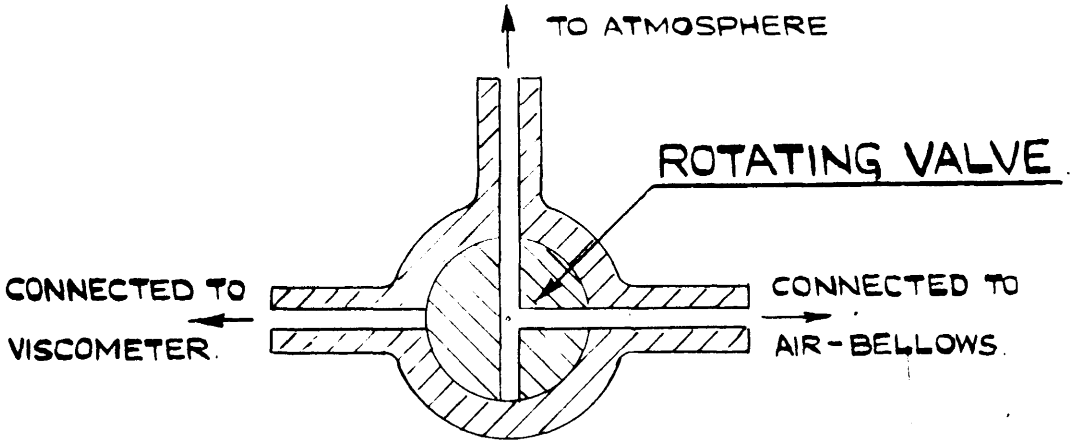
VISCOMETER.

FIG. 4.

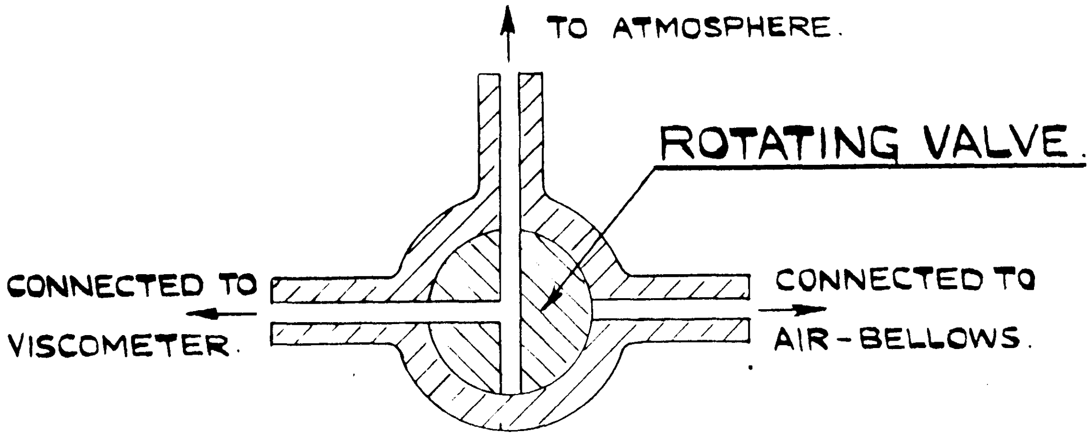
3-WAY VALVE



POSITION (1)



POSITION (2)



POSITION (3)

FIG 5.

With the valve in:-

Position 1 the air pressure in the limb could be increased by means of air bellows.

Position 2 the limb was sealed off and thereby the air pressure in it remained constant.

Position 3 the right-hand limb was open to atmospheric pressure.

Preparation of the Solutions.

1% C.T.A.B.

A 1% C.T.A.B. (cetyl trimethyl ammonium bromide) solution means 1 gm. of C.T.A.B. in 100 ml. of water (2.7 X 10^{-2}M). The C.T.A.B. was weighed out and washed into warm water at 30°C and the subsequent solution made up to a litre at 25°C. This solution was then placed in a thermostatically controlled water bath at 30°C for 12 hours before being stored at 25°C. The reason the C.T.A.B. was dissolved at 30°C was because it dissolves very slowly in water at 25°C.

The Addition of Phenolic Compound to 1% C.T.A.B.

The phenolic compound, if solid, was weighed out, if liquid, it was measured out by a micro burette and dissolved at 25°C in the prepared 1% C.T.A.B. solution. The resultant solution was then placed in a water bath at 30°C for 12 hours to ensure that there were no non-homogeneous regions in it and then stored at 25°C.

The Procedure in Measuring the Time of Flow.

Before use, the viscometer was thoroughly cleansed with warm water in order to free the capillary from any obstructions which might interfere with the flow of the liquid, If this procedure did not remove all the visible obstructions, then the viscometer was washed with chromic acid, followed by several washings with distilled water. Once the viscometer appeared to be thoroughly cleaned, it was rinsed with the particular liquid whose time of flow was to be measured.

The viscometer was filled to the graduation mark, C, by means of a pipette, which had been previously washed with the solution. To ensure uniformity of temperature, the solution was allowed to stand in the viscometer for one hour, beford any measurements were taken.

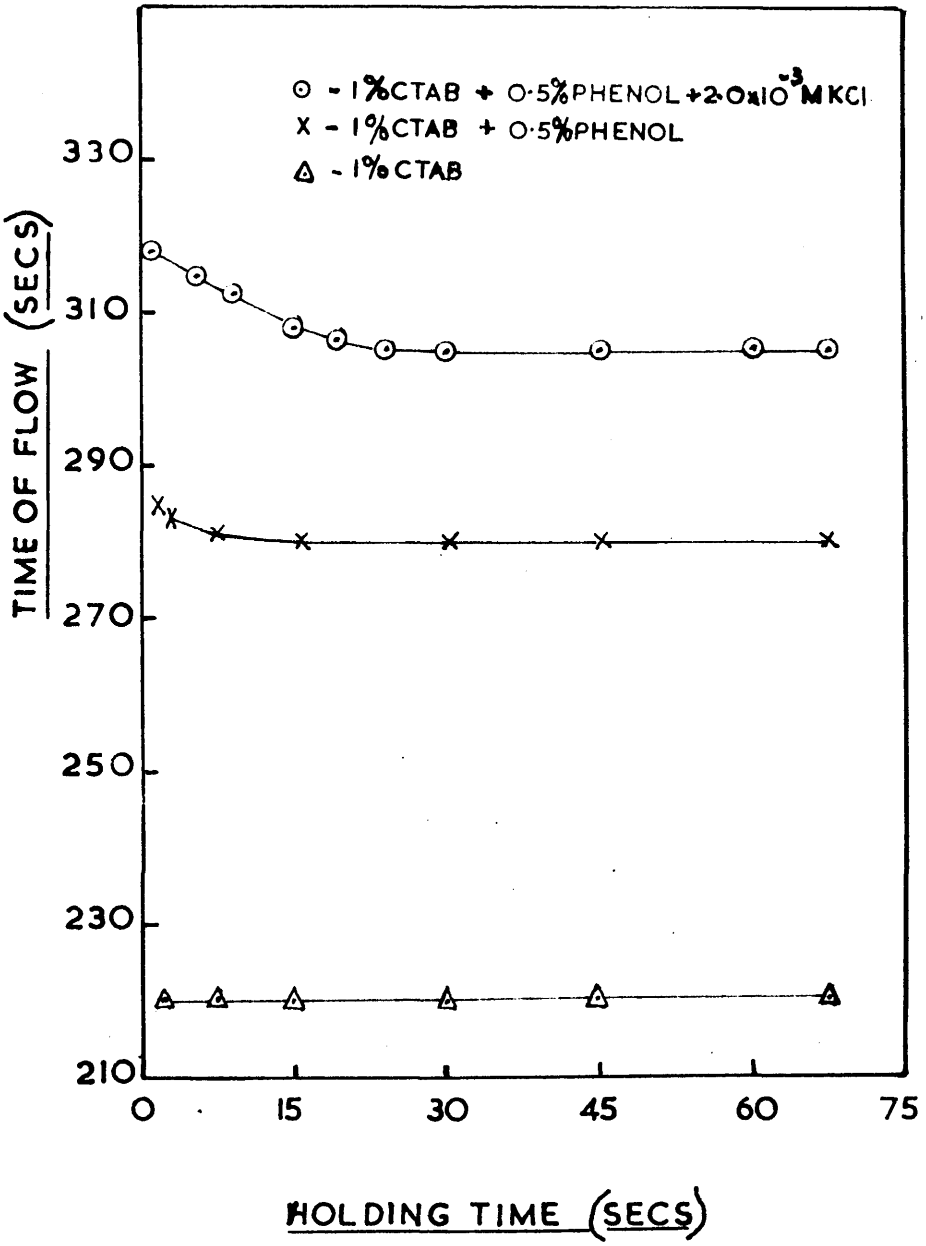
To measure the time of flow an air pressure was applied to the right-hand limb which caused the liquid to be forced up the left-hand limb to just above the timing mark, A. This procedure took approximately 5 seconds. Thereupon the air pressure was released and the time taken for the outflow of the solution from the timing marks A to B (see figure 4) was measured by a stop watch to ± 0.1 seconds. This was termed the <u>time of flow</u> of the solution. The measurements were repeated several times until three readings agreed. During these measurements care was taken that the solution in the viscometer was always below the water level in the thermostatic bath.

This method of measuring the time of flow of a liquid system was found to be very satisfactory for water and for 1% C.T.A.B. solution but for certain systems of 1% C.T.A.B. containing phenol great difficulty was experienced in obtaining reproducible results. It was found that, if the liquid was forced up the left-hand limb to above the timing mark, A, and then released immediately, the time of flow was greater than what was obtained when the same solution had been held for some time above the timing mark before being released. This meant that for these liquid systems of 1% C.T.A.B. + phenol the time of flow was a function of the holding time, (i.e. the period of time the liquid was held above the timing mark, A, before being released).

A study of the variation in time of flow with holding time was made using several systems and the results are plotted in figure 6 where it can be seen that the time of flow of a 1% C.T.A.B. system is independent of the holding time while the time of flow of a 1% C.T.A.B. + 0.5% phenol system decreases with holding time up to 15 seconds and thereafter remains constant. Also shown is that the time of flow of 1% C.T.A.B. + 0.5% phenol containing 2 X 10^{-3} moles/litre of potassium chloride decreases with holding time up to 20 seconds and, at greater holding times it is constant.

FIG 6

VARIATION IN TIME OF FLOW THROUGH VISCOMETER I WITH HOLDING TIME



From this information, it is obvious that the procedure for determining a characteristic time of flow of 1% C.T.A.B. systems, containing phenolic compounds, must allow for this effect and consequently the method for measuring the time of flow was modified to ensure a standard holding time. To force the liquid up the left-hand limb the 3-way valve was adjusted to position 1 allowing the air to pass from the bellows into the right-hand limb causing the liquid to be forced up the left-hand limb. When the liquid level was above the timing mark, A, the valve was placed in position 2 which closed the right-hand limb of the viscometer and thus kept the liquid level static for a specific holding time. Thereafter, the valve was turned to position 3 to open the right-hand limb to the atmosphere which released the liquid, and the time of flow was measured with a stop-watch.

Experimental Results.

From the work of Walker (100) it was known that 1% C.T.A.B. solutions containing certain concentrations of phenol were non-Newtonian in character and therefore not much significance could be attached to a coefficient of viscosity. A measure of the relative viscous properties of the systems was obtained by comparing their times of flow through the same viscometer.

The Addition of Phenol to 1% C.T.A.B.

The first investigation was to study the change in viscous properties caused by the addition of phenol to

1% C.T.A.B. system. The times of flow of 1% C.T.A.B. systems, containing various amounts of phenol, were determined in viscometer II with a holding time of 30 seconds.

The plot of the time of flow against concentration of phenol is shown in figure 7. It can be seen that, with increase in phenol concentration, the time of flow rises to a maximum at 0.5% and that the addition of more phenol causes it to decrease to a minimum at approximately 1.2% and thereafter with increase in phenol concentration the time of flow increases linearly. Also shown in figure 7 is the plot of the time of flow of phenol in water systems against concentration of phenol.

These plots obtained with phenol were similar to those reported previously by Good (99) and Walker (100).

Addition of Cresols to 1% C.T.A.B.

To obtain a clearer understanding of systems of phenol in 1% C.T.A.B. it was decided to investigate the change in viscous properties when cresols are added to 1% C.T.A.B.

It was found, as shown in figure 8, that the time of flow of a 1% C.T.A.B. system increased with the addition of p-cresol and reached a maximum at a concentration of approximately 0.4%. Further additions of p-cresol caused the time of flow to decrease. The value of the maximum time of flow varied with holding time, although the general shape of the curve remained constant.

• • FIG 7 • •

EFFECT OF THE ADDITION OF PHENOL ON THE TIME OF FLOW THROUGH VISCOMETER II

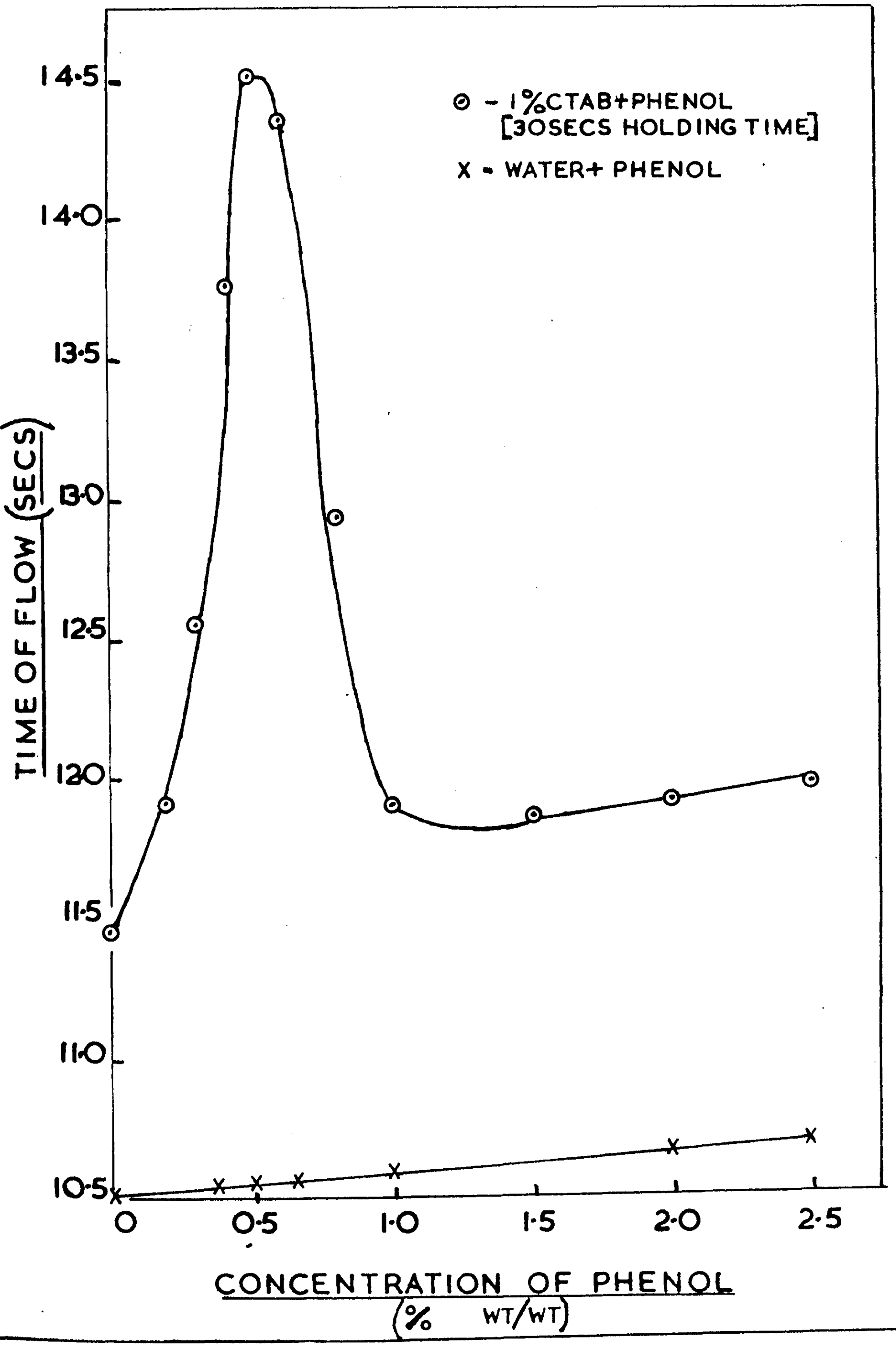
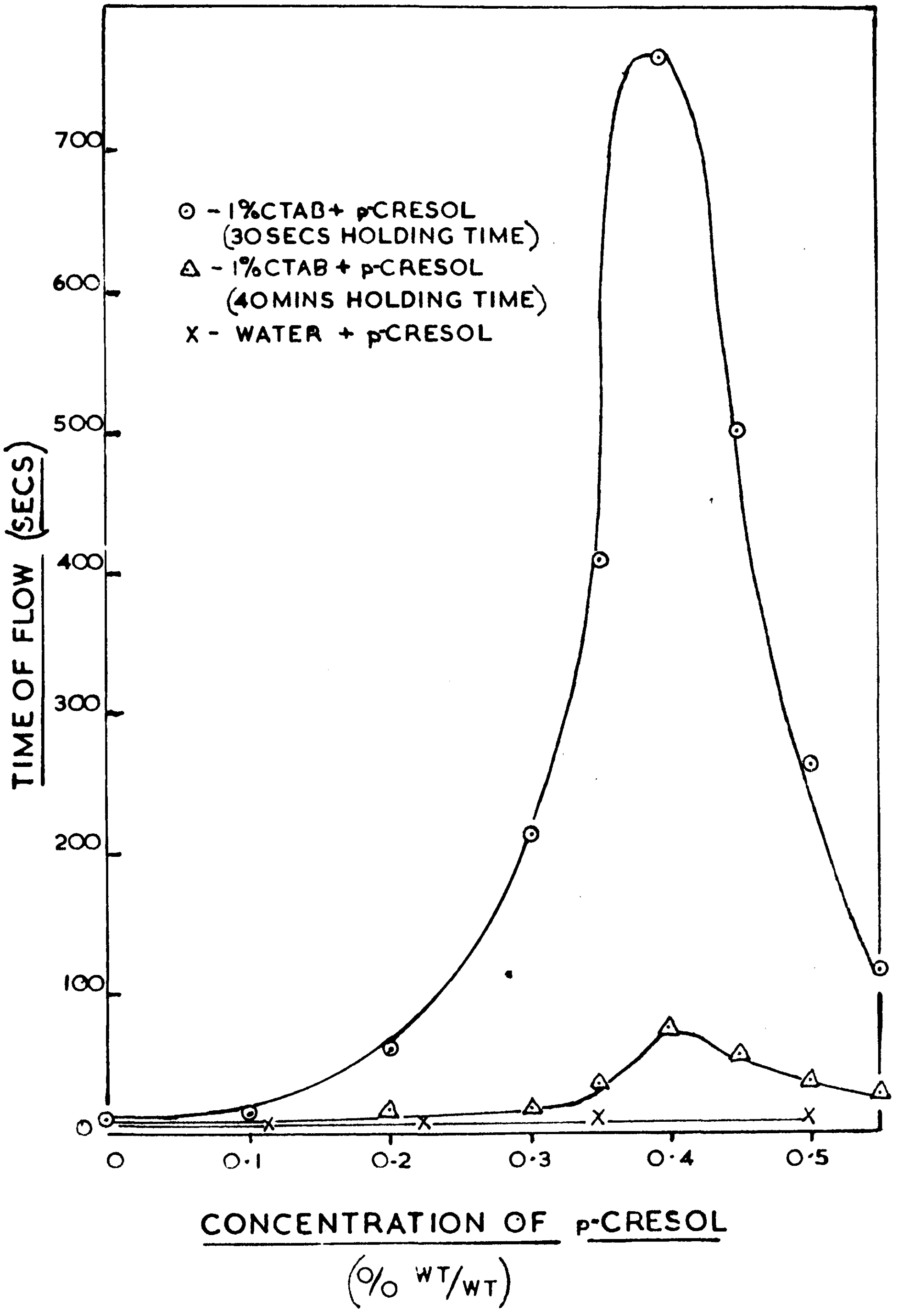


FIG 8

EFFECT OF THE ADDITION OF p-CRESOL ON THE TIME OF FLOW THROUGH VISCOMETER II

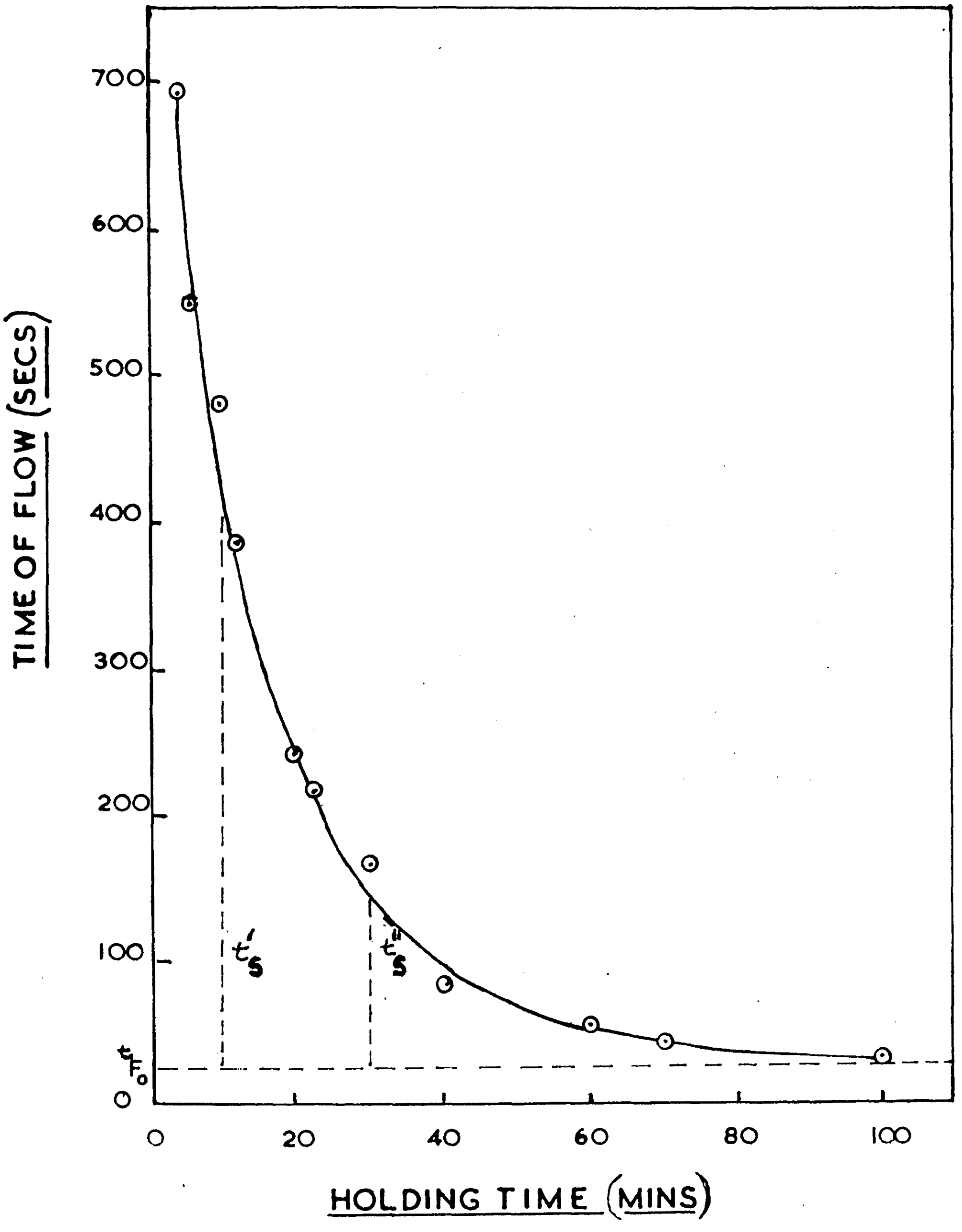


A plot for a 1% C.T.A.B. + 0.4% p-cresol system of time of flow through viscometer II against holding time is shown in figure 9. It can be seen that, as the holding time increases, the time of flow decreases, with the rate of decrease in time of flow being very rapid at small holding times but, with increase in holding time, the rate of decrease in time of flow becomes less. Thus, since the time of flow varied with holding time, the times of flow for 1% C.T.A.B. + p-cresol system could only be compared if all measurements were made with the same holding time. The times of flow of 1% C.T.A.B. + p-cresol systems were measured with holding times of 30 seconds and of 40 minutes. A holding time of 30 seconds was used so that the time of flow measurements on a 1% C.T.A.B. + p-cresol system could be compared with those determined for systems of 1% C.T.A.B. + phenol. Now, as the time of flow varied with holding time, even after 100 minutes, it was necessary to measure the time of flow using as large a holding time as was practical, and therefore it was decided arbitrarily to use 40 minutes as a holding time.

The addition of m-cresol and o-cresol to 1% C.T.A.B. was studied in a similar manner to that described for the addition of p-cresol. The results are shown in figures 10 and 11 respectively. It is noted that, like p-cresol, the addition of m-cresol or o-cresol to 1% C.T.A.B. produces a

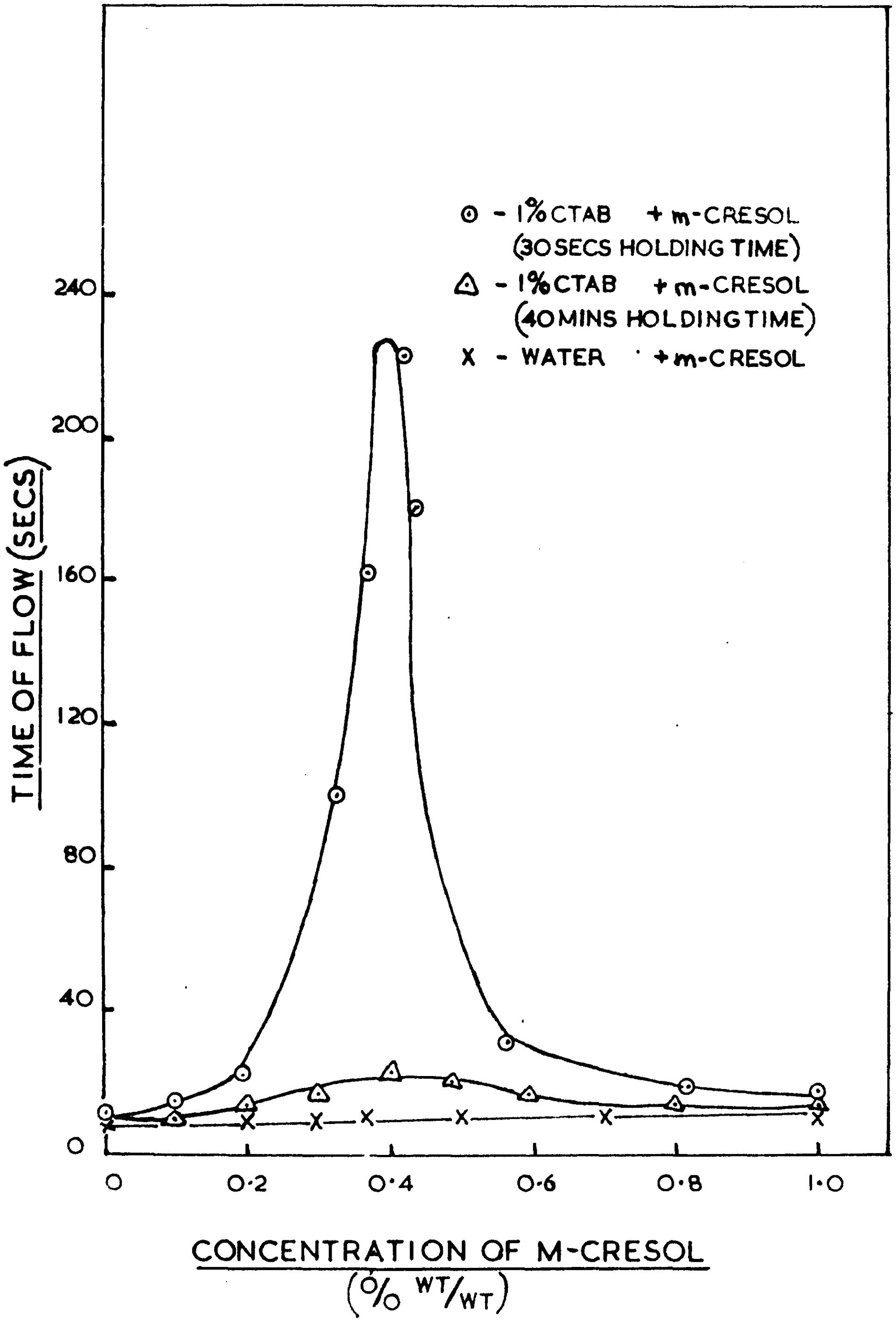
··FIG 9··

VARIATION IN TIME OF FLOW THROUGH VISCOMETER II OF THE 1% C.T.A.B. + 0·4% p-CRESOL SYSTEM WITH HOLDING TIME



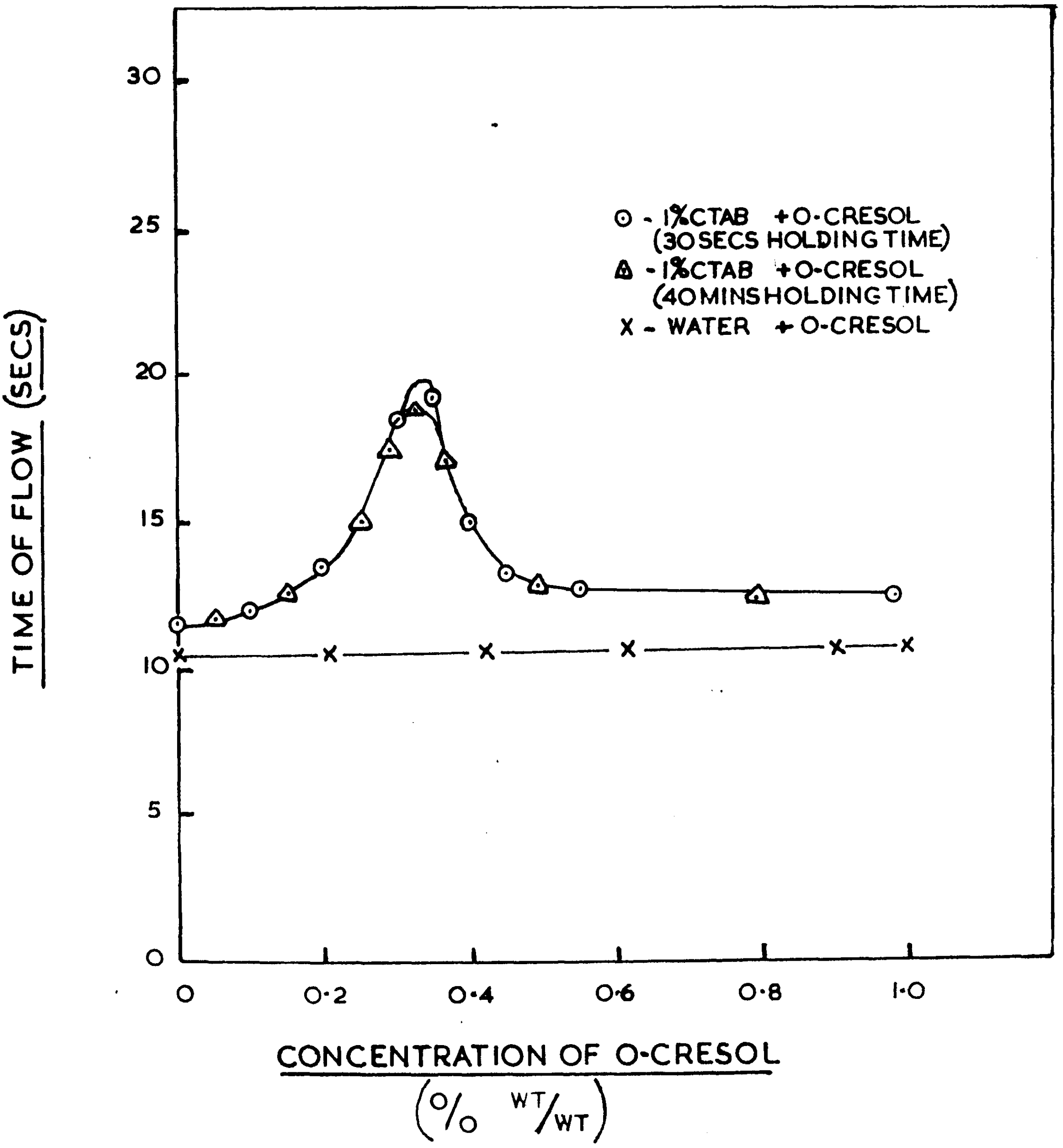
··FIG 10··

EFFECT OF THE ADDITION OF M-CRESOL ON THE TIME OF FLOW THROUGH VISCOMETER II



·· FIG 11 ··

EFFECT OF THE ADDITION OF O-CRESOL ON THE TIME OF FLOW THROUGH VISCOMETER II



maximum in the time of flow at a concentration of approximately 0.4% (probably 0.39% for m-cresol and 0.35% for o-cresol) and that the maximum time of flow varies with the holding time.

It can be seen in figures 10, 8 and 11 that the maximum time of flow produced by m-cresol is less than that produced with p-cresol while the maximum value produced by o-cresol is considerably less, being only slightly greater than that produced by phenol. Also, shown in figures 10 and 11 respectively, is the change in the time of flow when m-cresol and o-cresol are added to water.

THE ADDITION OF ETHYL-PHENOLS TO 1% C.T.A.B.

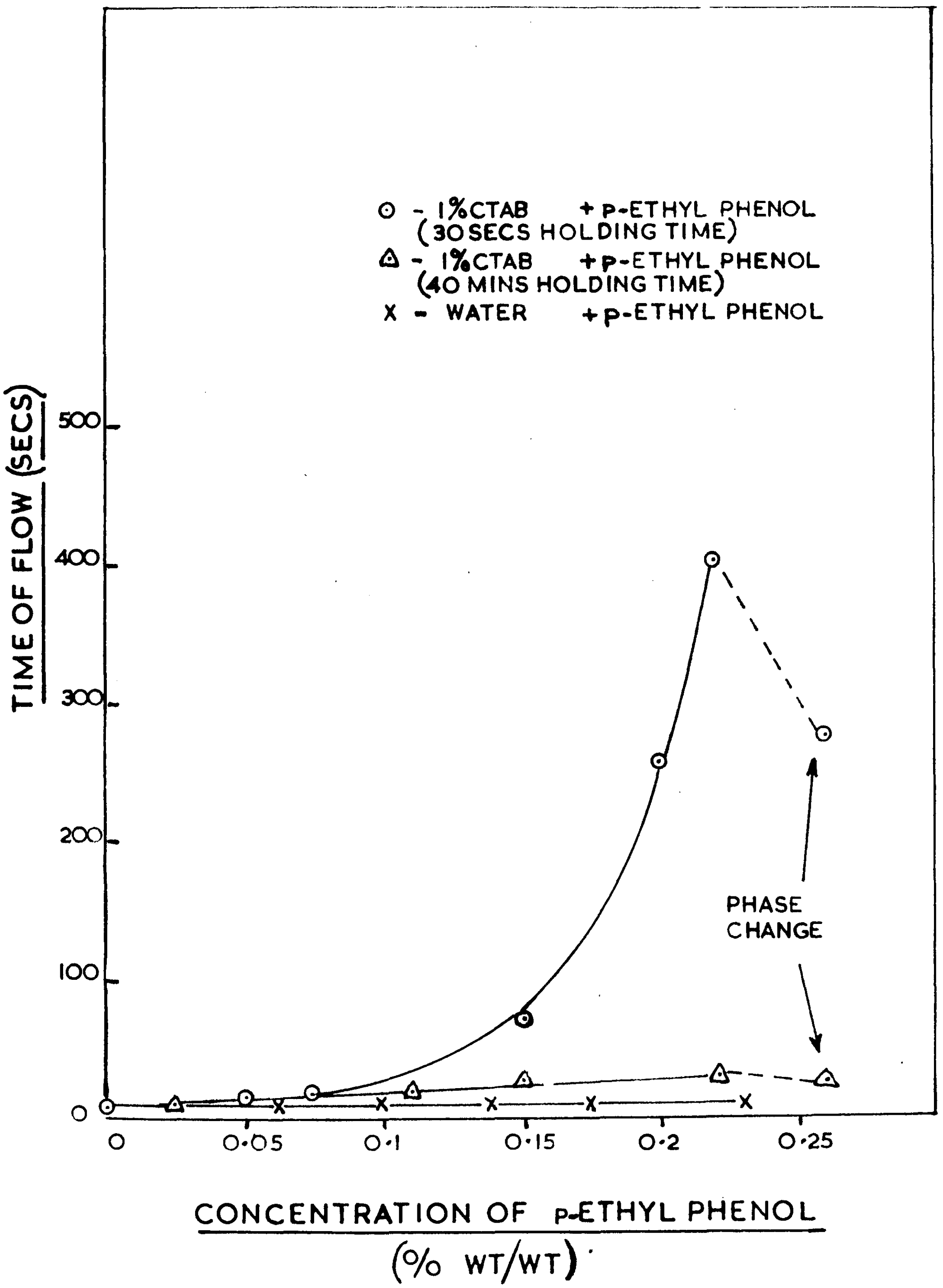
Since the addition of each cresol isomer to 1% C.T.A.B. appeared to produce maxima of different values, (in the curves of time of flow vs. concentration of additive) it was considered that the position of the CH_3- grouping on the phenolic nucleus affected the type of curve obtained.

This suggested that the effect of lengthening the side chain on the phenolic nucleus of the additive would produce an interesting curve.

The effect on the time of flow of a 1% C.T.A.B. system due to the addition of p- and of o-ethyl phenol with holding times of 30 seconds and 40 minutes are shown in figures 12 and 13 respectively. It can be seen that the addition of p-ethyl phenol causes the time of flow to increase until, at a concentration of 0.22% a phase change

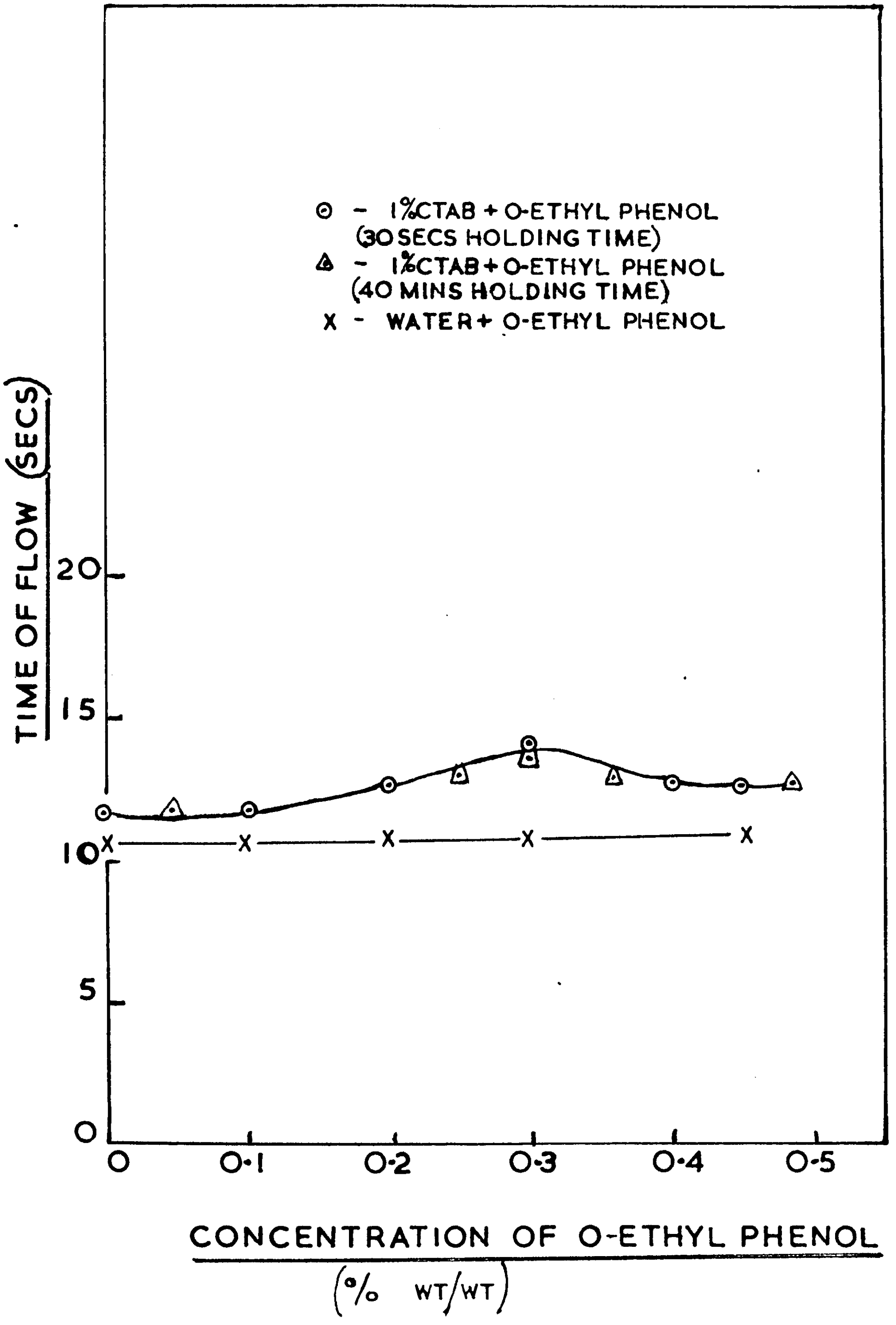
• • FIG 12 • •

EFFECT OF THE ADDITION OF p-ETHYL PHENOL ON THE TIME OF FLOW THROUGH VISCOMETER II



··FIG 13··

EFFECT OF THE ADDITION OF O-ETHYL PHENOL ON THE TIME OF FLOW THROUGH VISCOMETER II



(system appears turbid) seems to take place with the result that there is a sudden fall in the time of flow.

Now, the time of flow of 1% C.T.A.B. containing 0.22% p-ethyl phenol is greater than each of the maximum times of flow (having corresponding holding time) of 1% C.T.A.B. + m-cresol and of 1% C.T.A.B. + o-cresol, but it is less than the maximum time of flow of 1% C.T.A.B. + p-cresol.

The addition of 0.3% o-ethyl phenol to 1% C.T.A.B. produced a maximum in time of flow which was less than that produced by o-cresol in 1% C.T.A.B. Since as much as 0.5% o-ethyl phenol could be added to 1% C.T.A.B. without any observable phase change, it appears that the ortho isomer of ethyl phenol is very much more soluble in 1% C.T.A.B. than the para isomer.

The effects on the time of flow of the additions of p- and of o- ethyl phenol to water are shown in figures 12 and 13 respectively.

THE SIGNIFICANCE OF THE HOLDING TIME.

In all these systems of 1% C.T.A.B. containing phenolic additives it has been shown (figures 6 to 13), that the curves of time of flow vs. concentration of phenolic additive are dependent on the holding time. This indicates that the curves were dependent on the time which elapsed between the completion of the upward movement (i.e. the liquid being forced up through the capillary of the viscometer to the top timing mark, A, on the left-hand limb) and the commencement of the downward movement of the liquid (i.e. the liquid being released to flow down through the capillary of the viscometer for the purpose of measuring the time of flow). This means that the holding time is the duration of time in which the system is allowed to recover from any properties induced upon it by the process of forcing it through the capillary of the viscometer. It would seem that since the times of flow were greater when the holding times were very small that the process of forcing the liquid upwards through the capillary made the system more viscous, (i.e. the liquid system is made more viscous by being sheared by the walls of the capillary in the viscometer). This suggests that systems of 1% C.T.A.B. containing phenolic additives were capable of displaying the property of NEGATIVE THIXOTROPY.

As the maximum in time of flow decreases with increase in holding time, it seems possible that, if the holding time was sufficiently large, there would be no maximum in the curve of time of flow vs. concentration of phenolic additive. If this were the case then the experiments reported, e.g. on the addition of cresol isomers, simply show that shear produced a temporary structural viscosity which was greater with p-cresol than with m-cresol and even more so than with o-cresol. Thus it is not possible to say, with certainty from the data collected, that a system of 1% C.T.A.B.

containing 0.4% p-cresol is more viscous than one containing 0.4% m-cresol etc.

Consequently, systems of 1% C.T.A.B. containing phenolic additives, which show large maxima in the curves of time of flow vs concentration of additive, may have, in greater degree, a structure which possesses a viscosity, not necessarily greatly different from that of other systems, but which is more sensitive to the effect of shearing. Therefore, the maximum in the time of flow could be caused by the shearing inducing a greater viscosity.

Thus, it was necessary to try to establish if the addition of phenolic compounds changed the "zero-shear" viscous properties of a 1% C.T.A.B. system. Such experiments are described in Section B.

SECTION B

This investigation was an attempt to establish if the systems which show the longest time of flow, in figures 7, 8, 10 to 13, in fact, possess the greatest "zero-shear" viscous properties, (i.e. viscous properties not induced by shearing effects), and thereby prove that the maxima in the curve of time of flow vs concentration of additive were not produced entirely by shearing.

In order to determine the "zero-shear" viscous properties of these systems, it is necessary to measure them in such a way that extrapolation to zero shearing rate is feasible.

For the flow of a Newtonian liquid through a capillary, the volume discharged per second (Q) is proportional to the pressure (P) which produced the flow. The proportionality constant is the fluidity, which is the reciprocal of the viscosity. In this work it is assumed that, for a liquid system which is non-Newtonian in character, (the plot of Q against P is not linear), a measure of the "zero-shear" viscous properties of the system may be obtained by measuring the reciprocal of the gradient at zero pressure of the plot of Q against P (i.e. $\frac{dP}{dQ}$ at P = 0).

$^{dP}/_{dQ}$ at zero pressure, has been termed in this work, the "viscosity", $(\frac{1}{G})$.

THE APPARATUS FOR DETERMINING PLOT OF Q vs. P.

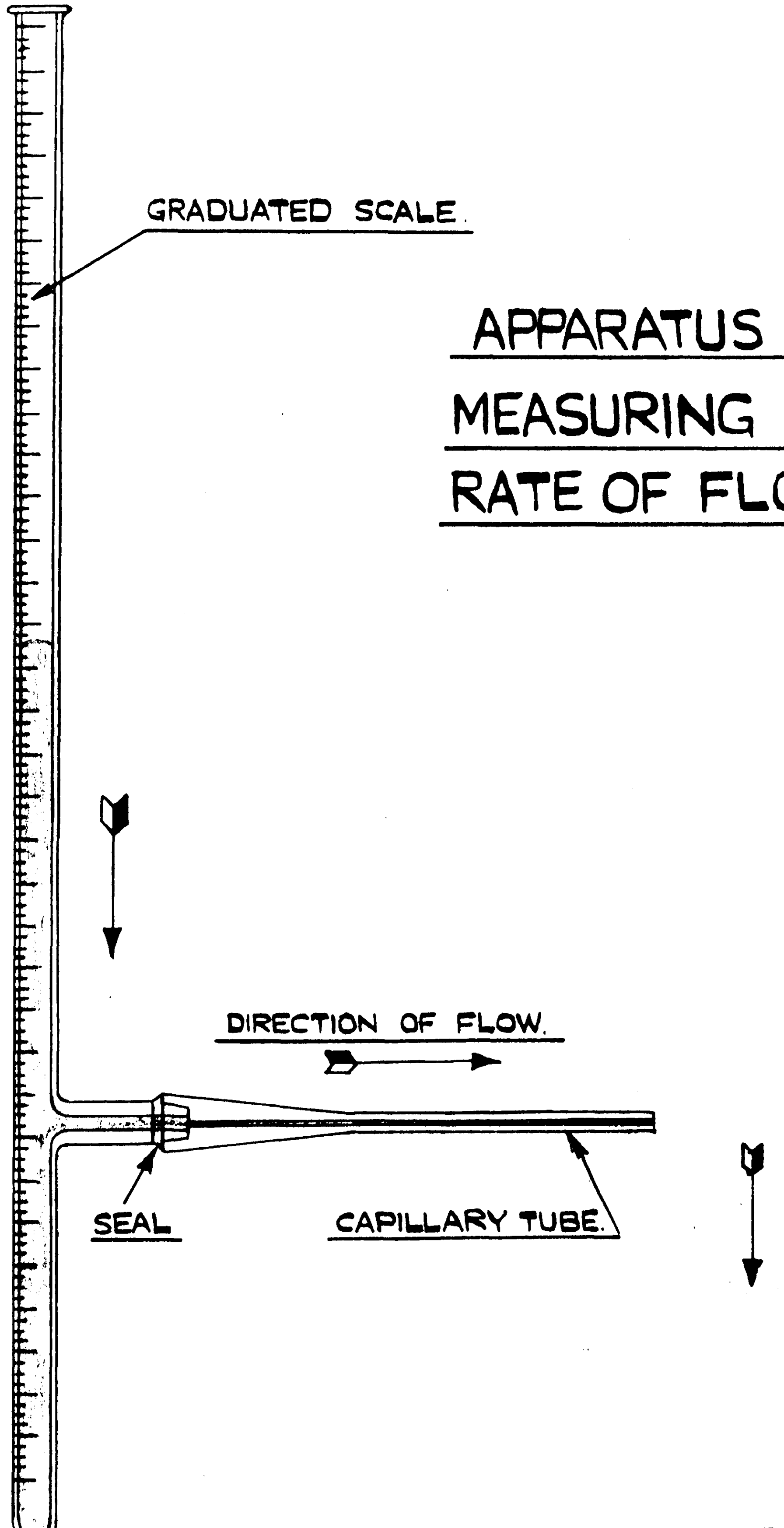
The apparatus used is shown in figure 14. It consists of a graduated tube 1.26 cm. in diameter, closed at one end and fixed in a vertical position. Attached to a side arm is a capillary tube 13.8 cm. long and 0.05 cm. in diameter. When the liquid was not flowing through the capillary a small rubber cap was placed over the end of it. The apparatus was contained in a thermostatically controlled air cabinet at $25^{\circ}C \pm 0.1^{\circ}C$.

THE PROCEDURE FOR DETERMINING PLOT OF Q vs. P.

The apparatus was set up as described above with a rubber cap over the exit end of the capillary. The liquid systems, which had been prepared as previously described, were introduced into the graduated tube by means of a pipette. Each system was always filled to the same mark on the graduated tube. Care was taken to remove all entrapped air. Before any measurements were taken, a period of one hour was allowed to elapse to ensure that the liquid had obtained a uniform temperature and had also recovered from shear induced viscosity.

To take readings the cap at the end of the capillary was removed, releasing the solution, which flowed through the capillary and discharged into air. The time for the liquid level on the graduated tube to fall from one position on the scale to another was measured with a stop-watch, to ± 0.1 seconds. The divisions on the graduated scale gave a measure of the volume of liquid discharged from the capillary and also the pressure causing the discharge of solution.

Using the apparatus in this manner, the liquid system



APPARATUS FOR MEASURING THE RATE OF FLOW.

FIG. 14.

undergoes little shearing because it can be assumed that the shearing in the graduated tube is negligible and therefore the only place where the liquid may be sheared is in the capillary tube where its retention time is comparatively small.

Experimental Results.

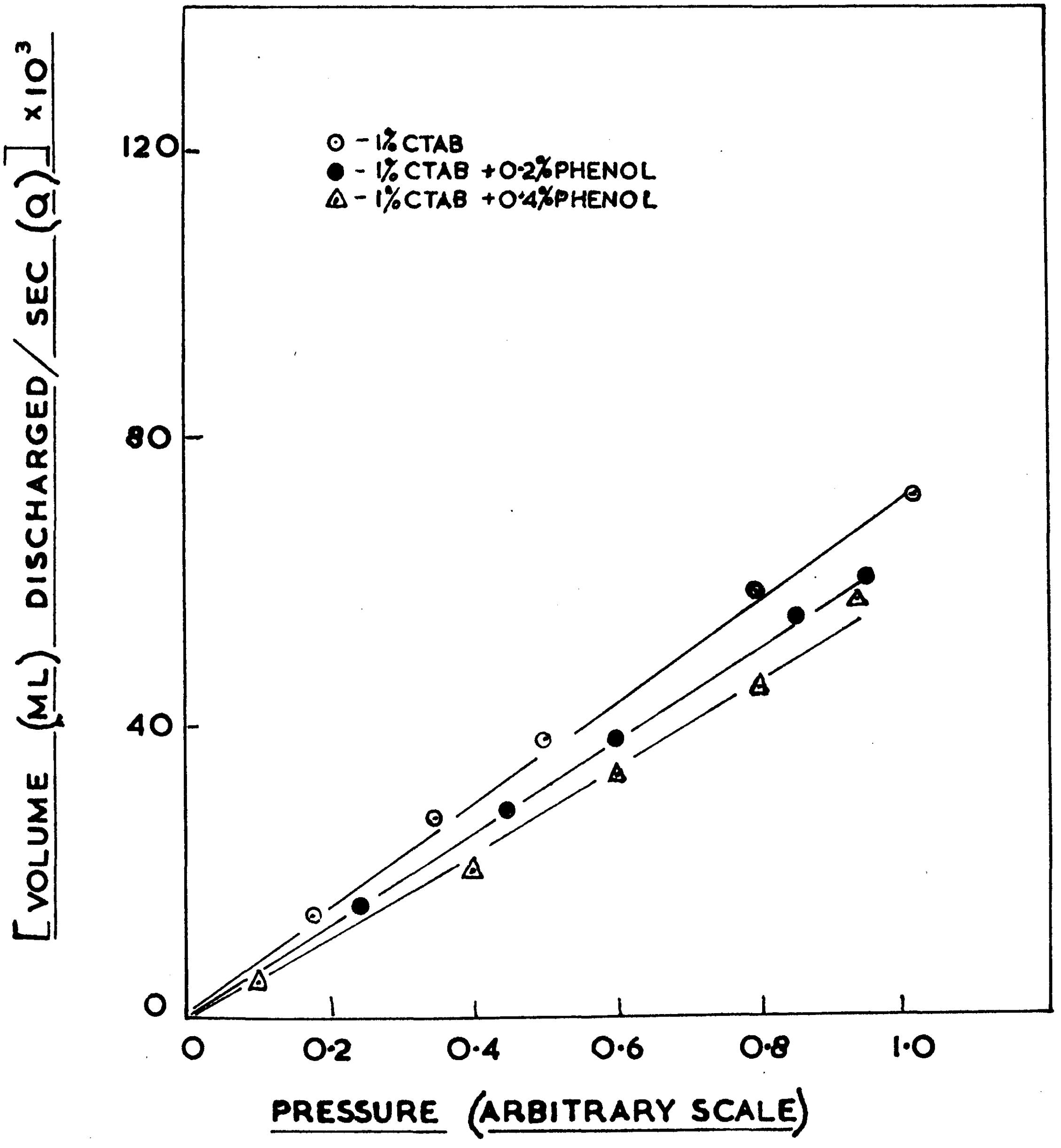
In figures 15 to 17 are shown the plots of the volume of 1% C.T.A.B. containing phenol discharged per second against pressure causing the discharge. The gradients of these plots at zero pressure were measured and thereby their "viscosities" $(\frac{1}{G})$ were determined. A plot of these "viscosities" against concentration of phenol added is shown in figure 19. It can be seen that the plot resembles the curve shown in figure 7 in that the "viscosity" increases with the addition of phenol to a maximum at 0.5% and thereafter the "viscosity" decreases to a minimum at approximately 1.2% phenol and further additions of phenol caused a linear increase in "viscosity".

Shown in figure 18 are the plots of the volume of phenol and water discharged per second against the pressure producing the discharge. The variation in "viscosity" of a water + phenol system with concentration of phenol is shown in figure 19.

Figures 20 and 21 show how the rate of flow of 1% C.T.A.B. systems containing p-cresol varies with pressure. It can be seen that the addition of p-cresol to 1% C.T.A.B. causes the curves to be deviated from a linear plot.

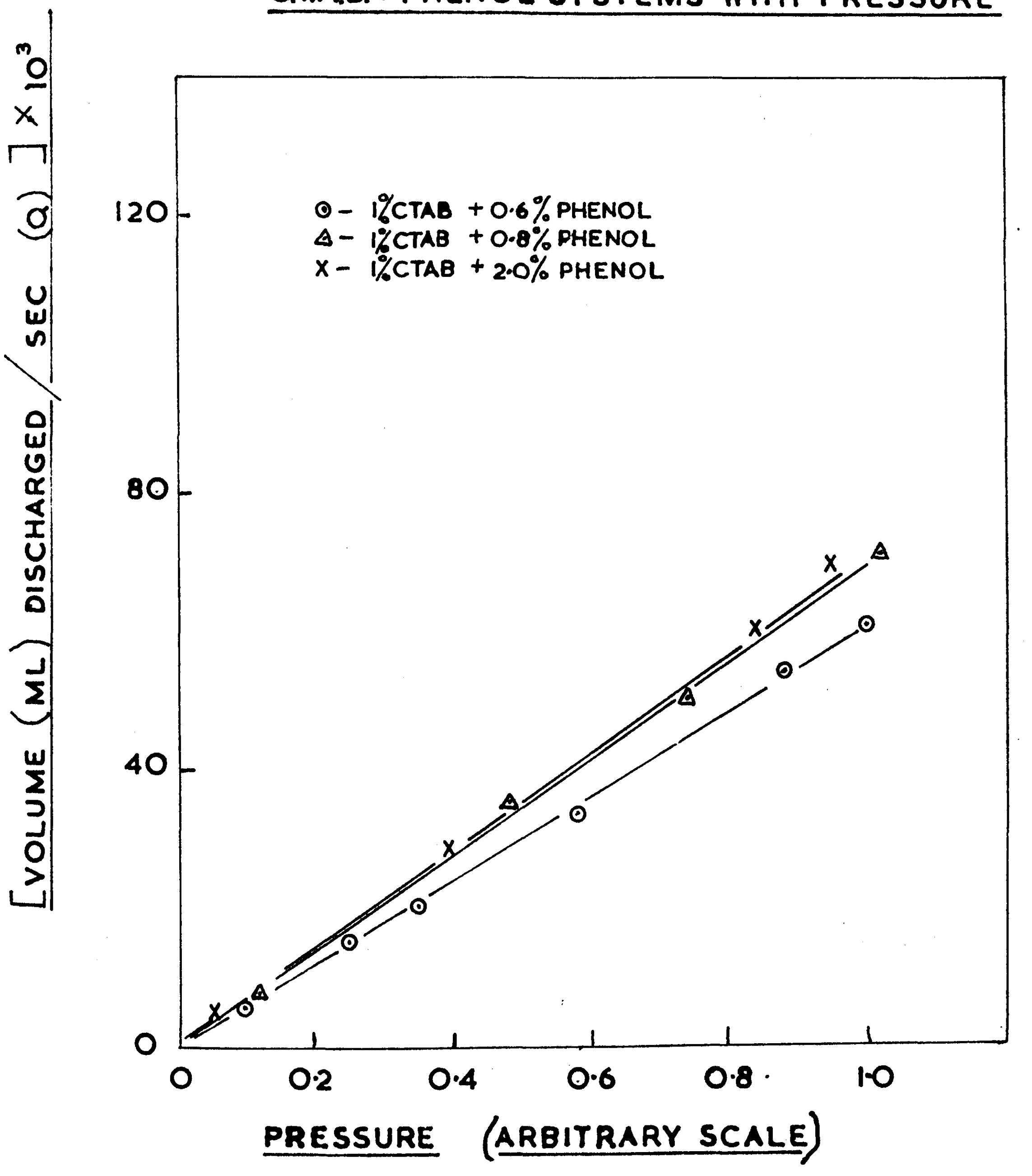
·· **FIG 15** ··

VARIATION OF THE RATE OF FLOW OF C.T.A.B.+ PHENOL SYSTEMS WITH PRESSURE



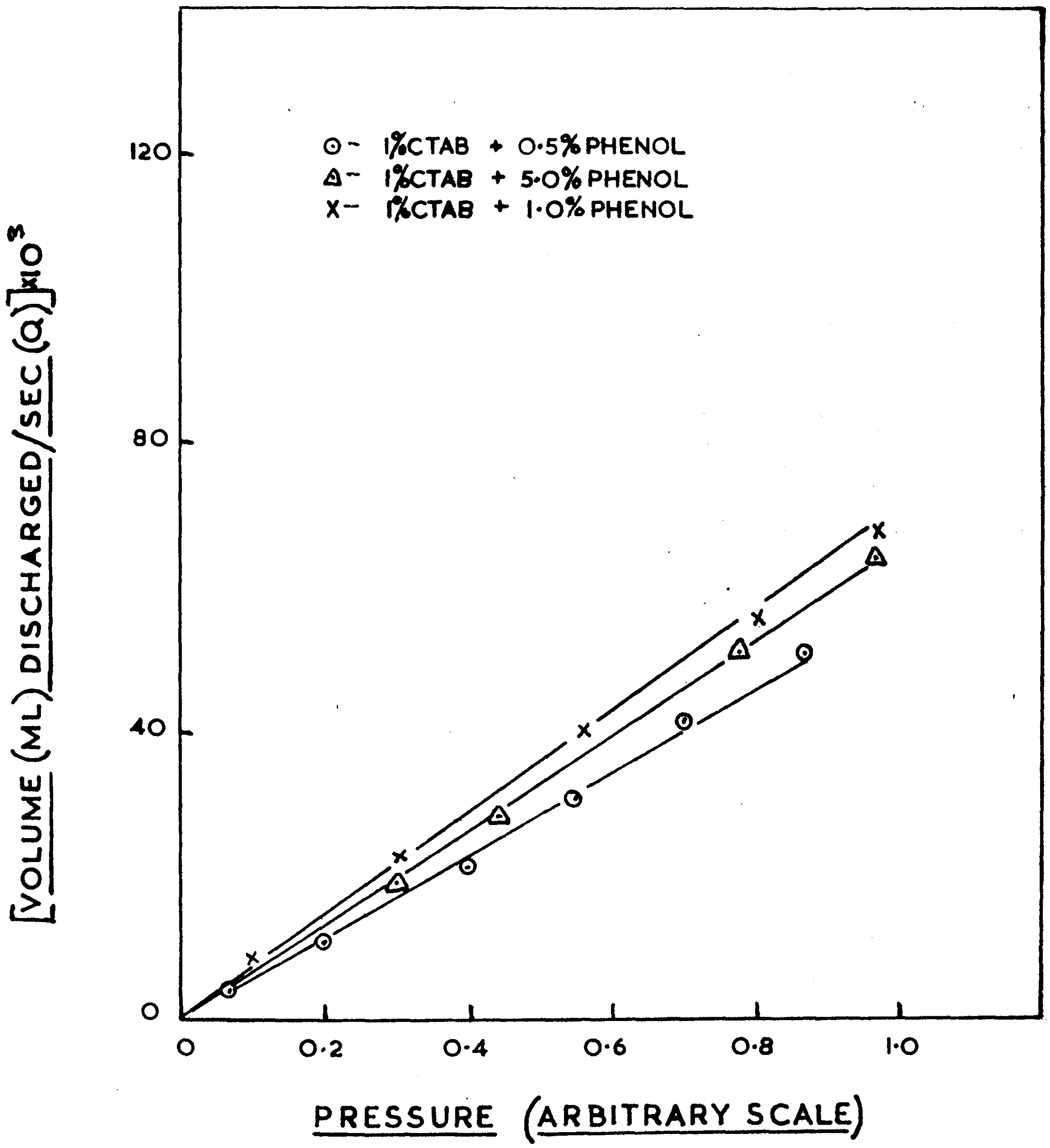
· · FIG 16 · ·

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + PHENOL SYSTEMS WITH PRESSURE



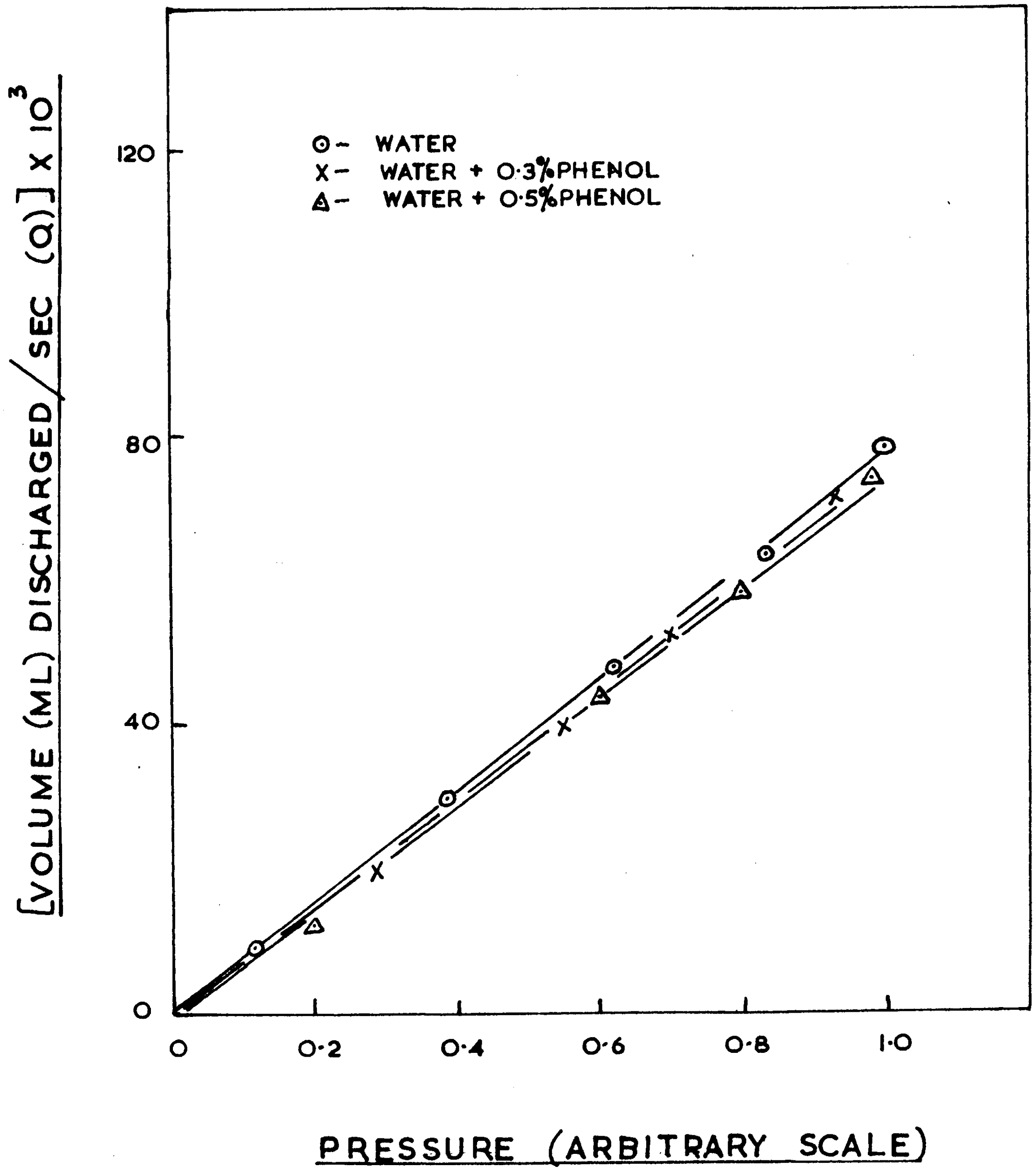
··FIG 17··

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + PHENOL SYSTEMS WITH PRESSURE



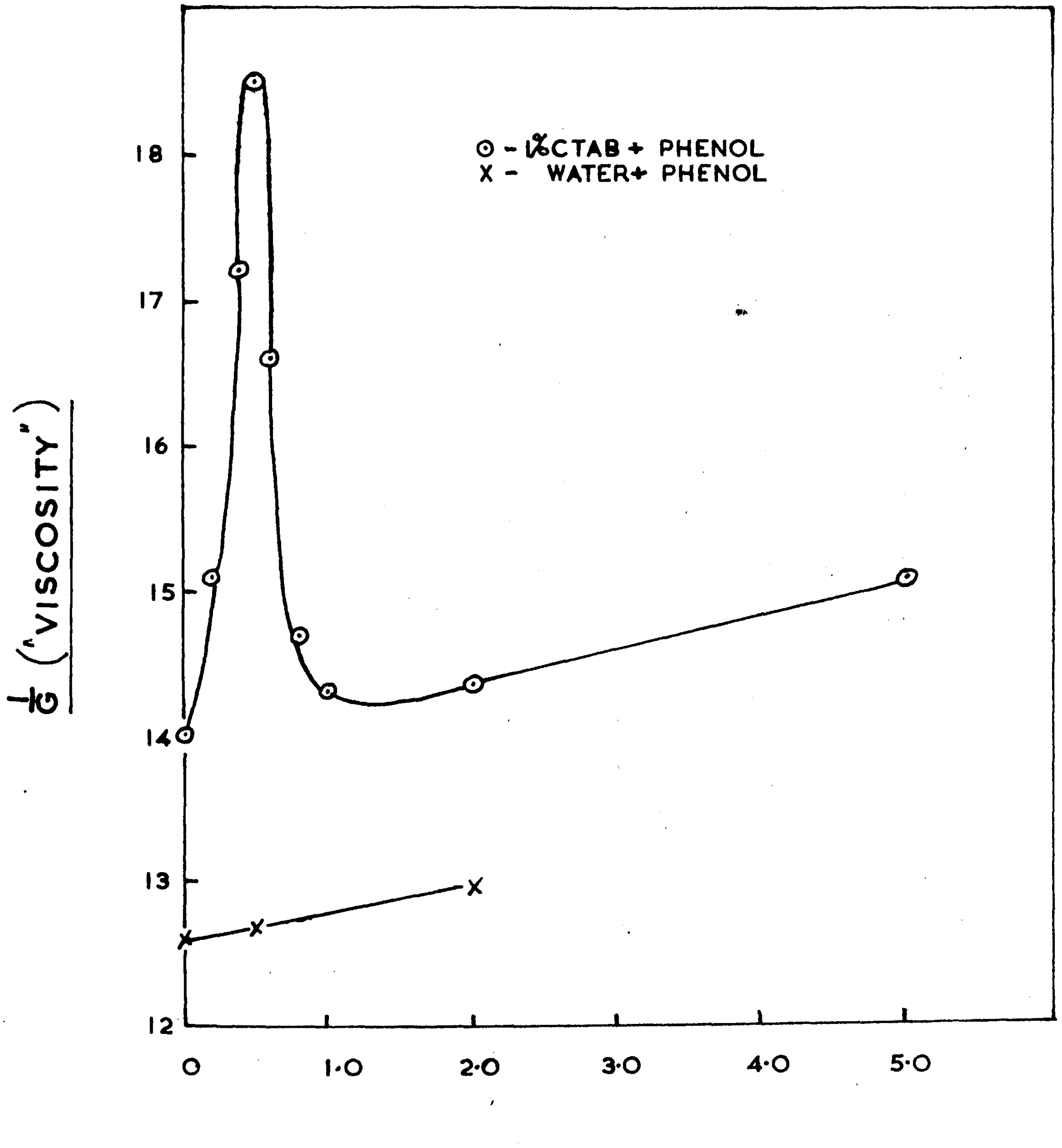
· · FIG 18 · ·

VARIATION OF THE RATE OF FLOW OF WATER + PHENOL SYSTEMS WITH PRESSURE



··FIG 19··

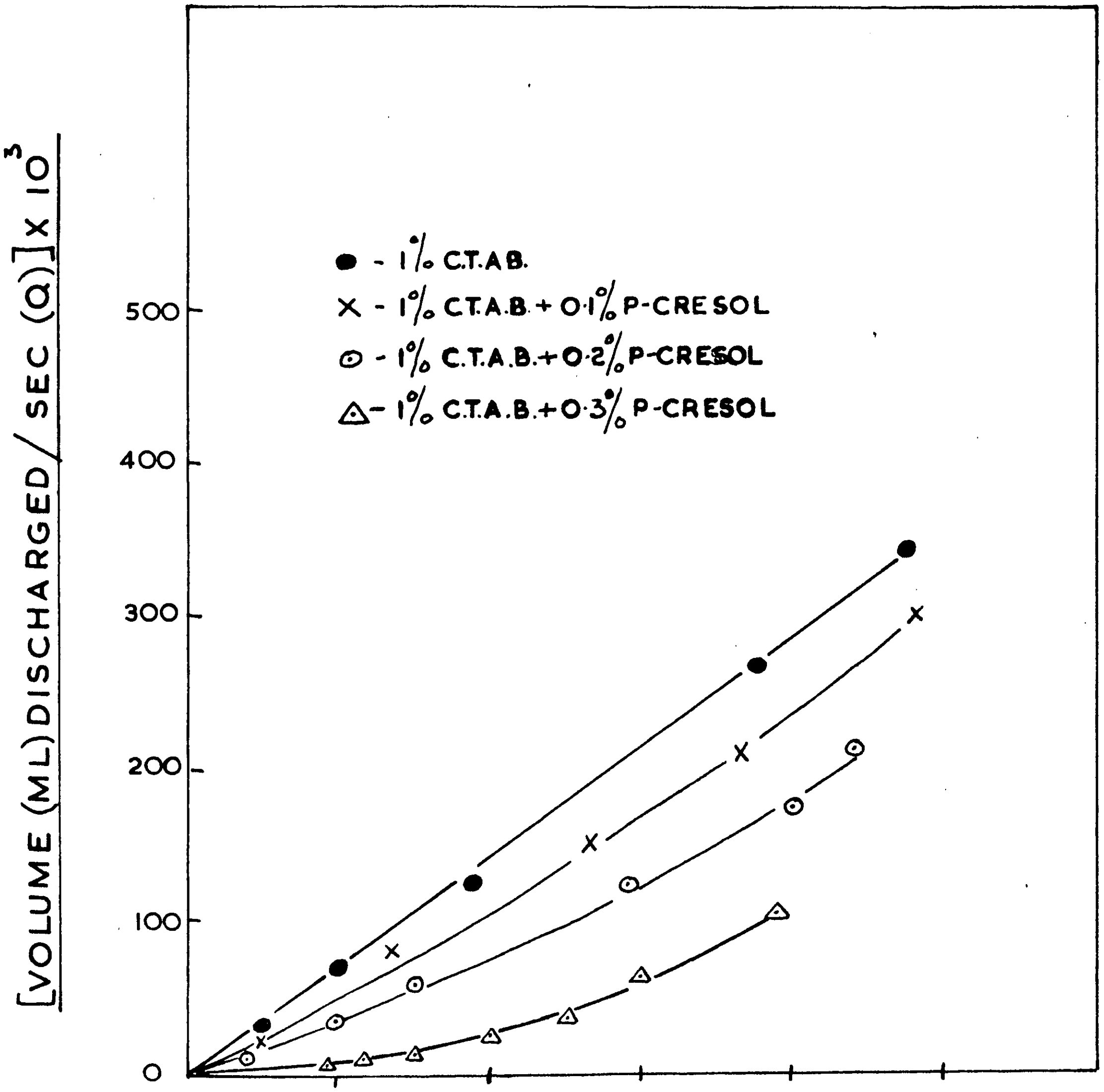
VARIATION IN "VISCOSITY" WITH CONCENTRATION OF PHENOL



CONCENTRATION OF PHENOL (% WT/WT)

··FIG 20··

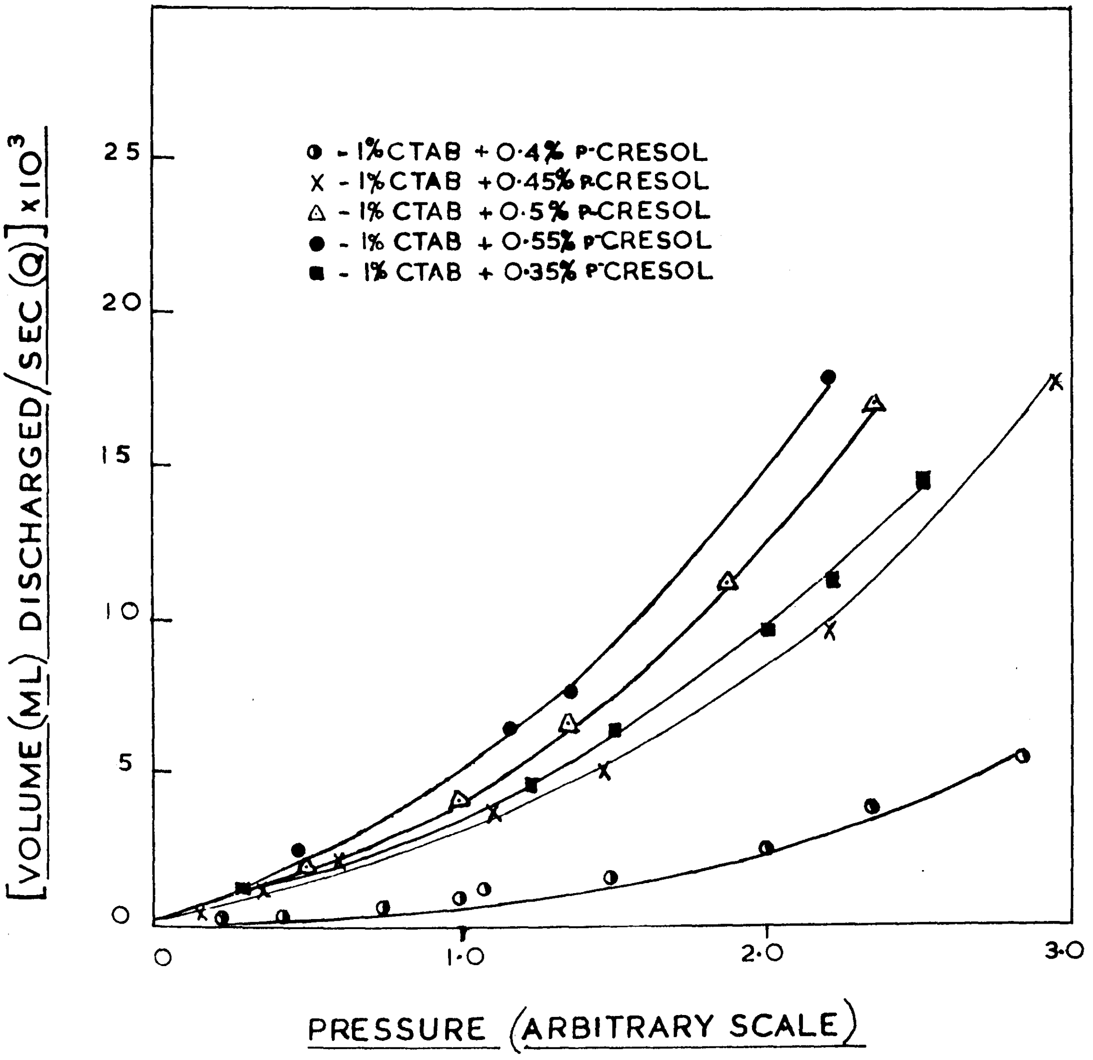
VARIATION OF THE RATE OF FLOW OF C.T.A.B. + p-CRESOL SYSTEMS WITH PRESSURE



PRESSURE (ARBITRARY SCALE)

• • FIG 21 • •

VARIATIONS OF THE RATE OF FLOW OF C.T.A.B.+P-CRESOL SYSTEMS WITH PRESSURE



The gradients of these curves at zero pressure were determined by drawing enlarged section of each curve, (see figure 20(a) and 21(a) at very low pressures (0 to 1.0). The reciprocal of the gradient, the "viscosity", was plotted against the concentration of p-cresol and it is shown in figure 23 that by increasing the p-cresol concentration the "viscosity" increases to a maximum at 0.4% and that further addition of p-cresol causes the "viscosity" to decrease. This plot, is similar in shape to the curve shown in figure 8.

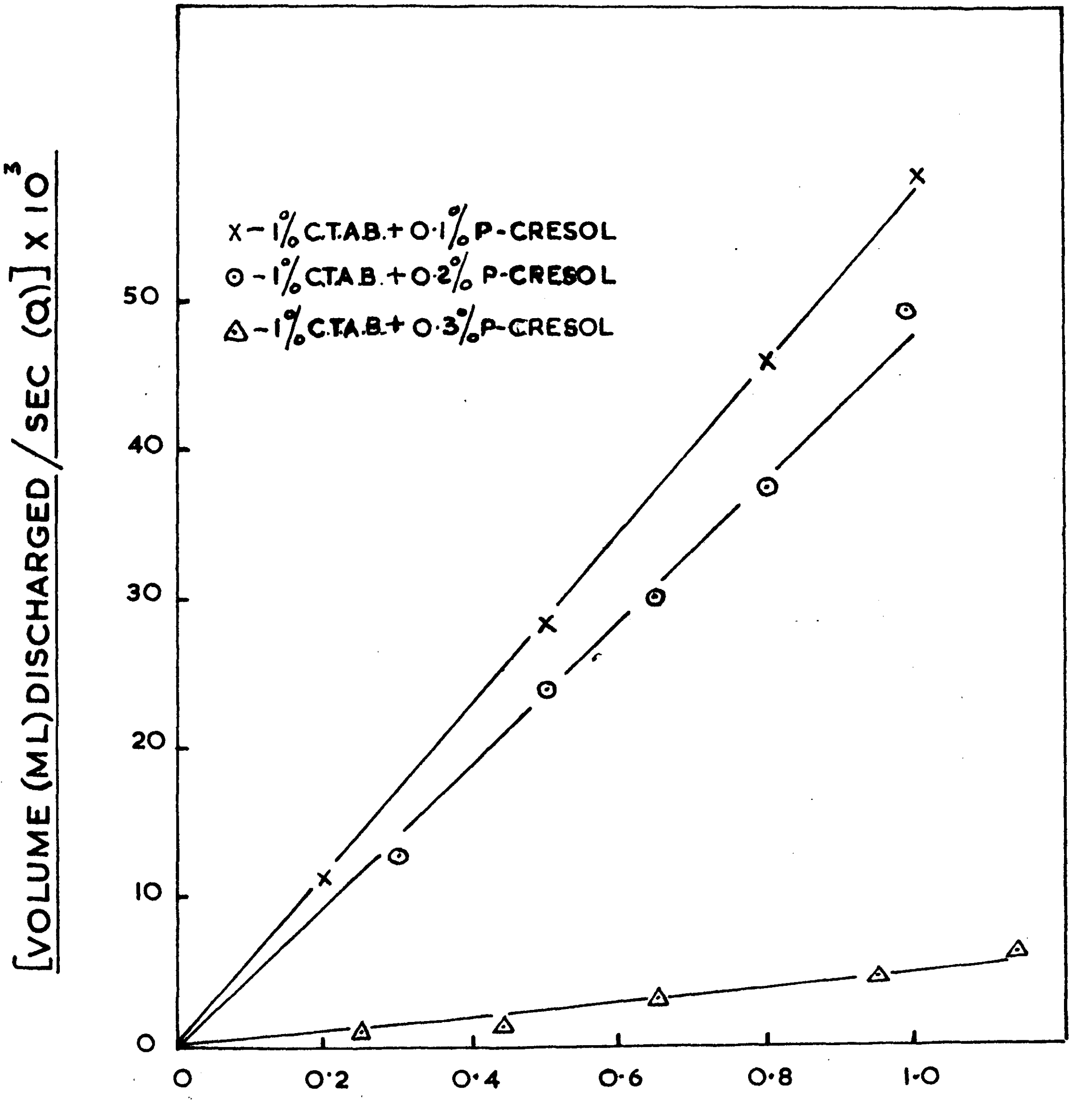
Also shown in figure 23 is the variation of the "viscosity" in p-cresol and water systems with concentration of p-cresol. These "viscosities" were determined from the curves shown in figure 22.

The variations of the rate of flow (volume discharged per second) with pressure for systems of 1% C.T.A.B. + m-cresol and of 1% C.T.A.B. + o-cresol are shown in figures 24, 25 and in 26, 27 respectively. The "viscosities" of these systems were determined from figures 24(a), 25(a) and from 26, 27 respectively, in a similar manner to that described for systems of 1% C.T.A.B. + p-cresol. The plots of these "viscosities" against the concentration of cresol are shown in figures 30 and 31. It can be seen that the curves shown in figures 30 and 31 are very similar in shape to the plots shown in figures 10 and 11 (time of flow vs. concentration of cresol) respectively.

Also, shown in figures 30 and 31 are the plots of the

FIG 20(a)

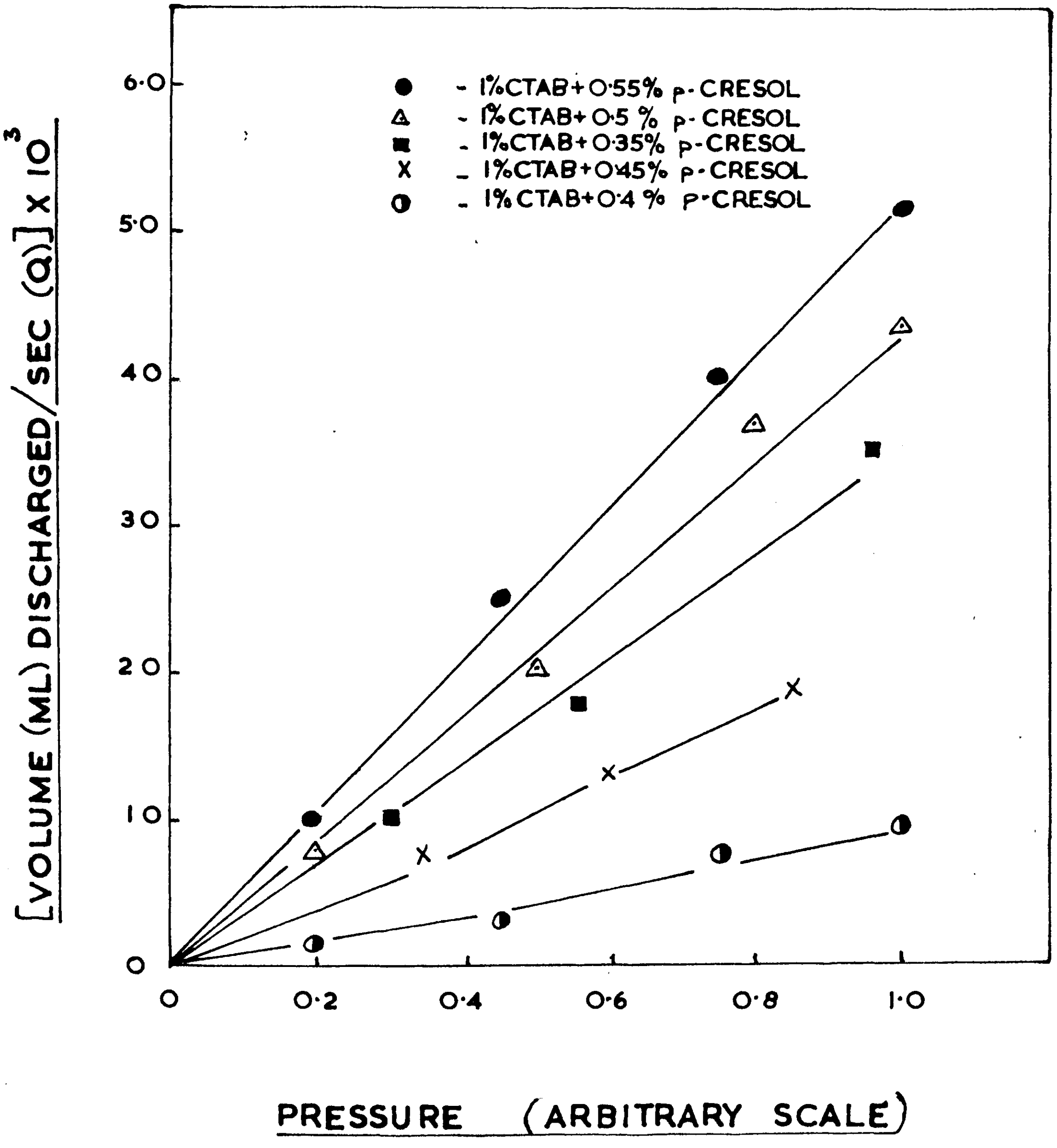
VARIATION OF THE RATE OF FLOW OF C.T.A.B.+ p-CRESOL SYSTEMS WITH LOW PRESSURES



PRESSURE (ARBITRARY SCALE)

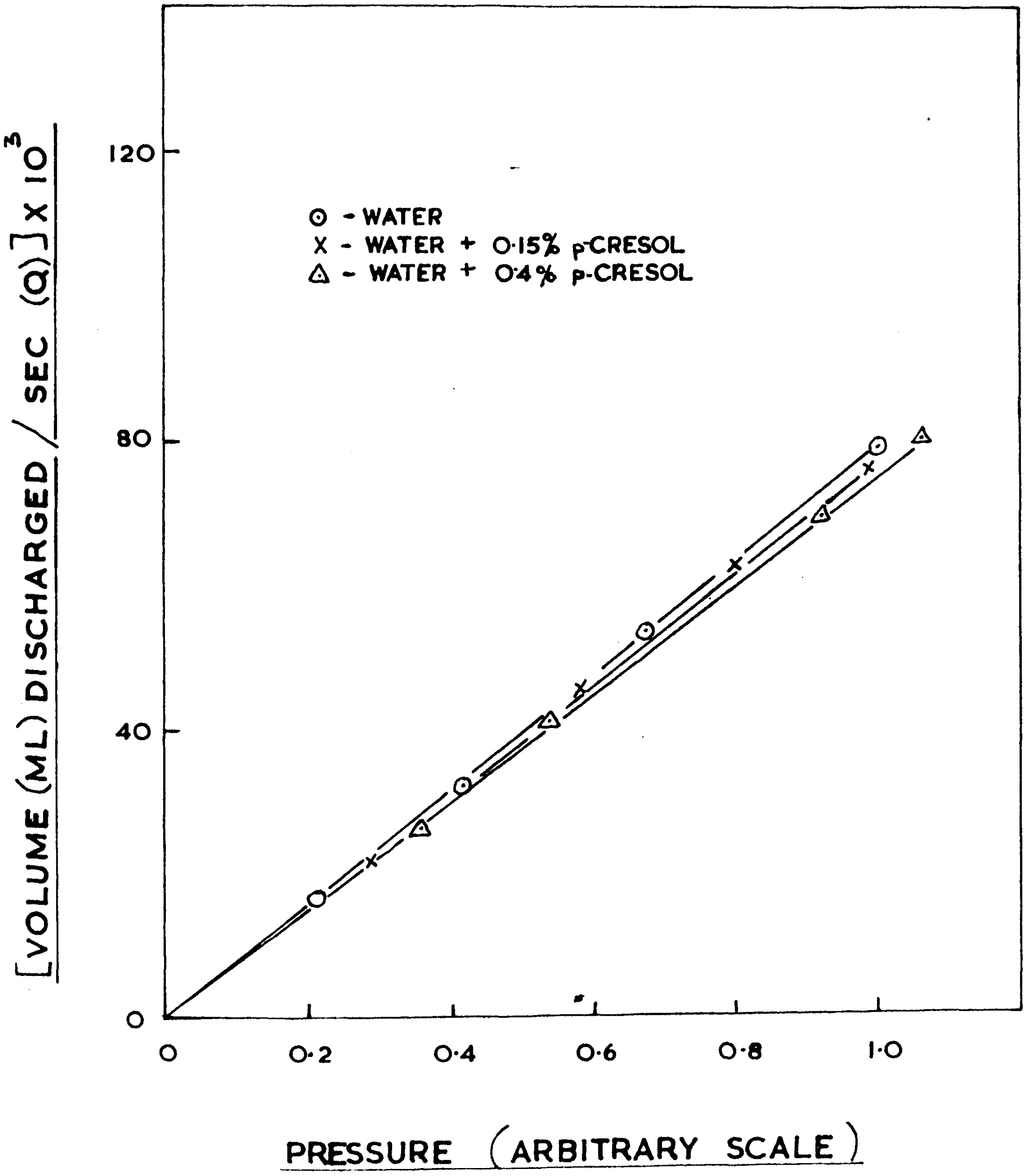
· · FIG 21(a) · ·

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + p-CRESOL SYSTEMS WITH LOW PRESSURES



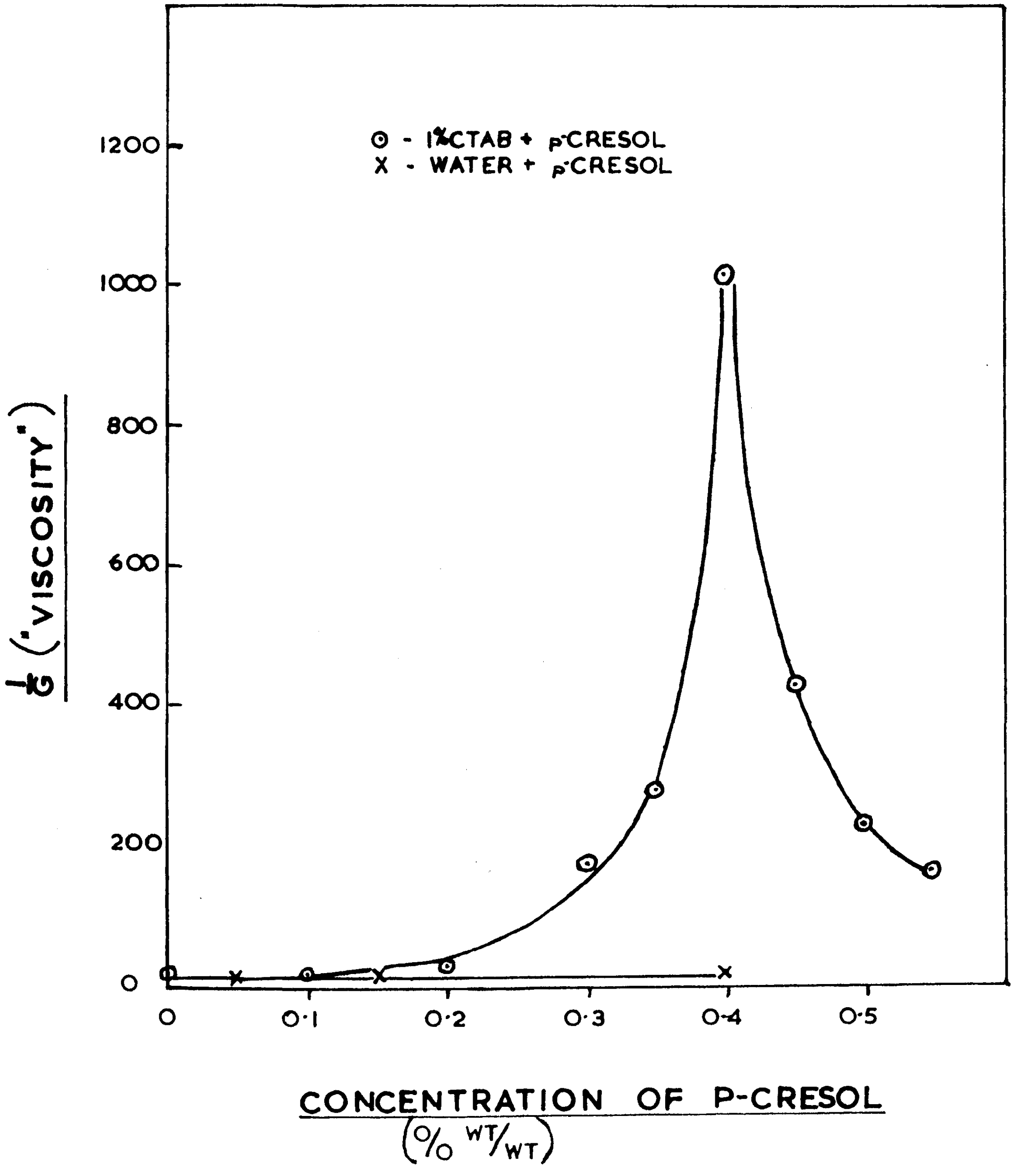
··FIG 22··

VARIATION OF THE RATE OF FLOW OF WATER + p-CRESOL SYSTEMS WITH PRESSURE



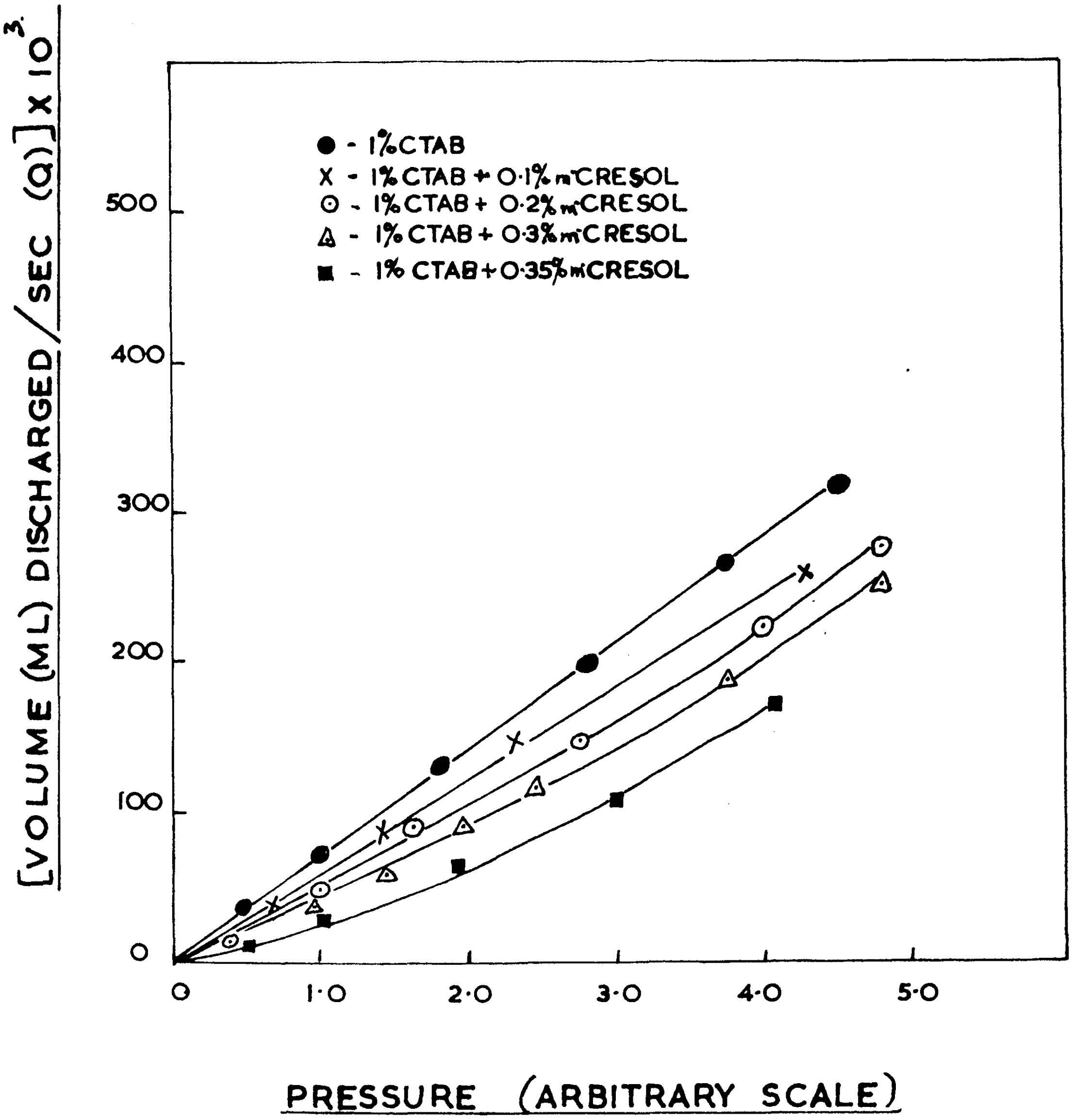
··FIG 23··

VARIATION IN "VISCOSITY" WITH CONCENTRATION OF P-CRESOL



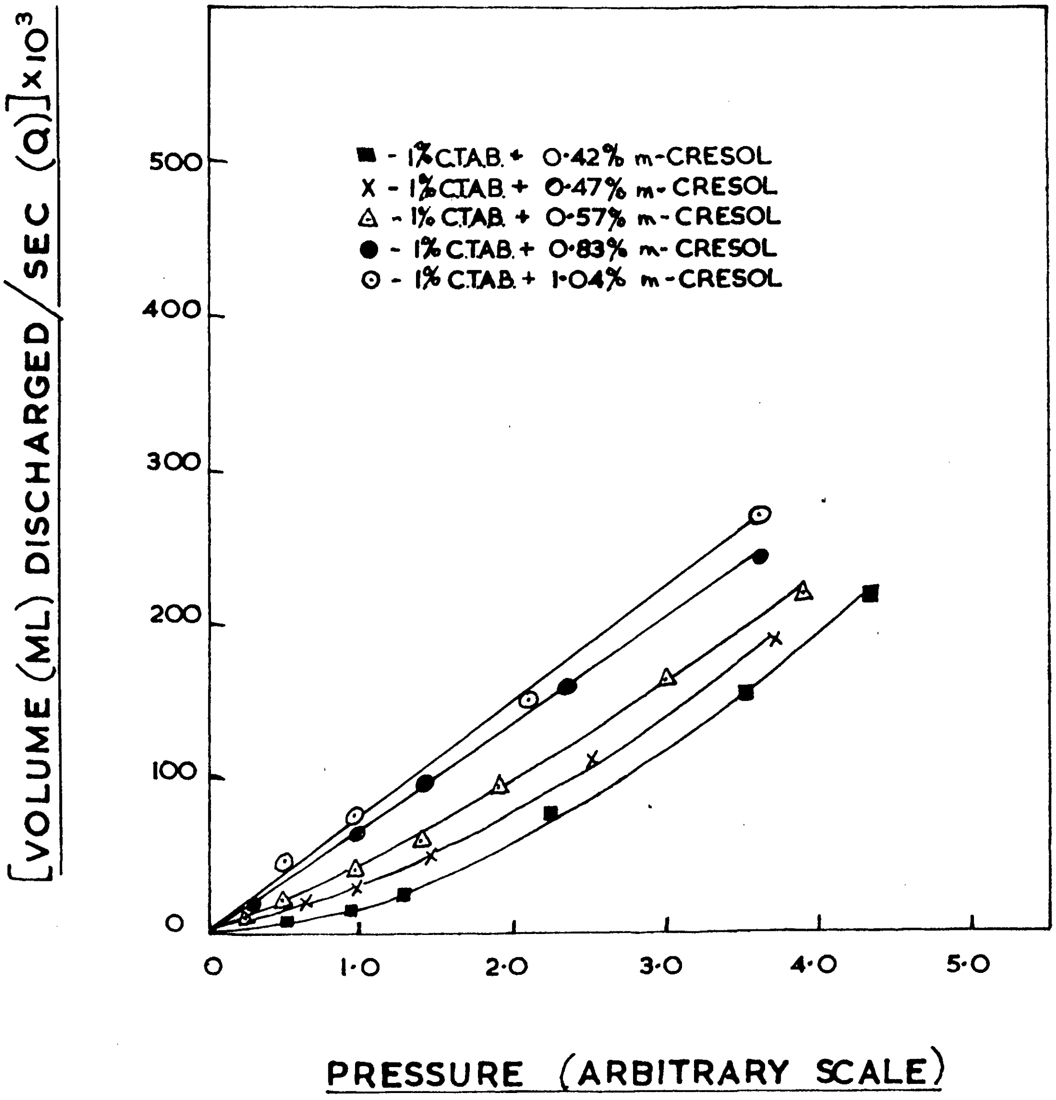
··FIG 24··

VARIATION OF THE RATE OF FLOW OF C.T.A.B + m -CRESOL SYSTEMS WITH PRESSURE



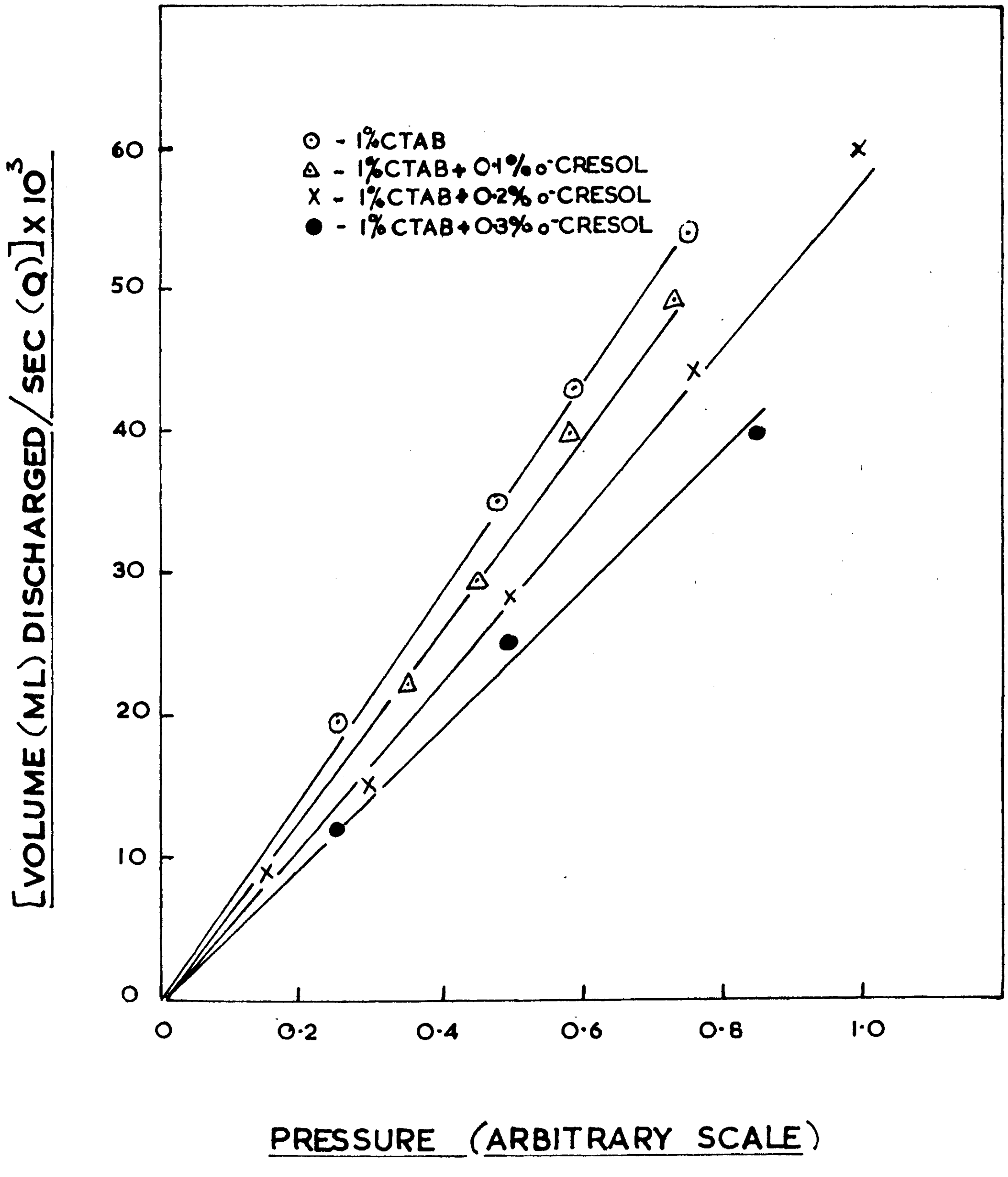
· · FIG 25 · ·

VARIATION OF THE RATE OF FLOW OF C.T.A.B.+ m-CRESOL SYSTEMS WITH PRESSURE



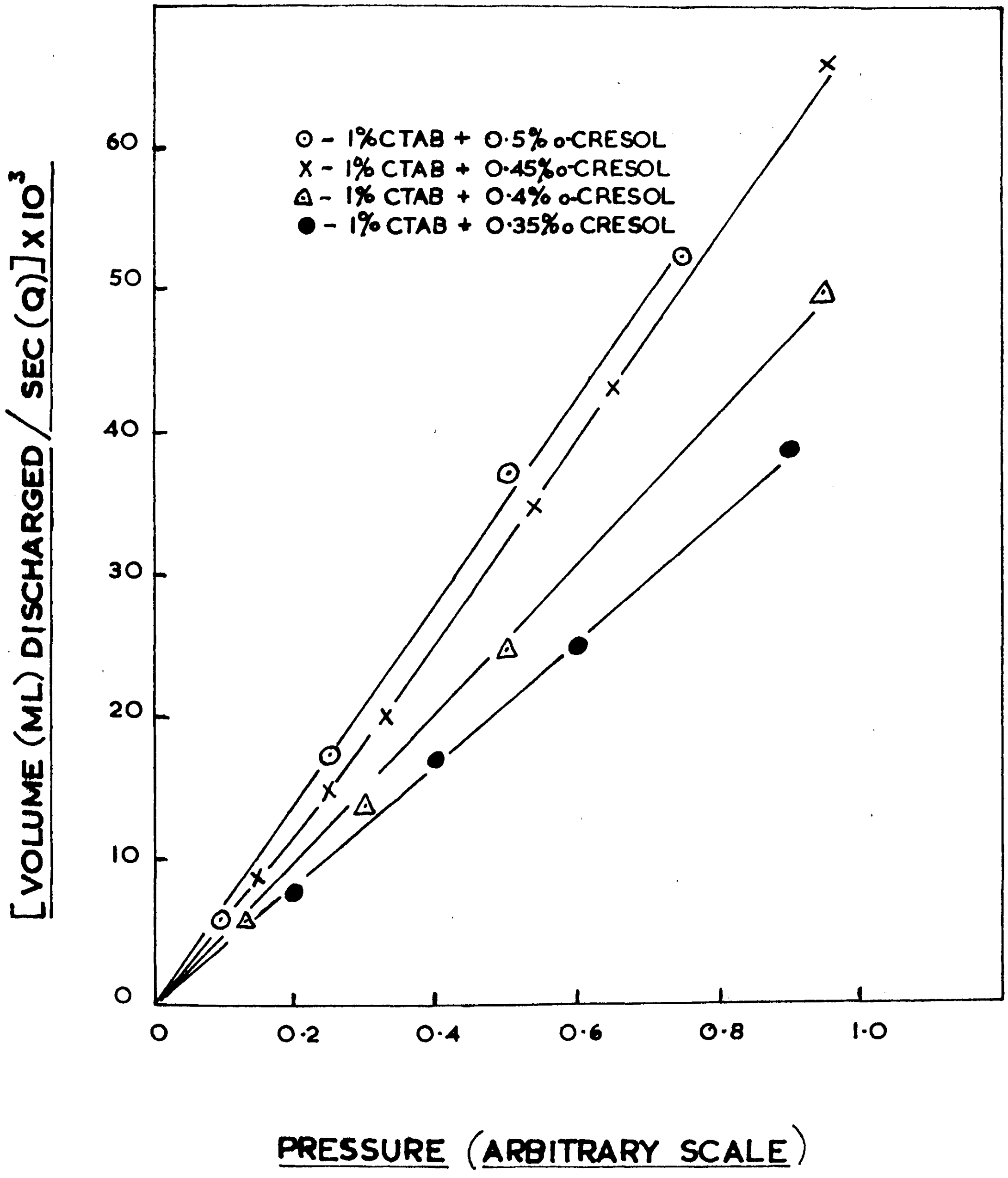
• • FIG 26 • •

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + o-CRESOL SYSTEMS WITH PRESSURE



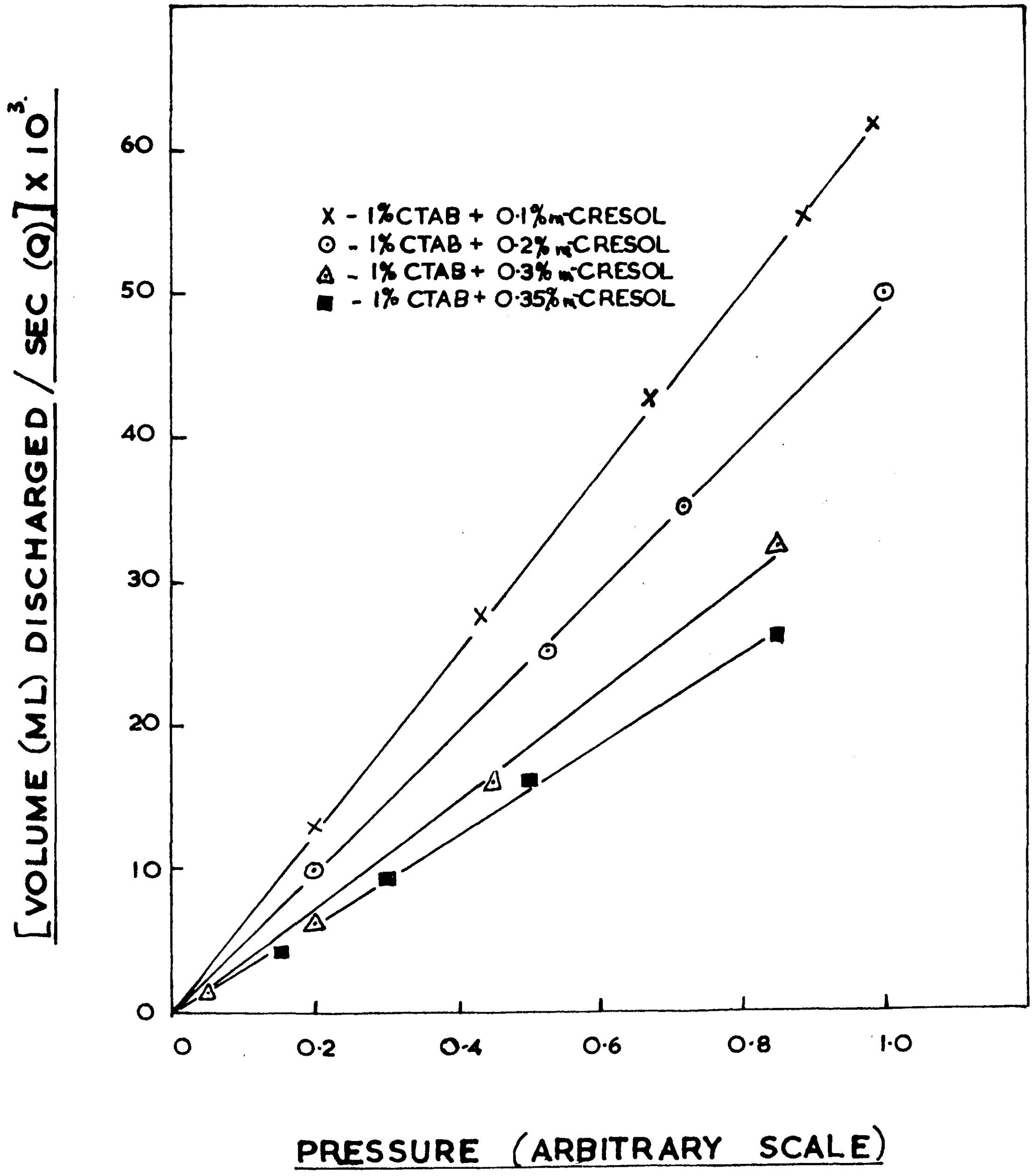
··FIG 27··

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + o-CRESOL SYSTEMS WITH PRESSURE



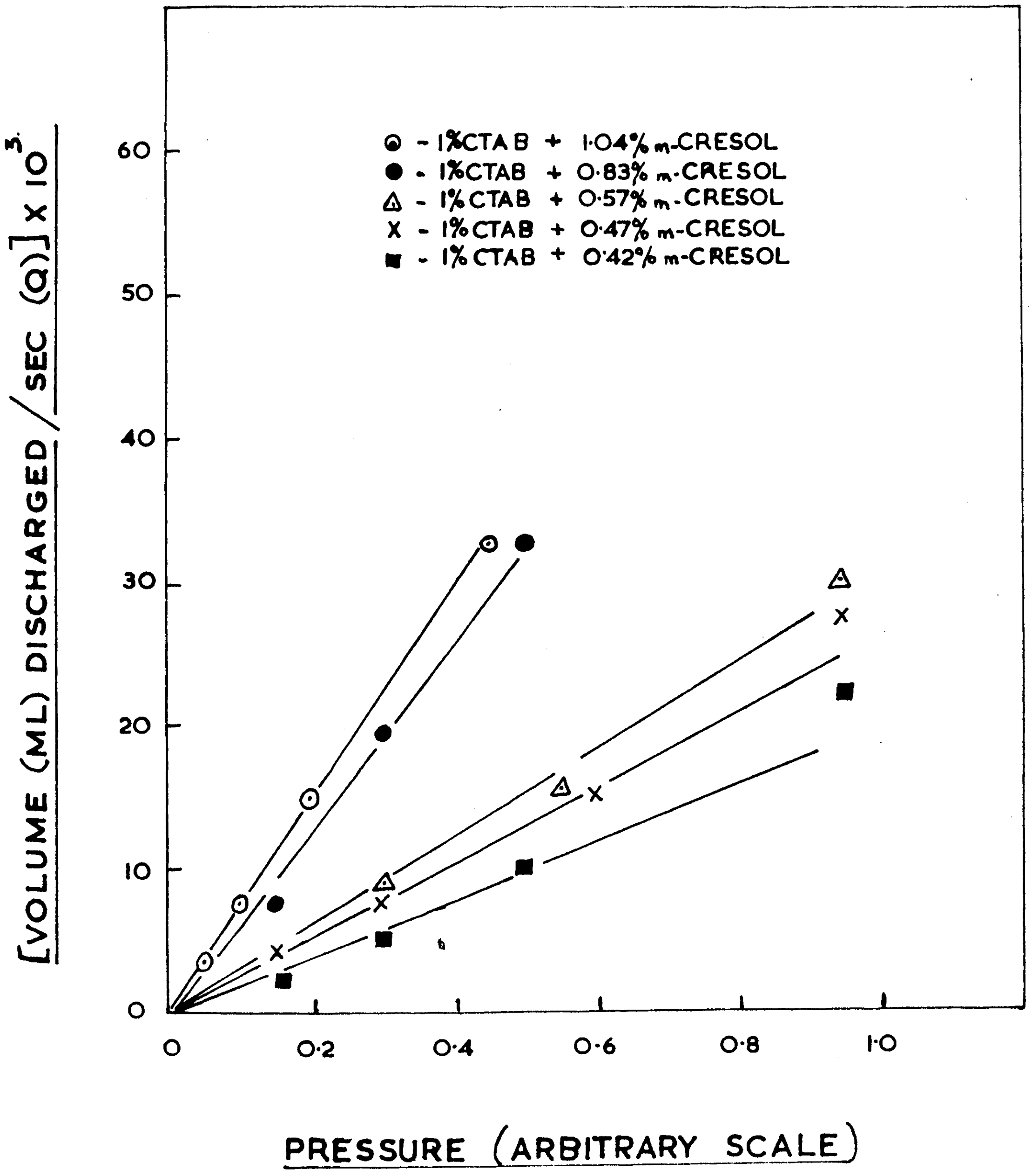
·· FIG 24(a) ··

VARIATION OF RATE OF FLOW OF C.T.A.B. + m-CRESOL SYSTEMS AT LOW PRESSURES



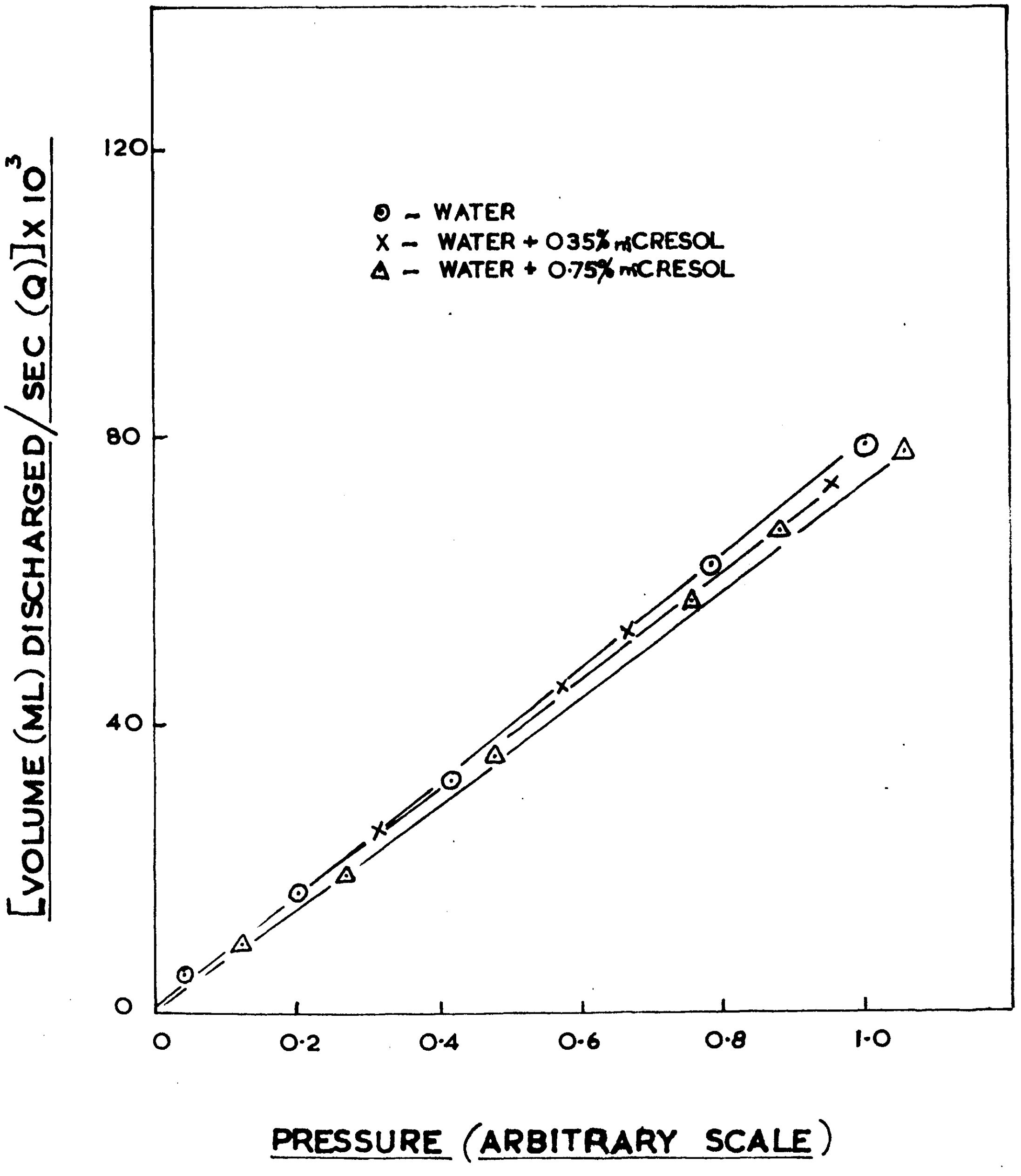
··FIG 25(a)··

VARIATION OF THE RATE OF FLOW OF C.T.A.B. + m-CRESOL SYSTEMS WITH LOW PRESSURES



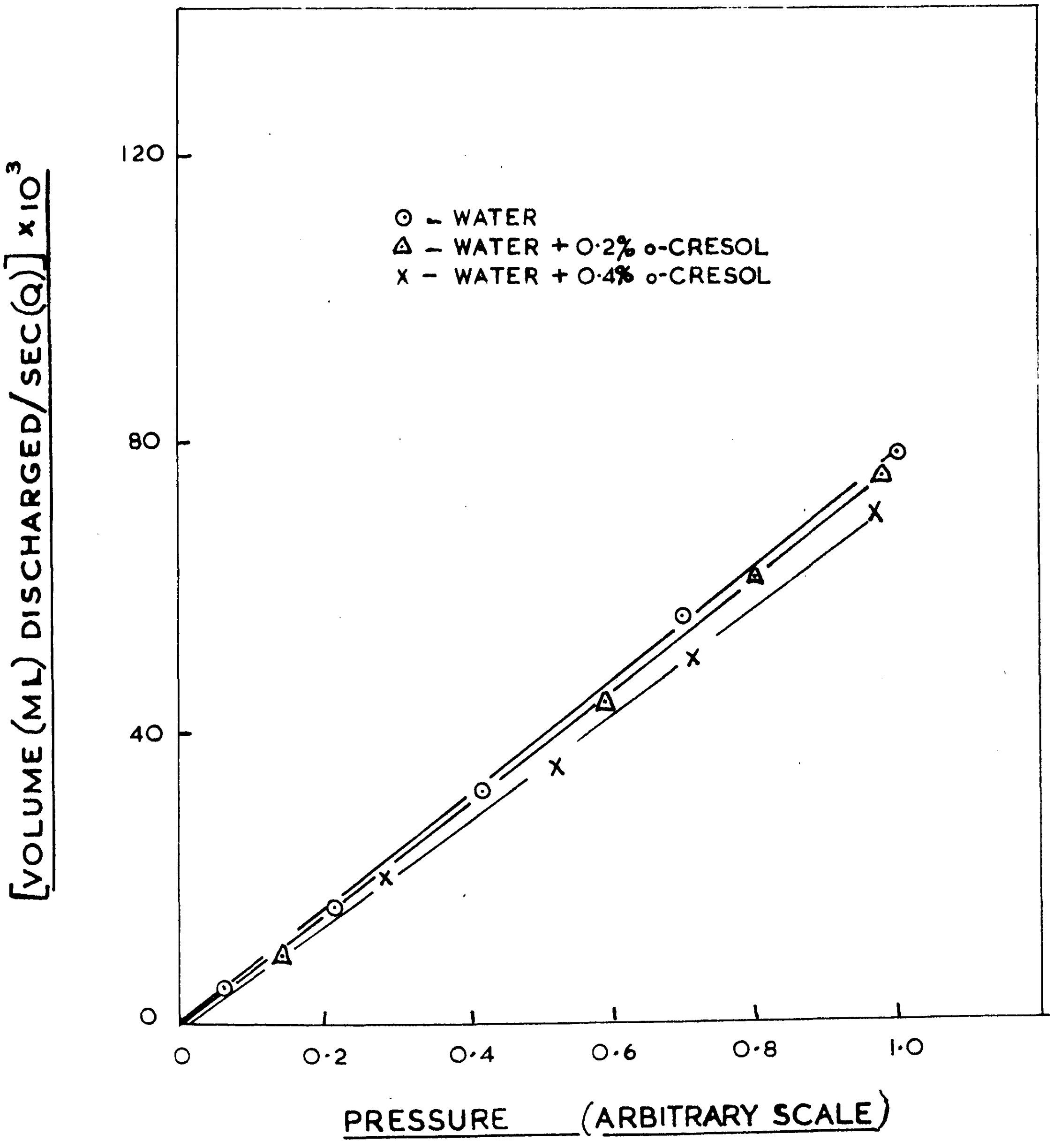
·· FIG 28 ··

VARIATION OF THE RATE OF FLOW OF WATER + M-CRESOL SYSTEMS



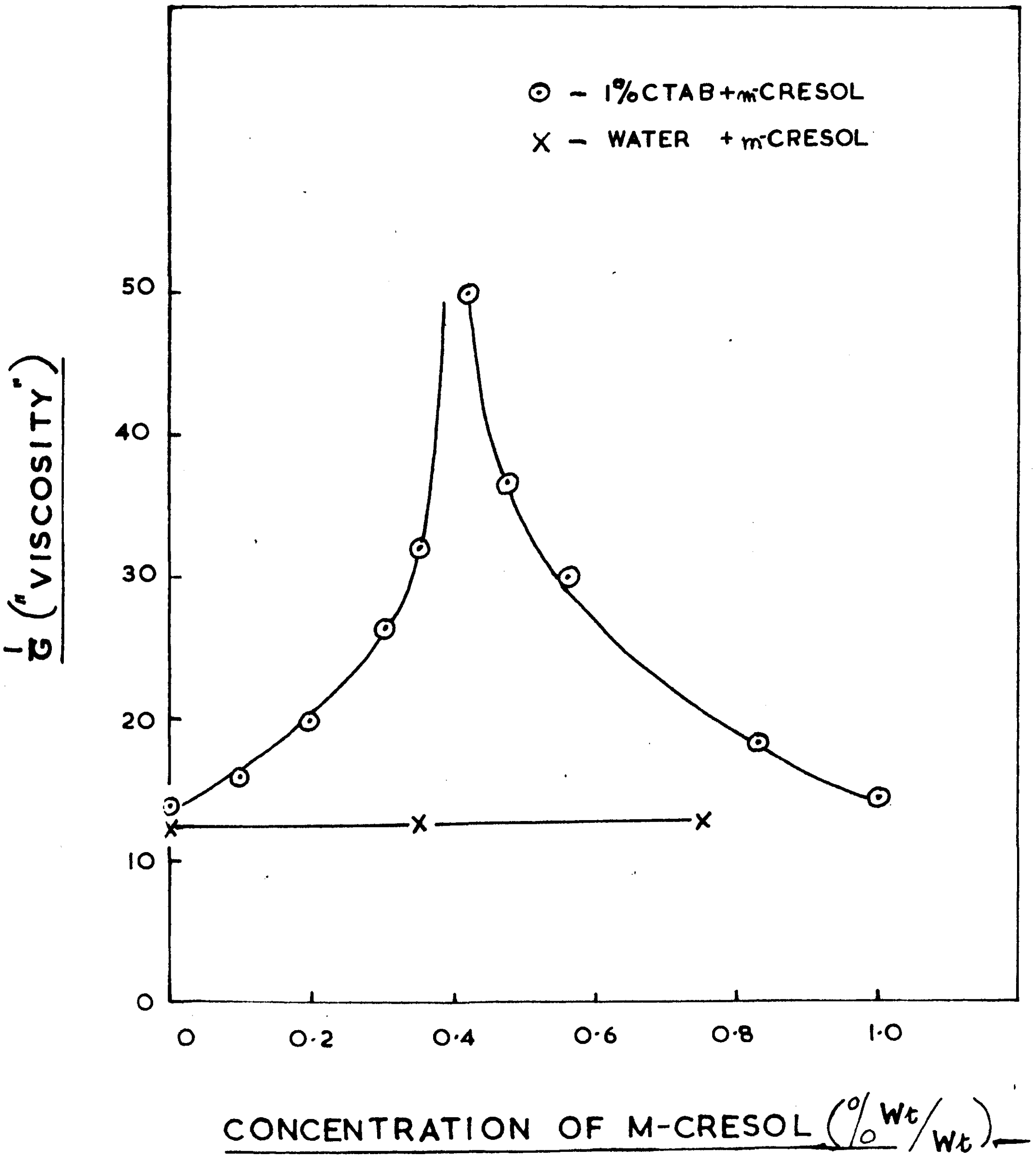
··FIG 29··

VARIATION OF THE RATE OF FLOW OF WATER + o-CRESOL SYSTEMS



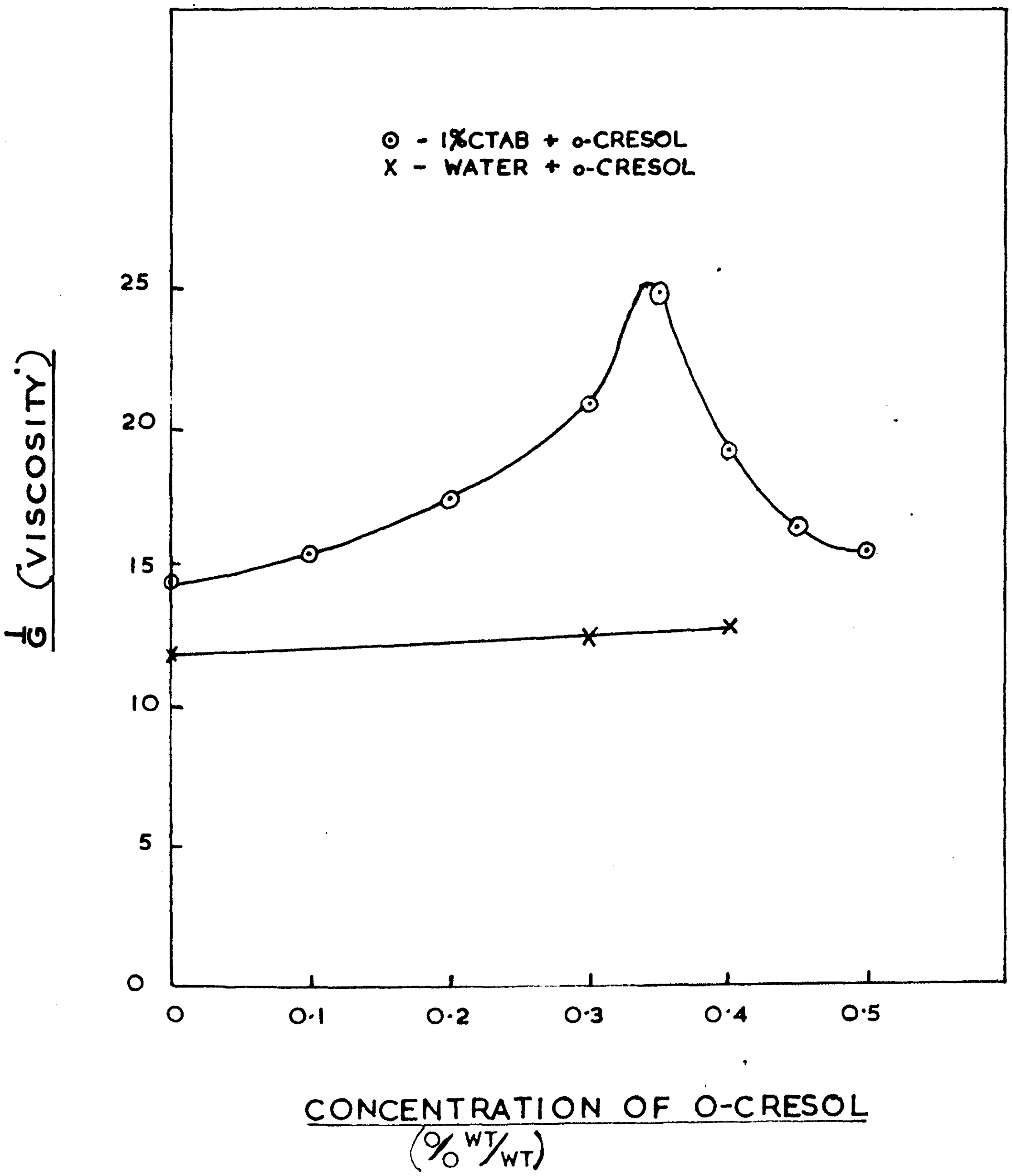
·· FIG 30 ··

VARIATION IN "VISCOSITY" WITH CONCENTRATION OF M-CRESOL



··FIG 31··

VARIATION IN "VISCOSITY" WITH CONCENTRATION OF O-CRESOL



Discussion.

The results reported here in Part I show that the addition of phenolic compounds to 1% C.T.A.B. causes changes in "zero-shear viscosity" (i.e. changes in viscous properties other than those produced by shearing) and at the same time makes the value of this viscosity very sensitive to the influence of shearing. To interpret these changes it is necessary to discuss them in terms of micellar configurations.

The existence of a viscosity maximum shows that phenol and C.T.A.B. molecules, or C.T.A. ions, must be interacting, and with optimum strength, at a certain phenol concentration.

It is assumed that the micelles in the 1% C.T.A.B. system are spheroidal in shape being in the form of Hartley micelles or of Winsor's S_1 micelles. When phenol is added, at first it will be strongly solubilised into the spheroidal hydrophilic micelles, possibly because phenol is a polar additive, by penetration of the palisade layer. Consequently, the phenyl group will be immersed in the hydrocarbon interior and the hydroxyl group will be situated on or near the surface of the micelle.

While the "zero-shear viscosity" increases very rapidly with concentration of phenol (and thus probably with the amount solubilised) the relative increase is so great that it does not seem likely to be due only to an increase in the diameter of the micelle. (i.e. swelling of the micelle).

Therefore, it is concluded that the solubilisation of phenol by the C.T.A.B. micelles must involve the spheroidal micelles rearranging themselves to form new micellar structures which result in a higher "viscosity". It is probable that this rearrangement entails the spheroidal micelles being transformed into lamellar or threadlike micelles.

If this is the micellar change brought about by the addition of phenol, then it apparently takes place only during the growth of the concentration of phenol to about 0.5% because thereafter the addition of more phenol causes the "viscosity" to decrease rapidly. This suggests a reversal of the process or the onset of a new one.

It is probable that, relative to the amount of C.T.A.B. present and the micellar structure being generated, at or near the viscosity maximum, the structure becomes saturated with phenol. Further phenol cannot now be accommodated with the phenyl groups embedded in the hydrocarbon interior of the cylindrical, or more probably, lamellar micelles. These groups are now constrained to exist on or within, the ionic double layer and are anchored in some degree by the polar hydroxyl groups. Now, this situation clearly represents the beginning of a gradual breaking up of the lamellar micelles, and with them the double layer, to give micellar organisations which become progressively less extensive in the liquid medium, with the result that there is a fall in viscosity.

These suggested micellar changes may be expressed in terms of Winsor's concept of Intermicellar Equilibrium. When phenol is added to 1% C.T.A.B. it is probably solubilised within the $\overline{C}$ regions of the system causing an increase in $A_{H\overline{c}\overline{o}}$ which increases $A_{\overline{c}\overline{o}}$. Therefore, the addition of phenol increases R̲ and displaces Winsor's Intermicellar Equilibrium to the right;

$$S_1 \rightleftharpoons \underrightarrow{(S_1 + G) \rightleftharpoons G \rightleftharpoons (G + S_2)} \rightleftharpoons S_2$$

R increasing

concentration of phenol increasing.

The "zero-shear viscosity" increases as the micellar changes proceed from S_1 to $(S_1 + G)$, reaches a maximum when $R = 1$ and begins to decrease as R̲ becomes greater than unity with the formation of $(G + S_2)$ regions. It is considered that only an equilibrium proportion of the S_1 micelles pass through the G phase structure and that the remaining micelles pass, more or less, directly to S_2 micelles.

While it seems certain that there must be an increase in $A_{H\overline{c}\overline{o}}$ when phenol is solubilised in the $\overline{C}$ regions of the system, it is difficult to determine the actual interactions which occur. The solubilisation of the phenol molecules takes place probably between the C.T.A. cations in the micelle (i.e. in the site of solubilisation of polar additive), and therefore tends to neutralise, by means of its dipole moment, the mutual repulsion between neighbouring C.T.A. cations on the surface of the micelle.

It has been shown by DeBoer (107) that there is an association, due to the π- electron attraction, which causes aromatic nucleii to arrange themselves in parallel rows. Thus, it is probable that the phenol molecules solubilised in the micelles tend to interact with each other in this way, trying to arrange themselves in parallel rows, so that the micelles containing phenol molecules have a tendency to become long and threadlike in shape, making the liquid system more viscous.

These interactions could account for the increase in $A_{H\overline{c}\,\overline{o}}$, with the resultant increase in "zero-shear viscosity", when phenol is added initially to 1% C.T.A.B.

If the interpretation of the micellar changes taking place when phenol is added to 1% C.T.A.B. is correct, then similar micellar changes are to be expected with other phenolic compounds as additives. The value of the maximum time of flow or viscosity and also the concentration of phenolic additive producing it are dependent on the nature and position of the groupings attached to the phenol skeleton.

From figures 23, 30 and 31, it can be seen that the additions of cresols to 1% C.T.A.B. produce curves of viscosity versus concentration of cresol in which p-cresol shows the greatest viscosity maximum and o-cresol the smallest one. This seems to indicate that p-cresol is more effective in forming the G phase with 1% C.T.A.B. than is m-cresol and even more effective than is o-cresol.

A probable explanation may be that p-cresol molecules, because of the para position and hydrophobic nature of the methyl groups in them, are more firmly enclosed within the C.T.A.B. micelle than the molecules of the other cresol isomers. The hydroxyl groups of these p-cresol molecules would be positioned very near to, if not at, the surface of the micellar organisation and would be interplaying electrically with the ions of the double layer. Consequently the concentration of p-cresol which interacts with the C.T.A.B. system with optimum strength would produce, in this way, a very extensive and co-herent G phase. The formation of such a phase at a certain p-cresol concentration would account for the large maximum in the curve of "viscosity" vs. concentration of p-cresol added to 1% C.T.A.B.

If o-cresol molecules are solubilised in a similar fashion, they would have on the surface of the micelle their hydrophobic groups which would tend to break up the ordered arrangement of the electrical units in the double layer and thereby hinder the formation of an extensive and co-herent G phase. Also, since the methyl groups of the o-cresol molecules are on the micellar surface there would be a lesser tendency for the o-cresol molecules to anchor themselves in the hydrocarbon interior of the micelles with the result that the micellar aggregates formed by o-cresol and C.T.A.B. are less compact than those formed by p-cresol and C.T.A.B. Thus, for these reasons o-cresol when added to 1% C.T.A.B. produces a relatively (compared with p-cresol) small maximum in the curve of "viscosity" vs. concentration of cresol added.

Using this concept of solubilisation of cresol molecules in the C.T.A.B. micelles, it is readily understood why the addition of m-cresol to 1% C.T.A.B. produces an intermediary (between p-cresol and o-cresol) behaviour. When m-cresol molecules are solubilised in the C.T.A.B. micelles their methyl groups, owing to their position on the phenyl groups, would be only partially "dissolved" in the hydrocarbon regions of the micelle. Consequently, although the micellar aggregates would form a G phase more extensive than that produced by o-cresol, it would not be so co-herent as that formed by p-cresol.

The fact that the addition of o-ethyl phenol to 1% C.T.A.B. yielded a maximum in time of flow smaller than that produced by o-cresol (o-methyl phenol) is consistent with the explanation put forward in this discussion. The o-ethyl phenol molecules would be solubilised in the micelle in a manner similar to the o-cresol molecules. This means that the lipophilic ethyl groups situated at or near the surface of the micelle would lessen, even more than in the case of the methyl groups, the ordered arrangement of the electrical units in the double layer. Therefore, the G phase is formed only to a small extent.

The addition of p-ethyl phenol to 1% C.T.A.B. caused the time of flow to increase until a phase change occurred at 0.22% (see figure 12). At this concentration, it was found that with the same holding time, the value of the time of flow was greater than the maximum time of flow produced by either o-cresol or by m-cresol although less than that produced by p-cresol. The shape of the curve suggests however that, were it not for the break-down into two phases, p-ethyl phenol would give an even greater maximum than p-methyl phenol (p-cresol).

When systems of 1% C.T.A.B. containing phenolic additives are sheared in a capillary tube a condition appears to be induced which causes the time of flow to increase. This condition created by shearing seems to be only temporary as the time of flow (a function of this condition) decreases with holding time (the time during which the system remains at rest after shearing i.e. the time for relaxation). It can be seen in figures 6 to 13, that the addition of different additives produced systems which were affected by shearing to different degrees because the time of flow varied considerably with the holding time. Provided the holding time was greater than 15 seconds, a system of 1% C.T.A.B. + 0.5% phenol gave a time of flow independent of the holding time, see figure 6, but the time of flow of a 1% C.T.A.B. + 0.4% p-cresol system varied with holding time even when the holding time was as long as about 100 minutes, see figure 9.

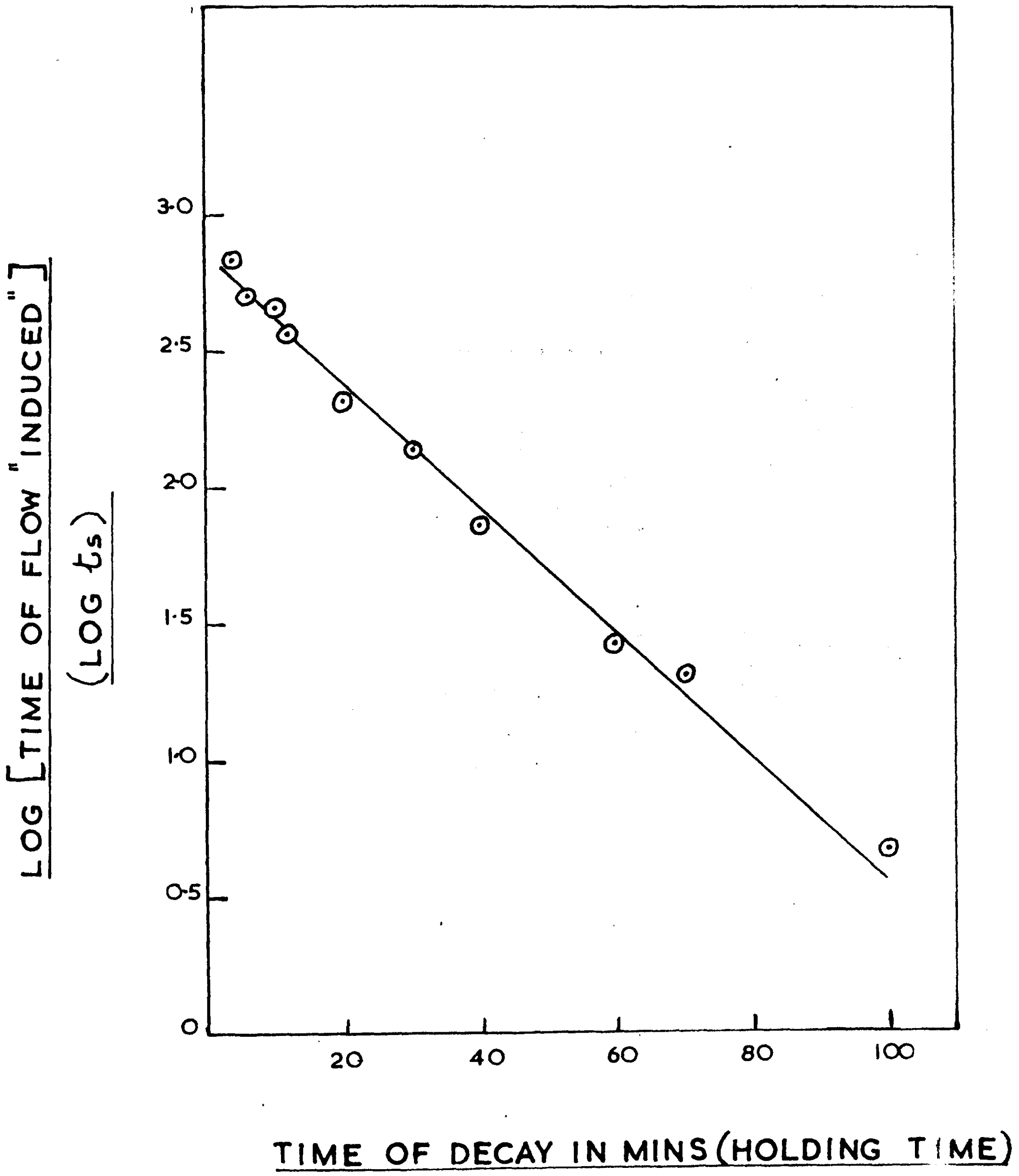
In figure 9, it can be seen that with increase in holding time, the time of flow decreased to an apparently constant value and this was taken as the time of flow which was independent of the holding time, t_{Fo}. The value of t_{Fo} was the asymptote to the curve drawn parallel to the holding time axis. Thus, t_{Fo} was taken as the time of flow of 1% C.T.A.B. + 0.4% p-cresol system in the absence of shearing effects other than those which may be induced on it while the time of flow was being measured. This meant that any time of flow values greater than t_{Fo}, were induced by the shearing in the capillary as the liquid was forced up the left-hand limb (see figure 4). Thus, at a holding time of 10 minutes, the time of flow due to shearing effects, t_S^1, was the difference between the time of flow measured after a holding time of 10 minutes and t_{Fo}. Similarly, t_S^{11} was the difference between the time of flow measured at a holding time of 30 minutes and t_{Fo}. In this way the time of flow induced by shearing, t_S, was determined and a plot of log (t_S) against holding time is shown in figure 32.

Now, since t_S is the time of flow induced by shearing, it can be regarded as a function of the "concentration" of the condition induced by shearing. The holding time is the time the system is allowed to relax. Thus, the linear plot shown in figure 32 shows that the log (concentration of the induced condition) decays according to a first order law. Now, this is the type of law which is consistent with the disintegration of aggregates. Therefore, it is possible that when systems of 1% C.T.A.B. + phenolic additive are forced up the capillary they may be distorted in different degrees, in such a way that structural aggregates are built up which give rise to the induced condition.

The curves of volume of liquid discharged per second against pressure for these systems (1% C.T.A.B. + phenolic additive - e.g. see figure 20) all show that the viscosity decreases with increase in pressure and resemble the curves produced by systems which have been described as showing quasi-viscous flow. Thus, it is interesting to note that while the time of flow of these systems increases with shearing, the "viscosity" measured at low pressures decreases with increase in pressure. This indicated that the shearing effect needed a closer investigation and this was carried out as described in Part II.

•• FIG 32 ••

THE RATE OF DECAY OF THE INDUCED CONDITION IN THE 1% CTAB + 0·4% P-CRESOL



EFFECT OF SHEARING ON THE VISCOUS PROPERTIES OF C.T.A.B. SYSTEMS CONTAINING PHENOLIC ADDITIVES.

INTRODUCTION.

It was noted in Section A of Part I that the times of flow of systems of 1% C.T.A.B. containing certain phenolic compounds were apparently increased by the shearing influence to which they were subjected while they flowed through the capillary tube in the viscometer. This effect needed more detailed study and Part II describes those experiments which were undertaken to verify it.

A system whose time of flow, or viscous property, is increased with shearing can be described as possessing the property of negative thixotropy. This phenomenon is rarely encountered in dilute solutions but, as was indicated in the historical review, Hartley (92) has observed this property at 80-90°C in a 0.02% solution of the copper salt of cetyl-phenyl-ether sulphonic acid.

Hartley found that, if a slow stream of air bubbles of suitable size was introduced at the bottom of a large beaker full of this solution, the bubbles rose through an undisturbed solution in a similar manner to that in which they rose through water and also in a similar time but, if the solution was gently stirred, the upward course of the bubbles took much longer and was extremely irregular. Also, he observed that they frequently collected in small clusters and, whether single or in clusters, the bubbles seemed to halt at, or be diverted

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Eliassaff, Silberberg and Katchalsky (108) have found that aqueous solutions of polymethacrylic acid also exhibited this phenomenon. Sufficiently concentrated aqueous solutions of polymethacrylic acid (about 8-15%) form clear stiff gels at room temperature. At lower concentrations, such systems are sols which, when heated, are converted into gels but on cooling, the gelation is reversed. Eliassaff and his co-workers found that a several hundred fold increase in consistency was easily induced by shaking or stirring and that some of the systems actually set into firm gels. If the systems were left undisturbed for one hour all transformations induced by shaking or stirring reversed to their original state.

Eliassaff envisages the field of flow within liquid systems as acting in two ways:

(1) structures being built up by more intermolecular bonds being formed and

(2) structures disintegrating due to the breaking of those molecular bonds which are insufficiently strong. Consequently, he suggests that liquid systems will show negative thixotropic or thixotropic properties depending on whether the former or the latter process predominates.

He considers that in solutions of polymethacrylic acid, intermolecular cross links of hydrogen bonds between carboxyl groups on neighbouring chains are formed while the liquid system is being stirred.

It has been known for a long time that laminar flow increases the velocity of aggregation of colloidal particles in unstable sols. An explanation of this phenomenon, on the basis of the collision theory, has been put forward by Smoluckowski (109).

More recently, a detailed study of the behaviour of suspended particles and liquid droplets in solution, under the influence of laminar shear, has been carried out by Mason and his co-workers (110). From their work, the following interesting information about these systems has been obtained.

(1) Particles suspended in a liquid when subjected to a velocity gradient, undergo rotational and translational movements.

(2) At low velocity gradients, fluid spheres rotate at the same angular velocity as rigid spheres but as the velocity gradient is increased, fluid particles are distorted into ellipsoids and the rotation is modified.

(3) The translational movements of equal sized spheres cause the particles to come into collision with one another and form doublets.

(4) The rate of formation, the lives and rotational velocities of the transitory doublets of rigid spheres have been found to be in excellent agreement with the values calculated on the basis of a rectinlear approach of two spheres.

(5) Rigid spheres approach one another very closely but

do not come into true physical contact.

(6) When the two interacting spheres are of different diameters the interactions appear to be very complex.

(7) Fluid spheres behave similarly to rigid spheres but in their case, the two particles under certain conditions may coalesce to form a single sphere. This phenomenon aids the formation of aggregates and consequently, the size of the aggregates in the solution is increased with rate of shear.

Bartok and Mason (111) have observed the deformations which liquid droplets, suspended in a liquid system, undergo when they are subjected to a rate of shear. They found that all liquid droplets did not undergo the same type of deformation. Some droplets were transformed, firstly, from spheroids to ellipsoids and then, with increase in shear, were deformed into sigmoidal shapes which had thin streaks of liquid disintegrating from the ends. As the rate of shear increased further these drops reverted to their more stable ellipsoidal shape. However, other droplets behaved differently and were transformed, firstly, from spheroids to ellipsoids, but as the rate of shearing increased these drops became more elongated and eventually a small neck was formed in the centre of each drop. With further increase in the rate of shear, this neck severed and two separate drops were formed.

The concept of decrease in particle size with high shearing forces had been suggested previously by Kuhn (112).

APPARATUS USED FOR STUDYING THE SHEARING EFFECTS.

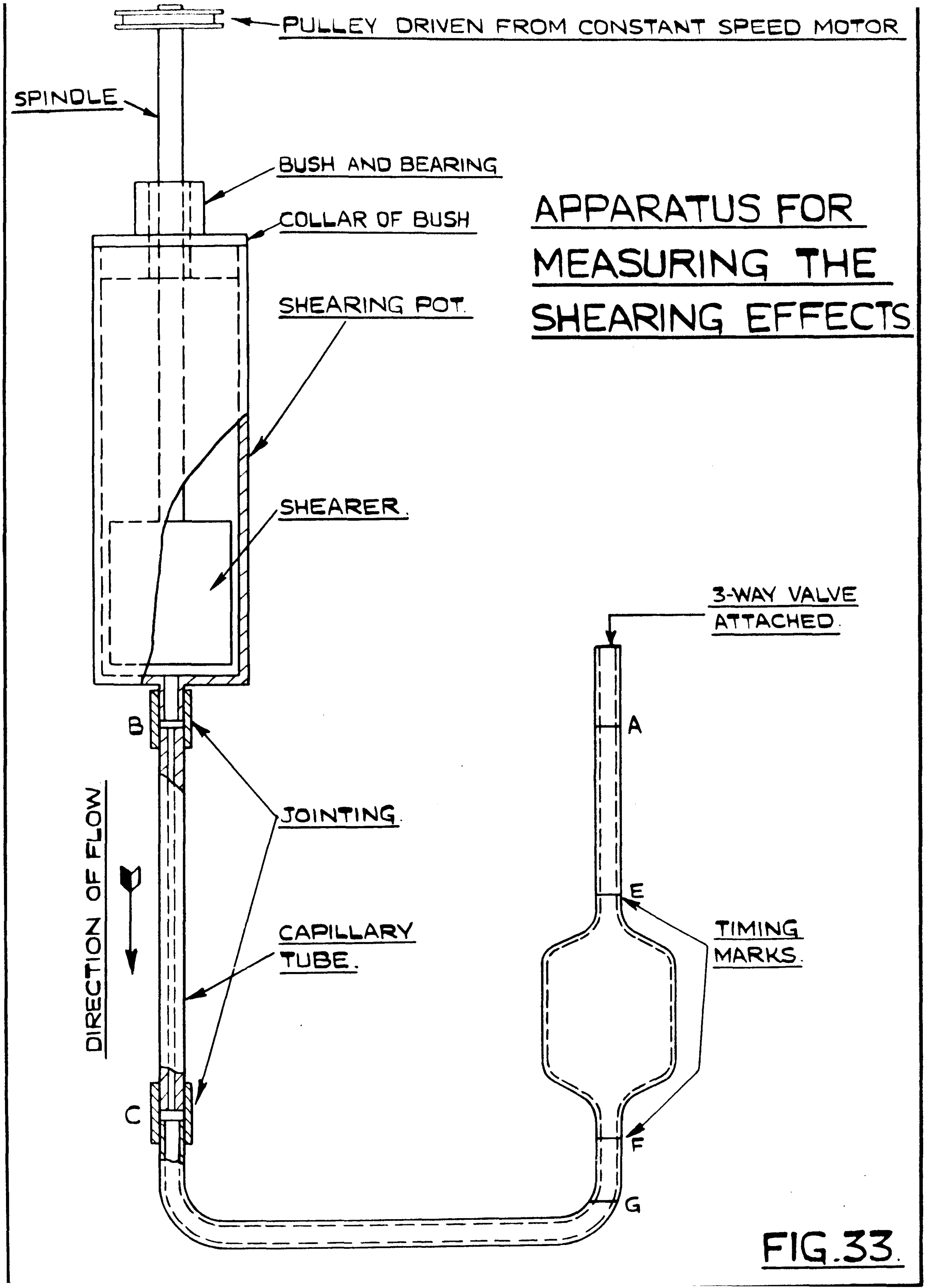
The apparatus used for studying the changes in time of flow of liquid systems caused by different shearing influences is shown in figure 33.

The liquid was sheared in a cylindrical nickel-plated shearing pot of internal diameter 3.9 cm. and 13 cm. in height. The shearing influence was produced by a solid nickel-plated cylinder (shearer) 3.2 cm. in diameter, rotating inside the shearing pot. A spindle, which passed through a bearing in a bush, connected the shearer to a pulley. Attached to the pulley was a belt driven from a multispeed motor. By regulating the speed of the motor, the drive to the spindle and the speed of revolution of the cylindrical shearer could be controlled. The bush which was made of brass, had a collar which fixed on to the top of the shearing pot and so set the position of the shearer in the pot.

The bush and bearing, spindle, pulley and shearer were made up as a complete unit so that it could be easily fixed into the shearing pot. Two such units were used each being dimensionally the same except that in unit A, the shearer was 8.3 cm. in length, while in unit B, the shearer was 3.6 cm. long.

There was a small air hole in the bush so that when the shearer units were in position in the shearing pot, the interior of the pot remained at atmospheric pressure.

At the centre of the base of the shearing pot there was an



APPARATUS FOR MEASURING THE SHEARING EFFECTS

FIG.33.

outlet 0.5 cm. in diameter. Attached to this outlet (see B in figure 33) was a capillary tube 15 cms. long and 1.0 m.m. in diameter. This capillary tube was joined to the left-hand limb of the U-tube (see C in figure 33). The right-hand limb of the U-tube was primarily a pipette having graduation marks A and G and two timing marks E and F on it (see figure 33). Thus the apparatus is really a capillary tube viscometer having a reservoir in its left-hand limb in which the system may be subjected to a specific shearing influence.

The right-hand limb of the U-tube was connected to a 3-way valve. This valve (see figure 5) could be set in three position, 1 to open the right-hand limb of the U-tube to air bellows, 2 to seal it off and 3 to open it to the atmosphere.

The apparatus was fixed in a vertical position, as shown in figure 33, and placed in an air cabinet thermostatically controlled to $25^{\circ}C \pm 0.1^{\circ}C$.

EXPERIMENTAL PROCEDURE.

Effect of Shearing on the Time of Flow of 1% C.T.A.B. + Phenol

A system of 1% C.T.A.B. + 0.5% phenol, which had been prepared as described in Part I, was investigated.

This liquid system was introduced into the right-hand limb of the U-tube and was filled to graduation mark, A. Before any measurements were made, the apparatus was allowed to stand in the thermostatically controlled air cabinet for one hour to ensure uniformity of temperature.

Method of Measuring the Time of Flow.

To take measurements, the liquid in the apparatus was forced up the left-hand limb into the shearing pot until the liquid level in the right-hand limb had fallen to graduation mark, G. The liquid level was held static at G and the liquid system in the pot was sheared (i.e. the cylindrical shearer rotated, for a given time, at a speed regulated by the speed of the motor driving the pulley). With the shearer still rotating, the liquid was allowed to flow from the shearing pot through the capillary tube and the time that elapsed for the liquid level to rise from timing mark F to E (i.e. the time of flow) was measured with a stop-watch to ± 0.1 second.

To force the liquid up the left-hand limb of the apparatus, the 3-way valve was adjusted so that the air flowed from the bellows into the right-hand limb causing the liquid to be pushed up into the shearing pot. When the liquid level in the right-hand limb had fallen to G, the valve was set so that no air entered or left the U-tube, thus maintaining the liquid at a static position. To release the liquid in order to measure the time of flow the valve was adjusted so that the right-hand limb of the apparatus was open to the atmosphere.

Experimental Investigations.

The first investigation to be carried out was to measure the times of flow at different shearing speeds (speeds of rotation of the shearer) using unit A (8.3 cm. long).

The apparatus was filled with a system of 1% C.T.A.B. + 0.5% phenol and its time of flow determined with the shearer not rotating (i.e. time of flow at zero speed of shearing). Once this had been done, the times of flow of the same liquid system were measured at shearing speeds from 50 to 500 R.P.M. The liquid system was sheared for 2 minutes at each of these speeds. The speed of the shearer was increased immediately the liquid level returned to graduation mark, A. Once the speed of the shearer had been adjusted to the next speed the liquid was forced back to the shearing pot to be sheared for 2 minutes at the new speed. It took approximately 20 seconds to force the liquid back to the shearing pot. After the time of flow, for a shearing speed of 500 R.P.M., had been determined, it was thereupon redetermined at this speed. The shearing speed was reduced to 430 R.P.M. and its time of flow measured. Then followed the determinations for shearing speeds decreasing from 430 to 0 R.P.M.

The measurements taken with <u>increasing</u> speeds of shearing, 0 to 500 R.P.M., were denoted as the FORWARD RUN while the measurements taken with <u>decreasing</u> speeds of shearing, 500 to 0 R.P.M. were denoted as the BACKWARD RUN.

It was observed that at the completion of the backward run the time of flow for zero speed of shearing was the same as the initial measurement in the forward run.

A plot of the time of flow vs. the speed of shearing is shown in figure 34. It can be seen that, as the shearing speed increases from 0 to 220 R.P.M., the time of flow of this liquid system increases. At shearing speeds greater than 220 R.P.M., the time of flow decreases with increase in shearing speed. Also, it is shown that the times of flow in the backward run are greater than those in the forward run (i.e. an hysteressis effect).

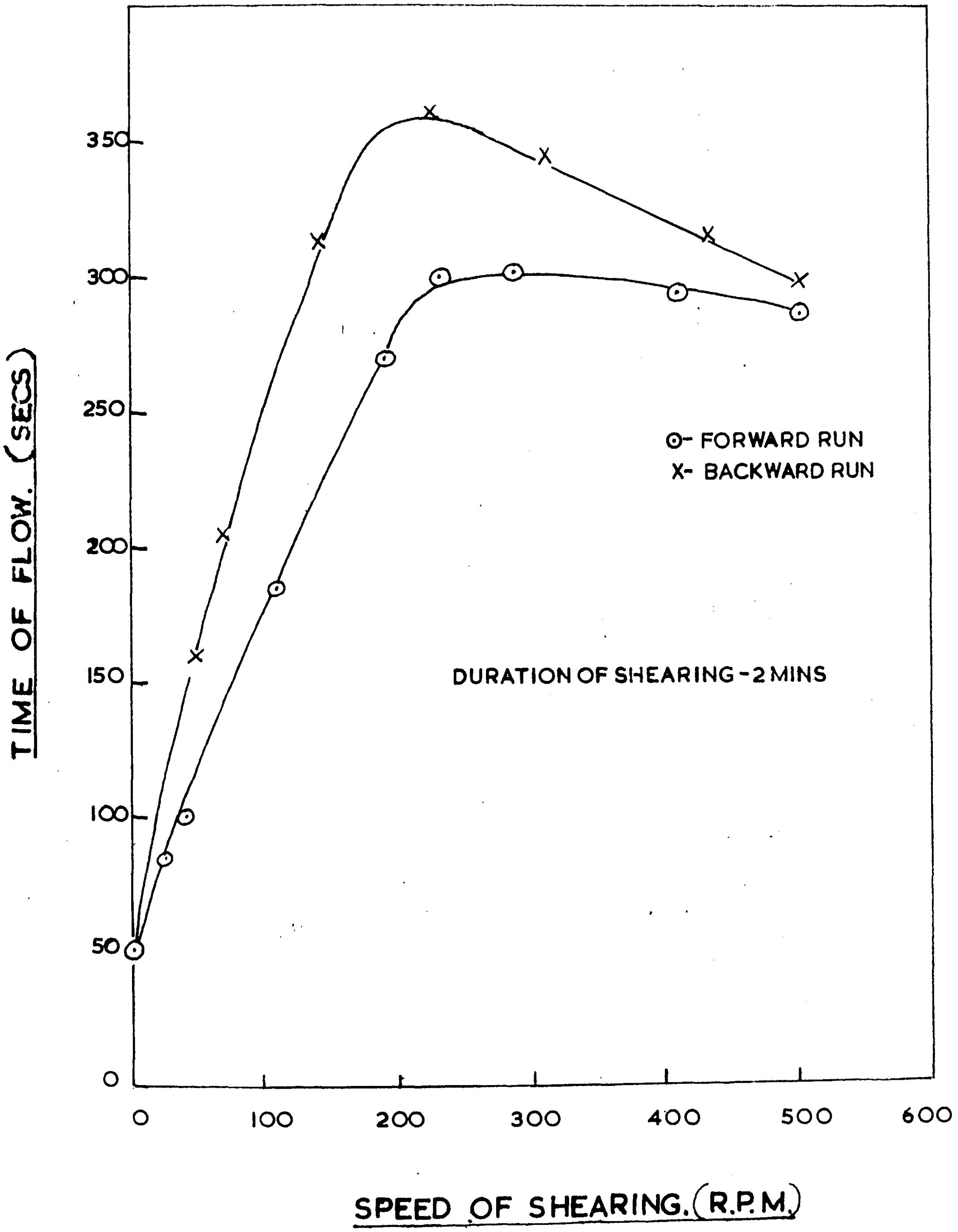
The fact that the backward run gave larger values of time of flow than those of the forward run indicates that the time of flow is influenced by the previous history of shearing. This suggested comparing the time of flow at a certain speed of shearing of a previously sheared (at lower speed) system with the time of flow of a similar amount of the same liquid system which had not been previously sheared.

The apparatus was filled with a 1% C.T.A.B. + 0.5% phenol system and the times of flow at seven speeds of shearing determined. The speeds of shearing were increased from 0 to 150 R.P.M. The plot of these times of flow vs. their speeds of shearing is shown as curve A in figure 35.

When these measurements had been completed, the apparatus was emptied and a fresh quantity of 1% C.T.A.B. + 0.5% phenol system introduced. The time of flow of this system was

··FIG 34··

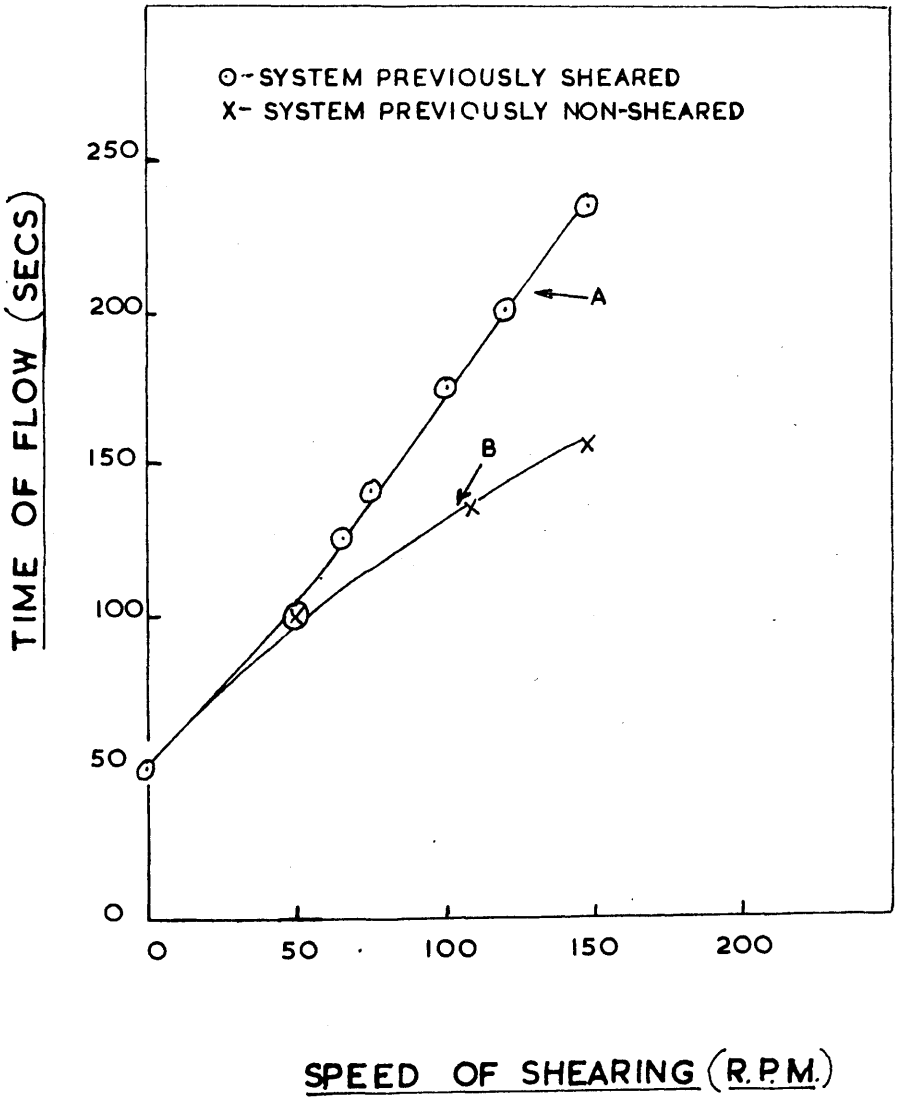
VARIATION IN TIME OF FLOW OF 1% C.T.A.B.+ 0·5% PHENOL SYSTEM WITH SPEED OF SHEARING



··FIG 35··

EFFECT ON THE TIME OF FLOW OF SHEARING SYSTEMS PREVIOUSLY SHEARED AND NON-SHEARED

(1% CTAB + 0·5% PHENOL SYSTEM SHEARED)



measured at a shearing speed of 50 R.P.M. The apparatus was again emptied and a further fresh unsheared quantity of the 1% C.T.A.B. + 0.5% phenol system introduced. Its time of flow at a shearing speed of 109 R.P.M. was determined. Then this procedure was repeated and the time of flow for another fresh quantity of this system, was measured at a shearing speed of 150 R.P.M. These measurements gave for various speeds of shearing the times of flow of previously non-sheared quantities of the system. The plot of these times of flow against their speeds of shearing is shown as curve B in figure 35.

From figure 35 it can be seen that for a system of 1% C.T.A.B. + 0.5% phenol the time of flow, besides being affected by the speed of shearing, is influenced by any previous shearing process. Thus, in order to study the effect of shearing speed on the time of flow it was necessary to use a previously non-sheared portion of the system for each measurement.

In figure 35, curve B shows the variation in the time of flow with speed of shearing for a 1% C.T.A.B. + 0.5% phenol system when the duration of shearing was two minutes + the time the system was being sheared in the pot while flowing through the capillary. Hence, before any interpretations from this curve could be made, it was clearly necessary to consider the effect on the time of flow of shearing the system at any constant speed for different periods of time.

To investigate this effect, the apparatus was filled with a 1% C.T.A.B. + 0.5% phenol system to graduation mark A. Then the liquid was forced into the shearing pot until the level in the right-hand limb had fallen to mark G. The shearer was then set rotating at a speed of 158 R.P.M. A stop-watch was used to measure the period of time the shearer was rotating (i.e. DURATION OF SHEARING). At various durations of shearing the time of flow was measured. After each time of flow measurement had been completed (i.e. the liquid level reverted to the graduation mark, A), the liquid was returned immediately to the shearing pot. Throughout these measurements the shearer was kept rotating and its speed checked at regular intervals. The plot of the time of flow against duration of shearing at 158 R.P.M. is shown in figure 36.

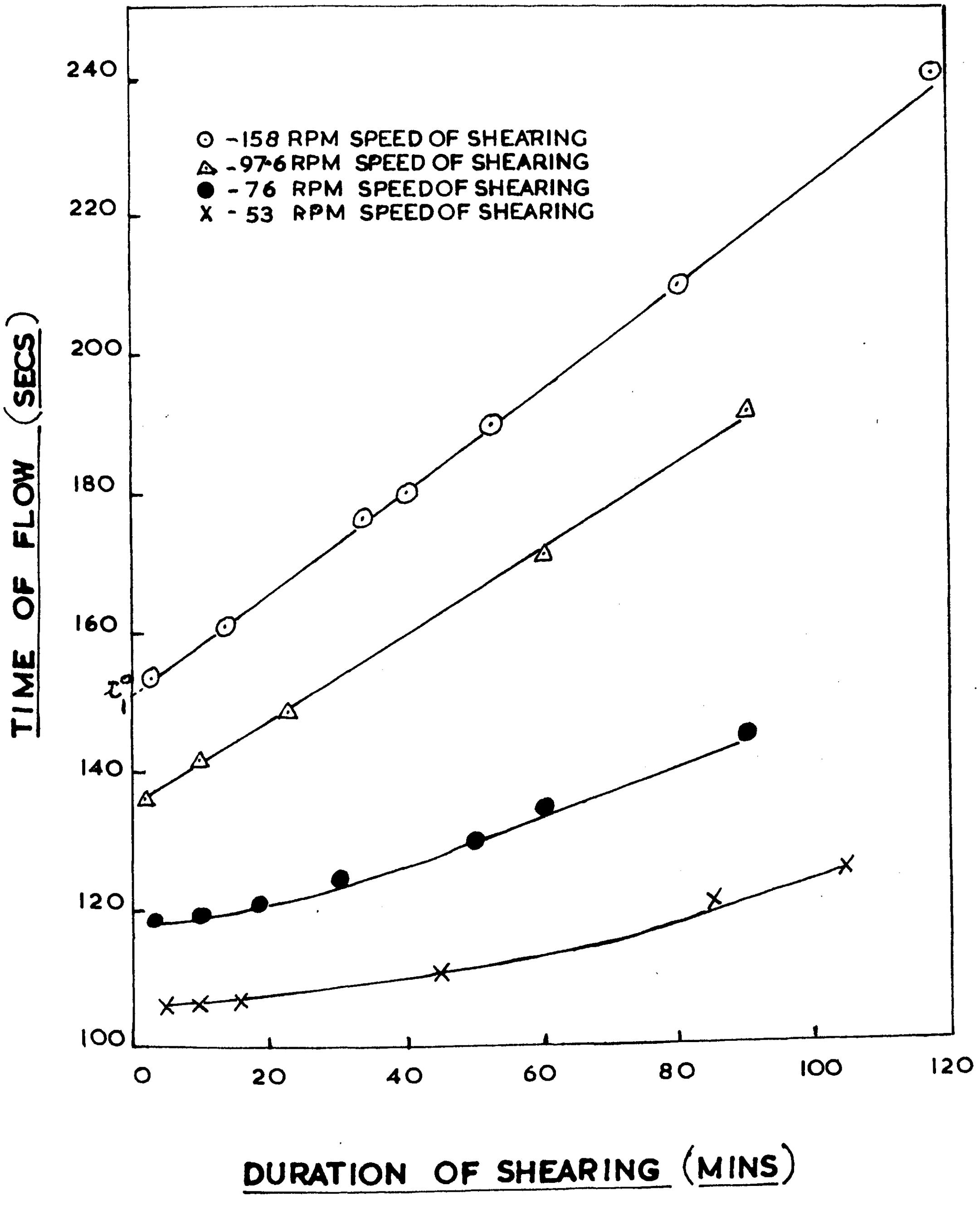
By a similar procedure, the plots for a 1% C.T.A.B. + 0.5% phenol system, of time of flow against duration of shearing at different shearing speeds, were obtained. These plots are shown in figure 36.

From these curves it appears that the time of flow of a system of 1% C.T.A.B. + 0.5% phenol is influenced by the duration of the shearing. This shearing effect was so pronounced with this system that it was decided to examine the shearing effect with other systems of C.T.A.B.

The first of these systems to be examined was 1% C.T.A.B.

••FIG 36••

VARIATION IN THE TIME OF FLOW OF THE 1% C.T.A.B.+ 0·5% PHENOL SYSTEM WITH DURATION OF SHEARING



alone and the plot of time of flow against duration of shearing for different shearing speeds are shown in figure 37. These plots showed that the time of flow of 1% C.T.A.B. was neither affected by the speed of shearing nor the duration of shearing. Similar experiments with a system of 0.05% C.T.A.B. alone also showed no variation in the time of flow with either speed of shearing or duration of shearing.

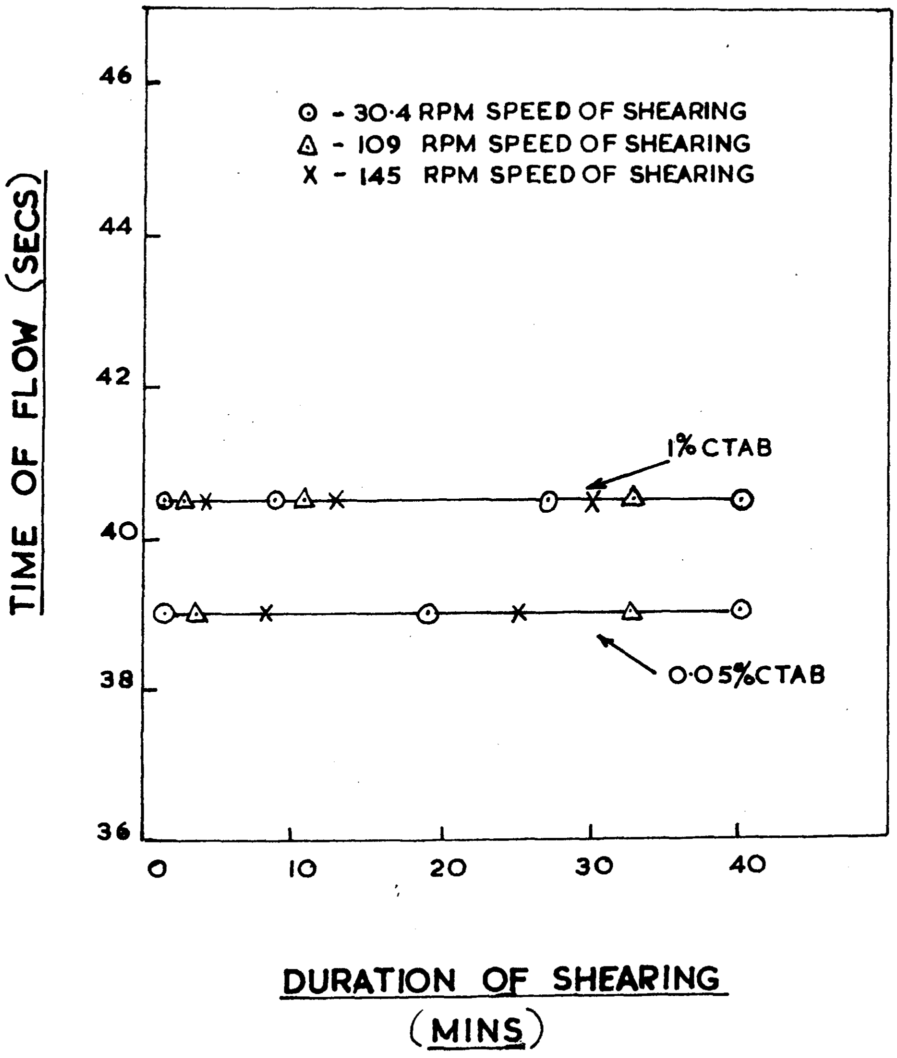
By the procedure described previously, the variations of the time of flow with duration of shearing for different speeds of shearing were determined for systems of 1% C.T.A.B. containing different percentages of phenol 0.3, 0.4, 0.6 and 0.8 and their respective plots are shown in figures 38, 39, 40 and 41.

It can be seen that the time of flow of each of the systems appeared to be increased with the speed and with the duration of shearing to which they had been subjected. To characterise the effect which the speed of shearing had on the time of flow it was obviously necessary to determine, by extrapolation, the times of flow obtained at zero duration of shearing, t^o, for several speeds of shearing.

The t^o values for the system of 1% C.T.A.B. + 0.5% phenol for several shearing speeds were obtained from figure 36. The time of flow at zero duration of shearing for a speed of shearing of 158 R.P.M., t_1^o, was that value of time of flow at which the curve of time of flow vs. duration of shearing for a speed of shearing at 158 R.P.M.

•• FIG 37 ••

VARIATION IN TIME OF FLOW OF C.T.A.B. SYSTEMS WITH DURATION OF SHEARING



··FIG 38··

VARIATION IN THE TIME OF FLOW OF THE 1% CTAB+0·3% PHENOL SYSTEM WITH DURATION OF SHEARING

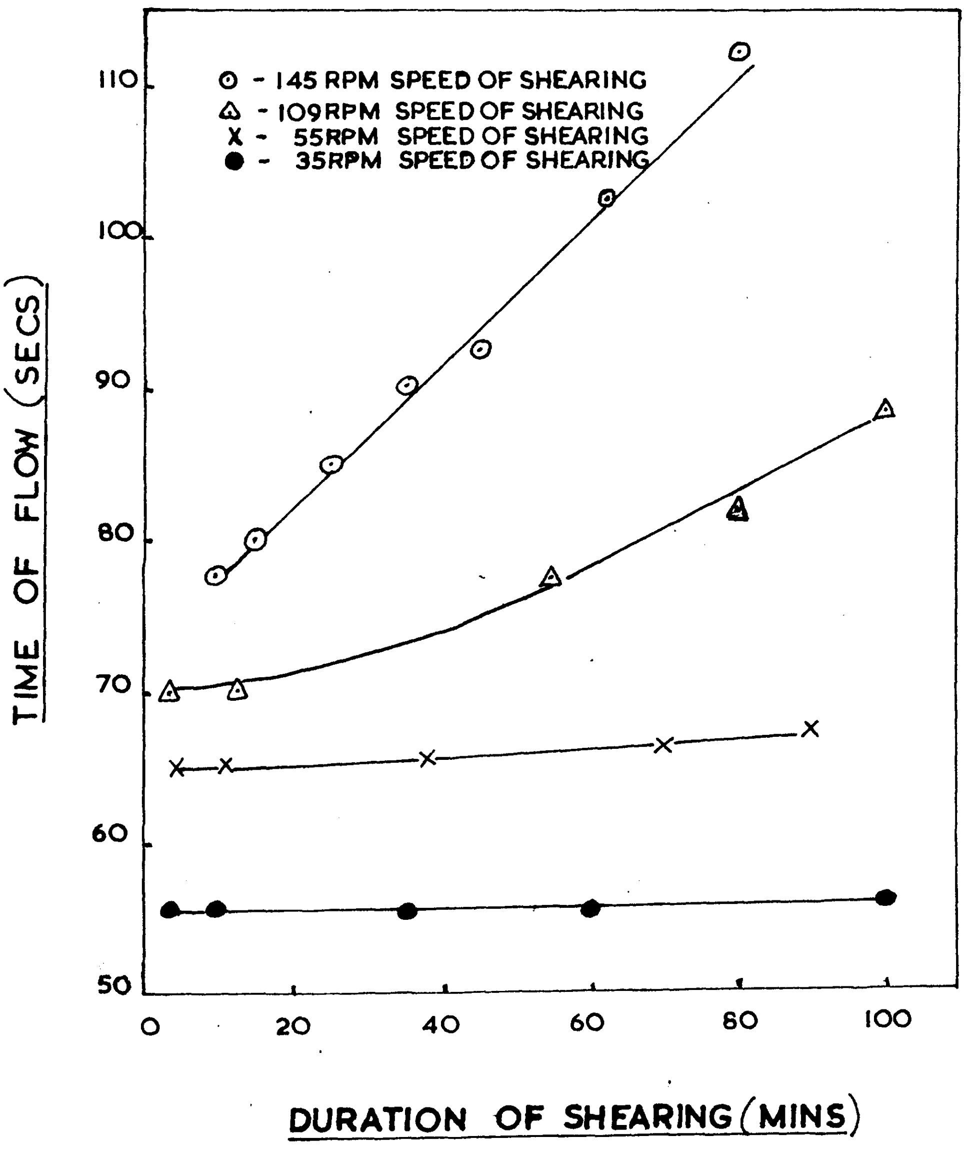
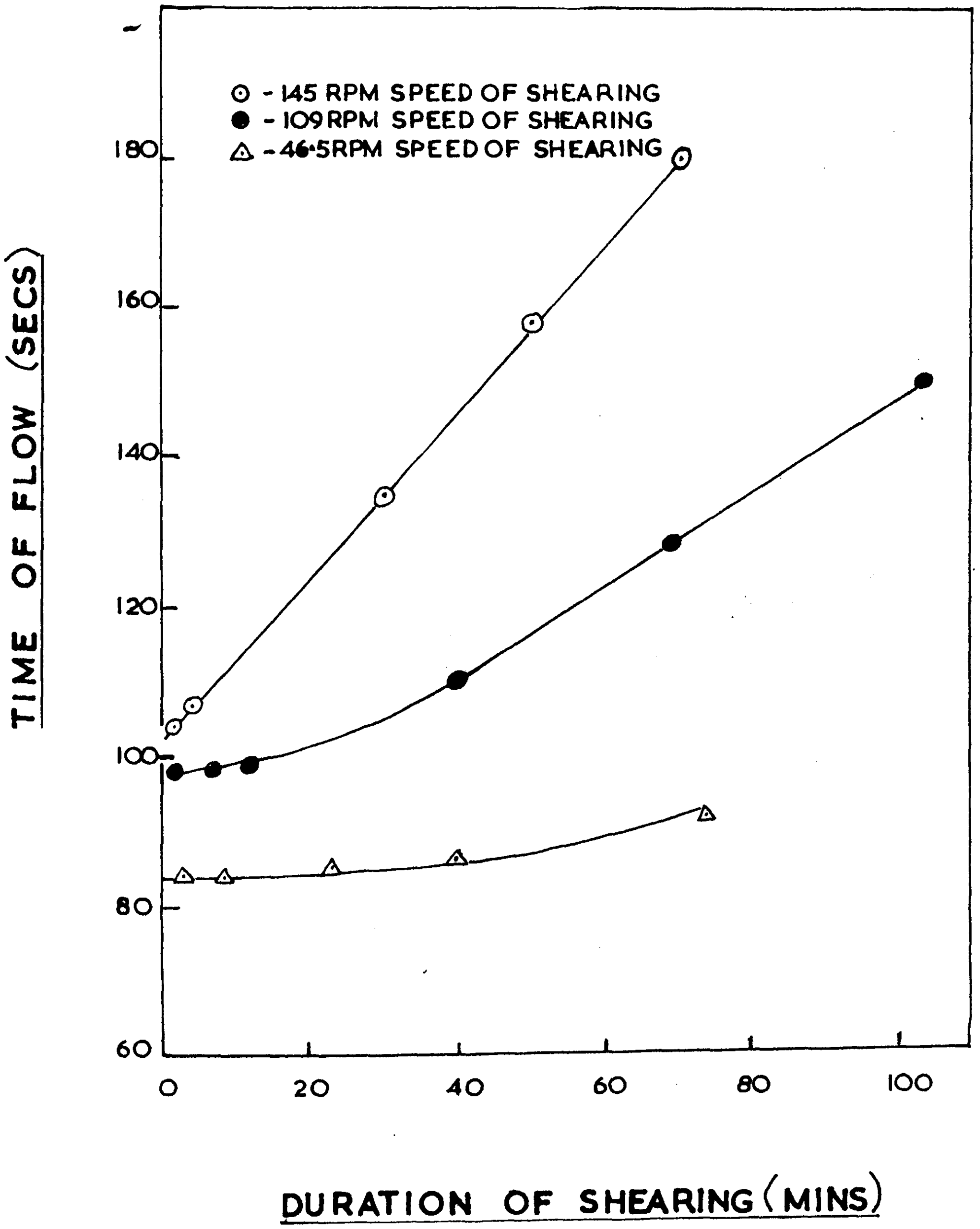


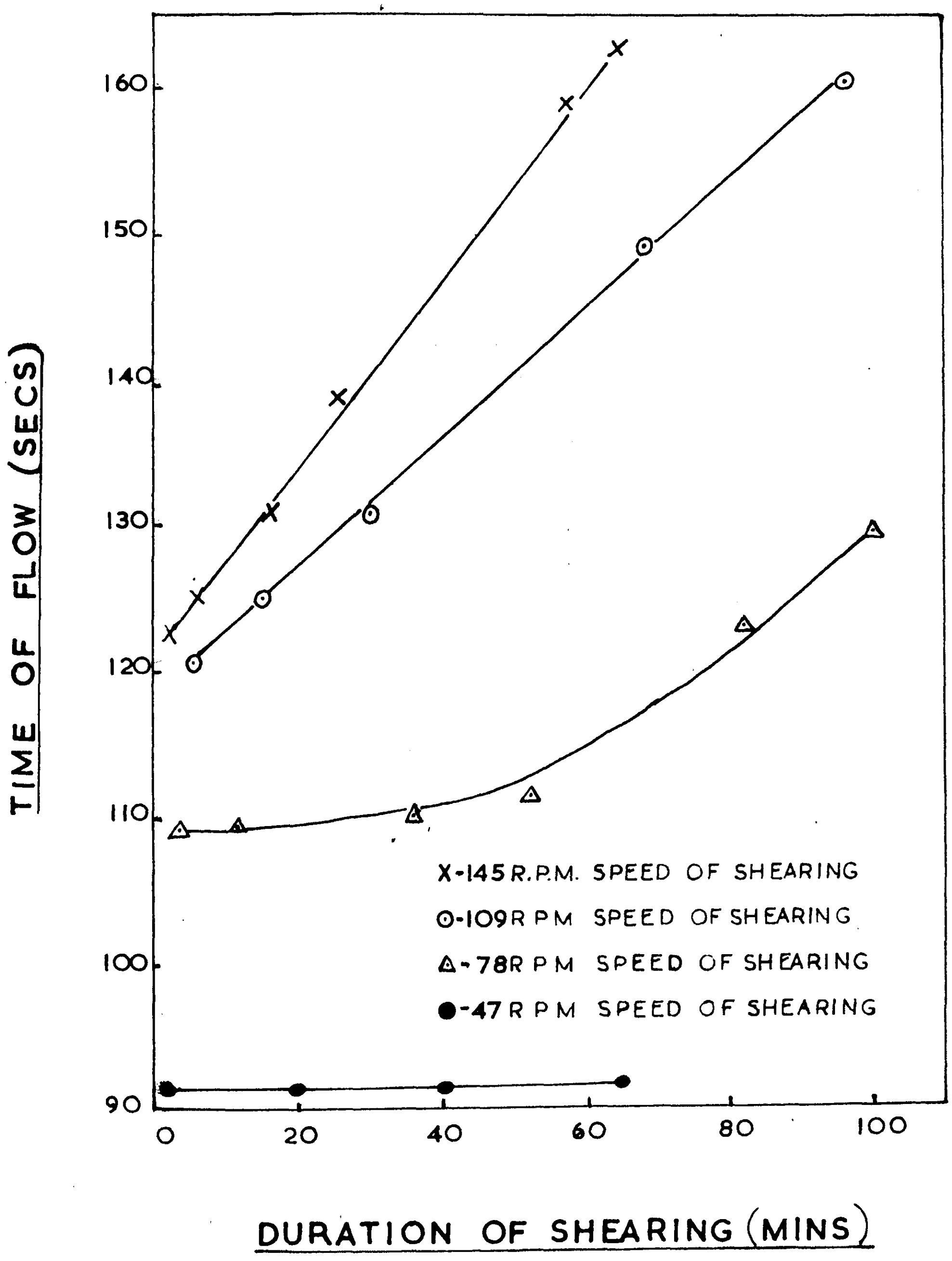
FIG 39

VARIATION IN THE TIME OF FLOW OF THE 1% CTAB + 0·4% PHENOL SYSTEM WITH DURATION OF SHEARING



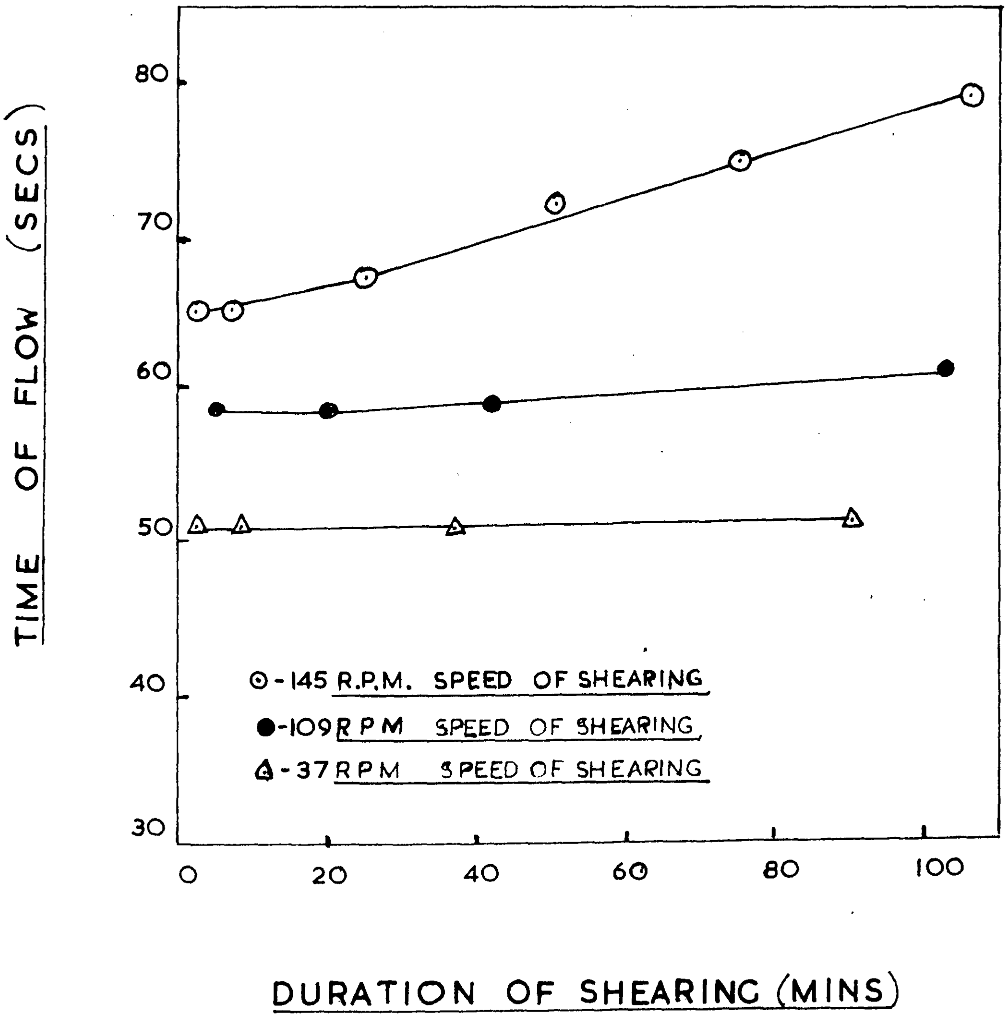
··FIG 40··

VARIATION IN THE TIME OF FLOW OF THE 1% C.T.A.B. + 0·6% PHENOL SYSTEM WITH DURATION OF SHEARING



••FIG 41••

VARIATION IN THE TIME OF FLOW OF THE 1% CTAB+0.8% PHENOL SYSTEM WITH DURATION OF SHEARING



cut the zero duration of shearing axis.

From figure 36, the t^o values for 1% C.T.A.B. + 0.5% phenol system were obtained for speeds of shearing of 97.6, 76 and 53 R.P.M. These values of t^o were then plotted against the speed of shearing and the curve is shown in figure 42.

From figures 38, 39, 40 and 41 the values of t^o were obtained for several speeds of shearing for systems of 1% C.T.A.B. containing 0.3, 0.4, 0.6 and 0.8 percentages of phenol respectively. These values of t^o were plotted against their speed of shearing and the curves are also shown in figure 42.

It was noted in figure 42 that the time of flow for zero duration of shearing, t^o, increases with speed of shearing and tends to come to a maximum value. These maximum time of flow, t^1, values. were determined for each curve as accurately as the experimental results permitted. The maximum time of flow, t_1^1, for a 1% C.T.A.B. + 0.5% phenol system is shown in figure 42.

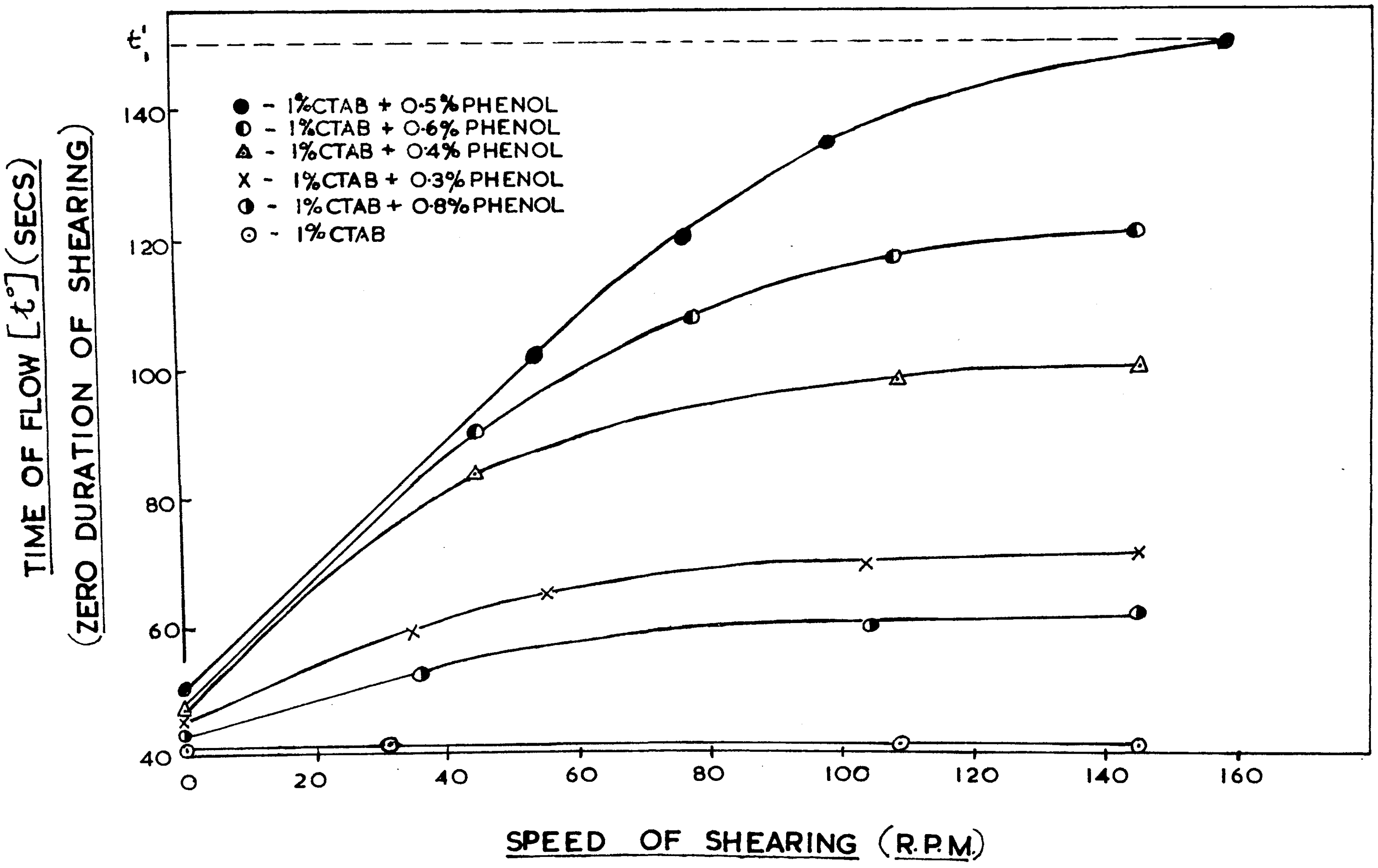
The t^1 values for several 1% C.T.A.B. + phenol systems were determined and are plotted against their concentration of phenol. The curve produced is shown in figure 43.

Also, shown in figure 43 is the plot of time of flow vs. concentration of phenol for non-sheared systems of 1% C.T.A.B. + phenol. The time of flow of a non-sheared system was the time of flow which was obtained with the shearer remaining static.

It can be seen that the two curves have the same characteristics but shearing makes the maximum time of flow more pronounced.

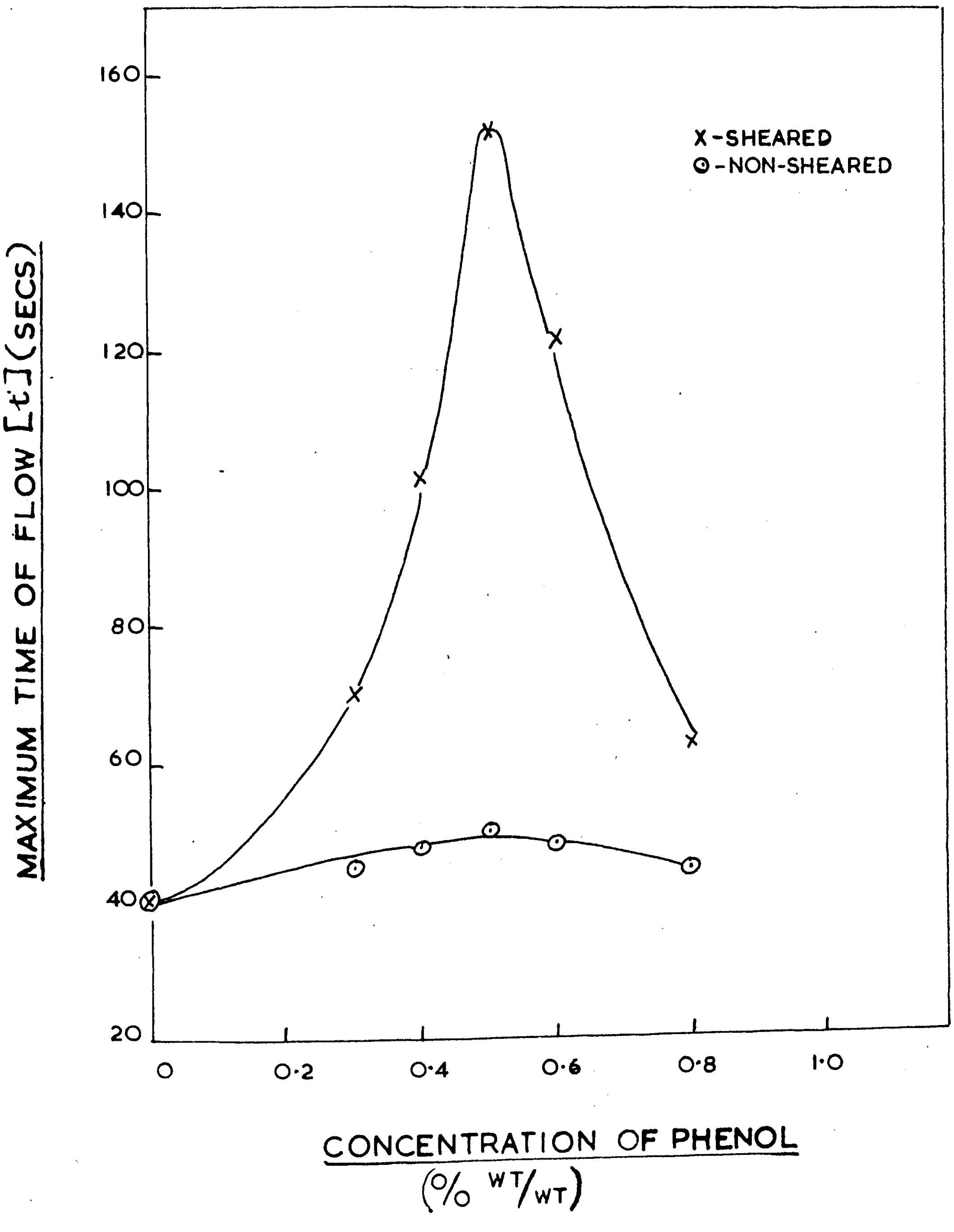
• • FIG 42 • •

VARIATION OF TIME OF FLOW (ZERO DURATION OF SHEAR) WITH SPEED OF SHEARING FOR 1% C.T.A.B. + PHENOL SYSTEMS



··FIG 43··

VARIATION IN THE MAXIMUM TIME OF FLOW WITH CONCENTRATION OF PHENOL FOR SHEARED AND NON-SHEARED SYSTEMS



Walker (100) has reported that systems of C.T.A.B. containing sodium salicylate show two maxima in the curve of time of flow vs. concentration of additive. Consequently, having found that, with systems of 1% C.T.A.B. containing phenol, the maximum in the curve of time of flow vs. concentration of phenol was made more pronounced by shearing, it was decided to examine the effect shearing would have on the curve of time of flow vs. concentration of additive in systems of C.T.A.B. containing sodium salicylate.

A system of 0.05% C.T.A.B. containing sodium salicylate showed times of flow, on non-sheared systems, which were similar to those produced by 1% C.T.A.B. systems containing phenol. Thus, as shearing measurements could be made in the same apparatus, it was possible for comparisons between the two systems to be made and so the effect of shearing on the time of flow of a 0.05% C.T.A.B. system containing sodium salicylate was investigated.

Effect of Shearing on the Time of Flow of Systems of 0.05% C.T.A.B. + Sodium Salicylate. (Na SAL).

The apparatus previously described (figure 33), was used and the procedure was similar to that adopted on 1% C.T.A.B. systems containing phenol.

It was found that the time of flow of a 0.05% C.T.A.B. + sodium salicylate system did not vary with the duration of shearing but it was greatly influenced by the speed of shearing to which it was subjected.

The variation in the time of flow of a 0.05% C.T.A.B. + 0.2% sodium salicylate system with duration of shearing, for speeds of shearing of 145, 97.6, 68.5 and 43 R.P.M., is shown in figure 44. It can be seen that there is no variation in the time of flow with duration of shearing.

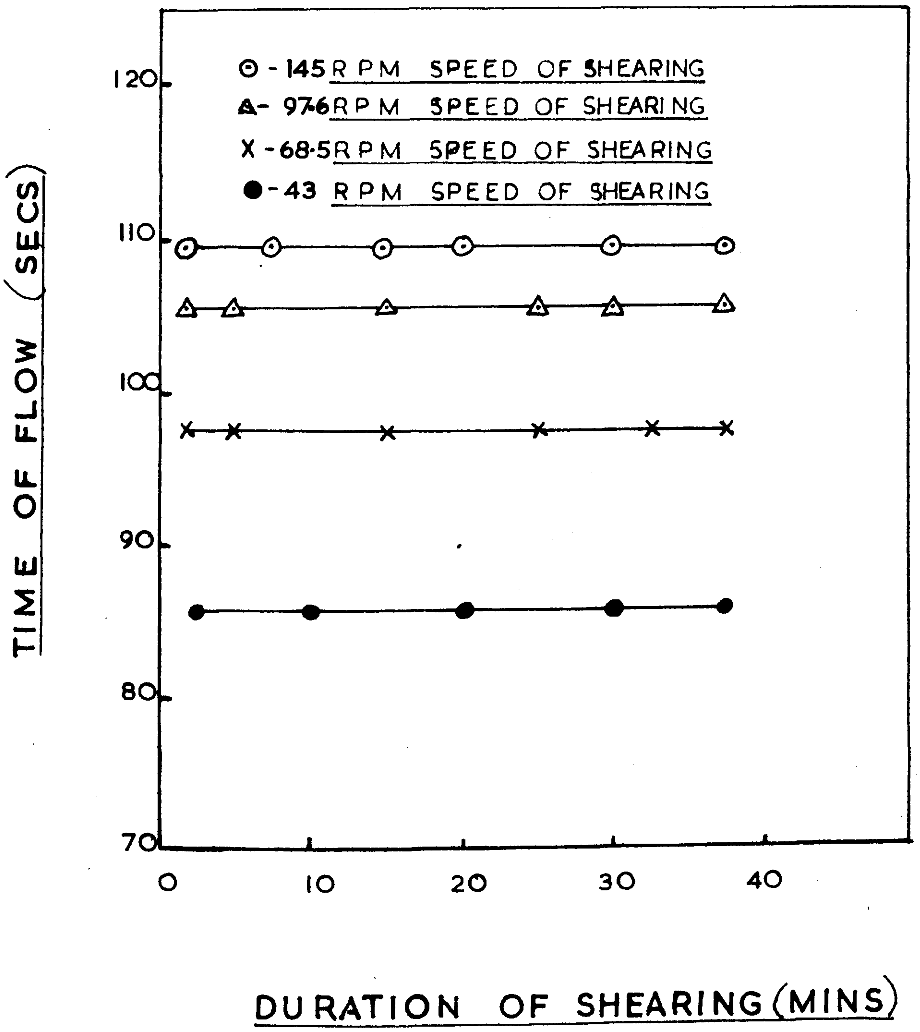
Similar plots were obtained for systems of 0.05% C.T.A.B. containing various percentages of sodium salicylate (0.25, 0.3, 0.1, 0.4, 0.5, 1.0, 1.5, 1.7, 2.0, 3.0 and 5.0) and they all showed that for various speeds of shearing there was no variation with duration of shearing.

From the plots of time of flow vs. duration of shearing the variation of time of flow (at zero duration of shearing) with speed of shearing was determined for various systems of 0.05% C.T.A.B. + sodium salicylate and are shown in figures 45 and 46.

It can be seen that these curves are similar to those produced by 1% C.T.A.B. + phenol systems.

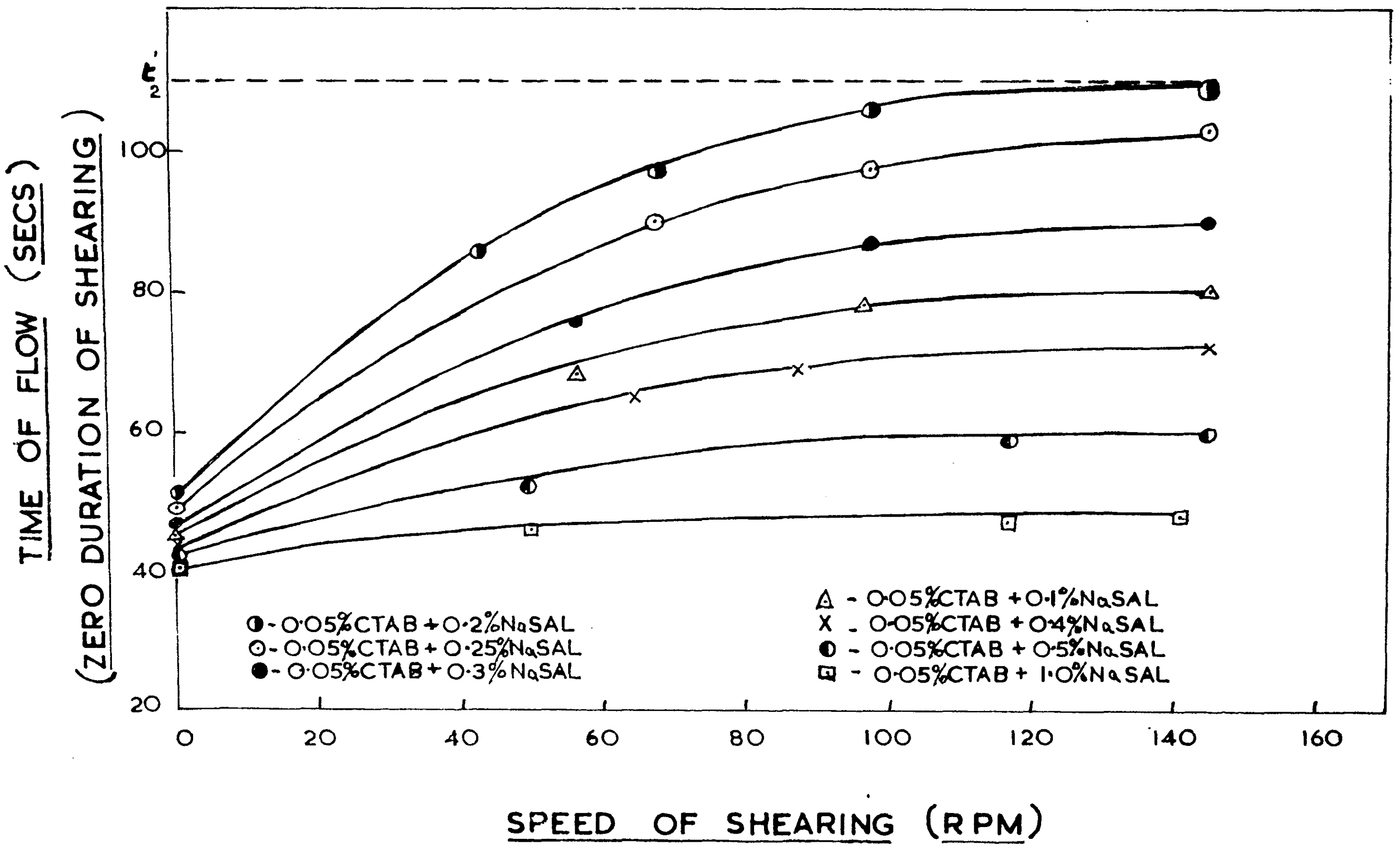
•• FIG 44 ••

VARIATION IN TIME OF FLOW OF THE 0·05% CTAB + 0·2% Na SAL SYSTEM WITH DURATION OF SHEARING



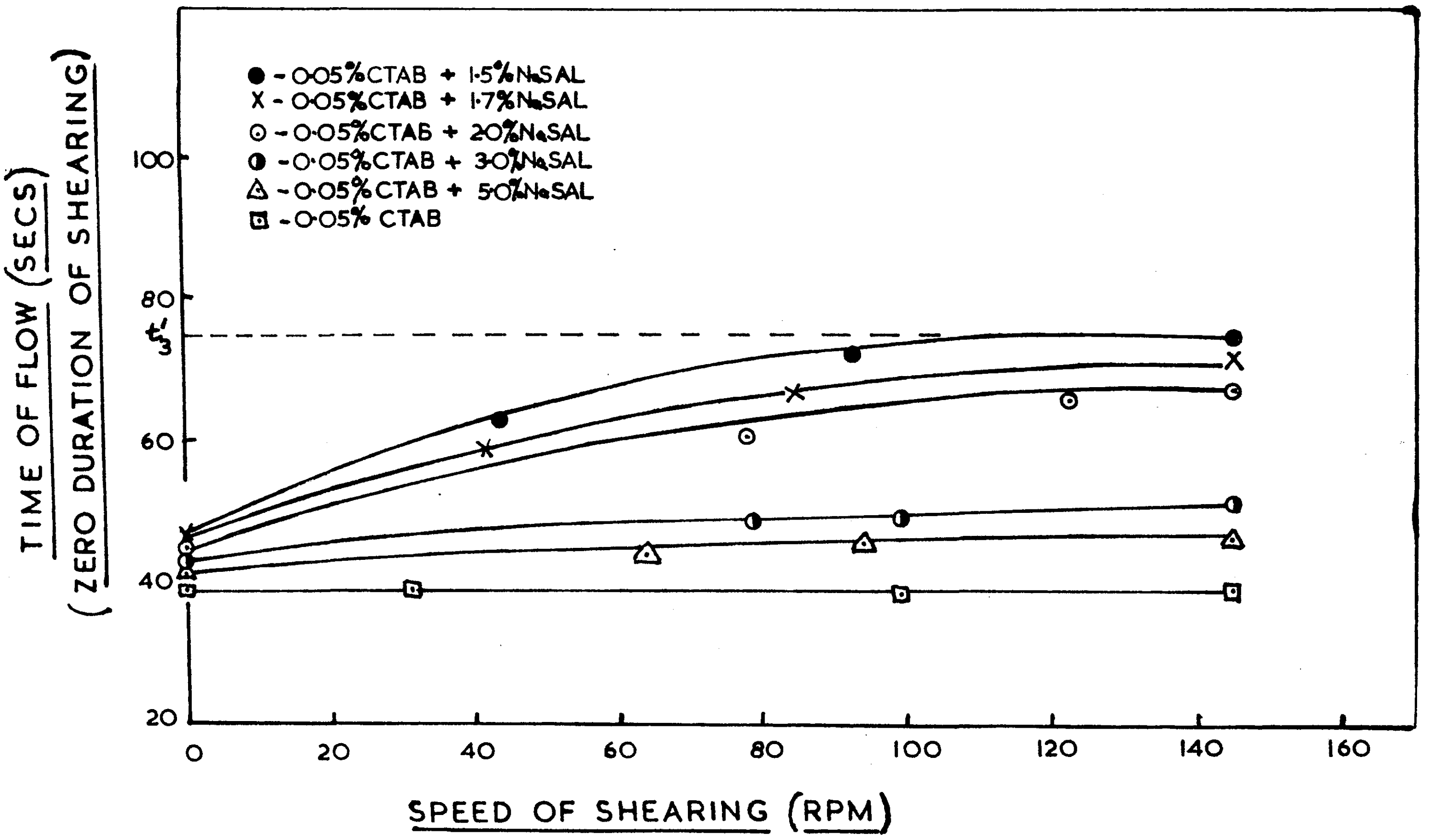
··FIG 45··

VARIATION OF TIME OF FLOW (ZERO DURATION OF SHEAR) WITH SPEED OF SHEARING FOR 0·05% CTAB + SODIUM SALICYLATE SYSTEMS



•• FIG 46 ••

VARIATION OF TIME OF FLOW (ZERO DURATION OF SHEAR) WITH SPEED OF SHEARING FOR 0·05% C.T.A.B.+ SODIUM SALICYLATE SYSTEMS



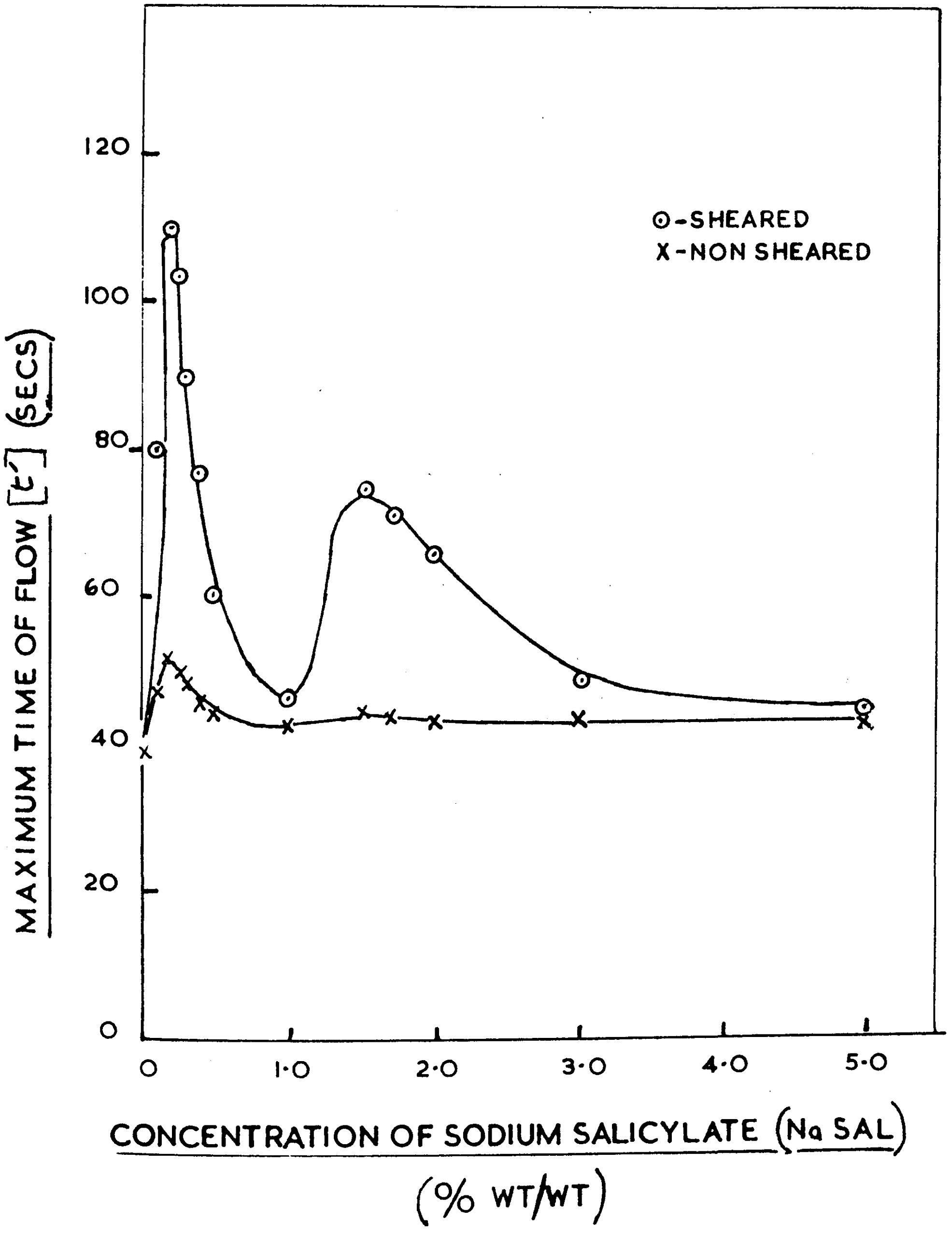
The maximum time of flow, t^1, was determined for each curve, e.g. the t^1 value for a system of 0.05% C.T.A.B. + 0.2% sodium salicylate, t^1_2, is indicated in figure 45 and that for a 0.05% C.T.A.B. + 1.5% sodium salicylate, t^1_3, in figure 46.

These t^1 values were plotted against the concentration of sodium salicylate in the system and the curve is shown in figure 47. Also shown in figure 47 is the plot of the time of flow measured on non-sheared systems of 0.05% C.T.A.B. and sodium salicylate vs. the concentration of sodium salicylate present.

A comparison of the two curves in figure 47 shows that shearing does not alter the general shape of the curve of time of flow vs. concentration of sodium salicylate, for systems of 0.05% C.T.A.B. containing sodium salicylate, but it greatly increases the values of the time of flow and makes the maxima in the curve very much more pronounced.

··FIG 47··

VARIATION IN THE MAXIMUM TIME OF FLOW WITH CONCENTRATION OF Na SAL FOR SHEARED AND NON-SHEARED SYSTEMS



The Effect on the Time of Flow of Shearing with Different Areas of Shearers.

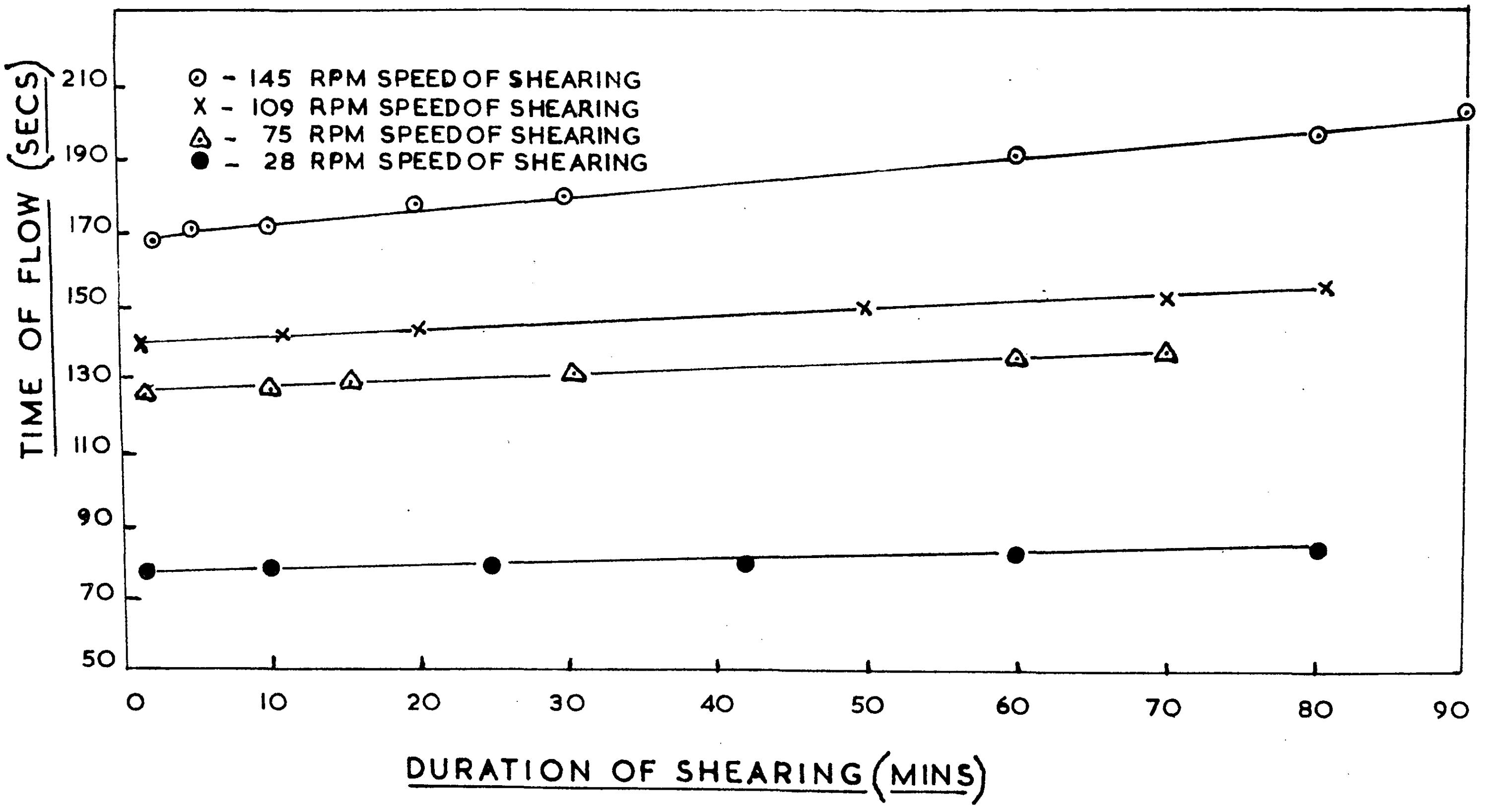
The shearing experiments on 1% C.T.A.B. + phenol and 0.05% C.T.A.B. + sodium salicylate systems were all carried out using the shearer unit A (8.3 cm. long). It was then decided to investigate if variation in the area of the cylindrical shearer influenced the time of flow. For this purpose a 1% C.T.A.B. + 0.5% phenol system was sheared with shearer B (3.6 cm. long), and time of flow measurements were taken.

The apparatus and the method used were the same as previously described, except that the shearer unit B had replaced shearer unit A. The variations in the time of flow of 1% C.T.A.B. + 0.5% phenol system with duration of shearing for speeds of shearing of 145, 109, 75 and 28 R.P.M. were determined and the results are plotted in figure 48.

When making these time of flow measurements, the liquid was forced up into the shearing pot until the liquid level in the right-hand limb had fallen to the graduation mark G. With shearer B, in the shearing pot, the liquid height in the pot was smaller than when shearer A was used because the volume of shearer B was smaller than that of shearer A. Thus, the head of liquid (i.e. the driving force in time of flow measurement) using shearer B was smaller than when shearer A was used. Therefore, any time of flow measurements made using shearer B,

••FIG 48••

EFFECT OF SHEARING A 1% C.T.A.B. + 0·5% PHENOL SYSTEM WITH THE SMALL CYLINDER (B)



which were to be compared with those obtained with shearer A, had to be corrected because of the change in liquid head.

To make this correction the time of flow with no shearing (shearer static) was measured using shearer A and then with shearer B. The ratio of these times of flow gave a measure of the effect of the change of liquid head on the time of flow. Using this ratio, the curves shown in figure 48, were corrected and then compared with those obtained with shearer A.

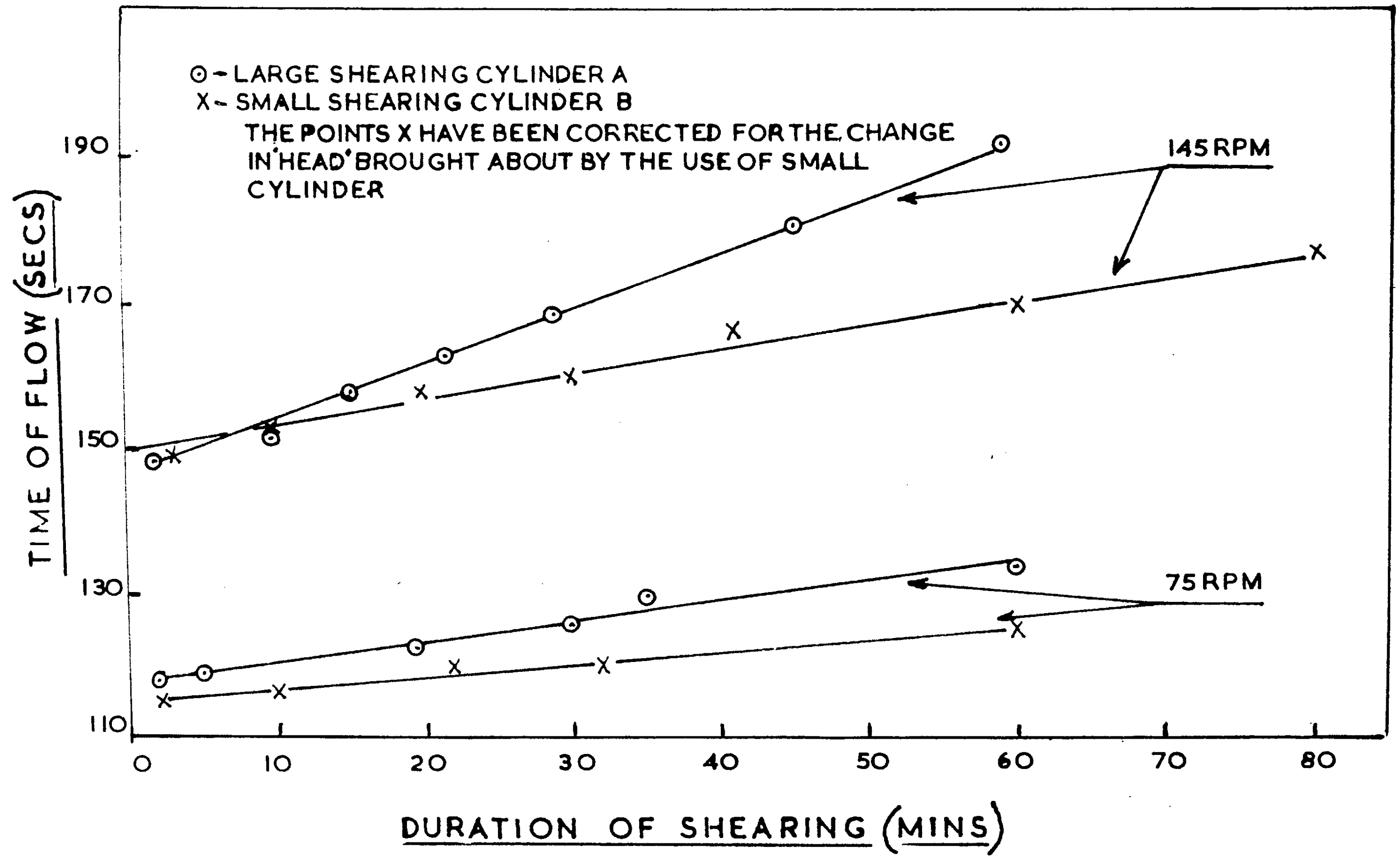
Comparisons of variations of time of flow of a 1% C.T.A.B. + 0.5% phenol system with duration of shearing for speeds of 145 and 75 R.P.M., measured by the shearers, are shown in figure 49. It can be seen that the variation in time of flow with duration of shearing for speeds of 75 and 145 R.P.M. are different for each area of shearer, but that the times of flow at zero duration of shearing at these speeds are approximately the same.

Therefore, since in this work only the times of flow at zero duration of shearing have been used to determine the times of flow induced by shearing, it appears that the results obtained are not necessarily dependent on the surface area of the cylindrical shearer.

• • FIG 49 • •

COMPARISON OF DIFFERENT AREAS OF SHEARERS

(1% C.T.A.B. + 0·5% PHENOL SYSTEM BEING SHEARED)



Effect of Temperature on the Time of Flow of a 1% C.T.A.B. + 0.5% Phenol System.

When these systems of C.T.A.B. + phenolic additive are subjected to shearing it is possible that an increase in temperature might result. If, by any chance, they were to become more viscous with rise in temperature, the temperature rise may be put forward as an explanation of the increase in time of flow caused by the shearing.

To test this, the effect of changes in temperature on the time of flow of a 1% C.T.A.B. + 0.5% phenol system was studied.

The apparatus used was viscometer B (described in Part I) and the method adopted was that used for measuring the time of flow through an ostwald viscometer. All the times of flow were measured with a holding time of 30 seconds. The viscometer was immersed in a thermostatically controlled water bath which could be regulated to any temperature.

Time of flow measurements were taken at temperatures from 23°C to 28°C. A plot of the log (time of flow) against the reciprocal of the [redacted] temperature at which they were measured is shown in figure 50.

It can be seen in this figure that the time of flow decreases with increase in temperature. Thus, any rise in temperature which may be produced by shearing this system must in fact tend to decrease the time of flow and therefore the increase in time of flow caused by shearing is not due to a thermal change.

Discussion.

It has been seen in Part I that the addition of phenol to aqueous 1% C.T.A.B. causes the time of flow property to increase and it has been suggested in the discussion of Part I that the increase is brought about by a change in the micellar structure from a spheroidal to a more elongated shape $(S_I \rightarrow G)$. It has now been experimentally established that when 1% C.T.A.B. systems containing phenol are subjected to shear, their times of flow are increased.

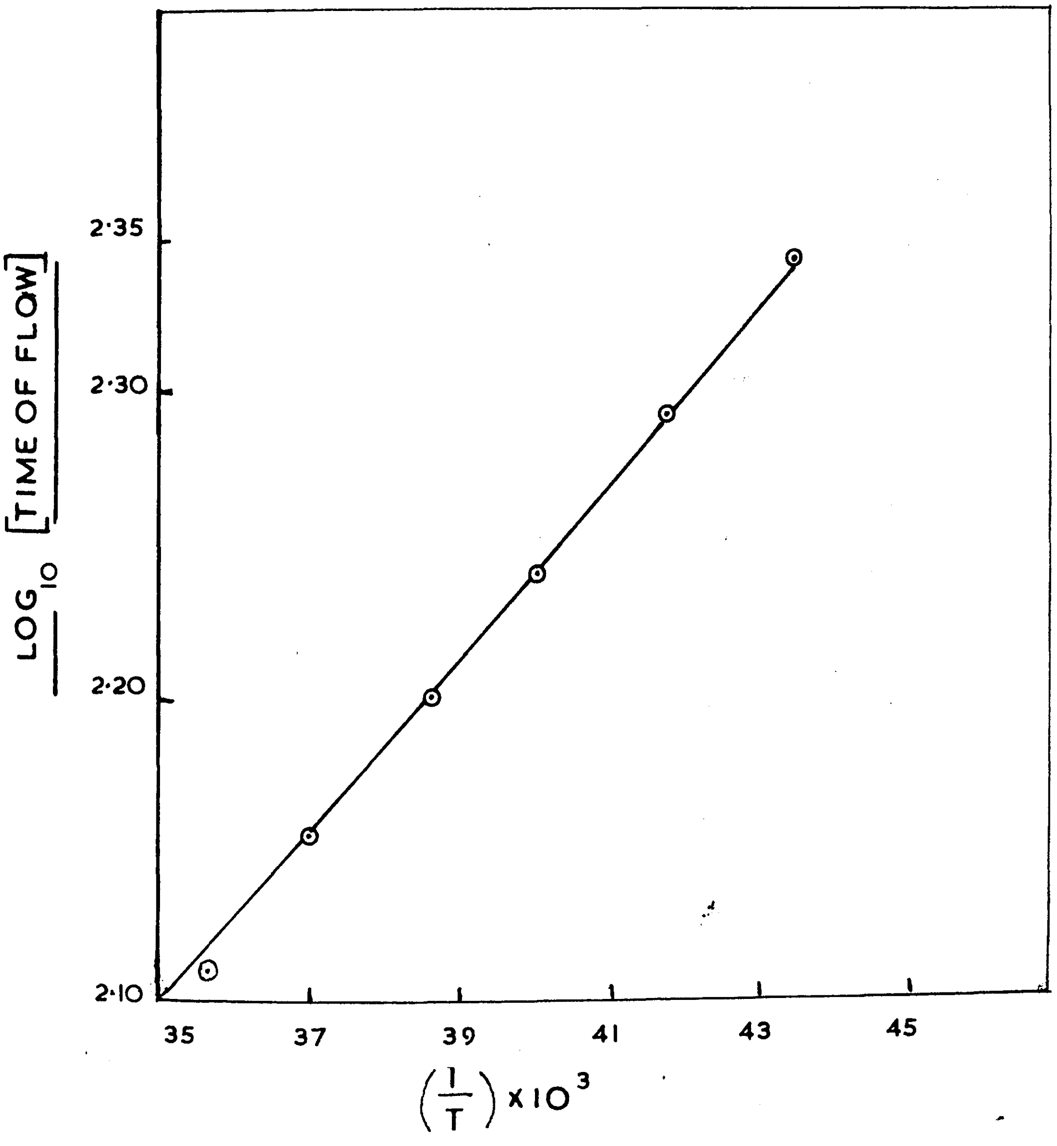
This increase can be considered to be due to the shearing causing the individual micelles to orientate into positions which are favourable to weak interaction and to cluster growth. Even if the shearing in these experiments were associated with a degree of turbulence, in the hydrodynamic sense, there would still be enough streamlined flow within the turbulence to produce favourable orientations for the growing aggregates.

Bartok and Mason (111) have shown, as already pointed out in the introduction to Part II, that liquid drops suspended in liquid media and when subjected to a shearing influence are transformed from a spheroidal shape into a more elongated form. It seems very probable that when micelles of C.T.A.B. + phenol are suspended in aqueous media and are subjected to shearing they also are transformed into elongated forms.

Thus, it is probable that shearing produces in micellar systems conditions in which:-

••FIG 50••

EFFECT OF TEMPERATURE ON THE TIME OF FLOW THROUGH VISCOMETER 'B' OF A 1% C.T.A.B.+0·5% PHENOL SYSTEM



(1) micelles aggregate,

(2) micelles form elongated structures.

In other words, the shearing of a liquid system produces conditions which would favour any inherent property of the individual micelles to aggregate into still larger micelles and to assume, more or less, threadlike or even lamellar forms.

While the time of flow of a 1% C.T.A.B. + phenol system varies with the speed of shearing, the time of flow of a 1% C.T.A.B. system, with no phenol addition, showed no variation. This suggests that the micelles in a 1% C.T.A.B. system do not form large aggregates or clusters during the shearing of the liquid and that the property of aggregation during shearing is that of the C.T.A.B. + phenol micelle.

On examining the curves of time of flow against speed of shearing for 1% C.T.A.B. + phenol systems, it can be seen, see figure 43, that the increase in the time of flow produced by shearing increased as the phenol concentration increased from 0 to 0.5%. Now, it has been suggested in the discussion of Part I, that the addition of phenol to 1% C.T.A.B. up to 0.5% increased the tendency for the C.T.A.B. + phenol micelles to form threadlike or lamellar micelles. Thus, it appears that the effect of shearing on the time of flow of a 1% C.T.A.B. + phenol system is connected with the presence of threadlike or lamellar micelles.

It was observed, while the time of flow of systems of

1% C.T.A.B. and phenol increased with shearing, the time of flow returned to its original value when the shearing ceased. This seems to imply that, when shearing ceases the micellar aggregates or clusters revert to their original form distribution.

Therefore, in this shearing process, we are apparently dealing with an equilibrium of forms,

$$\underset{\text{(micelles)}}{\text{aggregates}} \rightleftharpoons \underset{\text{(micelles)}}{\text{larger aggregates}}$$

and that the shearing of C.T.A.B. + phenol micelles causes this equilibrium to be displaced in some degree to the right-hand side, but, when the shearing ceases, this equilibrium reverts predominantly to the left-hand side.

Since shearing systems of C.T.A.B. of concentration 1% or less alone in water causes no increase in time of flow, it means that the energy of repulsion between the C.T.A.B. micelles is such that the energy introduced by the shearing is not sufficient to overcome it with the result that the equilibrium is not displaced to any extent. It may well be, that the shearing of the C.T.A.B. micelles causes them to be distorted, but if so, the distortion does not noticeably result in any aggregation of the micellar species present.

It is shown in figure 34 that, with increase in speed of shearing, the time of flow of a 1% C.T.A.B. + 0.5% phenol system increases to a maximum and then decreases gently. This suggests that the aggregation of C.T.A.B. + phenol micelles increases with speed of shearing to an optimum size and that further increase in shearing speed causes the existing aggregates or micellar clusters to deform to an extent that they gradually disintegrate into less large micellar configurations. This breakdown in the micellar aggregates may be very similar in form to the disintegrations, observed by Bartok and Mason (111), of liquid droplets when they were subjected to high shearing forces.

On examining the plots of volume of liquid discharged per second against pressure shown in figures 20 etc., it can be seen that the viscosities (i.e. the reciprocal of the gradient to the plot) of certain systems of 1% C.T.A.B. + phenolic compound tend to decrease with increase in pressure (i.e. at low shearing speeds). Figure 34 shows, on the other hand, that with increase in shearing speed the viscosity of a 1% C.T.A.B. + 0.5% phenol system increases to a maximum and then decreases. A study of these results seems to suggest that the viscosities of systems of 1% C.T.A.B. + phenolic compound which show maxima in viscous properties vary with speed of shearing in a complex manner. It appears that:-

(1) At low rates of shear the viscosities decrease with speed of shearing.

(2) At higher rates of shear the viscosities increase with speed of shearing.

(3) At still higher rates of shear the viscosities decrease with speed of shearing.

Also, it was found (see figure 34) that, at a specific shearing speed, the time of flow in the backward run is greater than in the forward run. This hysteresis effect shows that, when shearing ceases the micellar species do not revert within two minutes (i.e. holding time between measurements) to exactly their original form but are in another form which is more sensitive to shearing. Consequently, as is shown in figure 36, the time of flow of a 1% C.T.A.B. + 0.5% phenol system varies with <u>duration</u> of shearing.

The variation of time of flow with duration of shearing is displayed to a varying degree by all the 1% C.T.A.B. + phenol systems studied. This phenomenon suggests that there exists, within this system, micellar species which take a certain time to orientate into the sheared induced structure. Such a behaviour is consistent with the view that these micellar species are long and threadlike in structure and are capable of forming weakly bonded clusters.

If it is accepted that the system of0.05% C.T.A.B. and sodium salicylate which gave maxima in time of flow possess micellar structures which have a tendency to form elongated shapes and to aggregate into micellar clusters (i.e. having weak repulsive forces between the micelles), then the variation in time of flow with rate of shearing in these systems may be explained in a manner similar to that put forward for 1% C.T.A.B. + phenol systems.

The systems of 1% C.T.A.B. + phenol and of 0.05% C.T.A.B. + sodium salicylate resemble each other in that the time of flow varies with the rate of shearing. These systems, however, differ in that while the C.T.A.B. + phenol system varies with duration of shearing the salicylate system shows no variation.

This difference which is quite remarkable suggests that, on being sheared, the micelles in a 0.05% C.T.A.B. + sodium salicylate system interact with each other almost instantaneously and form an apparently stable aggregate while the micelles in a 1% C.T.A.B. + phenol system interact only very slowly. It is probable that salicylate, being an ion, confers on the aggegating clustering process the extreme rapidity associated, in general, with ionic as compared with non-ionic behaviour.

PART III

DETERMINATION OF THE MOLECULAR AREAS IN SURFACE FILMS OF C.T.A.B. SYSTEMS CONTAINING PHENOLIC ADDITIVES.

DETERMINATION OF THE MOLECULAR AREAS IN SURFACE FILMS OF C.T.A.B. SYSTEMS CONTAINING PHENOLIC ADDITIVES.

Introduction.

It was suggested in the discussion in Part I, that the initial addition of phenol to 1% C.T.A.B. involved phenol molecules being solubilised by the C.T.A. cations and, that once the concentration of phenol had become greater than about 0.5%, the phenol molecules became less firmly attached to the C.T.A. cations. It was therefore decided to measure molecular areas in the surface films of systems of 1% C.T.A.B. containing various percentages of phenol in the hope that these views might be reflected in the molecular area values.

In the late 19th century, Rayleigh (113) clearly established that certain water-insoluble substances, e.g. ricinoleic acid, tend to spread over a water surface as a monomolecular layer. At the same time, it was observed that the area which these surface films occupied could be varied at will by confining the film between movable barriers.

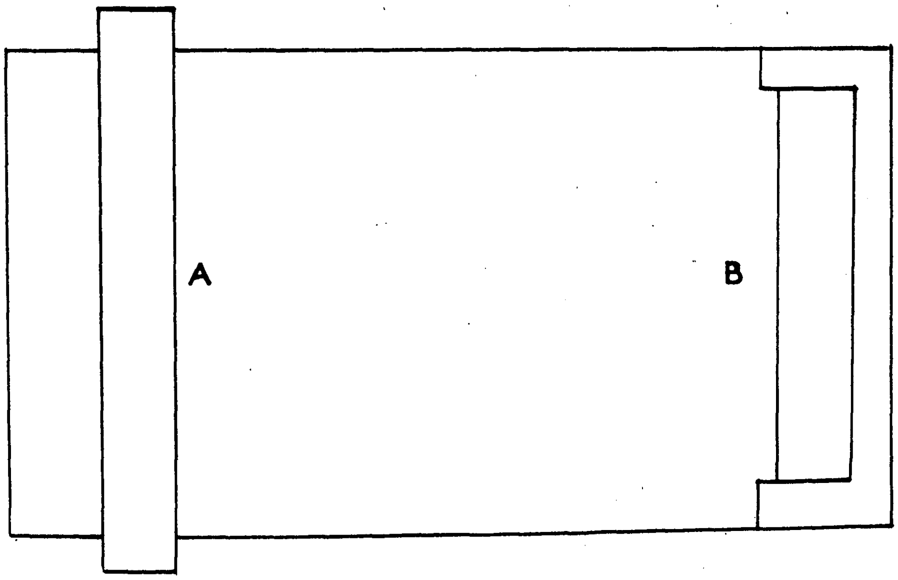
These observations were confirmed by Langmuir (114) and Adam (115) and they made use of them to devise a convenient method of determining cross-sectional areas of the molecules of material insoluble in water, such as fatty acids, barium soaps, long-chain alcohols and similar compounds.

The method consisted of spreading the "oil" dissolved in benzene on a clean surface of water which was contained in a shallow trough. The benzene evaporated leaving a film of oil which was confined between a movable barrier, A, (see figure 51) placed across the trough and a barrier B, fixed at the other end of the trough. Attached to barrier B, was a balancing system which measured the force the film exerted on it. Langmuir measured the force exerted on B by attaching a lever and balance pan to its centre and finding the weights required to bring it back to the original position. Adam measured the force by a torsion wire and optical lever system. To take measurements, barrier A was moved in stages towards barrier B, thus reducing the area occupied by the film and, at each stage, the force which the film exerted on the barrier was noted. The weight of oil introduced on to the water surface and the area of the surface between A and B were known, and by making use of the molecular weight of the oil and Avogadro's number, it was possible to calculate the area occupied by each single molecule.

The force-area curves obtained for such experiments were found to have a shape similar to that of the curve shown in figure 52. It is seen that, for relatively large areas, the pressure is very small but at a point, a, it commences to increase slowly and then from b onwards, the increase is rapid until at c the film collapses. This type of curve has been interpreted as showing that oil films consist of a single layer of molecules (monolayer) which are arranged so that their hydrocarbon chains are pointing

..FIG 51..

STUDY OF SURFACE FILMS

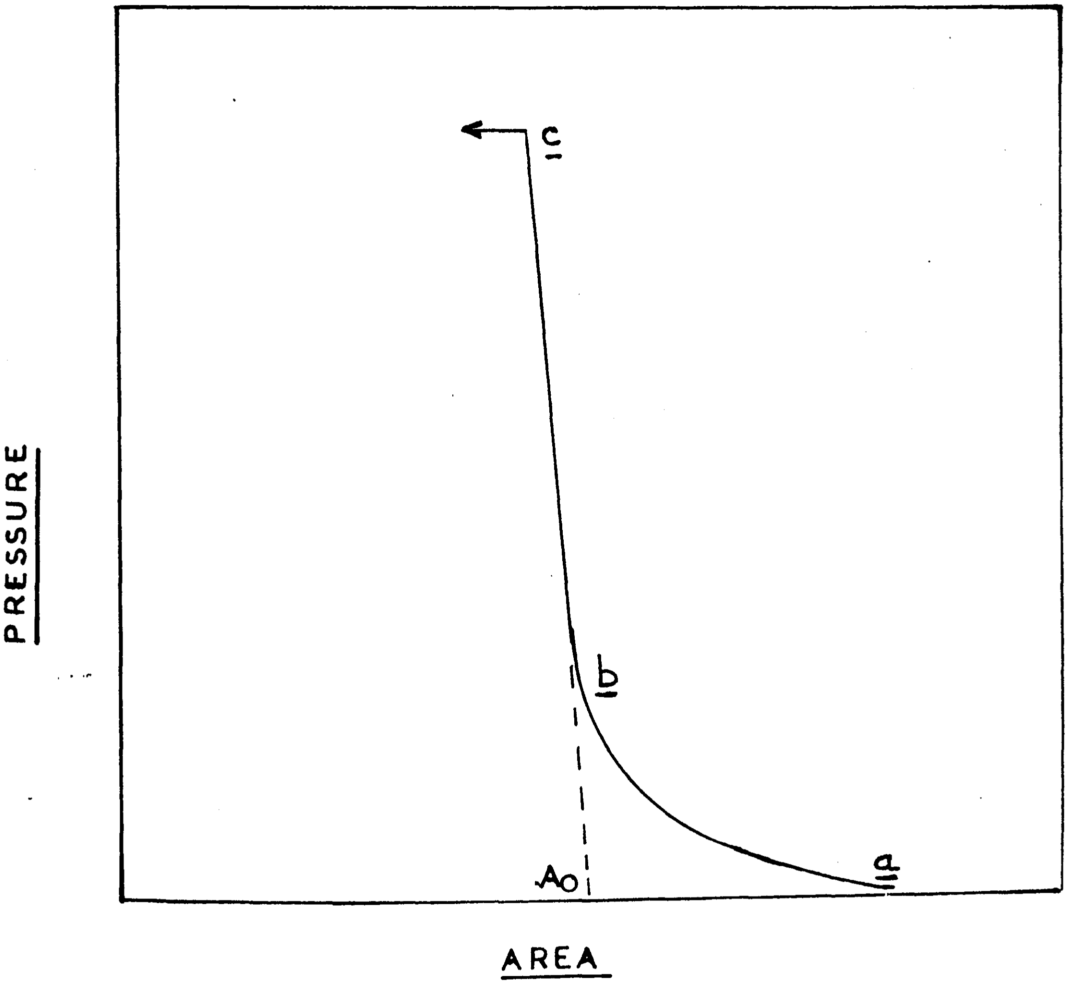


A = MOVABLE BARRIER

B = FIXED BARRIER

··FIG 52··

A DIAGRAMMATIC REPRESENTATION OF THE FORCE-AREA CURVE OF A FILM ON THE SURFACE OF WATER



outwards from the water with their polar groups immersed in the water or on its surface. It is considered that, as the film is compressed, by moving the enclosing barriers nearer each other, a point is reached, probably at about b, in figure 52, when the molecules are so closely packed together that any further attempt at compression demands exertion of an appreciable force.

It was regarded by Langmuir and Adam that the compression of molecules from b to c, in figure 52, involves molecules packing on top of one another, and if this view is correct then the extrapolation of curve c b to the zero axis of compression gives a measure of the area of a single molecule of the "oil" on the surface of the water, A_o.

Now, while this procedure has been found to be very successful in measuring the molecular areas of water-insoluble materials, it has to be modified to study soluble substances, such as paraffin-chain salts.

Brady (116) found that films of sodium 1-alkyl benzene sulphonate on water at 20°C were very unstable. He overcame this difficulty by using a salt solution as a substrate in place of water. Owing to the instability of the films, he used an automatic machine for advancing the barrier and a recording device for indicating the film pressure. The substrates he used were sodium chloride solutions of 0.5% to 16.6% and dilute solutions of calcium and barium chlorides. The films formed on barium chloride were found to be much too fragile to give reproducible results.

Meader and Criddle (117) obtained force-area curves of surface films of several soluble substances on a salt substrate. They used, at first, a substrate of 6% sodium chloride solution but the films obtained on it were found to be only slightly more stable than they were on water. Also, they used a saturated solution of sodium chloride but, as the sodium chloride in this substrate tended to crystallise at barrier B, they experienced difficulty in obtaining reproducible results.

Meader and Criddle found that, using a Cenco Hydrophil balance with a 95% saturated solution of sodium nitrate as a substrate, reproducible force-area curves for surface films of several soluble surface active agents could be obtained. In fact, they were able, with this apparatus and substrate, to detect certain types of structures in mixtures of surface active agents by measuring the force-area curves.

The Apparatus.

The apparatus used for measuring the cross sectional areas of the molecular structures was a type of Langmuir film balance which is similar to that described by Allan and Alexander (118). This balance consisted of three components - a trough, a balancing system and an optical lever arrangement.

The Trough.

The rectangular trough (21.4 X 11.3 X 0.6) c.c. was machined out of a solid polythene block, a material which is both inert and water repellant. This trough was screwed to a stainless steel plate and placed on a wooden stand, as shown in figure 53. The stand had four adjustable brass feet which ensured that thetrough could always be maintained in a level position.

Attached to the trough was a movable barrier consisting of a strip of polythene measuring (15 X 1.8 X 0.6) c.c. When this barrier was placed in position, see figure 53, it could be moved, by means of a screw mechanism, in stages along the trough so that its polythene face swept the surface of the liquid to ensure that it was perfectly clean.

At the other end of the trough was a fixed barrier in the form of a boom floating on the surface of the liquid. The boom had dimensions of (8.5 X 1.0 X 0.1) c.c. and was made of teflon, which made it quite rigid and also water repellant. There were two holes drilled near the centre of the boom,

APPARATUS USED FOR MEASURING SURFACE PRESSURES.

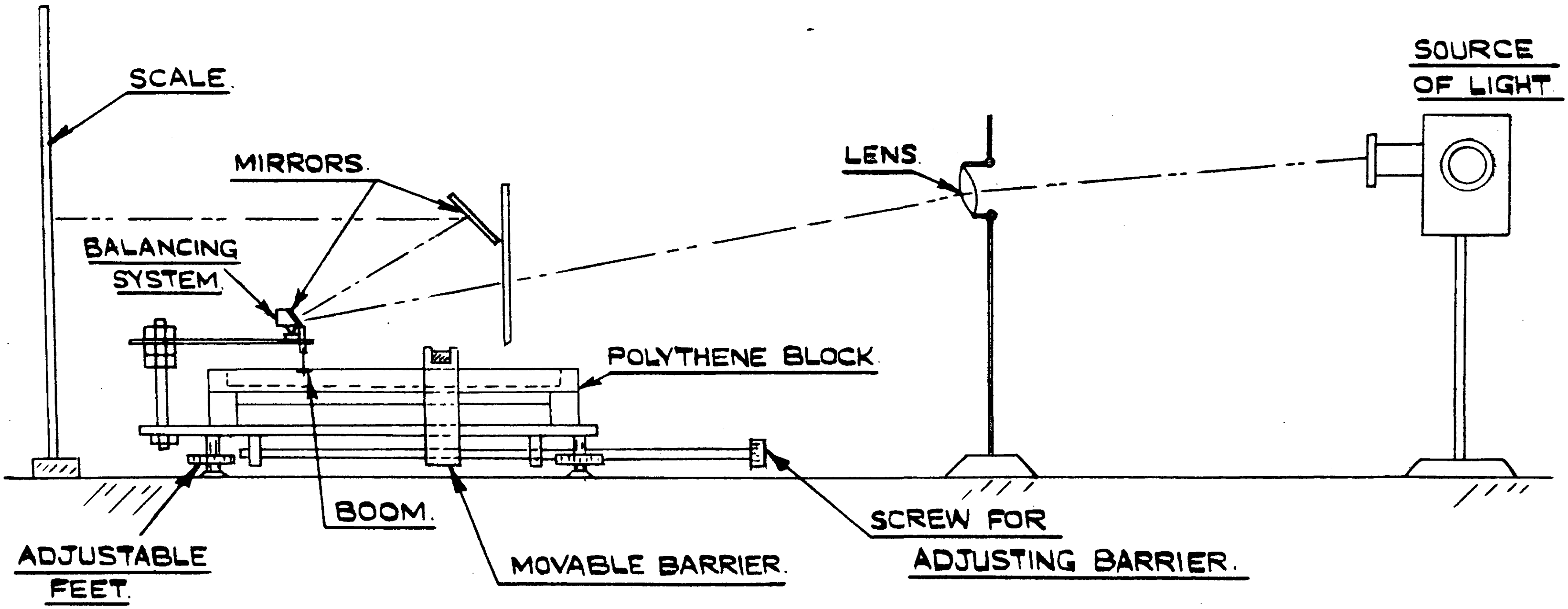


FIG.53.

3 cm. apart, to accommodate the wires from the balance head. Polythene threads were used to attach the boom to the sides of the trough. These threads were fixed to the boom and to the trough with paraffin wax.

The Balancing System.

The balancing system is shown in figure 54. The balance head consisted of a brass block into which two agate knife edges were clamped by a brass plate. In the centre of the balance head was a mirror, inclined at a suitable angle. The knife agate edges of the head rested on the agate seats on a brass strip above the trough so that the balance head was suspended over the trough. Fitted to the centre of the underside of the balancing head was a small brass block carrying a brass rod which had a wire brazed to each end. These two wires passed through the holes drilled in the boom. When the balance head is in this assembled position, it is very sensitive to the changes of surface pressure acting on the boom.

The advantages this system of measuring surface pressures had over other systems (e.g. torsion wire) were that its sensitivity was constant, it was robust and it could be easily cleaned.

The Optical Lever Arrangement.

The optical arrangement is shown in figure 53. The pressure exerted by the film on the boom was measured by means of an optical lever system, consisting of a light source, bi-convex lens and two mirrors, one of which was fitted to the

CROSS-SECTION OF TROUGH SHOWING BALANCING SYSTEM.

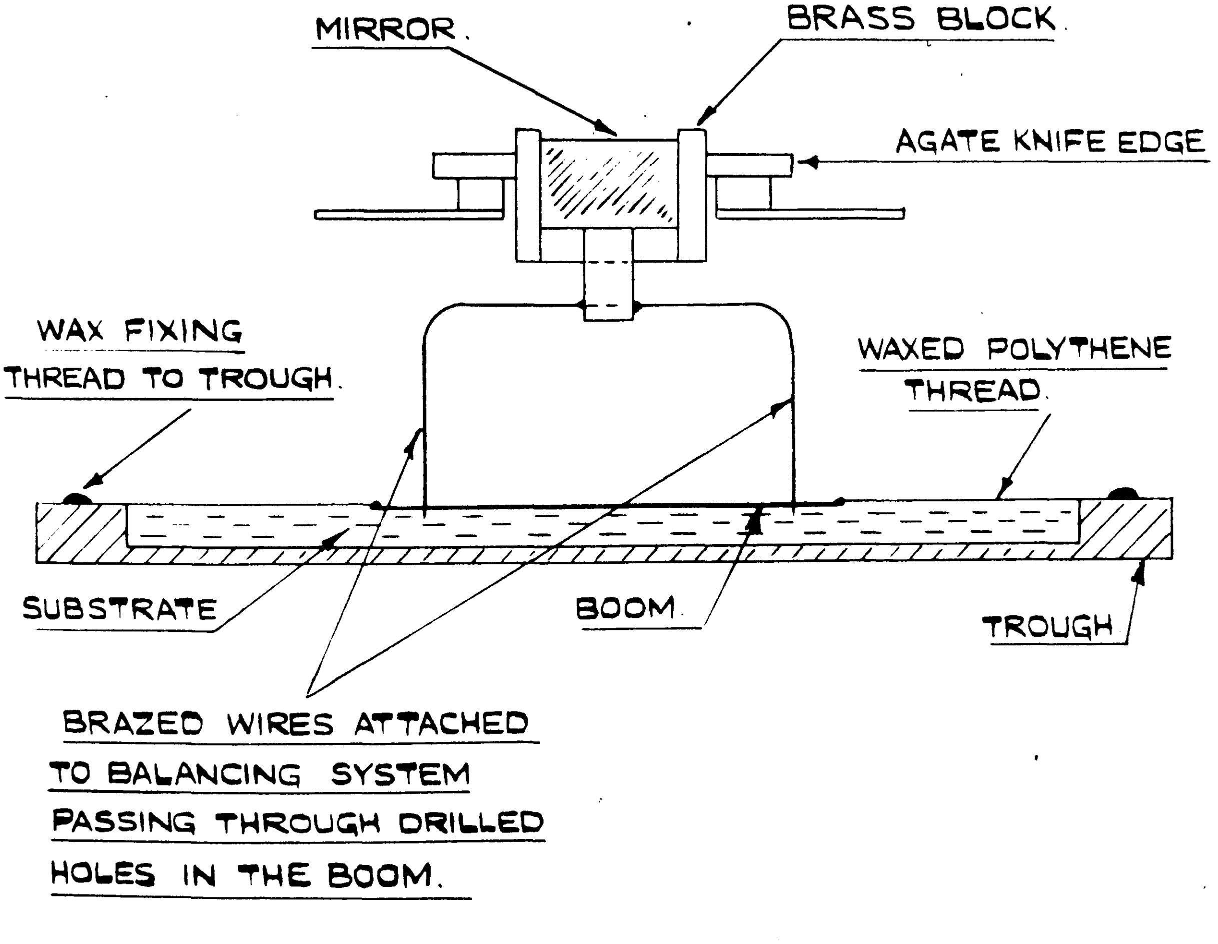


FIG. 54.

centre of the balance head.

The image of the light source was focussed on the mirror on the balance head by means of a bi-convex lens. The light was then reflected from the balance head mirror on to another mirror situated between the balance head and the lens. This mirror reflected the image on to a scale which was placed behind the balance head.

In this way any movement of the balance head was registered and therefore changes in surface pressure could be measured on the scale.

Procedure.

Before setting up the apparatus, great care was taken to ensure that the trough, boom and barrier were thoroughly cleaned. The apparatus was then assembled as shown in figures 53 and 54, making certain that the trough was level.

The trough was filled with the substrate solution. When this was done, an inspection was made to check that the threads connecting the boom to the trough lay flat on the surface of the solution so that there was no possibility of a surface film leaking under or around them. Such a leakage could be detected by dusting fine talc powder on to the surface of the solution and noting the movement of the powder particles under compression from the movable barrier.

After the inspection had been completed and the boom found to be in the correct position, the liquid surface on both sides of the boom was swept clean with the polythene bar. This removed any surface contamination and exposed a clean liquid surface between the boom and the barrier.

A known weight of film forming material was then ejected from an Alga micrometer syringe on to the liquid surface between the boom and the barrier. After the film had been spread on the surface, it was allowed to rest for one minute. Then the movable barrier was advanced 1 or 2 cm. at a time and the film pressure noted at each stage. When the film became unstable or collapsed, the readings were discontinued. The readings, which were always made on compression, were taken every 20 seconds and the entire run was made in about 5 or 6 minutes. The results obtained with all the systems studied were found to be reproducible, using this procedure. All the experiments were performed at room temperature (20 ± 1°C). The zero on the arbitrary pressure scale was taken as the reading on the scale before the film was spread on the liquid surface.

The first substrate used was a saturated solution of sodium chloride but was found to be unsatisfactory as the sodium chloride tended to crystallise on the barriers and on the edges of the trough and this caused the monolayer to leak away. Now, this same difficulty was encountered by Meader and Criddle (117) and they overcame it by using a 95% saturated solution of sodium nitrate. Consequently, a substrate of 95% saturated solution of sodium nitrate was tried but it was found that, while measurements were being taken, the substrate tended to crystallise and therefore the results so obtained using systems of C.T.A.B. + phenol could not be regarded as being reliable. After experimenting with different concentrations of sodium nitrate in the substrates, it was eventually found that the most satisfactory substrate upon which a stable film of 1% C.T.A.B. could be formed was an 80% sodium nitrate solution. This solution was used as a substrate in all measurements made in this investigation.

Calculation of Molecular Area.

The calculation of the area which a single molecule occupies in the monolayer on the substrate was as follows:-

Let the concentration of C.T.A.B. = Y% (Y g. in 100 ml. solution)

Volume ejected from syringe = 0.001 ml.

Now 100 ml. of solution contain Y g. C.T.A.B.

$\therefore$ Weight of C.T.A.B. in 0.001 ml. solution $= \frac{Y}{100} \times 0.001$ g.

Weight of C.T.A.B. present in film $= Y \times 10^{-5}$ g.

Molecular Weight of C.T.A.B. = 364.5

Now, the number of molecules in 364.5 g. C.T.A.B. $= 6.02 \times 10^{23}$

$\therefore$ Number of molecules in $Y \times 10^{-5}$ g. C.T.A.B. $= \frac{6.02 \times 10^{23} \times 10^{-5} \times Y}{364.5}$

Area of $\frac{6.02 \times 10^{23} \times 10^{-5} \times Y}{364.5}$ molecules $= \ell \times 11.3$ sq. cm.

$= \ell \times 11.3 \times 10^{16}$ sq. Å.

$\therefore$ Area of 1 molecule $= \frac{\ell \times 11.3 \times 10^{16} \times 364.5}{10^{23} \times 6.02 \times 10^{-5} \times Y}$ sq. Å.

$\underline{\ell}$ is the distance between the boom and barrier. Thus by knowing $\underline{\ell}$ and $\underline{Y}$ the area which 1 molecule of C.T.A.B. occupies in the surface film can be found.

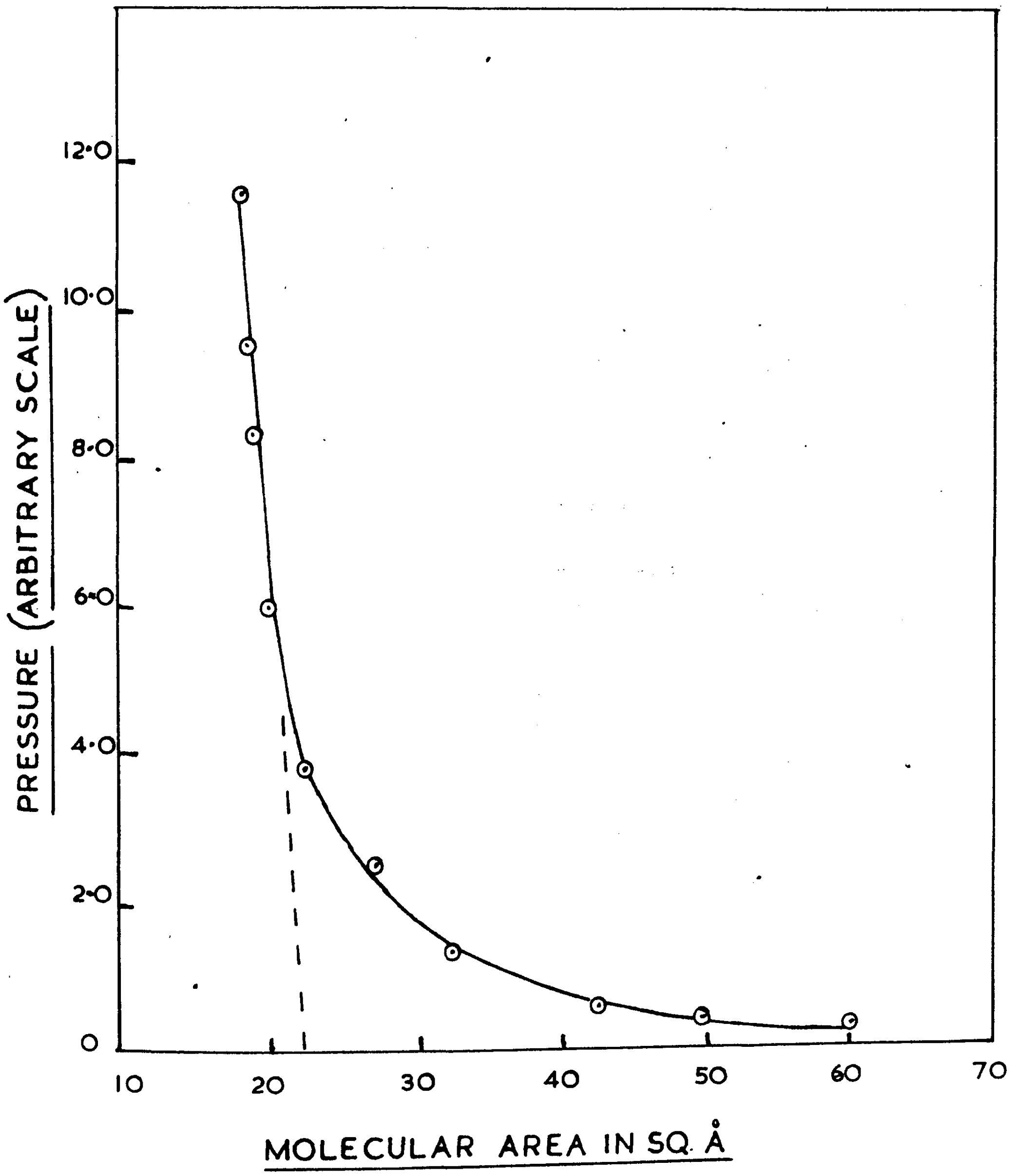
Results.

The first system to be spread on the 80% sodium nitrate solution was palmitic acid in benzene. The benzene evaporated off and the palmitic acid left formed a surface film on the substrate. The force-area curve for this film was determined and is shown in figure 55. The area obtained by extrapolating the straight portion of this curve to the zero pressure axis was 22.5 sq. Å. This value is similar to that reported in the literature (119) for the molecular area of long-chain fatty acids when spread on a water substrate.

A system of 1% C.T.A.B. was spread on the substrate and the force-area curve for the surface film was determined and it is shown in figure 56. The straight portion of this curve was extrapolated to the zero pressure axis and the area measured. Subsequently, systems of 1% C.T.A.B. containing various percentages of phenol (0.2, 0.4, 0.5, 0.6, 0.8, 1.0, 2.0, 3.0 and 5.0) were spread on the substrate and force-area curves for the surface films formed by each of these systems were determined. From each of these curves the area obtained by extrapolating the straight upper portion of the curve back to zero pressure was measured. This area was regarded as the effective molecular area associated with the C.T.A.B. in the surface film of each particular system. The force-area curves for systems of 1% C.T.A.B. containing percentages of phenol of 0.4, 0.5 and 1.0 are shown in figures 57, 58 and 59 respectively. The results for other 1% C.T.A.B. systems

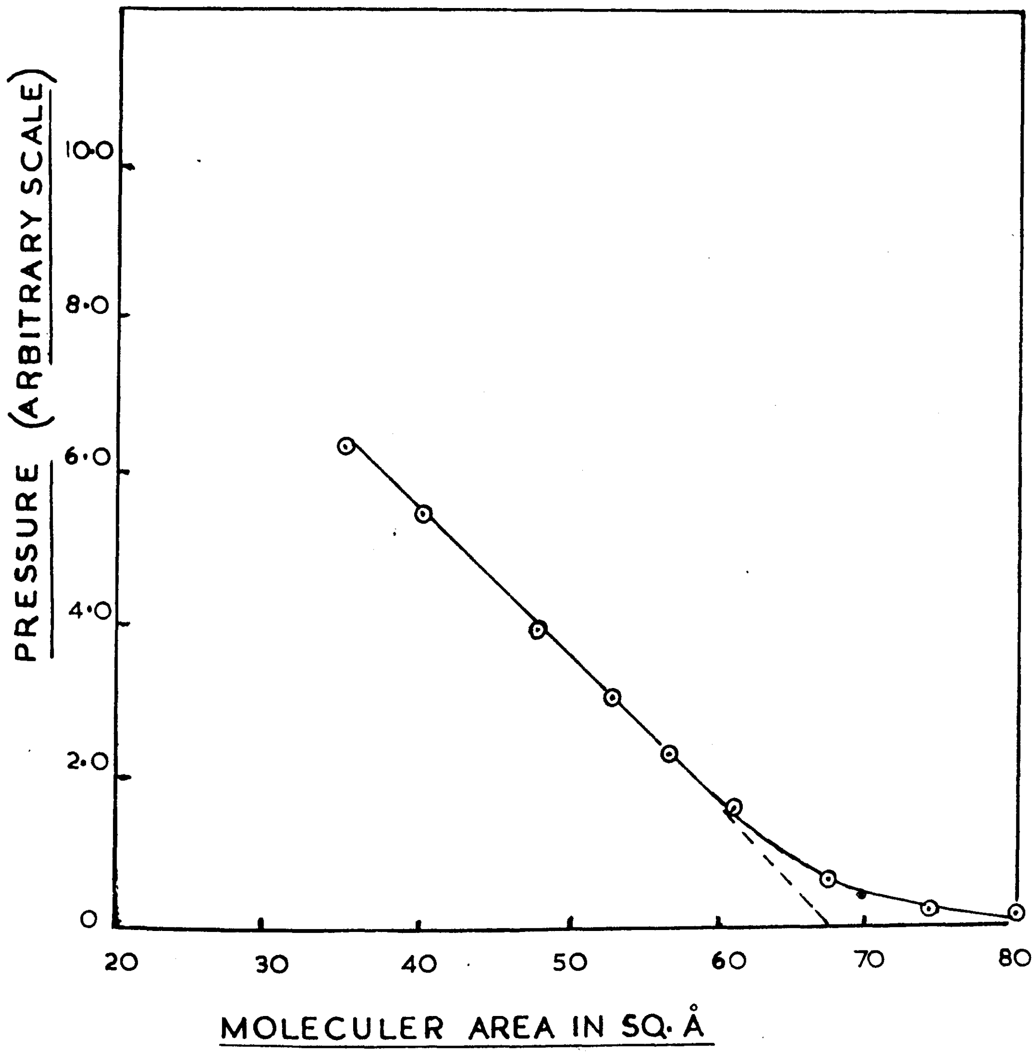
··FIG 55··

PRESSURE-AREA CURVE OF PALMITIC ACID FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



••FIG 56••

PRESSURE-AREA CURVE OF 1% C.T.A.B. FILM ON 80% (WT/WT) NaNO$_3$ SOLUTION



$\cdot\cdot$ FIG 57 $\cdot\cdot$

PRESSURE-AREA CURVE OF 1% C.T.A.B.+ 0·4% PHENOL FILM ON 80% $\left(^{WT}/_{WT}\right)$ $NaNO_3$ SOLUTION

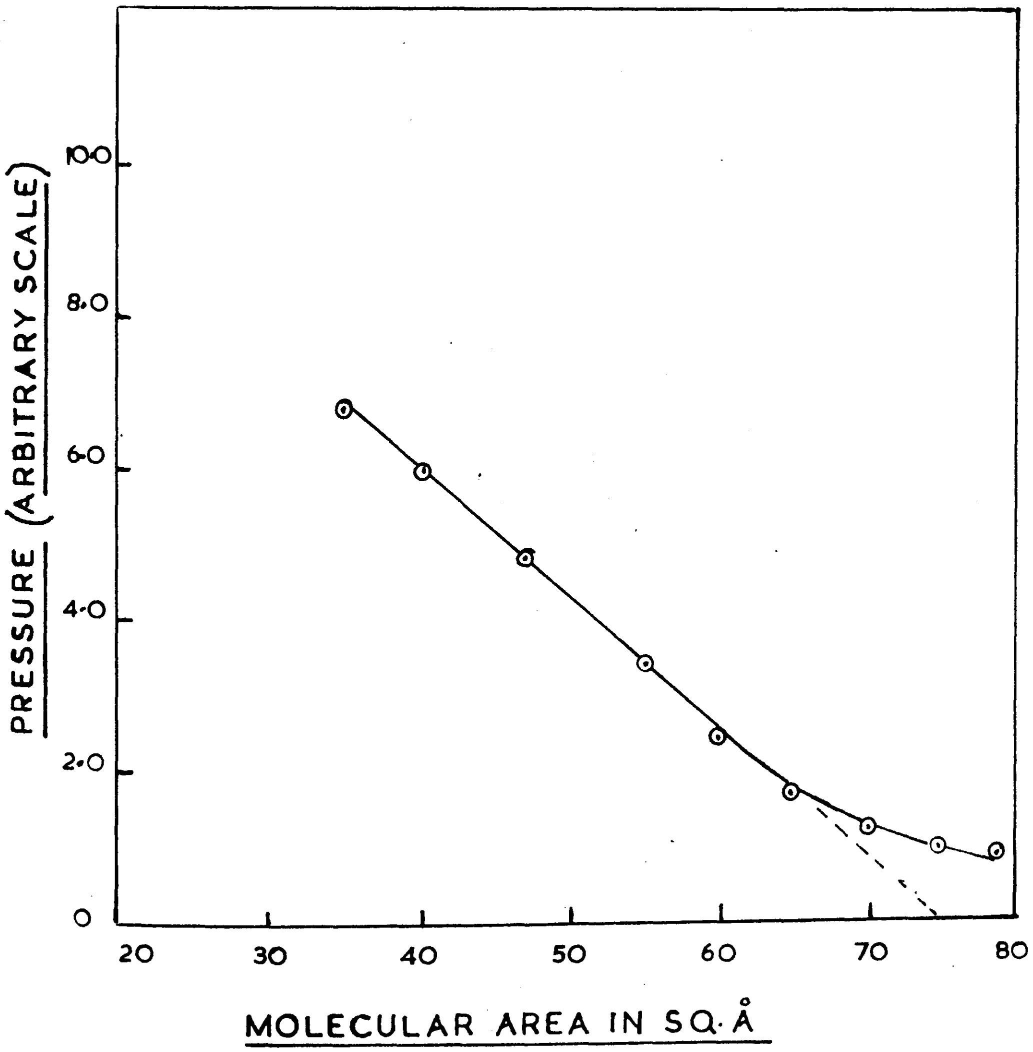


FIG 58

PRESSURE-AREA CURVE OF 1% C.T.A.B. + 0·5% PHENOL FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION

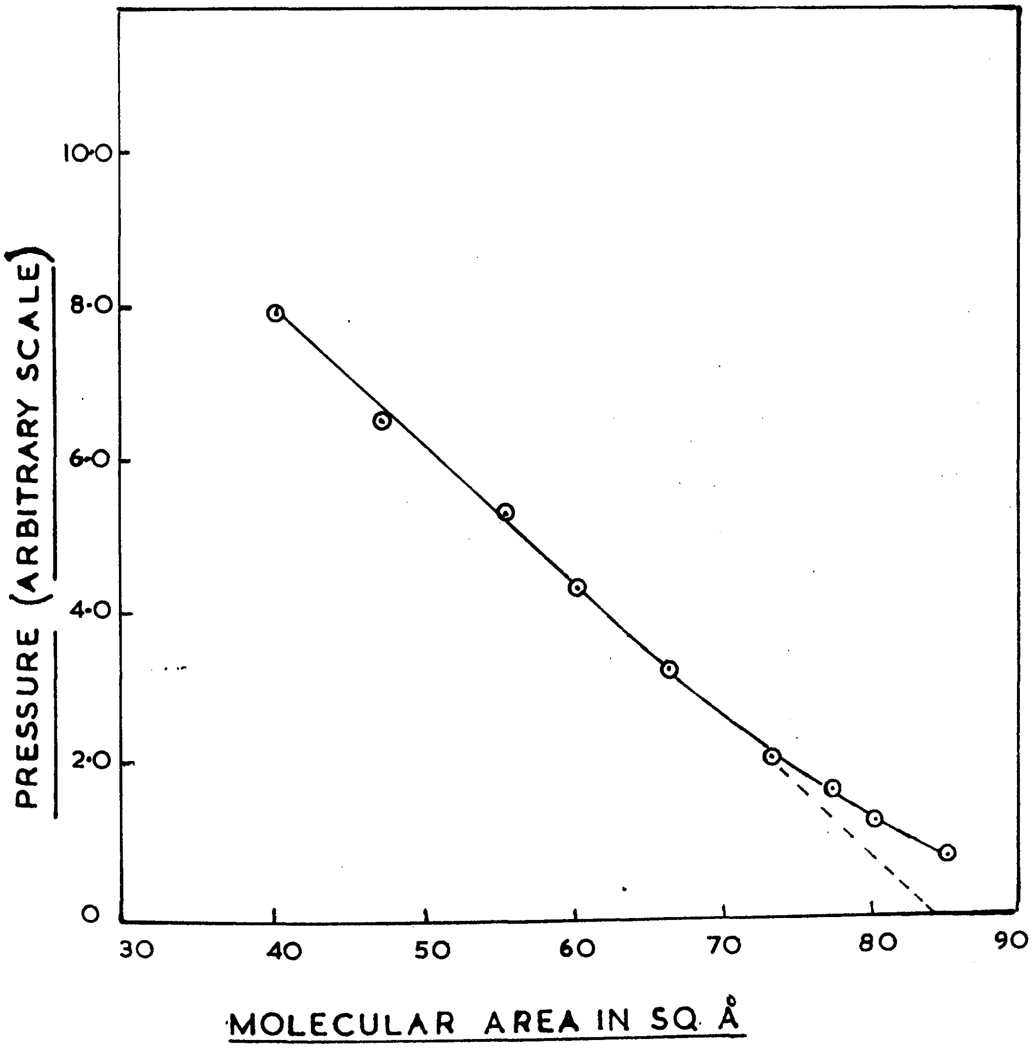
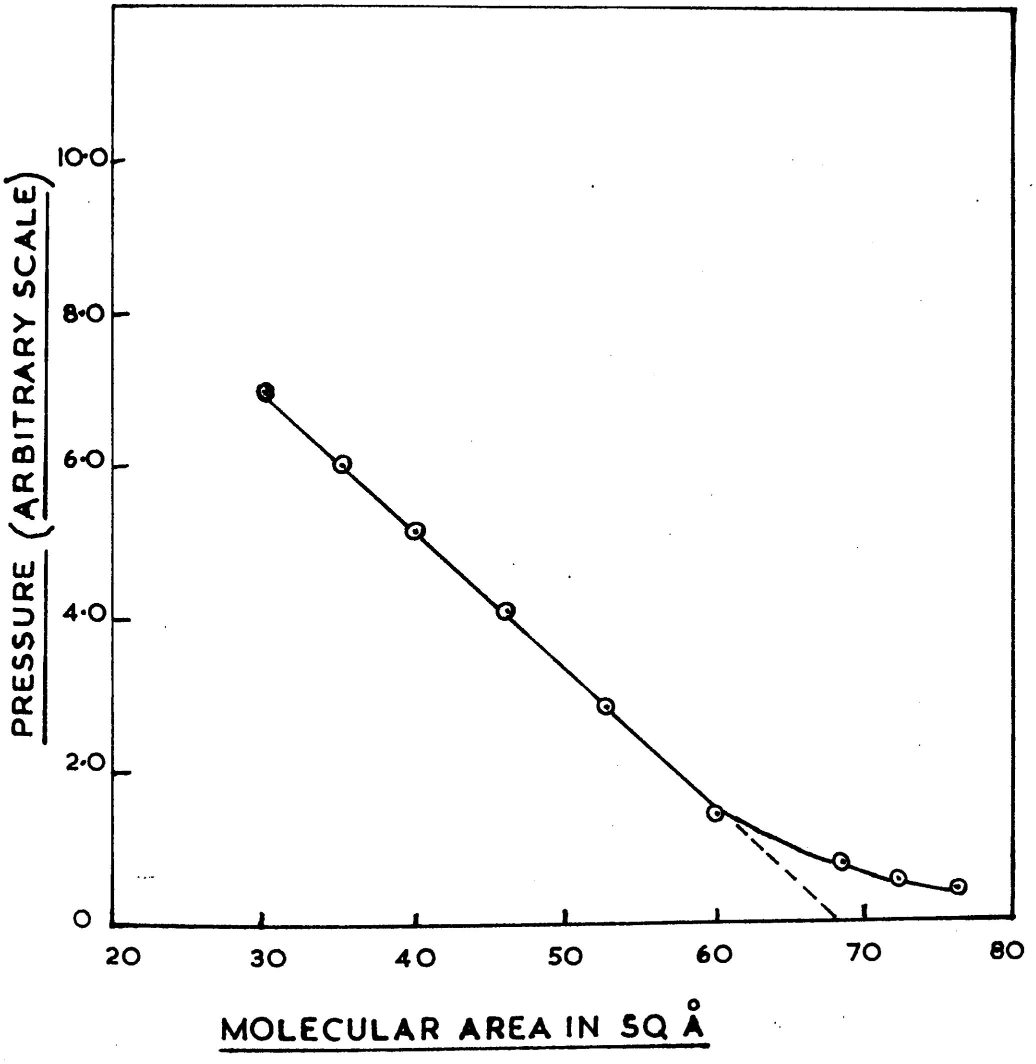


FIG 59

PRESSURE-AREA CURVE OF 1% CTAB + 1·0% PHENOL FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



containing 0.2, 0.6, 0.8, 2.0, 3.0 and 5.0, percentages of phenol are shown in tables 1-6 respectively.

A plot of the variation of molecular area of C.T.A.B. with concentration of phenol added is shown in figure 60. It can be seen that with initial increase in phenol concentration the molecular area reaches a maximum at a phenol concentration of 0.5%, but further additions of phenol cause the molecular area in the surface film to decrease.

Also, a 0.05% C.T.A.B. system was spread on the substrate and its force-area curve determined, shown in figure 61, and its molecular area in the surface film determined. Thereafter, systems of 0.05% C.T.A.B. containing various percentages (0.1, 0.2, 0.25, 0.3, 0.4, 0.5, 1.0, 1.5, 1.7, 2.0, 3.0 and 5.0) of sodium salicylate (NaSAL) were spread on the substrate and the molecular in their respective surface films measured. The force-area curves for systems of 0.05% C.T.A.B. containing percentages of sodium salicylate of 0.2, 1.0, 1.5 and 2.0 are shown in figures 62-65 respectively. The results for other 0.05% C.T.A.B. systems containing percentages of sodium salicylate of 0.1, 0.25, 0.3, 0.4, 0.5, 1.7, 3.0 and 5.0 are shown in tables 7-14 respectively.

A plot of the variation of molecular area of C.T.A.B. in the surface films with concentration of sodium salicylate (NaSAL) is shown in figure 66. It can be seen that this plot shows two maxima, one at 0.2% NaSAL and the other at 1.5% NaSAL.

TABLE 1

Measurements on a 1% C.T.A.B. + 0.2% phenol film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.9	76
1.15	71
1.5	66
2.1	60
3.0	53
4.0	46
4.6	42.5
5.5	38
6.3	34
7.0	30

Extrapolated Area = 70 Sq.Å.

TABLE 2

Measurements on a 1% C.T.A.B. + o.6% phenol film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale	Area (Sq.Å)
1.0	80
1.2	73.5
1.8	67
2.7	60
3.7	54
4.5	48.5
6.0	40
7.1	34

Extrapolated Area = 76 Sq.Å.

TABLE 3

Measurements on a 1% C.T.A.B. + 0.8% Phenol film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbtirary Scale)	Area (Sq.Å)
1.0	75
1.1	70
2.1	60
3.3	53
5.4	40
6.6	33
7.7	27

Extrapolated Area = 70 Sq.Å.

TABLE 4

Measurements on a 1% C.T.A.B. + 2.0% phenol film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.1	80
0.3	75
0.6	68
1.3	60
2.5	52.5
3.5	47.
4.4	41
5.8	33
6.7	28

Extrapolated Area = 67 Sq.Å

TABLE 5

Measurements on a 1% C.T.A.B.
+ 3.0% phenol film on an 80%
(Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.4	80
0.6	72.5
1.0	66
2.0	60
3.0	53
4.0	47
6.7	38.5
7.9	26.5

Extrapolated Area = 69 Sq.Å

TABLE 6

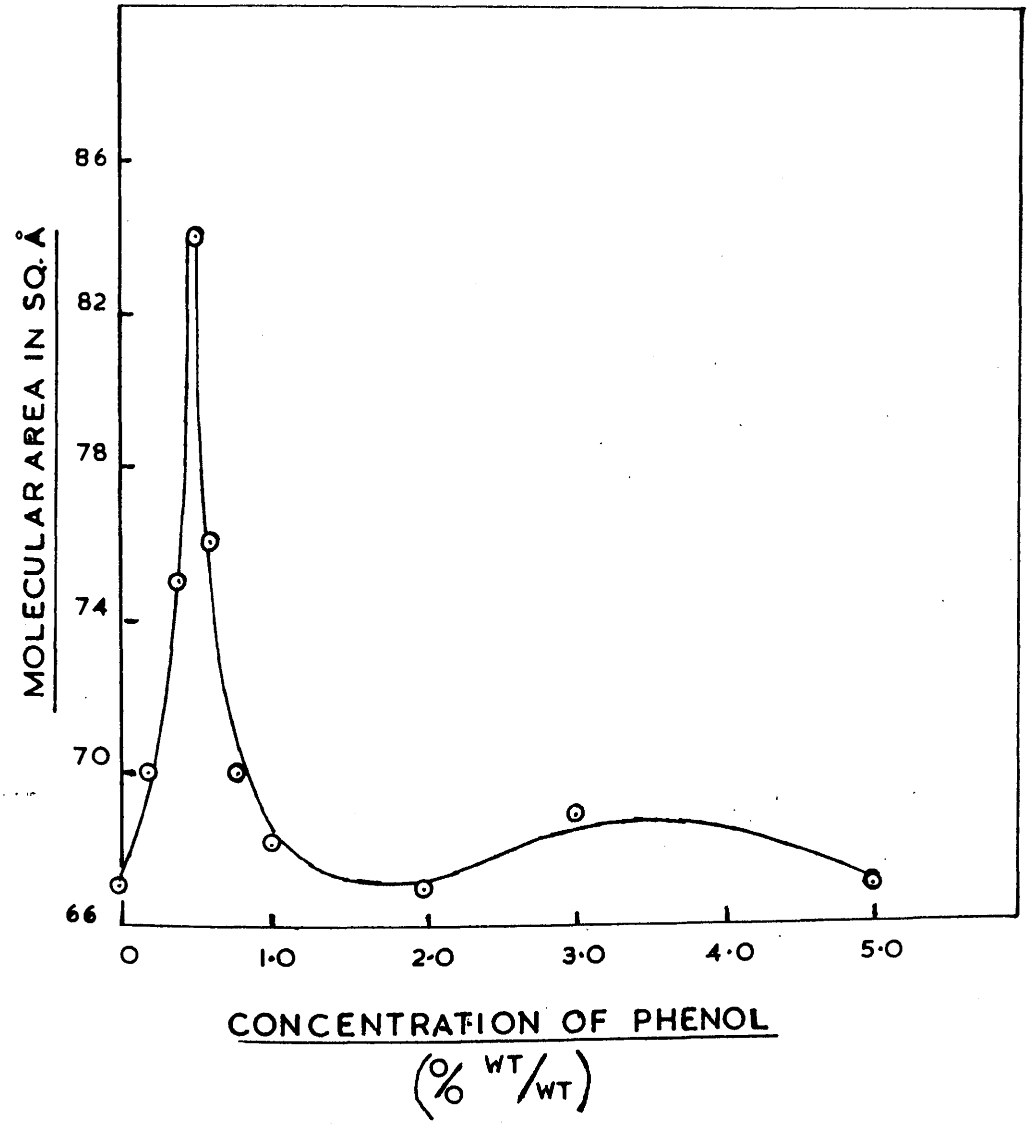
Measurements on a 1% C.T.A.B.
+ 5.0% phenol film on an 80%
(Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.2	80
0.6	66
1.0	61
2.6	53
3.7	47
5.1	40
6.4	33

Extrapolated Area = 67 Sq.Å

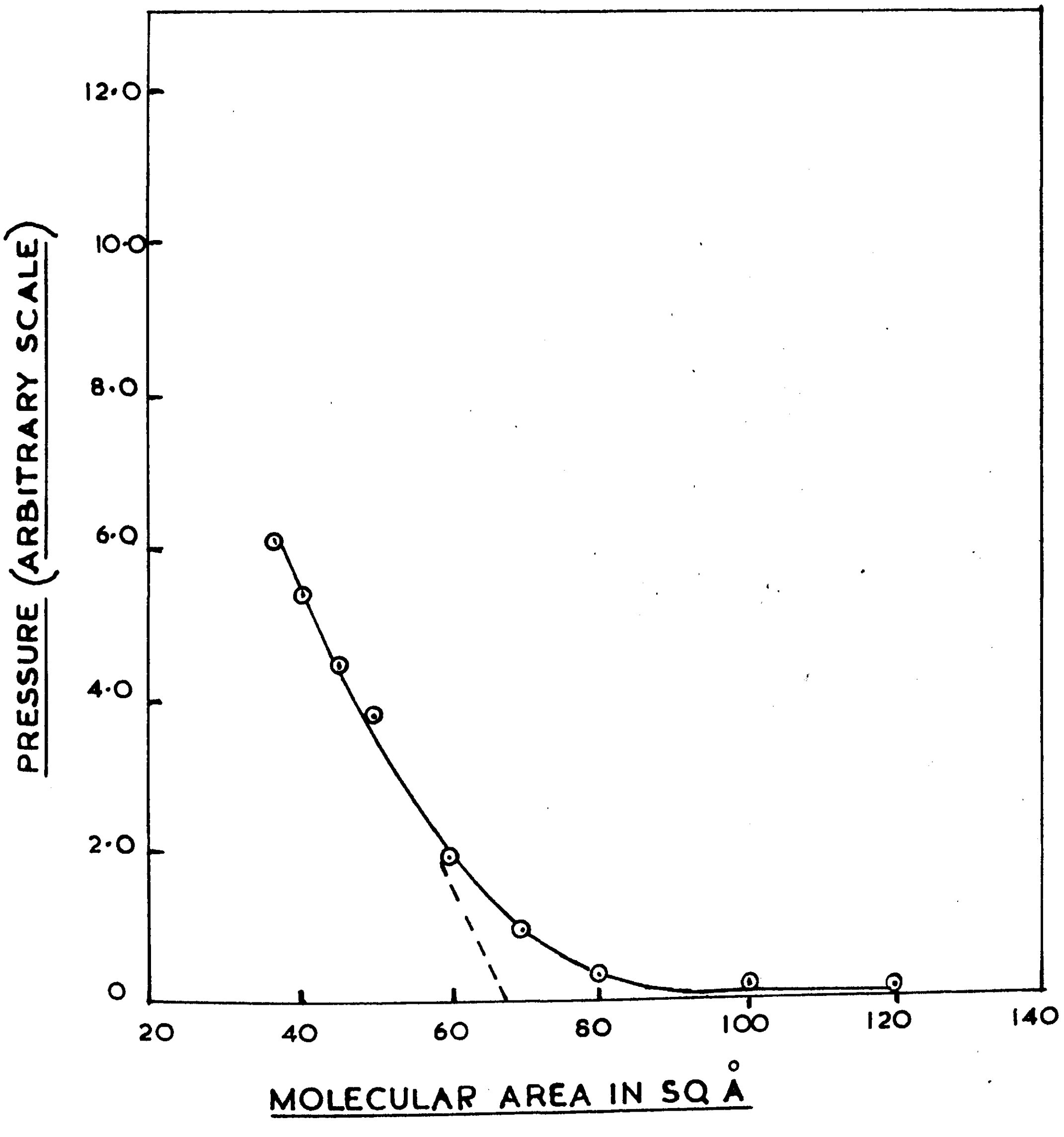
• • FIG 60 • •

VARIATION OF MOLECULAR AREA WITH CONCENTRATION OF PHENOL



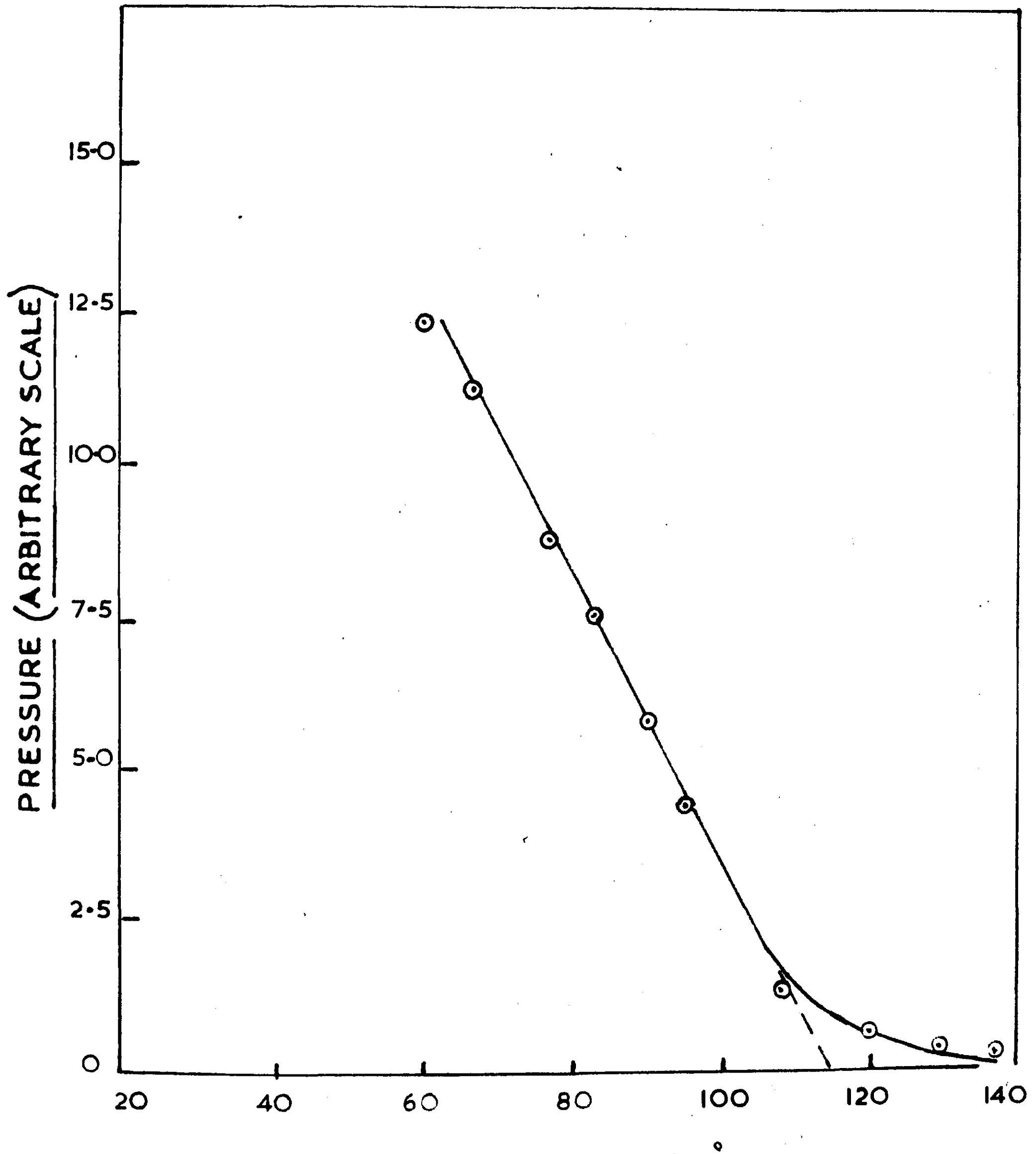
· · FIG 61 · ·

PRESSURE-AREA CURVE OF 0·05% C.T.A.B. FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



· · FIG 62 · ·

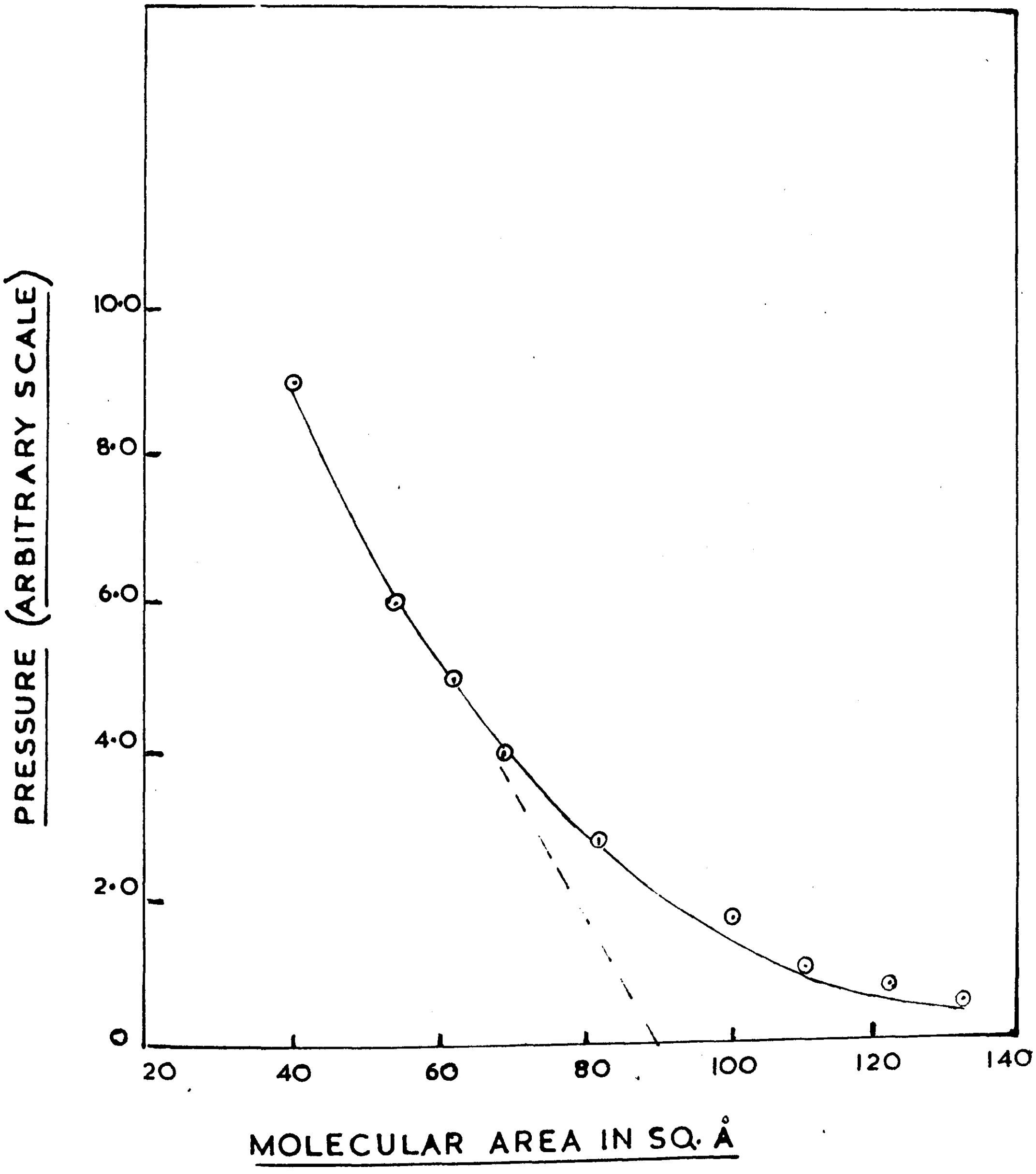
PRESSURE-AREA CURVE OF 0·05% CTAB + 0·2% Na SAL FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



MOLECULAR AREA IN SQ. Å

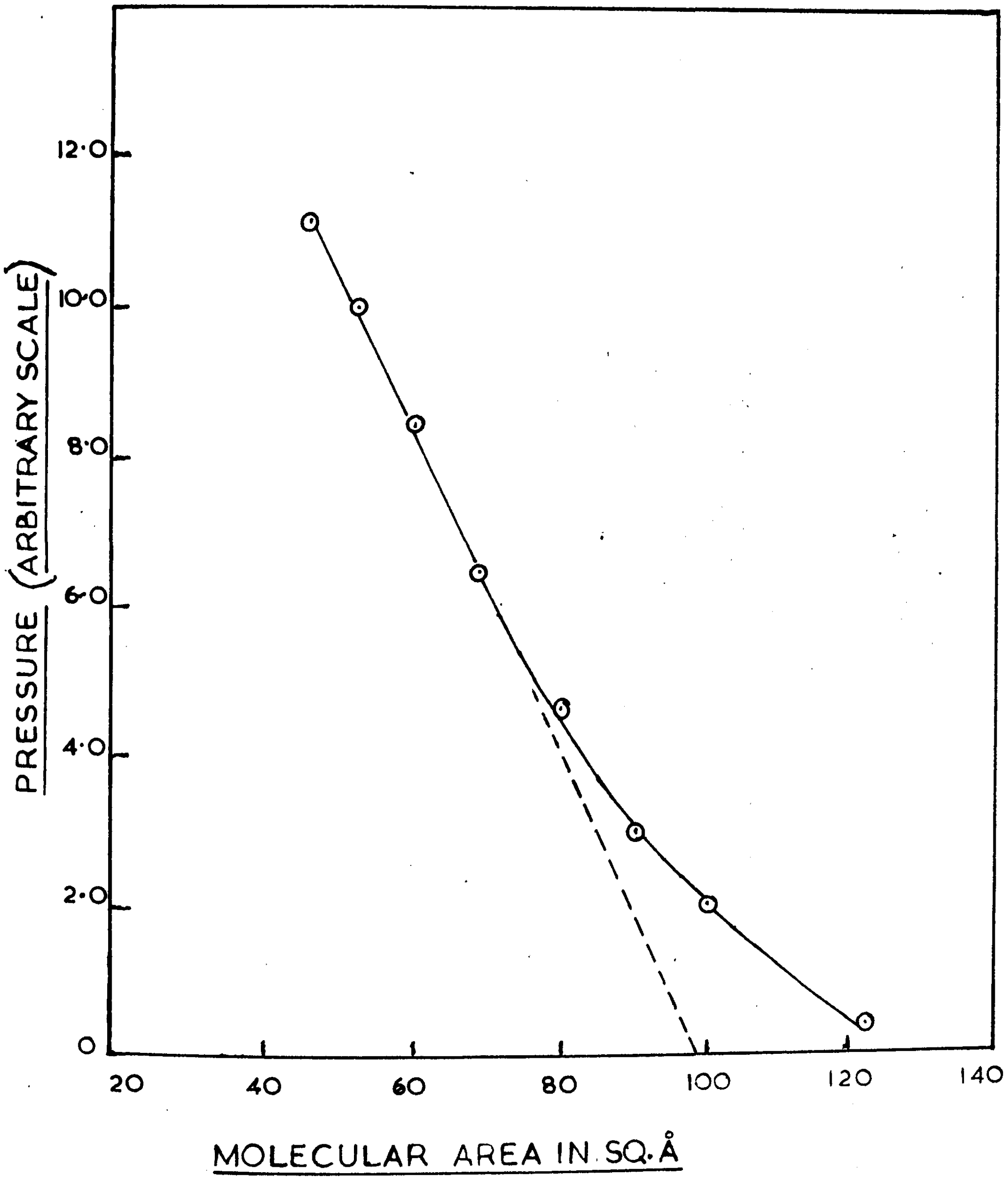
••FIG 63••

PRESSURE-AREA CURVE OF 0·05% C.T.A.B. + 1·0% Na SAL FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



··FIG 64··

PRESSURE-AREA CURVE OF 0·05% CTAB + 1·5% NaSAL FILM ON 80% (WT/WT) $NaNO_3$ SOLUTION



·· FIG 65 ··

PRESSURE-AREA CURVE OF 0·05% CTAB + 2·0% Na SAL FILM ON 80% ($^{WT}/_{WT}$) NaNO$_3$ SOLUTION

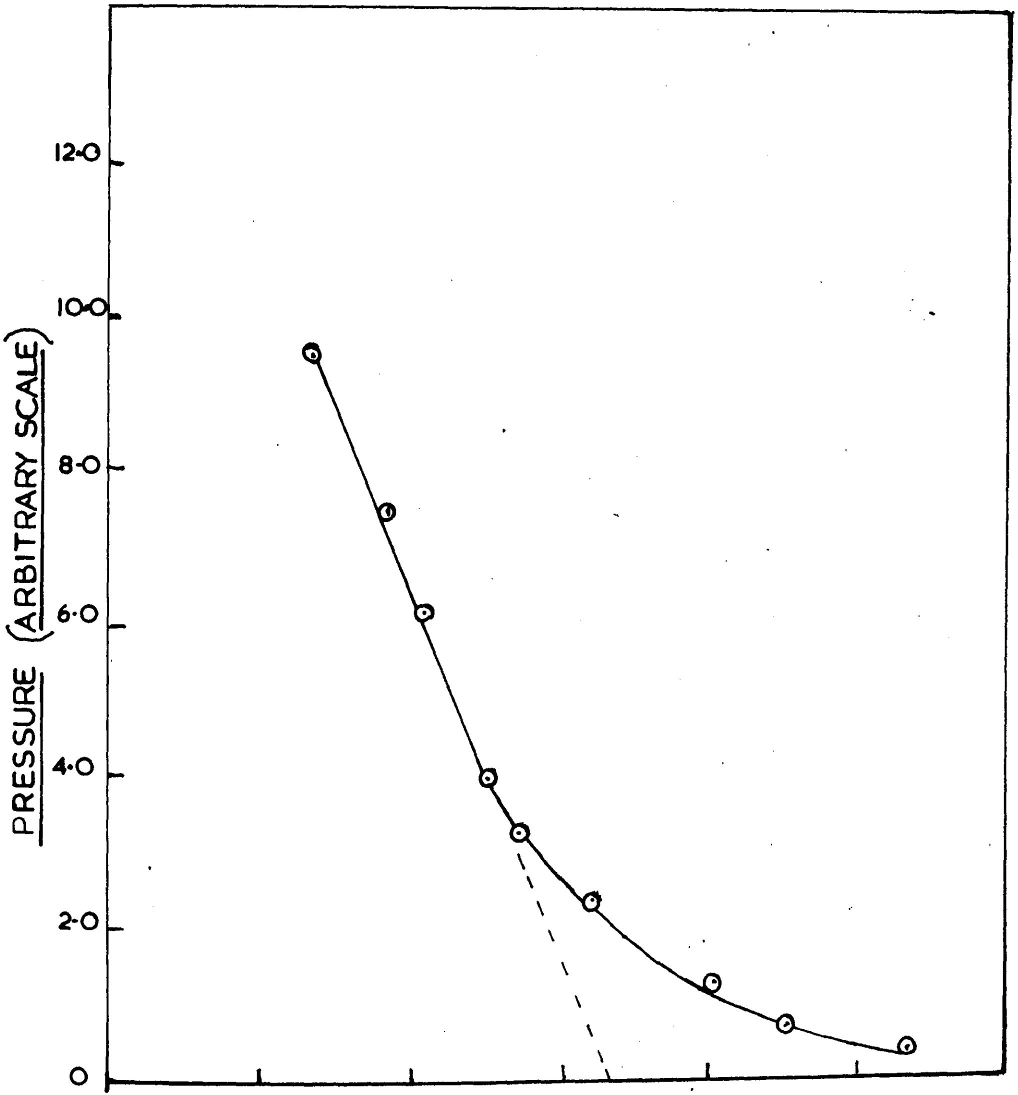


TABLE 7

Measurements on a 0.05% C.T.A.B. + 0.1% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.4	138
0.6	130
0.9	119
1.5	106
2.6	92
4.0	81
6.1	72
9.3	57
11.1	49

Extrapolated Area = 100 Sq.Å

TABLE 8

Measurements on a 0.05% C.T.A.B. + 0.25% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.3	138
0.8	120
1.5	107
3.5	93
4.5	83
6.0	76
7.3	70
9.4	60

Extrapolated Area = 113 Sq.Å

TABLE 9

Measurements on a 0.05% C.T.A.B. + 0.3% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.2	139
0.6	120
1.2	108
2.0	98
3.5	82
5.0	70
6.5	62
8.9	50

Extrapolated Area = 103 Sq.Å

TABLE 10

Measurements on a 0.05% C.T.A.B. + 0.4% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.2	140
0.5	126
1.0	110
1.9	97
3.7	80
5.0	70
6.8	60
8.0	53
9.0	48

Extrapolated Area = 100 Sq.Å

TABLE 11

Measurements on a 0.05% C.T.A.B. + 0.5% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.5	122
1.0	110
2.0	97
3.0	82
5.0	68
6.6	60
8.0	54
10.0	44

Extrapolated Area = 92 Sq.Å

TABLE 12

Measurements on a 0.05% C.T.A.B. + 1.7% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.2	137
0.4	125
0.9	110
1.6	100
2.6	80
5.2	69
6.6	62
8.2	55
10.0	47

Extrapolated Area = 97 Sq.Å

TABLE 13

Measurements on a 0.05% C.T.A.B. + 3.0% NaSAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale	Area (Sq.Å)
0.3	130
0.5	120
0.7	110
1.3	88
2.1	77
3.3	67
4.0	62
5.6	54
6.6	48
8.0	40

Extrapolated Area = 84 Sq.Å

TABLE 14

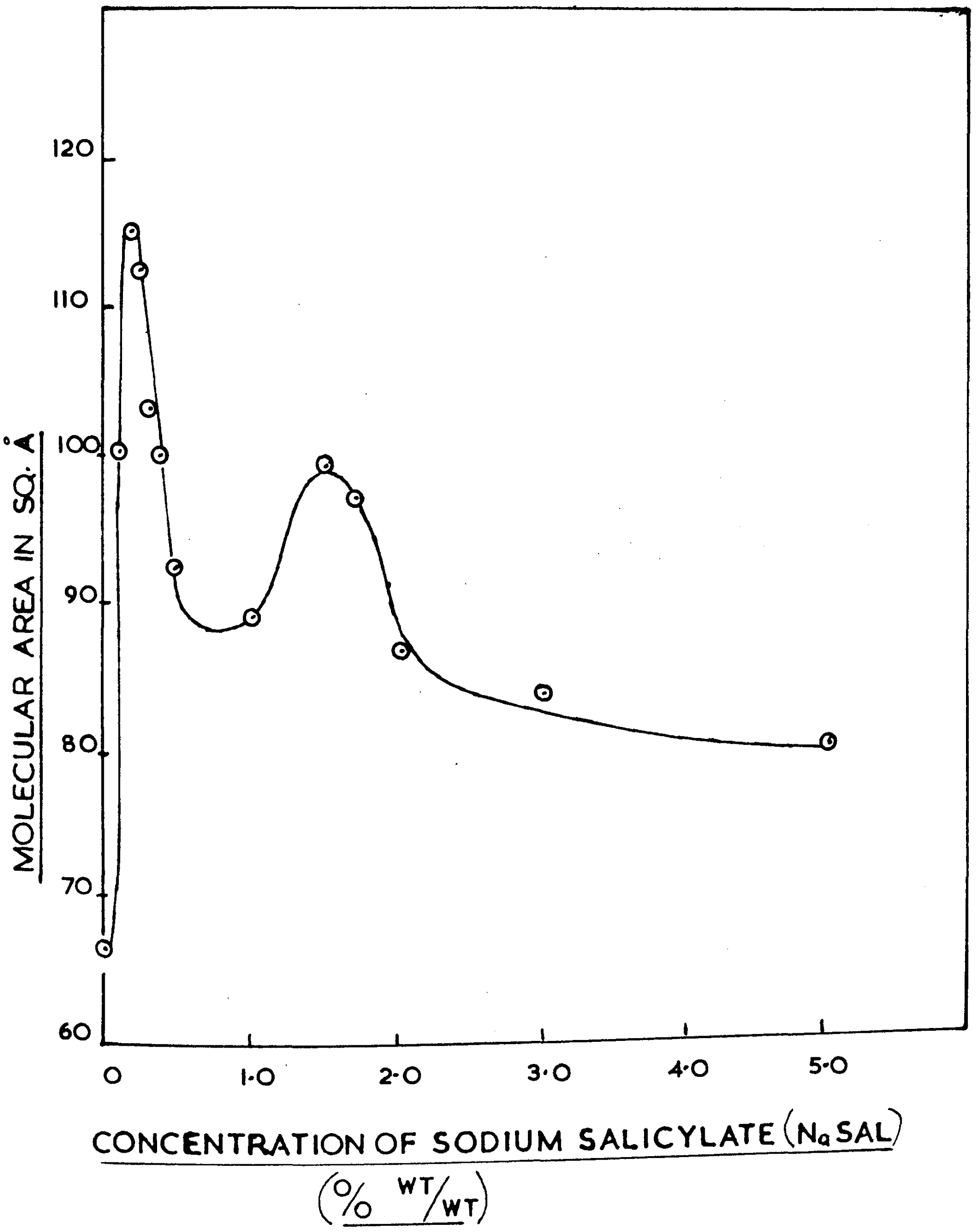
Measurements on a 0.05% C.T.A.B. + 5.0% Na SAL film on an 80% (Wt/Wt) $NaNO_3$ solution

Pressure (Arbitrary Scale)	Area (Sq.Å)
0.3	122
0.7	100
1.2	90
2.0	74
2.5	67
3.1	62
4.1	54
5.2	48
6.5	43

Extrapolated Area = 80 Sq.Å

• • FIG 66 • •

VARIATION OF MOLECULAR AREA WITH CONCENTRATION OF NaSAL



Discussion.

The molecular area of 22.5 sq. Å, in a film of palmitic acid on a substrate of 80% sodium nitrate solution was obtained by extrapolating the straight portion of the force-area curve to the zero pressure axis, see figure 55. This molecular area was in good agreement with those published for long chain fatty acids (119) which suggests that the area obtained by extrapolating the straight portion of the force-area curve to the zero pressure axis may be regarded as the effective molecular cross-sectional area operative in the surface film. Therefore, it is considered that the extrapolated areas, from the force-area curves, obtained for films of systems of 1% C.T.A.B. + phenol on a substrate of 80% sodium nitrate solution are measures of the molecular area in their respective surface films.

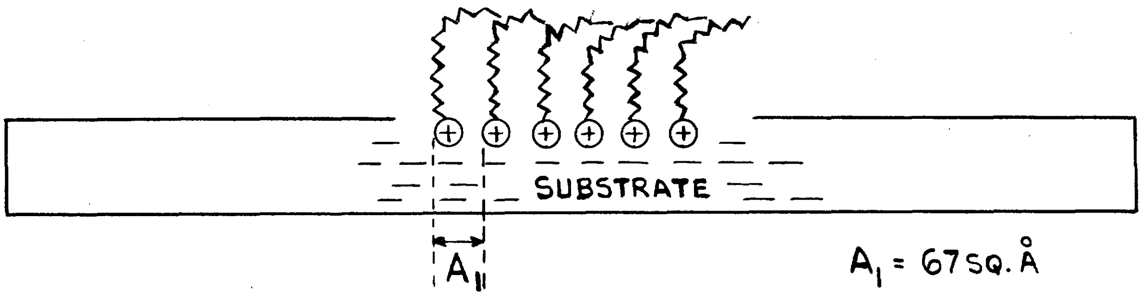
The molecular areas in these surface films varied with the concentration of phenol. It can be seen, in figure 60, that these molecular areas increased as the concentration of phenol increased up to 0.5% and that further additions caused them to decrease.

The molecular area obtained for a film of 1% C.T.A.B. or 0.05% C.T.A.B. was 67 sq. Å., see figures 56 and 61, and consequently it appears that this is the area occupied by the C.T.A. cation. Now, this area suggests (since the area of the quarternary ammonium ion is 30 sq. Å. (120) that the C.T.A. cations on the surface of the substrate cannot be closely packed together with their cetyl groups projecting as straight chains vertically outwards from the substrate. However, the arrangement in the surface film will be such that the tails, which are very flexible, are free to interact with one another with the result that they diverge from the vertical position and consequently the C.T.A. cation within the film assumes a greater area. A diagramatic representation, very idealised, of the probable configuration in the film produced by the C.T.A.B. system is shown in figure 67.

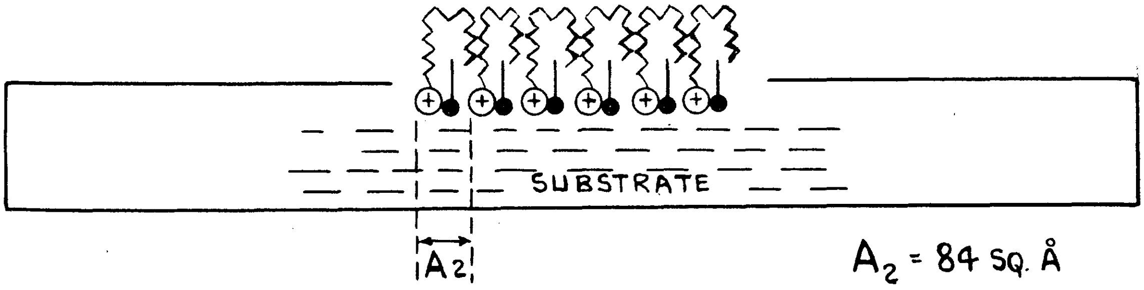
The molecular area of the surface film formed by a 1% C.T.A.B. + 0.5% phenol system was found to be 84 sq.Å., see figure 58. Using molecular models of the C.T.A. cations and of the phenol molecules the cross-sectional area for various configurations were measured. It was found, if the C.T.A. cation and the phenol molecule were arranged in vertical positions along side one another so that the quarternary ammonium ion of the C.T.A. cation and the hydroxyl group of the phenol molecule lie on the same surface, and if the tail of the cetyl chain forms a hook into which the phenyl group of the phenol molecule fits, then the overall cross-sectional area occupied by this arrangement of C.T.A. cation and phenol molecule was almost exactly 84 sq. Å. Therefore, it seems probable that the surface film produced by the 1% C.T.A.B. + 0.5% phenol system consists of a mixed film of C.T.A. cations and phenol molecules which are penetrating between neighbouring C.T.A.

··FIG. 67··

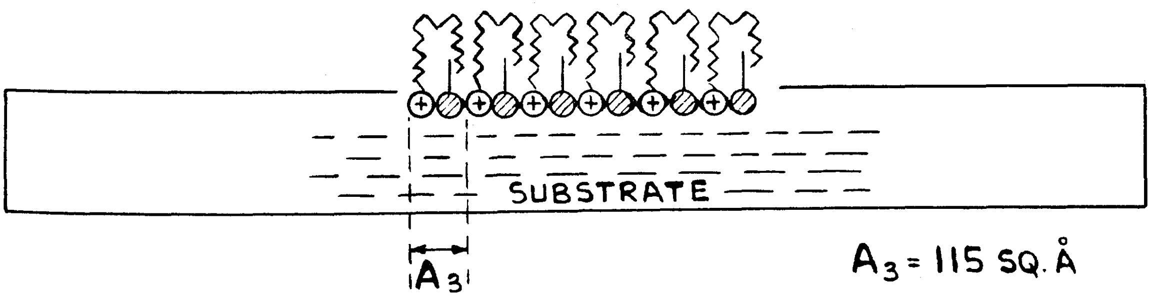
PROBABLE MOLECULAR ARRANGEMENTS IN THE SURFACE FILMS.



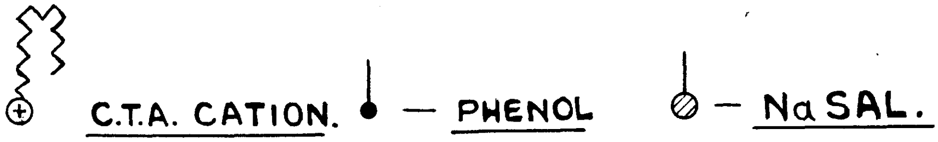
1% C.T.A.B.



1% C.T.A.B. + 0·5% PHENOL.



0·05% C.T.A.B. + 0·2% Na SAL.



cations in such a way that their phenyl groups are incorporated into the hydrophobic region of the surface film. Also, it seems that in this film the cetyl chains are, on the average, so arranged that they curl back on themselves and form hook-like shapes into which the phenyl groups of the phenol molecules position themselves. A diagramatic representation of this proposed molecular configuration in the surface film of 1% C.T.A.B. + 0.5% phenol is shown, in a very idealised form in figure 67.

Since the molecular area in these surface films increases with increase in phenol concentration and reaches a maximum at 0.5% phenol, it appears that the extent to which the phenol molecules are incorporated into the films increases with phenol concentration up to 0.5%. Also, the phenol and C.T.A.B. molecules appear most closely associated in the 1% C.T.A.B. + 0.5% phenol system. At phenol concentrations greater than 0.5% the measurements indicate a decrease in the association between the C.T.A.B. and the phenol molecules.

These results are consistent with the view put forward in the discussion of Part I in which it was suggested that the initial addition of phenol to 1% C.T.A.B. involved phenol molecules being solubilised by the C.T.A. cations and that, at a concentration of 0.5% phenol, this solubilisation was at a maximum but, at greater concentrations, the association between the phenol molecules and the C.T.A. cations decreased.

It has been found, see figure 66, that the curve of molecular area (in surface films) vs. concentration of sodium salicylate has two maxima which occur at the same sodium salicylate concentrations at which the viscosity maxima were observed. Thus, the variation of molecular area and viscosity with concentration of sodium salicylate showed a remarkable similarity which suggests that there is a close connection between the increase in viscosity and the tendency for the C.T.A. cationic film to incorporate salicylate ions.

It was observed that the polar area in the salicylate ion would be a combination of the hydroxyl group and of the carboxylate ion. By measuring a scaled molecular model of the salicylate ion, the diameter of the polar group was found to be approximately 5.3 Å. Since the area of the quarternary ammonium ion is 30 sq. Å. (120) the diameter of the C.T.A. cation must be approximately 5.5 Å. Therefore, the area occupied by the C.T.A. cation and the polar group in the salicylate ion is 116.6sq. Å. Now, this molecular area is very similar to the molecular area of 115 sq. Å. which was produced by a system of 0.2% sodium salicylate in 0.05% C.T.A.B. Thus, it is probable that the molecular area in a surface film of this system consisted of a mixed film of C.T.A. cations and salicylate ions, with the latter being incorporated between neighbouring C.T.A. cations in such a manner that their carboxylate ions and hydroxyl groups are on the surface of the substrate. Also, it is probable that the cetyl chains may, on the average, form hook-like shapes into which the hydrophobic part of the salicylate ion can be incorporated. A diagram of this proposed molecular arrangement in the surface film is shown in a very idealised form in figure 67.

The molecular area at the second maximum was 99 sq. Å. and was produced by a 0.05% C.T.A.B. + 1.5% sodium salicylate system. This area implies that the surface film of a system of 0.05% C.T.A.B. + 1.5% sodium salicylate possessed a molecular arrangement such that the cations and the salicylate ions formed a type of association which appears to be of a different form from that shown by a 0.05% C.T.A.B. + 0.2% sodium salicylate system. It is probable that this second maximum in molecular area is produced by an association which involves only partial incorporation of the salicylate ions into the C.T.A. cationic surface film.

Thus, this work shows that the two maxima in the curve of viscous properties vs. concentration of sodium salicylate for systems of 0.05% C.T.A.B. + sodium salicylate are connected with the tendency for the salicylate ions to "associate" with the C.T.A.B. molecules (i.e. to be solubilised in the C.T.A.B. micelles).

PART IV

EFFECT OF THE ADDITION OF ELECTROLYTES ON THE VISCOUS PROPERTIES OF 1% C.T.A.B. AND OF 1% C.T.A.B. + 0.5% PHENOL SYSTEMS.

EFFECT OF THE ADDITION OF ELECTROLYTES ON THE VISCOUS PROPERTIES OF 1% C.T.A.B. AND OF 1% C.T.A.B. + 0.5% PHENOL SYSTEMS.

Introduction.

During his work with aqueous solutions of C.T.A.B. Walker (100) reported that the respective additions of 0.128 moles of potassium chloride, of sodium chloride and of potassium bromide to a 1% C.T.A.B. + 0.5% phenol system caused in each case an increase in time of flow, measured through an ostwald viscometer and that potassium bromide produced the smallest increase.

To understand the significance of these observations it was necessary to investigate the effect which the addition of different electrolytes had on the time of flow of a 1% C.T.A.B. + 0.5% phenol system. Such an investigation is described in this Part.

Effect of the Addition of Electrolytes on the Viscosity of Aqueous Paraffin-Chain Salt Solutions.

As early as 1885, Morawski and Demski (121) found that the viscosity of Fuller's soap was altered considerably by the addition of small amounts of electrolyte. In 1910, Leimdorfer (122) observed that small additions of potassium chloride to cocoa-nut oil soap lowered the viscosity but larger amounts raised the viscosity to a high value.

Similar results were also observed by Farrow (123) who found that the addition of electrolyte to sodium palmitate caused the viscosity to fall at first and then to rise very sharply. He ascribed the first fall to be due to shrinkage of the colloidal species by the inability of the electrolyte to penetrate them and thereby causing the water to flow out of the colloidal particles as though through a semi-permeable membrane.

In 1940, Angelescu and Szász (124) suggested that the rise in viscosity found at higher concentrations of electrolyte was due to the electrolyte reducing the solubility of the soap, i.e. SALTING OUT. This reduction in solubility enhanced the aggregation of the soap ions and therefore caused a rise in viscosity. The process of aggregation envisaged by Angelescu was a fusion of micelles to form a large reticular structure which may enclose a large amount of water and so set up a high structural viscosity.

McBain considered that salts promote the formation of neutral micelles at the expense of ionic micelles by a reduction of the surface charges.

It has been shown (125) that the c.m.c. of soap solutions is reduced by the addition of simple electrolytes. Corrin and Harkins (126) have shown that for anionic and for cationic paraffin-chain salts the reduction in the c.m.c. is practically independent of the anion or of the cation respectively of the added electrolyte. This reduction of the c.m.c. was explained by them as being due to the ion from the electrolyte screening the repulsion of the ionic heads of the paraffin-chain ions and therefore making micelle formation more favourable.

Klevens (127) has shown that the addition of electrolyte increases the solubilisation of non-polar compounds in aqueous solutions of paraffin-chain salts. He suggested that the added electrolyte reduced the repulsion of the ionic heads on the surface of the micelle and therefore the area occupied per head decreased with the result that there was a decrease in the curvature of the micelle. This decrease in the curvature caused an increase in the size of the paraffinic interior and consequently there became a greater capacity within the micelle for non-polar solubilisation.

Also, Klevens (127) found that, at low concentrations of the paraffin-chain salts, polar solubilisation is increased by the addition of electrolyte but, at higher concentrations of paraffin-chain salt the addition of electrolyte caused a decrease in polar solubilisation. This increase in polar solubilisation, at low concentration of paraffin-chain salt, has been explained as being due to the lowering of the c.m.c. while the decrease in polar solubilisation found at higher concentrations of paraffin-chain salt, was considered to be due to the electrolyte decreasing the repulsion between ionic heads and therefore reducing the available space between paraffin-chain ions for polar solubilisation.

It appears from the work of Alexander (95) and Hubbard (128) that the concentration of paraffin-chain salt determines the effect that the addition of electrolyte has on the viscosity. Alexander observed that, the addition of sodium chloride to

0.44 M solution of cetyl pyridinium chloride caused the viscosity initially to decrease to a minimum, but that further electrolyte addition caused the viscosity to increase to a value many times greater than that of the original cetyl pyridinium chloride solution. However, he noted that the addition of sodium chloride to 0.118 M solution of cetyl pyridinium chloride showed initially only a slight decrease in viscosity and that there was no increase with further additions (i.e. additions of NaCl which showed a marked increase in viscosity with 0.44 M solution).

There seems to be no clear evidence that there is any change in micellar size when small amounts of electrolyte are added to a solution of paraffin-chain salt. Hartley (129) attempted to detect micellar changes by diffusion measurements but failed to find any change in size in the presence of electrolyte until the electrolyte concentration was 1.0 N. Similarly, from light scattering measurements, no apparent micellar change was observed at low concentrations of electrolyte. Debye and Anacker (87) using light-scattering techniques, could not detect any micellar changes in solutions of paraffin-chain salts containing simple electrolytes until the electrolyte concentration was 0.2 N. They suggested that the effect of the addition of electrolyte, at a concentration of 0.2 N or more, is to transform the spheroidal micelles into rod-like shaped micelles.

The effect of moderate additions of electrolyte to aqueous paraffin-chain salts has been studied by Schulmann, Van der Berg and Pilpel.

Schulmann and Van der Berg (130) found that the addition of electrolyte caused, in some cases, the formation of a visco-elastic system. They examined some of these systems with X-ray and found that the long spacing gave a very diffused pattern which suggested that the systems contained micellar aggregates of various sizes.

Pilpel (93) has studied the formation of visco-elastic systems when electrolyte is added to moderately concentrated solutions of paraffin-chain salts. He envisaged that the spheroidal micelles were transformed by the added electrolyte into plate-like shaped micelles which packed together into aggregates, shaped like long cylindrical rods in which the molecules are arranged radially to the axis with their polar heads outermost. According to him, it was the interlinking of these long rod-like micelles which produced the visco-elastic properties in these systems. Also, he noted that systems of paraffin-chain salts which formed a gel with a certain concentration of electrolyte showed a slight birefringence. This finding supported his view that a change from spheroidal to cylindrical micelles takes place on the addition of electrolyte.

Alexander et.al. (95) have reported that the addition of either chlorobenzene, toluene, n-octane, or p-dichlorobenzene to a system of cetyl pyridinium chloride containing sodium chloride caused the viscosity to increase to a maximum and with further additions to decrease. They observed that with decrease in concentration of cetyl pyridinium chloride, the curves of viscosity against concentration of additive (chlorobenzene etc.) to the cetyl pyridinium chloride + sodium chloride system showed sharper but lower maxima. In the absence of sodium chloride only small viscosity changes occurred and they were observed only in strong solutions of cetyl pyridinium chloride (0.3 to 0.5 M).

Apparatus.

The times of flow in this work were measured by two ostwald type viscometers A and B. Viscometer A had the larger capillary bore. The apparatus was set up as described in Part I.

Preparation of Solutions.

Addition of Electrolyte to 1% C.T.A.B. or 1% C.T.A.B. + 0.5% Phenol.

The electrolyte was weighed out, dissolved in either the 1% C.T.A.B. or in the 1% C.T.A.B. + 0.5% phenol system at 25°C and then placed for 12 hours in a water bath thermostatically controlled at 30°C. This was done to ensure that there were no non-homogeneous regions in the system. These systems containing electrolytes were stored in a second bath thermostatically controlled at 25°C. Time of flow measurements were not made on any of these systems until they had been stored at 25°C for at least 12 hours.

Procedure.

The method adopted for time of flow measurements was the same as described in Part I. All measurements were made at (25 ± 0.1°C) and with a holding time of 45 seconds.

Results.

The effect on the time of flow of the addition of potassium chloride and of sodium chloride to 1% C.T.A.B. and to 1% C.T.A.B. + 0.5% phenol system were studied. The plot of time of flow through viscometer A against concentration of electrolyte added is shown in figure 68. It can be seen that the addition of chloride salt to this system caused the time of flow to increase to a maximum at a concentration of 0.1 moles/litre and then to decrease until a phase change took place at which point the measurements were discontinued. The value of the maximum time of flow was found to be about 124 times that of an electrolyte-free system.

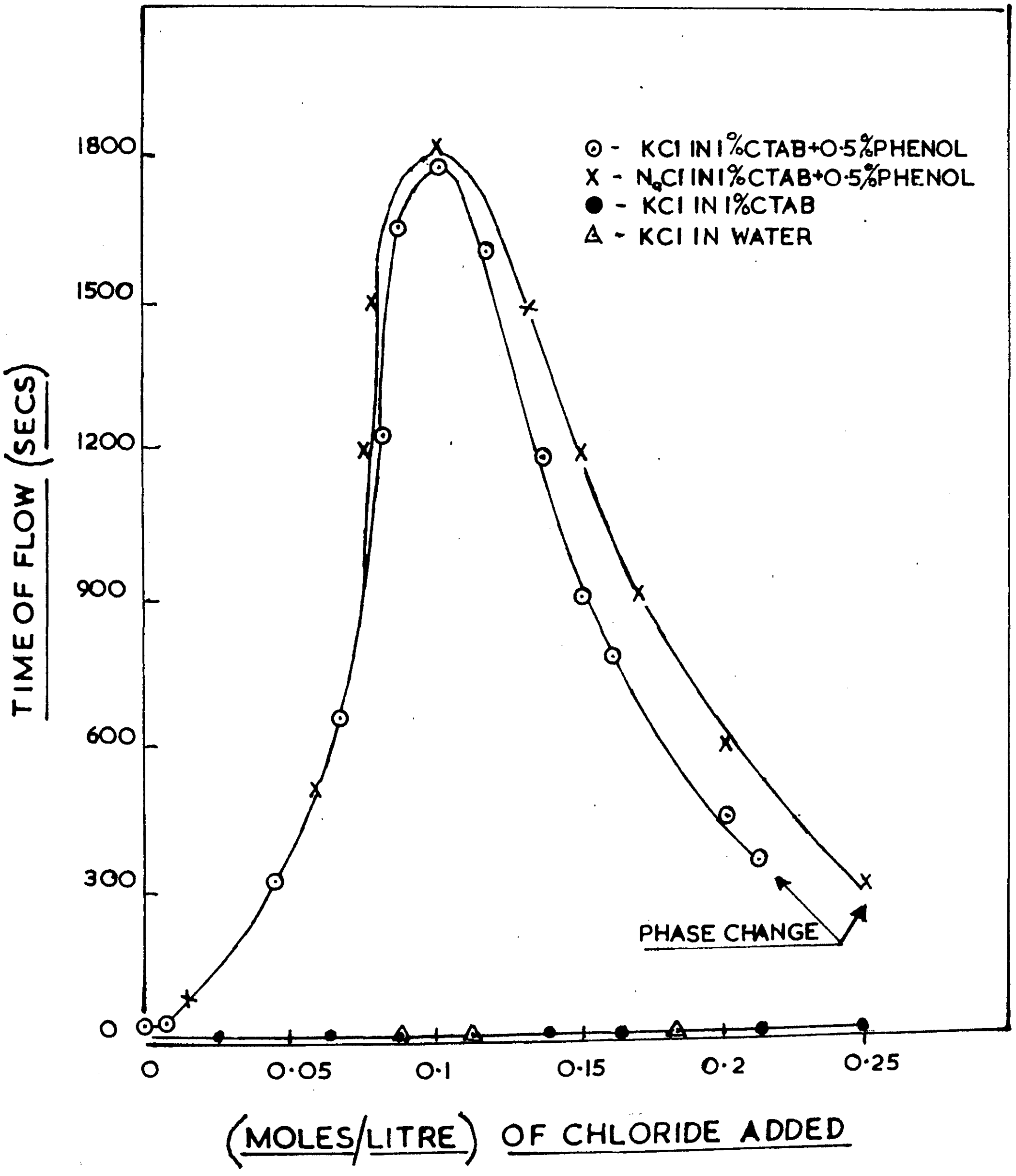
From the shape of the curves shown in figure 68, it appears that sodium chloride and potassium chloride have almost identical effects on the time of flow of a 1% C.T.A.B. + 0.5% phenol system. Also, it was observed that while the addition of potassium chloride to a 1% C.T.A.B. + 0.5% phenol system had a pronounced effect on the time of flow, its additions to a 1% C.T.A.B. system had practically no effect.

Increasing amounts of other electrolytes were added to a 1% C.T.A.B. + 0.5% phenol system and their times of flow measured. The plots of time of flow against concentration of potassium bromide, potassium nitrate, potassium sulphate and potassium phosphate are shown in figures 69, 70, 71 and 72 respectively.

It can be seen that the addition of all these salts

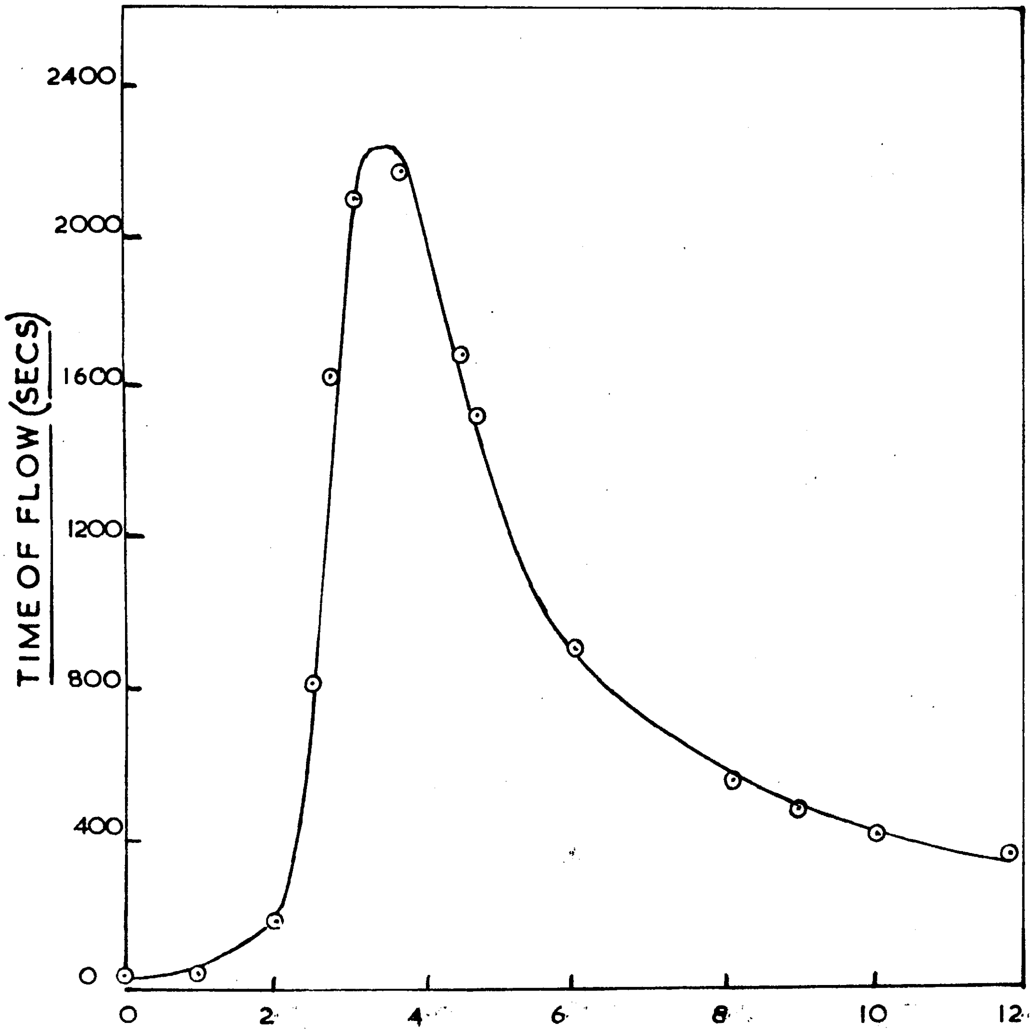
···FIG 68··

EFFECT OF THE ADDITION OF CHLORIDE ON TIME OF FLOW THROUGH VISCOMETER 'A'



·· FIG 69··

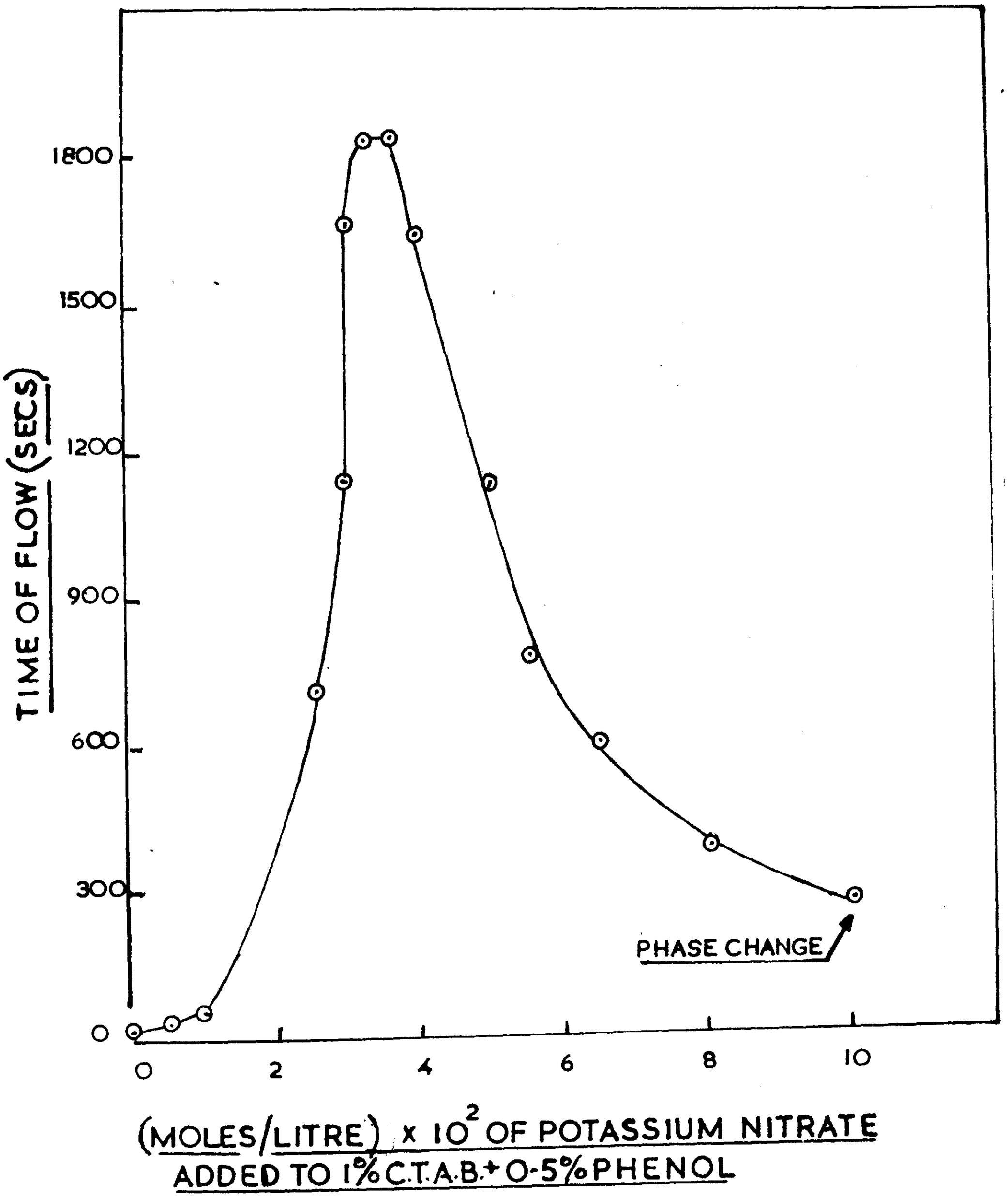
EFFECT OF THE ADDITION OF KBr
ON TIME OF FLOW THROUGH VISCOMETER "A"
OF A 1% C.T.A.B. + 0·5% PHENOL SYSTEM



(MOLES/LITRE) x 10^2 OF POTASSIUM BROMIDE
ADDED TO 1% C.T.A.B. + 0·5% PHENOL

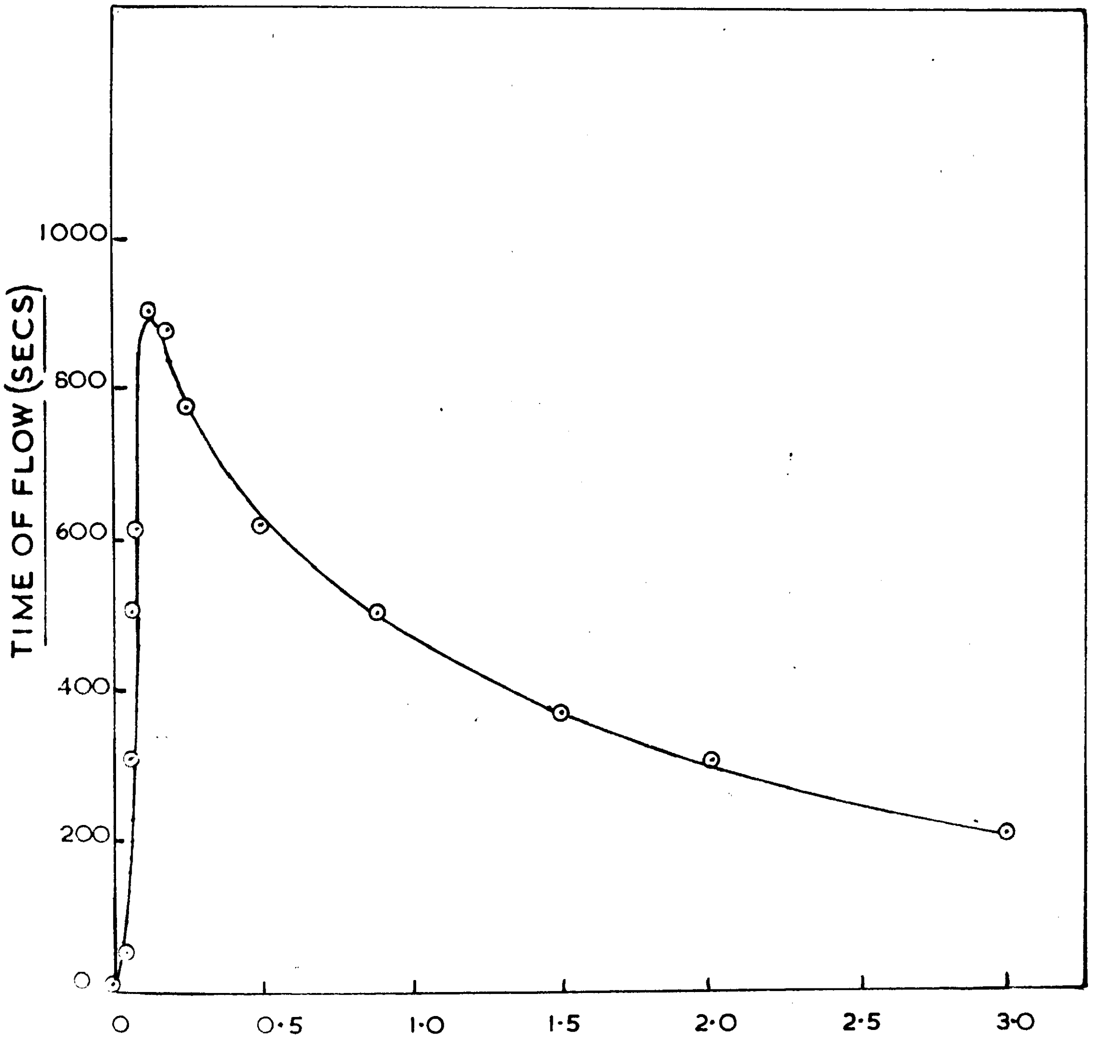
-- FIG 70 --

EFFECT OF THE ADDITION OF KNO_3 ON TIME OF FLOW THROUGH VISCOMETER "A" OF A 1% C.T.A.B + 0·5% PHENOL SYSTEM



•• FIG 71 ••

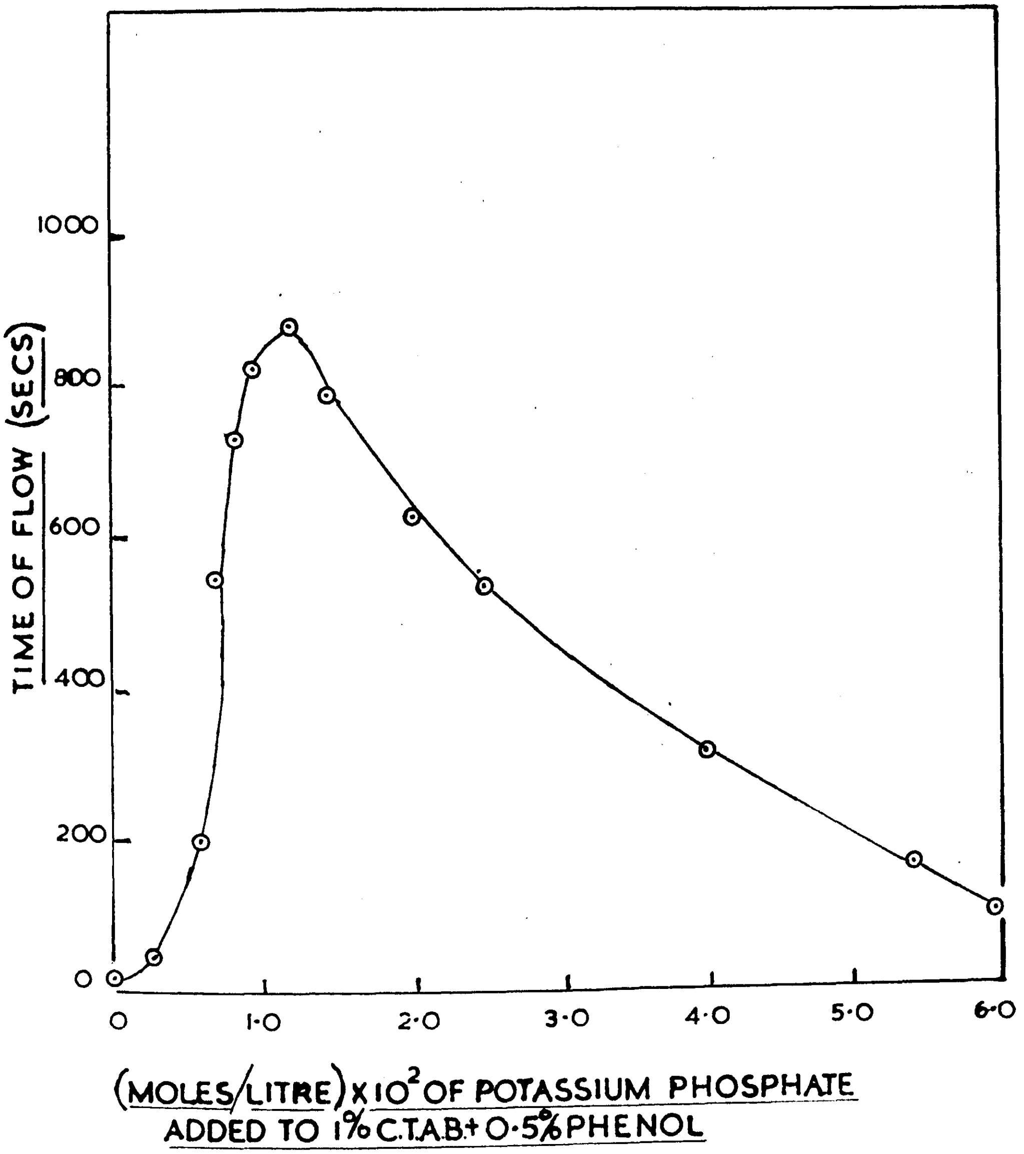
EFFECT OF ADDITION OF K_2SO_4 ON TIME OF FLOW THROUGH VISCOMETER "A" OF A 1% CTAB + 0·5% PHENOL SYSTEM



(MOLES/LITRE) x 10 OF POTASSIUM SULPHATE ADDED TO 1% C.T.A.B. + 0·5% PHENOL

··FIG 72··

EFFECT OF THE ADDITION OF K_3PO_4 ON TIME OF FLOW THROUGH VISCOMETER 'A' OF A 1% C.T.A.B.+0·5% PHENOL SYSTEM



caused the times of flow to increase to a maximum and then to decrease. The value of the maximum time of flow and the concentration of salt added to give this maximum was different for each salt.

Since the addition of each potassium salt produced a different curve and since the addition of sodium chloride and of potassium chloride gave almost identical curves, it appears that the shape of the curve is a characteristic of the anion added.

In order to study semi-quantitatively the effect produced by different anions, it was necessary to discover a parameter which could be measured with accuracy and which would be characteristic of the electrolyte anion added. A convenient parameter was found to be the gradient to the curve of time of flow against concentration of added electrolyte at zero concentration of electrolyte. It is referred to in this work simply as the "GRADIENT" and, as will be seen, is characteristic of the added anion.

If a sufficiently large holding time is used when making the time of flow measurements, then the "GRADIENT" obtained will not be dependent on the previous shearing influences to which the systems have been subjected.

The Effect of the Addition of Small concentrations of Electrolyte to a 1% C.T.A.B. + 0.5% Phenol System.

The determination of the "GRADIENT" for different anions.

To determine accurately the "GRADIENT", it was necessary to study the changes in time of flow of a 1% C.T.A.B. + 0.5% phenol system caused by small additions of electrolyte ($0 \rightarrow 3 \times 10^{-3}$ M).

A system of 1% C.T.A.B. + 0.5% phenol + approximately 3×10^{-3} moles/litre of electrolyte was prepared by the procedure previously described. In order to obtain systems of lower electrolyte concentration, this system was diluted with the 1% C.T.A.B. + 0.5% phenol system. After each dilution, the resultant system was placed for 12 hours in a bath thermostatically controlled at 30°C to ensure proper mixing. Before any measurements were made, these systems were stored for at least 12 hours at 25°C.

The time of flow of each of these systems was measured in viscometer B with a holding time of 45 seconds which according to figure 6. (Part I) would be large enough to ensure that the time of flow was not influenced by previous shearing effects.

The procedure adopted for making time of flow measurements was the same as described in Part I.

Results.

The effect on the time of flow of small additions of potassium chloride to 1% C.T.A.B. + 0.5% phenol system and to a 1% C.T.A.B. system is shown in figure 73. It was noted that while the addition of potassium chloride to 1% C.T.A.B. + 0.5% phenol caused an increase in the time of flow, its addition to 1% C.T.A.B. caused only a slight decrease in the time of flow.

The "GRADIENT" for the chloride anion was determined from figure 73 and was taken as being the ratio of AB:BC.

The effect on the time of flow of small additions to a 1% C.T.A.B. + 0.5% phenol system of the following potassium salts, fluoride, bromide, nitrate, iodide, iodate, bromate, chlorate, perchlorate, sulphate, phosphate, chromate and tungstate, were studied and their plots of time of flow against the small concentrations of electrolyte added are shown in figures 74(a), 74(b), 75(a), 75(b), 76(a), 76(b), 77(a), 77(b), 78, 79(a), 79(b) and 80(a) respectively.

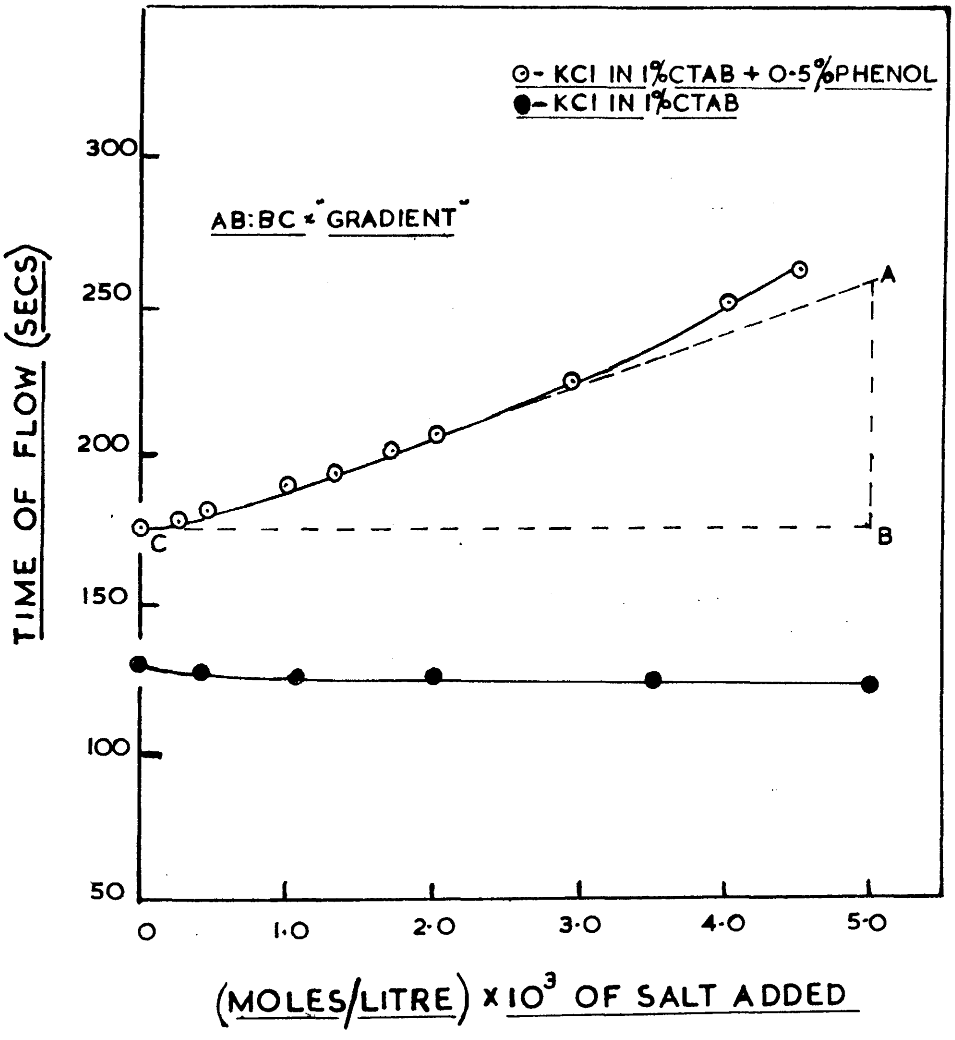
From these figures the "GRADIENTS" for the various anions were determined.

Correlation of the "GRADIENT" of the Anions

Attemps to correlate the "GRADIENTS" of the various anions with some of their other characteristics, such as, lyotropic numbers, parachors, etc., at first proved to be unsuccessful but eventually a simple correlation was obtained, as shown in figure 81, by plotting the "GRADIENT" of the anion against the cube of its "effective" radius. The "effective" radii of the anions were determined by a method proposed by

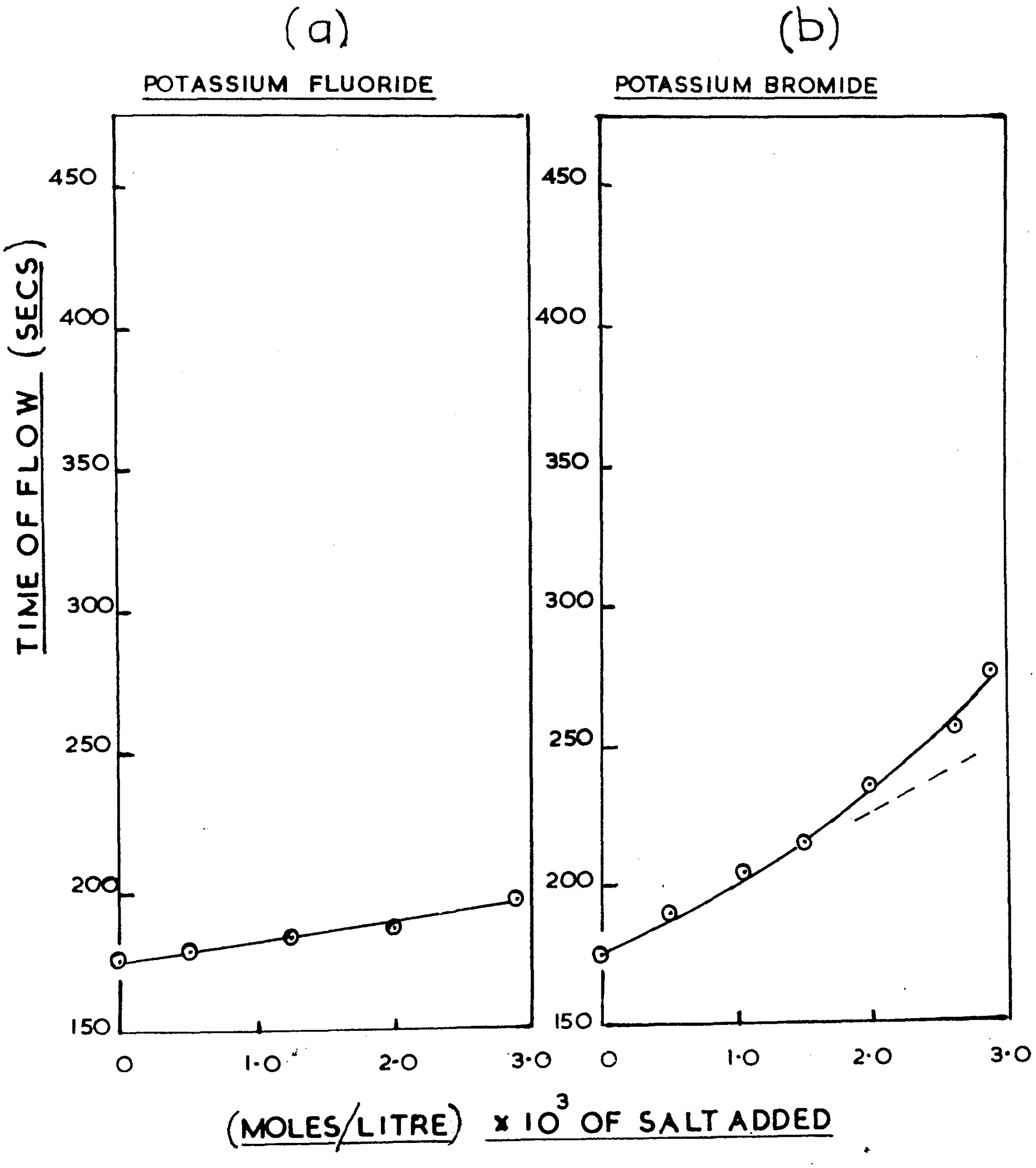
••FIG 73••

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF POTASSIUM CHLORIDE ON THE TIME OF FLOW THROUGH VISCOMETER "B"



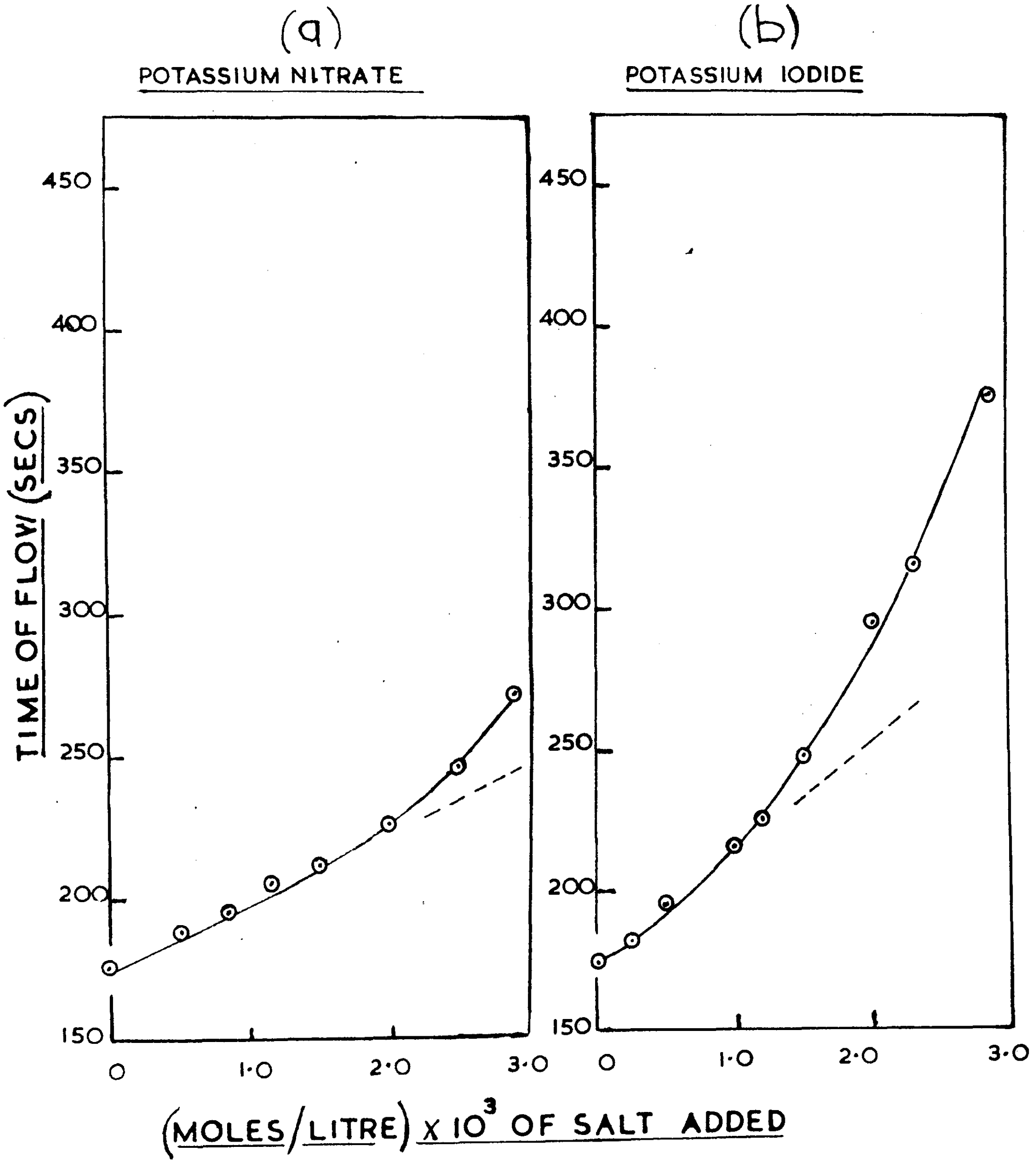
••FIG 74••

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% CTAB+0·5% PHENOL SYSTEM



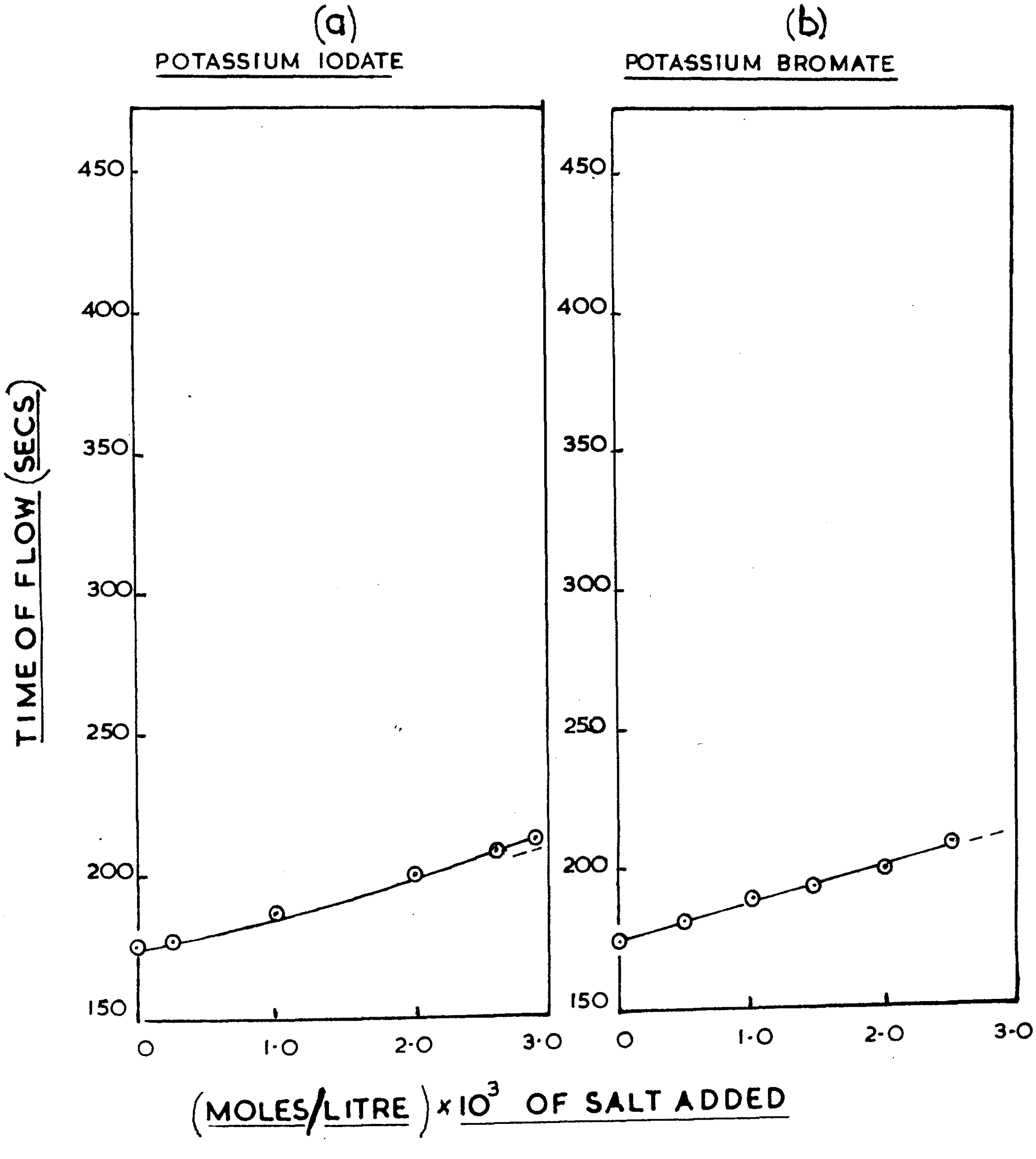
• • FIG 75 • •

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER 'B' OF 1% C.T.A.B. + 0·5% PHENOL SYSTEM



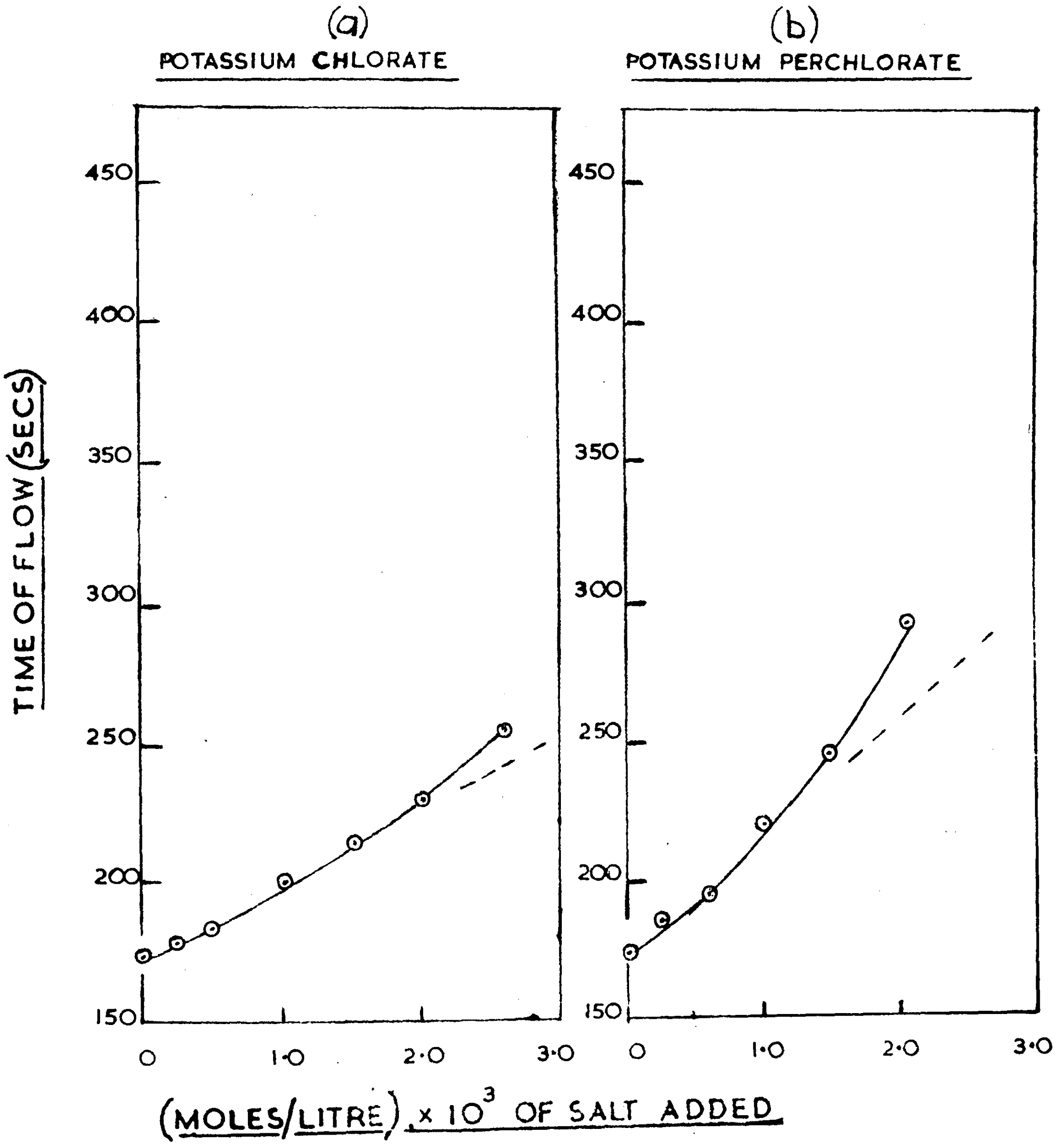
• • FIG 76 • •

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C.T.A.B. + 0·5% PHENOL SYSTEM



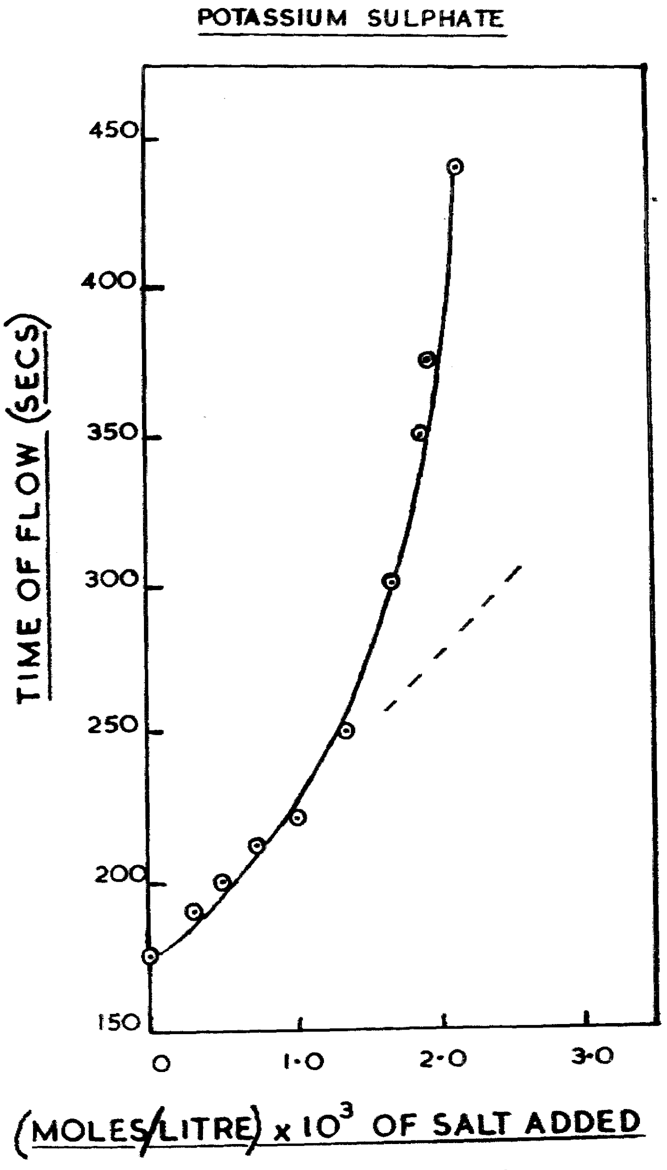
•• FIG 77 ••

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER 'B' OF 1% CTAB + 0.5% PHENOL SYSTEM



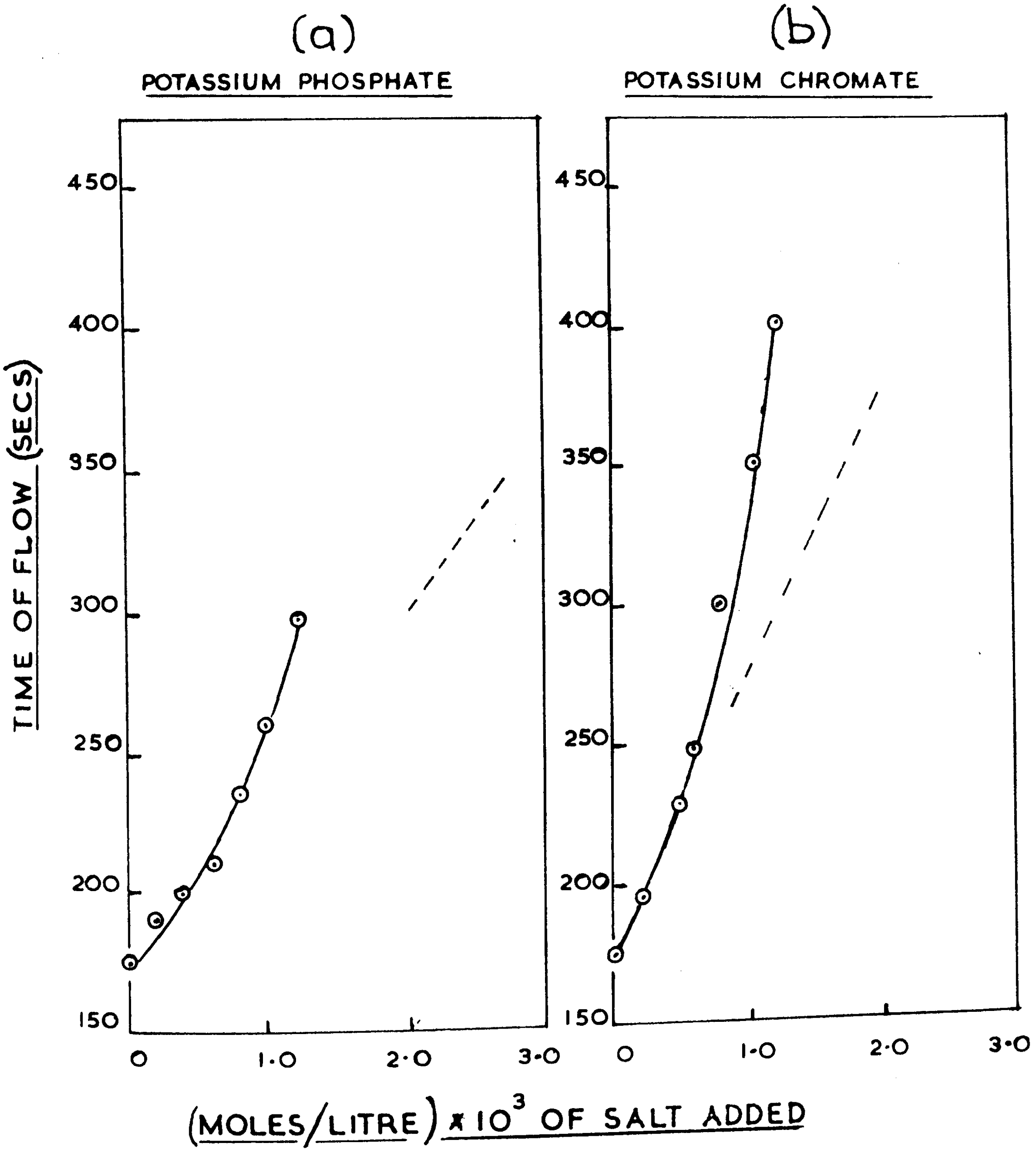
·· FIG 78 ··

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C.T.A.B.+O·5% PHENOL SYSTEM



·· FIG 79 ··

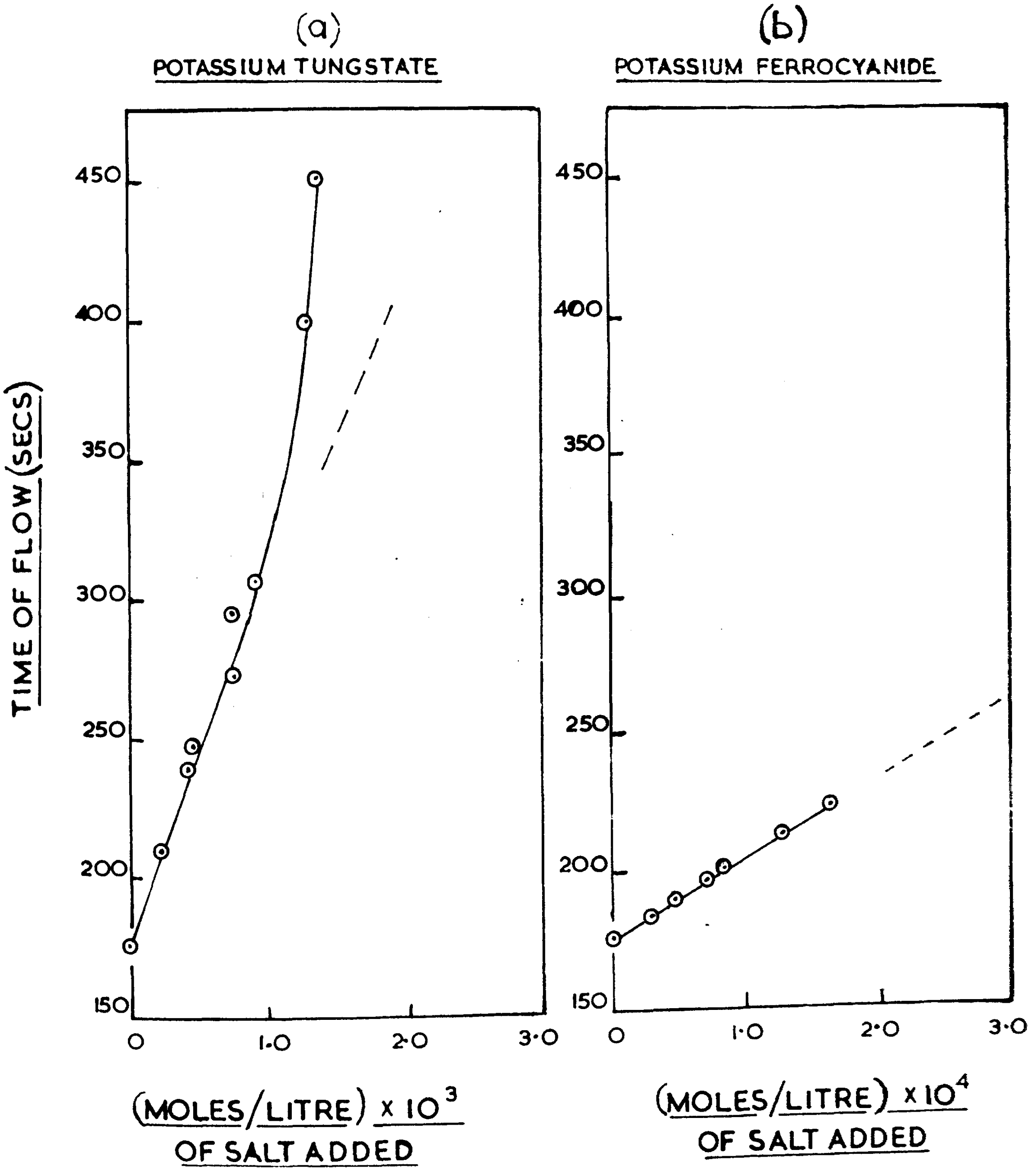
EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1%CTAB +0·5%PHENOL SYSTEM



··FIG 80··

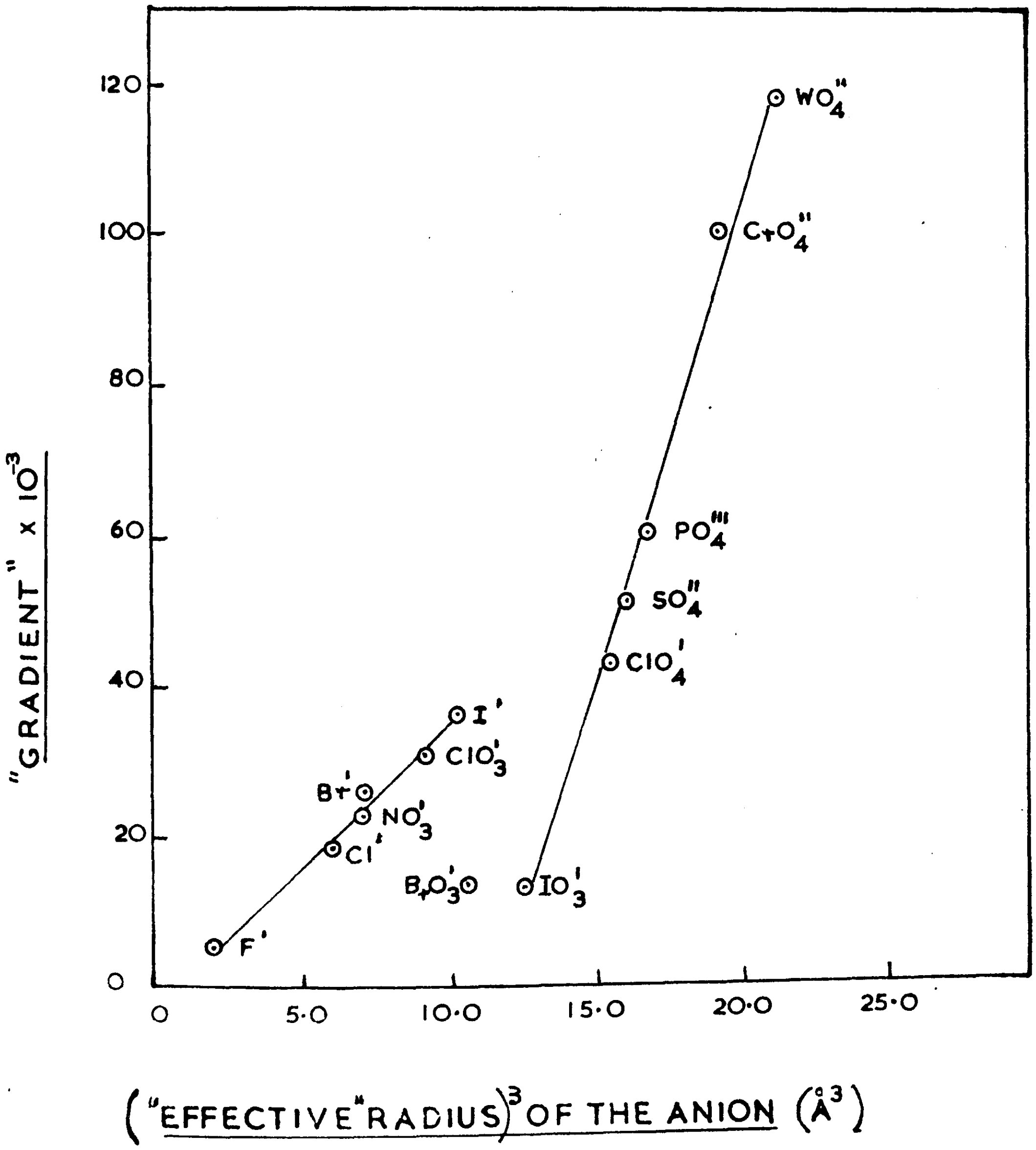
EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B"

1% C.T.A.B. + 0·5% PHENOL SYSTEM



·· FIG 81 ··

VARIATION OF "GRADIENT" WITH ("EFFECTIVE" RADIUS)^3 OF ANION



Stern and Amis (131) which made use of the covalent radii (132).

Determination of the "effective" Radii of Anions.

The method suggested by Stern and Amis (131), who reviewed the literature regarding the sizes of the anions, gave a convenient basis for comparing the relative sizes of the anions.

According to this method, to find the "effective" radius of an anion, it was first necessary to determine the radius of the sphere circumscribing the anion. The radius of this sphere (r) was calculated for oxyanions from the following formula:

$$r = r_{12} + 1.4$$

where r_{12} = covalent radius of the central atom + covalent radius of the oxygen atom.

and 1.4 = Van der Waals' radius for the oxygen atom, in Å.

The "effective" radius (R) of the anion could then be found from,

$$\frac{R}{r} = k = \text{a constant.}$$

The value of k depends on the type of anion,

k for spherical ion = 1

k for triangular ions, like NO_3' = 0.67

and k for tetrahedral ions, like SO_4'' = 0.79

ClO_3', IO_3' and BrO_3' were regarded as triangular ions, although they are triangular pyramids, and k for these ions was taken as 0.67.

In this manner the "effective" radii of the anions were determined as shown in table 15.

	TABLE 15	
Anion	Radius of Circumscribing Sphere (r) in Å	"Effective" Radius (R) Å
F'	1.36	1.36
Cl'	1.81	1.81
Br'	1.95	1.95
I'	2.16	2.16
NO_3'	0.74 + 0.74 + 1.4 = 2.88	1.93
ClO_3'	0.99 + 0.74 + 1.4 = 3.13	2.09
BrO_3'	1.14 + 0.74 + 1.4 = 3.28	2.19
IO_3'	1.33 + 0.74 + 1.4 = 3.47	2.32
ClO_4'	0.99 + 0.74 + 1.4 = 3.13	2.47
SO_4''	1.04 + 0.74 + 1.4 = 3.18	2.51
PO_4'''	1.10 + 0.74 + 1.4 = 3.24	2.56
CrO_4''	1.25 + 0.74 + 1.4 = 3.39	2.68
WO_4''	1.37 + 0.74 + 1.4 = 3.51	2.80

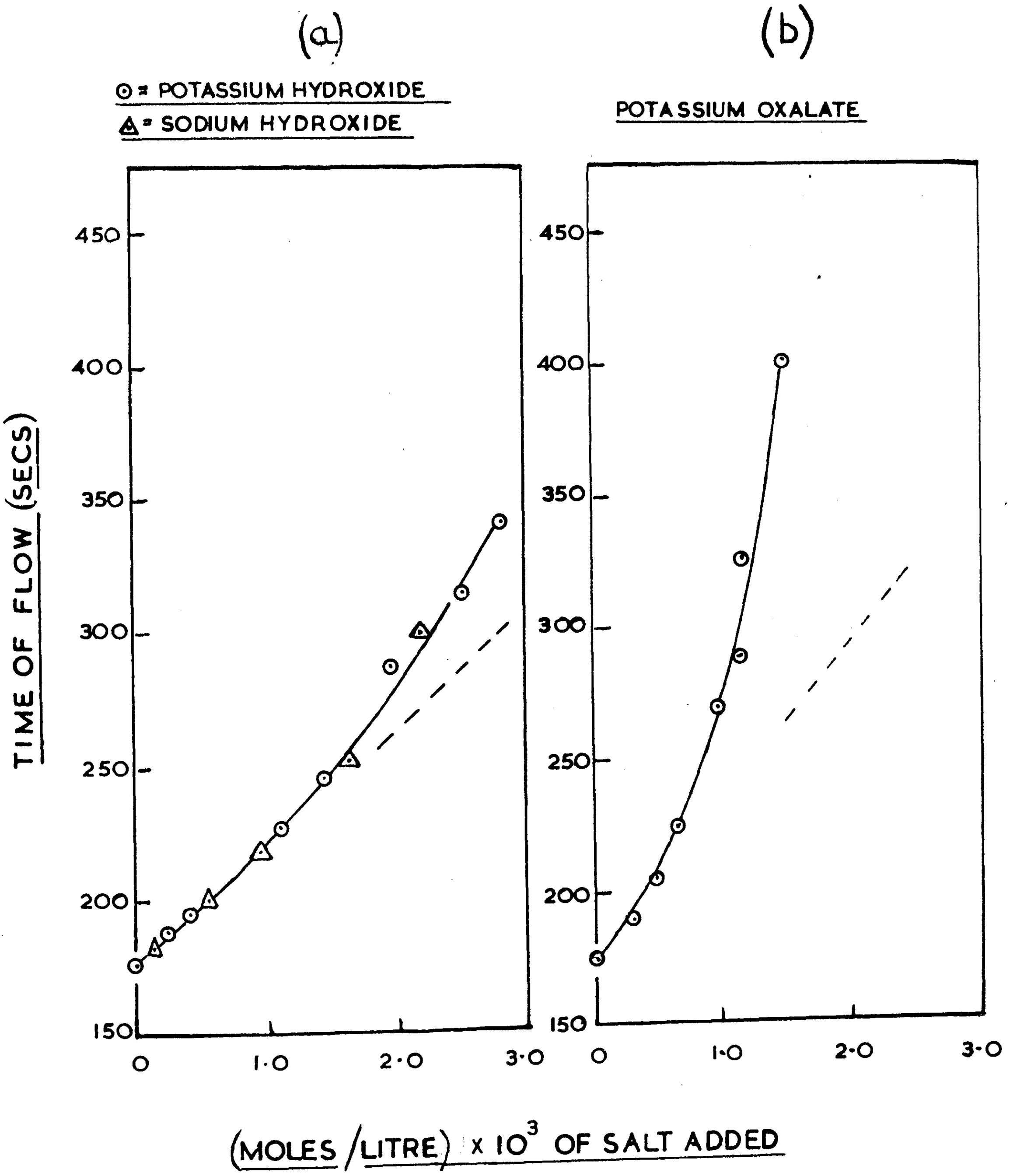
Correlation of the "GRADIENT" of the Anions (contd.)

In figure 81 (the plot of "GRADIENT" vs. cube of the "effective" radius of the anions) it can be seen that the anions lie on two straight lines with those anions having radius = 2.16 Å or less lying on the first straight line while those anions, with the exception of the bromate anion, which have a greater radius lie on the second straight line.

As shown in figure 82 (a), the variation in the time of flow of a 1% C.T.A.B. + 0.5% phenol system with small additions

··FIG 82··

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF ELECTROLYTE ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C T A B +0·5% PHENOL SYSTEM



of potassium hydroxide and of sodium hydroxide was found in each case to be very similar and it appeared that sodium hydroxide and potassium hydroxide gave the same "GRADIENT". This confirmed the previous suggestion that the "GRADIENT" was a characteristic of the added anion.

Now the "GRADIENT" produced by the addition of sodium hydroxide or potassium hydroxide i.e. the "GRADIENT" produced by the hydroxide anion, when plotted, as shown in figure 83, into the correlation obtained in figure 81, was found to correspond to an "effective" radius, R_H, which was greater than the "effective" radius of the hydroxide anion. This suggested that the hydroxide anion interacted with the C.T.A.B. + phenol micelles as though it was a much larger anion.

From figures 82(b) and 80(b) "GRADIENTS" were determined for oxalate and ferrocyanide anions respectively. It was found, as shown in figure 83, using the plot in figure 81 that the "effective" radius of the oxalate anion, R_O, was 2.53 Å and the "effective" radius of the ferrocyanide anion, R_F, was 3.35 Å.

The "effective" radii of the ferrocyanide and of the oxalate anions determined experimentally were examined to see if they agreed with a theoretical estimation of the values of their radii.

To estimate theoretically the "effective" radius of the ferrocyanide ion a value for the radius of the circumscribing sphere, r_F, must be found. From the following expression r_F may be obtained,

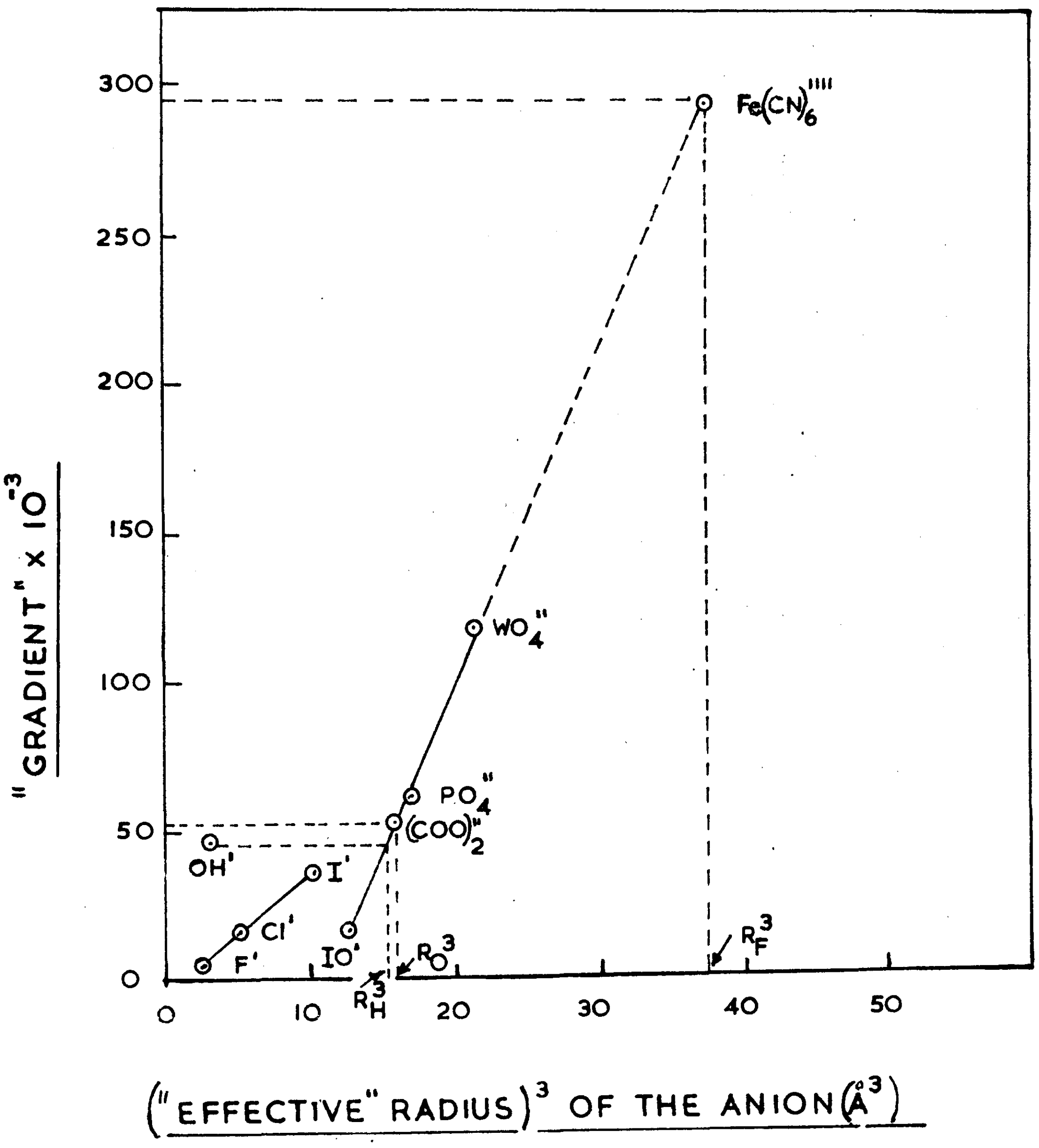
··FIG 83··

USING FIG.81, TO DETERMINE THE "EFFECTIVE" RADII OF:-

(1) HYDROXIDE ANION ····· R_H

(2) OXALATE ANION ········ R_O

(3) FERROCYANIDE ANION ···· R_F



i.e. r_F = sum of covalent radii of Fe atom and of C atom + radius of the cyanide ion.

i.e. $r_F = 1.23 + 0.77 + 1.92 = 3.92$.

Now, the "effective" radius of the ferrocyanide ion, R_F, may be found from

$$\frac{R_F}{r_F} = \text{a constant, } k_F, \text{ - - - - - - (a)}$$

where k_F depends on the type of anion. Since the value of k_F is unknown no accurate "effective" radius for the ferrocyanide can be obtained but as the ferrocyanide anion resembles a sphere to a greater extent than the tetrahedral anions, k_F probably has a value in the range of 0.79 - 1.0.

Now, if the experimentally determined value for the "effective" radius of the ferrocyanide anion is substituted in equation (a) then k_F has a value which is in the range 0.79 - 1.0. Thus, it may be concluded that R_F is in satisfactory agreement with the estimated value of the "effective" radius of the ferrocyanide ion.

Also, it was found that the "effective" radius of the oxalate anion, R_O, determined experimentally was similar to the radius obtained by measuring a scale model of the oxalate anion.

Potassium phosphotungstate was added to 1% C.T.A.B. + 0.5% phenol system but its solubility was so low that no accurate "GRADIENT" could be determined. However, the measurements showed that the "GRADIENT" appeared to be very large and therefore revealed that as would be anticipated the phosphotungstate anion possessed a very large "effective" radius.

Effect on the Time of Flow of Small Additions of Sodium Salts of Aliphatic Acids to a 1% C.T.A.B. + 0.5% Phenol System.

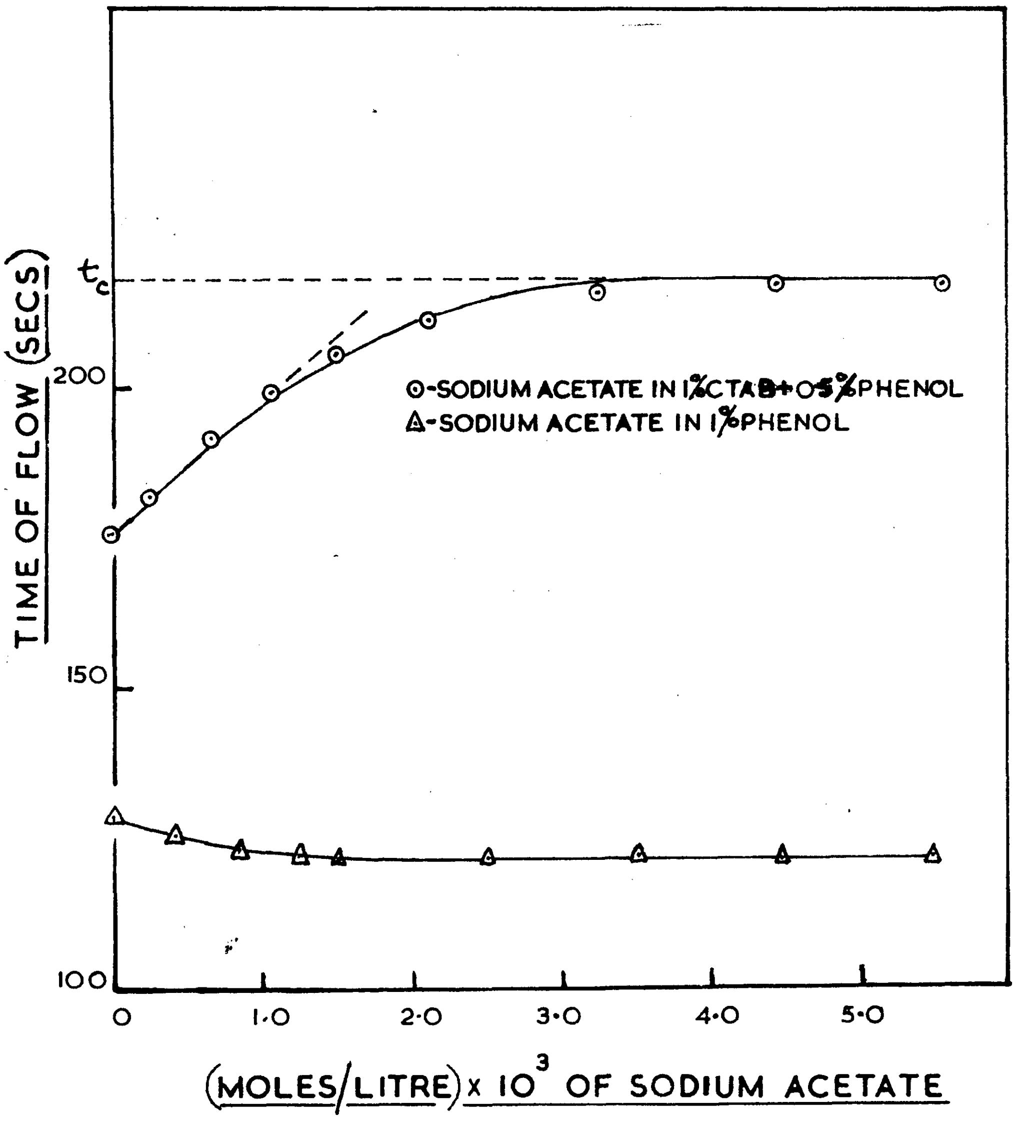
Having discovered that the "GRADIENT" produced by the addition of inorganic electrolytes was a function of the size of the added anion, it was thought necessary to determine whether the addition of the salts of organic acids to 1% C.T.A.B. + 0.5% phenol would also produce a "GRADIENT" which agreed with this relationship.

The variations in the time of flow through viscometer B, caused by small additions of sodium acetate to 1% C.T.A.B. and to 1% C.T.A.B. + 0.5% phenol, were studied and the plots obtained are shown in figure 84. It can be seen that, while the initial additions of sodium acetate to 1% C.T.A.B. caused a decrease in time of flow, the initial additions to 1% C.T.A.B. + 0.5% phenol brought about an increase. Although these initial additions of sodium acetate to a 1% C.T.A.B. + 0.5% phenol system produced an increase in the time of flow, it was found that further small additions caused the rate of increase to be less rapid and eventually the time of flow reached an apparently "constant" value. This "constant" time of flow, t_c, was measured.

Therefore, it appears that the effect on the time of flow of small additions of sodium acetate to a 1% C.T.A.B. + 0.5% phenol system is different in form from the effect produced by the inorganic electrolyte.

FIG 84

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF CH_3CO_2Na ON THE TIME OF FLOW THROUGH VISCOMETER "B"



Thus it was decided to investigate the effect of small additions of other sodium salts of aliphatic acids and the following sodium salts were used, formate, propionate, n-butyrate and i-butyrate. Their plots of time of flow against concentration of salt added are shown in figures 85, 86, 87 and 88 respectively.

It was found that the plots produced by small addition of these salts were of similar shape to that obtained on adding sodium acetate, i.e. with addition of salt the time of flow initially increased and reached, with further small additions, an almost constant value, t_c.

The "GRADIENTS" of these various salts were determined and their values are shown in table 16.

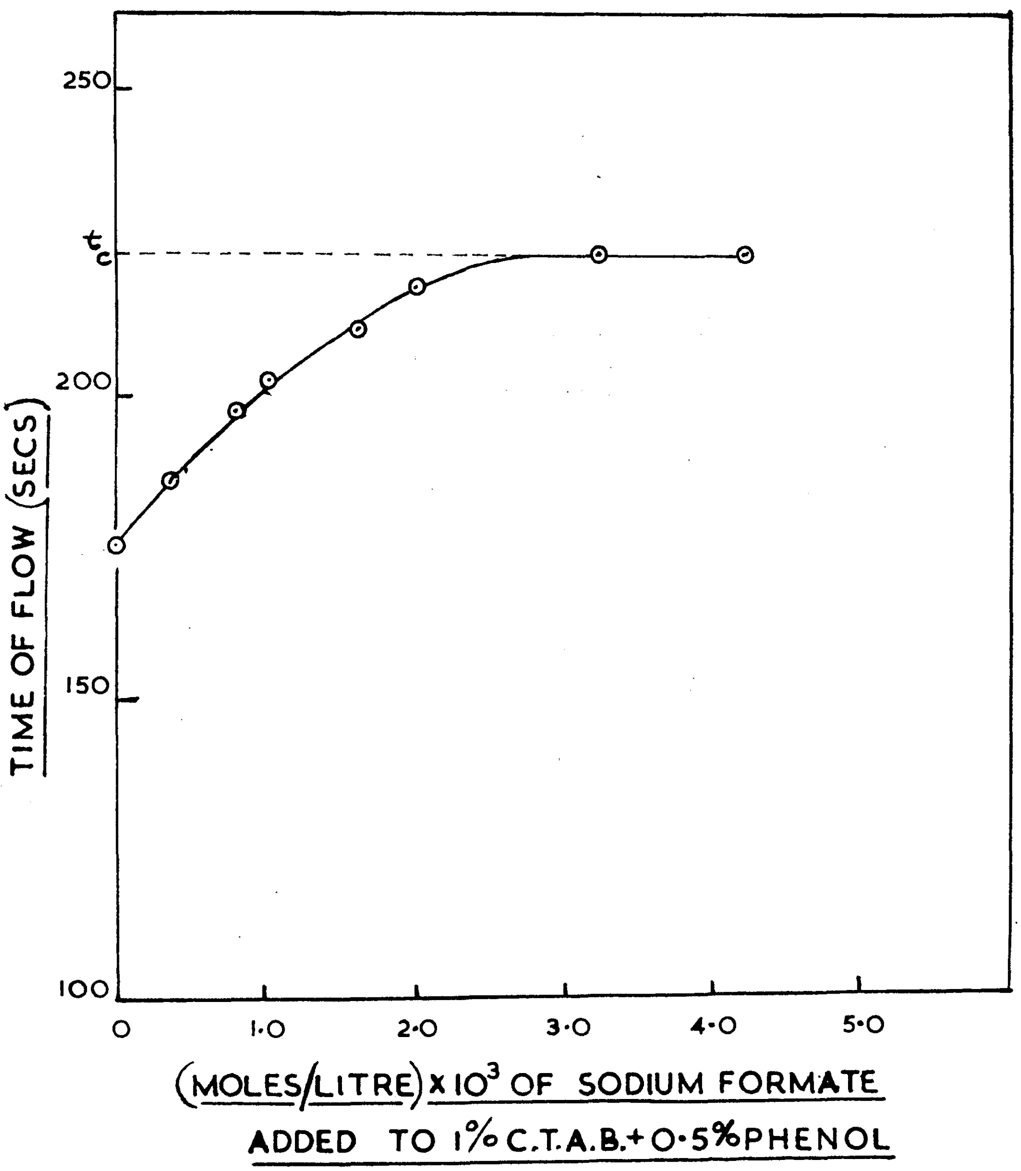
TABLE 16

ANION	$\left[\frac{\text{"GRADIENT"}}{\text{(Secs/Moles/Litre)}}\right] \times 10^{-3}$
FORMATE	26.0
ACETATE	25.5
PROPIONATE	25.0
n-BUTYRATE	24.0
i-BUTYRATE	23.5

It is shown, in this table, that the increase in the size of the hydrophobic group in these aliphatic anions and consequently the size of the anion, does not affect the value of the "GRADIENT" to any great extent. Therefore, it appears

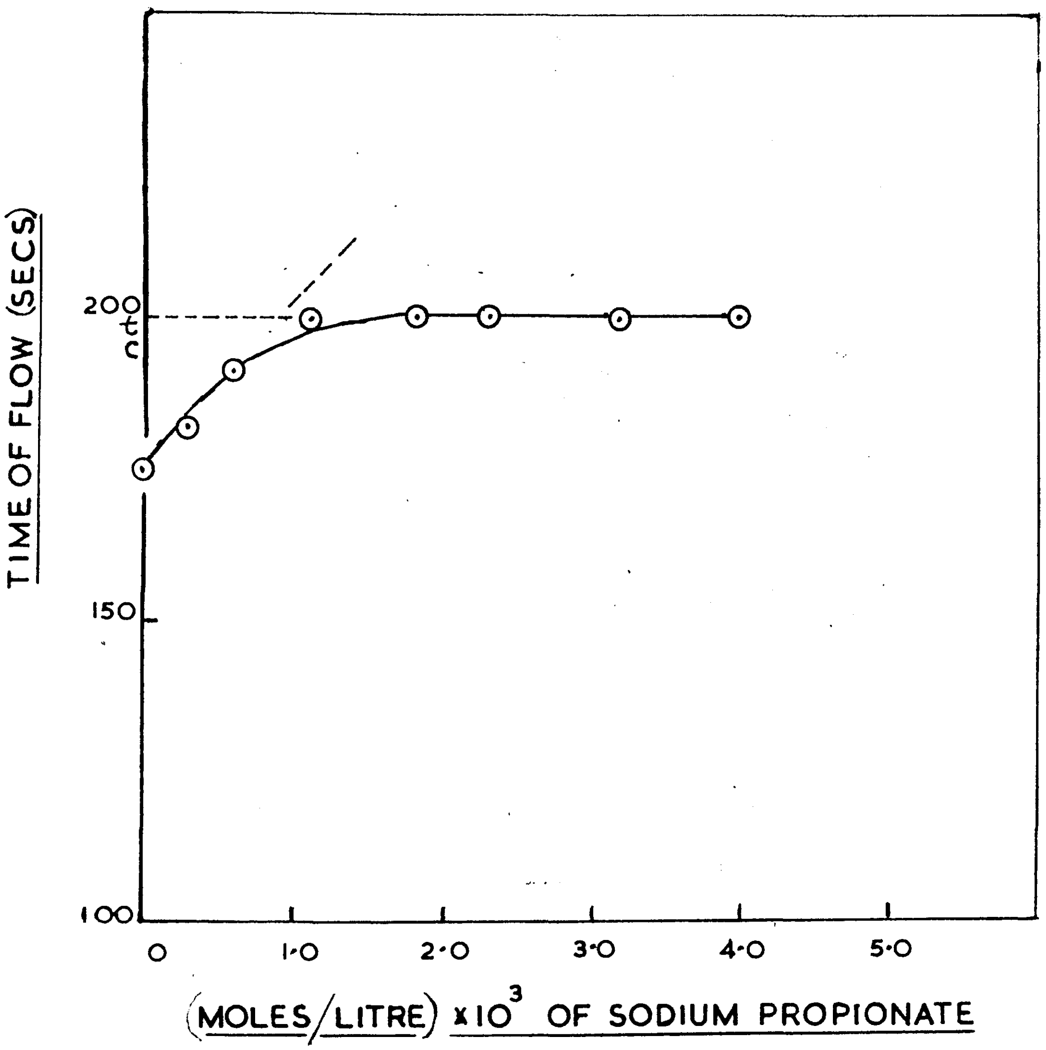
··FIG 85··

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF HCO_2Na ON TIME OF FLOW THROUGH VISCOMETER "B" OF A 1% C.T.A.B.+ 0·5% PHENOL SYSTEM



· · FIG 86 · ·

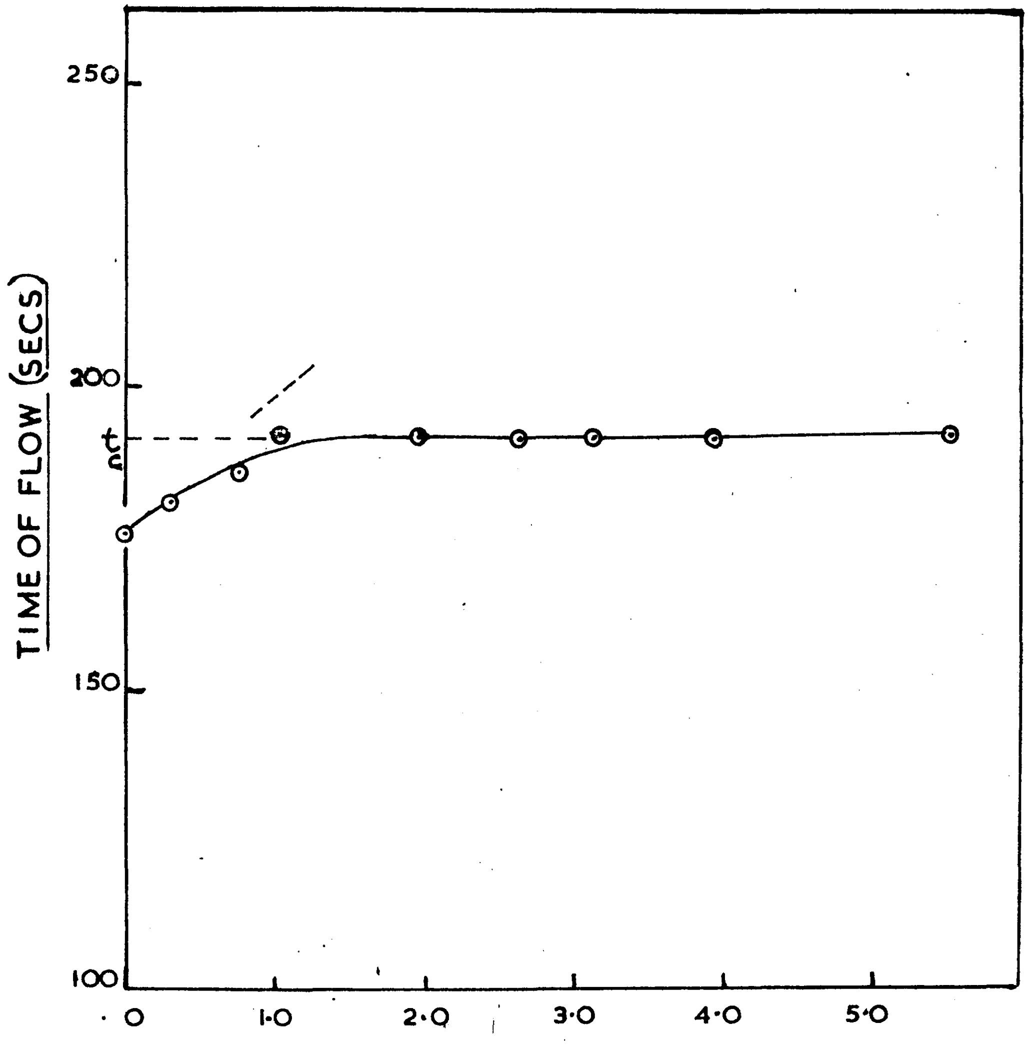
EFFECT OF THE ADDITION OF SMALL AMOUNTS OF $C_2H_5CO_2Na$ ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF A 1% C.T.A.B + 0·5% PHENOL SYSTEM



(MOLES/LITRE) $\times 10^3$ OF SODIUM PROPIONATE ADDED TO 1% C.T.A.B.+ 0·5% PHENOL

FIG 87

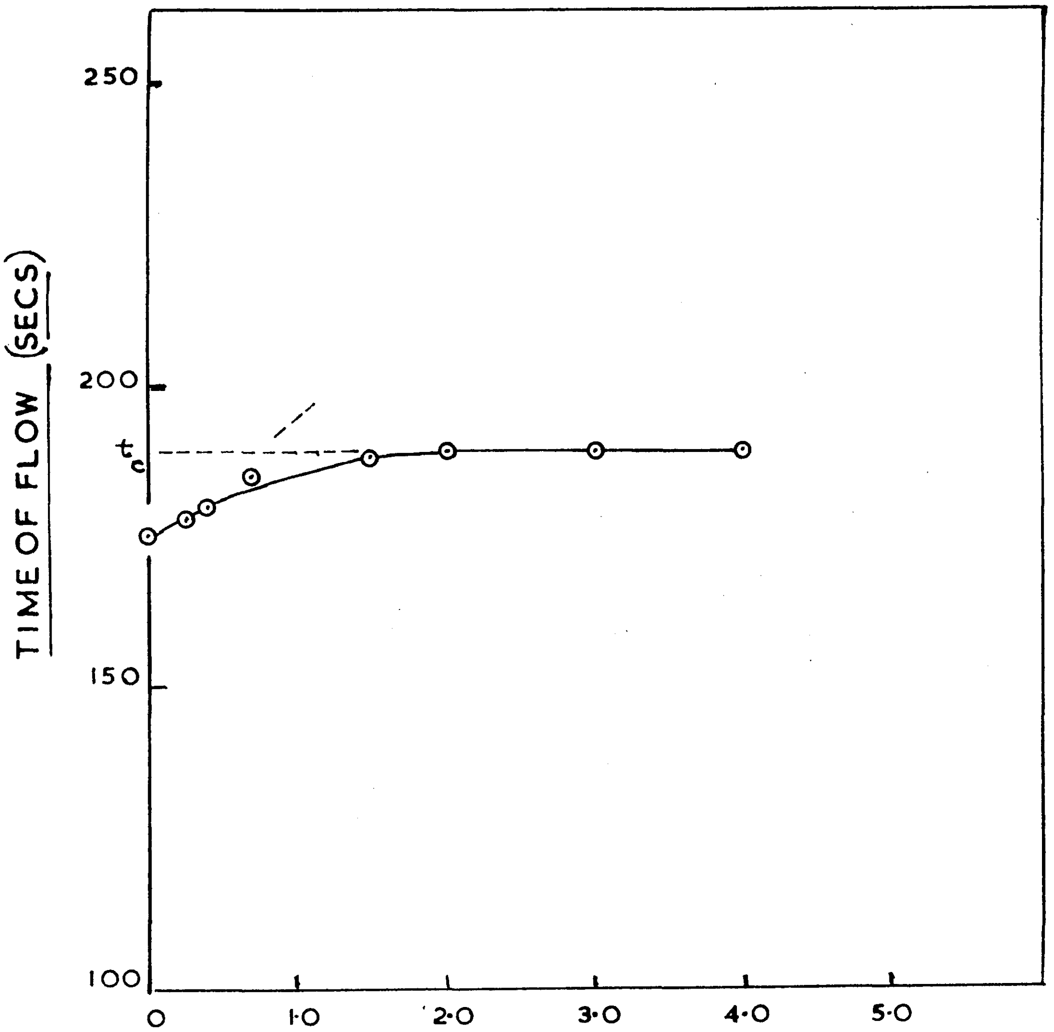
EFFECT OF THE ADDITION OF SMALL AMOUNTS OF $\eta - C_3H_7CO_2Na$ ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C.T.A.B. + 0·5% PHENOL SYSTEM



(MOLES/LITRE) x 10^3 OF SODIUM n-BUTYRATE ADDED TO 1% C.T.A.B. + 0·5% PHENOL

FIG 88

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF i-$C_3H_7CO_2Na$ ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C.T.A.B. + 0.5% PHENOL SYSTEM



(MOLES/LITRE) x 10^3 OF SODIUM i-BUTYRATE ADDED TO 1% C.T.A.B.+ 0·5% PHENOL that the "GRADIENTS" produced by the salts of aliphatic acids are not a function of the size of the anions.

It was noted that the "constant" time of flow, t_c, was different for each salt. The t_c value for each salt was determined and plotted against the number of carbon atoms in each respective salt. This plot is shown in figure 89.

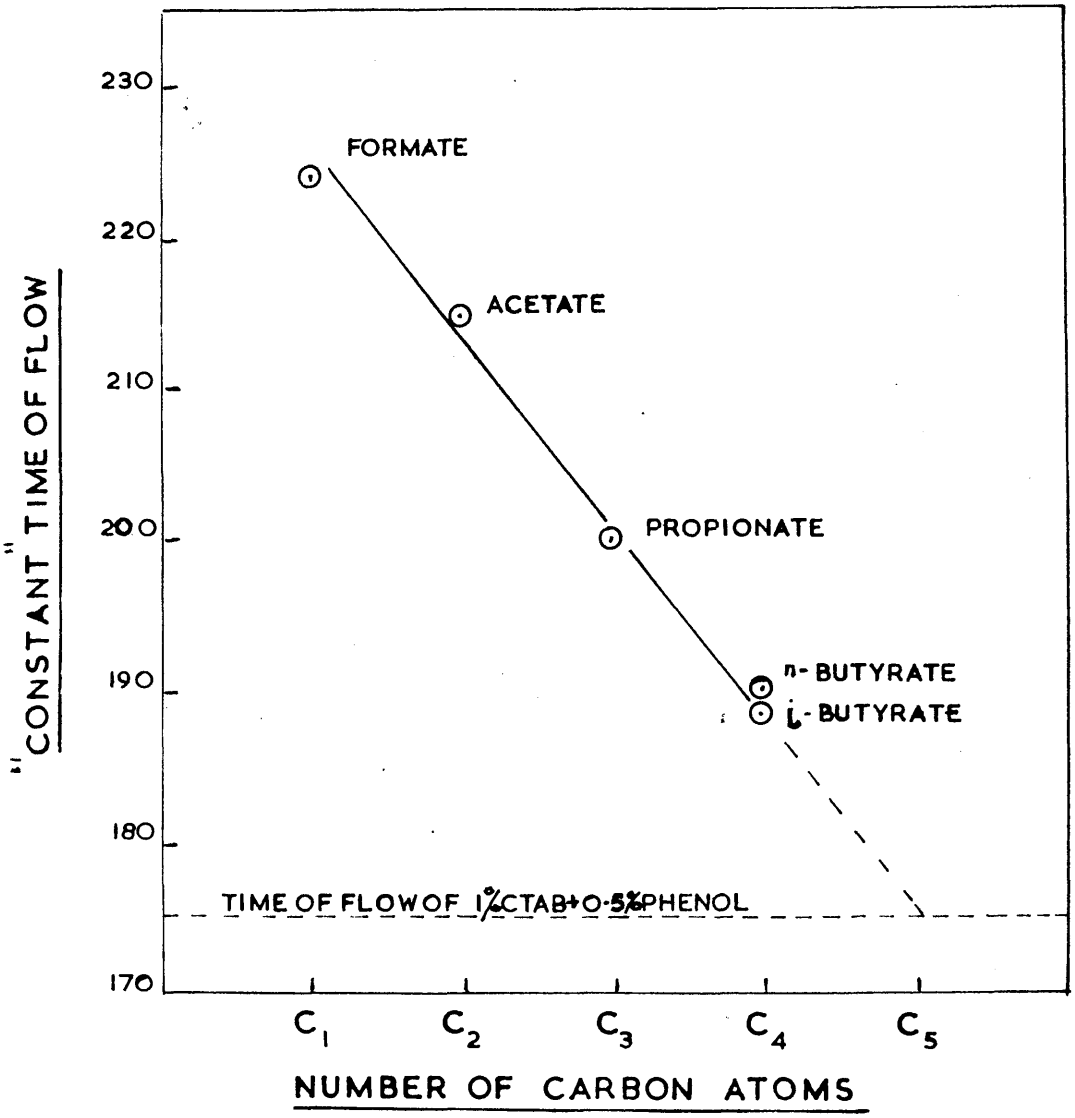
It can be seen that the t_c value decreases linearly with increase in the number of carbon atoms. If this linear plot, in figure 89, is extrapolated, it shows that the t_c value for an aliphatic anion containing five carbon atoms is equal to the time of flow of a 1% C.T.A.B. + 0.5% phenol system. This suggests that an aliphatic salt containing six or more carbon atoms would produce a different effect from the salts which have fewer than five carbon atoms.

Consequently, an investigation into the variation in the time of flow of a 1% C.T.A.B. + 0.5% phenol system produced by small additions of sodium hexoate and of sodium octoate was carried out and the results for each salt are plotted in figure 90.

It was found, as was suggested by figure 89, that the effect of sodium hexoate and of sodium octoate on the time of flow of a 1% C.T.A.B. + 0.5% phenol system was different from that produced by the salts of aliphatic acids containing fewer than five carbon atoms, because the rate of increase in time of flow increased with increase in concentration of salt added

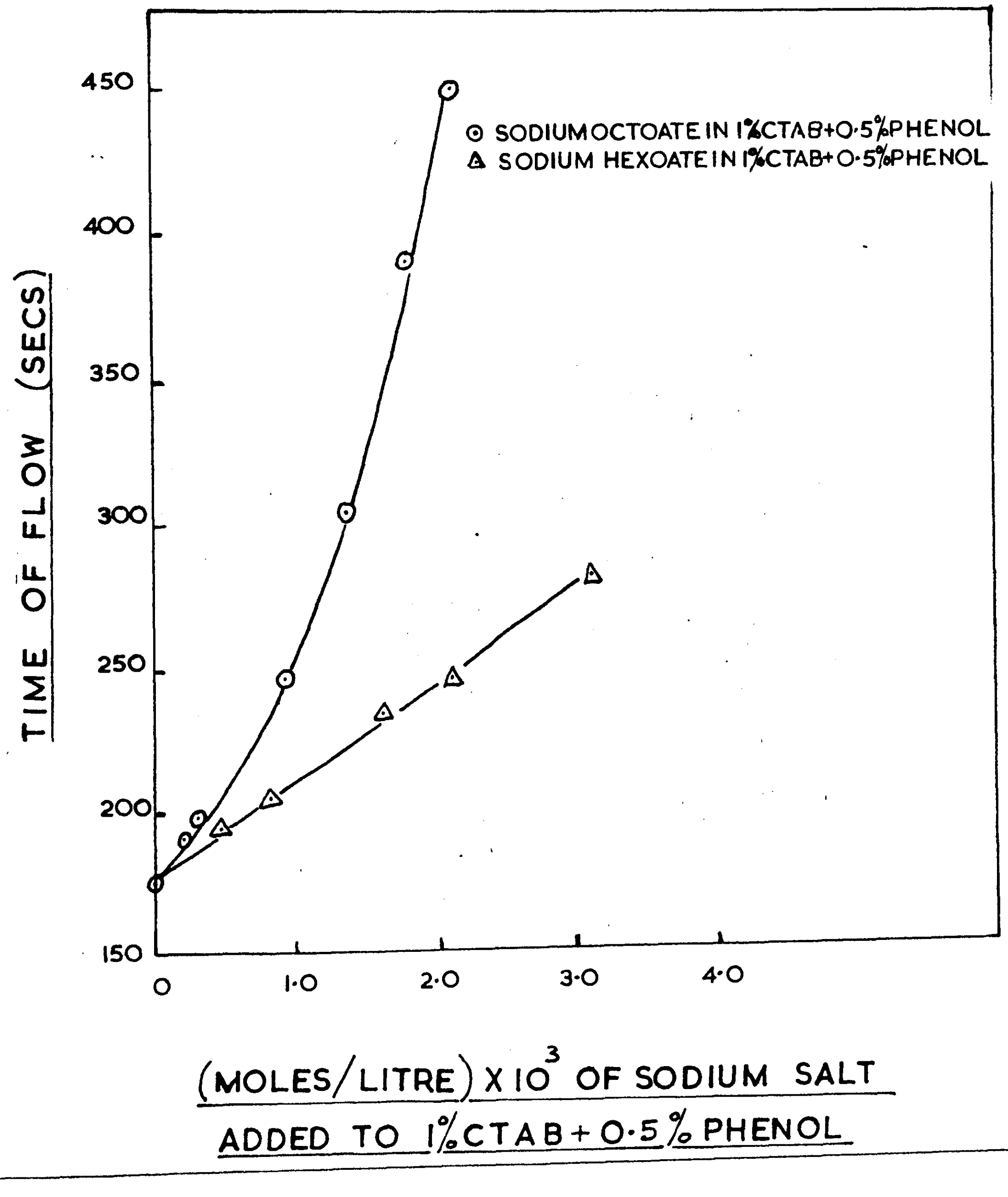
·· FIG 89 ··

VARIATION OF THE "CONSTANT" TIME OF FLOW (t_c) FOR THE SODIUM SALTS OF ALIPHATIC ACIDS WITH THEIR NUMBER OF CARBON ATOMS



··FIG 90··

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF SODIUM SALTS OF ALIPHATIC ACIDS ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% CTAB + 0·5% PHENOL SYSTEM



(i.e. d^2t/dc^2 is POSITIVE). In fact, the shape of the curve was similar to that produced by the inorganic anions as shown in figures 73-80.

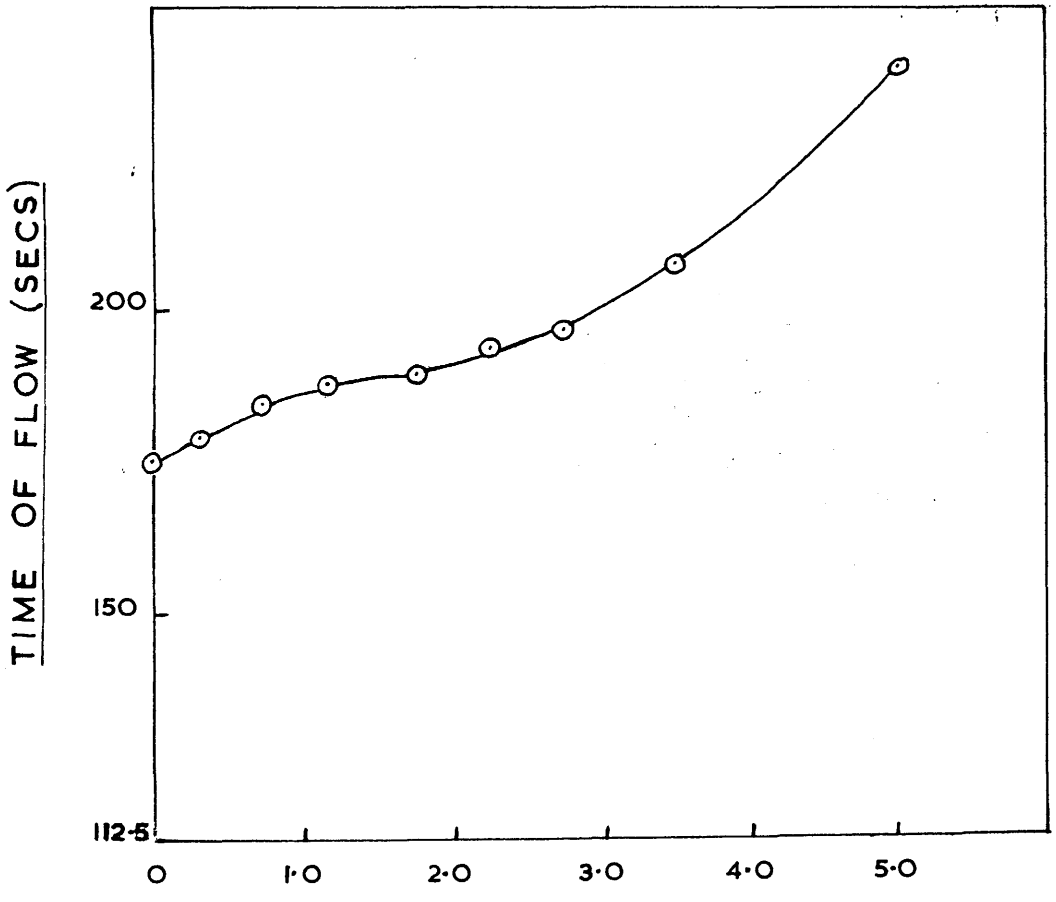
Thus, it has been observed that the effect on the time of flow of a 1% C.T.A.B. + 0.5% phenol system produced by small additions of sodium salts of aliphatic acids is dependent on whether the salt contains fewer or more than five carbon atoms. Therefore, it would be interesting to observe the effect produced by a sodium salt formed from an aliphatic acid containing exactly five carbon atoms and so sodium valerate was added to a 1% C.T.A.B. + 0.5% phenol system and its effect on the time of flow determined. A plot of time of flow against concentration of sodium valerate is shown in figure 91.

This curve shows features characteristic of those curves produced by both sodium salts of aliphatic acids containing fewer or more than five carbon atoms. The shape suggests that sodium valerate interacts with a 1% C.T.A.B. + 0.5% phenol system partly as a sodium salt of an aliphatic acid having fewer than five carbon atoms and partly as a sodium salt of an aliphatic acid having more than five carbon atoms.

Now, since it appears that the effect on the time of flow of a system of 1% C.T.A.B. + 0.5% phenol of small additions of an aliphatic acid salt depends on the number of carbon atoms in the hydrocarbon group or chain, it was decided to determine if at higher concentration of additive the length

·· FIG 91 ··

EFFECT OF THE ADDITION OF SMALL AMOUNTS OF n-$C_4H_9O_2Na$ ON THE TIME OF FLOW THROUGH VISCOMETER "B" OF 1% C.T.A.B. + 0·5% PHENOL SYSTEM



(MOLES/LITRE) X 10^3 OF SODIUM n-VALERATE ADDED TO 1% C.T.A.B. + 0·5% PHENOL of hydrocarbon chain or group still influenced the time of flow. In order to settle this point, larger amounts of sodium octoate and of sodium acetate were each added to 1% C.T.A.B. + 0.5% phenol systems and the times of flow, at various concentrations of added salt, were measured in viscometer A. The plots of time of flow against concentration of salt added are shown in figures 92 and 93.

It can be seen that the plots differ considerably. The addition of sodium octoate caused the time of flow to increase to 800 seconds at which point a phase change sets in at a concentration of 0.9×10^{-2} moles/litre. The addition of sodium acetate caused only a gradual increase in the time of flow and at a concentration of 1.1 moles/litre there is a broad maximum which has a time of flow of 152 seconds. Addition of more sodium acetate caused the time of flow to decrease until, at a concentration of 2.0 moles/litre, there is a phase separation.

It was noted that the phase change, caused by the addition of sodium octoate to 1% C.T.A.B. + 0.5% phenol, was the formation of a white curdy liquid which, on standing, showed no sign of separation while the phase change caused by the addition of sodium acetate was a separation of two phases which, when allowed to settle, produced two distinct liquid layers. These features appear to confirm the view that sodium acetate (i.e. a sodium salt of an aliphatic acid having fewer than five

··FIG 92··

EFFECT OF THE ADDITION OF $C_7H_{15}CO_2Na$ ON THE TIME OF FLOW THROUGH VISCOMETER "A"

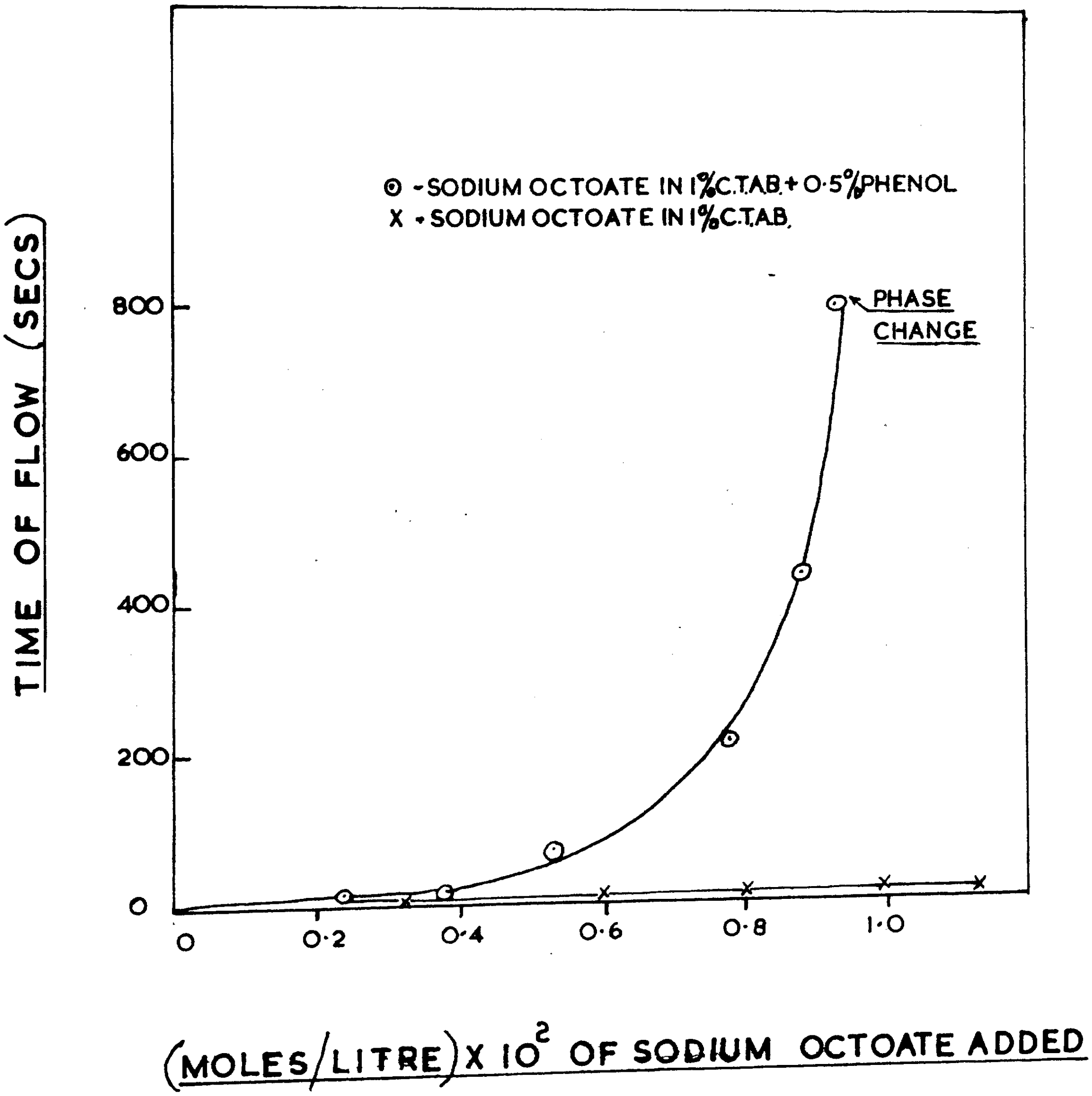
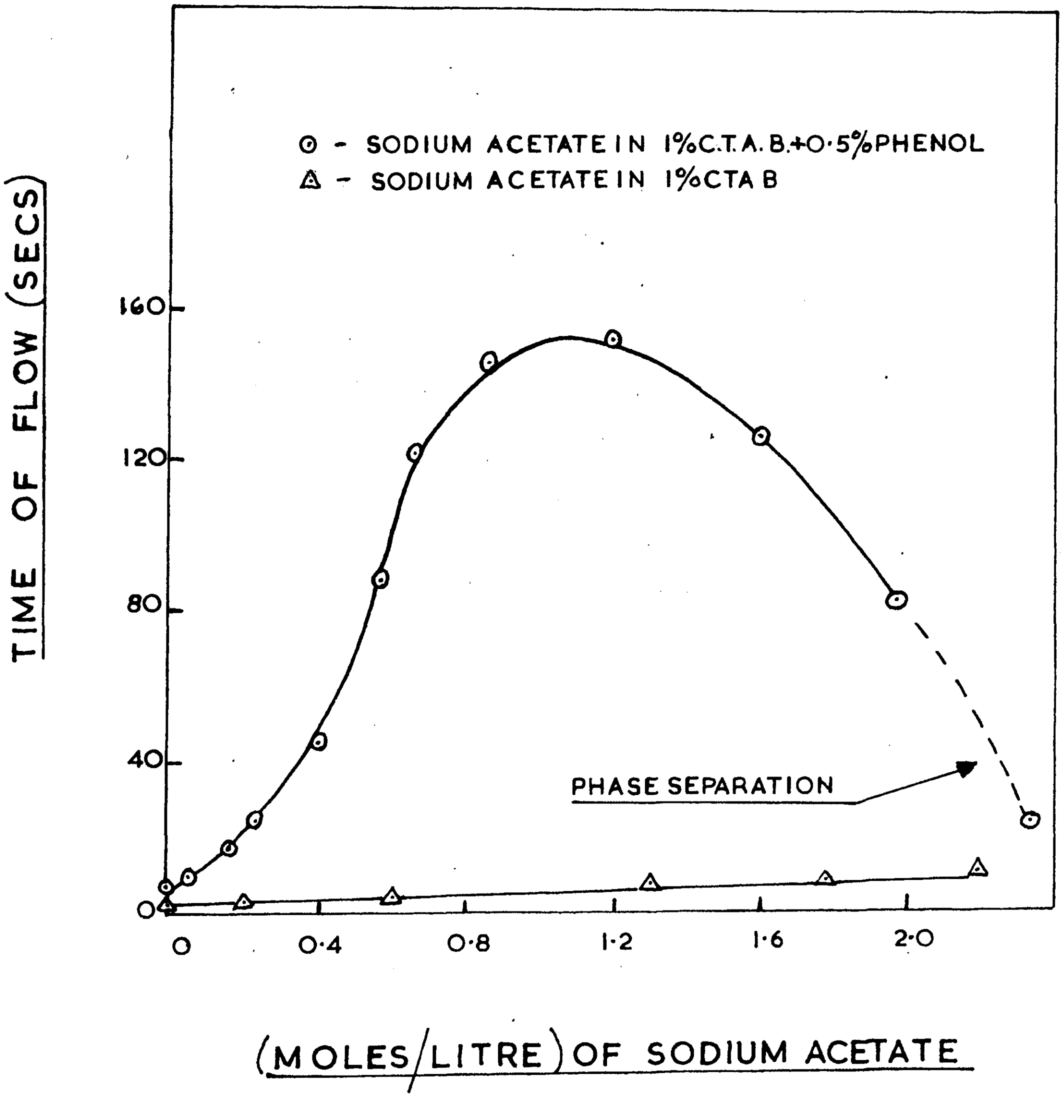


FIG 93

EFFECT OF THE ADDITION OF CH_3CO_2Na ON THE TIME OF FLOW THROUGH VISCOMETER 'A'



carbon atoms) has a different interaction with a 1% C.T.A.B. + 0.5% phenol system than sodium octoate (i.e. a salt of an aliphatic acid having more than five carbon atoms).

Thus, having established that sodium octoate and sodium acetate each behaved differently when added to a 1% C.T.A.B. + 0.5% phenol system, it seemed necessary to investigate if the addition of these salts to a 1% C.T.A.B. system would each produce a different effect on its time of flow. Subsequently, this investigation was carried out and the plots of time of flow against concentration of sodium salt are shown in figures 92 and 93 respectively. It is clear that the effect produced by the addition of sodium acetate is very similar to that produced by the addition of sodium octoate.

Therefore, it may be concluded that, since sodium acetate and sodium octoate each produce a different effect on the time of flow of a 1% C.T.A.B. + 0.5% phenol system but show no difference with a 1% C.T.A.B. system, the difference must be due to the 0. 5% phenol having modified the 1% C.T.A.B. system so that it is in a form whereby it interacts with potassium acetate by a different process from potassium octoate.

Discussion.

The shape of the curves of time of flow against concentration of electrolyte added, in figures 68-72, indicating initially an increase in viscosity, suggests that as inorganic anions are added to a system of 1% C.T.A.B. + 0.5% phenol large structural aggregates are built up which at a certain electrolyte concentration reach an optimum size. Further addition of electrolyte appears then to bring about changes such that the viscosity of the system decreases and eventually separation of two phases takes place.

It is probable that, on adding electrolyte to the C.T.A.B. + phenol system, the anions so added are attracted to the micelles, which are regions of positive charge, where they cause a decrease in mutual repulsion between ionic heads. This in turn increases the effectiveness of Van der Walls' forces in the attraction of the hydrophobic hydrocarbon chains for each other. Thus, the presence of electrolyte in increasing quantity tends gradually to promote further association or aggregation of micelles. Consequently, these micelles which are considered to be lamellar, or nearly so, in an environment of electrolyte and water form yet larger and more ordered lamellar structures incorporating more and more water. When the electrolyte reaches a certain concentration some of the bound water will begin to be extracted, by a kind of osmosis, leaving structures which become less and less soluble and then a phase separation (called by some authors "co-acervation") sets in. This phase appears to be liquid crystalline in character as it shows strong birefringence (133). The existence of flow birefringence in the solutions is regarded as evidence that the addition of electrolyte causes geometrically organised micellar aggregates to be built up.

Thus, it is suggested that, the general effect of the addition of inorganic ions on these C.T.A.B. + phenol micellar systems is to reduce the tendency for the 'heads' of the $\overline{C}$ layer to disperse into the $\overline{W}$ region with the result that $A_{\overline{c}\,\overline{w}}$ decreases and therefore Winsor's ratio, R, is increased. This means that the intermicellar equilibrium is displaced to the right, causing more S_1 micelles to be transformed into an extensive G phase which is eventually precipitated.

From this work, it appears that it is only the inorganic anions of the electrolyte which have a pronounced effect on the viscous properties of the C.T.A.B. + phenol systems and that each anion has a characteristic effect. Figures 81 and 83 in which the "GRADIENT" is plotted against the cube of the effective radius of the anion, show that the increase in viscous properties caused by the addition of electrolyte is a function of the size of the anion added. This supports the view that the anions are incorporated into the micellar structure.

It can be seen that the plot of "GRADIENT" against cube of the effective radius of the anion is in the form of two straight lines. All anions which have a radius equal to approximately 2.15 Å or less lie on the first straight line, while those with a greater radius lie on the second straight line.

It seems probable that the added anion must be attracted to the positive charge on the micellar surface. Therefore, as the threadlike micelles of C.T.A.B. + phenol pack together, possibly on top of one another, like a pack of cards, the anions would orientate themselves within the double layer so that they are situated near the environment of positive charge produced by the C.T.A. cation and the positive end of the oxygen dipole in the phenol molecule. A diagram of the probable structure of the micellar aggregate built up by the addition of inorganic anions to 1% C.T.A.B. + 0.5% phenol system is shown in figure 94. (the actual structure, will of course be far from as rigid, or as regular, as the diagram suggests).

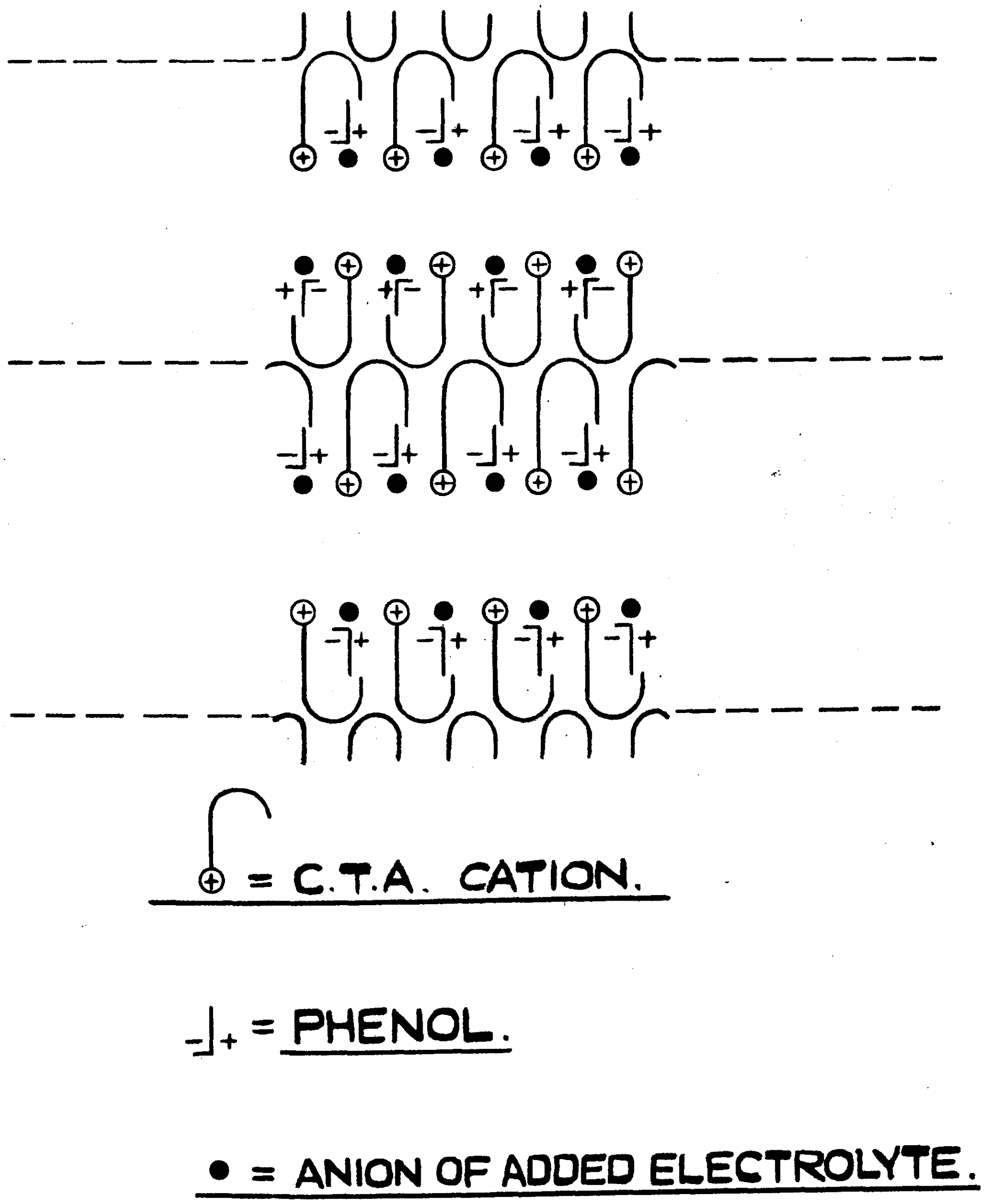
The presence of anions in such a structure as portrayed in figure 94 will have two effects:-

(1) To reduce the electrical repulsion between the ionic heads of the C.T.A.B. + phenol micelles and thereby cause the formation of very extensive lamellar structures (i.e. the micelles link two-dimensionally together to form large structures).

(2) To reduce the electrical repulsion between the micellar lamellar leaflets and thereby enable the leaflets to

··FIG. 94··

PROBABLE MICELLAR CONFIGURATION IN SYSTEMS OF 1% C.T.A.B. + 0.5% PHENOL + INORGANIC ELECTROLYTE.



pack on top of one another to form large three-dimensional aggregates.

This second effect will tend to cause the phenol molecules in neighbouring micellar leaflets, to pack together as close as possible. Now Pierce (134) has shown that the closest distance which aromatic nucleii may pack together in liquid media was approximately 4.3 Å. Thus, any inorganic anion which has an effective radius of approximately 2.15 Å, e.g. 2.16 Å, or less will cause micellar structures to pack together into the most ordered and compact micellar arrangement, but any anion of greater radius would be unable, owing to its size, to allow the phenol molecules to take up their most compact and ordered arrangement. A diagramatic representation of this variation is shown in figure 95.

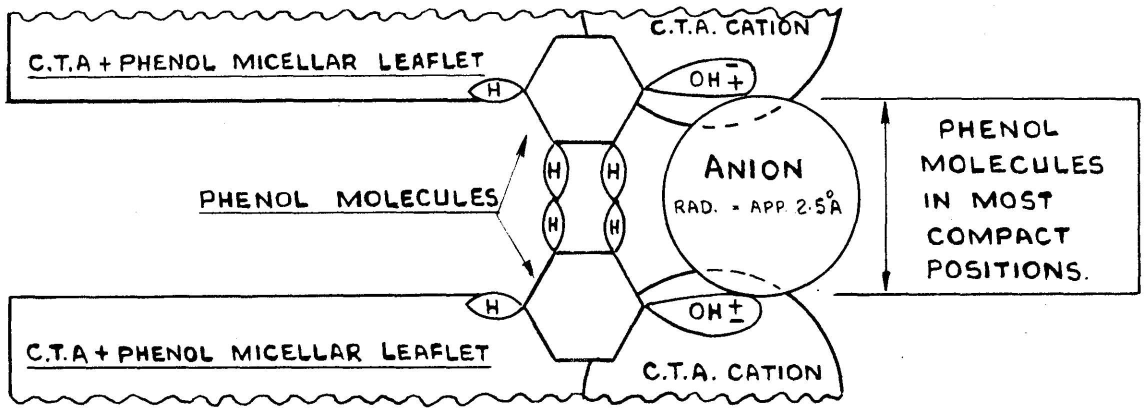
Thus it seems probable that inorganic anions which enable the C.T.A. + phenol micellar leaflets to form their most compact structure produce "GRADIENTS" which can be equated with the first straight line in figure 81, while other inorganic anions produce "GRADIENTS" which can be equated with the second straight line.

The radius of the bromate anion (2.19 Å) is almost coincident with the anionic radius at which this break in the curve of "GRADIENT" against the cube of the effective radius of the anion takes place. Thus, it seems probable that some of the bromate anions behave like anions which produce compact three-dimensional micellar structures with C.T.A.B. + phenol

FIG. 95

POSSIBLE MICELLAR 3-DIMENSIONAL STRUCTURES OF C.T.A.B.+ PHENOL MICELLAR LEAFLETS PRODUCED BY THE ADDITION OF ANIONS.

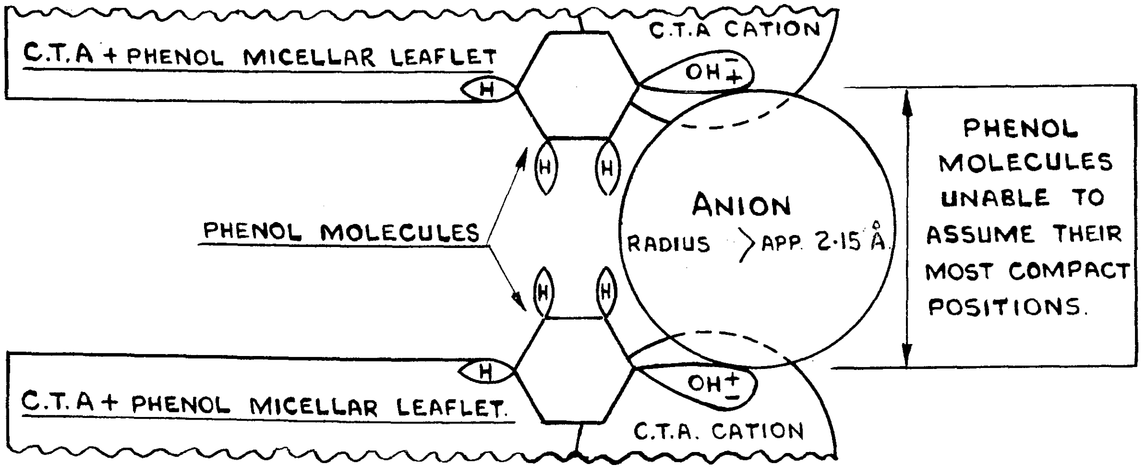
(1) MICELLAR AGGREGATION PRODUCED BY ANIONS OF RADIUS = 2·15 Å OR LESS.



THIS SIZE OF ANION ENABLES THE PHENOL MOLECULES TO ASSUME THEIR MOST COMPACT POSITIONS.

ANIONS OF RADIUS < APP. 2·15 Å. ALSO WILL ALLOW PHENOL MOLECULES TO ASSUME THESE COMPACT POSITIONS.

(2) MICELLAR AGGREGATION PRODUCED BY ANIONS OF RADIUS > 2·15 Å



THIS LARGER SIZE OF ANION DOES NOT ENABLE THE PHENOL MOLECULES TO ASSUME THEIR MOST COMPACT POSITIONS.

while other bromate anions do not. Therefore, for this reason the addition of the bromate anion produced a "GRADIENT" as shown in figure 81 which lies between the linear plots.

Also, it can be seen in figure 83 that, when sodium hydroxide or potassium hydroxide is added to 1% C.T.A.B. + 0.5% phenol system, the "GRADIENT" obtained appears to be too large to be a function of the size of the hydroxide anion but corresponds to a large anion of radius, $R_H = 2.47$ Å. It is possible that this large radius may be produced by the added hydroxide anion causing hydrogen bonding interactions within the micellar arrangement. On the other hand, since hydroxide anions are capable of interacting with the phenol molecules to produce phenoxide anions, it may well be that it is the interaction between phenoxide anions and the C.T.A.B. + phenol micelles which is responsible for the increase in viscous properties.

It seems probable, since the "GRADIENTS" produced by the oxalate and ferrocyanide anions are a function of their approximate radii that measurements of "GRADIENTS" may well be able to give useful information about the sizes of anions whose effective radii are unknown.

The effect on the viscous properties of C.T.A.B. + phenol systems of the addition of anions of salts of aliphatic acids appears not to be a direct function of the size of the anion although it seems to be dependent on the length of the hydrocarbon chain in the anion.

It can be seen in figures 84 to 88 that anions formed from aliphatic acids with fewer than five carbon atoms behave initially like the inorganic anions but, with further increase in their concentration, the time of flow did not increase as rapidly as in the case of inorganic anions. On the other hand, as is shown in figure 90, the addition of anions from aliphatic acids, containing more than five carbon atoms, caused the time of flow to increase rapidly with no tendency for this rate of increase to diminish.

It seems probable that these anions formed from aliphatic acids would orientate themselves near the micellar surface so that their carboxylate groups would be situated in the double layer in a similar position to that suggested for the inorganic anions. Therefore, the aliphatic anions would be so positioned that their hydrocarbon chains, or hydrophobic groups hinder the interplay of the electrical units within the double layer causing a reduction in the tendency for the micellar aggregates to form larger and more ordered micellar arrangements. If the hydrophobic group in the aliphatic anion is increased, then the energy considerations of the system may require it to be removed from the aqueous or $\overline{W}$ region with the result that the anion orientates itself so that this hydrophobic group is solubilised in the micelle, leaving the ionic region of the anion on the surface of the micelle.

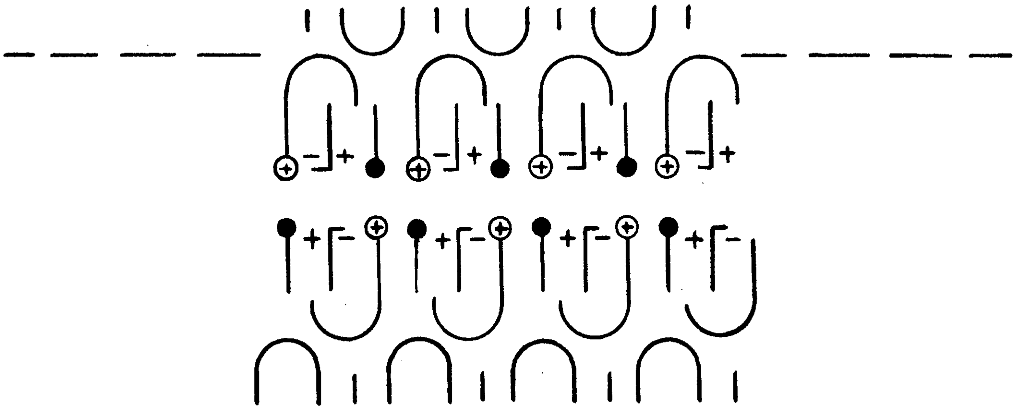
A probable explanation of the experimental results seems to be that, if the hydrocarbon chain contains five or more carbon atoms its hydrophobic nature is such that it cannot exist readily in the aqueous region and consequently the hydrophobic group penetrates into the C.T.A.B. + phenol micelle. The carboxylate group remains on the micellar surface so that it is able to promote micellar interactions which are similar to those produced by the inorganic anions. Thus, in this way, the addition of octoate anions to C.T.A.B. + phenol systems may form such a micellar configuration, as shown in figure 96. The addition of anions containing fewer than five carbon atoms to a 1% C.T.A.B. + 0.5% phenol system would therefore not necessarily involve the hydrophobic groups of the added anions being solubilised in the micelles. Consequently, the hydrophobic groups would be present in the micellar double layer where they could reduce the tendency for large micellar structures to be formed. Such a micellar configuration for a 1% C.T.A.B. + 0.5% phenol + sodium acetate system is shown in a very idealised form in figure 96.

It is apparent (see figures 84 to 89) that, as the size of the hydrophobic group in the anion increases, the initial increase in time of flow decreases. This suggests that as the hydrophobic group in the anion increases in size, the greater is the hinderance to the electrical interplay in the double layer and therefore there is a decrease in further micellar aggregation.

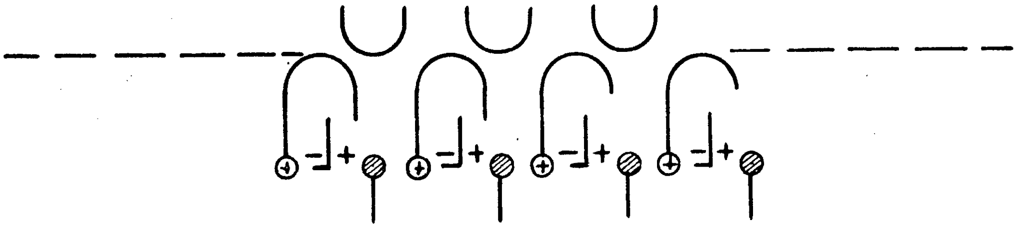
In this way, anions formed from aliphatic acids containing fewer than five carbon atoms form less viscous systems with 1% C.T.A.B. + 0.5% phenol than do those anions with more than five carbon atoms.

··FIG. 96.··

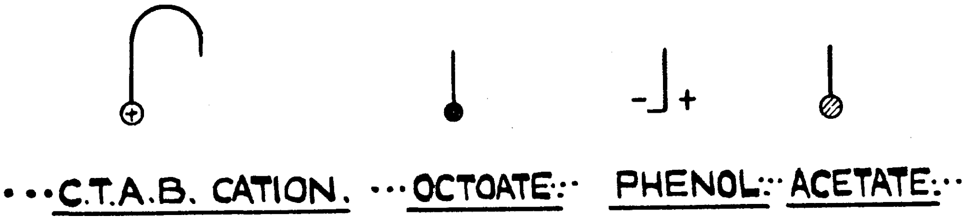
PROBABLE MICELLAR CONFIGURATIONS IN SYSTEMS OF 1% C.T.A.B. + 0·5% PHENOL + SODIUM SALTS OF ALIPHATIC ACIDS.



1% C.T.A.B. + 0·5% PHENOL + SODIUM OCTOATE.



1% C.T.A.B. + 0·5% PHENOL + SODIUM ACETATE.



It is interesting to note that Lawrence (135), while studying changes in viscosity produced by the addition of alcohols and of acids to a 36% Teepol solution, discovered that alcohols and acids which contained more than five carbon atoms formed with this Teepol solution a liquid crystalline phase.

While the addition of anions to a 1% C.T.A.B. + 0.5% phenol system has a marked effect on the time of flow, their addition to a 1% C.T.A.B. system without phenol, see figures 73 and 84, has little effect. Therefore, it seems that while the addition of anions causes C.T.A.B. + phenol micelles to aggregate it does not seriously disturb the micellar arrangement of the C.T.A.B. micelles containing no phenolic additive.

Now, it can be visualised, that if the micelles are lamellar or tending to become lamellar, then the addition of anions may easily cause them to pack into large and more ordered aggregates, (as described previously) but if the micelles are spheroidal in form then their shape is such that they would not aggregate easily with the result that the addition of anions would not readily promote the formation of larger structures.

Thus, it appears that the changes in viscosity caused by the addition of electrolytes support the view put forward in the discussion to Part I that the micelles in a 1% C.T.A.B. + 0.5% phenol system are lamellar or tending to become lamellar, while the micelles in a system of 1% C.T.A.B. without phenol are spheroidal.

REFERENCES.

REFERENCES.

1. Hartley, "Aqueous Solutions of Paraffin-Chain Salts", Hermann et Cie, Paris, (1936).
2. Winsor, Trans.Far.Soc. 44, 376 (1948).
3. McBain, Cornish & Bowden, Trans.Chem.Soc. 101, 2042 (1912).
4. McBain & Taylor, Zeit.Physik.Chem. 76, 179 (1912).
5. McBain & Martin, Trans.Chem.Soc. 105, 957 (1914).
6. Laing, Titley & McBain, Trans.Chem.Soc. 115, 1279 (1919).
7. Goldsmidt & Weismann, Koll.Zeit. 12, 18 (1913).
8. Reychler, Bul.Soc.Chim.Belg. 27, 110 217 (1913).
9. McBain & Salmon, J.A.C.S. 42, 426 (1920).
10. Burnbury & Martin, Trans. Chem.Soc. 105, 424 (1914).
11. McBain, Trans.Far.Soc. 9, 99 (1913).
12. Jones & Bury, Phil.Mag. 4, 841 (1927).
13. Grindley & Bury, J.Chem.Soc. 679 (1929).
14. Davis & Bury, J.Chem.Soc. 2263 (1930).
15. Lottermoser & Püschel, Koll.Zeit. 63, 175 (1933).
16. Hartley & Malesch, Zeit.Physik.Chem. 170A, 321 (1934).
17. Wright, Abbott, Sivertz & Tartar, J.A.C.S. 61, 549 (1939).
18. Ralston & Hoerr, J.A.C.S. 64, 772 (1942).
19. Ekwall, Koll.Zeit. 101, 135 (1942).
20. Johnson & McBain, Proc.Roy.Soc. 181, 119 (1943).
21. Bury & Parry, J.Chem.Soc. 626 (1935).

22. Adam & Shute, Trans.Far.Soc. 34, 758 (1938).

23. Wright & Tartar, J.A.C.S. 61, 545 (1939).

24. Hoerr & Ralston, J.A.C.S. 65, 976 (1943).

25. Howell & Robinson, Proc.Roy.Soc. A155, 386 (1936).

26. McBain, "Colloid Science", (Book) Heath & Co., Boston (1950).

27. Moilliet & Collie, "Surface Activity", Sponer & Co., London (1951).

28. Ralston, Ann.N.Y.Acad.Sci. 46, 351 (1946).

29. Tartar & Reed, J.A.C.S. 58, 322 (1936).

30. Hartley, J.A.C.S. 58, 2347 (1936).

31. McBain, "Colloid Science" (Book) London (1925).

32. Hartley, Kolloidzschr 88, 22 (1939).

33. Warren, Phys.Rev. 44, 969 (1933).

34. Hartley, Collie & Samis, Trans.Far.Soc. 32, 795 (1936).

35. Laing, J.Phys.Chem. 28, 673 (1924).

36. Murray & Hartley, Trans.Far.Soc. 31, 183 (1935).

37. McBain, "Colloid Chemistry" (Book) Reinhold Publishing Corp. N.Y. (1944).

38. McDowell & Kraus, J.A.C.S. 73, 2173 (1951).

39. Brown, Grieger & Kraus, J.A.C.S. 69, 1835 (1947).

40. Ralston, Eggenberger & DuBrow, J.A.C.S. 70, 977 (1948).

41. Evvers, Grieger & Kraus, J.A.C.S. 68, 1137 (1946).

42. Ralston & Hoerr, J.A.C.S. 68, 851, 2460 (1946).

43. McBain, "Advances in Colloid Science", Interscience Publishing Inc. N.Y. (1942).

44. Ward, Proc.Roy.Soc. 176A, 412 (1940).

45. McBain, "Frontiers in Colloid Chemistry" (Book) Interscience Publishing Inc. N.Y. (1950).

46. McBain, J.Phys.Chem. 47, 196 (1943).

47. Winsor, "Solvent Properties of Amphilic Compounds", (Book) Butterworths Science Publications (1954).

48. Lawrence, Trans.Far.Soc. 31, 189 (1935).

49. Lawrence, "Discussion on Colloidal Electrolytes", Trans.Far.Soc. (1935).

50. Klevens, 112th Meeting of American Chemical Society N.Y. (1947).

51. Harkins, J.Chem.Phys. 16, 156 (1948).

52. Klevens, Chem.Rev. 47, 1 (1950).

53. Hartley, J.Chem.Soc. 1968 (1938).

54. Krishnamurti, Indian J.Phys. 3, 307 (1929).

55. Hess & Gundermann, Ber. 70B, 1800 (1937).

56. Hess, Philipoff & Kiessig, Koll.Zeit. 88, 40 (1939).

57. Kiessig & Philipoff, Naturwiss 27, 593 (1939).

58. Stauff, Koll.Zeit. 89, 224 (1939).

59. Hughes, Sawyer & Vinograd, J.Chem.Phys. 13, 131 (1945).

60. Harkins, Mattoon & Corrin, J.Coll.Sci. 1, 105 (1946).

61. Mattoon, Stearns & Harkins, J.Chem.Phys. 15, 209 (1947).

62. Klevens, J.Phys.Chem. & Coll.Chem. 54, 283 (1950).

63. Schulman & Hughes, Biochem.J. 29, 1243 (1935).

64. Harkins & Mittleman, J.Coll.Sci. 4, 367 (1949).

65. Harkins, Mattoon & Corrin, J.A.C.S. 68, 220 (1946).

66. McBain & Hoffman, J.Phys. & Coll. Chem. 53, 39 (1949).

67. Samis & Hartley, Trans.Far.Soc. 34, 1928 (1938).

68. McBain & Richards, Ind.Eng.Chem. 38, 642 (1946).

69. Stearns, Oppenheimer, Simon & Harkins, J.Chem.Phys. 15, 496 (1947).

70. Harkins & Oppenheimer, J.A.C.S. 71, 808 (1949).

71. Klevens, J.A.C.S. 72, 3581 (1950).

72. Smith, J.Phys.Chem. 36, 1401, 1672 (1932).

73. Winsor, Trans.Far.Soc. 44, 376, 451, 471 (1948).

74. Winsor, Trans.Far.Soc. 46, 762 (1950).

75. Winsor, Disc.Far.Soc. 7, 205 (1950).

76. Winsor, J.Phys.Chem. 56, 391 (1952).

77. Winsor & Lumb, Ind.Eng.Chem. 45, 1086 (1953).

78. Winsor, J.Coll.Sci. 10, 88 (1955).

79. Winsor, Chem. & Ind. 632 (1960).

80. Hartley, Private Communication to Winsor cf (47) p7.

81. Schulman & Riley, J.Coll.Sci. 3, 383 (1948).

82. Mattoon, Stearns & Harkins, J.Chem.Phys. 16, 644 (1948).

83. Stewart & Morrow, Phys.Rev. 30, 232 (1927).
Morrow, Phys.Rev. 31, 10 (1928).
Stewart, Phys.Rev. 31, 174 (1928).

84. Bernal, Trans.Far.Soc. 42B, 197 (1946).

85. Hartley, Nature 163, 767 (1949).

86. Debye, J.Phys.Chem. 53, 1 (1949).

87. Debye & Anacker, J.Phys.Chem. 55, 644 (1951).

88. Tartar, J.Phys.Chem. 59, 1195 (1955).

89. Tartar, J.Coll.Sci. 14, 115 (1959).

90. Hatschek & Jane, Koll.Zeit. 38, 33 (1926).

91. Andrade & Lewis, Koll.Zeit. 38, 260 (1926).

92. Hartley, Nature 142, 161 (1938).

93. Pilpel, J.Coll.Sci. 9, 285 (1954).

94. Pilpel, Trans.Far.Soc. 51, 1307 (1955).

95. Stainsby & Alexander, Aus.J.Chem. 6, 123 (1953).

96. Smith & Alexander, Proc.Intern.Congr. of Surface Activity 349 (1957).

97. Angelescu & Manolescu, Koll. Zeit. 94, 319 (1941).

98. Nash, J.App.Chem. 6, 539 (1956).

99. Good & Milloy, Chem. & Ind. 872 (1956).

100. Walker, Ph.D.Thesis London University.

101. Ferguson, Ph.D.Thesis Glasgow University.

102. (a) Nash, J.Coll.Sci. 13, 134 (1958).
(b) Nash, J.Coll.Sci. 14, 6 (1959).
(c) Nash, J.App.Chem. 7, 392 (1957).
(d) Nash, J.App.Chem. 8, 440 (1958).
(e) Nash, Nature 180, 188 (1957).
(f) Nash, Chem. & Ind. 590 (1958).

123. Farrow, J.Chem.Soc. 347 (1912).

124. Angelescu & Szász, Koll.Zeit. 90, 302 (1940).

125. Tartar & Cadle, J.Phys.Chem. 43, 1173 (1939).

126. Corrin & Harkins, J.A.C.S. 69, 683 (1947).

127. Klevens, J.A.C.S. 72, 3780 (1950).

128. Kushner, Hubbard & Parker, Journal of Research of the National Bureau of Standards 59, 113 (1957).

129. Hartley & Runnicles, Proc. of Roy.Soc. A168, 420 (1938).

130. Schulman & Berg, Disc.Far.Soc. 11, 96 (1951).

131. Stern & Amis, Chem.Rev. 59, 28 (1959).

132. Pauling, "Nature of Chemical Bond" (Book) 224, 228 (1960).

Schomaker & Stevenson, J.A.C.S. 63, 37 (1941).

133. UNPUBLISHED WORK IN THIS LABORATORY.

134. Pierce, J.Chem.Phys. 5, 719 (1937).

135. Lawrence, Hyde & Langbridge, Disc.Far.Soc. 18, 249 (1954).