STUDIES ON THE PROPERTIES & PHYSICO-CHEMICAL BEHAVIOUR OF SOME ANIONIC & CATIONIC SOAPS

Thesis submitted in fulfilment of
the requirements for the
Doctor of Philosophy
in Chemistry.

By
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CERTIFICATE

Certified that the Thesis entitled" STUDIES ON THE PROPERTIES AND PHYSICO-CHEMICAL BEHAVIOUR OF SOME ANIONIC AND CATIONIC SOAPS" which being submitted by Shri Surendra Pal Verma for the award of the Degree of Doctor of Philosophy in Chemistry of the University of Roorkee, is his own work carried out under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other Degree of any University.

This is to certify that he has worked on the above mentioned problem for a period equivalent to 24 months of full time research.

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Surendra Pal Verma

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GENERAL INTRODUCTION

GENERAL INTRODUCTION

The name 'surface active agents' has been given to those substances which even in small quantity,alter the conditions prevailing at the interfaces. Different termenologies have been used from time to time to represent these compounds. In industry the term'syndet' is widely used which is a contraction for 'synthetic detergent'. 'Surfactant' a shorter term for surface active agent, represent an organic molecule or an unformulated compound having surface active properties while'syndet'represents primarily a detergent formulation.

Hartley has given the name'amphipathy',which shows by its meaning that the molecule or the ion contains two groups,one that has the sympathy for the phase in which the molecule or the ion is dissolved and the other group which is antipathetic to the medium. In the colloid chemistry these types of groups are known as'lyophilic' and 'lyophobic' respectively and hence these types of compounds are also known as'colloidal electrolytes'. McBain called all of them by the name of 'soap'.

The soaps are natural as well as synthetic products. The compounds like glue,egg white,the natural gums etc. are natural products. Synthetic surface active agents,as we understand,are substances which have been specially synthesised inorder to obtain the compound which has surface active properties,is a modern development,which has received its most active phase in the period between two World Wars.

Classification.

The synthetic surface active agents are classified as follows:

Oil-soluble surfactants:- They are of three types (i) long chain polar compounds, which lower the oil-water interfacial tension and are adsorbed on the polar surfaces; (ii) fluorocarbon compounds, whose polar groups are sufficiently soluble in oil and lower the surface tension of oils; and (iii) silicones, they are generally used as insoluble components of the system and serves antifoeming agents.

Water soluble surfactants:- Most of the interest of the workers is centered towards this class of soaps. These are generally classified depending upon the state of the soap in solution.

(i) Anionic surfactants:- In which on ionisation the hydrophobic portion contains negative charge. The most important among them are, Twichell's reagents (alkyl-aryl surphates and sulphonates), ester sulphonates, amide sulphonates, aliphatic sulphates etc..

(ii) Cationic surfactants:- In which on ionisation the long chain contains positive charge. This class generally consists long chain primary, secondary and tertiary amines, quarternary ammonium compounds, alkyl pyridinium chlorides.etc

(iii) Non-ionic surfactants:- They do not ionise in solution. These are fatty alkanol amides, ethylene oxides derived non-ionic surfactants, sugar esters etc..

(iv) Amphoteric or ampholytic surfactants:- They ionise in solution, with a long chain ion carrying either a positive or negative charge, depending upon the pH of the solution. They behave like amino acids. Their surface active properties are pH dependent. They are N-alkyl taurines, amino-sulphonic acids etc.. Amongst the newer ones are imidazolin derivaties.

Uses and industrial applications.

Almost all types of soaps have been put to use in industry, technology and allied fields. A very large proportion of the total surfactant production is used in washing textile fabrics. There are three major areas in which soap are used for washing fabrics. These are: (a) in mills where the fabrics are made and finished; (b) in home; and (c) in commercial laundries. The alkane sulphonates (Mersolates) were at one time very widely used in Europe for house hold detergents.

The soaps have also been used in cleaning the hard surfaces, generally includes, metal surfaces; glass, ceramic and other non-metallic inorganic surfaces; hard and relatively durable organic surfaces such as paints, plastics, linoleum; surfaces of senstitive materials, such as food stuffs, which are easily penetrated or injured.

In textile and dry cleaning industries, they are used for several textile processing operations such as dyeing, wetting, dispersing, emulsification and other similar gross effects(1). The use of soaps for various non-detersive applications in the field of medicine and hygine has increased appreciably within recent years. Anionic surfactants such as lauryl sulphate and non ionic surfactants such as the Tweens and Spans have been widely adopted for preparing skin lotions in which the effective medicament is suspended or emulsified. One of the most interesting applications of soaps in medicine is the use of an aerosol spray of sodium lauryl sulphate solution as an inhalant for children suffering with severe bronchial congestion. This treatment appears to loosen the excessive mucous secretion and to provide moisture more effectively than stream inhalations(2). The cationic germicides such as benzalkonium chloride can be incorporated into ointments based on methyl cellulose,starch polyglycol,gelatin,pectin or Tween emulsions but their activity is reduced or destroyed when anionic emulsifiers or bases are used(3). Surfactants are used internally as ingredients in many different dispersed or emulsified medicaments in which the surfactant itself play no important biological role but merely serves as a carrier for the active drug. Alkylaromatic sulphonates have been used as carriers for phenothiazine in anthelmintic preparations(4). Penicillin is itself a surface active,and has a relatively high critical micelle concentration,and its surface activity is negligible at the extremely low concentrations where it is still biologically active(5).

The fields of cosmetic technology which have derived most benefit from the recent advances in surfactants include: hand and skin cleansers and bath preparations; emulsion products,lotions, and creams;dentifrices;shaving preparations;and shampoos.

In metal and mineral technology,surfactants are used in flotation,electroplating and surface finishing of metals. The alkyl aryl sulphonates,including the long chain alkyl benzene sulphonates and the short chain alkyl napthalene sulphonates,as well as the fatty alcohol sulphates, have become more or less standard antipitting additives for nickel plating baths(6). For bright copper plates thiourea in combination with napthalene disulphonic acid have been used(7). Bright alloys of copper-tin or copper-tin-zinc,i.e. bronze or brass plates,have been obtained by using the ampholytic surfactant,dodecyl trimethyl bentaine in an alkaline cyanide(8,9).

In building and construction industries surfactants are being consumed on a large scale. Specific areas in which surfactants are widely used include the preparation and use of asphalt bonding materials,concrete,plaster board, and earth,clay,and ceramic products. Soaps and sulphonated anionic surfactants have been used as retarders in the preparation of Plaster of Paris(10). In the construction of dirt roads,aircraft runways,floors,and other load-bearing earth surfaces it is desirable to render the soil stable and compact. Cationic soaps are very effective stabilizers for certain types of soil and soil-aggregate(11). Fatty soaps and rosin soaps,folowed by an alun treatment,have been used to increase the water resistance of dirt roads. Hydrophobic and hydrophilic surface active substances have been shown to be effective in increasing the penetration of Portland cement suspensions into sand(12).

The use of soaps in the manufacture of fertilizers was first announced by Seymour(13). The major beneficial result from the soap is the improvement of the physical character of the fertilizer by reducing the hardness of the fertilizer,and by increasing the resistance to caking. The alkyl sulphonates,such as Santomerse,Oronite Detergent, and Kreelon are used commercially. The acid-stable non-ionics(alcohol or mercaptan-ethylene oxide condensates, alkylphenyl polyethylene glycol ether,or alkylphenoxy polyoxyphenyl ethanol) are the most effective surfactants for the treatment of fertilizers(14). In insecticides, fungicides and herbicides the demand of soaps has appreciably increased.

In the industries of leather,fur, paper, synthetic filaments and films, synthetic rubers, polymers,plastics, paints,petroleum and chemical-processing industries etc. the soaps have wide applications. Besides the aforesaid applications soaps have used in fire fighting and fire preventation recently. One of the well established methods for fighting fires is to lay down over the smouldering material a thick blanket of aqueous foam. This blanket serves to prevent reignition of combustible material, even though it rarely has sufficient cooling power to extinguish a vigorous flame.

Properties of soaps.

As has already been stated that the soap molecule contains hydrophobic and hydrophilic groups in a single molecule. When such a substance is put into water, the water molecules will try to repel the hydrophobic group and simultaneously has a loving tendency towards the hydrophilic portion. The least energy of water will be wasted in pushing away the hydrophobic portion if the system exhibit the smallest possible area of contact between the water molecules and the non-polar hydrocarbon chain of the soap molecule. There is such minimum contact when soap molecules go to the surface and orient with their polar group directed towards the water. This tendency of the soap molecules decreases the surface tension and the interfacial tension. This is what actually happens in the dilute solutions but in the concentrated solutions all the hydrophobic portion cannot remain at the surface. In that case the hydrophobic portion starts to aggregate and these aggregates are surrounded and hidden by polar groups. This aggregation of the soap molecules is called a micelle. A number of investigators like McBain(15), Hartley(16), Wright(17) and Tartar(18) etc., have all agreed on the presence of aggregates of the soap solutions.

These aggregates or micelles do not form at any arbitary concentration but they start forming only after passing an optimum concentration. The concentration at which micelle begins to form is known as critical micelle concentration(c.m.c.). The c.m.c. is not a specific concentration value, but it is a concentration range in which the dispersed soap molecules changes to an equilibrium between molecules (or ions) and aggregates. When practically any physical property of an aqueous soap solution is considered, it exhibits more or less abrupt change in the magnitude over a narrow concentration range (c.m.c.). This abruptness in the physical property has been utilized in the determination of the c.m.c. The values of the c.m.c. derived from various physico-chemical properties may not necessarily be identical since they will depend on the abruptness of the change of the property.

Any method that measures the deviation from ideal behaviour can be used to determine the c.m.c. of a surfactant. A number of physical methods,viz.,conductivity (19-23), surface tension(24) freezing point(25),osmotic pressure(26), vapour pressure(27),solubility(28),viscosity (29), etc., have been employed from time to time by workers. Because of its simplicity the spectral-change method involving the colour change of the dyes has been recently used for estimating the c.m.c. of soap solutions. This method has been critically studied by Mukerjee and Mysels(30).

Tracer technique(31) and electrophoretic mobility(32) methods have also been employed in investigating this property.

An indirect evidence of micelle formation is the phenomenon of solubilization. When such substances which are not very soluble in water,dissolve to an appreciable extent in the micellar soap solution,the phenomenon is known as solubilization. Direct evidence that solubilized materials are present within the micelles is provided by X-ray measurements(33).McBain (34) established that for solubilized systems,the components are in thermodynamically stable equilibrium. In their monograph on "Solubilization",McBain and Hutchinson(35) treat solubilization as a distribution phenomenon between two phases: One is aqueous phase and the other is micellar phase. This phenomena is discussed later.

Soap micelles in non-aqueous.

The oil soluble soaps forms their micelles in hydrocarbon solvents(36-43).(Micelles formed in non-polar solvents are considered that the polar groups are directed towards the interior of the micelles). These micelles are capable to solubilize water. Matton and Mathew (39) found that pure sodium bis(2-ethylhexyl) sulphosuccinate formed spherical micelles in n-dodecane. Kaufman and Singleterry(41,43) investigated micelle formation by a number of salts of dinonyl naphthalene sulphonate. Oil soluble non-ionic surfactants and amine-fatty acid soaps, form micelles at concentrations of about 10^{-2} molar and above and the size of the micelles varies substantially with concentration(44-47).

Shape of the micelle.

There is a general agreement on the presence of micelles in soap solution but a controversy still exist about their shape. McBain(48) was of the opinion that in aqueous soap solutions, two types of aggregates which are very dissimilar in structure, are in equilibrium with each other. One (the ionic micelle) is highly charged and spherical and the other (the lamellar micelle) has a small charge. Hartley(49) on the other hand, postulated only one type of micelle, spherical, essentially liquid in structure and is large compared with McBain's ionic micelle and contains in addition to the amphipathic ions a considerable number of counter ions. Debye(50) has proposed a cylindrical micelle with curved ends which are approximately Hartley spheres. An ellipsoid of rotation was proposed by Hughes(51) and Halsey has suggested that the micelle is rod like(52).

Viscosity(53,54) and birefringence (55) measurements suggest the spherical micelles in 5% soap concentration but beyond this concentration upto 20% the micelles are asymmetric or rod like and at still higher concentrations the micelles are microcrystallites of the lamellar kind(56).

By X-ray studies S-band is observed at 5%

concentration of soap and thus indicate a liquid arrangement in the micelle. It does not provide the evidence regarding the geometrical structure of the micelle. The M-band was also found at this concentration by Harkins(57) which is not inconsistent with a spherical micelle. With 10% of soap concentration the I-band was observed. McBain (58) and initially Harkins(59) interpreted the I-band on the basis of a lamellar micelle. With the data collected by Hartley on transport number (60) and of Corrin(61), Riley and Oster(62),Fournet(63) and others on X-ray,it can be concluded here that at present the size and shape of these micelles is still under dispute.

Size of the micelles.

A number of physical methods have been employed to estimate the size of the micelles. Among them the important one include light scattering (64-66),X-ray(58,67), diffusion(68-71) and ultracentrifuge measurements(72). Singleterry and associates (73,74) determined the micellar size and c.m.c. in non-aqueous systems by measuring the fluorescence and spectral absorption of a suitable dye. Rhodamine B is particularly suited to the detection of soap micelles in such solvents as benzene,cyclohexane, cetane and di-(2-ethylhexyl) -sebacate. Micellar size determined by fluorescence-depolarization method have been confirmed by cryoscopic(75) and osmotic pressure(74) measurements.

Environmental factors on the micelle formation.

The c.m.c. of a given soap and the other properties of the micelles are greatly influenced by such environmental factors as the presence of salts, the nature of the solvent, the presence of co-dissolved or solubilized material, temperature etc.. The effect of solvent is also an important factor. The c.m.c. of K soaps(C_8, C_{10}, C_{12}, C_{14}) is a linear function of the alcohol concentration in aqueous solutions. The specific effects of each alcohol differ quantitatively from each other(76). The effect of added organic solvent on the c.m.c. is variable, with the c.m.c. being raised in some instances and lowered in others (77,78). The studies on the effect of solvent on the micelle formation of soap had been a matter of great concern to Ralston(79-82), Klevens(83,84). The effect of inorganic salts on the micellar properties of surfactants in aqueous solution has also been examined extensively. Corrin and Harkins (85) found that the c.m.c. of soaps, anionic sulphates and sulphonates, cationic primary and quaternary amine salts, was lowered by the presence of salt. It has been found that a series of alkaline builder sodium salts lower the c.m.c. of soap to the same extent when the total sodium ion concentrations are equal(86). Regardless of their effect on the c.m.c., most inorganic salts increase the size of the micelles(87,88) and higher salt concentrations tend to salt-out the surfactants. Polyethenoxy nonionic surfactants of the ester or ether type in which the hydrophobic group is a straight fatty chain are salted out by sodium chloride but are salted in by salts of Ca,Mg, Ba or Al(89).

The c.m.c. increases with increasing temperature, but the slope of the curve is not as steep as might be expected (90,91).

Solubilization.

The phenomenon of solubilization is important in soaps from the theoritical as well as from the practical view point. Solubilization for an aqueous system may be defined as the spontaneous dissolving of a normally water-insoluble substance by a relatively dilute aqueous solution of a surfactant. The major factor which controls the amount of material solubilized in a given system is the chemical composition of the surfactant and the solubilizate. There appears to be no simple relationship between the solubilizing power of a surfactant and its other micellar or surface properties. The cationic surfactants have proved to be much better solubilizers than the anionic ones.

The state of the solubilizate in a solubilization system has been studied from many different points of view and by several different techniques. Methods like turbidimetry (92), surface tension(93),spectrophotometry (94),light scattering (95) etc. have been used to study the solubilization.

X-ray diffraction has very clearly distinguished between two different types of solubilization. In one type, the spacings representing the thickness of the micellar layers increase in proportion to the quantity of the material solubilized. In this case the hydrocarbon is visualized as occupying the space between the hydrophobic ion tails and the water layer. The second type is seen in fatty alcohols in dodecyl sulphate. Here micelle thickness does not change significantly. Kolthoff and Johnson(96) have described a somewhat different type of solubilization in which ion exchange is a key factor. In some cases of solubilization, for example, Cholesterol by non-ionic detergents(97) and certain hydrocarbon by soap(98), it is accomplished by the formation of relatively stable complexes. Ekwall and Co-workers(99) have recently reported a new solubilization which occurs when decane-1, 10-diol is solubilized in sodium oleate. In this case the solubilizate causes the formation of smaller and more lightly ionised micelles than are normally present.

Electrochemical phenomena.

Surface active agents effect certain electrochemical phenomena. Maluli's and Bodnevas(100) have described a rule for change in the cathode polarisation in deposition of metal in presence of surface active substances. Kheifets (101) has seen the effect of soaps on the over voltage for the liberation of hydrogen on platinium. Loser and Kabanov(102) studied the adsorption of surface active substances on the iron electrode. Levin and Co-workers(103) have found a shift in the electrode potential of copper and zinc electrodes in the presence of surface active agents. The effect of surface active agents on the dropping mercury electrodes is another worth mentioning problem. They generally decrease the limiting current, shift the half wave potential and some times change the entire wave. Holleck and Exner(104) had shown the mechanism of reduction of nitro compounds at the dropping mercury electrode. Silvestroni(105) had shown that the half wave potential of oxygen is shifted to more negative value by the presence of these compounds. Kemula(106,107) has studied the reduction wave of copper,while Kolthoff (108) found more reversible nature of copper wave in perchloric acid medium, in the presence of surface active substances. Doss and Co-workers(109) have studied the behaviour of bromocresol purple blue,bromothymol blue and cetyl pyridinium bromide at the dropping mercury electrode inorder to see their effect on the capacity of the double layer: Chaki(110) has studied the effect of these compounds in oscillography polarography and Nagi(111) has studied the effect on the chronopotentiograms of copper,lead, cadmium and bismuth in various supporting electrolytes.

Meits(112), Zuman(113) and others have studied the suppressive action of a number of surface active agents. Kolthoff(114) has recommended the use of poly-acryl amide as maximum suppressor in the case of rotated dropping electrode. Capitanio and Pittoni(115) have calculated the suppression coefficient of sulpho-naphthyl stearic acid and lauric acid. Reilley (116) and Smoler(117) have studied the effect of surface active agents on polarographic currents.

Thermodynamic functions.

Some authors had calculated the thermodynamical functions of micelle formation of soaps in aqueous solution. Molyneux, Rhodes and Swarbrik(118) have studied the c.m.c. at 20° of N-alkyl bentaines and had converted the results into free energy, enthalpy and entropy changes of micellisation and have compared these with corresponding values obtained from the literature data on the micellisation of other amphiphiles and on related processes. Corkil and Co-workers(119) have determined calorimetrically the heat of micelle formation for some members of a homologous series of n-alkyl hexaoxy ethylene glycol monoesters. Others have also determined the heat of micelle formation in a detergent system either by direct calorimetric measurements(120-124) or calculated from the temperature dependence of the critical micelle concentration(125). Stauff and Rasper(126) have determined the free energy of adsorption of dodecyl polyglycerols.

Interaction with proteins.

The interactions between proteins and various surfactants have been extensively studied from many different points of view. Most of the studies on protein-surfactant reactions have been done from the biochemical point of view. There are many other fields like textiles (wool and silk and synthetic protein fibres), leather and furs, proteinaceous plastics, cosmetics and others, in which the behaviour of proteins with surfactants is of great importance.

The higher fatty acyl derivatives of casein, egg albumin, zein, solybean protein, peanut protein and others have been prepared by Gordon and Co-workers(127,128). The typical effects which may be noted when a surfactant is added to protein are:(i) the protein may be denaturated which is a stereochemical phenomenon in which the spatial configuration of the protein molecule is altered, but primary interatomic linkages are not formed or broken, (ii) the protein may be precipitated, (iii) the protein may form complex with the surfactant, (iv) the protein may be stabilized against the denaturating effects of non-surface active denaturants such as heat and urea(129) and (v) conjugated proteins are frequently split by surfactant and the protein is liberated from the prosthetic groups.

The anionic or cationic soaps when react with proteins form complexes, ionic or coulombic in nature. The protein molecules contain both negative and positive charges which can combine with the surfactant ions of opposite charge. Steinhardt, Fugitt, and Harris(130) established on the basis of acid-base titration of keratin that electrical charge alone could not account for the strength of the binding effect.

Generally, soluble proteins have been used for the quantitative studies of protein-surfactant interactions: The quantity of the surfactant bound by the protein usually exceeds the stoichiometric quantity by a large factor. The reactions of beta-globulin, insulin and pepsin with carboxylic polyelectrolytes has been studied by Alexander and Cumper, using monolayer force-area curves and measurements of surface viscosity and surface elasticity(131). The reaction of serum albumins with dodecyl sulphate(132,133) has also been studied by surface tension and interfacial tension measurements. Interaction between albumins and cationic surfactants has been described by Foster and Yang (134). Pankhurst and Co-workers(135,136) studied extensively the reaction between dodecyl sulphate and gelatin. The reaction of carboxylic polyelectrolytes with serum albomin has been studied by absorption spectroscopy (137) and confirmed by viscosity and crystallographic measurements.

Electrophoresis and equilibrium dialysis are said to be good techniques for studying the reactions of alkyl aryl sulphonates and fatty alkyl sulphates with zein and various albumins(138-140). Jerchel and Co-workers (141,142) studied the reaction of cationic detergents with a wide variety of proteins by paper electrophoresis. Sedimentation technique which has proved so effective, has also been used on protein-surfactant combinations(143).

The anionic detergents unfold and stretch out the protein chains. The protein can thus be brought into the form of a viscous solution which can then be spun into fibrous form. The keratin solutions can be spun into fibrous form and regenerated(144). The surfactants also inactivate various enzymes. This effect appears to be highly specific and a particular enzyme may be strongly poisoned by one surfactant but scarcely affected by another. Similar considerations apply to the deactivation of toxins by surfactants(145-147).

Interaction with dyes.

The interaction of surface active agents with dyes present some interesting features worth considering. For a long time dyes have been used for the qualitative and quantitative determination of surfactants. Methylene blue in chloroform as an indicator(148) has been used for the determination of cetyl trimethyl ammonium bromide. Pinacyanol bromide is said to be an excellent indicator for the titration of the anionic surfactants with the cationics (149),pontamine Red 8 BLN has also been used (150) and also (151) eosine and rhodamine 6 GCP. A recently described colorimetric method involves measuring the quantity of bromocresol purple which is liberated from a protein complex of this dye when the complex is treated with an anionic detergent(152). Thymol blue has also been recommended as a reagent for anionic detergents(153). The cationic soaps may also be made to react with an acid dye to form a solvent-soluble complex which can be extracted and then estimated colorimetrically (154). The quaternary cationics has been determined using bromophenol blue as the precipitating agent(155). Hiskey and Downey(156),Mysels and Mukerjee(157),Hartley(158) etc. showed that colour change involved the formation of a dye-detergent complex. More references on the dye-detergent complexes have been given in the introduction of Chapter I.

Besides these two main fields of interaction, surfactants also interact with metal ions,polymers, nucleic acids etc.. Schulman(159) studied the reaction of copper with dodecyl sulphate. Walton(160), Van Voorst (161) have prepared the mercury salts of anionic surfactants. Cetyl trimethyl ammonium bromide is shown to form an insoluble complex of constant composition (162) with potassium dichromate. Anionic surfactants also react with zinc amine complexes(163) and this has been used for the recovering of the surfactant from the solution. Ottewill(164) studied the effect of surfactants on the stability of hydrophobic sols.

<u>Analysis and estimation of surfactants</u>.

The surfactants are generally identified by surface tension and elemental analysis. In a mixture of surfactants the problem of identification and separation can become very difficult. The help of dyes and certain other reagents is also taken to estimate them.

Anionic surfactants:- One of the earliest and the best known methods for determining sulphonates and sulphates was developed by Kling and Puschel who first applied it to the analysis of alkyl sulphates(165). The most widely used methods for determining anionic detergents is by titration with a long-chain quaternary ammonium salt, such as alkyl pyridinium halides,cetyl trimethyl ammonium bromide etc.(166). Preston(167) has described a tensiometric titration in which the sharp rise in surface tension of the solution indicates an equivalence of the reagent. Dye indicators such as pinacyanol bromide, bromophenol blue, eosine,rhodamine 6GCP etc.,have been widely used for the estimation of anionic detergents.

Cationic surfactant:- Methods for analysing cationics are quite similar to those used in analysing anionics. Titrations of the cationics with standard anionics may be carried out using methylene blue in chloroform as an indicator(loc.cit.). Wilson(168) has described a gravimetric method for quaternaries in which they are precipitated as the reineckates,purified,dried and weighed. The determination of quaternaries with the aid of phosphotungstic acid has also been used(169).

Non-ionic and ampholytic surfactants:- Despite the great commercial importance of the non-ionics relatively few quantitative analytical procedures for these substances have yet been developed. The method of Oliver and Preston(170) in which acidified sample is treated with barium chloride followed by hydrochloric acid and phosphomolybdic acid,is most satisfactory. The precipitate so obtained is filtered,washed,dried and weighed. This precipitation reaction is specific for polyethenoxy chain and has been used to estimate the polyethylene glycols and their surface active derivatives. Titration with aqueous phenol has been used as a method for determining the relations of hydrophobic and hydrophilic chain length in polyethenoxy ethers and esters (171). Spectrocopic methods have been proved to be very practical and useful for the polyethenoxy alkyl phenol ethers(172).

Potentiometric titrations are frequently of value in the analysis of surfactants and their auxiliaries(173). Conductometric titrations have been used in the determination of soaps in synthetic rubber latexes(174). Conductivity meters have also been used in controlling the strength of wool schouring baths(175). Polarographic analysis has also been used for the determination of various surfactants and builders(176). Gordon and Urner(177) have recently described a polarographic method for the determination of sulphite and sulphate in petroleum sulphanates.

The work described in this thesis deals with the investigations on some less familiar aspects of dye-soap interaction. Almost nothing has been done so far to determine quantitatively the extent of binding of the dyes with soaps. Quantitative studies on the interaction of malachite green and rhodamine 6G with sulphonated phenyl,tolyl and xylyl stearic acids and those on the interaction of alizarin red S with cetyl trimethyl ammonium bromide and cetyl pyridinium bromide were, therefore, carried out spectrophotometrically. Attempt has also been made to estimate the micellar size or aggregation number.

Determination of the critical micelle concentration of the anionic and cationic soaps by pH metric, conductrometric, spectrophotometric and potentiometric methods has been done. The effect of foreign electrolytes on the c.m.c. of anionic soaps has also been studied by pH metry.

The effect of methyl and ethyl alcohols, urea, acetamide, formamide and lauric acid diethanol amine condensate, on the critical micelle concentration of the above mentioned soaps has been studied by pH and conductivity measurements.

The polarography of soap-dye mixtures has not been worked out as yet. A preliminary study has been carried out using malachite green methylene blue and rhodamine 6G and anionic soaps to establish polarographically the nature of dye-soap interaction. Some of the salient features of the electrode process have been discussed.

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CHAPTER I.

Spectrophotometric study on the interaction of soaps with dyes.

INTRODUCTION

The problem of interaction of surface active agents with other substances like polymers(1,2) dyes(3), proteins(4-10),nucleic acid (11),hydrophobic sols(12,13), metal ions(14),complex ions(15) etc.has been referred to by many workers,but most of the work done in this direction has been qualitative in nature and lacks in many details. This remark is equally true for surfactant-dye interaction inspite of the pioneering work of Hartley(16,17) on the c.m.c. of soaps and its extension by Harkins and Corrin (18),Kolthoff and Stricks(19), Arkin and Singlettery (20) and Mysels and Mukerjee(21). The spectral changes accompany soap-dye interaction has not only proved to be a useful tool in determining the c.m.c. of soaps but successfully imployed to interpret structural changes taking place therein. Several articles on this aspect have appeared(22-26).

The concept of existence of dye-detergent complex in such systems was first introduced by Downey, Mysels and others. Mukerjee and Mysels (21),showed that the colour change involved the formation of a dye-detergent salt which was highly insoluble but formed a coarse and quite stable suspension in the presence of some what more than the stoichiometric amounts of the detergent. They also established the composition of methylene blue-lauryl sulphate,cetyl trimethyl ammonium-bromophenol blue and dicetyl.trimethyl ammonium-bromo phenol blue complexes by estimating C,H,N,S and Br.Hiskey and Downey (27) studied the interaction between octadecyl trimethyl ammonium ion and methyl orange spectrophotometrically. They had interpreted the spectral data in terms of association reaction between the quanternary salt and the basic form of the methyl orange. Hayashi(28) had studied the interaction of congo red with cetyl trimethyl ammonium bromide and Triton X-100 and interpreted the spectrophotometric data in terms of 1:2 dye-detergent complex.

Another feature of the interaction of surface active agents and dyes is the existence of the phenomenon of 'Metachromasy'. Linsove(29) and Holmes (30)used this word to explain the change in colour of dilute aqueous solutions of dyes caused by the addition of substances of high molecular weights. Solutions of dyes not obeying the Beer's law can very well be studied on the basis of this property. Michaclis and Granicks (31) during the course of their studies on 'Metacromasy of basic dyestuffs' showed that polymerization in presence of nucleic acid is always correlated with the metachromatic effect. The importance of dyes with induced 'metachromasy' in staining some histological morphological elements,such as cellular nuclei or the cyloplasma of lymphocytes is well established.

Although it is fairly well established that soap and dyes interact to give some sort of complexes, the problem still offers fresh avenues for further investigations. For example,nothing has been said so far about the extent of binding of the dyes with soaps. In this chanpter results of investigation on the binding of the dyes with anionic and cationic soaps and the actual mechanism of the soap-dye interaction are discussed.

The following set of soap-dye mixtures have been studied:

(i) Malachite green and sulphonated phenyl stearic acid.

(ii) Malachite green and sulphonated tolyl stearic acid.

(iii) Malachite green and sulphonated xylyl stearic acid.

(iv) Rhodamine 6G and sulphonated phenyl stearic acid.

(v) Rhodamine 6G and sulphonated tolyl stearic acid.

(vi) Rhodamine 6G and sulphonated xylyl stearic acid.

(vii) Alizarin red S and cetyl trimethyl ammonium bromide.

(viii) Alizarin red S and cetyl pyridinium bromide.

EXPERIMENTAL

Preparation of soap:- Sulphonated phenyl-,tolyl-and stearic acids were prepared by the method of Stirton and Coworkers(32). The aromatic hydrocarbons viz., benzene,toluene,xylene etc. were refluxed with oliec acid in presence of anhydrous aluminium chloride as a catalyst for about 4 hrs. The refluxed product was cooled to room temperature and dilute hydrochloric acid was added. Aluminium chloride separated out and the refluxed product was decanted and washed several times with hot water. During washing with hot water vigorous shaking was avoided otherwise emulsion was formed which caused difficulty in demulsifying. Steam distillation was carried out to make the product free from steam volatile impurities. The rest of the product was dried and was subjected to distillation under reduced pressure(5 mm) to obtain the different aryl stearic acids. To ensure complete purity of the product redistillation under reduced pressure(5 mm) was again done. The aryl stearic acids were then refluxed with conc. sulphuric acid(1:8) for about one hour at 80°C. The separation of these sulphonated stearates was done based on their insolubility in dilute sulphuric acid. Hence on addition of water to the sulphonated products,these eventually separate as an oily layer and was separated. This oily layer was extracted with ether and to the ethereal extract water was added to dissolve the corresponding soap which formed the lower layer and was thus separated. The water extract was concentrated and the last traces of the moisture were removed under vaccuum dessicator.

The solutions were prepared in doubly distilled water(all glass). Since these soaps behaves like di-basic acids,their strength were calculated by pH metric titrations against KOH of known strength.

Cetyl trimethyl ammonium bromide and cetyl pyridinium bromide were B.D.H. products. They were recrystallized from aceton. Malachite green,rhodamine 6G and alizarin red S were also B.D.H.products.The Walpole,McIlvaine and Borax(33) buffers were prepared in the laboratory.

Apparatus:- A Bouch and Lomb 'spectronic 20' was used for absorption measurements. The molar extinction coefficients were calculated from the relationship $\epsilon = \frac{1}{cd} \log_{10} \frac{I_0}{I}$. pH of the solutions were measured with the help of a Cambridge Bench Type pH meter.

Formula used: - Klotz(34) studied spectrophotometrically the interaction of proteins with organic anions. The concentration of bound and unbound dye was calculated using the formula:

$$\alpha = \frac{\epsilon_{app} - \epsilon_B}{\epsilon_F - \epsilon_B}$$

where ϵ_{app} is the apparant molar extinction

6

coefficient, ϵ_B molar extinction coefficient of the bound dye, ϵ_F molar extinction coefficient of free dye and α is the fraction of the free dye.

The validity of this equation was tried in the dye-soap interactions.

<u>Procedure:</u>- Stock solutions of dyes(1.0×10^{-3}M) and soaps(1.0×10^{-3}M) for anionic and (1.0×10^{-2}M) for cationic soaps were prepared in doubly distilled water (all glass). The absorption of the following sets of mixtures was measured in order to determine the binding of the dye:(i) 5 cc. of 10^{-3}M soap + a minute quantity of the dye(one or two drops of 10^{-3}M); total volume made up to 10 cc. by the addition of the requisite amount of the buffer,(ii) 0.5 cc. of 10^{-3}M malachite green or 0.3 cc. of 10^{-3}M rhodamine 6G + varying amount of soap(1 cc,2 cc,3 cc,5 cc, -----17 cc,21 cc of 10^{-3}M); total volume made up to 25 cc. with buffers and (iii) solutions of varying concentrations of dyes(0.1 cc, 0.2 cc ------0.7 cc,1.0 cc. of 10^{-3}M); total volume made up to 25 cc. with the buffers alone. A period of about one hour was allowed in each case to attain equilibrium.

The same procedure was adopted in the case of acid dye and cationic soaps combinations.

Set I,II and III were used to determine ϵ_B, ϵ_{app}

and ϵ_F respectively in Klotz equation.

On carrying out the preliminary experiments the following changes in the colour of the dye by the addition of surface active agents were observed.

(i) The colour of malachite green changes from bluish green to very dark green in presence of SPSA, STSA and SXSA irrespective of the pH of the medium.

(ii) The colour of the rhodamine 6G changes from yellowish to red in presence of SPSA, STSA and SXSA irrespective of the pH of the medium.

(iii) The colour of the alizarin red S in presence of CTMAB and CPB changes from yellow to greenish yellow in the acidic medium, red to violet in the neutral medium and from wine red to violet in the alkaline medium. In the vicinity of pH 7.00 a violet coloured precipitate was formed at low soap concentrations which got dissolved by further addition of the soap.

The absorption readings of the dyes in presence of surface active agents are given in the following tables:

TABLE 1.

Absorption spectra of different concentrations of malachite green.

Wave length in mμ	Absorbance for different concentrations of malachite green (x 10^{-6} M)					
	1	2	3	4	5	6
	4.0	8.0	20.0	28.0	40.0	60.0
400	0.02	0.04	0.13	0.15	0.26	0.30
425	0.02	0.06	0.19	0.24	0.35	0.40
450	0.02	0.03	0.11	0.15	0.23	0.35
475	0.02	0.02	0.03	0.07	0.05	0.10
500	0.03	0.03	0.04	0.07	0.07	0.15
525	0.03	0.04	0.09	0.09	0.15	0.30
550	0.04	0.05	0.18	0.25	0.35	0.72
575	0.05	0.11	0.38	0.48	0.75	1.00
600	0.08	0.19	0.62	0.80	1.22	1.50
625	0.10	0.26	0.90	1.15	1.52	1.95
640	0.07	0.21	0.70	0.88	1.30	1.40
650	0.06	0.15	0.48	0.59	0.78	0.90

Fig. 1 A

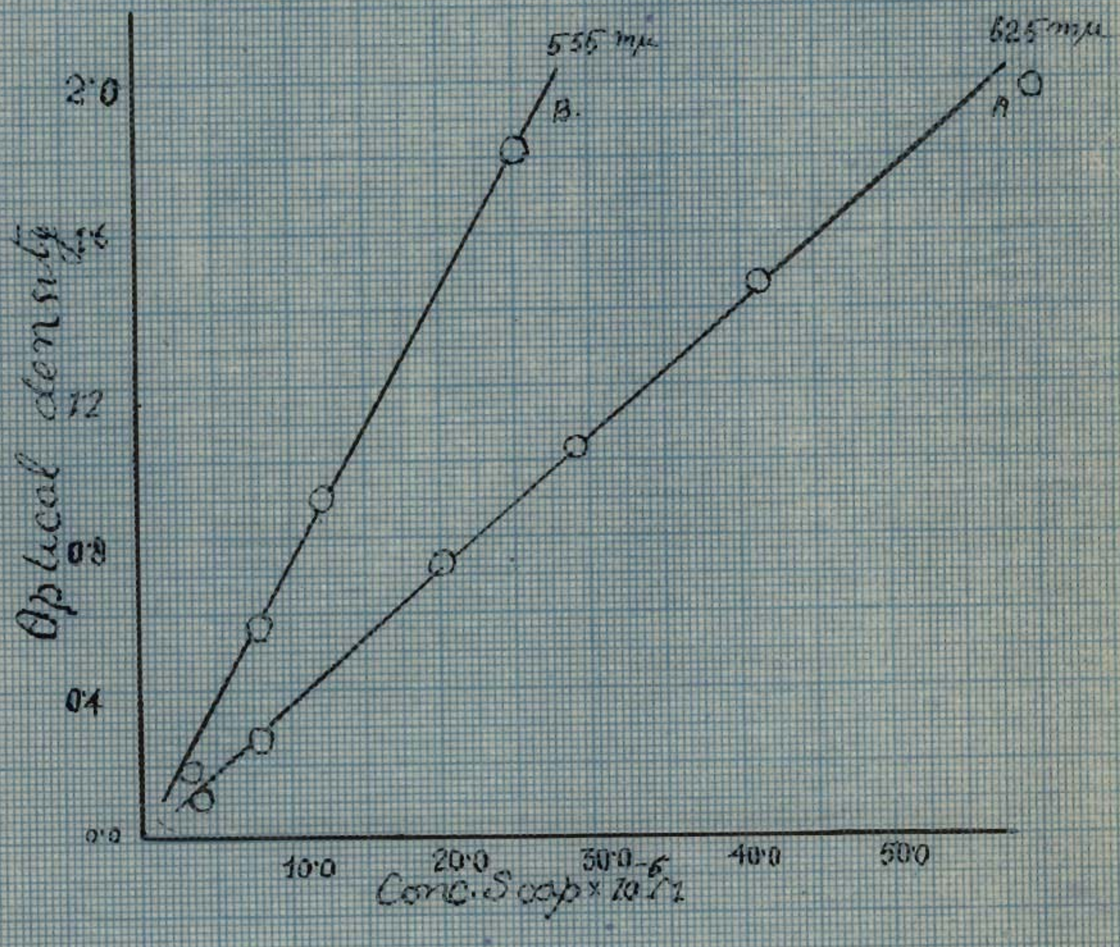

555 mμ
B.
625 mμ
A
Optical density
2·0
1·6
1·2
0·8
0·4
0·0
10·0
20·0
30·0
40·0
50·0
Conc. Soap × 10-6 M

Fig 1

Malachite green-sulphonated phenyl stearic acid.

TABLE 2.

Absorption spectra of 2.0×10^{-5}M malachite green in presence of different concentration of SPSA (order 10^{-5}M) at pH 2.72.

Wave length in mµ	Absorbance of malachite green for different concentration of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.12	0.15	0.17	0.23	0.23	0.33	0.44	0.52	0.58
425	0.13	0.17	0.19	0.24	0.27	0.35	0.44	0.52	0.60
450	0.11	0.12	0.16	0.20	0.22	0.25	0.36	0.41	0.52
475	0.07	0.08	0.06	0.11	0.17	0.21	0.26	0.32	0.36
500	0.06	0.07	0.05	0.07	0.14	0.17	0.21	0.24	0.27
525	0.10	0.05	0.09	0.08	0.10	0.15	0.20	0.17	0.27
550	0.11	0.11	0.11	0.12	0.13	0.15	0.21	0.22	0.25
575	0.21	0.21	0.19	0.18	0.23	0.14	0.22	0.29	0.30
600	0.34	0.35	0.35	0.32	0.36	0.36	0.40	0.40	0.38
625	0.49	0.49	0.50	0.52	0.52	0.57	0.58	0.57	0.54
640	0.47	0.56	0.60	0.62	0.66	0.68	0.72	0.69	0.69
650	0.42	0.51	0.56	0.57	0.63	0.64	0.68	0.68	0.64

Fig. 2 A

TABLE 3.

Absorption spectra of 2.0 x 10^{-5}M malachite green in presence of different concentration of SPSA (order 10^{-5}M) at pH 7.00

Wave length in mµ	Absorbance of malachite green for different concentration of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.14	0.13	0.16	0.21	0.25	0.35	0.43	0.50	0.58
425	0.14	0.15	0.17	0.22	0.25	0.38	0.44	0.50	0.62
450	0.12	0.11	0.13	0.17	0.21	0.33	0.36	0.41	0.52
475	0.06	0.04	0.07	0.09	0.15	0.21	0.22	0.26	0.36
500	0.07	0.02	0.02	0.07	0.11	0.16	0.18	0.19	0.27
525	0.12	0.03	0.03	0.10	0.10	0.11	0.14	0.19	0.23
550	0.17	0.09	0.07	0.11	0.13	0.15	0.17	0.19	0.24
575	0.30	0.17	0.21	0.23	0.24	0.26	0.28	0.27	0.34
600	0.59	0.33	0.38	0.42	0.46	0.43	0.43	0.45	0.47
625	0.56	0.54	0.62	0.65	0.65	0.68	0.69	0.71	0.75
640	0.50	0.62	0.70	0.79	0.79	0.85	0.86	0.86	0.90
650	0.44	0.56	0.64	0.73	0.74	0.80	0.81	0.82	0.86

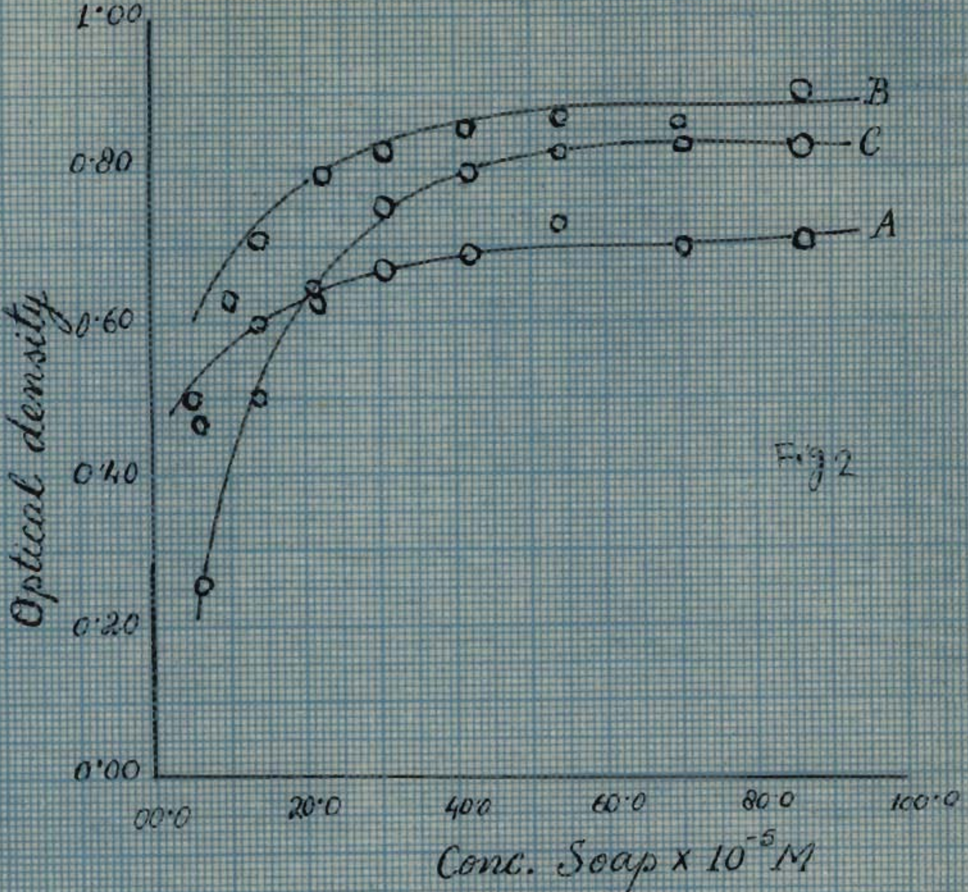
Fig. 2 B

TABLE 4.

Absorption spectra of 2.0 x 10^{-5} M malachite green in presence of different concentration of SPSA (order 10^{-5}M) at pH 9.12

Wave length in mμ	Absorbance of malachite green for different concentration of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.11	0.11	0.15	0.19	0.28	0.34	0.40	0.47	0.60
425	0.10	0.14	0.17	0.21	0.27	0.35	0.42	0.50	0.61
450	0.08	0.07	0.13	0.19	0.23	0.31	0.38	0.41	0.50
475	0.07	0.04	0.10	0.10	0.12	0.18	0.22	0.26	0.36
500	0.07	0.06	0.06	0.06	0.11	0.14	0.15	0.20	0.28
525	0.08	0.05	0.04	0.04	0.05	0.14	0.15	0.17	0.24
550	0.12	0.06	0.08	0.09	0.12	0.15	0.18	0.18	0.23
575	0.24	0.11	0.15	0.21	0.22	0.22	0.27	0.29	0.34
600	0.39	0.20	0.28	0.35	0.36	0.41	0.43	0.42	0.47
625	0.30	0.31	0.44	0.43	0.58	0.63	0.64	0.66	0.70
640	0.25	0.37	0.50	0.63	0.74	0.79	0.81	0.82	0.90
650	0.25	0.35	0.49	0.62	0.69	0.74	0.79	0.77	0.85

Fig. 2 C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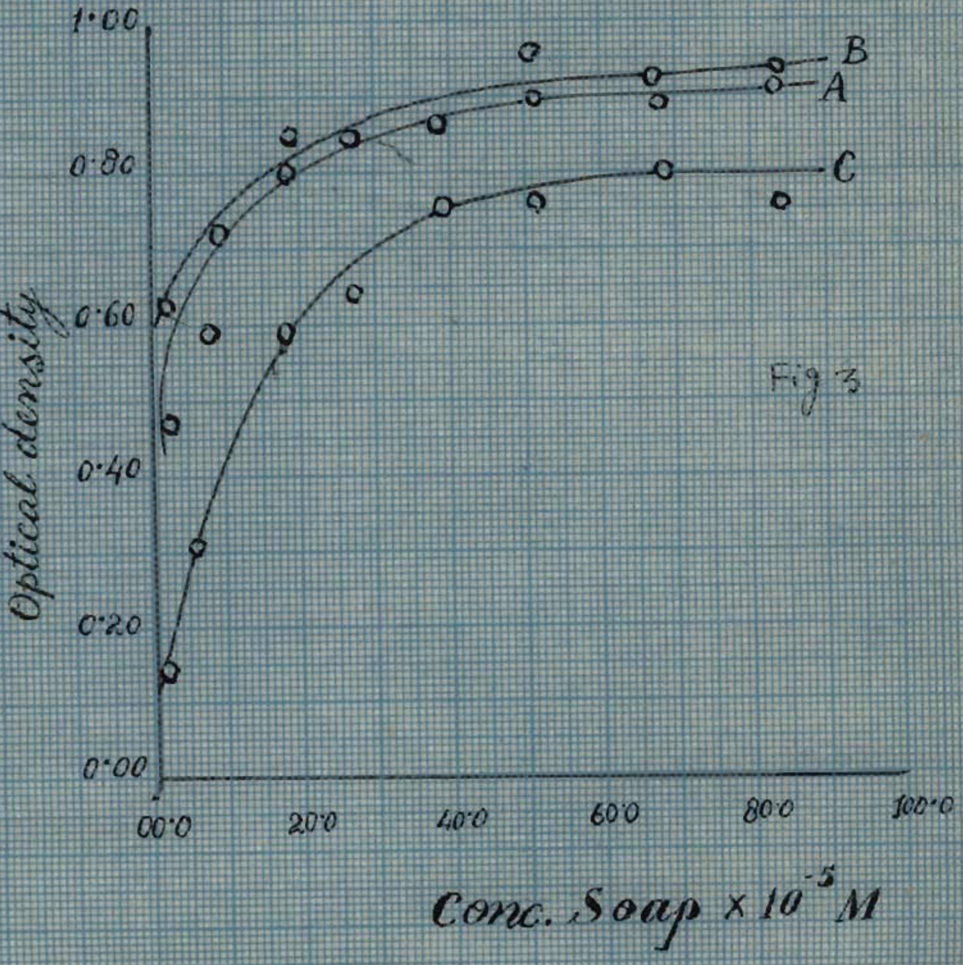
0·80
0·60
0·40
0·20
0·00
Optical density
00·0
20·0
40·0
60·0
80·0
100·0
Conc. Soap × 10^{-5} M
B
C
A

Fig 2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0·80
0·60
0·40
0·20
0·00
Optical density
00·0
20·0
40·0
60·0
80·0
100·0
Conc. Soap × 10^{-5} M
B
A
C

Fig 3

Malachite green - sulphonated tolyl stearic acid.

TABLE 5.

Absorption spectra of 2.0 x 10^{-5} M malachite green in presence of different concentration of STSA (order 10^{-5}M) at pH 2.72

Wave length in mμ	Absorbance of malachite green for different concentration of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.18	0.19	0.18	0.17	0.17	0.21	0.30	0.33	0.41
425	0.20	0.23	0.18	0.24	0.21	0.26	0.35	0.35	0.43
450	0.18	0.20	0.18	0.22	0.18	0.23	0.28	0.31	0.35
475	0.12	0.15	0.14	0.11	0.09	0.13	0.15	0.15	0.26
500	0.07	0.12	0.12	0.10	0.10	0.07	0.13	0.10	0.20
525	0.08	0.11	0.09	0.13	0.09	0.11	0.10	0.15	0.18
550	0.13	0.17	0.15	0.12	0.11	0.13	0.18	0.19	0.23
575	0.29	0.27	0.24	0.27	0.24	0.27	0.28	0.28	0.32
600	0.44	0.42	0.41	0.45	0.48	0.48	0.48	0.49	0.50
525	0.69	0.61	0.57	0.67	0.70	0.74	0.79	0.72	0.77
640	0.62	0.60	0.61	0.80	0.85	0.86	0.90	0.89	0.91
650	0.52	0.51	0.58	0.77	0.78	0.80	0.78	0.81	0.87

Fig. 3 A

TABLE 6.

Absorption spectra of 2.0×10^{-5} M malachite green in presence of different concentration of STSA (order 10^{-5}M) at pH 7.00

Wave length in mμ	Absorbance of malachite green for different concentration of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.09	0.09	0.11	0.17	0.17	0.18	0.25	0.31	0.33
425	0.11	0.12	0.14	0.20	0.19	0.27	0.28	0.36	0.40
450	0.10	0.11	0.13	0.17	0.18	0.24	0.25	0.30	0.34
475	0.04	0.04	0.06	0.10	0.10	0.11	0.16	0.16	0.19
500	0.03	0.02	0.06	0.07	0.09	0.07	0.09	0.12	0.17
525	0.04	0.04	0.06	0.06	0.07	0.08	0.09	0.09	0.14
550	0.10	0.08	0.11	0.12	0.09	0.10	0.11	0.17	0.17
575	0.16	0.18	0.18	0.25	0.25	0.24	0.24	0.22	0.29
600	0.29	0.38	0.40	0.43	0.40	0.42	0.45	0.46	0.48
625	0.45	0.50	0.64	0.66	0.66	0.70	0.71	0.74	0.74
640	0.48	0.58	0.74	0.84	0.84	0.86	0.90	0.91	0.92
650	0.43	0.56	0.69	0.78	0.76	0.77	0.78	0.80	0.81

Fig. 3 B

TABLE 7.

Absorption spectra of 2.0 x 10^{-5} M malachite green in presence of different concentration of STSA (order 10^{-5}M) at pH 9.12

Wave length in mµ	Absorbance of malachite green for different concentration of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
400	0.03	0.06	0.08	0.13	0.14	0.22	0.27	0.32	0.26
425	0.05	0.07	0.12	0.14	0.16	0.26	0.29	0.35	0.30
450	0.04	0.05	0.09	0.13	0.14	0.22	0.23	0.32	0.24
475	0.03	0.03	0.04	0.07	0.06	0.16	0.15	0.19	0.15
500	0.02	0.02	0.07	0.04	0.03	0.09	0.12	0.13	0.14
525	0.02	0.01	0.06	0.03	0.05	0.10	0.11	0.13	0.14
550	0.03	0.04	0.03	0.09	0.06	0.15	0.13	0.20	0.21
575	0.07	0.11	0.11	0.17	0.14	0.23	0.21	0.28	0.29
600	0.09	0.13	0.21	0.30	0.32	0.39	0.39	0.48	0.40
625	0.17	0.27	0.33	0.49	0.54	0.63	0.65	0.75	0.70
640	0.15	0.31	0.47	0.59	0.64	0.75	0.75	0.79	0.75
650	0.14	0.27	0.39	0.53	0.58	0.69	0.70	0.72	0.68

Fig. 3 C

Malachite green-sulphonated xylyl stearic acid.

TABLE 8.

Absorption spectra of 2.0×10^{-5} M malachite green in presence of different concentration of SXSA (order 10^{-5}M) at pH 2.72

Wave length in mμ	Absorbance of malachite green for different concentration of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.08	0.09	0.09	0.12	0.15	0.16	0.17	0.20	0.21
525	0.09	0.09	0.10	0.13	0.16	0.18	0.19	0.22	0.25
575	0.13	0.12	0.10	0.20	0.25	0.28	0.32	0.39	0.40
600	0.29	0.26	0.21	0.25	0.40	0.43	0.50	0.46	0.44
625	0.39	0.35	0.29	0.28	0.53	0.56	0.60	0.56	0.55
640	0.34	0.32	0.27	0.26	0.63	0.64	0.70	0.64	0.66
650	0.27	0.28	0.28	0.27	0.56	0.58	0.62	0.62	0.64
675	0.14	0.16	0.19	0.20	0.30	0.36	0.50	0.45	0.49

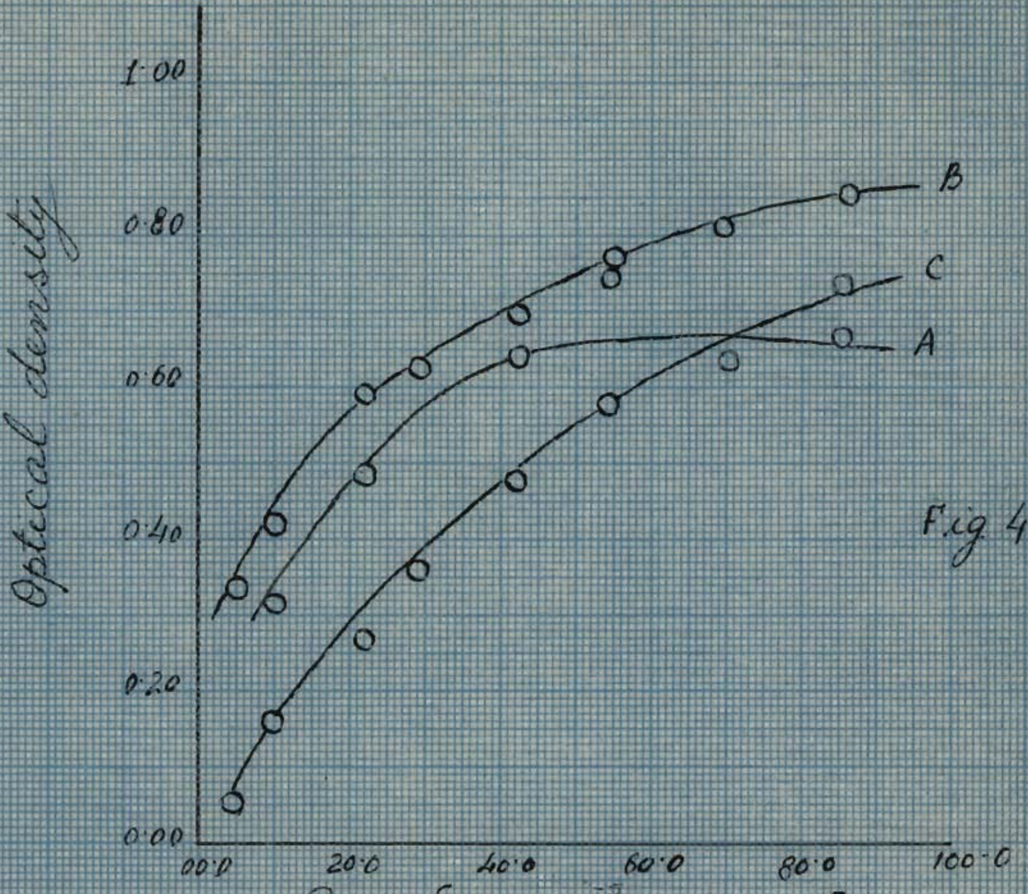
Fig. 4 A

TABLE 9.

Absorption spectra of 2.0×10^{-5} M malachite green in presence of different concentration of SXSA (order 10^{-5}M) at pH 7.00

Wave length in mμ	Absorbance of malachite green for different concentration of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.05	0.09	0.09	0.10	0.15	0.17	0.18	0.20	0.22
525	0.10	0.10	0.12	0.12	0.18	0.19	0.20	0.22	0.25
575	0.15	0.17	0.18	0.19	0.21	0.23	0.26	0.28	0.32
600	0.30	0.32	0.35	0.37	0.40	0.45	0.48	0.52	0.58
625	0.35	0.40	0.46	0.48	0.54	0.57	0.62	0.68	0.75
640	0.35	0.43	0.48	0.60	0.62	0.68	0.75	0.81	0.82
650	0.29	0.37	0.44	0.56	0.61	0.66	0.70	0.72	0.73
675	0.16	0.19	0.24	0.32	0.35	0.36	0.39	0.42	0.46

Fig. 4 B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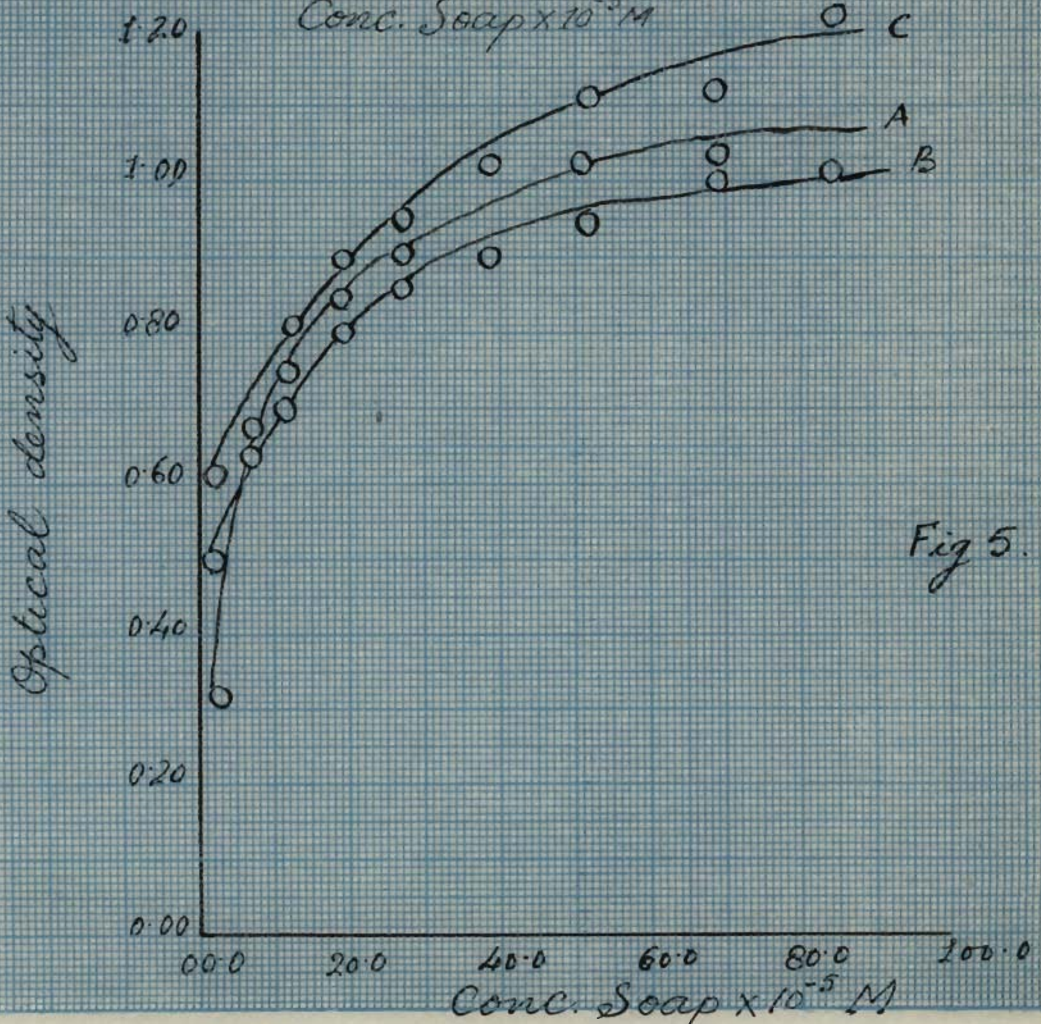
0·80
0·60
0·40
0·20
0·00
Optical density
B
C
A
00·0
20·0
40·0
60·0
80·0
100·0
Conc. Soap × 10^{-5} M

Fig 4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1·00
0·80
0·60
0·40
0·20
0·00
Optical density
C
A
B
00·0
20·0
40·0
60·0
80·0
100·0
Conc. Soap × 10^{-5} M

Fig 5.

TABLE 10

Absorption spectra of 2.0 x 10^{-5}M malachite green in presence of different concentration of SXSA (order 10^{-5}M) at pH 9.12

Wave length in mµ	Absorbance of malachite green for different concentration of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.03	0.04	0.03	0.07	0.10	0.11	0.13	0.14	1.15
525	0.08	0.09	0.13	0.15	0.17	0.19	0.22	0.25	0.26
575	0.10	0.12	0.15	0.17	0.18	0.19	0.22	0.25	0.28
600	0.06	0.13	0.14	0.18	0.28	0.30	0.47	0.43	0.50
625	0.05	0.13	0.15	0.22	0.32	0.40	0.47	0.55	0.68
640	0.04	0.17	0.17	0.27	0.36	0.47	0.58	0.64	0.70
650	0.04	0.06	0.15	0.26	0.32	0.42	0.52	0.61	0.68
675	0.03	0.08	0.12	0.15	0.20	0.24	0.28	0.37	0.42

Fig. 4 C

TABLE 11.

Absorbance of varying concentration of malachite green in presence of different concentrations of SPSA, STSA and SXSA at 640 mμ: pH 2.72.

Conc. of dye $\times 10^{-5}$ M	Conc. of soap $\times 10^{-5}$ M	Absorbance		
		SPSA	STSA	SXSA
4.0	33.3	1.30	1.23	1.23
4.0	53.3	1.34	1.25	1.38
4.0	80.0	1.32	1.19	1.60
6.0	33.3	1.73	1.68	1.62
6.0	53.3	1.78	1.70	1.79
6.0	80.0	1.73	1.64	1.96

TABLE 12

Absorbance of varying concentrations of malachite green in presence of different concentrations of SPSA, STSA and SXSA at 640 mμ: pH 7.00

Conc. of dye $\times 10^{-5}$ M	Conc. of soap $\times 10^{-5}$ M	Absorbance SPSA	Absorbance STSA	Absorbance SXSA
4.0	33.3	1.34	1.48	1.42
4.0	53.3	1.37	1.52	1.56
4.0	80.0	1.43	1.51	1.62
6.0	33.3	1.78	1.94	1.92
6.0	53.3	1.80	2.00	2.00
6.0	80.0	1.85	1.94	2.00

TABLE 13

Absorbance of varying concentrations of malachite green in presence of different concentrations of SPSA, STSA and SXSA at 640 mμ: pH 9.12

Conc. of dye x 10^{-5} M	Conc. of soap x 10^{-5} M	Absorbance SPSA	Absorbance STSA	Absorbance SXSA
4.0	33.3	1.05	1.60	1.42
4.0	53.3	1.35	1.50	1.56
4.0	80.0	1.51	1.54	1.62
6.0	33.3	1.40	2.00	1.92
6.0	53.3	1.71	2.00	2.00
6.0	80.0	1.93	2.02	2.02

TABLE 14

Absorption spectra of different concentrations of rhodamine 6G.

Wave length in mμ	Absorbance for different concentrations of rhodamine 6G ($\times 10^{-6}$M)			
	1	2	3	4
	4.0	8.0	12.0	28.0
450	0.02	0.02	0.03	0.09
475	0.04	0.04	0.14	0.26
500	0.07	0.25	0.45	0.70
525	0.19	0.56	0.90	1.30
535	0.26	0.62	0.95	1.70
545	0.13	0.38	0.60	0.88
575	0.08	0.26	0.45	0.60
600	0.04	0.20	0.30	0.50

Fig. 1B

Rhodamine 6G - sulphonated phenyl stearic acid.

TABLE 15

Absorption spectra of 1.2 x 10^{-5} M rhodamine 6G in presence of different concentrations of SPSA(order 10^{-5}M) at pH 2.72.

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.20	0.25	0.36	0.40	0.48	0.52	0.60	0.63	0.68
525	0.30	0.52	0.62	0.64	0.64	0.74	0.79	0.77	0.80
535	0.38	0.58	0.69	0.72	0.84	0.88	0.95	0.95	1.00
545	0.28	0.62	0.72	0.82	0.88	1.00	1.04	1.04	1.10
575	0.04	0.14	0.14	0.15	0.19	0.20	1.26	0.24	0.27
600	0.02	0.10	0.10	0.09	0.11	0.12	0.13	0.12	0.13

Fig. 5 A

TABLE 16

Absorption spectra of 1.2 x 10^{-5} M rhodamine 6G in presence of different concentrations of SPSA (order 10^{-5}M) at pH 7.00

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.09	0.35	0.40	0.42	0.45	0.48	0.50	0.54	0.60
525	0.54	0.55	0.59	0.62	0.65	0.66	0.72	0.79	0.85
535	0.56	0.62	0.64	0.74	0.77	0.82	0.85	0.92	0.98
545	0.48	0.61	0.68	0.78	0.85	0.88	0.92	1.00	1.04
575	0.16	0.12	0.16	0.20	0.20	0.18	0.24	0.22	0.28
600	0.08	0.06	0.06	0.10	0.11	0.09	0.14	0.12	0.15

Fig. 5 B

TABLE 17.

Absorption spectra of 1.2 x 10^{-5} M rhodamine 6G in presence of different concentrations of SPSA (order 10^{-5} M) at pH 9.12

Wave length in mµ	Absorbance of rhodamine 6G for different concentrations of SPSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.30	0.32	0.34	0.32	0.38	0.40	0.42	0.48	0.50
525	0.62	0.61	0.64	0.68	0.67	0.77	0.72	0.77	0.95
535	0.64	0.66	0.77	0.82	0.85	0.88	0.77	0.92	1.10
545	0.58	0.65	0.79	0.88	0.92	1.00	1.00	1.10	1.20
575	0.13	0.12	0.13	0.12	0.20	0.23	0.17	1.21	0.29
600	0.08	0.07	0.08	0.08	0.10	0.12	0.14	1.15	0.18

Fig. 5 C

Rhodamine 6G-sulphonated tolyl stearic acid.

TABLE 18A

Absorption spectra of 1.2×10^{-5} M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5} M) at pH 2.72.

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.12	0.13	0.18	0.24	0.29	0.32	0.40	0.39	0.38
525	0.31	0.35	0.53	0.60	0.62	0.70	0.72	0.72	0.75
535	0.35	0.38	0.58	0.74	0.75	0.89	0.87	0.85	0.89
545	0.31	0.42	0.68	0.82	0.82	0.95	1.00	0.95	1.00
575	0.13	0.35	0.46	0.32	0.36	0.21	0.20	0.25	0.24
600	0.06	0.20	0.23	0.23	0.24	0.13	0.12	0.14	0.13

Fig. 6 A

TABLE 18B

Absorption spectra of 1.2 x 10^{-5} M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5}M) at pH 7.00

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.40	0.37	0.32	0.34	0.40	0.41	0.42	0.46	0.49
525	0.56	0.50	0.52	0.56	0.60	0.61	0.64	0.69	0.70
535	0.59	0.52	0.58	0.66	0.69	0.74	0.80	0.82	0.88
545	0.52	0.54	0.62	0.72	0.75	0.79	0.85	0.88	0.92
575	0.08	0.14	0.11	0.12	0.13	0.16	0.13	0.17	0.20
600	0.03	0.08	0.07	0.07	0.07	0.10	0.08	0.11	0.12

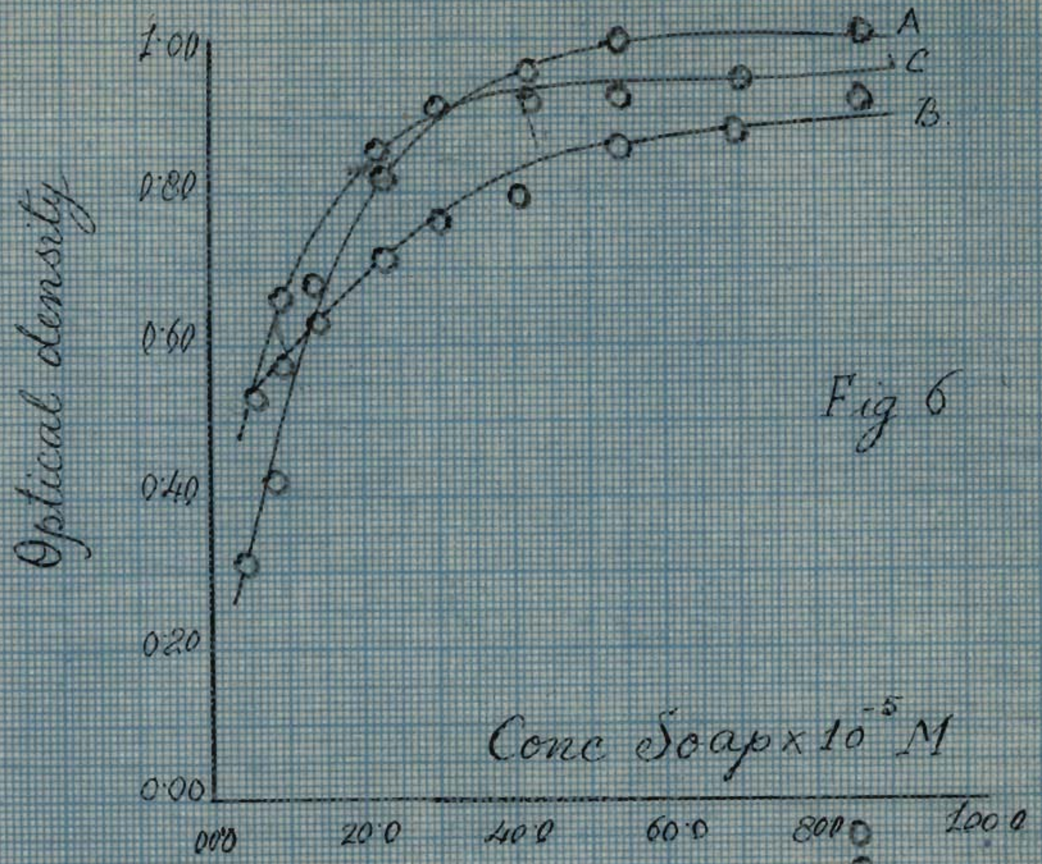
Fig. 6 B

TABLE 19

Absorption spectra of 1.2×10^{-5} M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5} M) at pH 9.12

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of STSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.36	0.37	0.26	0.32	0.36	0.40	0.42	0.45	0.46
525	0.60	0.62	0.56	0.66	0.69	0.71	0.70	0.72	0.75
535	0.64	0.68	0.64	0.82	0.85	0.88	0.85	0.92	0.90
545	0.52	0.67	0.64	0.85	0.92	0.92	0.92	0.95	1.00
575	0.08	0.10	0.07	0.13	0.11	0.18	0.11	0.13	0.18
600	0.03	0.03	0.02	0.05	0.07	0.09	0.02	0.08	0.10

Fig. 6 C


1·00
0·80
0·60
0·40
0·20
0·00
Optical density
Conc Soap × 10⁻⁵ M
00·0
20·0
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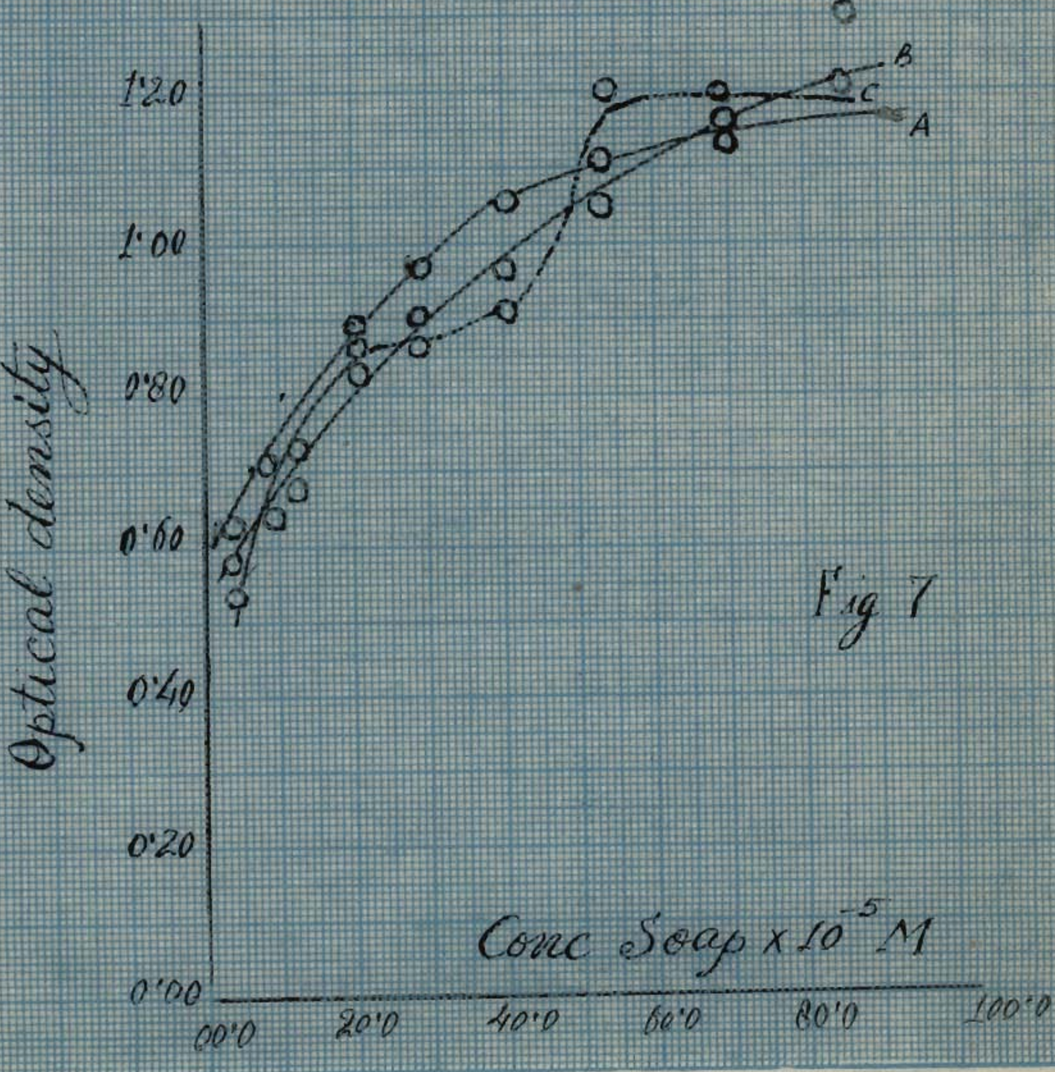
60·0
80·0
100·0
A
C
B.

Fig 6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0·80
0·60
0·40
0·20
0·00
Optical density
Conc Soap × 10⁻⁵ M
00·0
20·0
40·0
60·0
80·0
100·0
B
C
A

Fig 7

Rhodamine 6G -sulphonated xylyl stearic acid.

TABLE 20

Absorption spectra of 1.2×10^{-5}M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5}M) at pH 2.72.

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.40	0.41	0.38	0.43	0.48	0.52	0.60	0.63	0.78
525	0.60	0.52	0.52	0.72	0.80	0.85	0.85	0.95	1.10
535	0.68	0.54	0.64	0.77	0.88	0.95	1.00	1.04	1.22
545	0.62	0.65	0.66	0.88	0.95	1.04	1.10	1.12	1.34
575	0.21	0.20	0.50	0.56	0.52	0.50	0.56	0.56	0.64
600	0.08	0.09	0.20	0.26	0.25	0.22	0.20	0.20	0.23

Fig. 7 A

TABLE 21

Absorption spectra of 1.2 x 10^{-5}M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5}M) at pH 7.00

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.38	0.40	0.38	0.37	0.40	0.40	0.48	0.52	0.70
525	0.60	0.66	0.69	0.68	0.79	0.79	0.88	0.95	1.15
535	0.68	0.69	0.70	0.77	0.82	0.90	1.00	1.10	1.20
545	0.62	0.70	0.72	0.82	0.88	0.95	1.04	1.15	1.30
575	0.29	0.25	0.21	0.25	0.37	0.35	0.39	0.52	0.58
600	0.12	0.10	0.10	0.10	0.20	0.20	0.21	0.26	0.27

Fig.7 B

TABLE 22.

Absorption spectra of 1.2×10^{-5} M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5} M) at pH 9.12

Wave length in mμ	Absorbance of rhodamine 6G for different concentrations of SXSA								
	1	2	3	4	5	6	7	8	9
	4.0	8.0	12.0	20.0	28.0	40.0	52.0	68.0	84.0
500	0.32	0.41	0.38	0.43	0.42	0.43	0.54	0.56	0.58
525	0.58	0.61	0.60	0.70	0.71	0.80	0.98	0.99	1.00
535	0.60	0.66	0.60	0.75	0.86	0.90	1.10	1.12	1.12
545	0.56	0.64	0.65	0.84	0.90	0.95	1.20	1.18	1.20
575	0.14	0.21	0.25	0.25	0.30	0.36	0.45	0.46	0.50
600	0.08	0.10	0.13	0.12	0.14	0.20	0.21	0.23	0.25

Fig. 7 C

TABLE 23

Absorbance of varying concentrations of rhodamine 6G in presence of different concentrations of SPSA, STSA and SXSA at 545 mμ: pH 2.72

Conc. of dye $\times 10^{-5}$ M	Conc. of soap $\times 10^{-5}$ M	Absorbance		
		SPSA	STSA	SXSA
1.80	33.3	1.45	1.34	1.59
1.80	53.3	1.44	1.37	1.65
1.80	80.0	1.46	1.33	1.81
2.40	33.3	1.85	1.75	2.22
2.40	53.3	1.79	1.65	2.08
2.40	80.0	1.83	1.68	2.26

TABLE 24

Absorbance of varying concentrations of rhodamine 6G in presence of different concentrations of SPSA, STSA and SXSA at 545 mμ: pH 7.00

Conc. of dye	Conc. of soap	Absorbance		
x 10^{-5}M	x 10^{-5}M	SPSA	STSA	SXSA
1.80	33.3	1.31	1.28	1.54
1.80	53.3	1.26	1.27	1.56
1.80	80.0	1.36	1.26	1.70
2.40	33.3	1.62	1.67	2.03
2.40	53.3	1.64	1.59	2.03
2.40	80.0	1.70	1.59	2.08

TABLE 25

Absorbance of varying concentrations of rhodamine 6G in presence of different concentrations of SPSA,STSA and SXSA at 545 mμ: pH 9.12

Conc.of dye $\times 10^{-5}$M	Conc.of soap $\times 10^{-5}$M	Absorbance		
		SPSA	STSA	SXSA
1.80	33.3	1.37	1.30	1.42
1.80	53.3	1.40	1.28	1.56
1.80	80.0	1.45	1.29	1.60
2.40	33.3	1.70	1.64	1.80
2.40	53.3	1.73	1.62	1.90
2.40	80.0	1.77	1.56	2.00

Alizarin red S -cetyl trymethyl ammonium bromide.

TABLE 26

Absorption spectra of 6.66×10^{-5} M alizarin red S in presence of different concentrations of CTMAB (order 10^{-5} M) pH 2.00

Wave length in mμ	Absorbance of alizarin red S for different concentrations of CTMAB							
	1	2	3	4	5	6	7	8 .
	0.0	3.3	6.6	10.0	13.3	33.3	53.3	80.0
325	0.12	0.11	0.11	0.11	0.12	0.12	0.13	0.14
350	0.11	0.09	0.09	0.09	0.09	0.09	0.09	0.11
375	0.13	0.11	0.10	0.10	0.10	0.10	0.11	0.12
400	0.19	0.16	0.14	0.14	0.15	0.16	0.16	0.17
415	0.20	0.17	0.17	0.17	0.16	0.18	0.20	0.19
425	0.19	0.16	0.17	0.17	0.18	0.20	0.20	0.21
450	0.12	0.12	0.14	0.14	0.15	0.16	0.17	0.18
475	0.04	0.06	0.08	0.08	0.07	0.07	0.08	0.10
500	0.005	0.02	0.03	0.03	0.02	0.01	0.02	0.05

Fig. 8A

TABLE 27

Absorption spectra of 6.66×10^{-5} M alizarin red S in presence of different concentrations of CTMAB (order 10^{-5} M) at pH 7.00

Wave length in mμ	Absorbance of alizarin red S for different concentrations of CTMAB							
	1	2	3	4	5	6	7	8
	0.00	3.3	6.6	10.0	13.3	33.3	53.3	80.0
325	0.48	0.35	ppt	ppt	ppt	0.31	0.37	0.38
350	0.27	0.22				0.30	0.31	0.36
375	0.10	0.09				0.15	0.18	0.18
400	0.07	0.06				0.07	0.10	0.09
425	0.11	0.09				0.06	0.07	0.07
450	0.19	0.17				0.11	0.11	0.11
475	0.29	0.26				0.18	0.19	0.19
500	0.35	0.31				0.27	0.28	0.27
515	0.37	0.32				0.29	0.31	0.30
525	0.36	0.31				0.31	0.32	0.33
550	0.29	0.28				0.31	0.34	0.36
575	0.18	0.21				0.29	0.31	0.32
600	0.08	0.14				0.22	0.25	0.25

TABLE 28

Absorption spectra of 6.66×10^{-5} M alizarin red S in presence of different concentrations of CTMAB (order 10^{-5}M) at pH 9.12

Wave length in mμ	Absorbance of alizarin red S for different concentrations of CTMAB							
	1	2	3	4	5	6	7	8
	0.0	3.3	6.6	10.0	13.3	33.3	53.3	80.0
325	0.20	0.24	0.27	0.32	0.32	0.26	0.33	0.38
350	0.16	0.17	0.24	0.32	0.30	0.23	0.29	0.31
375	0.17	0.14	0.19	0.28	0.25	0.14	0.16	0.18
400	0.21	0.18	0.16	0.19	0.18	0.11	0.11	0.12
425	0.28	0.22	0.16	0.17	0.16	0.12	0.13	0.13
445	0.30	0.24	0.18	0.17	0.17	0.16	0.15	0.14
475	0.21	0.22	0.19	0.19	0.21	0.21	0.22	0.24
500	0.11	0.20	0.22	0.24	0.26	0.22	0.25	0.27
525	0.05	0.18	0.24	0.29	0.30	0.22	0.27	0.28
550	0.02	0.16	0.22	0.29	0.31	0.22	0.28	0.30
575	0.01	0.12	0.20	0.27	0.30	0.20	0.25	0.26
600	0.006	0.07	0.17	0.23	0.26	0.17	0.20	0.21

Fig. 8 B

TABLE 29

Absorbance of varying concentrations of alizarin red S for different concentrations of CTMAB at different pHs.

Conc. of dye $\times 10^{-5}$ M	Conc. of soap $\times 10^{-5}$ M	Absorption at different pH		
		(2.00) at 415 mμ	(7.00) at 515 mμ	(9.12) at 445 mμ
1.33	33.3	0.025	0.065	0.035
10.0	200.0	0.32	0.45	0.28
10.0	466.6	0.33	0.46	0.24
13.3	200.0	0.42	0.61	0.40
13.3	466.6	0.44	0.60	0.33

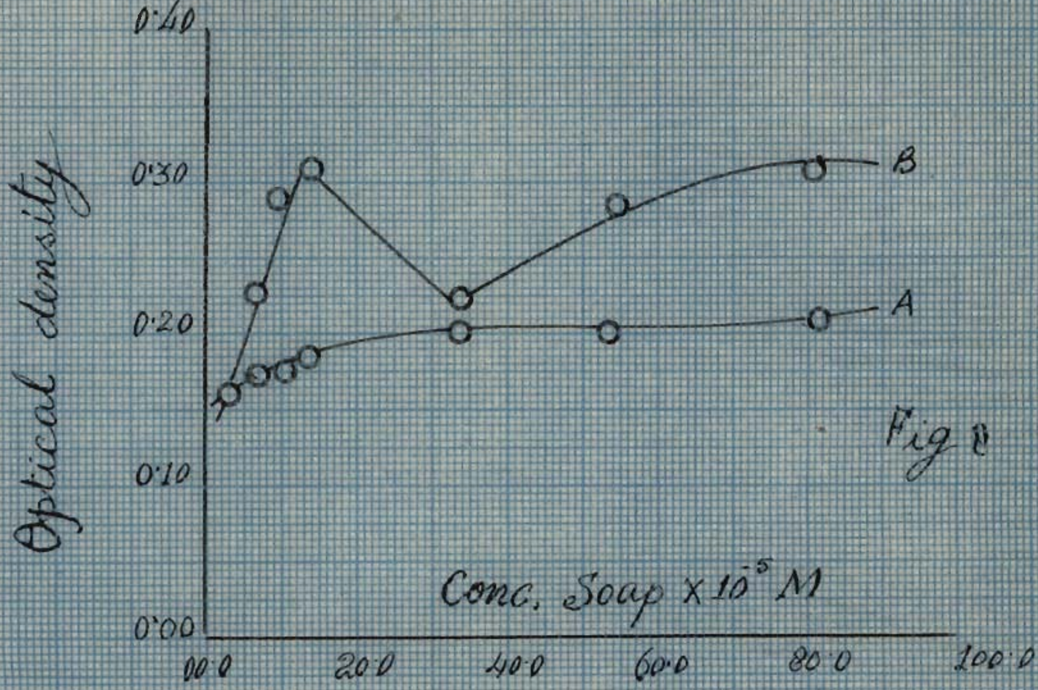

0·40
0·30
0·20
0·10
0·00
Optical density
B
A
Conc. Soap x 10^{-5} M
00·0
20·0
40·0
60·0
80·0
100·0

Fig 8

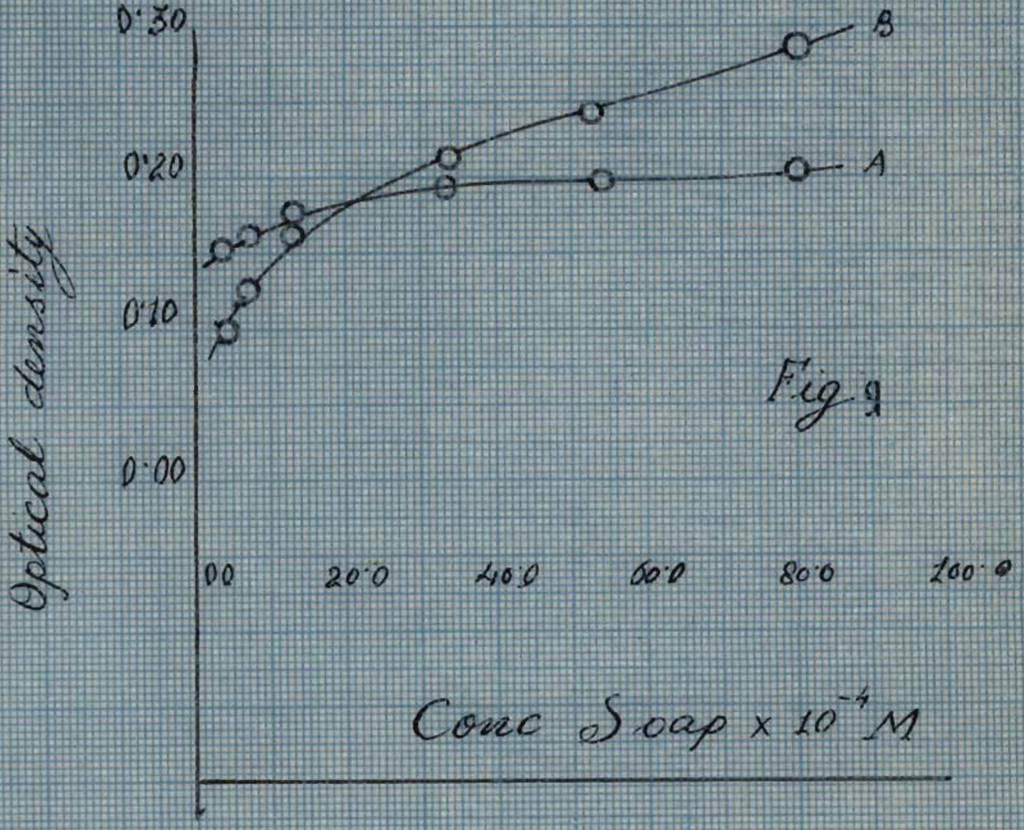

0·30
0·20
0·10
0·00
Optical density
B
A
00
20·0
40·0
60·0
80·0
100·0
Conc Soap x 10^{-4} M

Fig 9

Alizarin red S - cetyl pyridinium bromide.

TABLE 30

Absorption spectra of 6.66 x 10^{-5} M alizarin red S in presence of different concentrations of CPB (order 10^{-3} M) at pH 2.00

Wave length in mμ	Absorbance of alizarin red S for different concentrations of CPB						
	1	2	3	4	5	6	7
	3.3	6.6	10.0	13.3	33.3	53.3	80.0
325	0.11	0.11	0.11	0.12	0.12	0.13	0.14
350	0.09	0.09	0.09	0.09	0.09	0.09	0.11
375	0.11	0.10	0.10	0.10	0.10	0.10	0.12
400	0.16	0.14	0.14	0.15	0.16	0.16	0.17
415	0.17	0.17	0.17	0.16	0.18	0.20	0.19
425	0.16	0.17	0.17	0.18	0.20	0.20	0.21
450	0.12	0.14	0.14	0.15	0.16	0.17	0.18
475	0.06	0.08	0.08	0.07	0.07	0.08	0.10
500	0.02	0.03	0.03	0.02	0.01	0.02	0.04

Fig. 9 A

TABLE 31

Absorption spectra of 6.66×10^{-5} M alizarin red S in presence of different concentrations of CPB (order 10^{-4}M) at pH 7.00

Wave length in mµ	Absorbance of alizarin red S for different concentrations of CPB						
	1	2	3	4	5	6	7
	3.3	6.6	10.0	13.3	33.3	53.3	80.0
325	0.40	ppt	ppt	ppt	ppt	0.36	0.39
350	0.27					0.33	0.37
375	0.12					0.18	0.19
400	0.08					0.10	0.10
425	0.11					0.07	0.06
450	0.18					0.10	0.10
475	0.27					0.17	0.17
500	0.32					0.25	0.25
515	0.34					0.29	0.30
525	0.33					0.31	0.32
550	0.29					0.34	0.35
575	0.22					0.31	0.31
600	0.19					0.24	0.24

TABLE 32

Absorption spectra of 6.66×10^{-5} M alizarin red S in presence of different concentrations of CPB (order 10^{-4} M) at pH 9.12

Wave length in mμ	Absorbance of alizarin red S for different concentrations of CPB						
	1	2	3	4	5	6	7
	3.3	6.6	10.0	13.0	33.3	53.3	80.0
325	0.26	0.24	0.25	0.24	0.28	0.31	0.36
350	0.18	0.19	0.20	0.19	0.24	0.28	0.32
375	0.16	0.17	0.17	0.13	0.13	0.15	0.17
400	0.22	0.20	0.18	0.12	0.10	0.11	0.11
425	0.28	0.24	0.20	0.15	0.13	0.13	0.10
445	0.29	0.26	0.21	0.19	0.17	0.17	0.13
475	0.25	0.22	0.25	0.21	0.22	0.22	0.19
500	0.18	0.17	0.18	0.21	0.22	0.23	0.23
525	0.13	0.15	0.17	0.19	0.22	0.24	0.26
550	0.11	0.13	0.16	0.17	0.21	0.25	0.28
575	0.09	0.12	0.16	0.15	0.19	0.22	0.26
600	0.07	0.11	0.14	0.12	0.15	0.18	0.20

Fig. 9 B

TABLE 33

Absorbance of varying concentrations of alizarin red S in presence of different concentrations of CPB at different pHs

Conc.of dye x 10^{-5} M	Conc.of soap x 10^{-5} M	Absorbance at different pH		
		(2.00) at 415 mμ	(7.00) at 515 mμ	(9.12) at 445 mμ
1.33	33.3	0.025	0.065	0.035
10.0	200.0	0.30	0.44	0.30
10.0	466.6	0.30	0.44	0.29
13.3	200.0	0.39	0.60	0.37
13.3	466.6	0.40	0.57	0.30

RESULTS AND DISCUSSION

There can be several causes for the spectral shift in the dye maximum on the addition of soaps. These are: change in the pH of the dye solution, disturbance in the monomer-polymer equilibrium of the dye(31,35), interaction between the dye and the soap molecules(3,31,36) etc. Therefore, it was considered necessary, before arriving at some conclusion on the possible interaction between the dye and the soap on the basis of spectrophotometric studies, to know the molecular state of the dye in solution. It was observed that no shift in the dye spectra took place with change in concentration and Beer Lambert's law was obeyed over wide concentration ranges: 4.0×10^{-6}M to 6.0×10^{-5}M, 4.0×10^{-6}M to 4.0×10^{-5}M and 4.0×10^{-5}M to 15.0×10^{-5}M for malachite green, rhodamine 6G and alizarin red S respectively(Fig.1 A,B,). This indicated that in the reported concentrations the three dyes remained in the monomeric form and thus the possibility of the existence of associated molecules in these concentration ranges was completely ruled out.

Anionic soaps and basic dyes: The effect of SPSA, STSA and SXSA on the maximum of malachite green and rhodamine 6G is given in table 1 and the amount of the soap which brings the change in maximum are also reported.

TABLE 1

The amount of the soap which changes the maximum of the dye: malachite green-shift in maximum from 625 mμ to 640mμ.

pH	Concentration of the soap(order 10^{-5}M)		
	SPSA	STSA	SXSA
2.72	8.0	8.0	8.0
7.00	8.0	8.0	12.0
9.12	12.0	12.0	20.0
Rhodamine 6G-shift in maximum from 535 mμ to 545 mμ.			
2.72	8.0	8.0	12.0
7.00	8.0	10.0	12.0
9.12	10.0	12.0	18.0

It was, therefore, inferred that the addition of small amount of soap, as low as 8.0×10^{-5}M, brought about a shift in maximum from 625 mμ to 640 mμ in the case of malachite green and from 535 mμ to 545 mμ in the case of rhodamine 6G. Moreover absorption measurements carried out at the new wavelengths(640 mμ and 545 mμ respectively) revealed large initial increases in the optical density in presence of the soaps(Figs 2-7). This observation was quite significant since it indicated definite binding of the dye with the soap, probably in the form of complex ions. At higher concentrations of the soap more or less a constant value of the optical density was reached.

Experiments carried out with basic dyes over a wide pH range(in buffers of pH 2.72,7.00 and 9.12) did not provide any evidence for the shift in the dye maximum with the change in pH.

The only possible way to explain the spectral shift under these conditions could be in terms of compound formation between the dye and the soap. The existence of such a complex could also be concluded from the dependence of the spectrum of the dye on soap concentration. The addition of gradually increasing amount of the soap to a fixed dye concentration should result in an increase in optical density up to a certain point. After this further addition should produce no appreciable changes in optical density due to all the possible dye cations entering into the complex formation. This is what was actually observed.

From the above observations it could be safely concluded that the spectral shifts were due to dye-detergent complex formation and other factors like pH of the dye solution,the monomer-polymer equilibrium etc. exert but little influence on soap-dye interaction. The data on the extent of binding calculated by Klotz's method are summarized in the following tables.

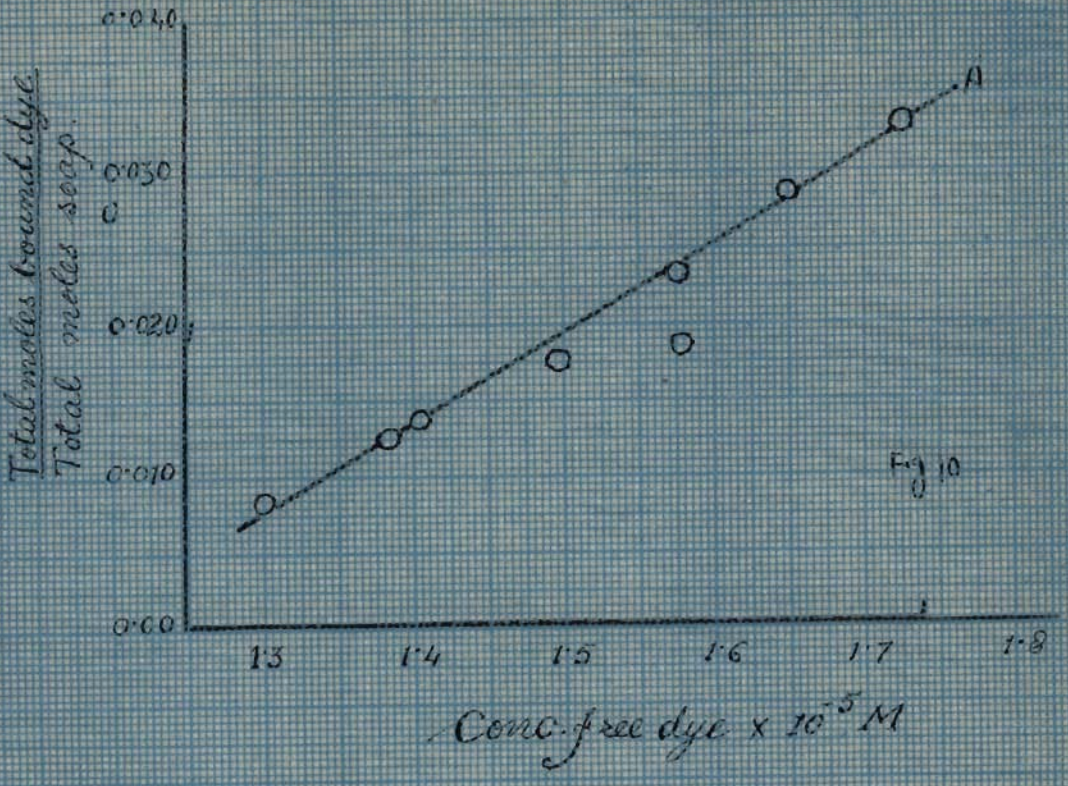
Sulphonated phenyl stearic acid-malachite green.

TABLE 2

Calculation of binding at pH 2.72

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app.	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	8.0	28000	0.86	1.72	0.28	0.035
2.0	12.0	30000	0.81	1.62	0.38	0.031
2.0	20.0	31000	0.80	1.60	0.40	0.020
2.0	28.0	33000	0.73	1.49	0.54	0.019
2.0	40.0	34000	0.70	1.40	0.60	0.015
2.0	52.0	34500	0.69	1.38	0.72	0.014
2.0	68.0	36000	0.65	1.30	0.70	0.010
2.0	84.0	34500	0.69	1.38	0.72	0.008
4.0	33.3	30700	0.80	3.20	0.80	0.024
4.0	53.3	31500	0.77	3.08	0.92	0.017
4.0	80.0	29700	0.82	3.28	0.18	0.002
6.0	33.3	28000	0.86	5.16	0.84	0.025
6.0	53.3	28300	0.86	5.14	0.86	0.016
6.0	80.0	26000	0.92	5.52	0.48	0.006

Fig.10 A


0·040
0·030
0·020
0·010
0·00
Total moles bound dye / Total moles soap.
1·3
1·4
1·5
1·6
1·7
1·8
Conc. free dye × 10⁻⁵ M
A
Fig 10

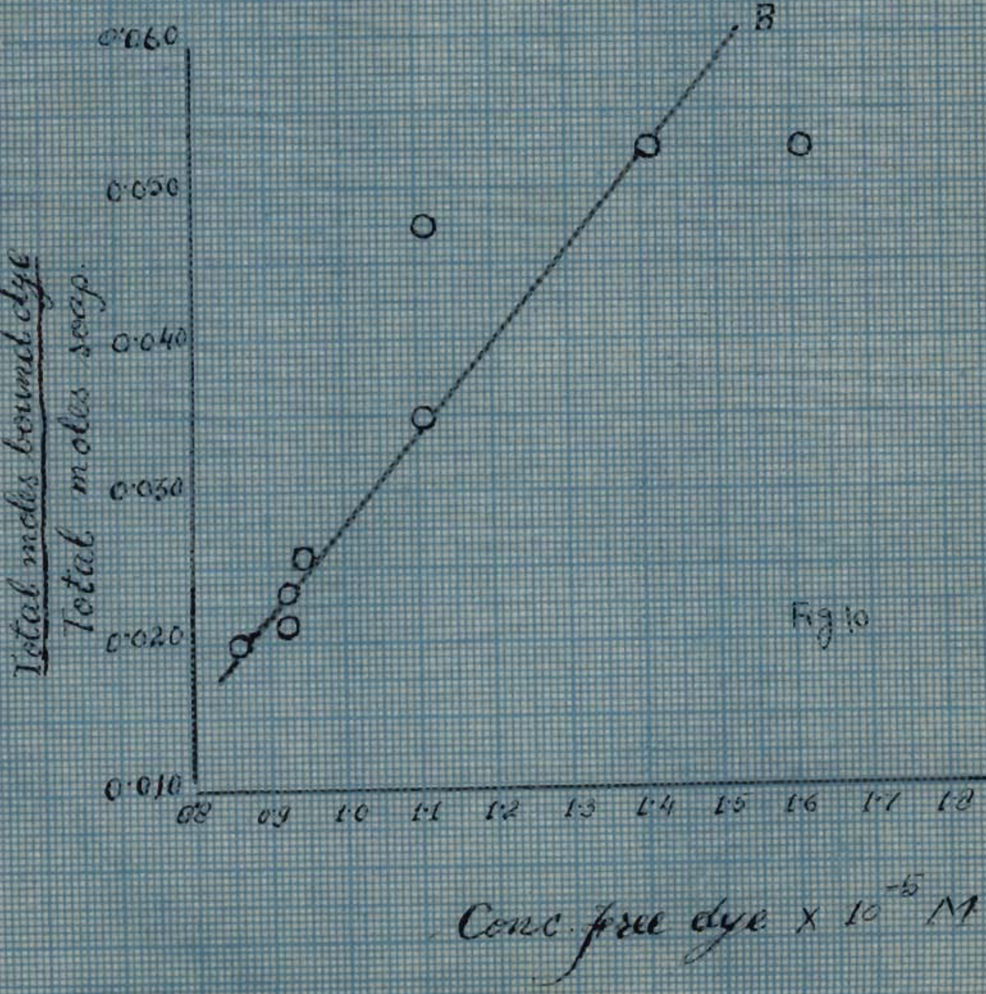

0·060
0·050
0·040
0·030
0·020
0·010
Total moles bound dye / Total moles soap.
0·8
0·9
1·0
1·1
1·2
1·3
1·4
1·5
1·6
1·7
1·8
Conc. free dye × 10⁻⁵ M
B
Fig 10

TABLE 3.

Calculation of binding at pH 7.00

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	8.0	31000	0.80	1.60	0.40	0.050
2.0	12.0	35000	0.70	1.40	0.60	0.050
2.0	20.0	39500	0.55	1.10	0.90	0.045
2.0	28.0	39500	0.55	1.10	0.90	0.032
2.0	40.0	42500	0.47	0.94	1.06	0.026
2.0	52.0	43000	0.46	0.92	1.08	0.020
2.0	68.0	43000	0.46	0.92	1.08	0.016
2.0	84.0	45000	0.40	0.80	1.20	0.014
4.0	33.3	37000	0.62	2.48	1.52	0.045
4.0	53.0	38000	0.60	2.40	1.60	0.030
4.0	80.0	38000	0.60	2.40	1.60	0.020
6.0	33.3	32300	0.75	4.50	1.50	0.045
6.0	53.3	33300	0.72	4.32	1.68	0.031
6.0	80.0	32300	0.75	4.50	1.50	0.019

Fig. 10.B

TABLE 4

Calculation of binding at pH 9.12

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵapp	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	12.0	26000	0.94	1.88	0.12	0.010
2.0	20.0	31500	0.77	1.54	0.46	0.023
2.0	28.0	37000	0.62	1.22	0.78	0.028
2.0	40.0	39500	0.55	1.12	0.90	0.022
2.0	52.0	40500	0.52	1.04	0.96	0.018
2.0	68.0	41000	0.50	1.00	1.00	0.014
2.0	84.0	45000	0.40	0.80	1.20	0.014
4.0	33.3	40000	0.54	2.16	1.84	0.055
4.0	53.3	37500	0.60	2.40	1.60	0.030
4.0	80.0	38500	0.58	2.32	1.68	0.021
6.0	33.3	33300	0.72	4.32	1.68	0.051
6.0	53.3	33300	0.72	4.32	1.68	0.031
6.0	80.0	33600	0.71	4.26	1.74	0.021

Fig. 10 C

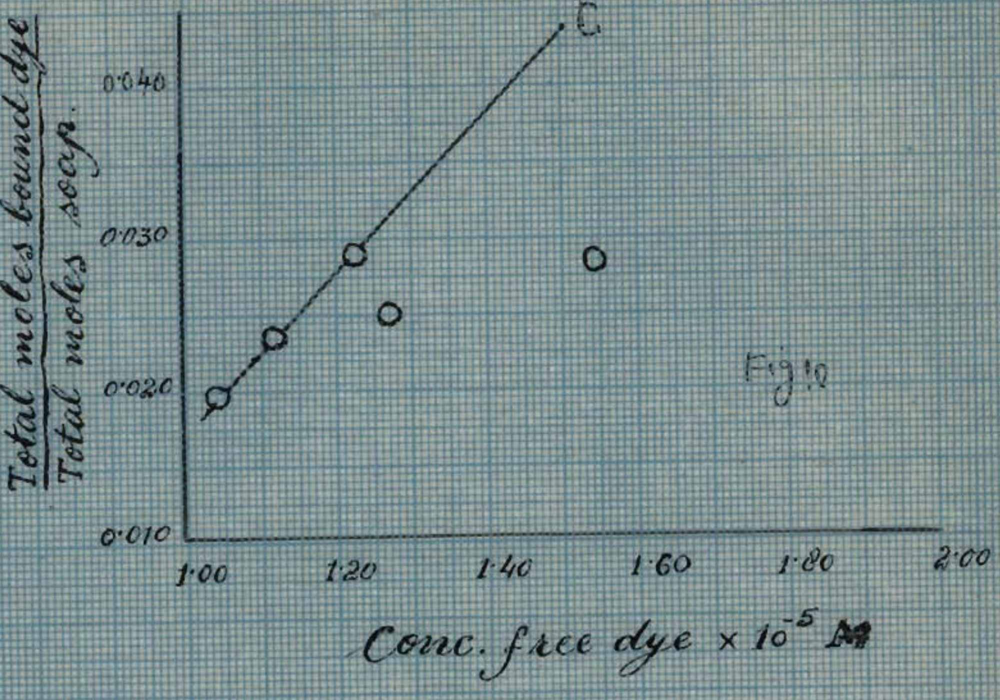

Total moles bound dye / Total moles soap.
0·040
0·030
0·020
0·010
C
1·00
1·20
1·40
1·60
1·80
2·00
Conc. free dye × 10^{-5} M

Fig 10

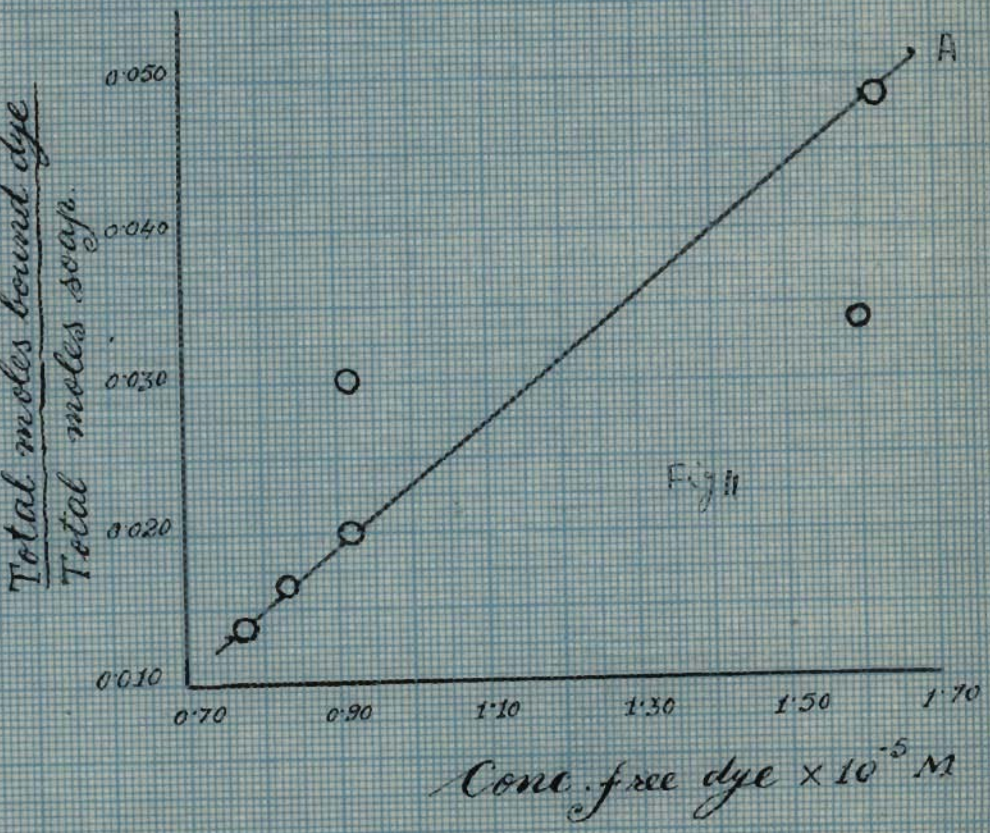

Total moles bound dye / Total moles soap.
0·050
0·040
0·030
0·020
0·010
A
0·70
0·90
1·10
1·30
1·50
1·70
Conc. free dye × 10^{-5} M

Fig 11

Sulphonated tolyl stearic acid-malachite green.

TABLE 5.

Calculation of binding at pH 2.72

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	8.0	30000	0.81	1.62	0.38	0.048
2.0	12.0	30500	0.80	1.60	0.40	0.033
2.0	20.0	40000	0.54	1.08	0.92	0.046
2.0	28.0	42500	0.47	0.94	1.06	0.039
2.0	40.0	43000	0.46	0.92	1.08	0.030
2.0	52.0	43000	0.46	0.92	1.08	0.020
2.0	68.0	44500	0.42	0.82	1.18	0.018
2.0	84.0	45500	0.39	0.78	1.22	0.014
4.0	33.3	32500	0.74	2.96	1.04	0.031
4.0	53.3	33500	0.72	2.88	1.12	0.021
4.0	80.0	33000	0.73	2.92	1.08	0.012
6.0	33.3	28800	0.84	5.04	0.96	0.029
6.0	53.3	29300	0.83	4.98	1.02	0.019
6.0	80.0	28800	0.84	5.04	0.96	0.012

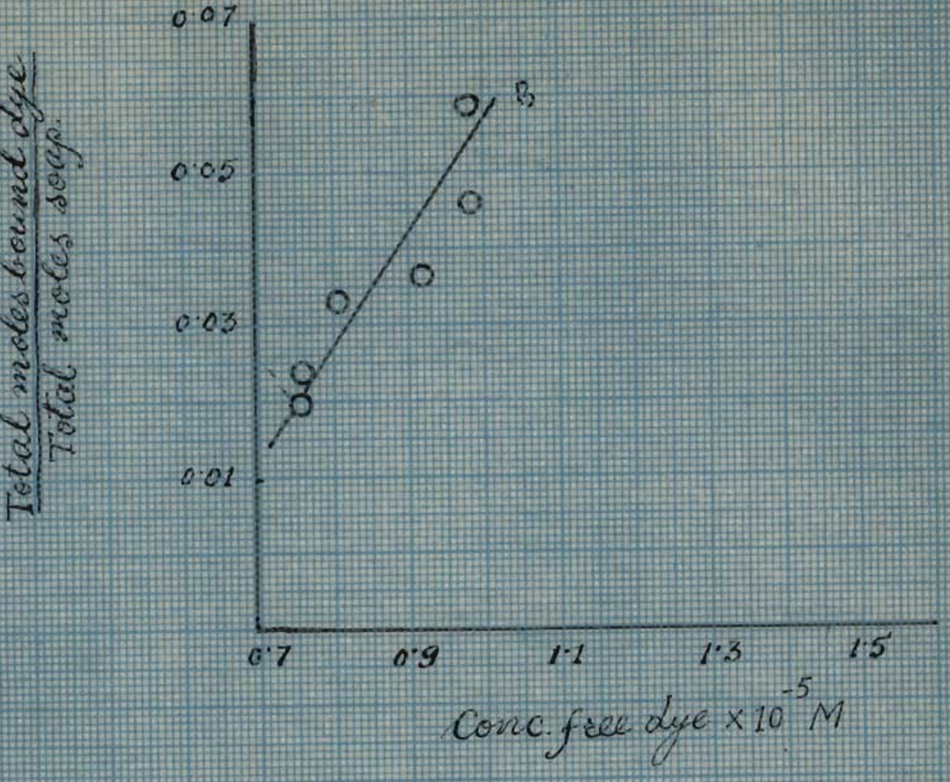
Fig. 11 A

TABLE 6

Calculation of binding at pH 7.00

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵapp	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	8.0	29000	0.84	1.68	0.32	0.040
2.0	12.0	38000	0.60	1.20	0.80	0.067
2.0	20.0	42000	0.49	0.98	1.02	0.050
2.0	28.0	42000	0.49	0.98	1.02	0.036
2.0	40.0	43000	0.46	0.92	1.08	0.027
2.0	52.0	45000	0.40	0.80	1.20	0.023
2.0	68.0	45500	0.39	0.78	1.22	0.018
2.0	84.0	46000	0.38	0.76	1.24	0.014
4.0	33.3	33500	0.72	2.88	1.12	0.033
4.0	53.3	34200	0.70	2.80	1.20	0.022
4.0	80.0	35700	0.66	2.64	1.36	0.017
6.0	33.3	29600	0.82	4.92	1.08	0.032
6.0	53.3	30000	0.81	4.86	1.14	0.021
6.0	80.0	30800	0.80	4.80	1.20	0.015

Fig. 11 B



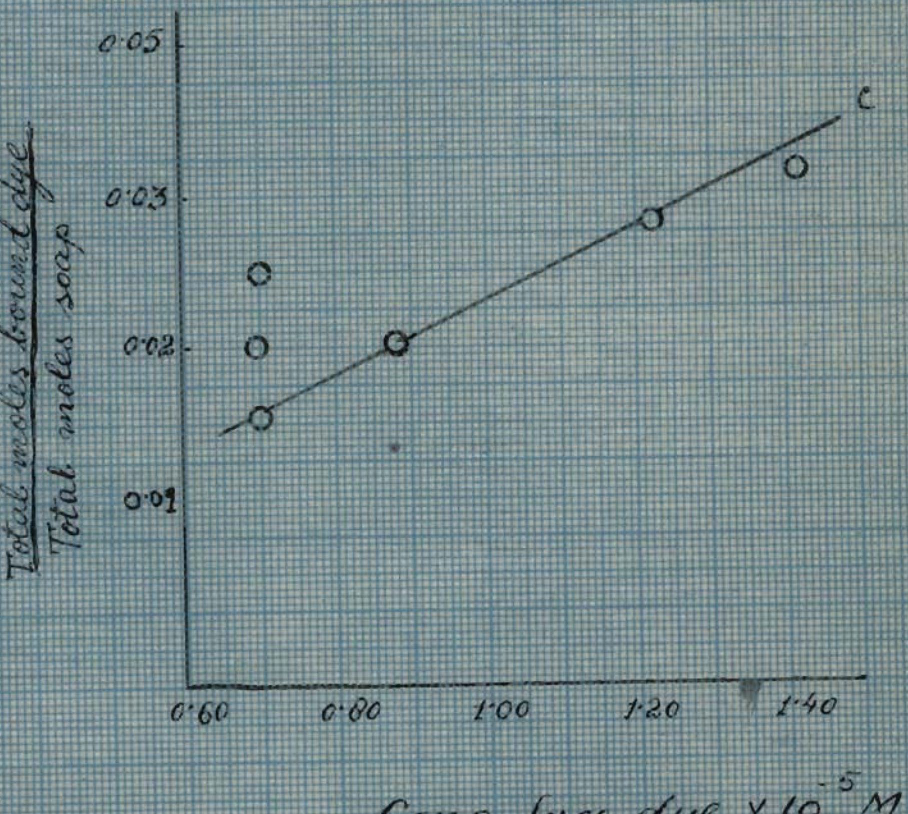


Fig 11

Conc. free dye × 10^{-5} M

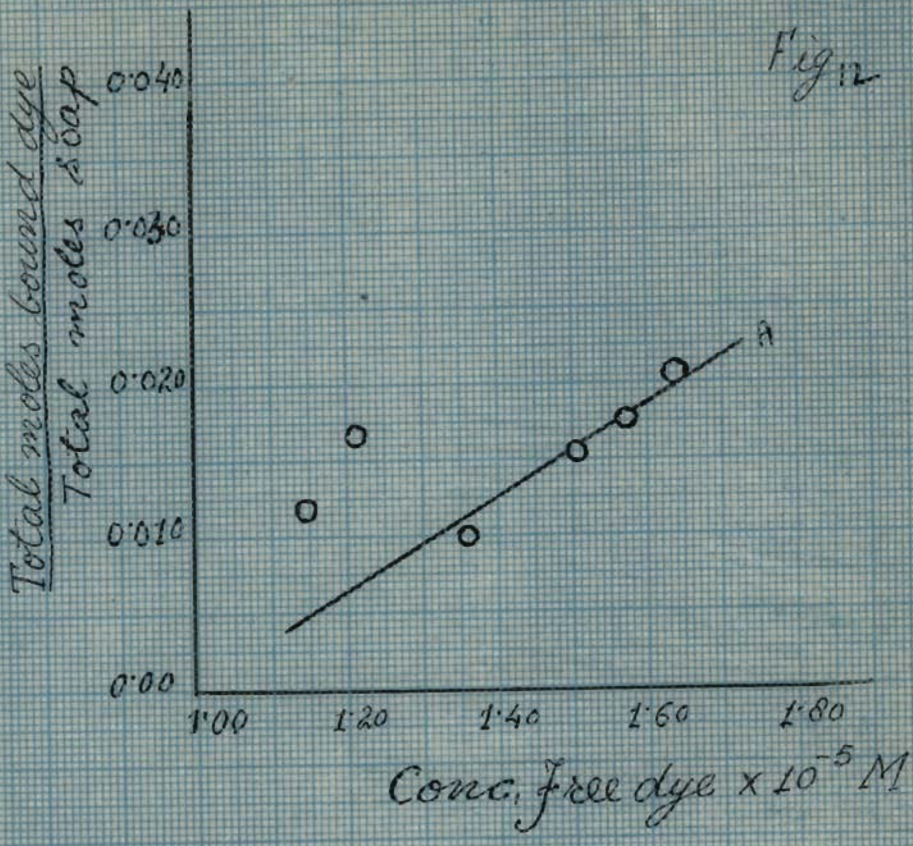


Fig 12

Total moles bound dye / Total moles soap
0·040
0·030
0·020
0·010
0·00
1·00
1·20
1·40
1·60
1·80
A
Conc. free dye x 10⁻⁵ M

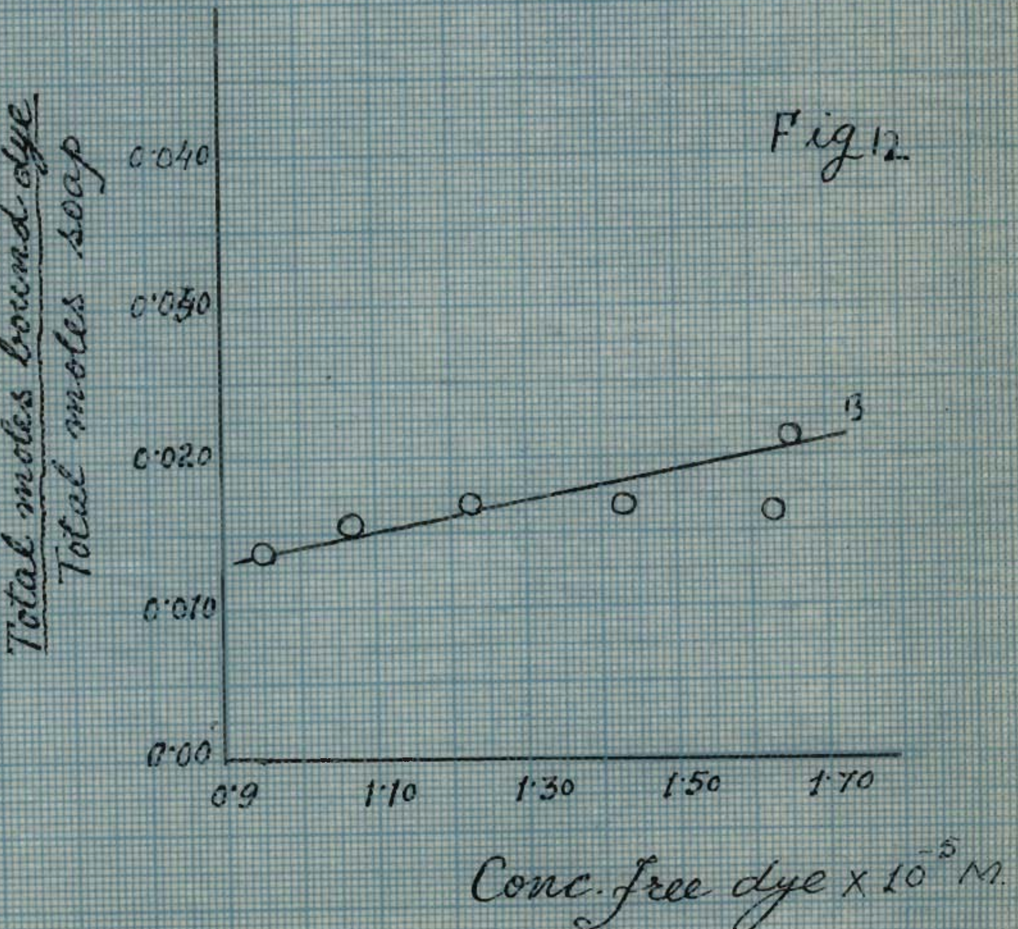


Fig 12

Total moles bound dye / Total moles soap
0·040
0·030
0·020
0·010
0·00
0·9
1·10
1·30
1·50
1·70
B
Conc. free dye x 10⁻⁵ M.

TABLE 9

Calculation of binding at pH 7.00

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵ_{app}	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	12.0	24000	0.97	1.94	0.06	0.005
2.0	20.0	30000	0.81	1.62	0.38	0.019
2.0	28.0	31000	0.80	1.60	0.40	0.014
2.0	40.0	34000	0.70	1.40	0.60	0.015
2.0	52.0	37000	0.60	1.20	0.80	0.015
2.0	68.0	40000	0.52	1.04	0.96	0.014
2.0	84.0	43000	0.46	0.92	1.08	0.012
4.0	33.3	35500	0.66	2.64	1.36	0.041
4.0	53.3	39000	0.57	2.28	1.72	0.032
4.0	80.0	40500	0.53	2.12	1.88	0.023
6.0	33.3	32000	0.75	4.50	1.50	0.045
6.0	53.3	33300	0.72	4.32	1.68	0.031
6.0	80.0	33700	0.71	4.26	1.74	0.021

Fig. 12 B

TABLE 10

Calculation of binding at pH 9.12

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵ_{app}	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	20.0	23500	0.98	1.96	0.04	0.002
2.0	28.0	29000	0.72	1.44	0.56	0.020
2.0	40.0	32000	0.60	1.20	0.80	0.020
2.0	52.0	35000	0.50	1.00	1.00	0.019
2.0	68.0	36500	0.40	0.80	1.20	0.018
2.0	84.0	37000	0.36	0.72	1.28	0.015
4.0	33.3	27500	0.87	3.48	0.52	0.016
4.0	53.3	38500	0.58	2.32	1.68	0.031
4.0	80.0	39000	0.56	2.24	1.76	0.022
6.0	33.3	27000	0.88	5.28	0.72	0.021
6.0	53.3	31030	0.78	4.68	1.32	0.024
6.0	80.0	32300	0.75	4.50	1.50	0.019

Fig. 12 C

Fig 12

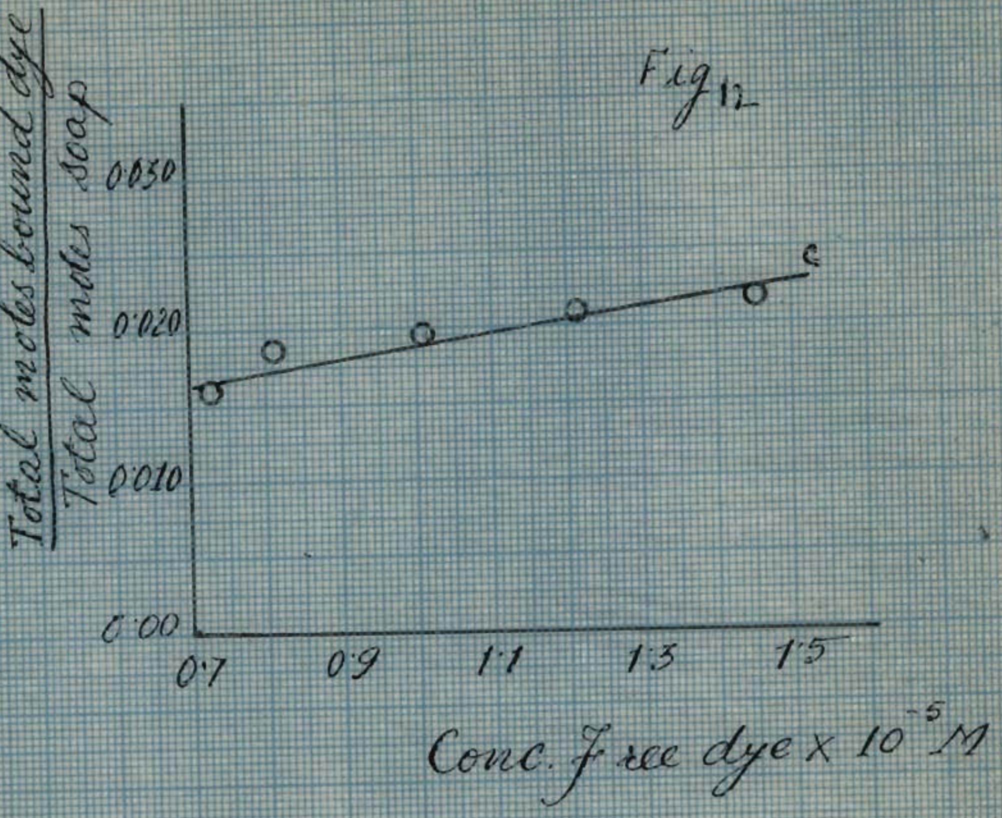
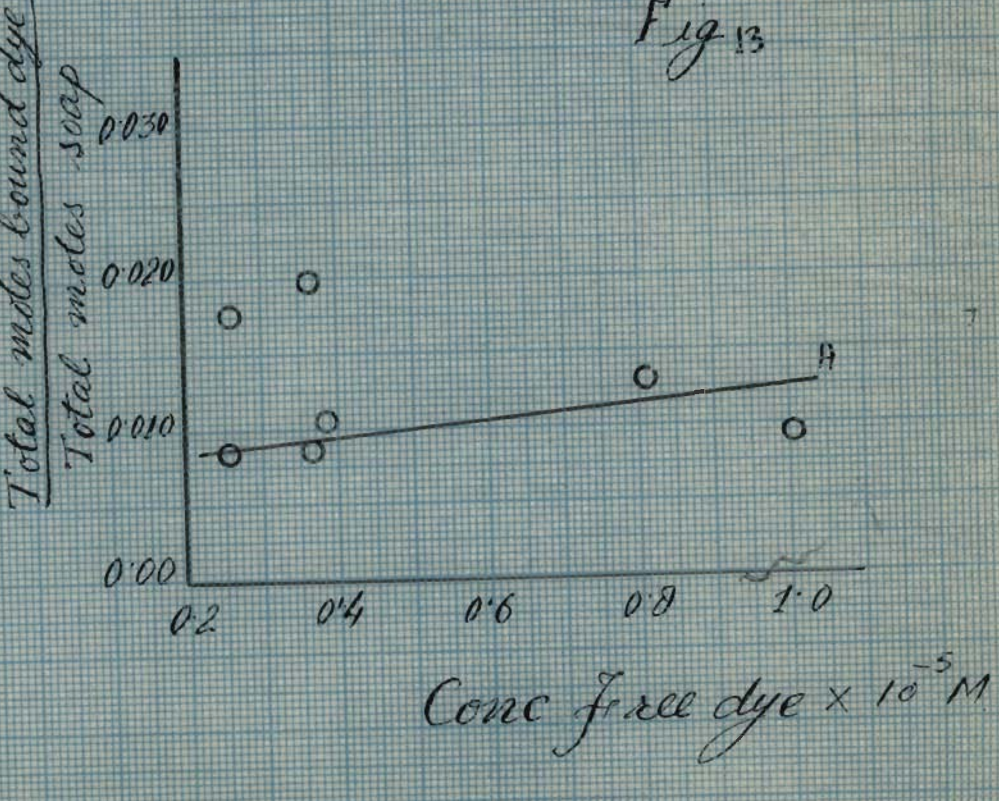

Total moles bound dye / Total moles soap
0·030
0·020
0·010
0·00
0·7
0·9
1·1
1·3
1·5
C
Conc. free dye × 10⁻⁵ M

Fig 13


Total moles bound dye / Total moles soap
0·030
0·020
0·010
0·00
0·2
0·4
0·6
0·8
1·0
A
Conc free dye × 10⁻⁵ M

Sulphonated phenyl stearic acid-rhodamine 6G

TABLE 11

Calculation of binding at pH 2.72

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵapp	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	68300	0.84	1.00	0.20	0.010
1.20	28.0	72000	0.67	0.80	0.40	0.014
1.20	40.0	80000	0.30	0.36	0.84	0.021
1.20	52.0	81600	0.22	0.26	0.94	0.018
1.20	68.0	78000	0.32	0.38	0.82	0.012
1.20	84.0	80000	0.30	0.36	0.84	0.010
1.80	33.3	80600	0.31	0.56	1.24	0.037
1.80	53.3	80000	0.30	0.56	1.24	0.023
1.80	80.0	81000	0.22	0.40	1.40	0.017
2.40	33.3	77000	0.44	1.06	1.34	0.040
2.40	53.3	75000	0.54	1.30	1.10	0.020
2.40	80.0	26200	0.48	1.15	1.25	0.015

Fig. 13 A

TABLE 12

Calculation of binding at pH 7.00

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	66000	0.95	1.14	0.06	0.003
1.20	28.0	67000	0.90	1.08	0.12	0.043
1.20	40.0	70000	0.77	0.92	0.30	0.007
1.20	52.0	72500	0.65	0.78	0.42	0.008
1.20	68.0	73300	0.61	0.73	0.47	0.007
1.20	84.0	75000	0.54	0.65	0.55	0.006
1.80	33.3	73000	0.63	1.13	0.67	0.021
1.80	53.3	70000	0.77	1.39	0.41	0.007
1.80	80.0	76000	0.49	0.88	0.92	0.011
2.40	33.3	67000	0.86	2.06	0.34	0.010
2.40	53.3	68000	0.80	1.92	0.48	0.009
2.40	80.0	70000	0.77	1.85	0.54	0.006

Fig. 13 B

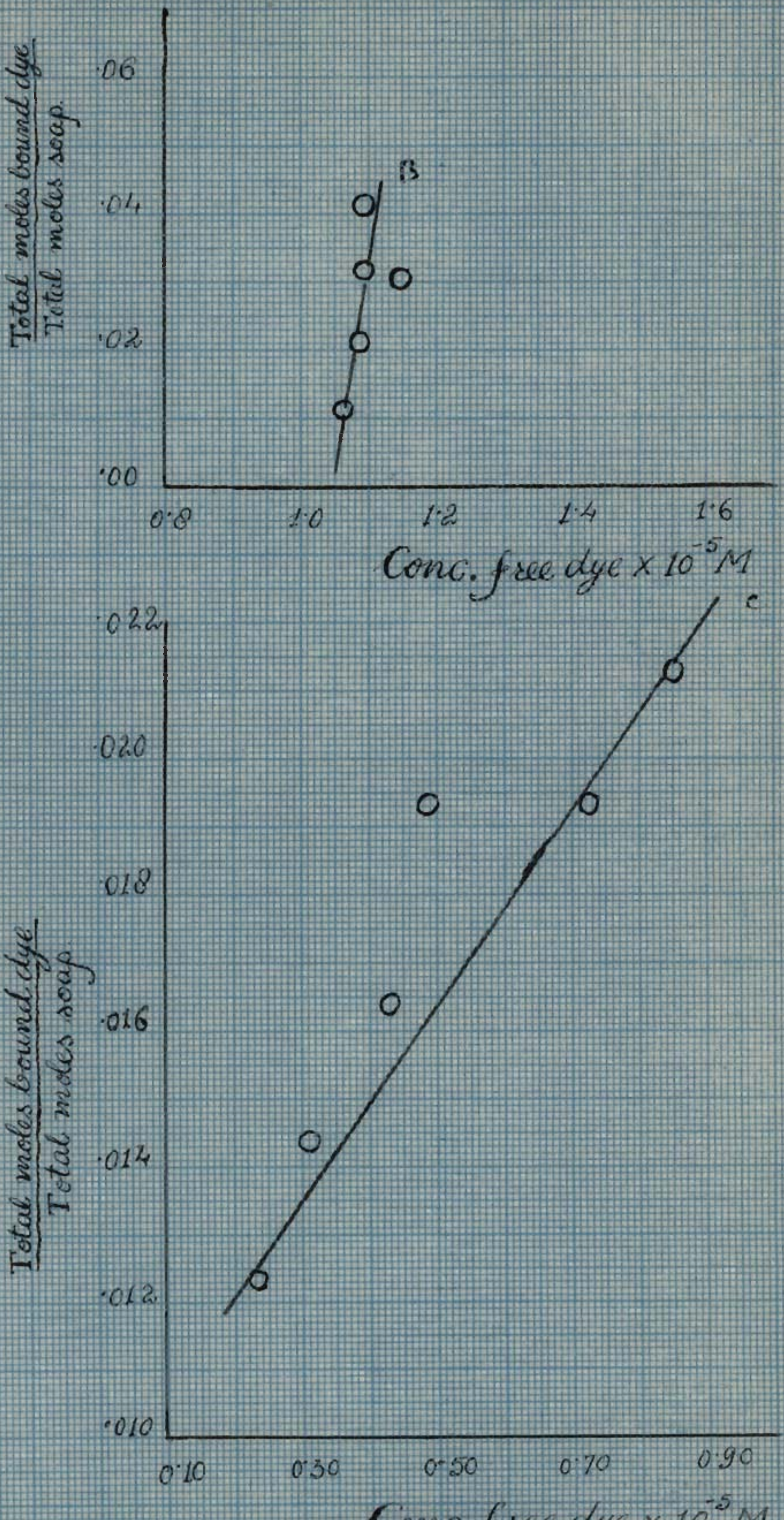


Fig 13

Total moles bound dye / Total moles soap
·06
·04
·02
·00
B
0·8
1·0
1·2
1·4
1·6
Conc. free dye × 10^{-5}M
Total moles bound dye / Total moles soap
·022
·020
·018
·016
·014
·012
·010
c
0·10
0·30
0·50
0·70
0·90
Conc. free dye × 10^{-5}M

TABLE 13

Calculation of binding at pH 9.12

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	Moles bound dye / Moles total soap
1.20	20.0	72500	0.65	0.78	0.42	0.021
1.20	28.0	75000	0.54	0.65	0.55	0.019
1.20	40.0	79000	0.34	0.41	0.79	0.019
1.20	52.0	80000	0.30	0.36	0.84	0.016
1.20	68.0	81800	0.22	0.26	0.94	0.014
1.20	84.0	83300	0.16	0.19	1.01	0.012
1.80	33.3	76000	0.48	0.86	0.94	0.022
1.80	53.3	77800	0.41	0.72	1.08	0.020
1.80	80.0	80000	0.31	0.56	1.24	0.015
2.40	33.3	70800	0.73	1.75	0.65	0.020
2.40	53.3	72080	0.67	1.61	0.79	0.014
2.40	80.0	74000	0.52	1.25	0.15	0.014

Fig. 13 C

Sulphonated tolyl stearic acid-rhodamine 6G

TABLE 14

Calculation of binding at pH 2.72

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵ app	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	68300	0.84	1.01	0.19	0.009
1.20	28.0	68300	0.84	1.01	0.19	0.007
1.20	40.0	78300	0.38	0.45	0.75	0.019
1.20	52.0	79000	0.35	0.41	0.79	0.015
1.20	68.0	80000	0.31	0.37	0.83	0.012
1.20	84.0	81700	0.23	0.28	0.92	0.011
1.80	33.3	74400	0.57	1.03	0.77	0.023
1.80	53.3	76000	0.48	0.86	0.94	0.017
1.80	80.0	74000	0.58	1.03	0.77	0.009
2.40	33.3	73000	0.63	1.61	0.79	0.024
2.40	53.3	68700	0.83	1.99	0.41	0.008
2.40	80.0	70000	0.77	1.85	0.55	0.007

Fig. 14 A

Fig 14

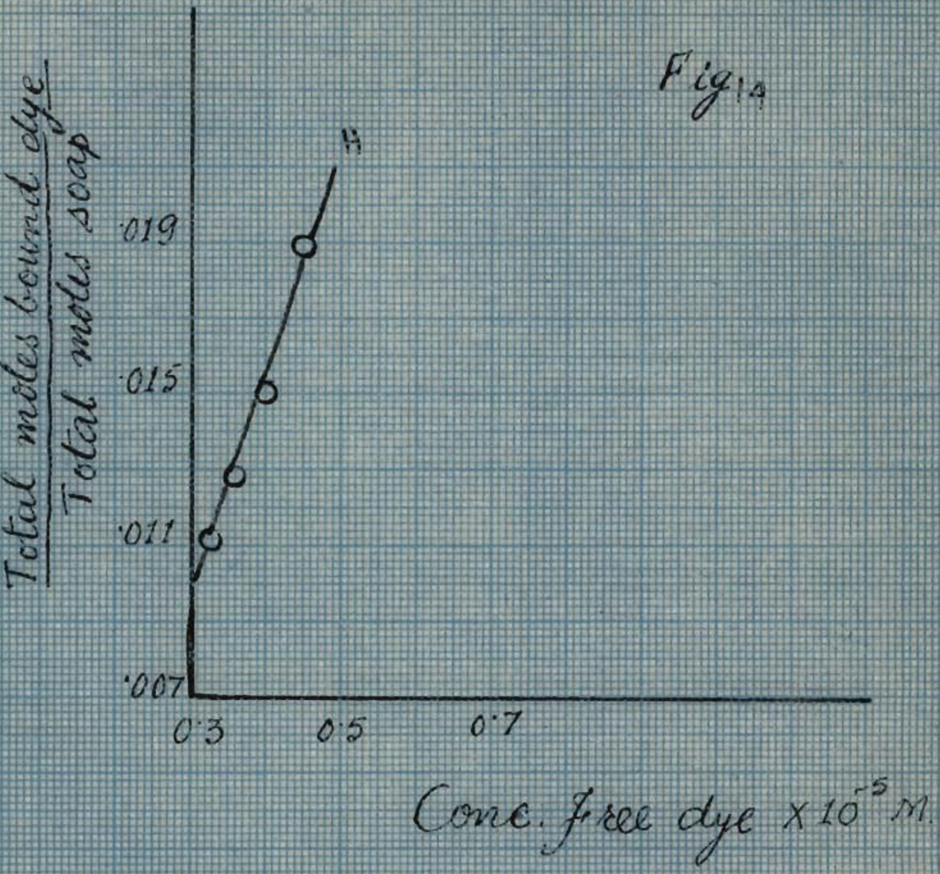

A
·019
·015
·011
·007
0·3
0·5
0·7
Total moles bound dye / Total moles soap
Conc. free dye × 10^{-5} M.

Fig 14

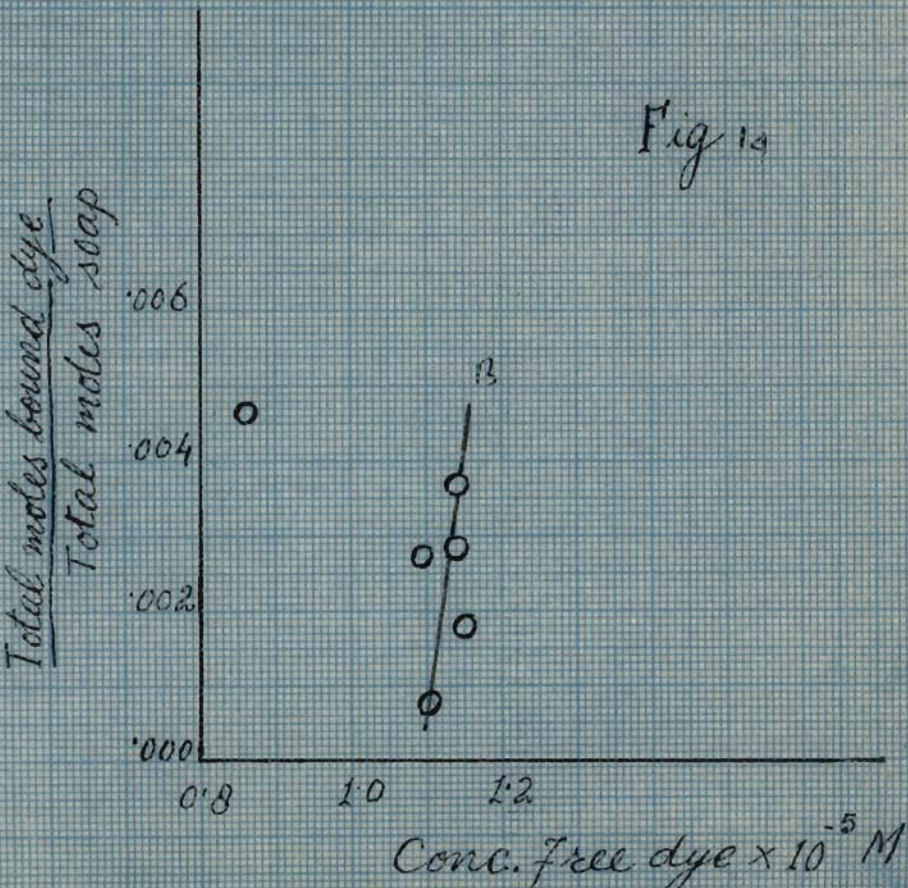

B
·006
·004
·002
·000
0·8
1·0
1·2
Total moles bound dye / Total moles soap
Conc. free dye × 10^{-5} M

TABLE 15

Calculation of binding at pH 7.00

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ_{app}	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	Moles bound dye / Moles total soap
1.20	20.0	66000	0.95	1.14	0.06	0.003
1.20	28.0	66800	0.91	1.09	0.11	0.004
1.20	40.0	67000	0.90	1.08	0.12	0.003
1.20	52.0	67000	0.90	1.08	0.12	0.002
1.20	68.0	67500	0.88	1.06	0.14	0.001
1.20	84.0	75000	0.68	0.82	0.48	0.005
1.80	33.3	71000	0.72	1.30	0.50	0.015
1.80	53.3	70600	0.74	1.33	0.47	0.009
1.80	80.0	70000	0.77	1.34	0.41	0.005
2.40	33.3	70000	0.77	1.85	0.54	0.016
2.40	53.3	67500	0.88	2.11	0.29	0.005
2.40	80.0	67500	0.88	2.11	0.29	0.003

Fig. 14 B

TABLE 16

Calculation of binding at pH 9.12

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	68300	0.84	1.00	0.20	0.010
1.20	28.0	70000	0.77	0.90	0.27	0.009
1.20	40.0	76000	0.49	0.59	0.61	0.015
1.20	52.0	76000	0.49	0.59	0.61	0.012
1.20	68.0	77500	0.43	0.52	0.68	0.010
1.20	84.0	81700	0.23	0.28	0.92	0.011
1.80	33.3	72200	0.67	1.21	0.59	0.017
1.80	53.3	71100	0.72	1.30	0.50	0.009
1.80	80.0	71700	0.70	1.26	0.54	0.007
2.40	33.3	68400	0.84	2.02	0.38	0.011
2.40	53.3	67500	0.88	2.11	0.29	0.005
2.40	80.0	67000	0.90	2.16	0.24	0.006

Fig. 14 C

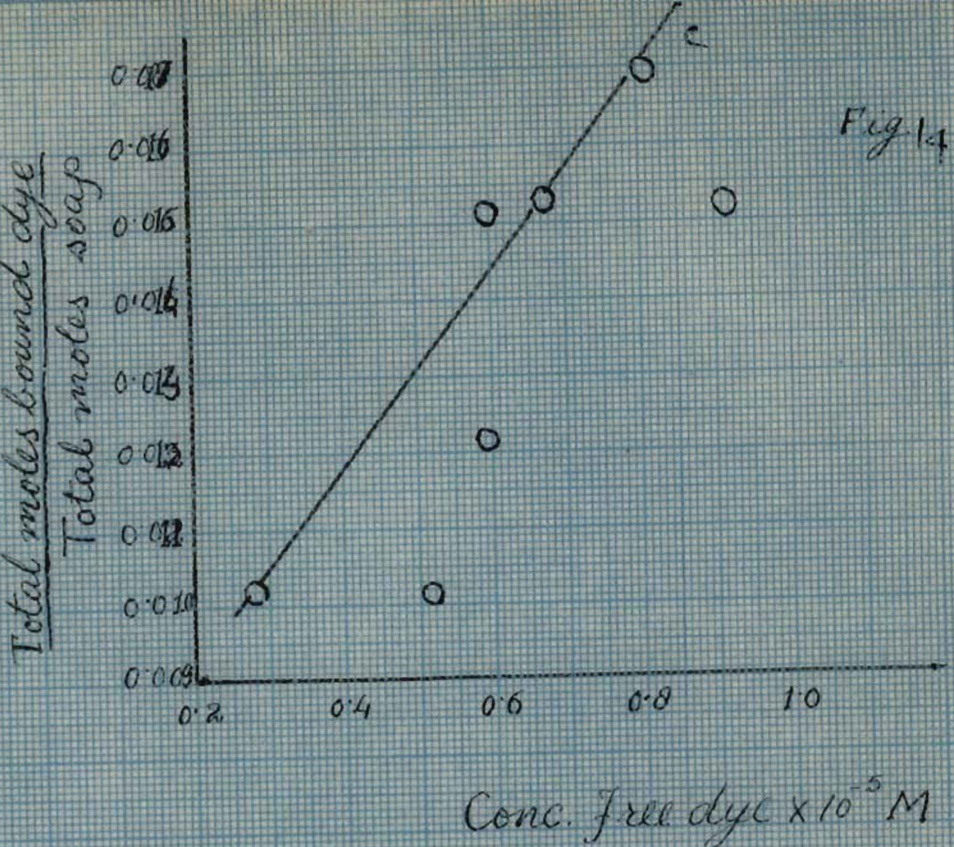

C
Total moles bound dye / Total moles soap
0·017
0·016
0·015
0·014
0·013
0·012
0·011
0·010
0·009
0·2
0·4
0·6
0·8
1·0
Conc. Free dye × 10⁻⁵ M

Fig 14

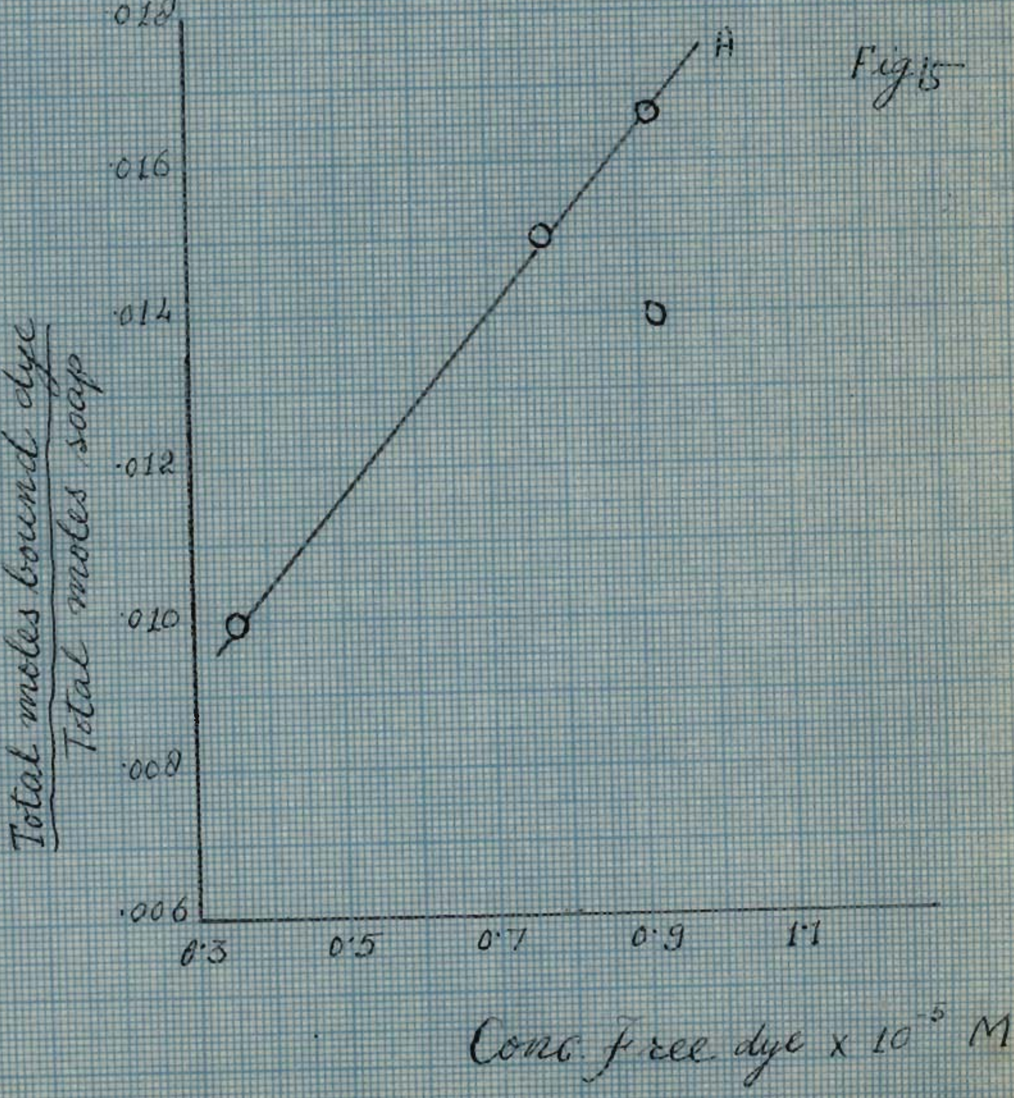

A
Total moles bound dye / Total moles soap
·018
·016
·014
·012
·010
·008
·006
0·3
0·5
0·7
0·9
1·1
Conc. Free dye × 10⁻⁵ M

Fig 15

Sulphonated xylyl stearic·acid-rhodamine 6G

TABLE 17

Calculation of binding at pH 2.72

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵapp	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	70000	0.77	0.92	0.28	0.014
1.20	28.0	70000	0.77	0.92	0.28	0.010
1.20	40.0	72500	0.65	0.78	0.42	0.015
1.20	52.0	71000	0.72	0.86	0.34	0.006
1.20	68.0	73300	0.61	0.73	0.47	0.007
1.20	84.0	80000	0.30	0.36	0.84	0.010
1.80	33.3	74400	0.57	1.03	0.77	0.023
1.80	53.3	73000	0.63	1.13	0.67	0.012
1.80	80.0	75600	0.51	0.92	0.88	0.011
2.40	33.3	74500	0.56	1.34	1.06	0.032
2.40	53.3	72500	0.65	1.56	0.84	0.015
2.40	80.0	75400	0.52	1.25	1.15	0.014

Fig. 15 A

TABLE 18

Calculation of binding at pH 7.00

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ_{app}	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	66000	0.95	1.14	0.06	0.003
1.20	28.0	66700	0.92	1.10	0.10	0.003
1.20	40.0	67000	0.90	1.08	0.12	0.003
1.20	52.0	68000	0.86	1.03	0.17	0.003
1.20	68.0	70000	0.77	0.92	0.28	0.004
1.20	84.0	77000	0.41	0.48	0.72	0.008
1.80	33.3	73300	0.61	1.10	0.70	0.021
1.80	53.3	71100	0.72	1.30	0.50	0.009
1.80	80.0	70000	0.77	1.39	0.41	0.005
2.40	33.3	70400	0.75	1.80	0.60	0.018
2.40	53.3	70400	0.75	1.80	0.60	0.012
2.40	80.0	68000	0.86	2.06	0.34	0.004

Fig. 15 B

TABLE 7

Calculation of binding at pH 9.12

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵ_{app}	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	12.0	23500	0.98	1.96	0.04	0.003
2.0	20.0	29500	0.70	1.40	0.60	0.030
2.0	28.0	32000	0.60	1.20	0.80	0.028
2.0	40.0	37500	0.34	0.68	1.32	0.033
2.0	52.0	37500	0.34	0.68	1.32	0.025
2.0	68.0	37500	0.34	0.68	1.32	0.020
2.0	84.0	37500	0.34	0.68	1.32	0.015
4.0	33.3	26100	0.90	3.60	0.40	0.012
4.0	53.3	33700	0.71	2.84	1.16	0.021
4.0	80.0	38000	0.61	2.60	1.40	0.0175
6.0	33.3	23300	0.99	5.94	0.06	0.002
6.0	53.3	28500	0.85	5.10	0.90	0.017
6.0	80.0	32100	0.75	4.70	1.30	0.016

Fig. 11 C

Sulphonated xylyl stearic acid-malachite green

TABLE 8

Calculation of binding at pH 2.72

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
2.0	12.0	23500	0.96	1.92	0.08	0.007
2.0	20.0	30000	0.81	1.62	0.38	0.019
2.0	28.0	31000	0.78	1.56	0.44	0.016
2.0	40.0	32500	0.74	1.49	0.56	0.014
2.0	52.0	38000	0.60	1.20	0.80	0.015
2.0	68.0	41000	0.51	1.02	0.98	0.014
2.0	84.0	39000	0.57	1.14	0.86	0.010
4.0	33.3	30800	0.79	3.16	0.84	0.025
4.0	53.3	34500	0.70	2.80	1.20	0.022
4.0	80.0	40000	0.54	2.14	1.86	0.021
6.0	33.3	27000	0.90	5.40	0.60	0.020
6.0	53.3	30000	0.80	4.80	1.20	0.022
6.0	80.0	32700	0.74	4.44	1.56	0.019

Fig. 12 A

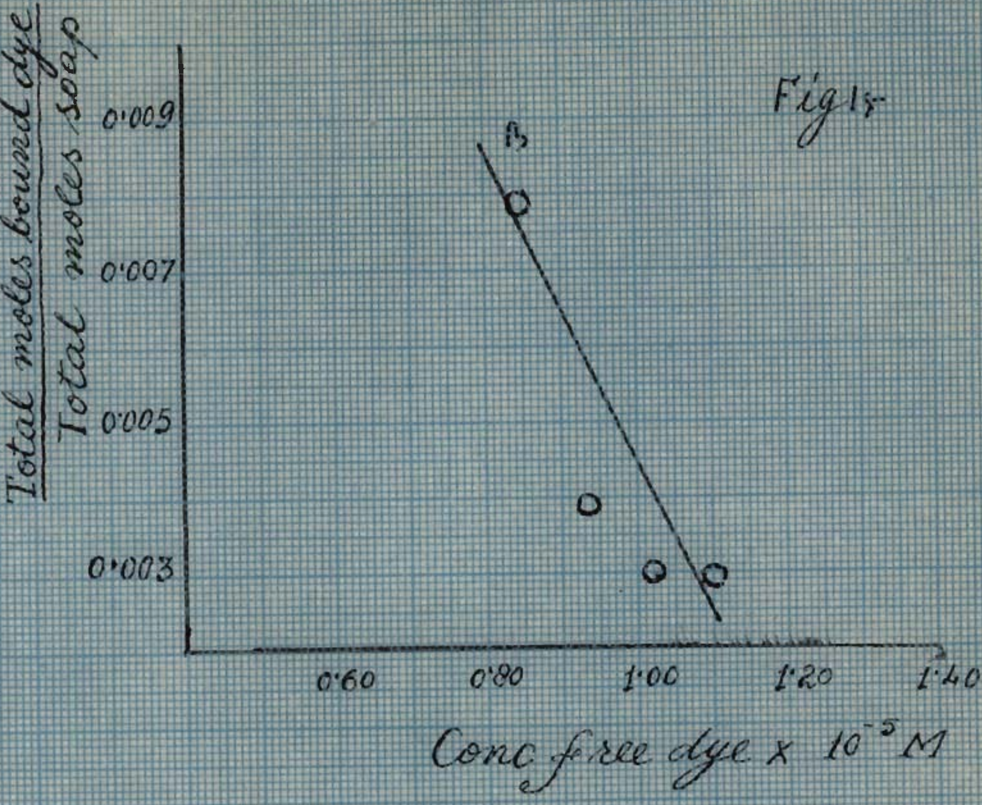


Fig 15

Total moles bound dye / Total moles soap
0·009
0·007
0·005
0·003
B
0·60
0·80
1·00
1·20
1·40
Conc free dye × 10^{-5} M

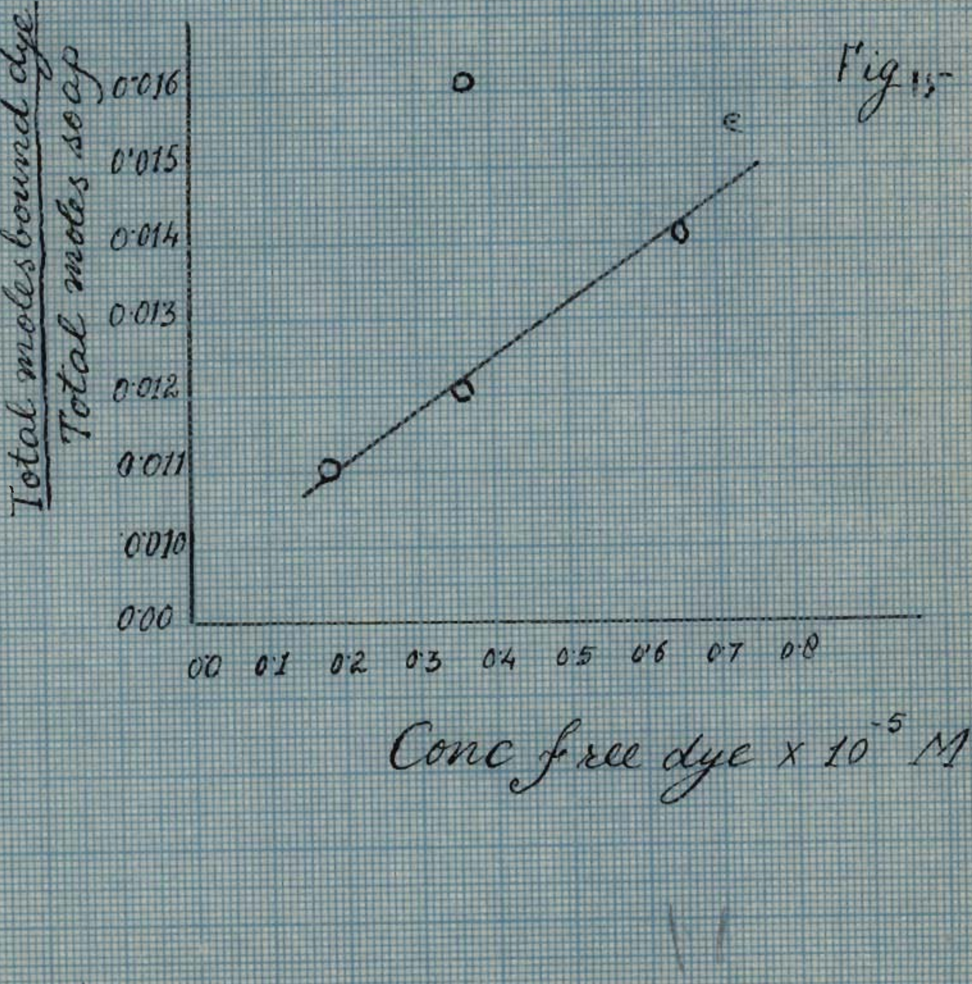


Fig 15

Total moles bound dye / Total moles soap
0·016
0·015
0·014
0·013
0·012
0·011
0·010
0·00
C
0·0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
Conc free dye × 10^{-5} M

TABLE 19

Calculation of binding at pH 9.12

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	ϵapp	α	Conc.free dye $\times 10^{-5}$M	Conc.bound dye $\times 10^{-5}$M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
1.20	20.0	66700	0.92	1.10	0.10	0.005
1.20	28.0	66700	0.92	1.10	0.10	0.004
1.20	40.0	75000	0.54	0.65	0.55	0.014
1.20	52.0	80000	0.30	0.36	0.84	0.016
1.20	68.0	80000	0.30	0.36	0.84	0.012
1.20	84.0	81700	0.23	0.28	0.92	0.011
1.80	33.3	72200	0.67	1.40	0.59	0.017
1.80	53.3	71100	0.72	1.34	0.50	0.009
1.80	80.0	70000	0.77	1.34	0.41	0.005
2.40	33.3	70000	0.77	1.86	0.54	0.016
2.40	53.3	69100	0.81	1.94	0.46	0.008
2.40	80.0	675	0.88	2.11	0.29	0.003

Fig. 15 C

TABLE 20

Micelle size(anionic soaps in presence of malachite green).

Conc.dye $\times 10^{-5}$M	Conc.soap $\times 10^{-5}$M	Total soap molecule/dye molecule(bound)								
		SPSA			STSA			SXSA		
		(2.72)	(7.00)	(9.12)	(2.72)	(7.00)	(9.12)	(2.72)	(7.00)	(9.12)
2.0	12.0	32	20	100	30	15	300	150	200	300
2.0	20.0	50	22	43	22	20	33	66	53	36
2.0	40.0	67	38	44	31	31	30	71	70	50
2.0	84.0	118	70	70	70	70	63	100	78	70
4.0	33.3	32	30	33	42	22	18	40	25	64
4.0	53.3	48	44	46	58	44	44	44	31	32
4.0	80.0	74	60	58	-	50	50	43	32	45
6.0	33.3	35	31	-	40	22	20	55	22	46
6.0	53.3	52	47	59	62	32	32	44	32	40
6.0	80.0	83	67	61	-	53	46	51	47	53

TABLE 21

Micelle size(anionic soaps in presence of rhodamine 6G).

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	Total soap molecule/dye molecule(bound)								
		SPSA			STSA			SXSA		
		(2.72)	(7.00)	(9.12)	(2.72)	(7.00)	(9.12)	(2.72)	(7.00)	(9.12)
1.2	20.0	100	100	50	100	333	100	71	143	167
1.2	40.0	48	133	51	54	290	67	95	200	74
1.2	84.0	100	153	84	91	152	91	100	155	91
1.8	33.3	27	50	35	43	67	56	43	48	56
1.8	53.3	42	130	50	56	113	106	80	106	106
1.8	80.0	57	88	70	104	195	146	90	195	195
2.4	33.3	25	98	51	42	62	87	31	55	62
2.4	53.3	48	111	67	130	140	140	63	89	116
2.4	80.0	64	150	70	145	280	333	70	239	280

From the above data (Tables 2-19) it could be concluded that the nature of the dye as well as the pH greatly influnced the extent of binding(as calculated for a particular spectral shift). Thus it was observed that rhodamine 6G combined with the anionic soaps to a greater extent than malachite green, the relative binding capacity being 4:3. It was further observed that the binding was larger in the alkaline range than in the acidic.

The plots between concentration of free dye and moles of bound dye/moles total soap gave straight lines in all the three pH ranges(Fig. 10-15). These results were similar in many respects to those of Klotz on dye-protein interaction except for the fact that low values were obtained in this case in contrast to Klotz's values which were always higher than one. Such low values in our case might be explained in the light of micelle formation. It can be said that dye molecules interact with the ionic micelles and not with the single soap molecules. On the other hand in the case of dye-protein mixtures greater possibility for monomer-monomer interaction exists.These values could be higher if calculations were made on the basis of miceller weights.

The total molecules of soap/bound dye molecules are calculated and reported in tables(20,21). Any attempt to determine the micelle size from these data is fraught with difficulties since this would be based on the fact that each micelle holds one dye molecule,which need not be true. Although these data do not provide information on true micelle size, it can be said that the micelle size would be an integral part of these values. The above results lead to the important generalisation: the micelle size is a function of three variables, viz., concentration of the soap, pH of the medium and bound dye molecules.

Since the addition of dyes do not bring about any change in pH of the soap, it may be concluded that the hydrogen ions of the soap do not take part in the dye-soap interaction. The mechanism of interaction would, therefore involve the interaction between the anionic micelle and the cationic part of the dye.

Cationic soaps and acid dye:- Unlike malachite green and rhodamine 6G, the absorption maximum of alizarin red S shifts with pH (Table 22).

TABLE 22

Influence of CTMAB on the absorption maximum of Alizarin red S.

Conc.soap	Absorption maximum at different pHs		
x 10^{-5}M	(2.00)	(7.00)	(9.12)
0.0	415 mμ	515 mμ	445 mμ
3.3	415 "	515 "	525 "
6.6	415 "	-	525,540 " (Ill defined)
10.0	415,425 "(Ill defined)	-	"
13.3	425 "	-	550 "
33.3	425 "	550 "	550 "
53.3	425 "	550 "	550 "
80.0	425 "	550 "	550 "

Influence of CPB on the absorption maximum of Alizarin red S

Conc.soap	Absorption maximum at different pHs		
x 10^{-4}M	(2.00)	(7.00)	(9.12)
0.0	415 mμ	515 mμ	445 mμ
3.3	415 "	515 "	445 "
6.6	415 "	-	445 "
10.0	415 "	-	500 "
13.3	415 "	-	500 "
33.3	425 "	-	500 "
53.3	425 "	550 "	550 "
80.0	425 "	550 "	550 ."

The experiments on the binding were, therefore, performed in buffered systems.

Preliminary experiments provided the following interesting observations: in the lower pH range only a small shift in the maximum(415 mμ to 425 mμ) was observed even after the addition of a large amount of the soap; at pH 7.00 a similar behaviour was observed with the only difference that precipitation was found to set in the early stages followed by dispersion of the precipitate with further addition of the soap and a marked shift in the maximum (515 mμ to 550 mμ); the spectral shift was, however, very much marked (445 mμ to 550 mμ) at high pH 9.12, even in presence of very small quantity of the soap. Here again the results of spectrophotometry may be interpreted in terms of chemical binding between the two species. The results of binding calculated by Klotz equation are given in tables(23 to 28).

Alizarin red S-cetyl trimethyl ammonium bromide.

TABLE 23.

Calculation of binding at pH 2.00

Conc.dye x 10^{-5} M	Conc.soap x 10^{-5} M	ϵapp	α	Conc.free dye x 10^{-5} M	Conc.bound dye x 10^{-5} M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
6.66	3.3	3153	0.80	5.33	1.33	0.403
6.66	6.6	3153	0.80	5.33	1.33	0.201
6.66	10.0	2852	0.60	4.00	2.66	0.266
6.66	13.3	2777	0.59	3.93	2.73	0.205
6.66	33.3	3078	0.76	5.06	1.60	0.050
6.66	53.3	3153	0.80	5.33	1.33	0.025
6.66	80.0	3228	0.85	5.66	1.00	0.012
10.00	200.0	3200	0.83	8.30	1.70	0.008
10.00	466.6	3300	0.90	9.00	1.00	0.002
13.30	200.0	3158	0.81	10.77	2.53	0.012
13.30	466.6	3308	0.90	11.97	1.33	0.003

Fig. 16 A

Fig 16

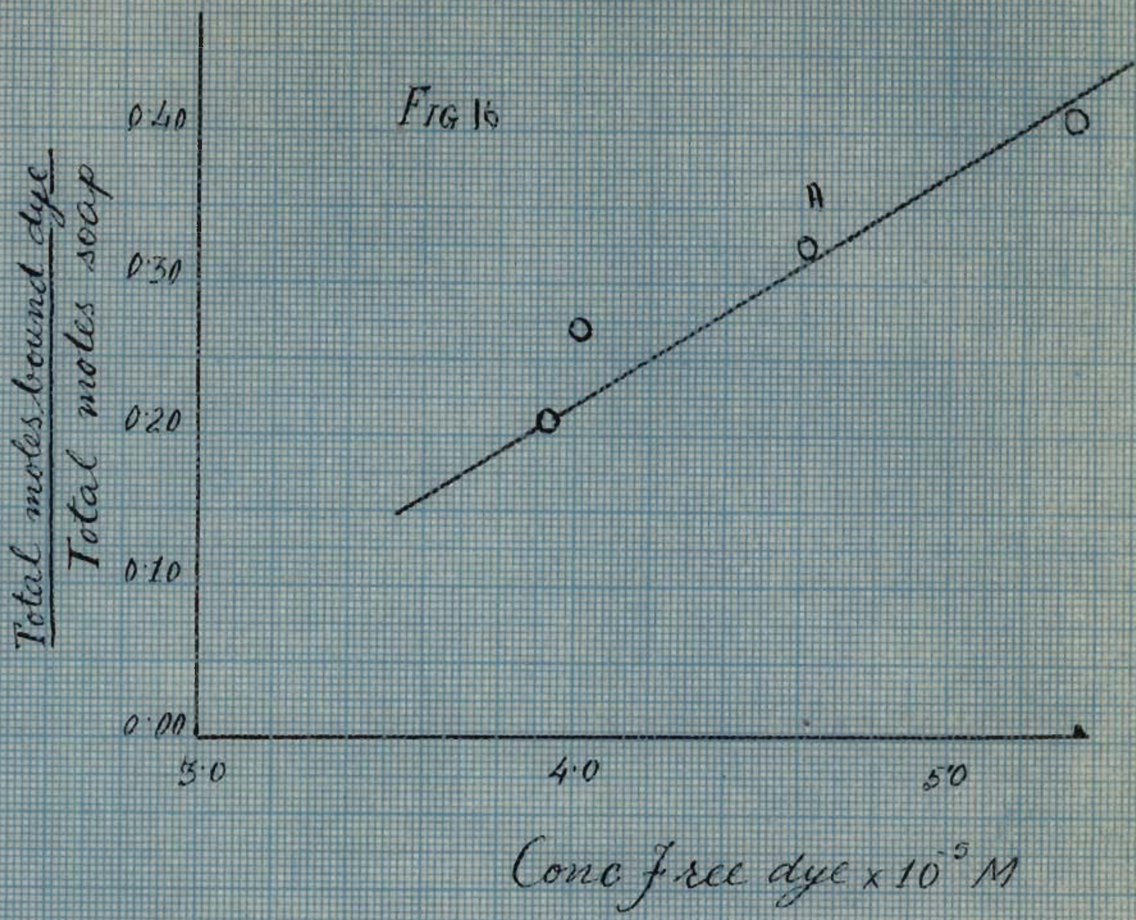

0·40
0·30
0·20
0·10
0·00
Total moles bound dye / Total moles soap
A
3·0
4·0
5·0
Conc free dye × 10^{-5} M

Fig 16

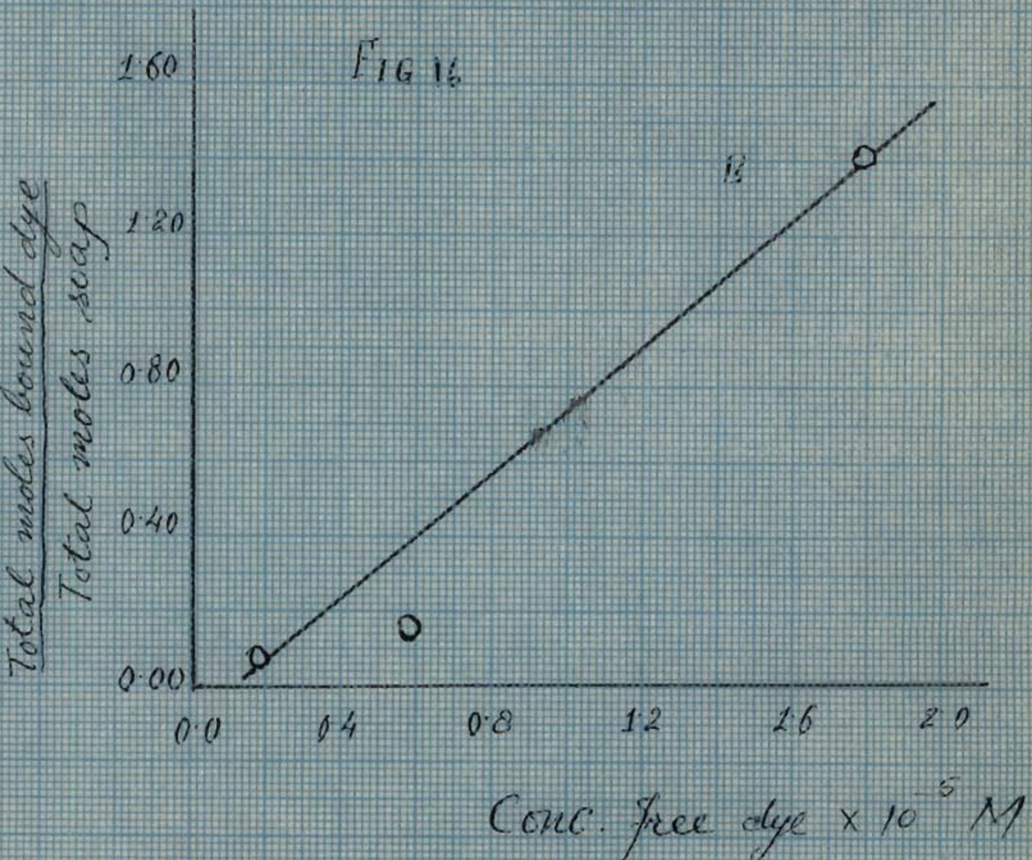

1·60
1·20
0·80
0·40
0·00
Total moles bound dye / Total moles soap
B
0·0
0·4
0·8
1·2
1·6
2·0
Conc. free dye × 10^{-5} M

TABLE 24

Calculation of binding at pH 7.00 F = 5606 B=4511

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵapp	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$
6.66	3.3	4820	0.30	1.99	4.67	1.41
6.66	6.6	ppt	-	-	-	-
6.66	10.0	"	-	-	-	-
6.66	13.3	"	-	-	-	-
6.66	33.3	4654	0.12	0.80	5.86	0.17
6.66	53.3	4654	0.12	0.80	5.86	0.11
6.66	80.0	4580	0.06	0.40	6.26	0.078
10.00	200.0	4550	0.036	0.36	9.64	0.048
10.00	466.6	4550	0.036	0.36	9.64	0.020
13.30	200.0	4586	0.068	0.90	12.40	0.062
13.30	466.0	4549	0.035	0.47	12.83	0.027

Fig. 16 B

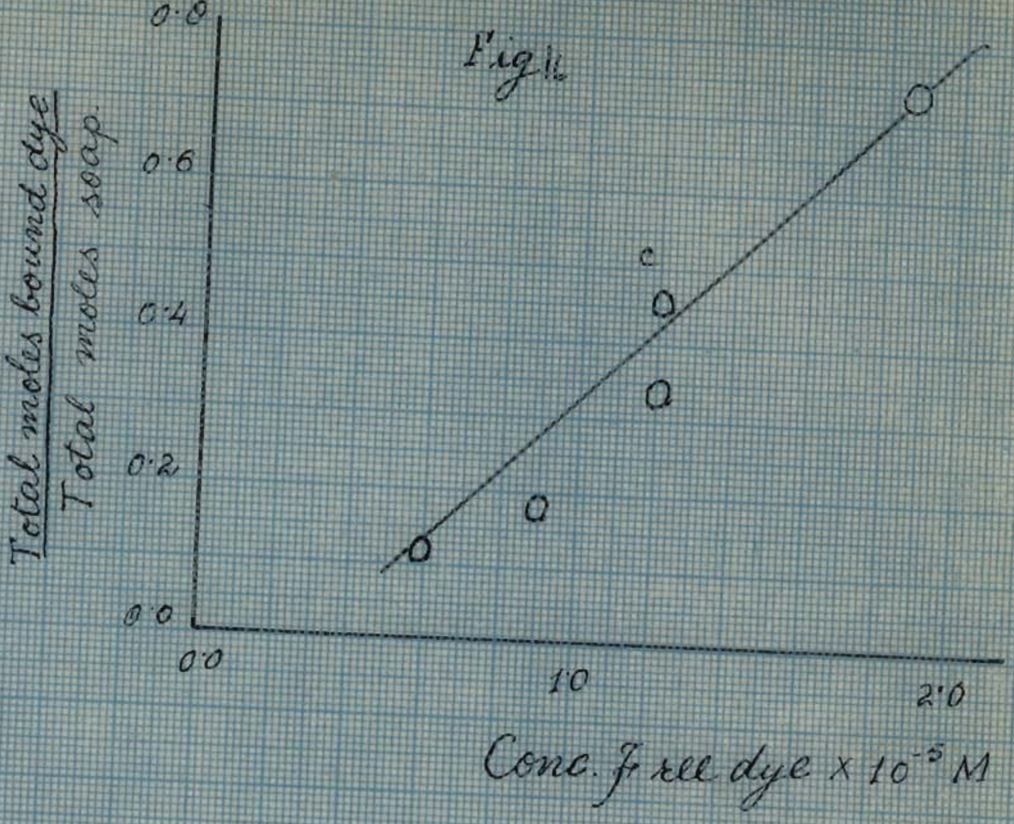
TABLE 25

Calculation of binding at pH 9.12 F=4545 B=2100

Conc.dye x 10^{-5}M	Conc.soap x 10^{-5}M	ϵapp	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap.}}$
6.66	3.3	3700	0.65	4.33	2.33	0.70
6.66	6.6	2780	0.28	1.86	4.80	0.73
6.66	10.0	2552	0.18	1.19	4.47	0.45
6.66	13.3	2552	0.18	1.19	4.47	0.32
6.66	33.3	2450	0.14	0.93	5.73	0.17
6.66	53.3	2330	0.09	0.60	6.06	0.11
6.66	80.0	2000	0.07	0.48	6.18	0.077
10.00	200.0	2800	0.28	2.80	7.20	0.036
10.00	466.6	2400	0.12	1.20	8.80	0.019
13.30	200.0	3000	0.36	4.80	8.50	0.042
13.30	466.6	2460	0.14	1.86	11.44	0.024

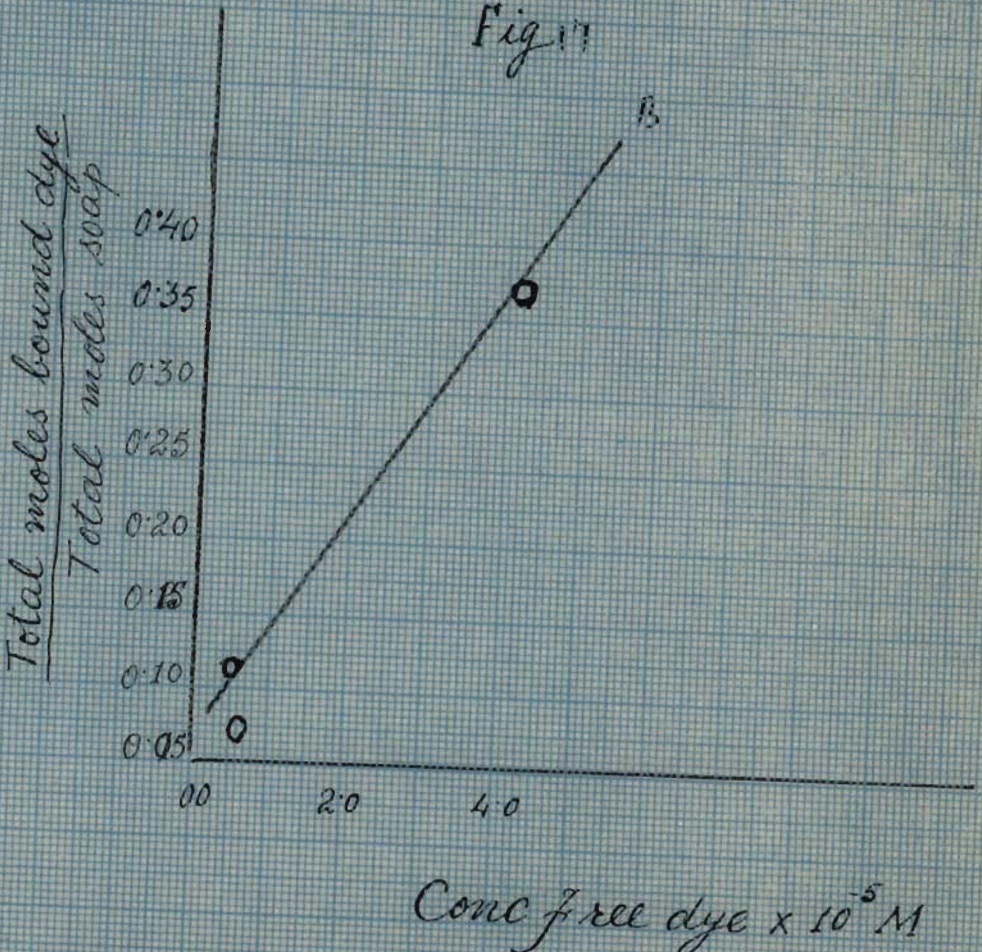
Fig. 16 C

Fig 16



Total moles bound dye / Total moles soap
0·8
0·6
0·4
0·2
0·0
0·0
1·0
2·0
Conc. free dye × 10⁻⁵ M

Fig 17



B
Total moles bound dye / Total moles soap
0·40
0·35
0·30
0·25
0·20
0·15
0·10
0·05
0·0
2·0
4·0
Conc free dye × 10⁻⁵ M

Alizarin red S-cetyl pyridinium bromide.

TABLE 26

Calculation of binding at pH 2.00 F = 3453 B = 1880

Conc.dye x 10^{-5} M	Conc.soap x 10^{-4} M	ε app	α	Conc.free dye x 10^{-5} M	Conc.bound dye x 10^{-5} M	$\frac{\text{Moles bound dye}}{\text{Moles total soap.}}$
6.66	3.3	2627	0.47	3.13	3.53	1.069
6.66	6.6	2552	0.42	2.80	3.86	0.585
6.66	10.0	2552	0.42	2.80	3.86	0.386
6.66	13.3	2477	0.36	2.40	4.26	0.320
6.66	33.3	2778	0.57	3.80	2.86	0.086
6.66	53.3	3000	0.70	4.66	2.00	0.037
6.66	80.0	2852	0.61	4.10	2.56	0.032
10.00	200.0	3000	0.70	7.00	3.00	0.015
10.00	466.6	3000	0.70	0.70	3.00	0.007
13.30	200.0	2900	0.64	8.51	4.79	0.024
13.30	466.6	3000	0.70	9.31	3.99	0.008

Fig. 17 A

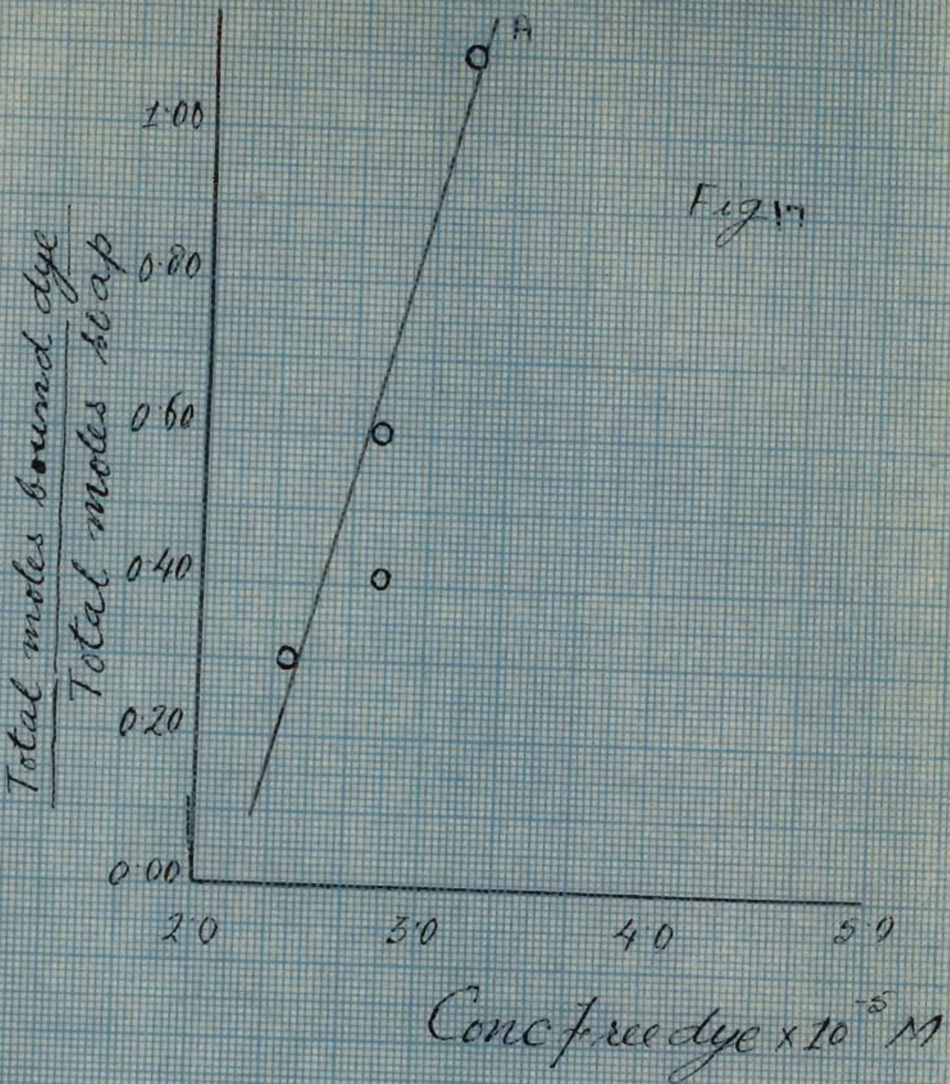

A
1·00
0·80
0·60
0·40
0·20
0·00
Total moles bound dye / Total moles soap
2·0
3·0
4·0
5·0
Conc free dye × 10⁻⁵ M

Fig 17

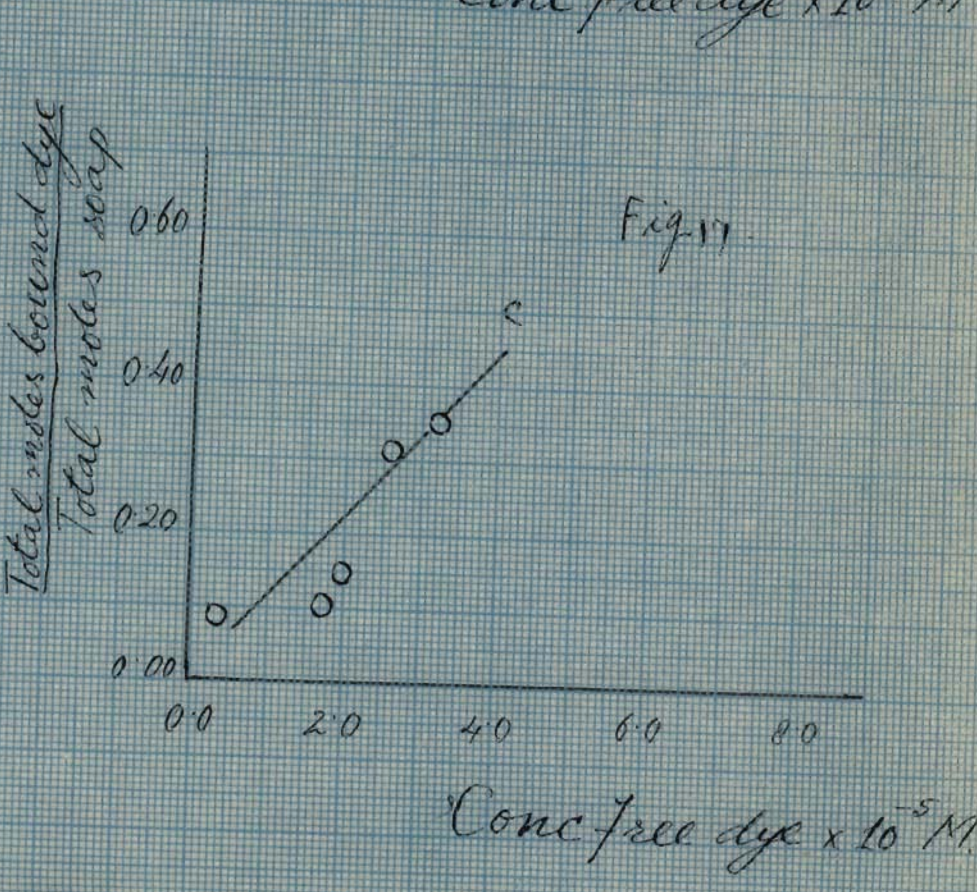

Total moles bound dye / Total moles soap
0·60
0·40
0·20
0·00
C
0·0
2·0
4·0
6·0
8·0
Conc free dye × 10⁻⁵ M.

Fig 17.

TABLE. 27

Calculation of binding at pH 7.00 F=5606 B= 4340

Conc.dye x 10^{-5}M	Conc.soap x 10^{-4}M	ϵ app	α	Conc.free dye x 10^{-5}M	Conc.bound dye x 10^{-5}M	$\frac{\text{Moles bound dye}}{\text{Moles total soap.}}$ x 1/10
6.66	3.3	4105	0.60	4.00	2.66	0.363
6.66	6.6	ppt	-	-	-	-
6.66	10.0	"	-	-	-	-
6.66	13.3	"	-	-	-	-
6.66	33.3	"	-	-	-	-
6.66	53.3	4433	0.07	0.48	6.18	0.114
6.66	80.0	4433	0.07	0.48	6.18	0.077
10.00	200.0	4450	0.08	0.86	9.14	0.046
10.00	466.6	4400	0.04	0.40	9.60	0.020
13.30	200.0	4500	0.12	1.60	11.70	0.058
13.30	466.6	4436	0.07	1.00	12.30	0.026

Fig. 17 B

TABLE 28.

Calculation of binding at pH 9.12 F=4545 B=1800

Conc.dye x 10^{-5} M	Conc.soap x 10^{-4} M	εapp	α	Conc.free dye x 10^{-5} M	Conc.bound dye x 10^{-5} M	$\frac{\text{Moles bound dye}}{\text{Moles total soap}}$ x 1/10
6.66	3.3	4354	0.85	5.56	1.10	0.350
6.66	6.6	3900	0.76	5.06	1.60	0.243
6.66	10.0	3153	0.49	3.26	3.40	0.340
6.66	13.3	2870	0.39	2.60	4.06	0.305
6.66	33.3	2627	0.30	2.00	4.66	0.140
6.66	53.3	2553	0.27	1.80	4.86	0.090
6.66	80.0	2000	0.07	0.48	6.18	0.077
10.00	200.0	3000	0.43	4.30	5.70	0.028
10.00	466.6	2900	0.40	4.00	6.00	0.013
13.30	200.0	2800	0.36	4.80	8.50	0.024
13.30	466.6	2480	0.24	3.20	10.10	0.021

Fig. 17 C

TABLE 29

Size of the micelle(cationic soap in presence of alizarine red S).

Conc.dye x 10^{-5}M	Conc.soap (CTMAB$\times10^{-5}$M) (CPB$\times10^{-4}$M)	Total soap molecule/dye molecule(bound) CTMAB (2.00)	CTMAB (7.00)	CTMAB (9.12)	CPB x 10 (2.00)	CPB x 10 (7.00)	CPB x 10 (9.12)
6.66	3.3	2	1	1	1	3	3
6.66	6.6	5	-	1	2	-	4
6.66	10.0	4	-	2	3	-	3
6.66	13.3	5	-	3	3	-	3
6.66	33.3	21	6	6	12	-	7
6.66	66.6	50	11	11	33	11	14
6.66	80.0	80	13	13	31	13	13
10.00	200.0	118	21	21	67	22	35
10.00	466.6	466	48	58	155	48	78
13.30	200.0	90	16	24	42	17	24
13.30	466.6	350	36	41	116	37	47

Thus it is observed that in the case of cationic soaps the influence of pH on the extent of binding is slightly complicated. Here it is observed that the binding is greater both in the neutral and alkaline ranges than in the acidic range. Such a behaviour is possible since at pHs 7.00 and 9.12 the ionisation of the phenolic groups side by side with that of the sulphonate group takes place providing more negative sites for interaction with the positively charged micelles of the cationic soap.

The data on the soap molecules per bound dye molecule are given in table(29). Here too the micelle size tends to be larger at pH 2.00 and about constant at pH 7.00 and 9.12, increases with the increase in soap concentration and increases with the increase in dye concentration.

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CHAPTER II.

Critical micelle concentration of anionic and cationic soaps by pH metric,conductometric, spectrophotometric and potentiometric methods.

INTRODUCTION

An important factor in studying the behaviour of surface active agents is its state of solution in the medium in which it is used. The numerous investigators who have worked on aqueous solutions of soaps-McBain on the soaps and the higher sulphonic acids;Lottermoser on the higher alkyl sulphates;Hartley on the alkyl quaternary ammonium salts;Wright and Tartar on the salts of alkane sulphonic acids and Ralston and Hoerr on the alkyl amine hydrochlorides-have all agreed on the presence of aggregates of the amphipathic ions in aqueous solutions. McBain named them as"ionic micelles".

The exact nature of these particles has,however, been a matter of great controversy. The contention of McBain and others (1-4) has been that at least two types of micelles exist: an associated ion or ionic micelle,which is highly ionic and spherical in shape and an associated molecule or lameller micelle,which is feebly ionic. The former may exist in quite dilute solutions while the latter exist in conjuction with the former (ionic micelle) in the more concentrated solutions. Hartley and others(5,6), on the other hand,maintain that only one type of particle is present,an associated ion to which are attached a number of oppositely charged ions,termed gegen ions or counter ions. This particle is formed at a certain critical concentration below which the solute acts as an ordinary electrolyte

Most investigators agree that these associated particles must be highly hydrated and that this bound water constitutes an integral part of the micelle.

Most of the investigations in the field of surfactant have been devoted to the formation,structure and behaviour of micelles. The determination of c.m.c. is, therefore,most fundamental aspect of study in this field. The methods usually employed are: vapour pressure(7,8), osmotic pressure(9),freezing point(10-17),surface tension(18-23), refractive index(24,25),turbidity (26),partial molal volume(27-29),viscosity(30-34), solubility(35-39),electrical conductance (40-44), transport number(45),Wien effect(46),suppressing the polarographic maxima(47,48),dialysis(49,50) etc. One of the most widely used method for determining the c.m.c. is by means of the marked colour change which occurs in solution containing both the surfactant and an appropriate dyestuff. Mysels(51),Raison(52),Harkins(53,54), Walton(55) etc. used this method for determining the c.m.c. of surfactants.

Kolthoff and Johnson(56) have shown that H^+ ions associated with the micelles of dodecane sulphonic acid catalyze the reaction between acetone and iodine much more effectively than free H^+ ions. This difference affords an unusual method for determining the c.m.c. of dodecane sulphonic acid by plotting the catalytic effect against the concentration. Recently Boyd(57) has introduced the tracer technique in studying the formation of micelles in detergents.

c.m.c.of anionic soaps.

Another method,which has attracted very little attention, can be the pH metric method. Although this method cannot claim general applicability,it can be successfully employed in anionic soaps of the sulphate and the sulphonated types. The plots of 1/concentration (reciprocal of soap concentration) against pH would give a sharp break corresponding to the formation of micelle. The effect of foreign electrolytes can very well be studied by this method.

In this chapter the c.m.c. of sulphonated phenyl-, tolyl-,and xylyl-stearic acids have been determined by pH measurements using glass and hydrogen electrodes. The values so obtained have been compared with the earlier results by polarography(58), conductometry and spectrophotometry.

EXPERIMENTAL

Reagents:- The anionic soaps,viz.,sulphonated phenyl-, tolyl-,and xylyl-stearic acids were prepared in the laboratory(chapter 1). Their stock solutions were prepared in doubly distilled water and strength were determined by titrating pH metrically against KOH of known strength. The foreign electrolytes were of A.R. grade and their solutions were prepared in doubly distilled water.

Procedure:- The pH measurements of different concentrations of soap were made with the help of a Cambridge Bench Type pH meter. To confirm our results, pH of the solutions were also measured with the help of hydrogen electrode.

Conductometric measurements were carried out using a Kohlrausch Universal Bridge and the spectrophotometric data were taken from chapter I.

TABLE 1

pH for different concentrations of soap solutions measured by Cambridge Bench Type pH meter.

Conc.soap $\times 10^{-5}$M	1/Conc.soap $\times 10^{5}$M	pH		
		SPSA	STSA	SXSA
3.84	0.2604	4.20	4.19	4.12
7.40	0.1351	3.92	3.93	3.80
13.80	0.0724	3.69	3.68	3.48
19.30	0.0518	3.56	3.53	3.32
24.20	0.0413	3.46	3.42	3.22
28.60	0.0349	3.38	3.36	3.14
32.40	0.0307	3.30	3.30	3.08
37.50	0.0267	3.26	3.24	3.00
44.50	0.0225	3.19	3.18	2.93
50.00	0.0200	3.16	3.11	2.87
Fig. 1		A	B	C

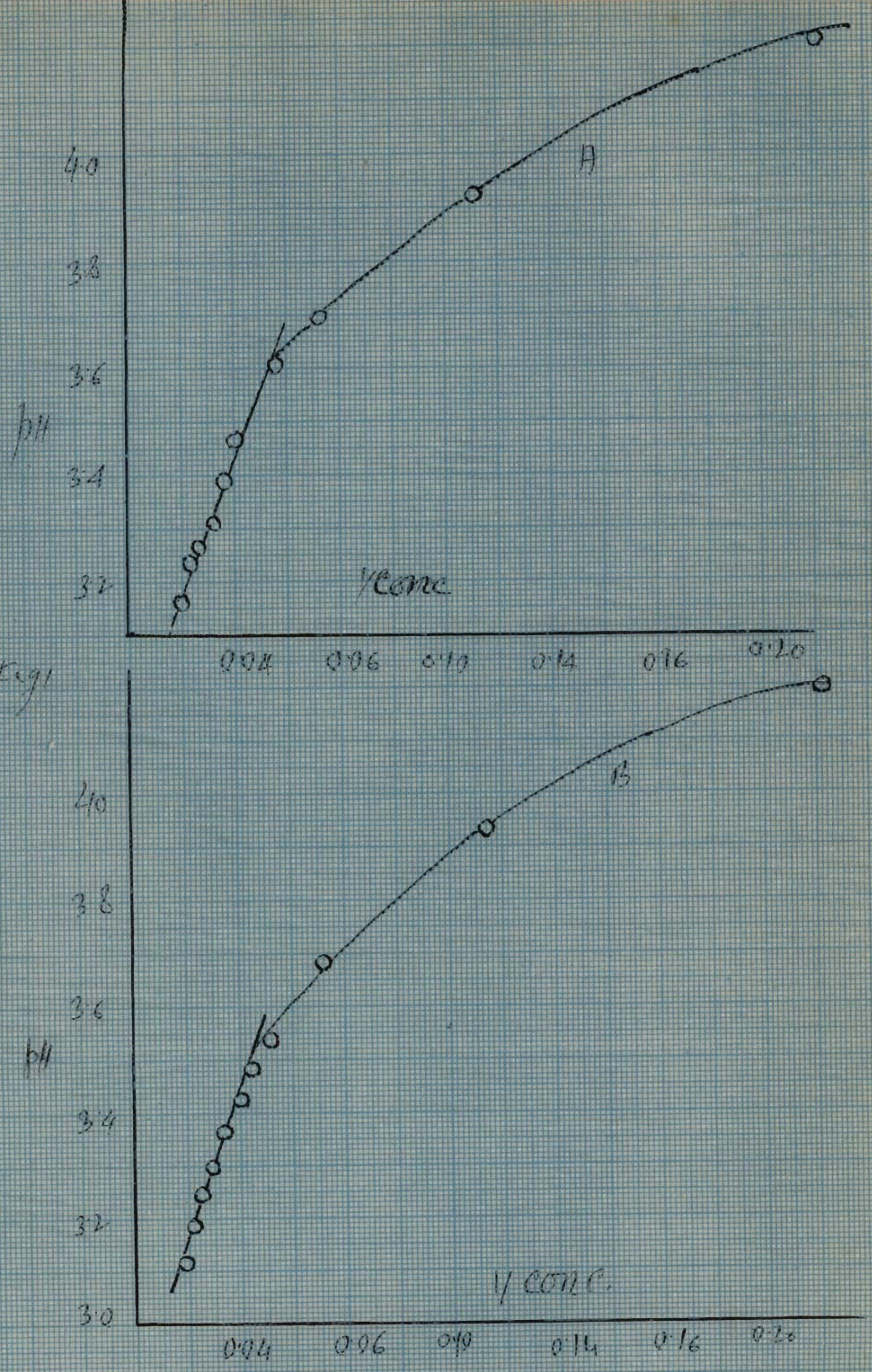

4·0
3·8
3·6
3·4
3·2
pH
A
1/conc.
0·04
0·06
0·10
0·14
0·16
0·20
4·0
3·8
3·6
3·4
3·2
3·0
pH
B
1/ conc.
0·04
0·06
0·10
0·14
0·16
0·20

Fig 1

TABLE 2

pH for different concentrations of soap solutions measured by hydrogen electrode.

Conc.soap $\times 10^{-5}$ M	pH SPSA	pH STSA	pH SXSA
3.84	4.30	4.20	4.21
7.40	3.90	3.92	3.84
13.80	3.71	3.66	3.50
19.30	3.50	3.50	3.35
24.20	3.42	3.40	3.25
28.60	3.40	3.35	3.19
32.40	3.36	3.31	3.12
37.50	3.29	3.25	3.06
44.50	3.20	3.20	3.00
50.00	3.15	3.13	2.95

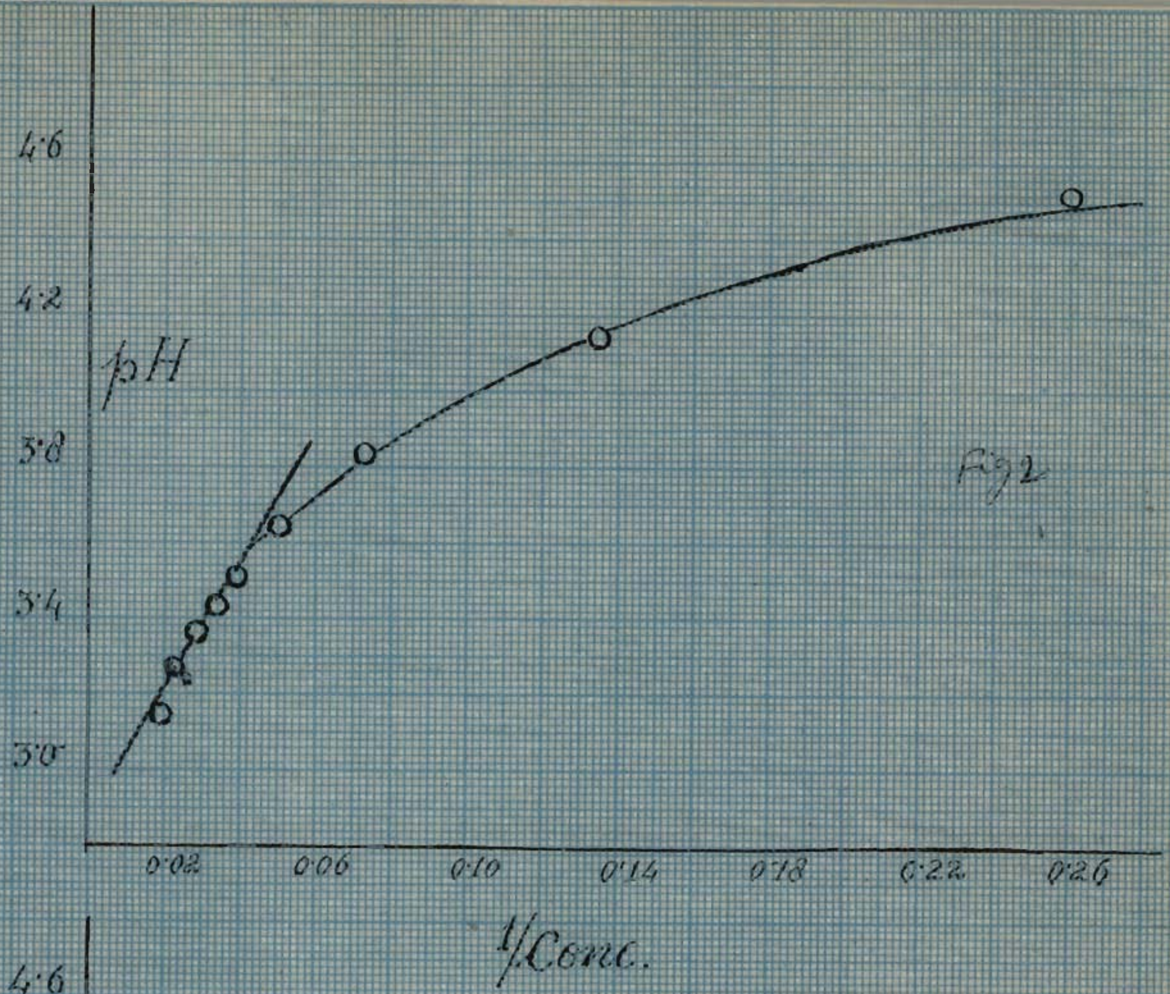

4·6
4·2
pH
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Conc.

Fig 2

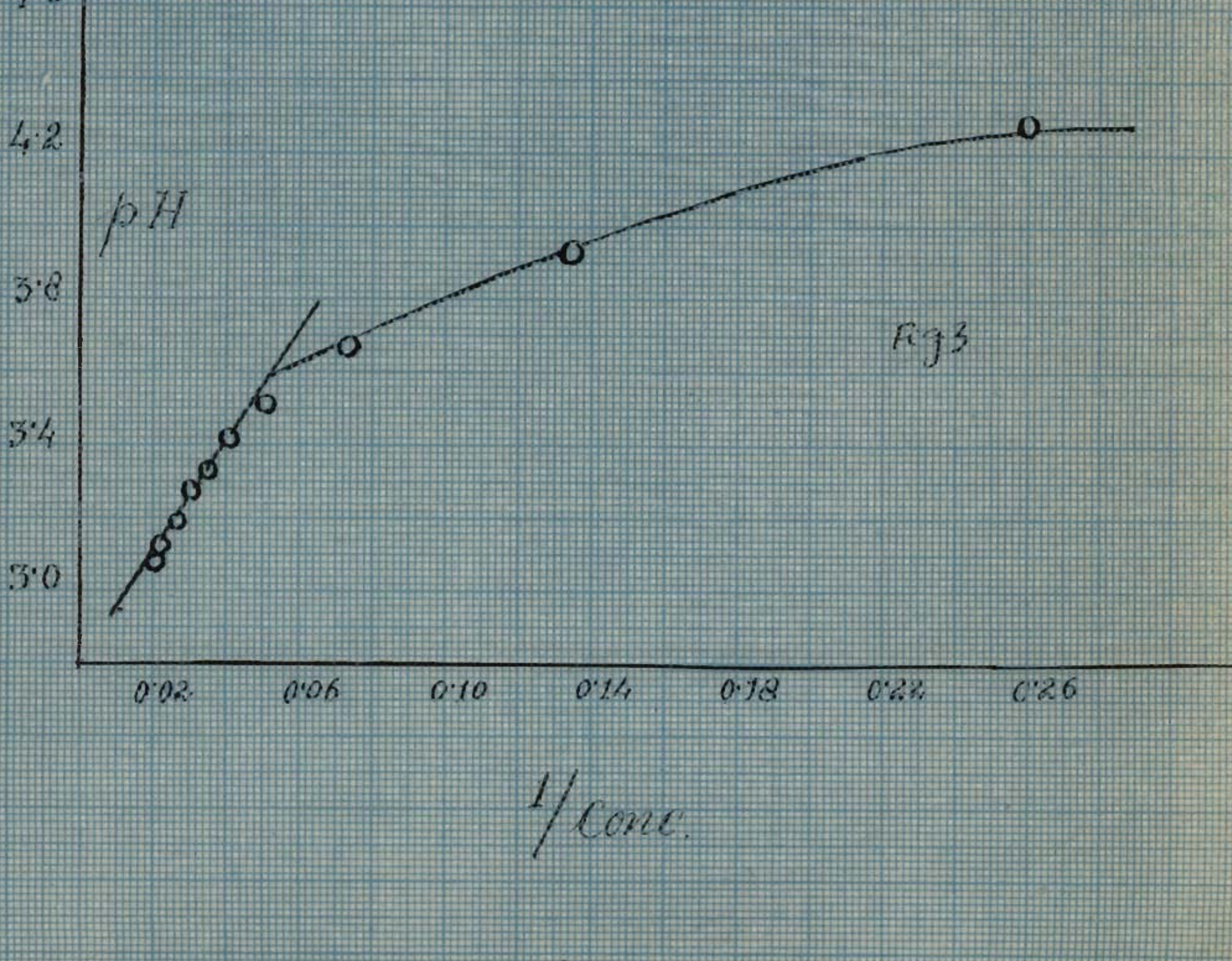

4·6
4·2
pH
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Conc.

Fig 3

Variation in pH of soap solutions in presence of different metal ions.

TABLE 3.

Variations in pH for different concentrations of SPSA in presence of the following:

0.005 M $NiCl_2$ + 0.2 M KCl; 0.0025M $Cd\text{-}I_2$ + 0.2M KI;

0.005M $Pb(NO_3)_2$ + 0.2 M KNO_3

Conc.soap x 10^{-5}M	1/Conc.soap x 10^{5}M	pH		
		$NiCl_2$+KCl	CdI_2+KI	$Pb(NO_3)_2$+KNO_3
0.0	-	4.92	6.03	5.15
3.80	0.2604	4.26	4.48	4.23
7.40	0.1351	3.92	4.11	3.94
13.80	0.0725	3.66	3.80	3.64
19.30	0.0518	3.50	3.61	3.49
24.20	0.0413	3.40	3.48	3.39
28.60	0.0350	3.32	3.40	3.30
32.40	0.0309	3.26	3.34	3.24
37.50	0.0267	3.19	3.24	3.18
44.50	0.0225	3.12	3.16	3.11
50.00	0.0200	3.06	3.10	3.04
		Fig. 2	Fig. 3	Fig.4

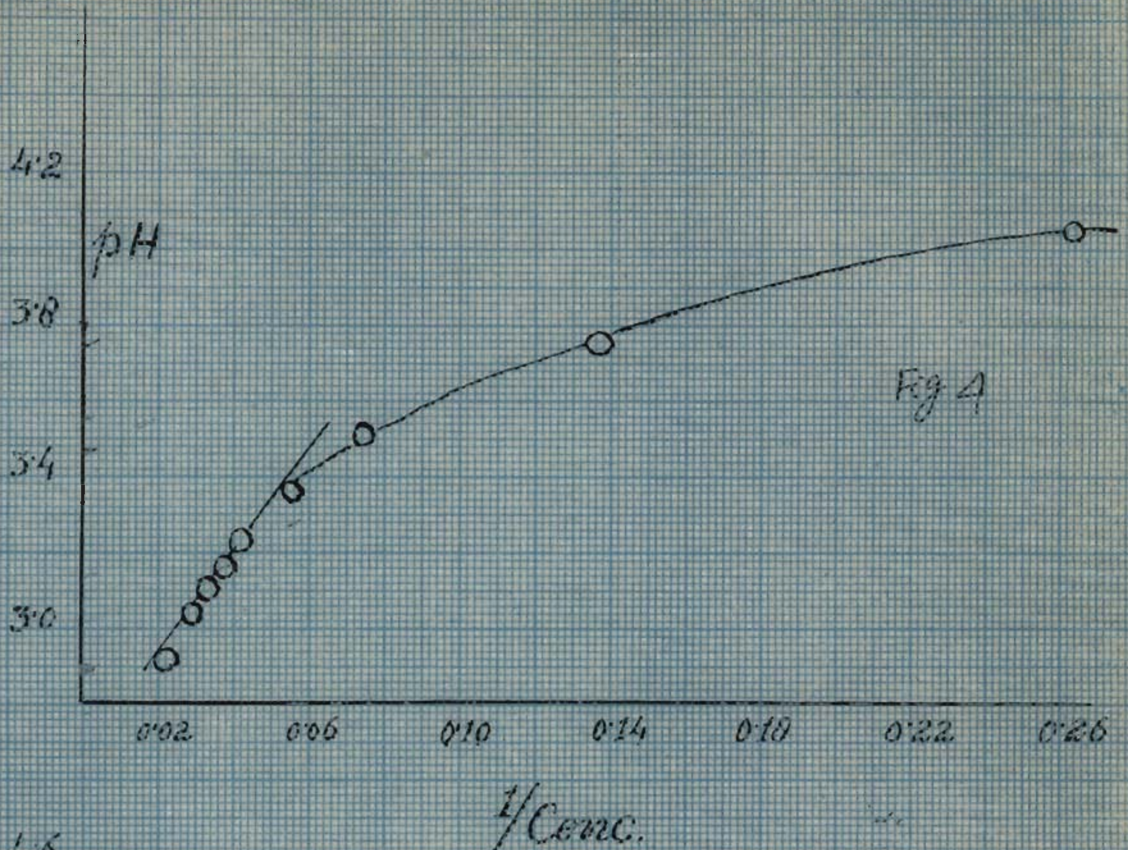

4·2
pH
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Conc.

Fig 4

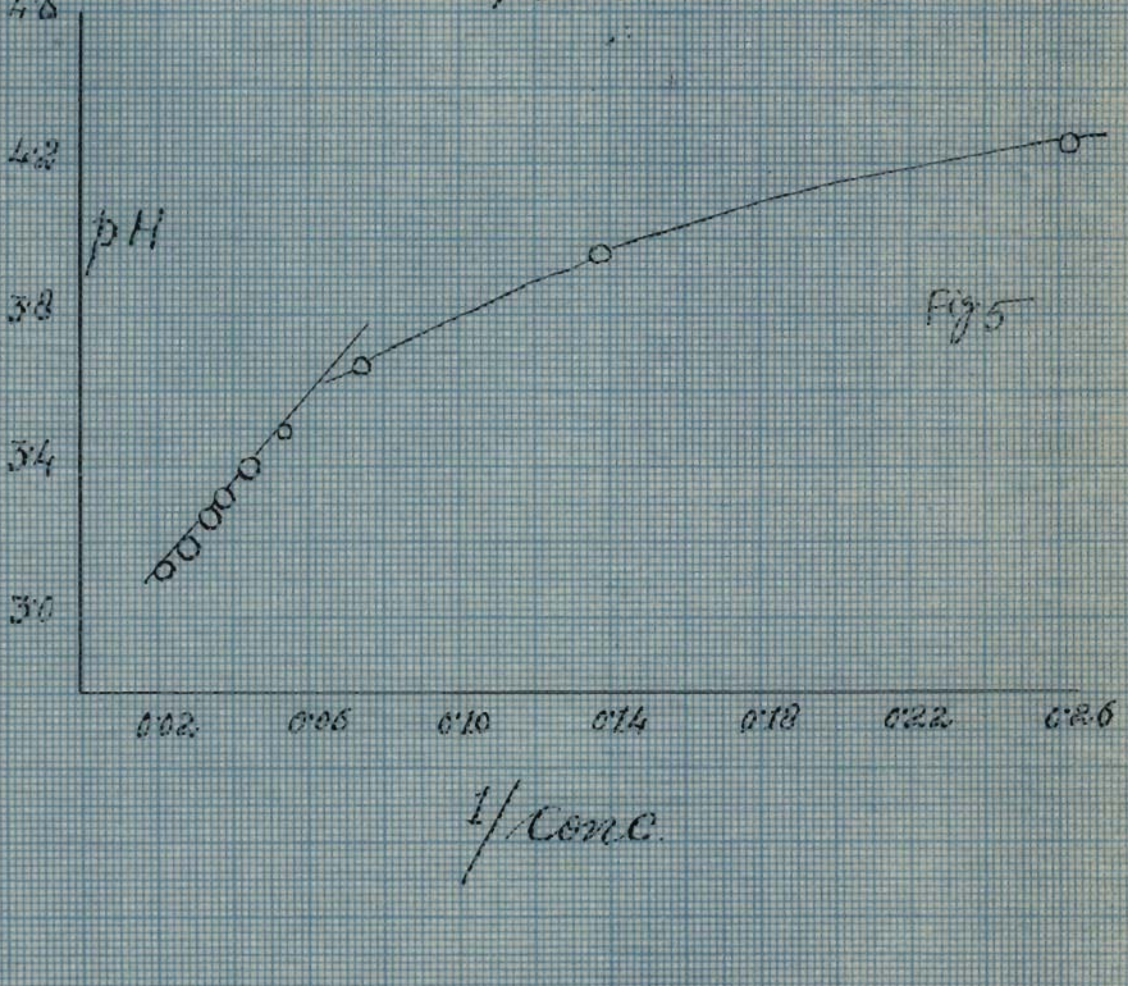

4·6
4·2
pH
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Conc.

Fig 5

TABLE 4.

Variation in pH for different concentrations of STSA in presence of the following:

0.005 M $NiCl_2$ + 0.2 M KCl; 0.0025M CdI_2+0.2M KI;

0.005M $Pb(NO_3)_2$ + 0.2M KNO_3

Conc.soap x 10^{-5}M	1/Conc.soap x 10^{5}M	pH		
		$NiCl_2$+KCl	CdI_2+KI	$Pb(NO_3)_2$+KNO_3
0.0	-	4.93	6.03	5.15
3.80	0.2604	4.02	4.48	4.20
7.40	0.1351	3.72	4.06	3.88
13.80	0.0725	3.48	3.74	3.63
19.30	0.0518	3.31	3.54	3.48
24.20	0.0413	3.20	3.40	3.40
28.20	0.0350	3.13	3.31	3.32
32.40	0.0308	3.08	3.26	3.27
37.50	0.0267	3.00	3.15	3.20
44.50	0.0225	2.92	3.05	3.12
50.00	0.0200	2.86	2.97	3.07
		Fig.5	Fig.6	Fig.7

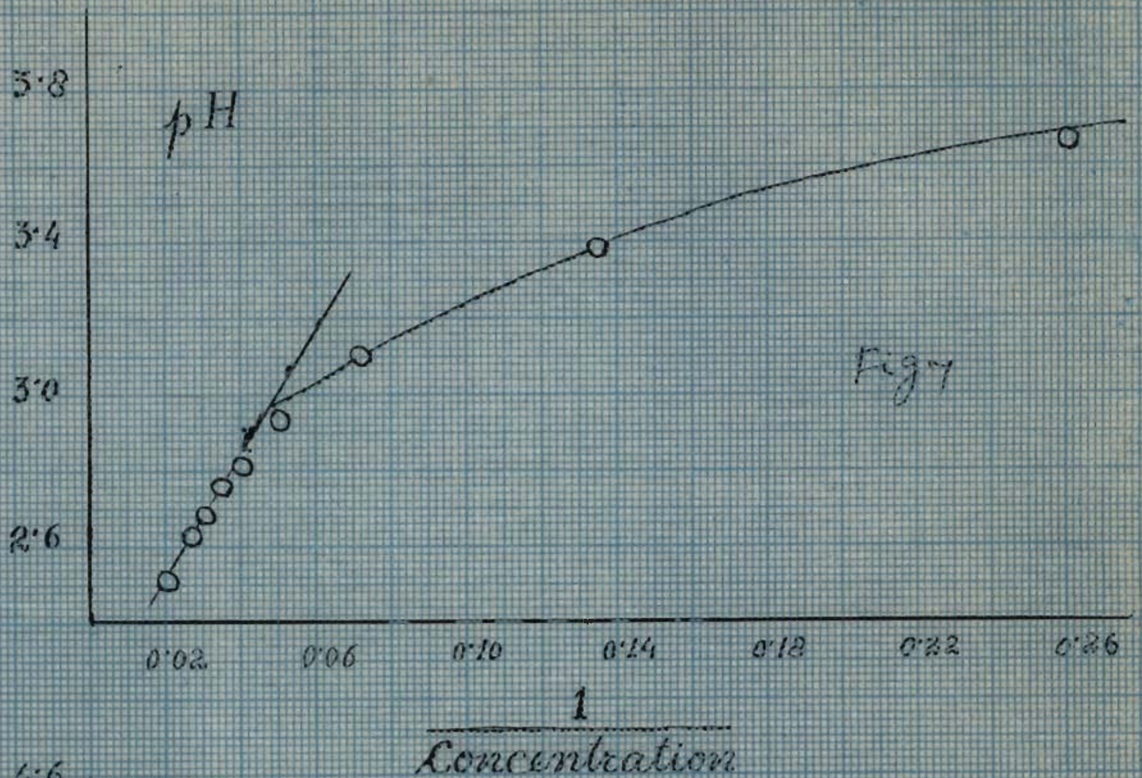


Fig 7
pH
3·8
3·4
3·0
2·6
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Concentration

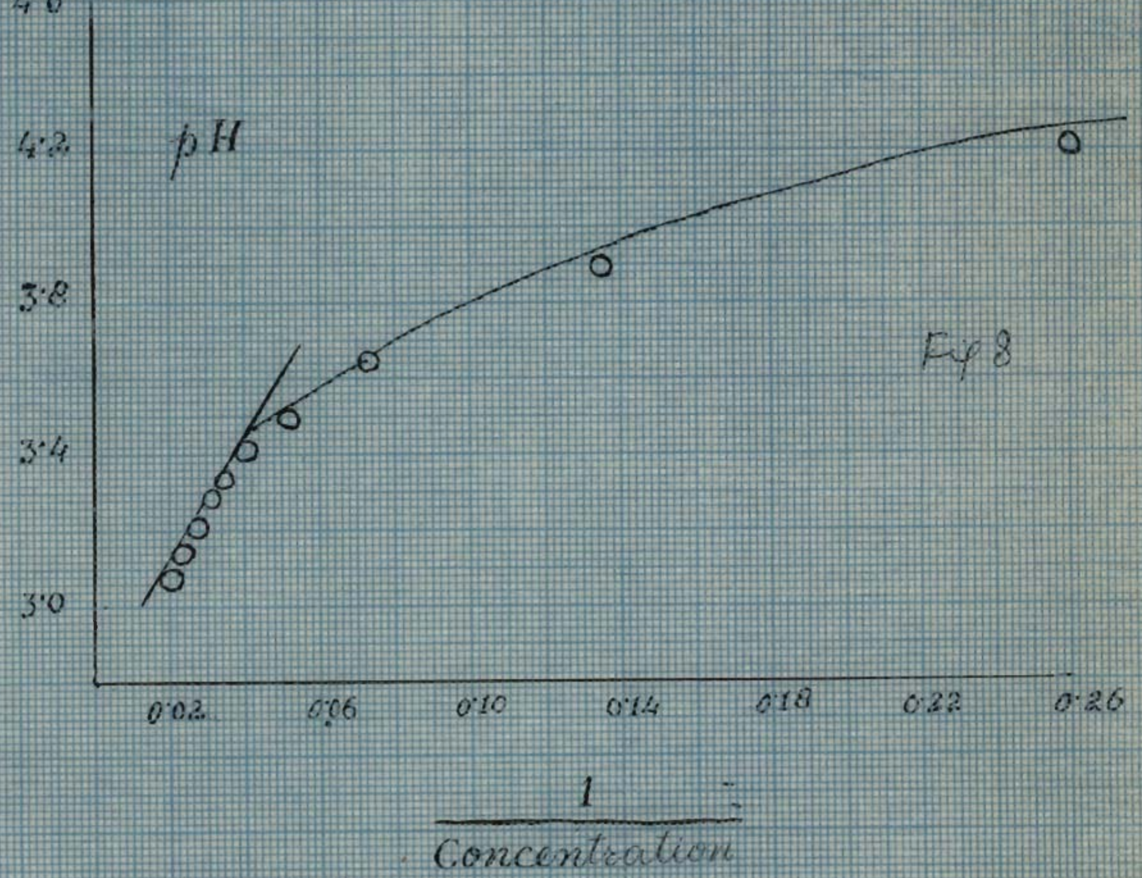


Fig 8
4·6
pH
4·2
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1/Concentration

TABLE 5

Variation in pH for different concentrations of SXSA in presence of the following:

0.005M $NiCl_2$+0.2M KCl; 0.0025M CdI_2+0.2M KI;

0.005M $Pb(NO_3)_2$+ 0.2M KNO_3

Conc.soap x 10^{-5}M	1/Conc.soap x 10^{5}	pH		
		$NiCl_2$+KCl	CdI_2+KI	$Pb(NO_3)_2$+KNO_3
0.0	-	4.92	6.03	5.15
3.80	0.2604	3.82	4.50	4.31
7.40	0.1351	3.54	3.89	3.93
13.80	0.0725	3.28	3.50	3.59
19.30	0.0518	3.10	3.29	3.43
24.20	0.0413	2.99	3.15	3.30
28.20	0.0350	2.92	3.05	3.24
32.40	0.0308	2.86	2.97	3.18
37.50	0.0267	2.80	2.89	3.09
44.50	0.0225	2.72	2.80	3.00
50.00	0.0200	2.67	2.71	2.92
		Fig.8	Fig.9	Fig.10A

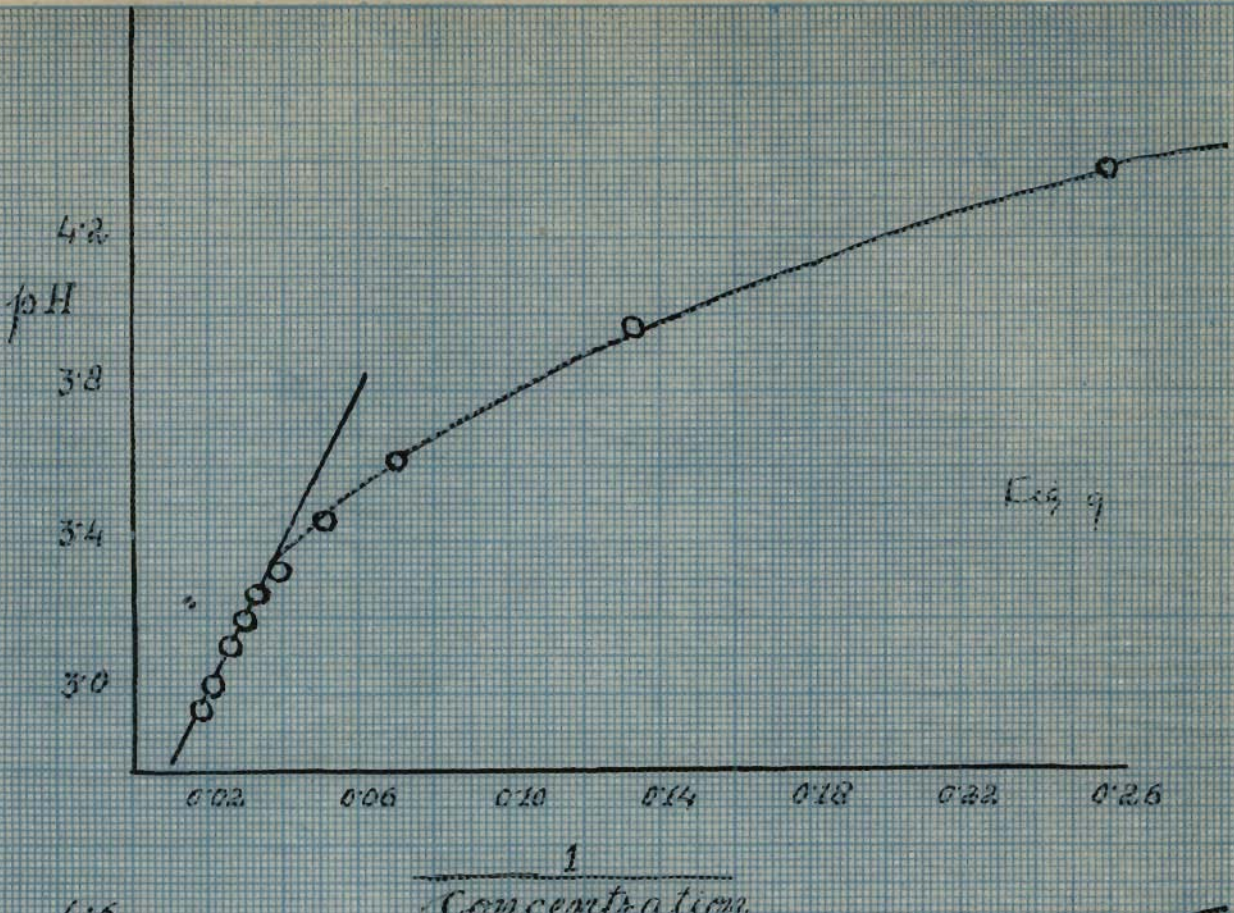


Fig 9

pH
4·2
3·8
3·4
3·0
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1
Concentration

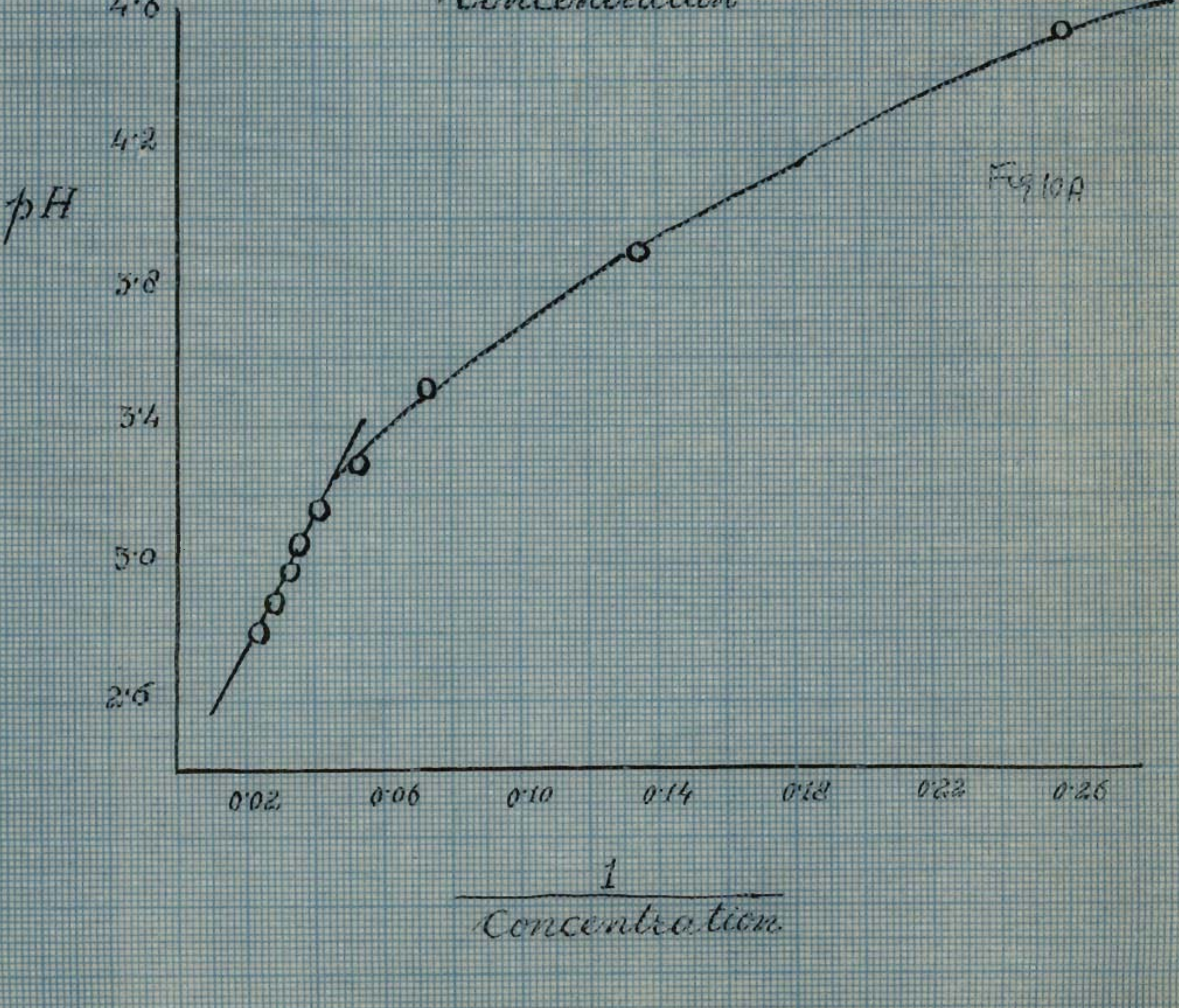


Fig 10A

pH
4·6
4·2
3·8
3·4
3·0
2·6
0·02
0·06
0·10
0·14
0·18
0·22
0·26
1
Concentration

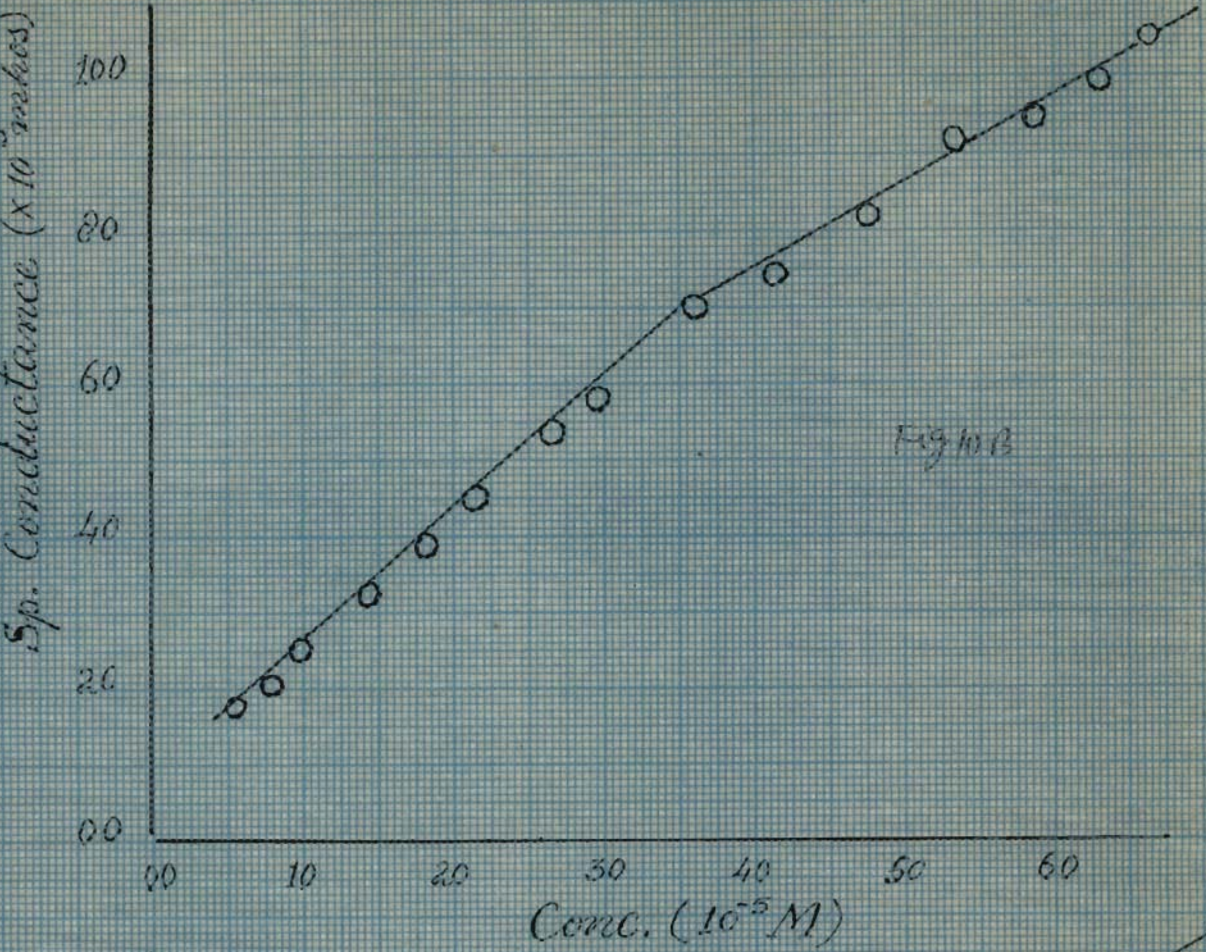


Fig 10B

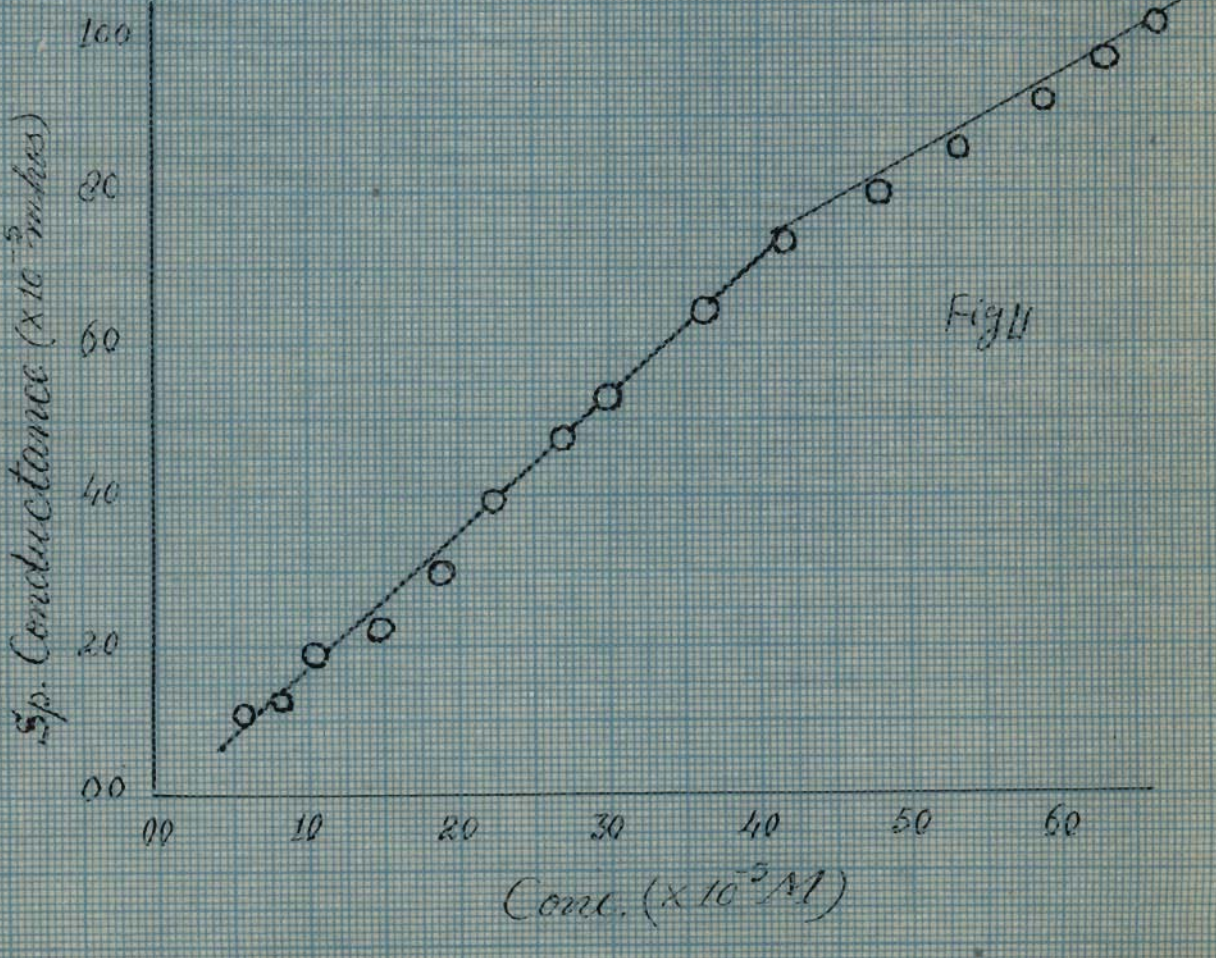


Fig 11

TABLE 6

Specific conductivity of SPSA, STSA and SXSA at different dilutions.

Conc.soap	Conductance (mhos)		
x 10^{-5} M	SPSA	STSA	SXSA
5.4	5.17 x 10^{-5}	3.50 x 10^{-5}	0.95 x 10^{-5}
7.8	7.00 "	4.00 "	2.75 "
10.2	8.00 "	6.30 "	4.40 "
14.6	10.23 "	7.33 "	6.87 "
18.6	12.30 "	9.63 "	11.20 "
22.2	14.70 "	12.97 "	11.90 "
27.1	17.50 "	15.71 "	17.20 "
30.0	19.13 "	17.58 "	20.50 "
36.4	23.10 "	21.18 "	24.80 "
41.7	24.54 "	24.20 "	28.40 "
46.1	27.16 "	26.27 "	31.20 "
53.3	30.34 "	28.50 "	35.70 "
58.8	31.50 "	30.50 "	38.20 "
63.2	33.00 "	32.30 "	40.10 "
66.6	35.00 "	34.00 "	41.50 "
	Fig.10B	Fig.11	Fig.12

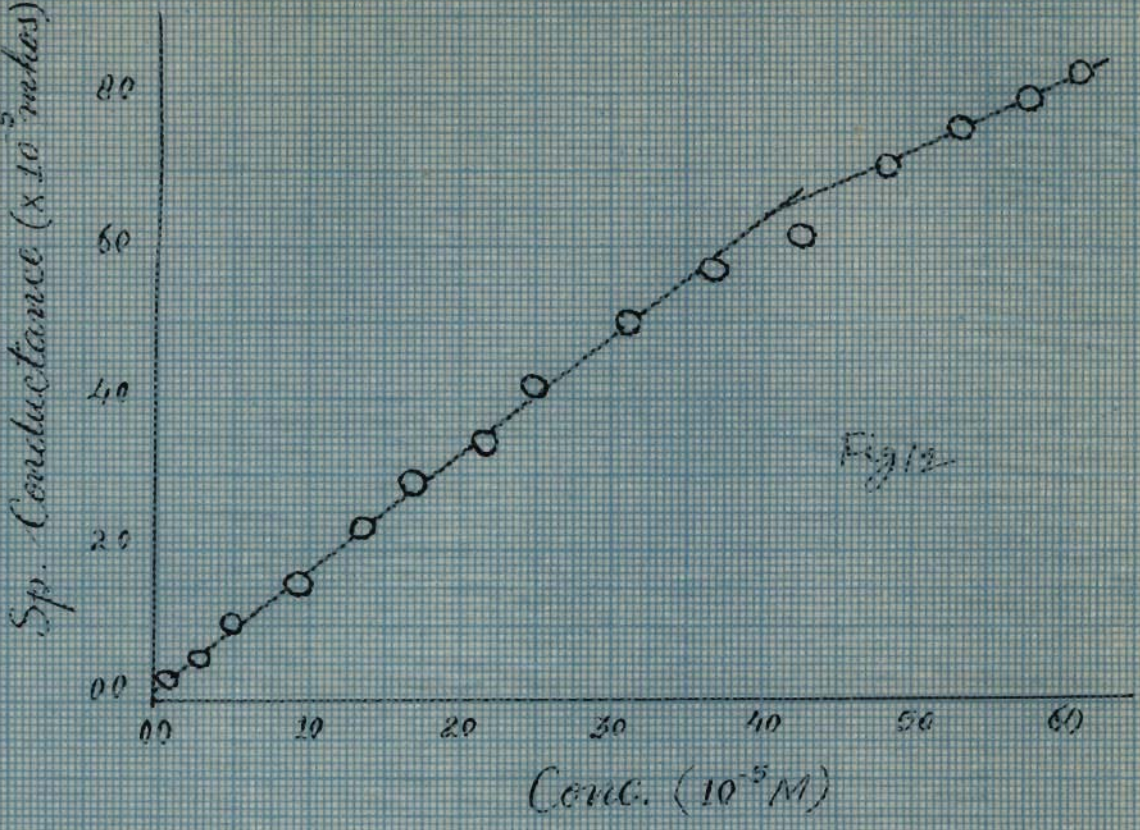

Sp. Conductance (x 10⁻⁵ mhos)
80
60
40
20
00
00
10
20
30
40
50
60
Conc. (10⁻⁵ M)

Fig 12

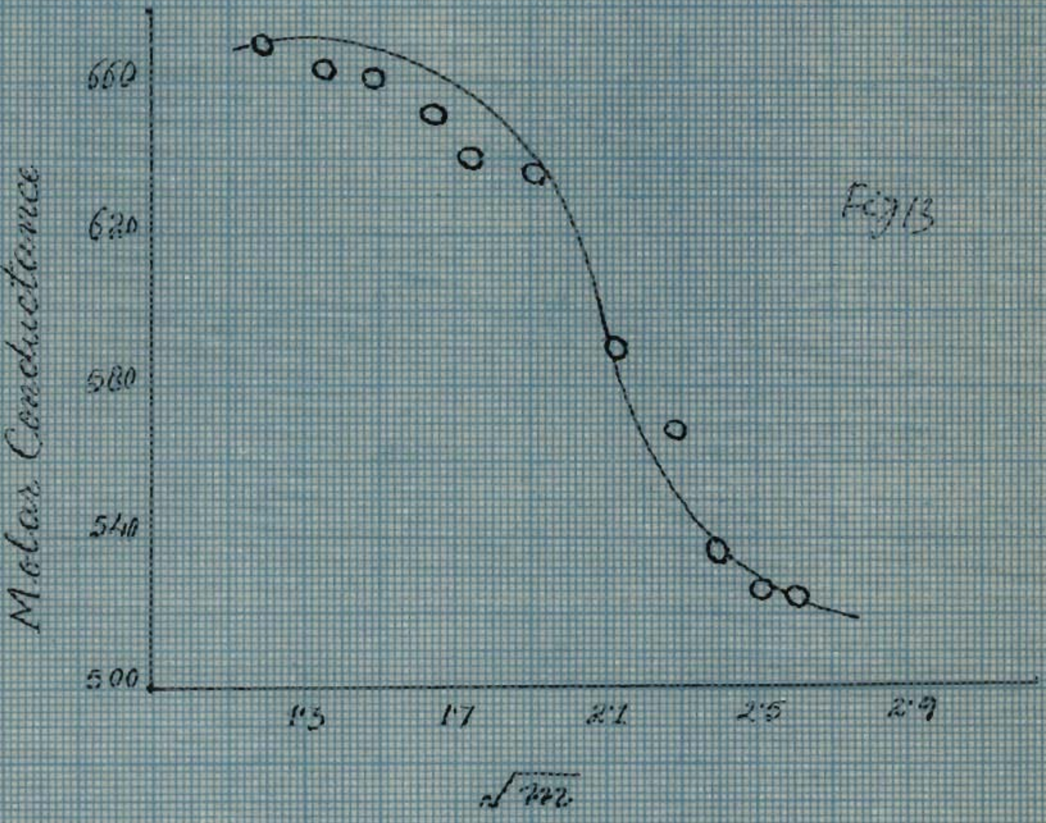

Molar Conductance
660
620
580
540
500
1·3
1·7
2·1
2·5
2·9
√m

Fig 13

TABLE 7

Molar conductance of SPSA,STSA and SXSA.

$\sqrt{m}$	Molar conductance in mhos.		
	SPSA	STSA	SXSA
0.0073	958.5	648.0	352.5
0.0081	786.2	513.0	431.3
0.0101	784.3	617.6	470.0
0.0121	700.0	502.0	600.0
0.0136	661.0	517.2	536.0
0.0149	660.6	589.0	634.6
0.0164	648.0	580.0	683.0
0.0173	637.6	586.0	681.3
0.0191	634.6	582.0	681.3
0.0204	545.4	580.0	678.9
0.0214	589.0	570.0	669.7
0.0231	569.0	534.0	649.0
0.0250	522.0	511.0	634.0
0.0258	525.0	510.5	623.0
	Fig.13	Fig.14	Fig.15

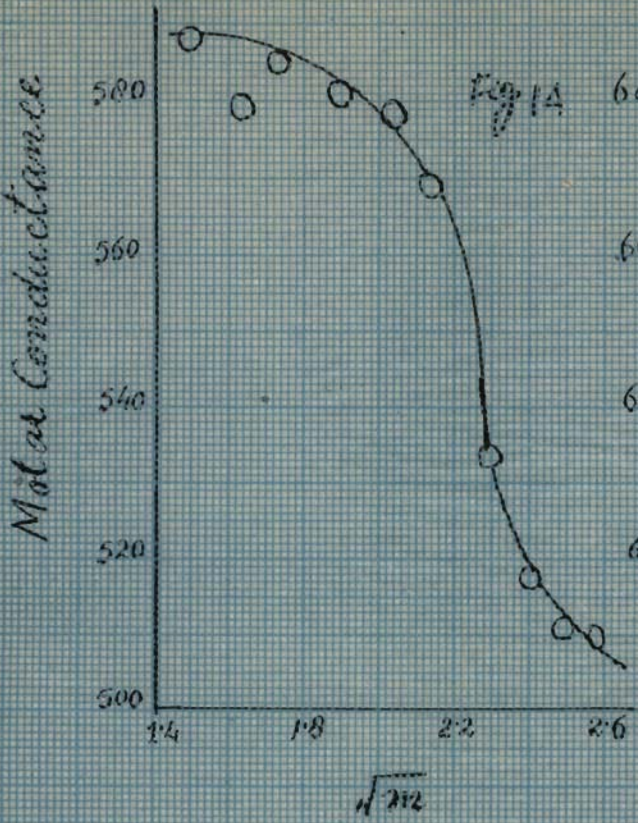


Fig14

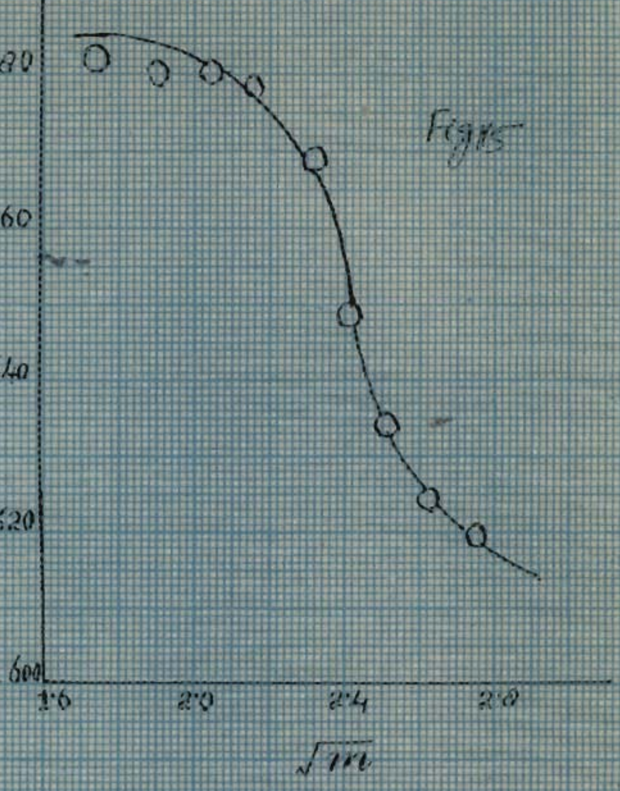


Fig15

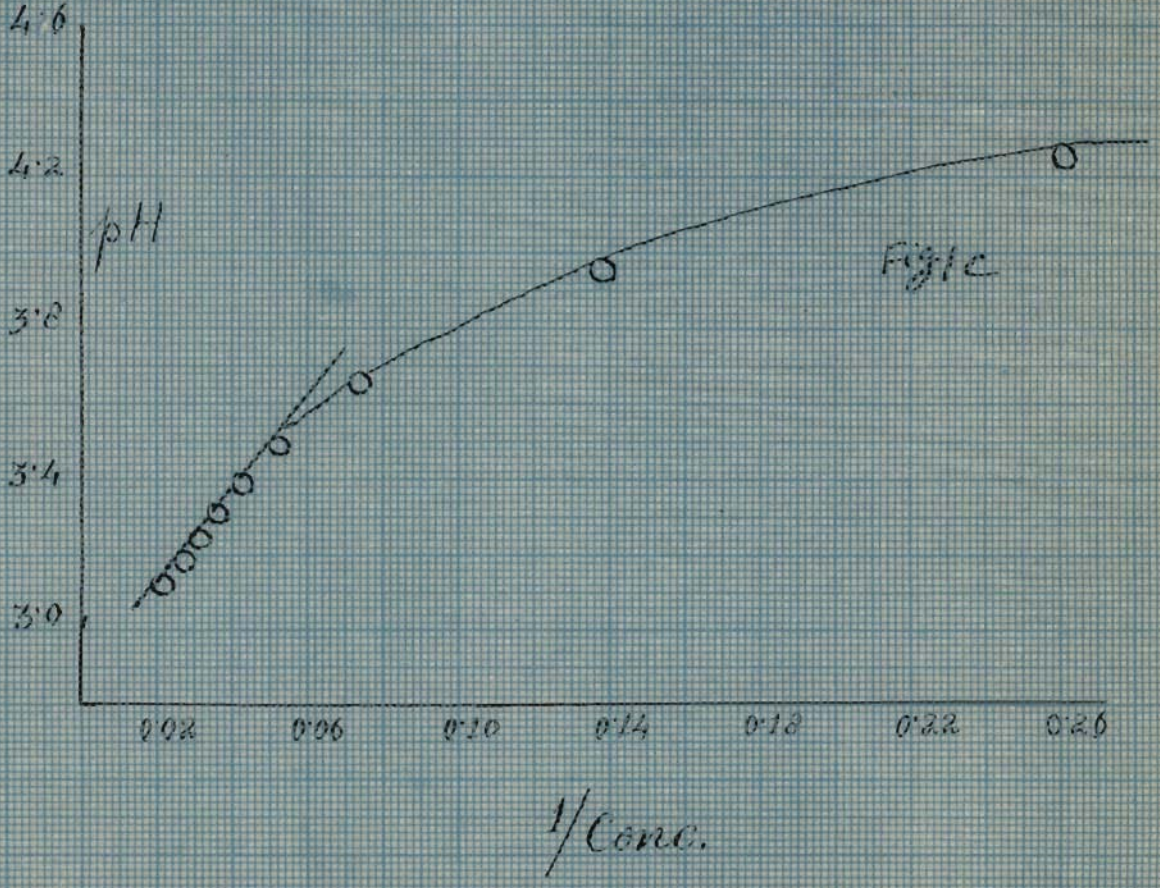
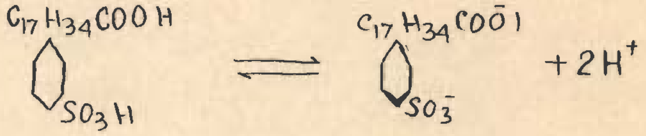


Fig16

RESULTS AND DISCUSSION

The behaviour of these soaps in aqueous medium is quite interesting. On the addition of 1 cc.of 10^{-3}M soap in 25 cc.of double distilled water, a considerable decrease in pH was observed. It means that the soaps under consideration behave as strong electrolytes,ionising as follows:



This behaviour is in agreement with the views of Hartley (loc.cit.) according to which surface active agents behave in dilute solutions as ordinary electrolytes up to a certain concentration.

Further addition of the soap although results in a decrease in pH but it reaches a constant value after a certain concentration. It appears that the charged micelles so formed contain an appreciable amount of negative charge and the hydrogen ions present therein are attracted electrostatically by these negatively charged micelles, resulting in the formation of a diffused double layer around the negatively charged micelles. Under these circumstances the hydrogen ions would show an irregular decrease in pH before and after the micelle formation. In a solution of HCl,the pH of which was the same as that of the soap, different concentrations of soap solution was added,it was found that there was no change in the pH (Table 8). This shows that soap micelles do not dissociate after a certain pH.

TABLE 8

Variation in the pH of HCl(pH 2.8)on addition of increasing amounts of soap and water respectively.

Vol.HCl. in cc.	*Vol.SPSA (10^{-3}M) in cc.	pH with Soap	pH with Water
14.0	1.0	2.81	2.89
13.0	2.0	2.81	2.91
12.0	3.0	2.81	2.93
10.0	5.0	2.81	3.01
8.0	7.0	2.81	3.12
5.0	10.0	2.82	3.30

* Refers to two different sets:one with SPSA and the other with double distilled water.

On plotting the concentration against pH a curve with a straight line portion in the lower and a hyperbolic portion in the higher concentration ranges is obtained. A curve just reverse to the first one,with the straight line portion in the higher concentration range and the hyperbolic portion in the lower concentration range was obtained exhibiting sharp in flexion points.

The c.m.c. values obtained from the inflexion points of the 1/C vs.pH curve are given the table 9.

TABLE 9

c.m.c. values of SPSA, STSA and SXSA.

Soap	Critical micelle concentration (order 10^{-5}M)
SPSA	13.8
STSA	15.6
SXSA	20.0

Further experiments were performed in presence of foreign electrolytes in order to compare the results of polarography for the c.m.c. values of alkyl-aryl sulphonates determined earlier in this laboratory. These results together with the results of polarography and conductometry (determined with out electrolyte) are summarised in table 10.

TABLE 10

Comparative c.m.c. values of SPSA, STSA and SXSA from different methods.

Method	c.m.c. value (order 10^{-5} M)			
		Ion or complex		
	With out electrolyte	Ni^{+2} in KCl	Pb^{+2} in KNO_3	$Cd-I_2$ complex
Conductometric				
SPSA	36.4	-	-	-
STSA	41.7	-	-	-
SXSA	46.1	-	-	-
Polarographic				
SPSA	-	8.20	9.80	121.00
STSA	-	48.98	2.19	7.94
SXSA	-	36.31	1.29	5.37
pH metric				
SPSA	13.8	16.7	16.0	23.8
STSA	15.6	13.8	16.7	23.8
SXSA	20.0	16.7	17.8	26.0

Spectrophotometry:- The data of chapter I was utilized here to calculate the c.m.c. of anionic soaps. The concentration of the soap, correponding to the c.m.c. value, was that which shifted the maximum of malachite green from 625 mμ to 640 mμ and of rhodamine 6G from 535 mμ to 545 mμ. The exact values were obtaind by plotting the optical density of the dye-soap mixture against

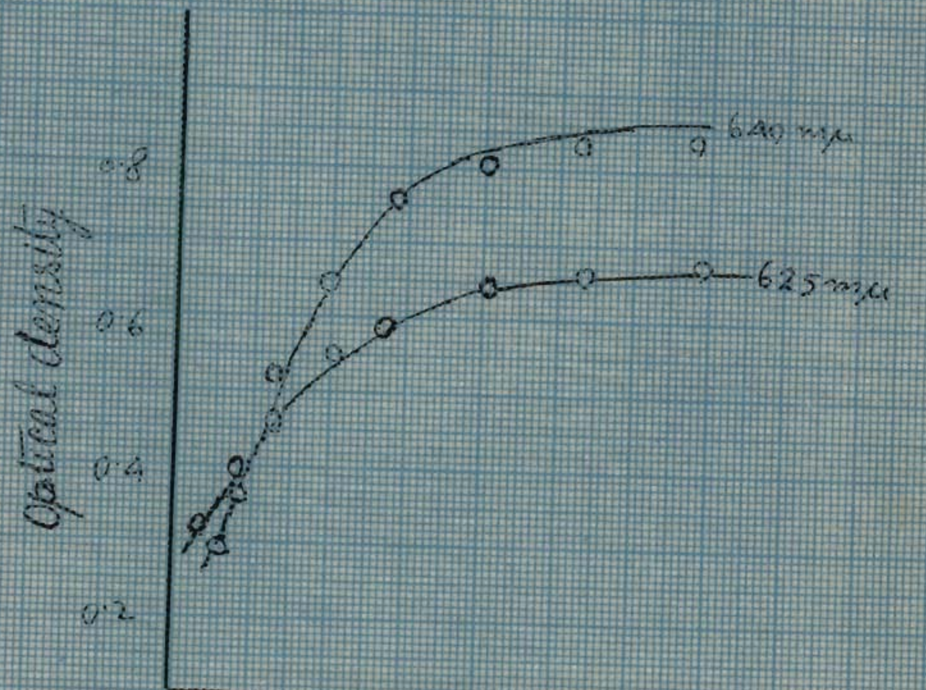


Fig 16

SPSA + malachite green
pH 9.12

soap concentration at 640 mu and 625 mu in the case of malachite green and at 535 mu and 545 mu in the case of rhodamine 6G. The intercept of the two curves were taken as the c.m.c. value(Fig. 16) . The values are given in tables 11 and 12.

TABLE 11

Concentration of soap which shift the maximum of malachite green from 625 mμ to 640 mμ.

pH	Soap concentration(order 10^{-5}M)		
	SPSA	STSA	SXSA
2.72	8.0	8.0	8.0
7.00	8.0	8.0	12.0
9.12	12.0	12.0	20.0

TABLE 12

Concentration of soap which shift the maximum of rhodamine 6G from 535 mμ to 545 mμ.

pH	Soap concentration(order 10^{-5}M)		
	SPSA	STSA	SXSA
2.72	8.0	8.0	12.0
7.00	8.0	10.0	12.0
9.12	10.0	12.0	18.0

The values obtained by different methods show the same order of c.m.c., that is, 10^{-5}M. The plots of specific conductivity vs. soap concentration give c.m.c. values which are higher but nevertheless the same order, viz., SXSA > STSA > SPSA exists.

On plotting the curves between $\sqrt{m}$ and molar conductance further evidence regarding the existence of ionic micelles in the solution as well as the tendency of these soaps to behave as a strong electrolyte up to a certain concentration was obtained. From these results it can also be concluded that the c.m.c. values decrease with the decrease in length of the carbon chain.

Although the same order (10^{-5}M) of c.m.c. was obtained both by polarography and pH metric methods but the order is changed in presence of different electrolytes. The values are lower in the case of polarography in presence of Pb^{+2} in KNO_3 and Cd-I_2 complex ions in comparision to the values obtained by pH metrically, while in the case of Ni^{+2} in KCl the values are higher.

The values obtained spectrophotometrically show that the micelles form earlier in lower pH ranges than that to alkaline and neutral medium. This is due to because anionic soaps ionise more in alkaline and neutral medium than in acidic. Both pH metric and spectrophotometric methods gave the higher values of the c.m.c. when the soap solution was added to a solution of pH about 7.00 or more. Both show that the micelle formation depends upon the ionisation of the soap.

*****

c.m.c. of cationic soaps.

E.m.f. measurements: A number of electrometric methods have been used to study soap solution but the potentiometric methods have received a little attention. If a suitable indicator electrode is made available this method may prove quite convenient for the calculation of c.m.c. activity coefficient, dimerization etc.

Walton(60) used this method to study the effect of temperature and added electrolytes on ionic soaps. He measured the e.m.f. of the cell,

$$Ag\text{-}AgCl/HCl(\ 0.1M\ )/\text{glass electrode}/C_{12}H_{25}SO_3H/Hg_2(C_{12}H_{25}SO_3)_2\text{-}Hg$$

to determine the c.m.c. and the activity coefficient of 1-n dodecane sulphonic acid and also the solubility product of mercurous dodecane sulphonate.

Hutchinson(61) and Van Voorst(62) used e.m.f. measurements method constructing similar types of concentration cells to find temperature dependency and pre-association of surfactant ions respectively.

In this part of the chapter 2 results of our investigations on the suitability of the cell,

$$Ag,AgBr/\underset{(\ C_1)}{\text{CTMAB or CPB}}/\ KNO_3,\text{Agar Bridge}/KCl(\text{Sat.})Hg_2Cl_2,Hg.$$

for determining the c.m.c. and activity coefficient of cationic soaps are reported. The c.m.c. values obtained by this method are compared with those obtained conductometrically and spectrophotometrically.

EXPERIMENTAL

Reagents:- The cationic soaps, cetyl trimethyl ammonium bromide (CTMAB) and cetyl pyridinium bromide (CPB) were BDH products. They were recrystalized from acetone. Solutions were prepared in doubly distilled water(all glass) in molar concentrations taking the molecular weights of CTMAB as 364.47 and CPB as 384.46 respectively.

The silver-silver bromide electrode was prepared by depositing silver on platinium wire from the solution of $AgNO_3$(0.2M) and KCN(0.2M) under the potential of 2 volts for about 45 minutes. It was then washed with doubly distilled water and was put finally in 0.1N solution of hydrobromic acid keeping silver deposited platinium wire as positive. Electrolysis was carried under a potential of 2 volts for about 20 minutes. The Ag-AgBr electrode thus formed was washed under distilled water. The e.m.f$.data at 30°C for different concentrations of cationic soaps are given in tables 1&2 and the results of conductometry are given in tables 3&4 .

Spectrophotometry:- The spectrophotometric method as used in the case of the alkyl-aryl sulphonates was also employed in studying the solutions of cetyl trimethyl ammonium bromide and cetyl pyridinium bromide by employing alizarin red S. The experimental data have been taken from chapter I.

TABLE 1

E.M.F. of the cell for different concentrations of cetyl trimethyl ammonium bromide.

Conc.soap x 10^{-5}M	1/ Conc.soap x 10^{+5}M	e.m.f.involts
3.22	0.3106	0.0925
6.25	0.1600	0.0820
9.03	0.1107	0.0750
11.80	0.0850	0.0690
16.70	0.0599	0.0630
21.00	0.04762	0.0570
25.00	0.04000	0.0530
28.60	0.03497	0.0500
34.80	0.02874	0.0460
40.00	0.02500	0.0430
50.00	0.02000	0.0380
57.10	0.01751	0.0350
66.70	0.01499	0.0320

Fig. 1

TABLE 2.

E.M.F. of the cell for different concentrations of cetyl pyridinium bromide.

Conc.of soap ($x10^{-4}M$)	1/Conc. ($x10^{4}M$)	e.m.f. in volts
3.20	0.3125	0.392
5.86	0.1707	0.380
8.92	0.1121	0.370
11.80	0.0847	0.365
17.00	0.0600	0.355
22.00	0.0454	0.348
30.00	0.0333	0.341
35.00	0.0286	0.338
40.40	0.0247	0.335
47.50	0.0211	0.332
53.80	0.0186	0.329
60.10	0.0166	0.327
66.70	0.0149	0.324

Fig.2

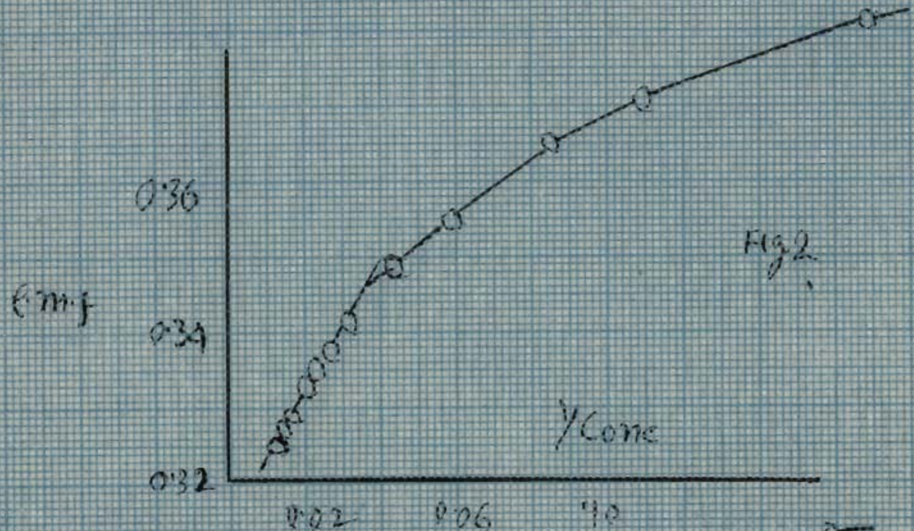
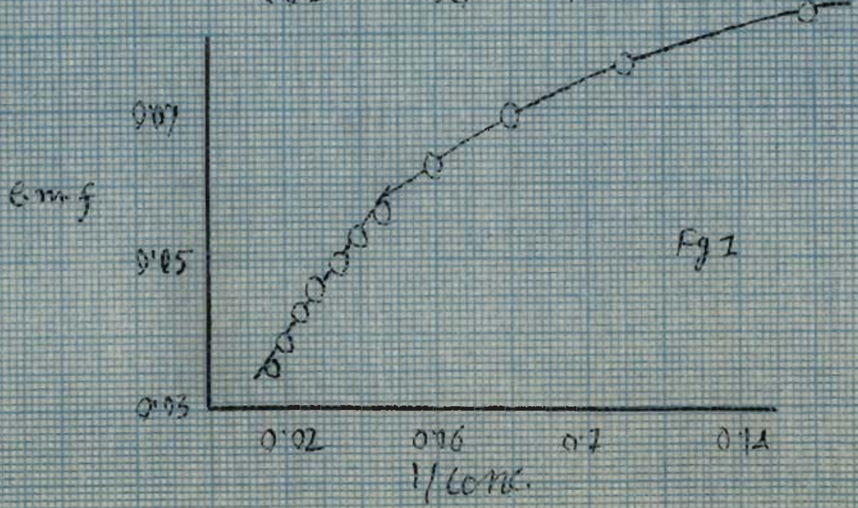


Fig 2



Fg 1

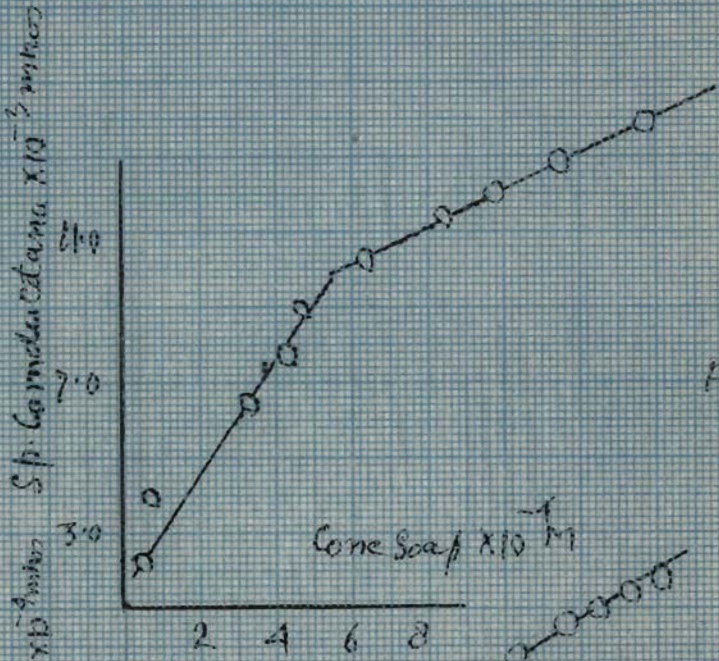


Fig 4

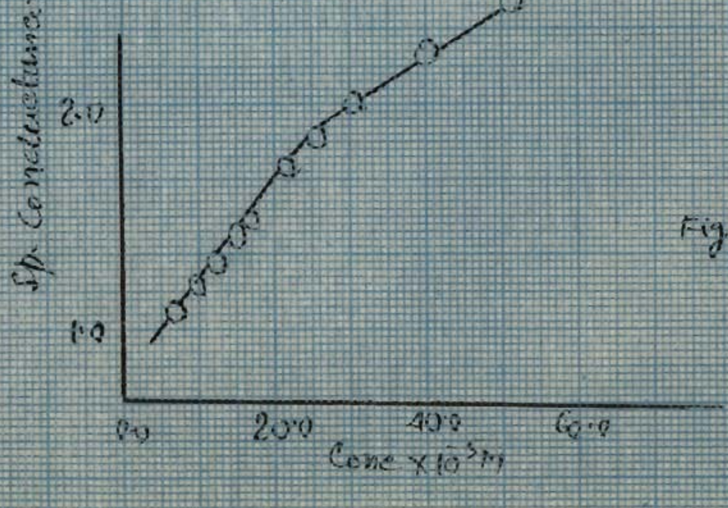


Fig 3

TABLE 3

Specific conductivity of cetyl trimethyl ammonium bromide at different dilutions.

Conc.soap $\times 10^{-5}$ M	Sp.conductivity $\times 10^{-3}$ mhos	Conc.soap $\times 10^{-5}$ M	Sp.conductivity $\times 10^{-3}$ mhos
3.33	0.0667	30.80	0.2083
6.25	0.1053	40.00	0.2222
9.03	0.1094	44.40	0.2564
11.80	0.1136	51.60	0.2600
14.30	0.1163	57.10	0.2642
16.70	0.1198	62.50	0.2702
21.00	0.1482	66.70	0.2842
25.00	0.1613	70.00	0.2898
28.60	0.1786	72.10	0.3021

Fig. 3

TABLE 4

Specific conductivity of cetyl pyridinium bromide at different dilutions.

Conc.soap x 10^{-3} M	Sp.conductivity x 10^{-3} mhos	Conc.soap x 10^{-3} M	Sp.conductivity x 10^{-3} mhos
0.82	0.924	4.60	8.812
1.12	2.000	5.85	9.803
1.64	3.000	6.70	10.311
2.22	4.132	8.50	11.200
2.67	5.112	9.86	11.815
3.33	6.220	11.40	12.632
4.10	7.600	13.33	13.572

Fig. 4

RESULTS AND DISCUSSION

The electrode reaction in the concentration cell

$Ag\text{-}AgBr/\underset{(C_1)}{CTMAB}/KNO_3$, Agar Bridge/KCl(sat.)$Hg_2Cl_2, Hg$

is as follows:-

$AgBr = Ag^+ + Br^-$

$Ag^+ + e = Ag$

The over all reaction will be

$$AgBr + e = Ag + Br^-$$

The electrode is reversible to the bromide ions and can help in knowing the amount of dissociated bromide ions from cationic soaps. Applying the Nernst equation

$$E = E_o + \frac{RT}{nF} \ln \frac{\text{Product of activities of reactants}}{\text{Product of activities of resultants}}$$

or $$E = E_o + \frac{RT}{nF} \ln \frac{a_{AgBr}}{a_{Br^-} \times a_{Ag}}$$

or
$$E = E_o - \frac{RT}{nF} \ln a_{Br^-}$$

Since the activity coefficient of Ag and AgBr is taken as unity.

The change in potential in the half cell was measured against saturated calomal electrode. The oberved potential(E_{ob}) will then be equal to

$$E_{ob} = E_{Ag\text{-}AgBr} - E_{cal.}$$

or $$E_{ob} = E_{o\ Ag\text{-}AgBr} - \frac{RT}{nF} \ln a_{Br^-} - E_{cal.}$$

or $$E_{ob} = 0.07 - 0.059 \ln a_{Br^-} - 0.249$$

($E^*_{o\,Ag - AgBr} = 0.07$ and $E_{cal.} = 0.249$ are taken from the literature).

or $$E_{ob} = - 0.179 - 0.059 \ln a_{Br^-}$$

From the above equation activity and activity coefficient of Br^- ions have been calculated and are reported in table I and II. The plots between soap concentration vs.activity coefficient give a break corresponding to the c.m.c. value(Fig. 5).

TABLE I.

Activity and activity coefficient of CTMAB.

Conc.soap($x10^{-5}$M)	Activity($x10^{-5}$M)	Activity coefficient
3.22	2.455	0.76
6.25	3.802	0.61
9.03	4.955	0.55
11.80	6.266	0.53
16.70	9.247	0.56
21.00	10.000	0.48
25.00	11.690	0.46
28.60	13.150	0.46
34.80	15.350	0.44
40.00	17.306	0.43
50.00	20.990	0.42
57.10	23.600	0.41
66.70	26.550	0.40

Fig. 5

TABLE II

Activity and activity coefficient of cetyl pyridinium bromide.

Conc.soap (x10^{-4}M)	Activity (x10^{-4}M)	Activity coefficient
3.20	2.559	0.79
5.86	3.917	0.66
8.92	5.794	0.64
11.80	8.241	0.61
17.00	11.220	0.66
22.00	13.680	0.62
30.00	17.950	0.59
35.00	20.180	0.57
40.40	22.700	0.56
47.50	25.120	0.53
53.80	28.710	0.53
60.10	31.050	0.52
66.70	35.590	0.50

Fig. 6

From the potential measurements it is evident that in dilute solutions these soaps behave just like an ordinary electrolytes but after a certain concentration the variation in e.m.f. are extremely small.The concentration beyond which such abrupt changes take place would indicate the formation of ionic micelles. The plots of the inverse of the concentration of soap vs.e.m.f. give breaks which may be taken to correspond to c.m.c.value. It is worth mentioning that similar results were obtained with alkyl-aryl sulphonates on plotting 1/conc.soap vs.pH (chapter II A).

A comparision of these data with the c.m.c. values determined by conductometry(Table III) shows that the conductivity results are a little higher than those of e.m.f. but the same order of c.m.c.values is obtained (10^{-5}M). It appear that the e.m.f. method provides more reliable results since the c.m.c.values of cetyl pyridinium bromide determined by other methods are more close to this method than the conductometric method.

TABLE III

Comparative c.m.c. values of cetyl trimethyl ammonium bromide and cetyl pyridinium bromide.

Method	Critical micelle concentration	
	CTMAB x 10^{-5}M	CPB x 10^{-4}M
Spectrophotometric	26.0	42.0
Conductometric	25.0	53.0
Potentiometric	23.8	38.0

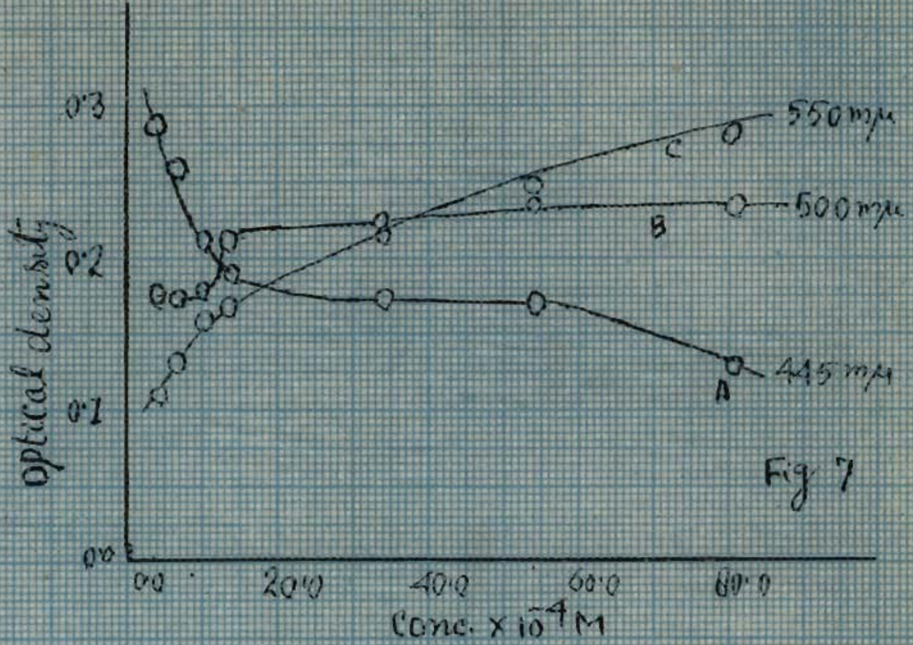


Fig 7

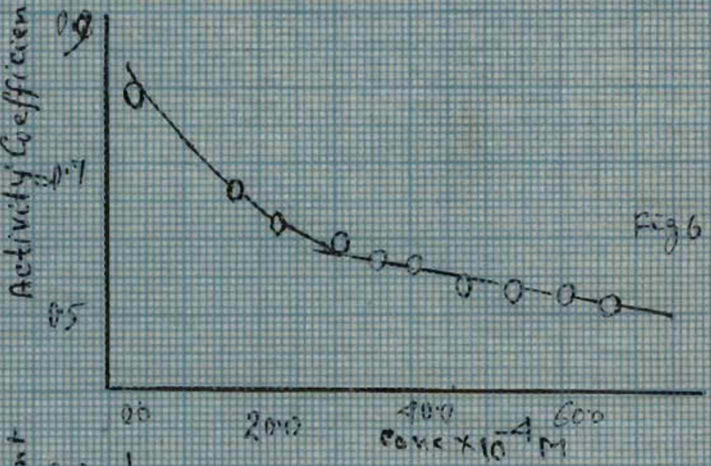


Fig 6

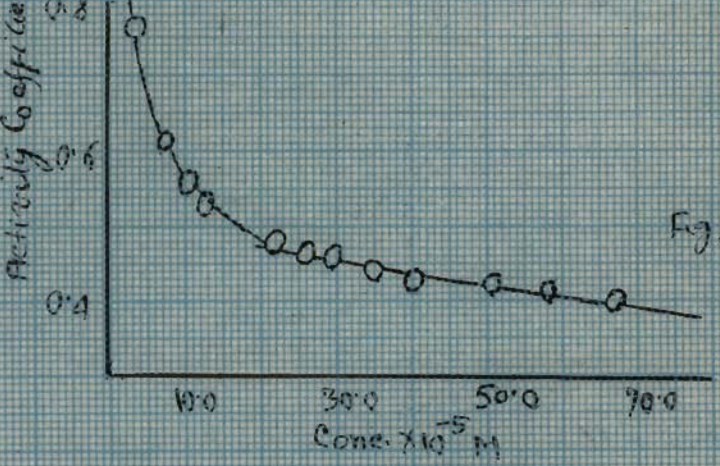


Fig 5

Spectrophotometric method:- The spectra of alizarin red S solutions changes very markedly with increasing concentration of cationic soaps. At pH 9.12 the shift in the maximum of the dye in presence of cationic soap is very large (445 mμ to 550 mμ) in comparision to those observed at the other two pHs. At pH 7.00 in the initial concentrations of the soap, precipitation occurs which might be attributed to dye-soap complex. However, on further addition of soap, the precipitate redissolves and the dye gives the same maximum as in alkaline range, the shift being from 515 mμ to 550 mμ. At pH 2.00 no appreciable shift in dye maximum could be observed (415 mμ to 425 mμ).

We have shown in chapter I that in dilute soap solutions the binding ratio between the soap and the dye molecule is 1:1. This ratio, however, changes with the increase in soap concentration due to the appearence of micelles in the solution. At pH 9.12 two maximum shifts were observed, viz., from 445 mμ to 525 mμ and 525 mμ to 550 mμ in presence of cetyl trimethyl ammonium bromide. The first shift takes place with soap concentration 6.66×10^{-5}M while the second one was observed by increasing a little beyond than this concentration. While in the case of cetyl pyridinium bromide the shift in maximum was from 445 mμ to 500 mμ for the concentration 13.3×10^{-4}M and the second maximum i.e. 550 mμ was observed after this concentration. The maximum at 550 mμ remains uneffected by further addition of the soap.

We conclude here that the first change in maximum is due to the compound formation between the soap and dye and that the next change in maximum is because the dye-detergent complex solubilized in the micelles of the soap. Although this complex is soluble at pH 9.12, but, however, in-soluble at pH 7.00 with the result that the first maximum at 525 mμ or 500 mμ realised at pH 9.12 is not observed here. Further addition of the soap results in its dissolution with the formation of micelles giving a maximum at 550 mμ.

The colour of the alizarin red S changes from red to violet on addition of soap and this change is spectrophotometrically characterized.

<u>The Transition Region</u>:- Fig. 7 shows the typical changes in the absorbance in the dye-soap mixtures. The optical density of the dye-soap mixtures have been plotted vs. soap concentration at 445 mμ, 500 mμ and 550 mμ for cetyl pyridinium bromide and at 445 mμ, 525 mμ and 550 mμ for cetyl trimethyl ammonium bromide. The curve A decreases at an accelerated rate. The B curve of the violet solution increases simultaneously and flattens out at higher concentrations of the soap. Curve C begins

by increasing just like B but does not flatten until much beyond the point corresponding to micelle formation. The intersection of B and C is taken as the c.m.c. point. This provide a proof of the fact that micelles are formed in the colour transition region.

The values of c.m.c. are given in Table III.

The values of CPB are about same as reported in the literature but the c.m.c.value of CTMAB differ very much than that reported so far. We got lower values than those reported in the literature. Other methods, viz., the conductometric and e.m.f.measurement methods also confirmed our results on the c.m.c. values of CTMAB.

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CHAPTER III.

Effect of alcohols, urea and amides on the behaviour of anionic and cationic soaps.

INTRODUCTION

The addition of foreign substances to soap solutions markedly effects the c.m.c. of soaps. This behaviour has been found in presence of salts, organic solvents and other solubilized materials. Shinoda(1) observed a linear relationship between the number of carbon atoms in the alcohol and the fatty acids and the rate of change of c.m.c. with concentration. Ralston and Hoarr(2,3) on the basis of solubility data, found a simple correlation between solubility and micelle forming ability in cationic soap solutions prepared in water-ethanol solutions.

The effect of solubilized material on the c.m.c. and micellar size, although not uniform, was also found quite marked. For example, Ralston and Eggenberge(4) had studied the effects of several solubilised long chain hydrocarbon, alcohols, halides, amides and nitrides on the c.m.c. of dodecyl amine hydrochloride. They found that all except two compounds, dodecane and octadecane, lowered the c.m.c.. Similar behaviour(5) was found with solubilised benzene in regard to the c.m.c. of fatty acid soaps and the fatty alkene sulphonates. The solubilised fatty alcohols were, however, found to exert an opposite influence (6).

The influence of salts on micelle forming ability of the soaps is also interesting. The benzene rings present in the salicylate group influenced strongly the micelle formation of the system cetyl trimethyl ammonium bromide-sodium salicylate(7). With inorganic salts, Corrin and Harkins(8) found that the c.m.c. of both anionic (sulphates and sulphonates) and cationic (primary and quaternary ammonium salts), was lowered by their presence but the effectiveness was solely controlled by the ions carrying charge opposite to that of the soaps.

Recent investigations(9) had proved that water structure had played an important role in the micelle formation and the effects of various additives on the c.m.c. of soaps may be explained on this basis. Urea, wellknown for its denaturation capacity and its characteristic property of breaking off the protein-protein hydrogen bonds, had usually been employed to study the micellar properties of soap solutions. Bruning and Holzer(10) had tested the effect of this compound on the hydrophobic bonds in aqueous solution of cationic detergents. Mukerjee and Ray(11) had carried out spectrophotometric studies with this compound to study the structure contribution to micelle formation and hydrophobic bonds in the case of dodecyl pyridinium iodide.

Schick(12) had made a systematic study of the influence of different counter ions, viz., sodium, potassium, lithium and trimethyl ammonium ions of n-alkyl sulphonate soaps on critical micelle concentration and hydrophobic bonding in presence of urea. He had also explained the results in terms of structural concepts of water.

Since the influence of compounds other than urea on the c.m.c. of soaps has been less extensively studied,ivestigations was,therefore,undertaken to increase our knowledge on this subject. The work reported in this chapter also includes data on the effect of urea for the sake of comparision and that of the non-ionic soap,lauric acid diethanolamine condensate,which by virtue of its composition is expected to influence as an amide in these studies. The effect of methyl and ethyl alcohols on the c.m.c. of anionic and cationic soaps has also been reported.

EXPERIMENTAL

Reagents:- The anionic soaps,viz., sulphonated phenyl, tolyl and xylyl stearic acids were prepared in the laboratory by the method of Stirton and Co-workers (Chapter I).

The cationic soaps,viz.,cetyl trimethyl ammonium bromide and cetyl pyridinium bromide were B.D.H. products and were recrystallized from acetone. Their solutions were also prepared in doubly distilled water.

The non-ionic soap,lauric acid diethanol amine condensate was prepared in the laboratory by condensing lauric acid(B.D.H.) with diethanol amine(13).

Urea,acetamide and formamide were B.D.H. products and were used without further purification.

Procedure:- Solutions of different concentrations of the anionic and cationic soaps were prepared by diluting their stock solutions (10^{-3}M).

The lauric acid diethanol amine condensate was mixed with the anionic or cationic soaps in the molar ratio 1:49, 1:9 and 1:4 (10^{-3}M). These solutions were then diluted to the desired concentration. The amount of alcohols added was in percentage by volume. The pH measurements were carried out with Cambridge Bench Type pH meter using glass electrode and the conductance was measured with Philips condustivity bridge.

The pH and conductance values in presence of alcohols,urea and amides of anionic and cationic soaps are given in the following tables:

Effect of methyl alcohol on the behaviour of soaps.

TABLE 1.

Effect of methyl alcohol on the behaviour of sulphonated phenyl stearic acid.

Methyl alcohol 6%		Methyl alcohol 12%		Methyl alcohol 17%		Methyl alcohol 25%	
Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH
3.10	4.24	2.94	4.40	2.78	4.68	2.50	5.10
6.25	3.92	5.88	3.96	5.55	3.98	5.00	4.14
9.35	3.46	8.82	3.62	8.33	3.61	7.50	3.70
13.50	3.37	11.77	3.42	11.10	3.42	10.00	3.38
19.75	3.34	17.65	3.30	16.65	3.18	15.00	3.24
25.00	3.20	23.53	3.20	22.20	3.04	20.00	3.26
31.25	3.11	29.42	3.12	27.75	3.18	25.00	3.20
37.50	3.10	35.30	3.02	33.30	3.01	30.00	3.10
50.00	3.08	47.06	3.10	44.40	3.17	40.00	3.18
62.50	3.02	58.83	3.10	55.55	3.16	50.00	3.23
75.00	2.98	70.60	3.06	66.60	3.08	60.00	3.16
93.75	2.90	88.24	3.00	83.25	3.02	75.00	3.04
Fig.1		Fig.2		Fig.3		Fig.4	

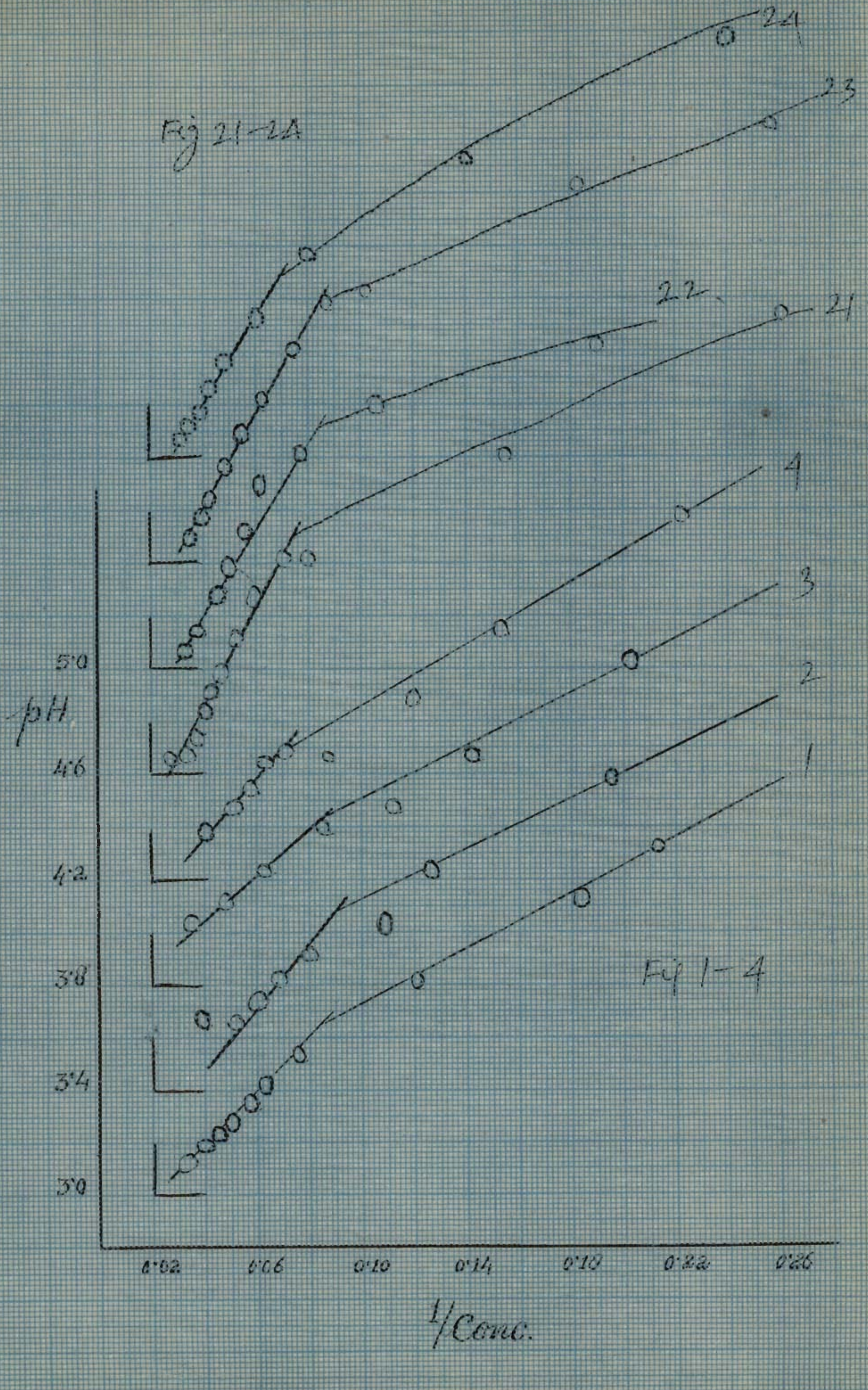
Fig 21-24
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23
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Fig 1-4
pH
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4·6
4·2
3·8
3·4
3·0
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0·06
0·10
0·14
0·18
0·22
0·26
1/Conc.

TABLE 2.

Effect of methyl alcohol on the behaviour of sulphonated tolyl stearic acid.

Methyl alcohol 6%		Methyl alcohol 12%		Methyl alcohol 17%		Methyl alcohol 25%	
Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH
3.10	4.70	2.94	4.75	2.78	4.95	2.50	5.45
6.25	4.20	5.88	4.10	5.55	4.15	5.00	4.20
9.35	3.95	8.82	3.96	8.33	4.00	7.50	4.05
13.50	3.77	11.77	3.80	11.10	3.85	10.00	3.95
19.75	3.60	17.65	3.56	16.65	3.60	15.00	3.70
25.00	3.72	23.53	3.48	22.20	3.45	20.00	3.50
31.25	3.30	29.42	3.30	27.75	3.35	25.00	3.40
37.50	3.22	35.30	3.20	33.30	3.22	30.00	3.30
50.00	3.13	47.06	3.10	44.40	3.15	40.00	3.20
62.50	3.10	58.83	3.03	55.55	3.00	50.00	3.10
75.00	3.02	70.60	2.94	66.60	2.95	60.00	3.05
93.75	2.92	88.24	2.90	83.25	2.90	75.00	3.00

Fig.5 Fig.6 Fig.7 Fig.8

TABLE 3.

Effect of methyl alcohol on the behaviour of sulphonated xylyl stearic acid.

Methyl alcohol 6%		Methyl alcohol 12%		Methyl alcohol 17%		Methyl alcohol 25%	
Conc.soap $\times 10^{-5}M$	pH	Conc.soap $\times 10^{-5}M$	pH	Conc.soap $\times 10^{-5}M$	pH	Conc.soap $\times 10^{-5}M$	pH
3.10	4.72	2.94	4.90	2.78	5.10	2.50	5.00
6.25	4.48	5.88	4.55	5.55	4.52	5.00	4.80
9.35	4.10	8.82	4.15	8.33	4.20	7.50	4.32
13.50	4.02	11.77	4.01	11.10	4.08	10.00	4.15
19.75	3.72	17.65	3.75	16.65	3.79	15.00	3.85
25.00	3.63	23.53	3.65	22.20	3.68	20.00	3.72
31.25	3.50	29.42	3.52	27.75	3.53	25.00	3.58
37.50	3.42	30.30	3.43	33.30	3.46	30.00	3.50
50.00	3.30	47.06	3.32	44.40	3.33	40.00	3.38
62.50	3.20	58.83	3.20	55.55	3.22	50.00	3.30
75.00	3.12	70.60	3.14	66.60	3.12	60.00	3.18
93.75	3.00	88.24	3.01	83.25	3.00	75.00	3.10
Fig.9		Fig.10		Fig.11		Fig.12	

Fig 33-36

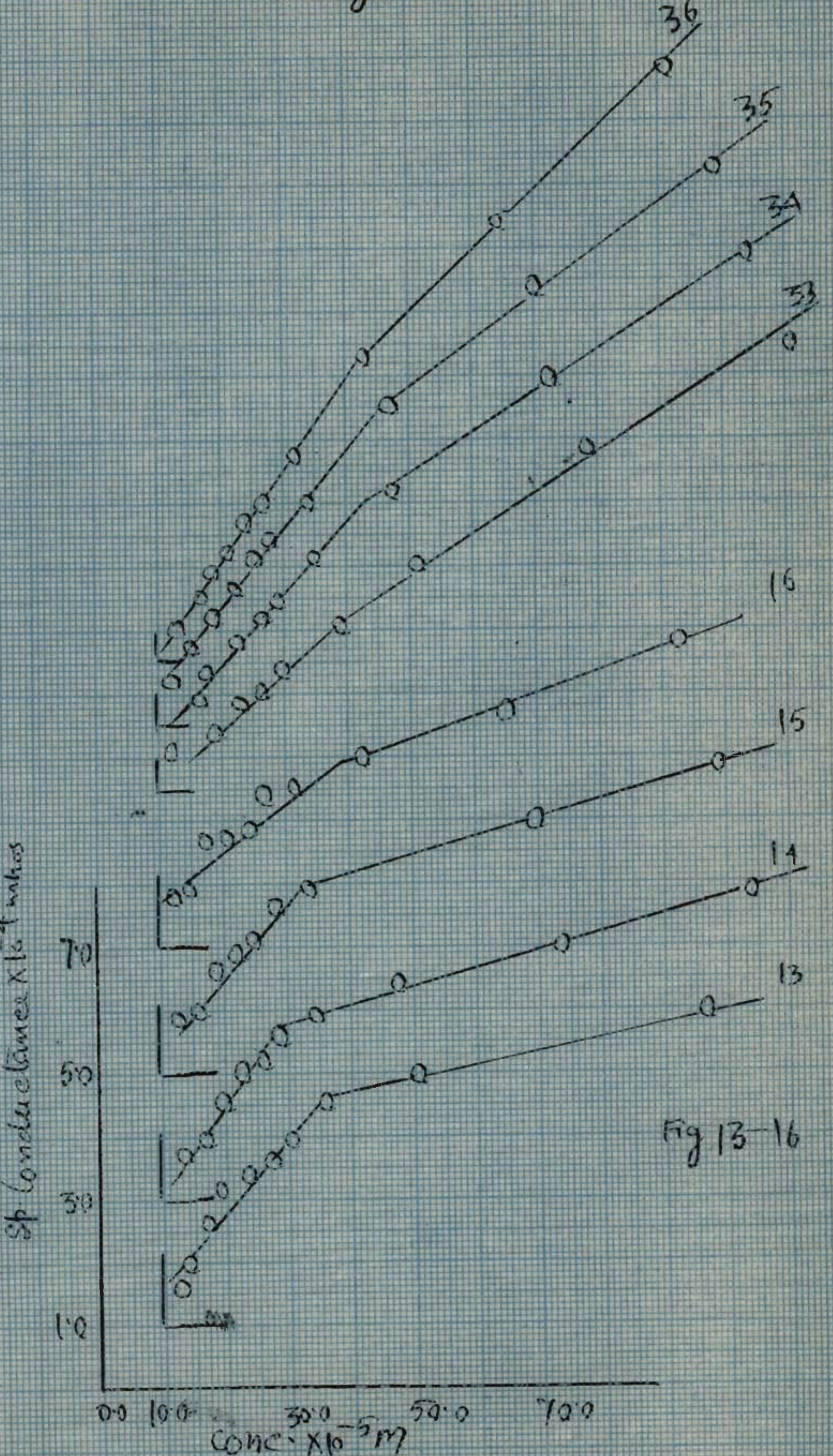


Fig 13-16

TABLE 4

Effect of methyl alcohol on the behaviour of cetyl trimethyl ammonium bromide.

Methyl alcohol 6%		Methyl alcohol 12%		Methyl alcohol 17%		Methyl alcohol 25%	
Conc.soap x 10^{-5}M	Sp.Cond. x 10^{-4}mhos	Conc.soap x 10^{-5}M	Sp.Cond. x 10^{-4}mhos	Conc.soap x 10^{-5}M	Sp.Cond. x 10^{-4}mhos	Conc.soap x 10^{-5}M	Sp.Cond. x 10^{-4}mhos
2.66	0.625	2.50	0.588	2.36	0.833	2.22	0.833
6.65	0.952	6.25	0.952	5.90	0.952	5.55	0.869
9.31	1.613	8.75	1.538	8.26	1.681	7.77	1.626
13.33	2.110	12.50	2.020	11.80	1.887	11.11	1.626
16.66	2.222	15.62	2.618	14.70	2.000	14.70	1.802
20.00	2.632	18.75	2.029	17.70	2.597	16.65	2.439
26.66	2.985	25.00	2.857	23.60	2.779	22.20	2.532
40.00	3.390	37.50	3.279	35.40	3.175	33.30	2.985
66.50	3.846	62.50	3.817	59.00	3.802	55.50	3.369
100.00	4.831	93.75	4.762	80.00	4.651	83.33	4.762

Fig.13 Fig.14 Fig.15 Fig.16

TABLE 5

Effect of methyl alcohol on the behaviour of cetyl pyridinium bromide.

Methyl alcohol 6%		Methyl alcohol 12%		Methyl alcohol 17%		Methyl alcohol 25%	
Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos
2.66	1.021	2.50	1.035	2.36	1.025	2.22	1.100
6.65	1.837	6.25	1.937	5.90	1.530	5.55	1.530
9.31	2.235	8.75	2.300	8.26	1.820	7.77	1.653
13.33	2.812	12.50	3.233	11.80	2.200	11.11	2.000
16.66	3.625	15.62	3.750	14.70	2.556	14.10	2.325
20.00	4.120	18.75	4.289	17.70	2.950	16.65	2.702
26.66	5.112	25.00	5.287	23.60	3.700	22.20	3.185
40.00	6.800	37.50	6.823	35.40	5.300	33.30	4.700
66.50	7.735	62.50	7.438	59.00	7.125	55.50	6.439
100.00	8.750	93.75	8.532	84.00	7.823	83.33	7.400

Fig.17 Fig.18 Fig.19 Fig.20

Fig 37-40

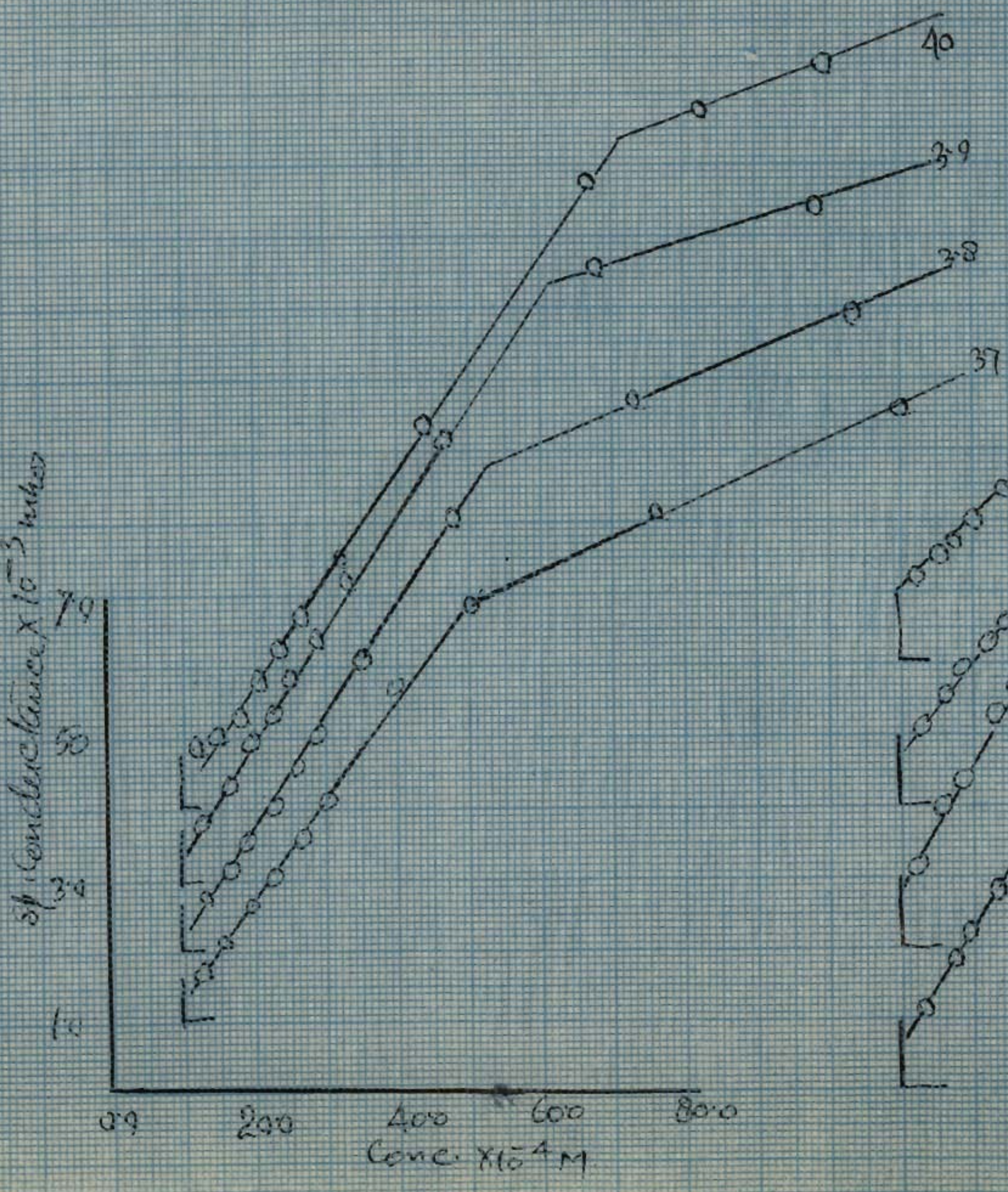
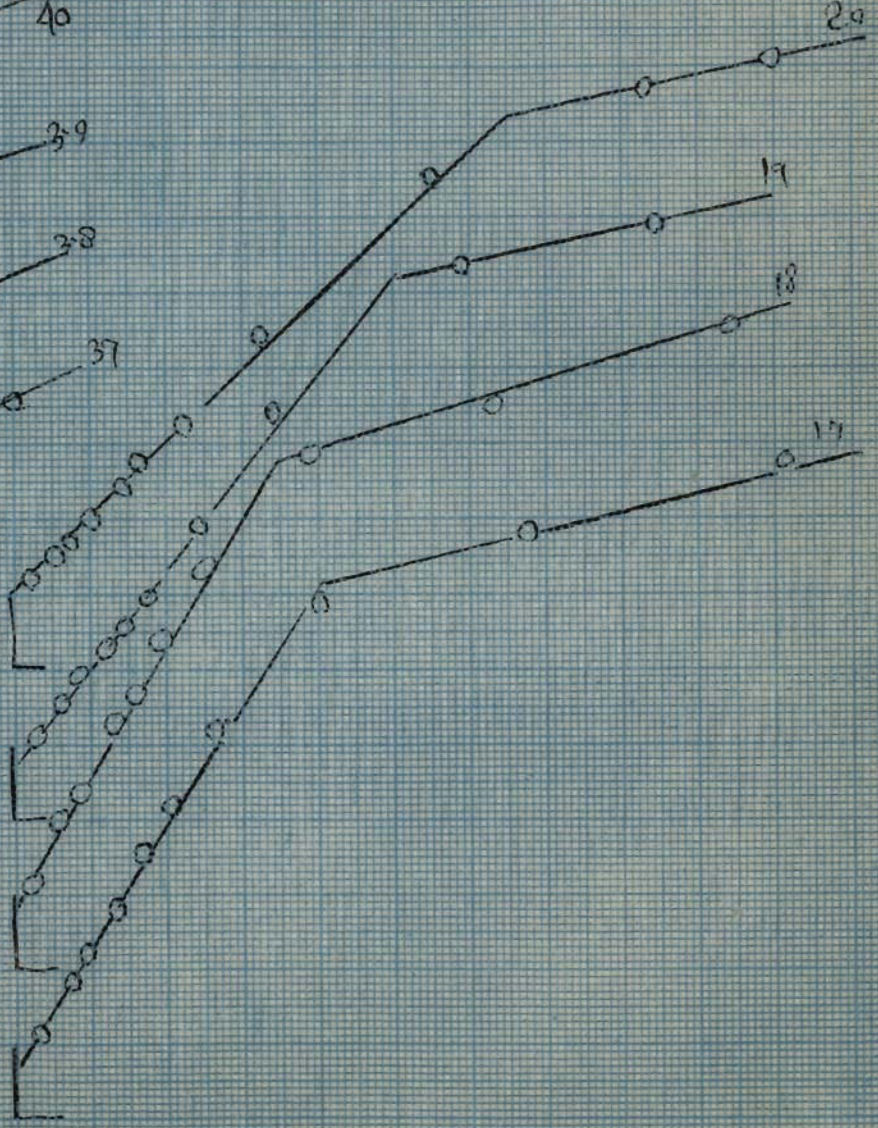


Fig 17-20



Effect of ethyl alcohol on the behaviour of soaps.

TABLE 6.

Effect of ethyl alcohol on the behaviour of sulphonated phenyl stearic acid.

Ethyl alcohol 6%		Ethyl alcohol 12%		Ethyl alcohol 17%		Ethyl alcohol 25%	
Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH
3.33	5.98	3.13	6.25	3.00	6.35	2.63	6.48
6.60	5.18	6.25	5.50	5.88	5.60	5.26	5.75
13.30	4.40	12.50	4.98	11.76	5.20	10.52	5.30
20.00	3.98	18.80	4.55	17.64	4.85	15.78	5.05
26.70	3.75	25.00	4.22	23.52	4.65	22.05	5.90
33.30	3.58	31.25	3.90	29.40	4.33	26.31	4.68
40.00	3.45	37.50	3.40	35.28	4.03	31.58	4.50
46.60	3.33	43.75	3.55	41.16	3.81	36.84	4.34
53.30	3.26	50.00	3.45	47.04	3.68	42.10	4.20
60.00	3.20	56.25	3.35	52.92	3.50	47.37	4.00
66.60	3.12	62.50	3.25	58.80	3.44	52.63	3.86
80.00	3.05	75.00	3.18	70.56	3.30	63.16	3.65
93.20	3.00	87.50	3.10	82.30	3.20	74.68	3.46
Fig.21		Fig.22		Fig.23		Fig.24	

TABLE 7

Effect of ethyl alcohol on the behaviour of sulphonated tolyl stearic acid.

Ethyl alcohol 6%		Ethyl alcohol 12%		Ethyl alcohol 17%		Ethyl alcohol 25%	
Conc.soap $\times 10^{-5}$ M	pH	Conc.soap $\times 10^{-5}$ M	pH	Conc.soap $\times 10^{-5}$ M	pH	Conc.soap $\times 10^{-5}$ M	pH
3.10	4.80	2.94	4.90	2.78	5.00	2.50	5.10
6.25	4.12	5.88	4.12	5.55	4.30	5.00	4.50
9.35	4.00	8.82	4.00	8.33	4.00	7.50	4.15
13.50	3.65	11.77	3.75	11.10	3.80	10.00	3.90
19.75	3.45	17.65	3.50	16.65	3.52	15.00	3.60
25.00	3.30	25.53	3.35	22.20	3.40	20.00	3.45
31.25	3.20	29.42	3.30	27.75	3.45	25.00	3.32
37.50	3.12	35.30	3.20	33.30	3.30	30.00	3.35
50.00	3.10	47.06	3.15	44.40	3.22	40.00	3.28
62.50	3.05	58.83	3.10	55.55	3.12	50.00	3.20
75.00	3.03	70.60	3.05	66.60	3.10	60.00	3.12
93.75	3.00	88.24	3.02	83.25	3.05	75.00	3.08

Fig.25 Fig.26 Fig.27 Fig.28

TABLE 8

Effect of ethyl alcohol on the behaviour of sulphonated xylyl stearic acid.

Ethyl alcohol 6%		Ethyl alcohol 12%		Ethyl alcohol 17%		Ethyl alcohol 25%	
Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH	Conc.soap x 10^{-5}M	pH
3.10	4.50	2.94	4.50	2.78	4.55	2.50	4.50
6.25	4.22	5.88	4.22	5.55	4.22	5.00	5.40
9.35	4.10	8.83	4.10	8.33	4.10	7.50	4.18
13.50	4.09	11.77	4.00	11.10	4.02	10.00	4.12
19.75	3.70	17.65	3.80	16.65	3.80	15.00	3.85
25.00	3.78	23.53	3.78	22.20	3.70	20.00	3.90
31.25	3.72	29.42	3.60	27.75	3.60	25.00	3.72
37.50	3.50	35.30	3.42	33.30	3.40	30.00	3.50
50.00	3.30	47.06	3.30	44.40	3.35	40.00	3.40
62.50	3.20	58.83	3.25	55.55	3.25	50.00	3.35
75.00	3.15	70.60	3.20	66.60	3.20	60.00	3.30
93.75	3.05	88.24	3.10	83.25	3.12	75.00	3.20

Fig.29 Fig.30 Fig.31 Fig.32

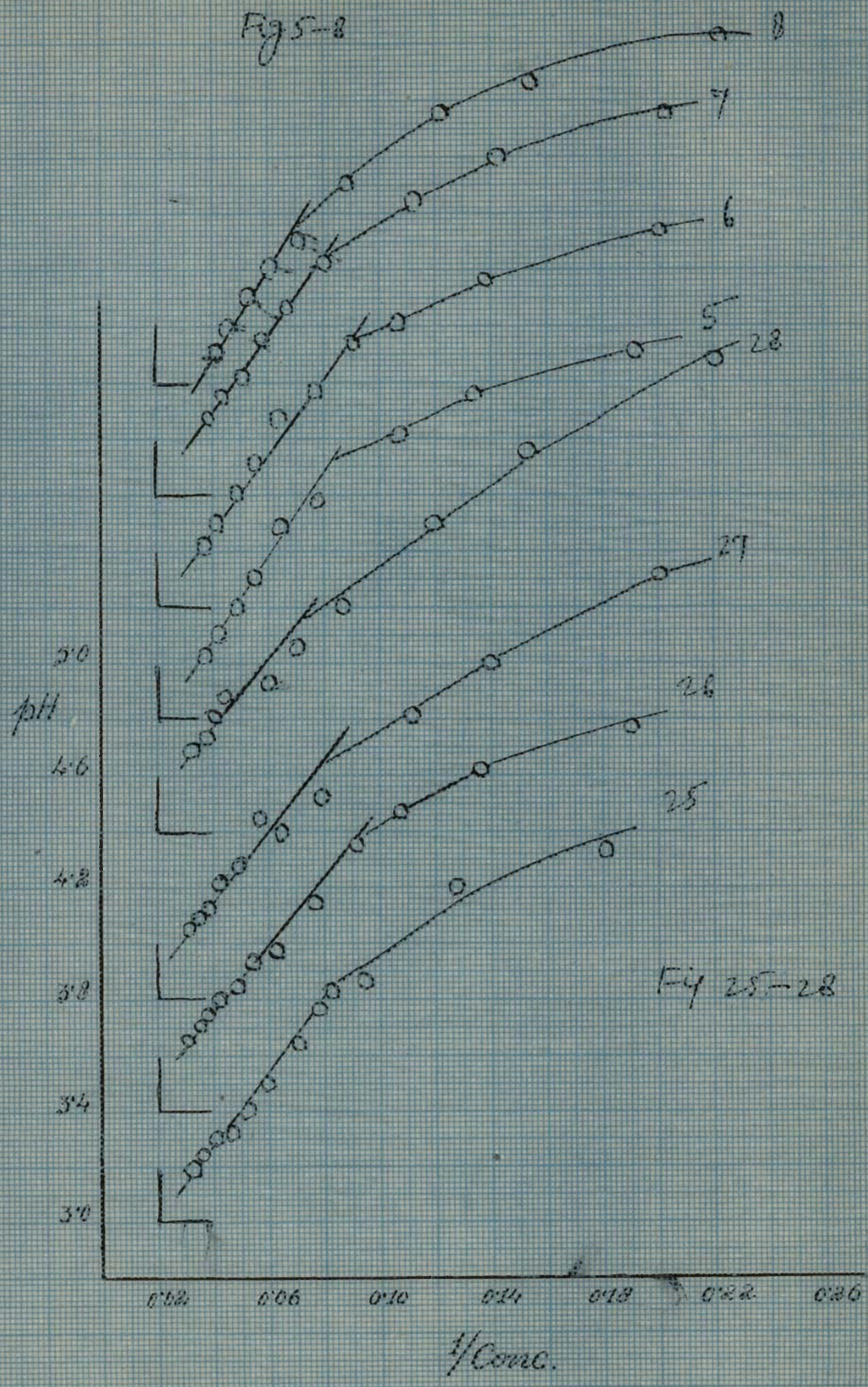

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Fig 25-28
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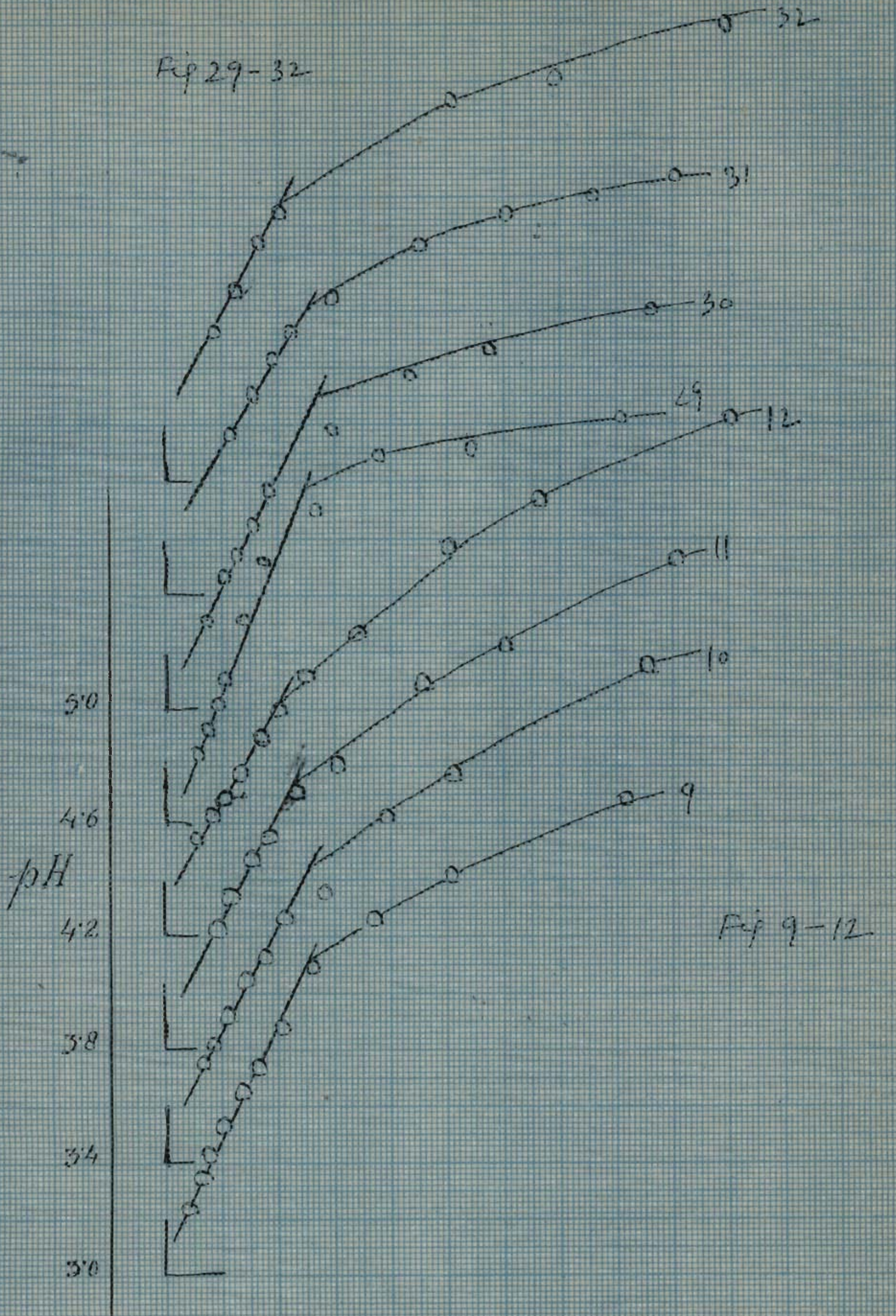
Fig 29-32
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Fig 9-12
pH
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1/Conc.

TABLE 9.

Effect of ethyl alcohol on the behaviour of cetyl trimethyl ammonium bromide.

Ethyl alcohol 6%		Ethyl alcohol 12%		Ethyl alcohol 17%		Ethyl alcohol 25%	
Conc.soap x 10^{-5}M	Sp.Cond. x 10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond. x 10^{-4} mhos	Conc.soap x10^{-5} M	Sp.Cond. x10^{-4} mhos	Conc.soap x10^{-5} M	Sp.Cond. x10^{-4} mhos
2.66	0.689	2.50	0.633	2.36	0.595	2.22	0.521
6.65	0.756	6.25	1.408	5.90	1.258	5.55	1.020
9.31	2.000	8.75	1.852	8.26	1.724	7.77	1.399
13.33	2.392	12.50	2.299	11.80	2.222	11.10	1.802
16.66	2.667	15.62	2.667	14.70	2.625	14.70	2.193
20.00	3.012	18.75	3.030	17.70	3.030	16.65	2.564
28.66	3.546	25.00	3.636	23.60	3.704	22.20	3.226
40.00	4.857	37.50	4.739	35.40	5.000	33.30	4.762
66.50	6.451	62.50	6.452	59.00	6.897	55.50	6.897
100.00	8.333	93.75	8.403	88.00	8.850	83.33	9.090

Fig.33 Fig.34 Fig.35 Fig.36

TABLE 10

Effect of ethyl alcohol on the behaviour of cetyl pyridinium bromide.

Ethyl alcohol 6%		Ethyl alcohol 12%		Ethyl alcohol 17%		Ethyl alcohol 25%	
Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos
2.66	0.784	2.50	0.784	2.36	0.790	2.22	0.899
6.65	1.047	6.25	1.100	5.90	1.211	5.55	1.128
9.31	1.580	8.75	1.580	8.26	1.920	7.77	1.340
13.33	2.000	12.50	2.052	11.80	2.345	11.11	1.789
16.66	2.645	15.62	2.538	14.70	2.837	14.70	2.238
20.00	3.130	18.75	3.000	17.70	3.350	16.65	2.789
28.66	4.728	25.00	4.100	23.60	4.200	22.20	3.539
40.00	5.823	37.50	6.000	35.40	6.235	33.30	5.400
66.50	7.012	62.50	6.699	59.00	8.200	55.50	8.800
100.00	8.500	93.75	8.800	88.00	9.400	83.33	9.635
Fig.37		Fig.38		Fig.39		Fig.40	

Effect of urea on the behaviour of soaps.

TABLE 11

Effect of urea on the behaviour of sulphonated phenyl stearic acid.

Urea 0.5M		Urea 1M		Urea 3M		Urea 6M	
Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH
3.10	5.00	2.94	5.10	2.78	5.50	2.50	6.00
6.25	4.75	5.88	4.80	5.55	4.80	5.00	4.85
9.35	4.55	8.83	4.50	8.33	4.57	7.50	4.60
13.50	4.55	11.77	4.35	11.10	4.40	10.00	4.48
19.50	4.28	17.65	4.30	16.65	4.41	15.00	4.50
25.00	4.10	23.53	4.15	22.20	4.20	20.00	4.30
31.25	4.00	29.42	4.08	27.75	4.26	25.00	4.20
37.50	3.90	35.30	4.00	33.30	4.12	30.00	4.15
50.00	3.80	47.06	3.90	44.40	4.00	40.00	4.00
62.50	3.50	58.83	3.80	55.55	3.90	50.00	3.95
75.00	3.45	70.60	3.70	66.60	3.75	60.00	3.80
93.75	3.40	88.24	3.60	83.25	3.63	15.00	3.75

Fig.41 Fig.42 Fig.43 Fig.44

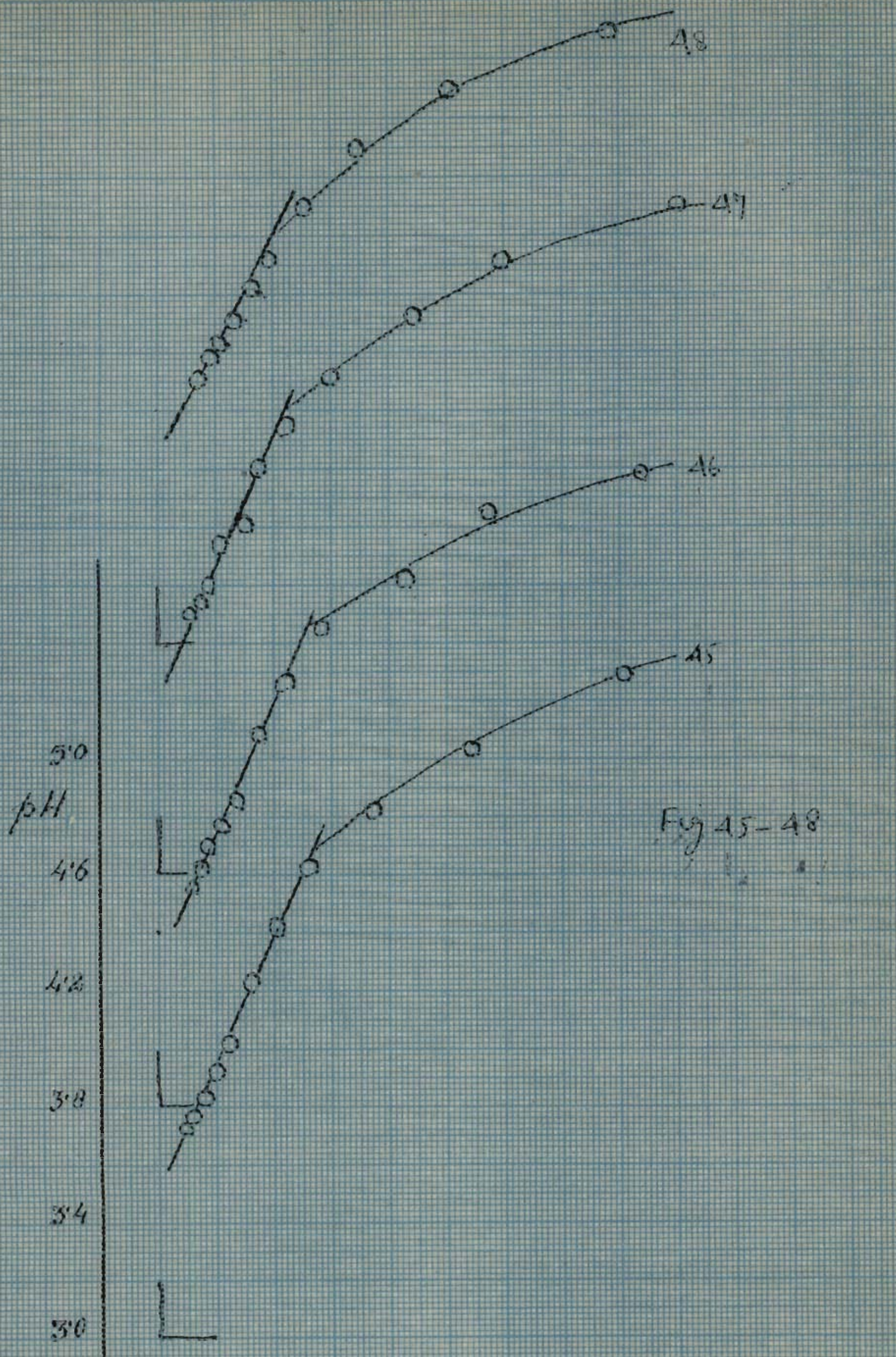


Fig 45-48

TABLE 12

Effect of urea on the behaviour of sulphonated tolyl stearic acid.

Urea 0.5M		Urea 1M		Urea 3M		Urea 6M	
Conc.soap $\times10^{-5}$M	pH	Conc.soap $\times10^{-5}$M	pH	Conc.soap $\times10^{-5}$M	pH	Conc.soap $\times10^{-5}$M	pH
3.10	5.80	2.94	5.9	2.78	6.10	2.50	6.50
6.25	5.20	5.88	5.25	5.55	5.40	5.00	5.60
9.35	4.80	8.83	4.83	8.33	4.90	7.50	5.00
13.50	4.60	11.77	4.60	11.10	4.70	10.00	4.80
19.50	4.40	17.65	4.43	16.65	4.50	15.00	4.60
25.00	4.20	23.53	4.25	22.20	4.35	20.00	4.40
31.25	4.00	29.42	4.08	27.75	4.20	25.00	4.20
37.50	3.80	35.30	3.84	33.30	4.00	30.00	4.10
50.00	3.70	47.06	3.75	44.40	3.95	40.00	4.00
62.50	3.60	58.83	3.68	55.55	3.80	50.00	3.95
75.00	3.55	70.60	3.60	66.60	3.75	60.00	3.90
93.75	3.50	88.24	3.55	83.25	3.70	75.00	3.85
Fig.45		Fig.46		Fig.47		Fig.48	

TABLE 13.

Effect of urea on the behaviour of sulphonated xylyl stearic acid.

Urea 0.5M		Urea 1M		Urea 3M		Urea 6M	
Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH
3.10	5.70	2.94	5.75	2.78	5.90	2.50	6.10
6.25	5.10	5.88	5.15	5.55	5.30	5.00	5.50
9.35	4.80	8.83	4.87	8.33	4.95	7.50	5.00
13.50	4.50	11.77	4.60	11.10	4.70	10.00	4.69
19.50	4.30	17.65	4.35	16.65	4.40	15.00	4.50
25.00	4.10	23.33	4.20	22.20	4.23	20.00	4.30
31.25	3.90	29.42	4.00	27.75	4.10	25.00	4.18
37.50	3.80	35.30	3.90	33.30	3.90	30.00	3.95
50.00	3.70	47.06	3.80	44.40	3.82	40.00	3.85
62.50	3.63	58.83	3.74	55.55	3.76	50.00	3.81
75.00	3.57	70.60	3.67	66.60	3.72	60.00	3.78
93.75	3.50	88.24	3.60	83.25	3.68	75.00	3.75
Fig.49		Fig.50		Fig.51		Fig.52	

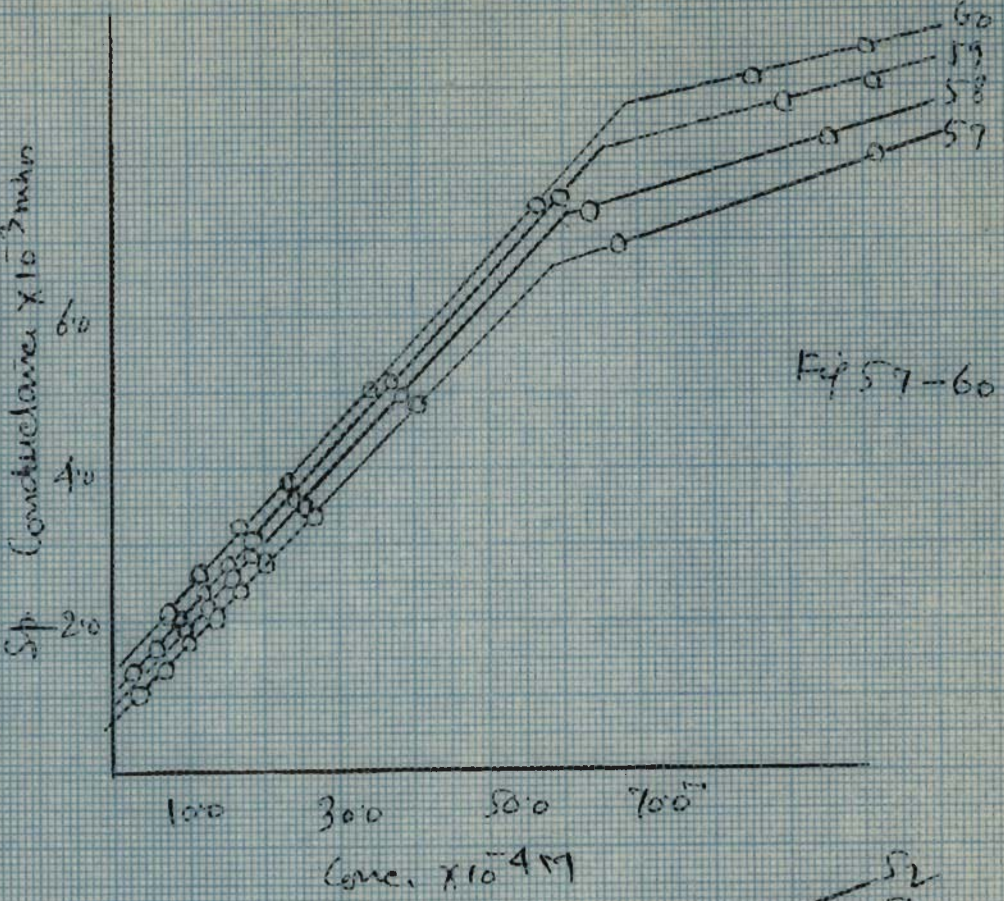


Fig 57-60

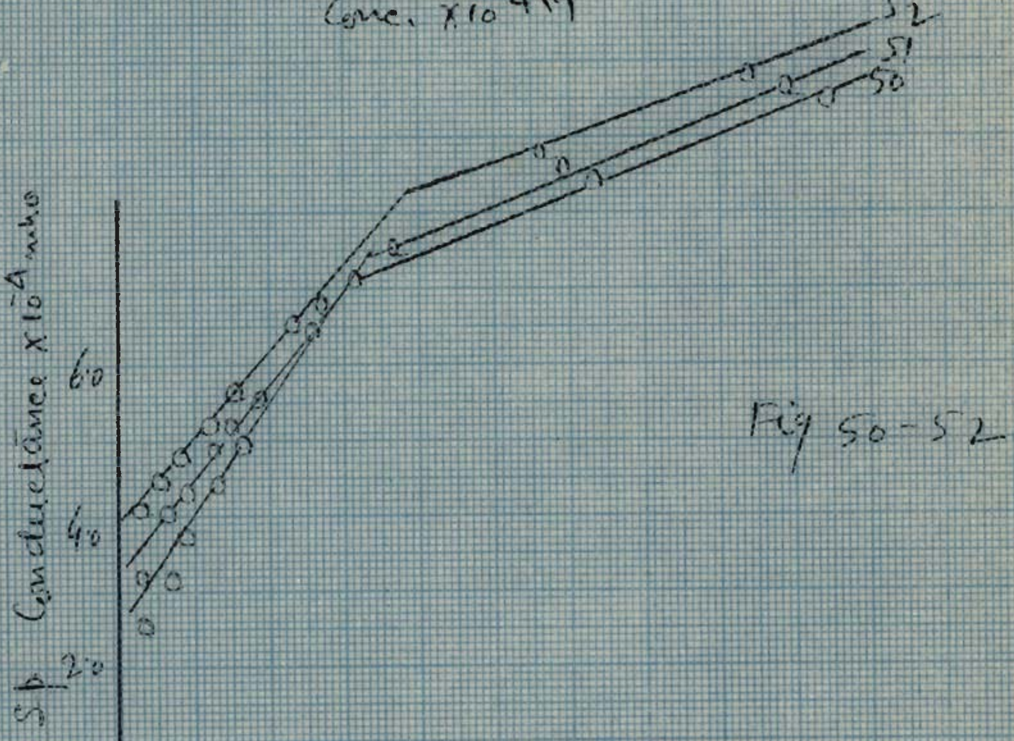


Fig 50-52

TABLE 14

Effect of urea on the behaviour of cetyl trimethyl ammonium bromide.

Urea 0.5M		Urea 1M		Urea 3M		Urea 6M	
Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond x10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos
2.66	1.234	2.50	2.500	2.36	3.200	2.22	3.920
6.65	2.435	6.25	3.237	5.90	4.032	5.55	4.438
9.31	3.043	8.75	3.712	8.26	4.389	7.77	4.752
13.33	3.836	12.50	4.431	11.80	4.804	11.11	5.117
16.66	4.634	15.62	5.012	14.70	5.231	14.70	5.629
20.00	5.432	18.75	5.534	17.70	5.634	16.65	5.852
26.66	6.534	25.00	6.531	23.60	6.531	22.20	6.534
40.00	7.432	37.50	7.321	35.40	7.639	33.30	7.721
66.50	8.200	62.50	8.415	59.00	8.550	55.50	8.706
100.00	9.024	93.75	9.238	88.00	9.631	83.33	9.721

Fig.53 Fig.54 Fig.55 Fig.56

TABLE 15

Effect of urea on the behaviour of cetyl pyridinium bromide.

Urea 0.5M		Urea 1M		Urea 3M		Urea 6M	
Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos.
2.66	0.993	2.50	1.253	2.36	1.253	2.22	1.835
6.65	1.399	6.25	1.550	5.90	1.554	5.55	2.000
9.31	1.633	8.75	1.850	8.26	1.951	7.77	2.153
13.33	2.000	12.50	2.150	11.80	2.301	11.11	2.605
16.66	2.341	15.62	2.539	14.70	2.650	14.70	2.950
20.00	2.781	18.75	2.800	17.70	3.000	16.65	3.151
26.66	3.351	25.00	3.501	23.60	3.550	22.20	3.801
40.00	4.753	37.50	4.913	35.40	5.058	33.30	4.950
66.50	6.851	62.50	7.358	59.00	7.513	35.50	7.305
100.00	8.025	93.75	8.211	88.00	8.730	83.33	9.055
Fig.57		Fig.58		Fig.59		Fig.60	

Effect of acetamide on the behaviour of soaps.

TABLE 16

Effect of acetamide on the behaviour of sulphonated phenyl stearic acid.

Acetamide 0.2M		Acetamide 0.4M		Acetamide 0.5M		Acetamide 0.75M	
Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH
3.10	4.68	2.94	4.51	2.78	4.52	2.50	4.56
6.25	4.80	5.88	4.58	5.55	4.60	5.00	4.65
9.35	4.60	8.83	4.60	8.33	4.61	7.50	4.64
13.50	4.52	11.77	4.58	11.10	4.61	10.00	4.65
19.50	4.40	17.65	4.52	16.65	4.60	15.00	4.63
25.00	4.42	23.53	4.51	22.20	4.58	20.00	4.60
31.25	3.80	29.42	4.10	27.75	4.30	25.00	4.30
37.50	3.85	35.30	4.05	33.30	4.20	30.00	4.20
50.00	3.70	47.06	4.00	44.40	4.10	40.00	4.20
62.50	3.68	58.83	3.95	55.55	4.05	50.00	4.10
75.00	3.50	70.60	3.80	66.60	4.00	60.00	4.05
93.75	3.40	88.24	3.70	83.25	3.90	75.00	4.00
Fig.61		Fig.62		Fig.63		Fig.64	

Fig 61- 64

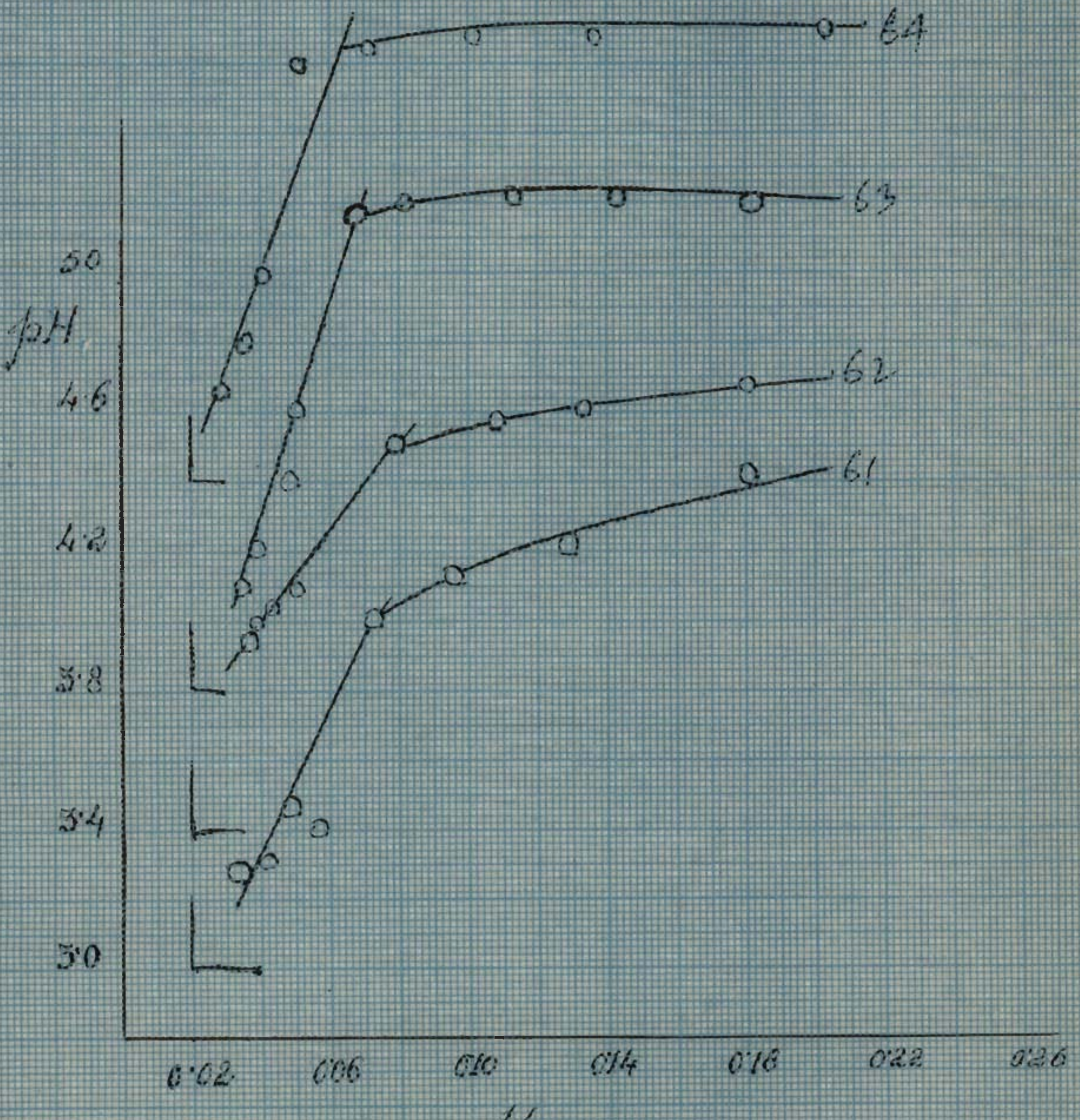


TABLE 17

Effect of acetamide on the behaviour of sulphonated tolyl stearic acid.

Acetamide 0.2M		Acetamide 0.4M		Acetamide 0.5M		Acetamide 0.75M	
Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH
3.10	4.70	2.94	4.68	2.78	4.70	2.50	4.78
6.25	4.80	5.88	4.60	5.55	4.65	5.00	4.70
9.35	4.70	8.83	4.41	8.33	4.43	7.50	4.50
13.50	4.55	11.77	4.35	11.10	4.40	10.00	4.48
19.50	4.41	17.65	4.30	16.65	4.35	15.00	4.40
25.00	4.38	23.53	4.23	22.20	4.27	20.00	4.28
31.25	3.90	29.42	4.10	27.75	4.15	25.00	4.20
50.00	3.68	47.06	4.05	44.40	3.95	40.00	4.00
62.50	3.60	58.83	3.80	55.55	3.85	50.00	3.90
75.00	3.52	70.60	3.75	66.60	3.80	60.00	3.84
93.75	3.40	88.24	3.70	83.25	3.76	75.00	3.80
Fig.65		Fig.66		Fig.67		Fig.68	

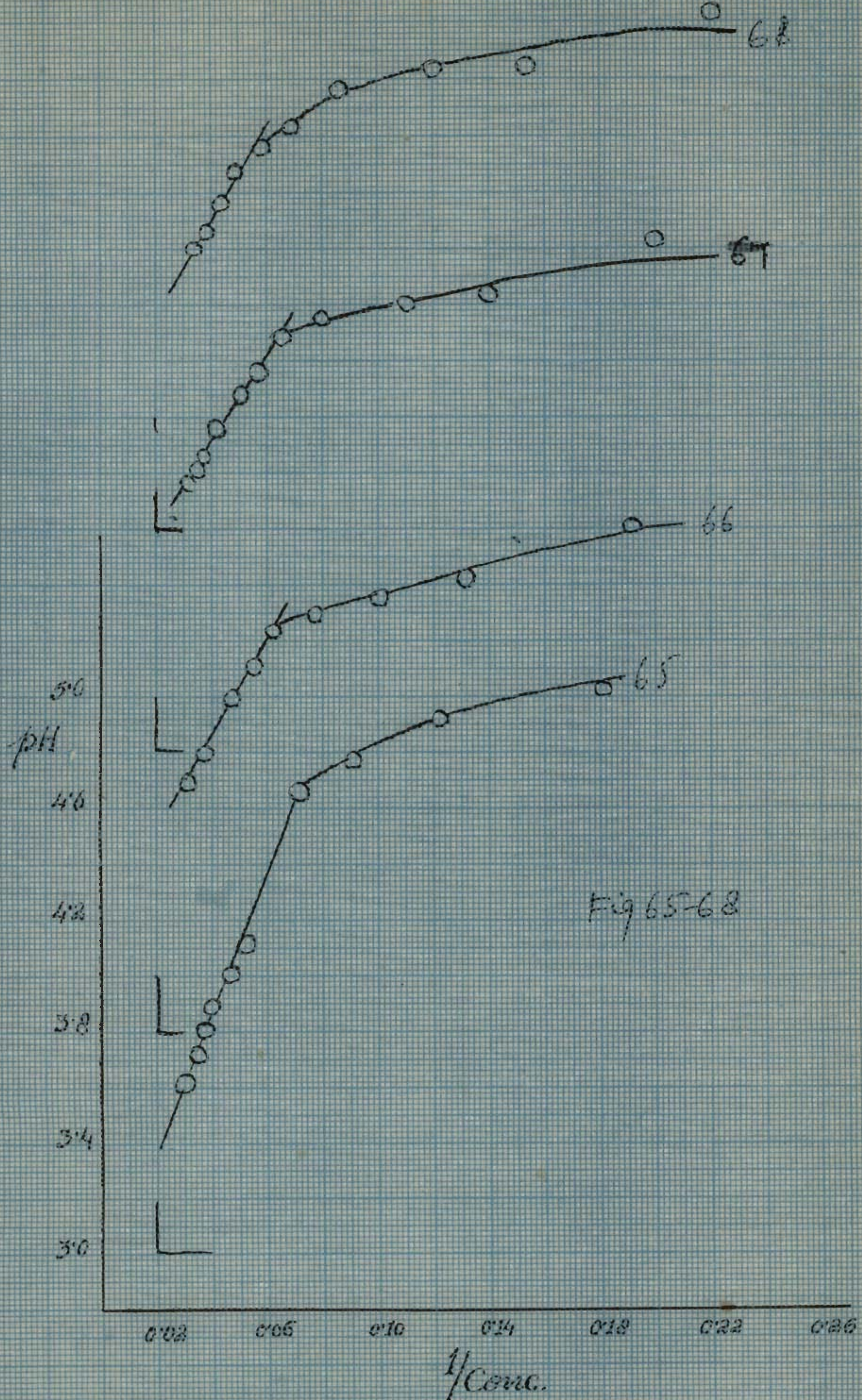


Fig 65-68

TABLE 18

Effect of acetamide on the behaviour sulphonated xylyl stearic acid.

Acetamide 0.2M		Acetamide 0.4M		Acetamide 0.5M		Acetamide 0.75M	
Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH	Conc.soap $x10^{-5}M$	pH
3.10	4.80	2.94	4.86	2.78	4.92	2.50	5.00
6.25	4.80	5.88	4.70	5.55	4.74	5.00	4.80
9.35	4.60	8.83	4.61	8.83	4.63	7.50	4.70
13.50	4.40	11.77	4.43	11.10	4.48	10.00	4.50
19.50	4.25	17.65	4.25	16.65	4.29	15.00	4.35
25.00	4.18	23.53	4.12	22.20	4.15	20.00	4.20
31.25	4.10	29.42	4.12	27.75	4.08	25.00	4.10
37.50	4.00	35.30	4.04	33.30	4.00	30.00	4.07
50.00	3.90	47.06	4.00	44.40	3.91	40.00	3.95
62.50	3.85	58.83	3.83	55.55	3.85	50.00	3.87
75.00	3.81	70.60	3.80	66.60	3.82	60.00	3.85
93.75	3.75	88.24	3.76	83.25	3.78	75.00	3.80

Fig.69 Fig.70 Fig.71 Fig.72

TABLE 19

Effect of acetamide on the behaviour of cetyl trimethyl ammononium bromide.

Acetamide 0.2M		Acetamide 0.4M		Acetamide 0.5M		Acetamide 0.75M	
Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos	Conc.soap x10^{-5}M	SP.Cond. x10^{-4}mhos	Conc.soap x10^{-5}M	Sp.Cond. x10^{-4}mhos.
2.66	1.818	2.50	2.381	2.36	2.899	2.22	3.704
6.65	2.632	6.25	3.226	5.90	3.636	5.55	4.255
9.31	3.125	8.75	3.636	8.26	4.082	7.77	4.651
13.33	3.509	12.50	4.000	11.80	4.348	11.11	5.000
16.66	3.922	15.62	4.444	14.70	4.762	14.70	5.260
20.00	3.968	18.75	4.545	17.70	4.831	16.65	5.405
26.66	4.484	25.00	4.878	23.60	5.208	22.20	5.714
40.00	5.714	37.50	6.061	35.40	6.452	33.30	6.849
66.50	7.246	62.50	7.407	59.00	7.752	55.50	8.064
100.00	9.259	93.75	9.524	88.00	9.524	83.33	9.709
Fig.73		Fig.74		Fig.75		Fig.76	

TABLE 20

Effect of acetamide on the behaviour of cetyl pyridinium bromide.

Acetamide 0.2M		Acetamide 0.4M		Acetamide 0.5M		Acetamide 0.75M	
Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos
2.66	1.538	2.50	1.818	2.36	3.333	2.22	3.921
6.65	1.808	6.25	2.108	5.90	3.649	5.55	4.166
9.31	2.217	8.75	2.451	8.26	3.890	7.77	4.437
13.33	2.500	12.50	2.817	11.80	4.167	11.11	4.651
16.66	3.030	15.62	3.125	14.70	4.339	14.70	4.817
20.00	3.436	18.75	3.508	17.70	4.761	16.65	5.029
26.66	4.167	25.00	4.329	23.60	5.128	22.20	5.523
40.00	5.714	37.50	5.618	35.40	6.135	33.30	6.345
66.50	7.143	62.50	7.936	59.00	8.064	55.50	8.196
100.00	8.928	93.75	9.174	88.00	9.259	83.33	9.346

Fig.77 Fig.78 Fig.79 Fig.80

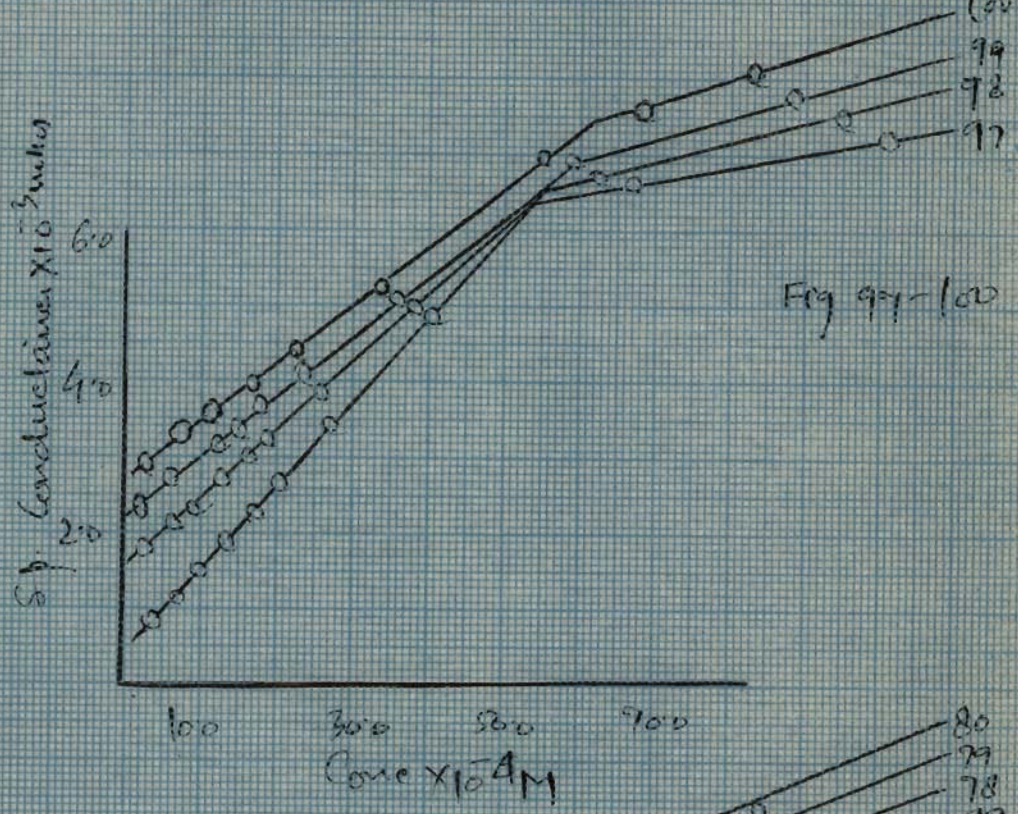


Fig 97-100

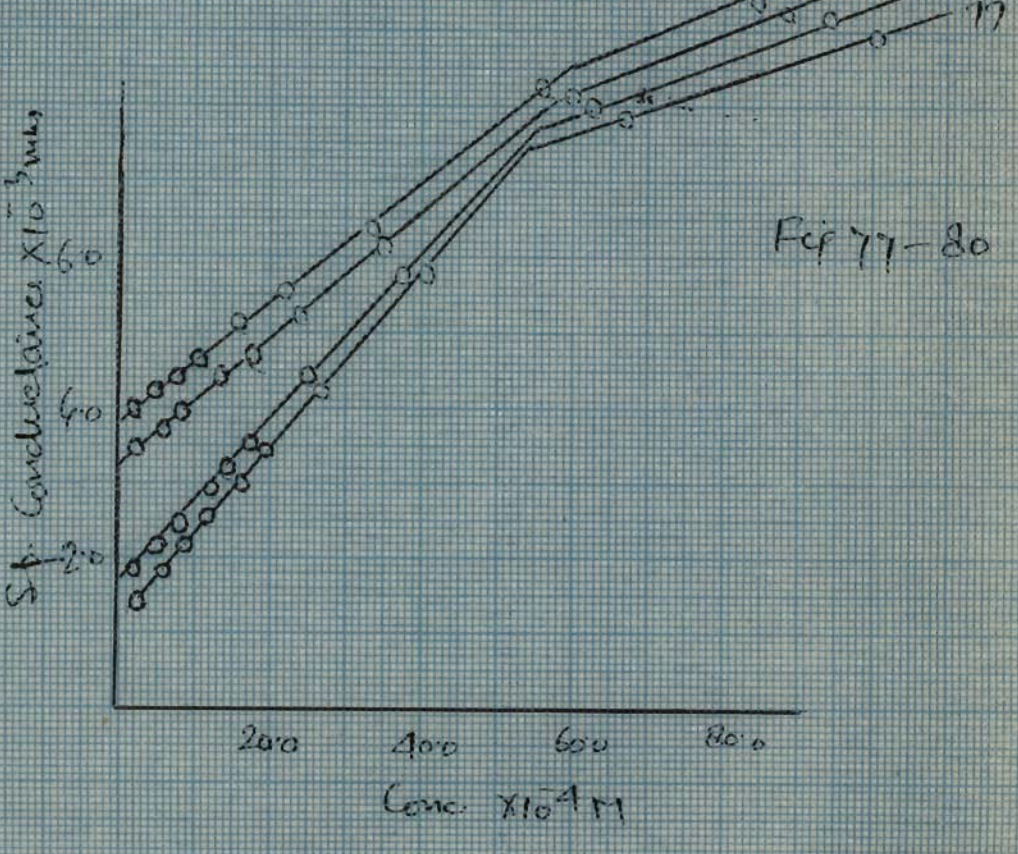


Fig 77-80

Effect of formamide on the behaviour of soaps.

TABLE 21

Effect of formamide on the behaviour of sulphonated phenyl stearic acid.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH	Conc.soap x10^{-5}M	pH
3.10	4.42	2.94	5.35	2.78	5.51	2.50	5.80
6.25	4.38	5.88	4.65	5.55	4.88	5.00	5.22
9.35	4.10	8.83	4.25	8.33	4.47	7.50	4.78
13.50	4.00	11.77	4.15	11.10	4.36	10.00	4.60
19.50	3.90	17.65	3.95	16.65	4.03	15.00	4.20
25.00	3.80	23.53	4.05	22.20	4.15	20.00	4.40
31.25	3.70	29.42	3.80	27.75	4.05	25.00	4.25
37.50	3.45	35.30	3.65	33.30	3.75	30.00	3.94
50.00	3.35	47.06	3.52	44.40	3.55	40.00	3.60
62.50	3.30	58.83	3.47	55.55	3.40	50.00	3.50
75.00	3.25	70.60	3.40	66.60	3.41	60.00	3.45
93.75	-	88.24	3.32	83.25	3.35	75.00	3.40

Fig. 81 Fig. 82 Fig. 83 Fig. 84

Fig 81–84

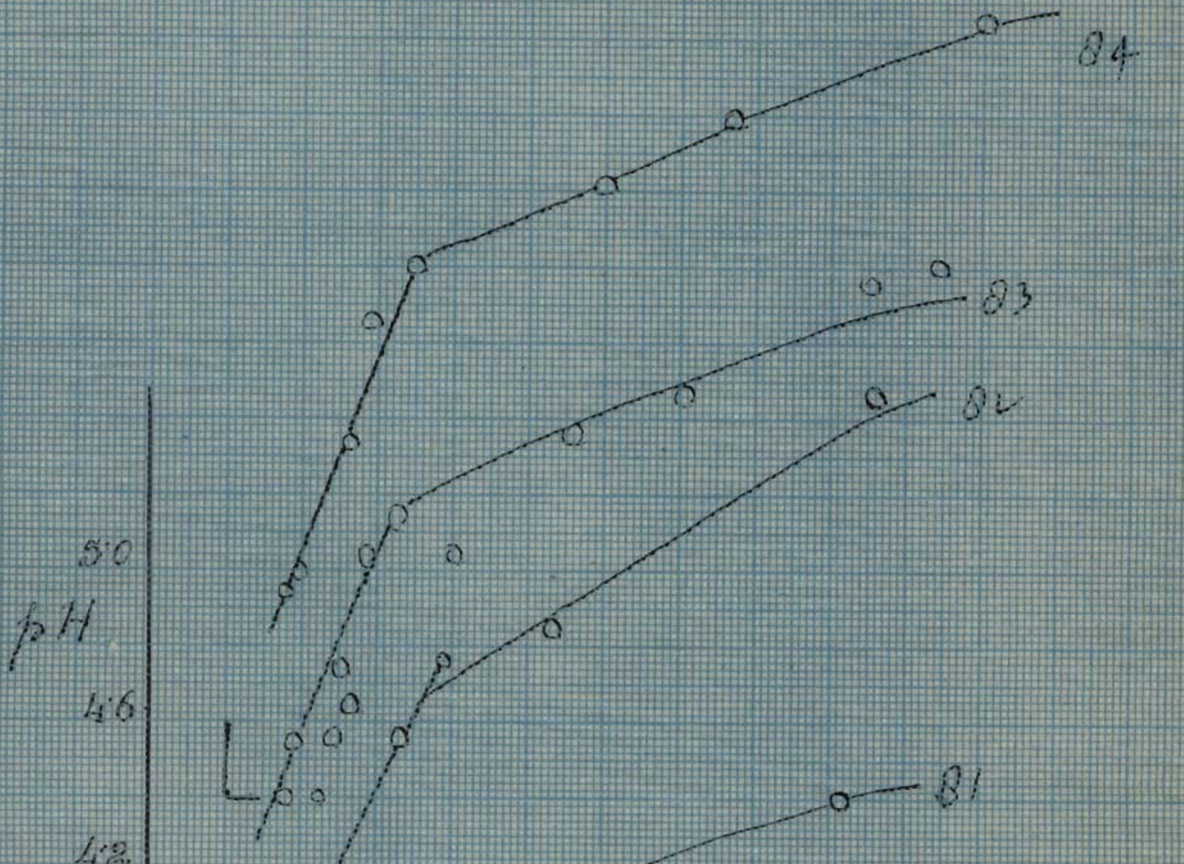


TABLE 22

Effect of formamide on the behaviour of sulphonated tolyl stearic acid.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH
3.10	5.00	2.94	5.10	2.78	5.20	2.50	5.35
6.25	4.50	5.88	4.65	5.55	4.80	5.00	4.98
9.35	4.25	8.83	4.45	8.33	4.60	7.50	4.80
13.50	4.15	11.77	4.25	11.10	4.45	10.00	4.63
19.50	3.90	17.65	4.10	16.65	4.25	15.00	4.42
25.00	3.73	23.53	3.90	22.20	4.03	20.00	4.30
31.25	3.56	29.42	3.75	27.75	3.90	25.00	4.10
37.50	3.50	35.30	3.70	33.30	3.80	30.00	4.00
50.00	3.35	47.06	3.47	44.40	3.60	40.00	3.80
62.50	3.20	58.83	3.30	55.55	3.40	50.00	3.70
75.00	3.12	70.60	3.20	66.60	3.30	60.00	3.58
93.75	3.00	88.24	3.10	83.35	3.20	75.00	3.40
Fig. 85		Fig. 86		Fig. 87		Fig. 88	

TABLE 22

Effect of formamide on the behaviour of sulphonated tolyl stearic acid.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH
3.10	5.00	2.94	5.10	2.78	5.20	2.50	5.35
6.25	4.50	5.88	4.65	5.55	4.80	5.00	4.98
9.35	4.25	8.83	4.45	8.33	4.60	7.50	4.80
13.50	4.15	11.77	4.25	11.10	4.45	10.00	4.63
19.50	3.90	17.65	4.10	16.65	4.25	15.00	4.42
25.00	3.73	23.53	3.90	22.20	4.03	20.00	4.30
31.25	3.56	29.42	3.75	27.75	3.90	25.00	4.10
37.50	3.50	35.30	3.70	33.30	3.80	30.00	4.00
50.00	3.35	47.06	3.47	44.40	3.60	40.00	3.80
62.50	3.20	58.83	3.30	55.55	3.40	50.00	3.70
75.00	3.12	70.60	3.20	66.60	3.30	60.00	3.58
93.75	3.00	88.24	3.10	83.35	3.20	75.00	3.40

Fig.85 Fig.86 Fig.87 Fig.88

TABLE 24

Effect of formamide on the behaviour of cetyl trimethyl ammonium bromide.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos
2.66	1.351	2.50	1.880	2.36	2.532	2.22	3.279
6.65	1.653	6.25	2.439	5.90	3.837	5.55	4.545
9.31	2.597	8.75	3.125	8.26	3.509	7.77	4.082
13.33	2.500	12.50	2.899	11.80	3.279	11.11	3.846
16.66	2.667	15.62	3.077	14.70	3.448	14.70	4.000
20.00	3.175	18.25	3.571	17.70	3.922	16.65	4.444
26.66	3.226	25.00	3.636	23.60	4.082	22.20	4.651
40.00	3.571	37.50	3.922	35.40	4.348	33.30	4.878
66.50	4.000	62.50	4.444	59.00	4.762	55.50	5.555
100.00	4.878	93.75	5.263	88.00	5.556	83.33	6.061
Fig.93		Fig.94		Fig.95		Fig.96	

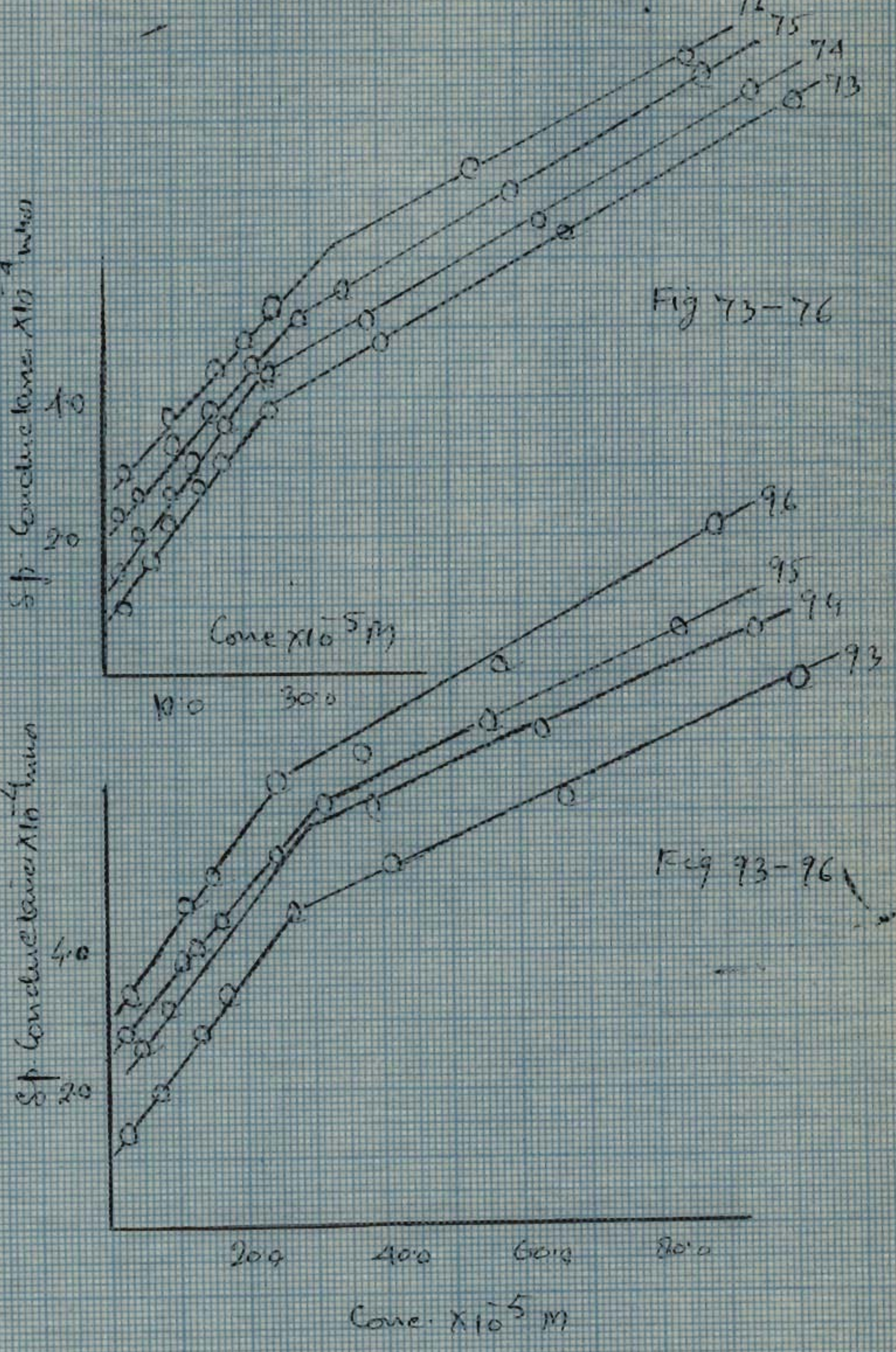


Fig 73-76

Fig 93-96

TABLE 24

Effect of formamide on the behaviour of cetyl trimethyl ammonium bromide.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $x10^{-5}M$	Sp.Cond. $x10^{-4}$ mhos	Conc.soap $x10^{-5}M$	Sp.Cond. $x10^{-4}$ mhos	Conc.soap $x10^{-5}M$	Sp.Cond. $x10^{-4}$ mhos	Conc.soap $x10^{-5}M$	Sp.Cond. $x10^{-4}$ mhos
2.66	1.351	2.50	1.880	2.36	2.532	2.22	3.279
6.65	1.653	6.25	2.439	5.90	3.837	5.55	4.545
9.31	2.597	8.75	3.125	8.26	3.509	7.77	4.082
13.33	2.500	12.50	2.899	11.80	3.279	11.11	3.846
16.66	2.667	15.62	3.077	14.70	3.448	14.70	4.000
20.00	3.175	18.25	3.571	17.70	3.922	16.65	4.444
26.66	3.226	25.00	3.636	23.60	4.082	22.20	4.651
40.00	3.571	37.50	3.922	35.40	4.348	33.30	4.878
66.50	4.000	62.50	4.444	59.00	4.762	55.50	5.555
100.00	4.878	93.75	5.263	88.00	5.556	83.33	6.061
Fig.93		Fig.94		Fig.95		Fig.96	

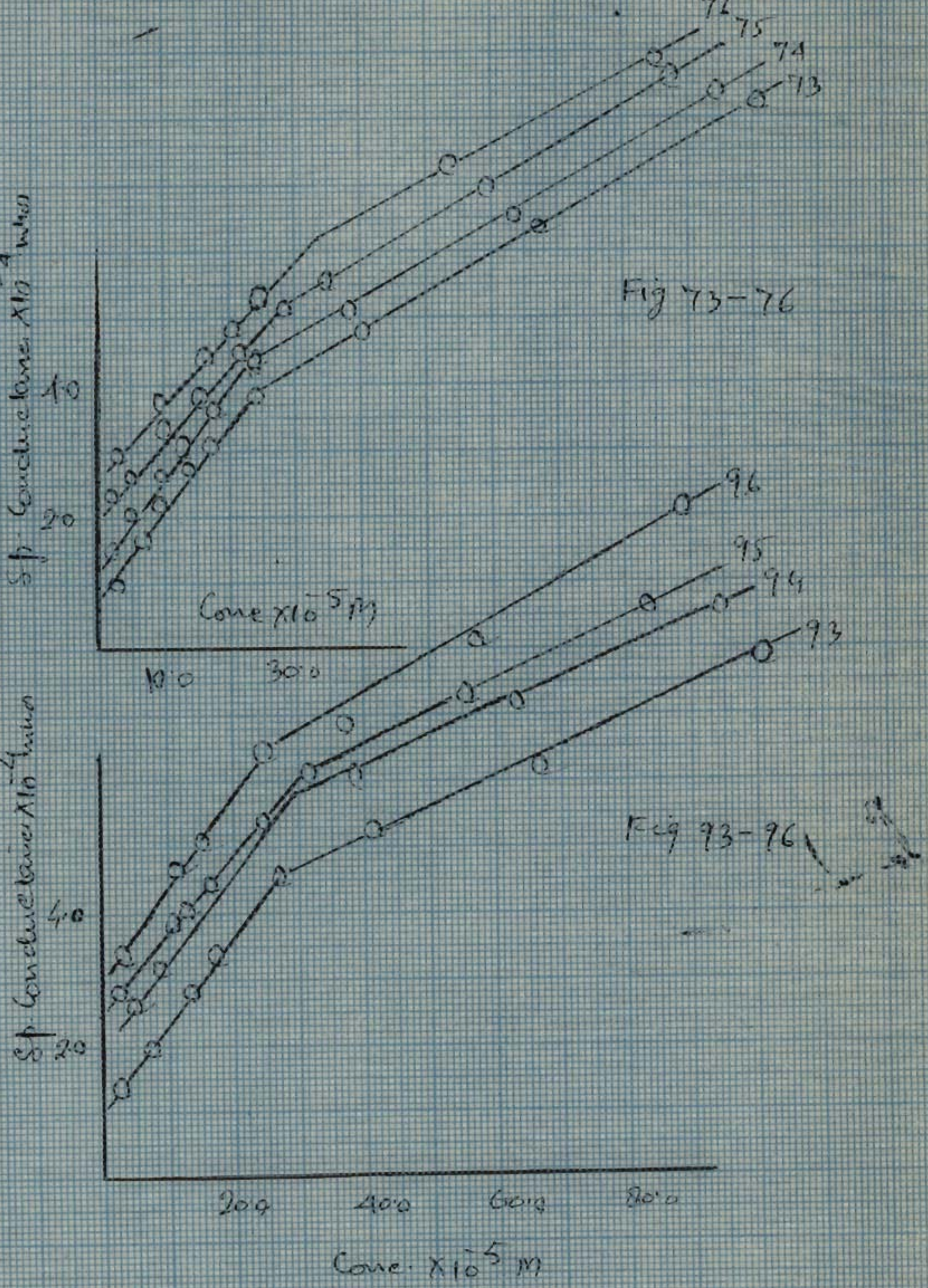


Fig 73-76

Fig 93-96

TABLE 25

Effect of formamide on the behaviour of cetyl pyridinium bromide.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos	Conc.soap $x10^{-4}$M	Sp.Cond. $x10^{-3}$mhos.
2.66	0.894	2.50	1.729	2.36	2.400	2.22	2.931
6.65	1.294	6.25	2.100	5.90	2.734	5.55	3.010
9.31	1.524	8.75	2.328	8.26	2.931	7.77	3.234
13.33	1.934	12.50	2.719	11.80	3.213	11.11	3.628
16.66	2.309	15.62	3.013	14.70	3.429	14.70	3.871
20.00	2.631	18.75	3.294	17.70	3.782	16.65	4.000
26.66	3.436	25.00	3.821	23.60	4.100	22.20	4.435
40.00	4.807	37.50	4.926	35.40	5.032	33.30	5.238
66.50	6.536	62.50	6.724	59.00	6.831	55.50	6.931
100.00	7.246	93.75	7.462	88.00	7.751	83.33	8.000

Fig.97 Fig.98 Fig.99 Fig.100

Effect of lauryl diethanol amine condensate (LDC) on the behaviour of soaps.

TABLE 26

Effect of LDC on the behaviour of sulphonated phenyl stearic acid mole ratio of LDC/ SPSA: A-1:49; B - 1:9; C - 1:4.

Conc.soap (x10^{-5}M)	pH		
	A	B	C
2.4	4.22	4.70	4.62
4.8	3.88	4.24	4.18
7.0	3.78	4.02	4.02
9.0	3.69	3.89	3.89
11.1	3.58	3.79	3.78
13.0	3.54	3.73	3.69
16.7	3.45	3.61	3.60
20.0	3.37	3.52	3.52
23.0	3.32	3.44	3.45
28.6	3.25	3.38	3.37
33.3	3.20	3.31	3.31
37.5	3.14	3.26	3.27
44.4	3.08	3.19	3.19
50.0	3.05	3.13	3.13
60.0	3.00	3.07	3.06
66.7	2.95	3.02	3.00
	Fig.101	Fig.102	Fig.103

Fig 101-103

Fig 104-106

Fig 107-109

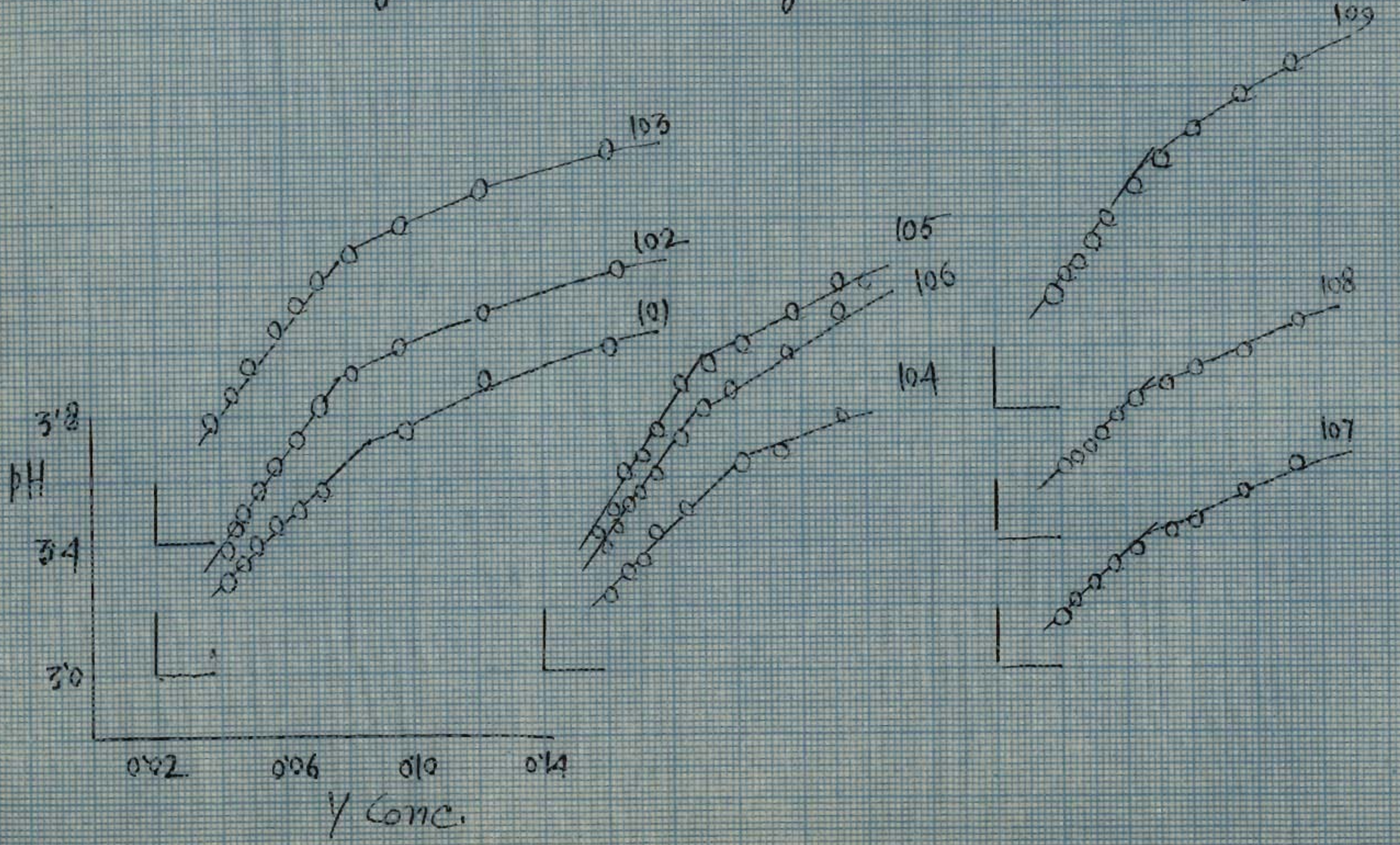


TABLE 27

Effect of LDC on the behaviour of sulphonated tolyl stearic acid mole ratio of LDC/STSA: A-1:49; B - 1:9; C - 1:4.

Conc.soap(x10^{-5}M)	pH		
	A	B	C
2.4	4.37	4.60	4.60
4.8	4.00	4.26	4.24
7.0	3.82	4.16	4.10
9.0	3.69	4.06	3.98
11.1	3.58	3.98	3.90
13.0	3.45	3.88	3.77
16.7	3.41	3.78	3.65
20.0	3.35	3.74	3.58
23.0	3.28	3.69	3.50
28.6	3.20	3.54	3.40
33.3	3.14	3.44	3.34
37.5	3.08	3.38	3.28
44.4	3.00	3.27	3.22
50.0	2.90	3.19	3.17
60.0	2.90	3.14	3.06
66.7	2.86	3.10	3.01
	Fig.104	Fig.105	Fig.106

TABLE 28

Effect of LDC on the behaviour of sulphonated xylyl stearic acid mole ratio LDC/SXSA A-1:49; B - 1:9; C - 1:4.

Conc.soap (x 10^{-5}M)	pH		
	A	B	C
2.4	4.48	4.65	4.68
4.8	4.10	4.20	4.20
7.0	3.95	4.00	4.10
9.0	3.65	3.85	3.90
11.1	3.42	3.50	3.80
13.0	3.32	3.40	3.70
16.7	3.25	3.30	3.65
20.0	3.20	3.25	3.40
23.0	3.15	3.20	3.30
28.6	3.10	3.15	3.25
33.3	3.06	3.10	3.20
37.5	3.00	3.07	3.15
44.4	2.96	3.04	3.08
50.0	2.94	3.00	3.00
60.0	2.90	2.98	3.00
66.7	2.68	2.96	2.95
	Fig.107	Fig.108	Fig.109

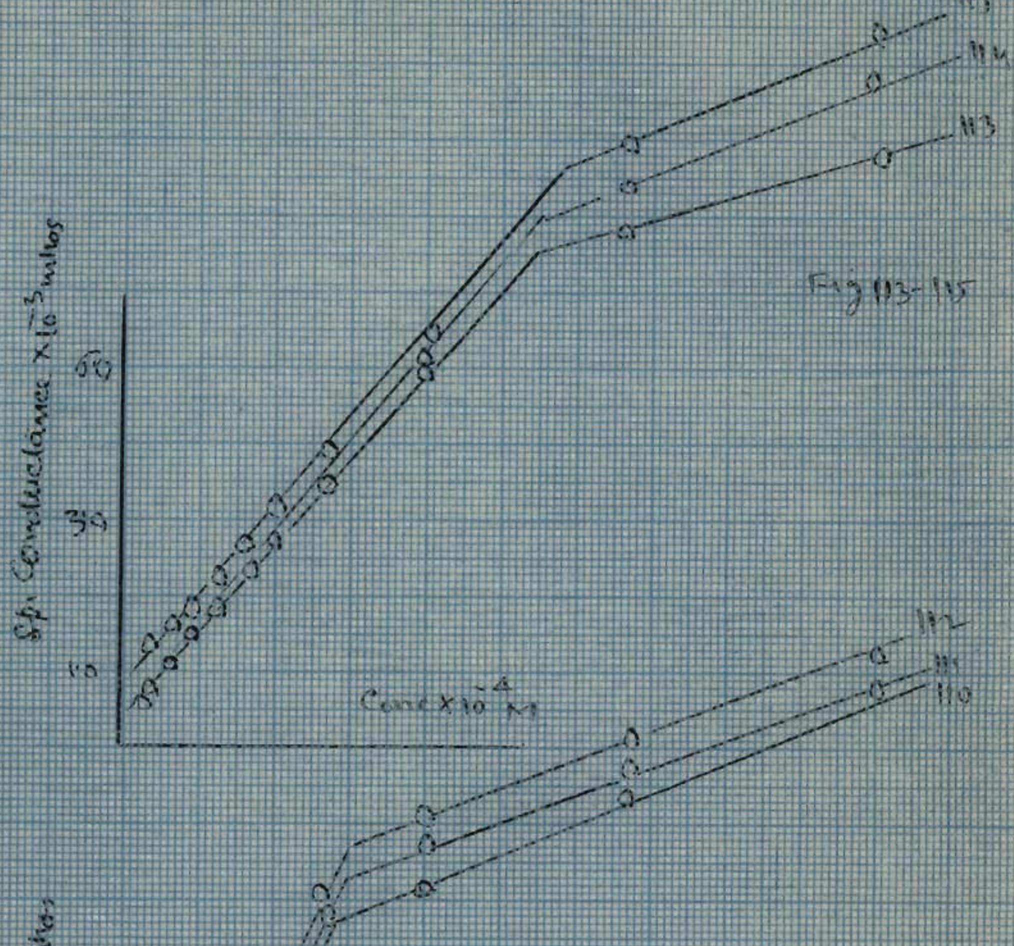


Fig 113-115

Fig 110-112

Polarography in phosphate buffer (pH 8.40) of malachite green in presence of different concentrationsof soap.

TABLE 1

Polarograms of 6.7 x 10^{-5}M malachite green in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.40	0.10	-0.05	-0.10	-0.20	-0.25	-0.25
0.1	1.95	1.00	0.00	-0.05	-0.05	-0.10	-0.15
0.2	2.65	1.95	0.50	0.70	0.20	0.20	0.25
0.3	2.85	2.15	0.70	0.90	0.80	1.00	1.25
0.4	2.95	2.20	0.80	1.00	1.20	1.50	1.80
0.5	3.50	2.25	0.85	1.15	1.25	1.65	2.00
0.6	3.85	2.30	0.90	1.25	1.30	1.70	2.15
0.7	4.50	2.40	1.00	1.35	1.40	1.75	2.20
0.8	5.20	2.80	1.15	1.50	1.50	1.80	2.25
0.9	5.50	3.50	1.50	1.65	1.60	1.90	2.30
1.0	6.50	4.50	1.80	1.90	1.70	2.10	2.40
1.1	7.20	4.80	2.20	2.50	2.00	2.45	2.50
1.2	7.40	5.20	2.50	2.85	2.65	3.30	3.50
1.3	7.55	5.35	2.65	3.00	3.20	3.80	4.30
1.4	7.50	5.45	2.70	3.15	3.40	3.85	4.80
1.5	7.55	5.50	2.80	3.20	3.55	3.95	5.00
1.6	7.60	5.60	2.90	3.30	3.60	4.00	5.15
Fig.1	A	B	C	D	E	F	G

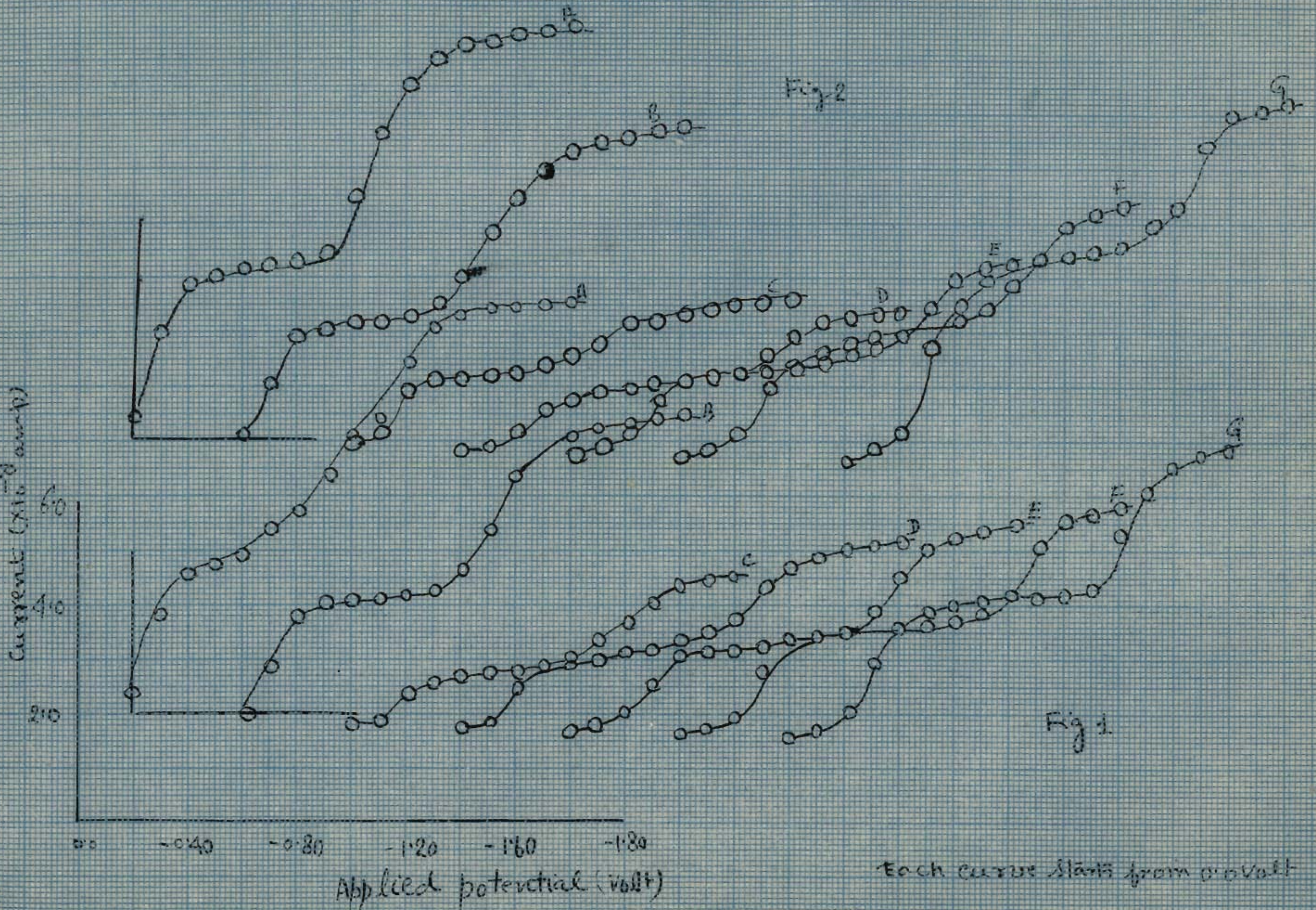


Fig 2

Fig 1

Each curve starts from 0·0 volt

Scale for Fig 1 & 2.

TABLE 2

Polarograms of 6.7×10^{-5} M malachite green in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.35	0.05	-0.05	-0.15	-0.20	-0.25	-0.25
0.1	1.95	0.95	0.10	-0.05	-0.05	-0.15	-0.15
0.2	2.85	1.95	0.95	0.20	0.22	0.20	0.20
0.3	3.00	2.00	1.10	0.65	0.85	1.00	1.80
0.4	3.15	2.15	1.15	0.85	1.20	1.45	2.50
0.5	3.20	2.20	1.20	0.95	1.30	1.65	3.00
0.6	3.25	2.25	1.25	1.00	1.35	1.85	3.25
0.7	3.40	2.50	1.40	1.15	1.45	1.95	3.35
0.8	4.40	3.00	1.60	1.20	1.60	2.00	3.45
0.9	5.58	3.80	1.80	1.25	1.65	2.15	3.50
1.0	6.50	4.50	2.20	1.40	1.80	2.30	3.65
1.1	7.00	5.00	2.25	1.65	2.00	2.50	4.00
1.2	7.25	5.35	2.35	1.95	2.50	2.95	4.35
1.3	7.30	5.55	2.40	2.25	3.00	3.45	5.55
1.4	7.45	5.60	2.50	2.30	3.25	4.00	6.00
1.5	7.50	5.70	2.55	2.40	2.35	4.25	6.15
1.6	7.60	5.90	2.65	2.45	3.40	4.15	6.15
Fig.2	A	B	C	D	E	F	G

TABLE 3

Polarograms of 6.7×10^{-5} M malachite green in presence of different concentrations of SXSA (order 10^{-5} M).

Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.45	0.00	-0.15	-0.25	-0.30	-0.30	-0.15
0.1	2.05	0.95	-0.05	-0.05	-0.05	-0.15	-0.05
0.2	3.15	2.00	0.95	0.25	0.30	0.90	0.20
0.3	3.55	2.25	1.10	0.75	1.05	1.40	1.35
0.4	3.70	2.30	1.15	1.10	1.55	1.65	2.50
0.5	3.80	2.35	1.20	1.20	1.80	1.75	3.15
0.6	3.85	2.40	1.25	1.30	1.90	1.80	3.35
0.7	4.15	2.50	1.40	1.40	1.95	1.90	3.45
0.8	5.10	3.30	1.70	1.50	2.00	2.95	3.50
0.9	6.15	4.35	2.00	1.55	2.10	3.00	3.50
1.0	6.75	4.55	2.50	1.65	2.25	3.20	3.65
1.1	7.35	4.80	3.00	1.95	2.53	3.70	3.80
1.2	7.55	5.00	3.25	2.30	3.30	4.10	4.35
1.3	7.70	5.20	3.45	2.80	4.45	5.25	6.00
1.4	7.65	5.20	3.50	3.15	4.95	4.85	8.10
1.5	7.70	5.30	3.60	3.20	4.85	5.00	7.60
1.6	7.75	5.35	3.70	3.35	5.15	5.15	7.70
Fig.3	A	B	C	D	E	F	G

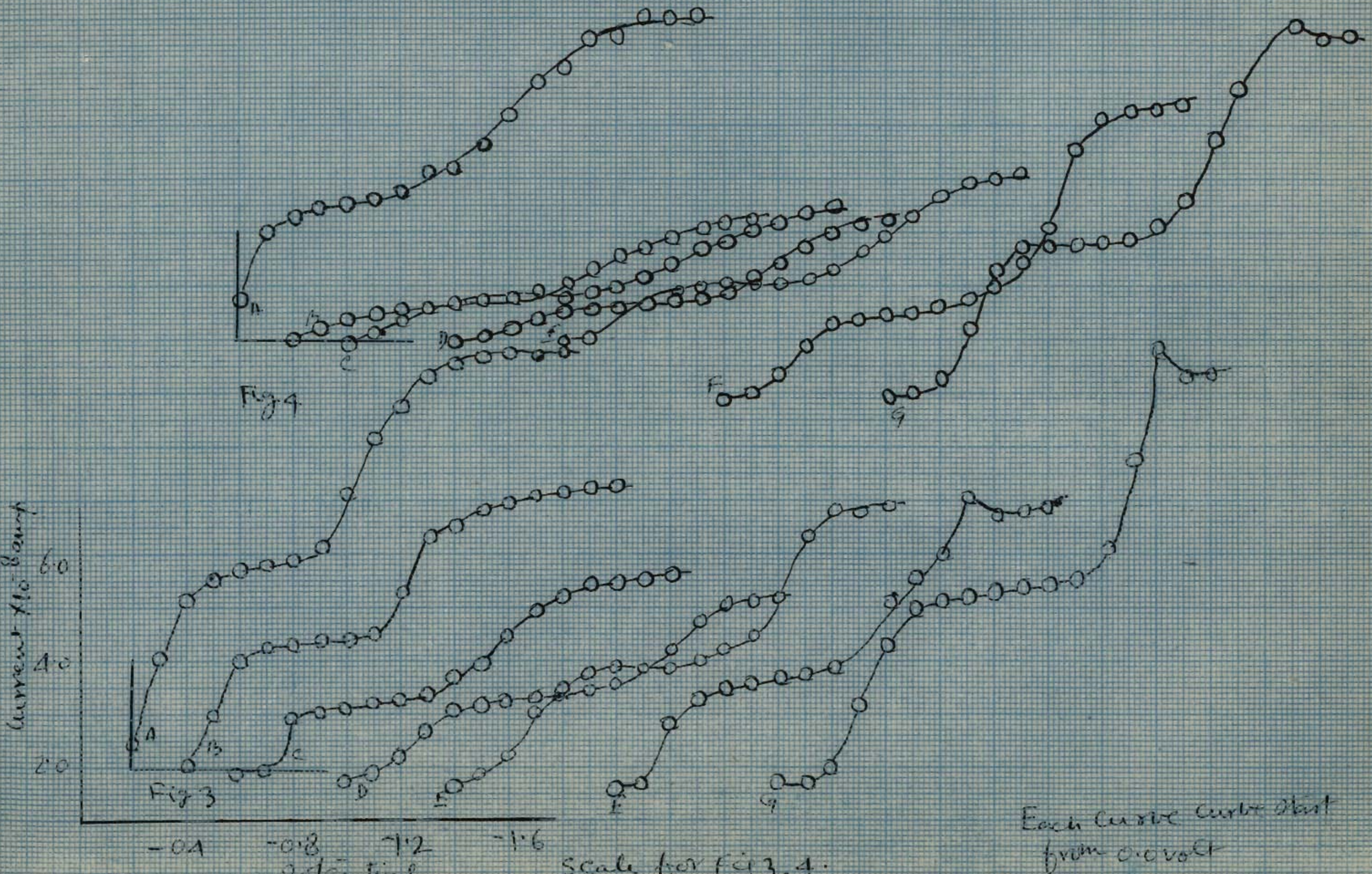


Fig. 4

Fig 3

Scale for Fig 3, 4.

Each Curve curve start from 0.0 volt

Polarography in phosphate buffer(pH 8.40) of rhodamine 6G in presence of different concentrations of soap.

TABLE 4.

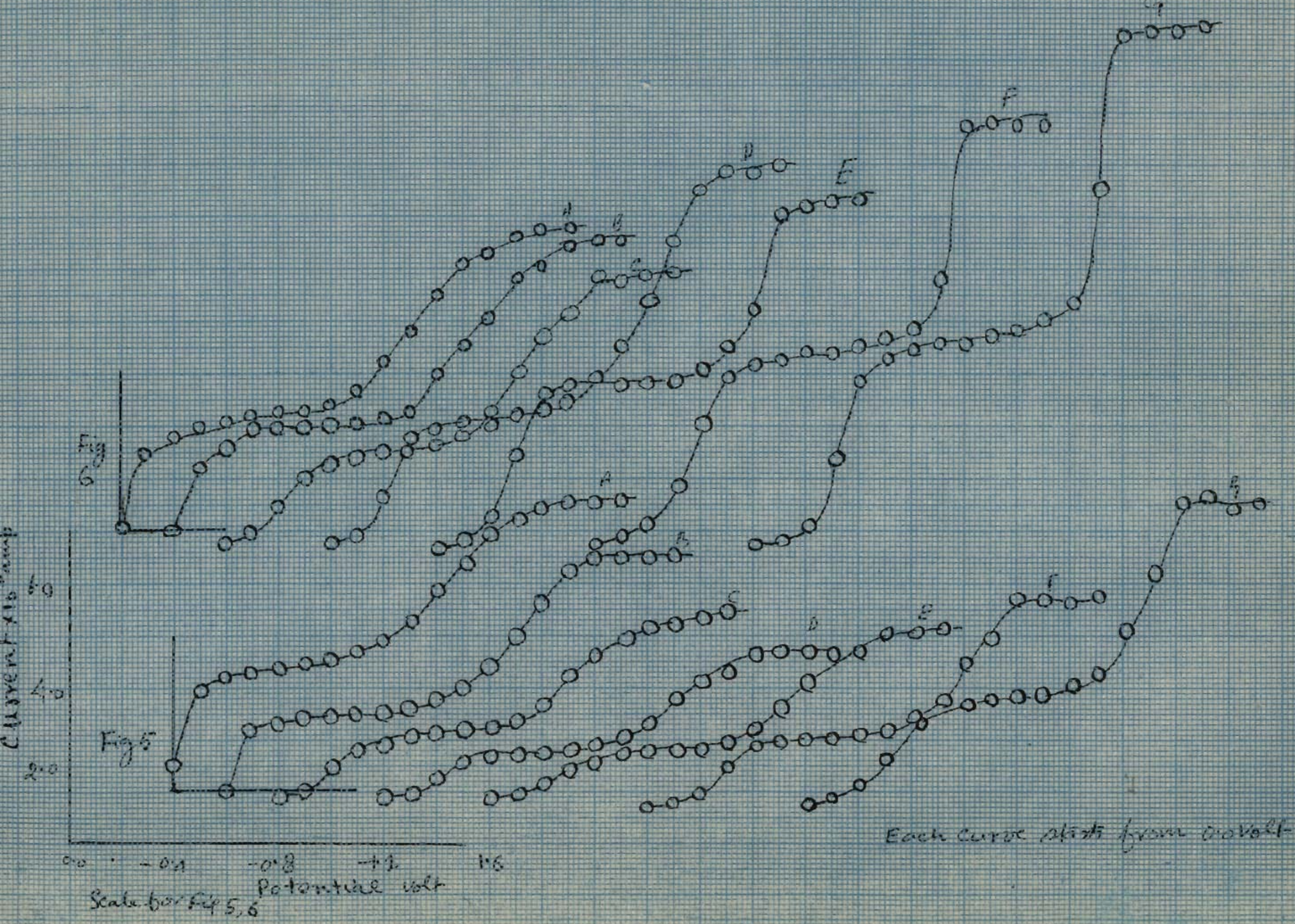
Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of SPSA(order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8}amp) for different concentration of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.6	-0.10	-0.15	-0.15	-0.20	-0.25	-0.25
0.1	1.95	0.10	0.05	-0.05	-0.05	-0.05	-0.05
0.2	2.20	0.25	0.25	0.15	0.20	0.20	0.15
0.3	2.35	0.35	0.50	0.35	0.55	0.80	1.05
0.4	2.40	0.40	0.55	0.40	0.70	1.20	2.05
0.5	2.50	0.45	0.55	0.45	0.80	1.30	2.50
0.6	2.65	0.55	0.65	0.45	0.90	1.40	2.60
0.7	3.00	0.60	0.70	0.55	0.90	1.40	2.60
0.8	3.05	0.65	0.75	0.60	0.95	1.50	2.65
0.9	3.50	0.75	0.85	0.65	1.05	1.60	2.75
1.0	4.05	0.90	1.05	0.80	1.25	1.85	3.00
1.1	4.70	1.20	1.35	1.10	1.60	2.35	3.45
1.2	5.00	1.40	1.55	1.35	2.00	2.95	4.60
1.3	5.50	1.60	1.75	1.70	2.30	3.40	5.50
1.4	5.55	1.80	2.00	1.90	2.55	4.00	6.40
1.5	5.90	1.90	2.10	2.00	2.80	4.10	6.65
1.6	5.85	2.00	2.30	2.10	2.80	4.15	6.45
Fig.4	A	B	C	D	E	F	G

TABLE 5

Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.50	0.05	-0.16	-0.15	-0.15	-0.30	-0.30
0.1	1.90	1.20	0.05	0.05	-0.05	-0.15	-0.15
0.2	2.15	1.30	0.45	0.30	0.15	0.05	0.10
0.3	2.25	1.35	0.80	0.55	0.40	0.50	0.65
0.4	2.35	1.40	0.90	0.65	0.55	0.90	1.25
0.5	2.40	1.45	1.00	0.70	0.70	0.95	1.60
0.6	2.50	1.50	1.10	0.75	0.75	1.00	1.65
0.7	2.65	1.60	1.15	0.80	0.75	1.00	1.70
0.8	2.85	2.00	1.20	0.85	0.80	1.10	1.80
0.9	3.25	2.40	1.35	1.05	0.90	1.20	1.80
1.0	3.90	3.00	1.60	1.30	1.20	1.40	2.00
1.1	4.40	3.60	2.15	1.80	1.60	1.70	2.25
1.2	4.90	4.20	2.85	2.30	2.00	2.45	2.00
1.3	5.20	4.40	3.10	2.60	2.50	2.90	4.10
1.4	5.40	4.45	3.20	2.70	2.60	3.70	5.45
1.5	5.55	4.50	3.30	2.70	2.00	3.65	5.60
1.6	5.50	4.60	3.40	2.75	3.00	3.65	5.25
Fig.5	A	B	C	D	E	F	G



Each curve starts from 0.0 volt

Scale for Fig 5, 6

TABLE 6

Polarograms of 6.7×10^{-5} M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5} M).

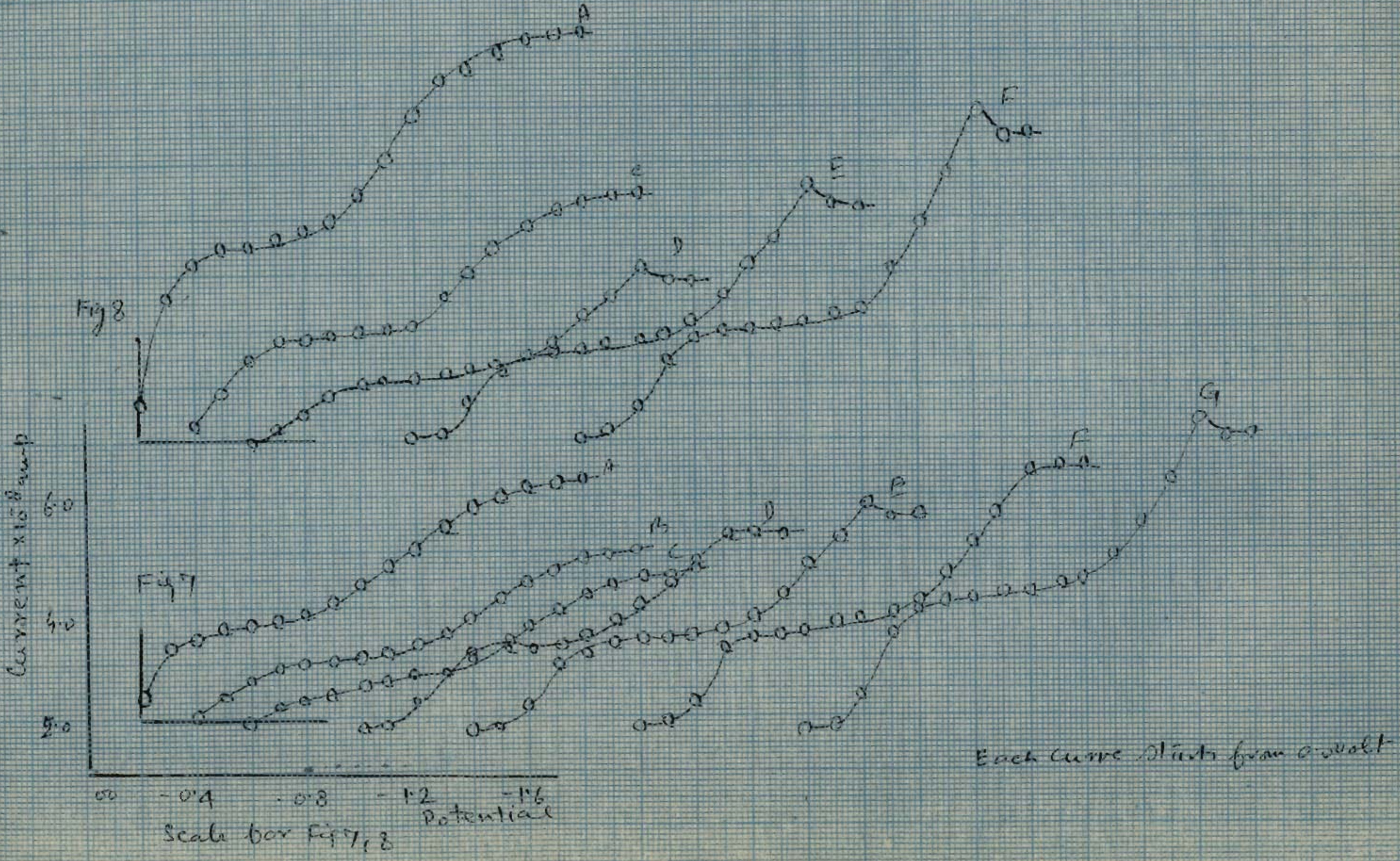
Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.00	-0.05	-0.20	-0.20	-0.25	-0.25	-0.35
0.1	1.95	1.20	0.00	-0.05	-0.15	-0.15	-0.15
0.2	1.75	1.60	0.50	0.60	0.25	0.10	0.05
0.3	2.05	2.00	1.10	1.85	1.45	1.30	0.80
0.4	2.15	2.00	1.30	1.90	2.55	2.85	2.05
0.5	2.20	2.00	1.45	1.95	2.70	3.25	2.90
0.6	2.25	2.05	1.55	2.00	2.70	3.40	3.10
0.7	2.25	2.15	1.60	2.20	2.75	3.50	3.20
0.8	2.40	2.20	1.65	2.30	2.75	3.50	3.30
0.9	2.70	2.22	1.80	2.40	2.75	3.65	3.30
1.0	3.20	3.00	2.20	2.90	3.00	3.75	3.45
1.1	3.75	3.50	2.95	3.50	3.50	4.95	3.60
1.2	4.40	4.00	3.65	4.30	4.20	4.55	3.75
1.3	5.05	4.85	1.10	5.50	6.00	6.40	4.75
1.4	5.25	5.00	4.80	6.40	6.10	8.30	7.70
1.5	6.65	4.95	4.75	6.80	6.15	8.35	7.75
1.6	5.75	5.50	4.80	6.80	6.25	8.40	7.60
Fig. 6	A	B	C	D	E	F	G

Polarography in phosphate buffer(pH 8.40) of methylene blue in presence of different concentrations of soap.

TABLE 7

Polarograms of 6.7×10^{-5}M methylene blue in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.35	-0.15	-0.20	-0.20	-0.25	-0.25	-0.25
0.1	1.25	0.30	0.15	-0.05	-0.10	-0.15	-0.15
0.2	1.35	0.60	0.30	0.40	0.30	0.35	0.50
0.3	1.55	0.80	0.40	0.95	1.00	1.20	1.50
0.4	1.65	0.90	0.50	1.15	1.20	1.40	2.00
0.5	1.75	0.90	0.60	1.20	1.30	1.45	2.15
0.6	1.85	1.10	0.65	1.25	1.40	1.55	2.20
0.7	2.05	1.20	0.90	1.30	1.45	1.70	2.30
0.8	2.35	1.40	1.10	1.60	1.55	1.75	2.40
0.9	2.75	1.70	1.30	1.80	1.65	1.80	2.50
1.0	3.00	2.05	1.70	2.25	1.90	2.10	2.06
1.1	3.40	2.30	2.00	2.60	2.35	2.65	3.00
1.2	3.70	2.50	2.30	2.95	2.85	3.25	3.50
1.3	3.90	2.80	2.00	3.55	3.30	3.70	4.20
1.4	4.10	2.80	2.55	3.35	4.10	4.50	5.50
1.5	4.15	2.85	2.60	3.45	3.70	4.45	5.00
1.6	4.20	3.05	2.70	3.55	3.75	4.45	5.10
Fig.7	A	B	C	D	E	F	G



Scale for Fig 7, 8

Each Curve starts from 0 volt

TABLE 8.

Polarograms of 6.7×10^{-5} M methylene blue in presence of different concentrations of STSA (order 10^{-5} M).

Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.40	-0.10	-0.15	-0.20	-0.20	-0.25	-0.25
0.1	2.30	0.55	0.30	0.00	-0.05	-0.05	-0.10
0.2	2.90	1.20	1.30	0.25	0.45	0.40	0.55
0.3	3.20	1.50	2.05	0.70	1.10	1.25	2.55
0.4	3.30	1.55	2.25	0.80	1.40	1.60	3.95
0.5	0.40	1.65	2.35	0.85	1.55	1.75	4.65
0.6	3.55	1.70	2.45	0.90	1.55	1.85	4.80
0.7	3.65	1.75	2.60	0.95	1.65	1.84	4.90
0.8	4.20	1.90	2.60	1.05	1.65	1.90	0.55
0.9	4.85	2.40	3.10	1.10	1.70	2.10	5.15
1.0	5.65	2.80	3.45	1.25	2.00	2.15	5.40
1.1	6.30	3.30	4.45	1.60	2.55	2.85	6.55
1.2	6.45	3.60	5.00	2.00	3.05	2.90	8.70
1.30	6.85	3.90	5.40	2.40	3.60	4.60	10.30
1.4	7.10	4.10	5.60	2.95	4.50	6.10	12.40
1.5	7.10	4.15	5.70	2.60	4.05	5.10	12.00
1.6	6.80	4.20	5.80	2.70	4.10	5.30	12.20
Fig.8	A	B	C	D	E	F	G

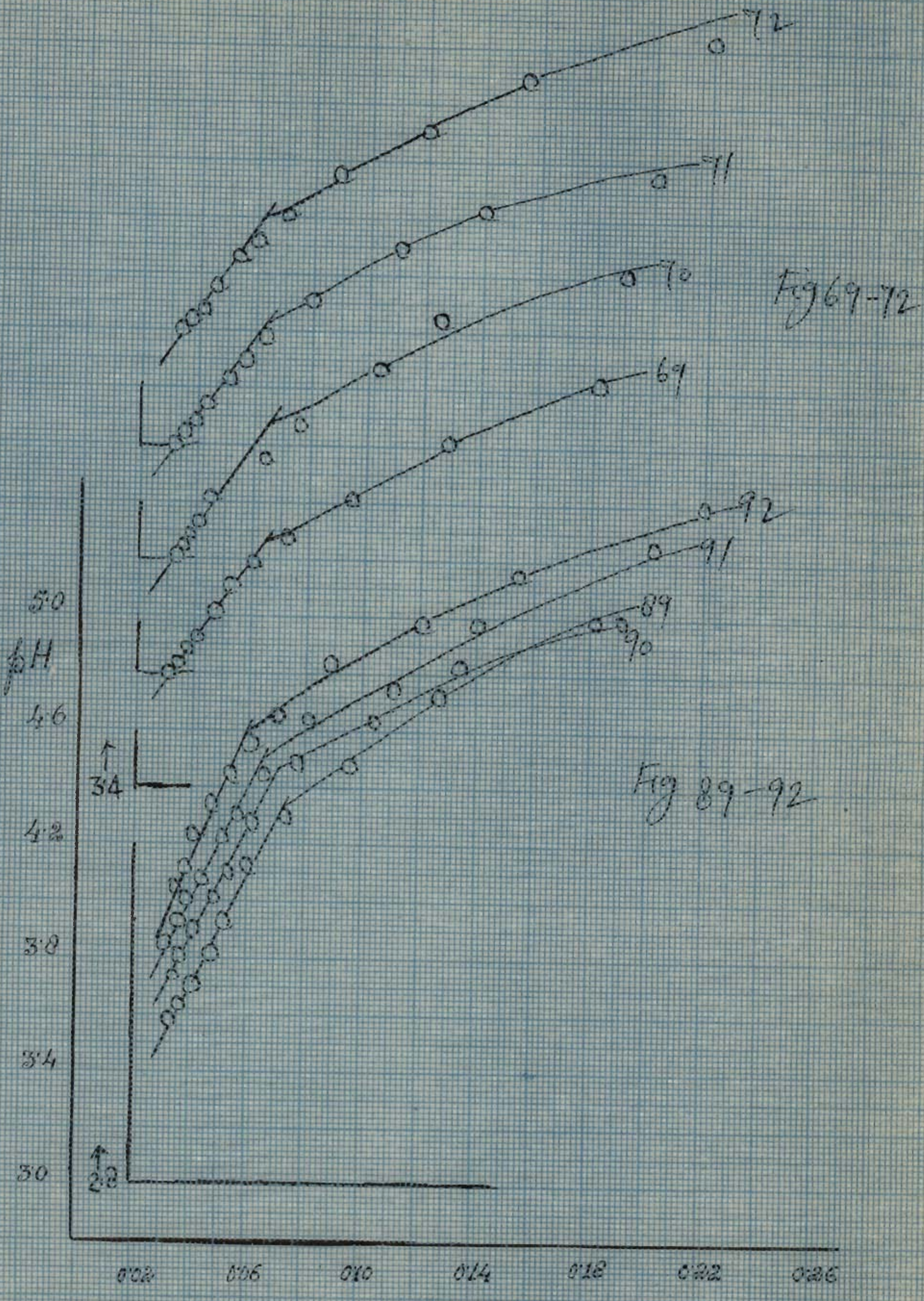


Fig 69-72

Fig 89-92

TABLE 23

Effect of formamide on the behaviour of sulphonated xylyl stearic acid.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH	Conc.soap $\times 10^{-5}$M	pH
3.10	5.15	2.94	5.30	2.78	5.40	2.50	5.50
6.25	4.95	5.88	5.05	5.55	5.15	5.00	5.30
9.35	4.50	8.83	4.60	8.33	4.75	7.50	4.90
13.50	4.25	11.77	4.40	11.10	4.50	10.00	4.70
19.50	4.05	17.65	4.25	16.65	4.40	15.00	4.60
25.00	3.90	23.53	4.05	22.20	4.20	20.00	4.40
31.25	3.70	29.42	3.90	27.75	4.05	25.00	4.30
37.50	3.60	35.30	3.80	33.30	4.00	30.00	4.20
50.00	3,48	47.06	3.70	44.40	3.85	40.00	4.10
62.50	3.40	58.83	3.60	55.55	3.78	50.00	4.00
75.00	3.35	70.60	3.52	66.60	3.70	60.00	3.85
93.75	3.22	88.24	3.40	83.25	3.51	75.00	3.80
Fig.89		Fig.90		Fig.91		Fig.92	

Fig 85-88

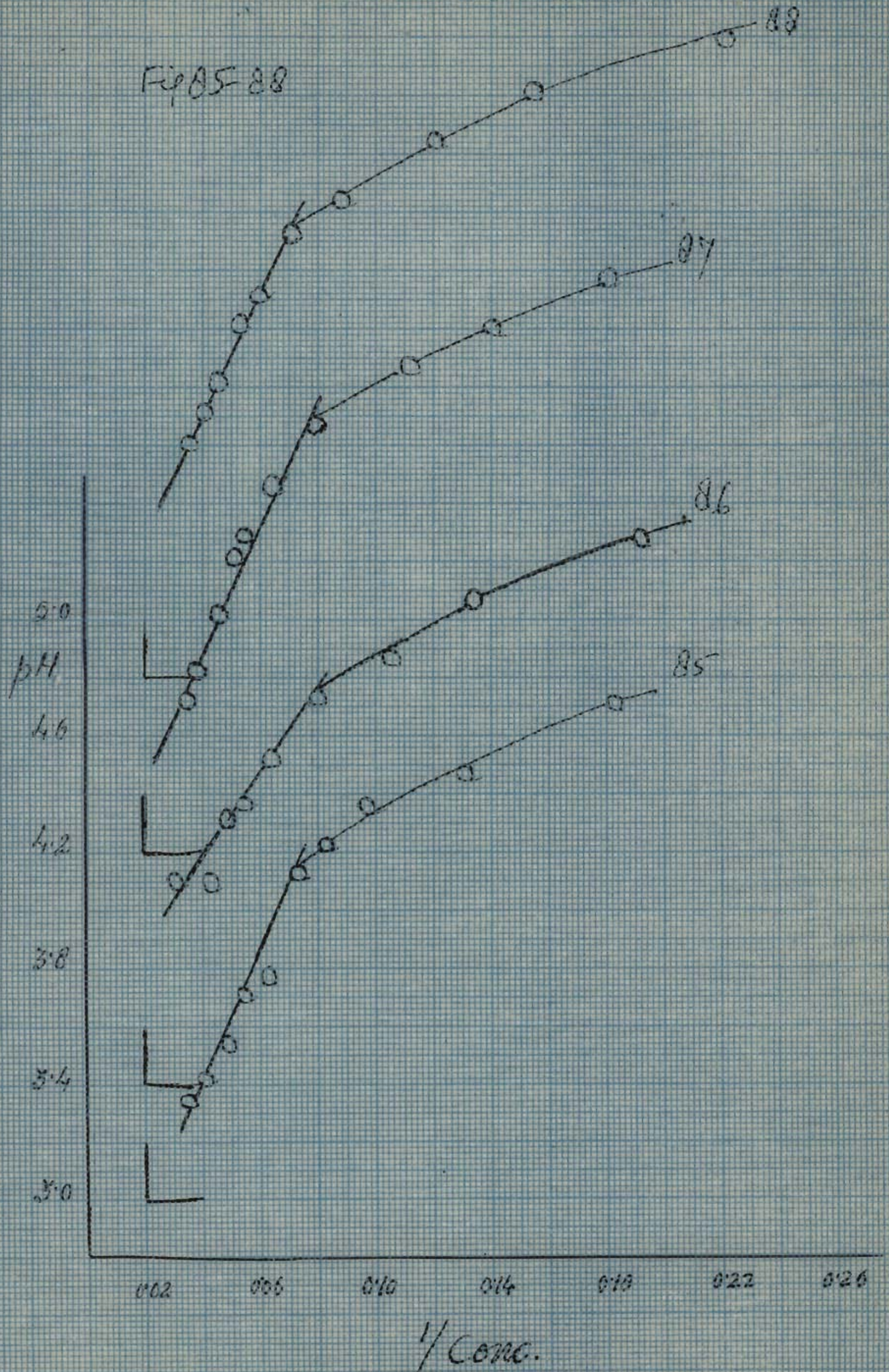


TABLE 24

Effect of formamide on the behaviour of cetyl trimethyl ammonium bromide.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos	Conc.soap $\times 10^{-5}$M	Sp.Cond. $\times 10^{-4}$mhos
2.66	1.351	2.50	1.880	2.36	2.532	2.22	3.279
6.65	1.653	6.25	2.439	5.90	3.837	5.55	4.545
9.31	2.597	8.75	3.125	8.26	3.509	7.77	4.082
13.33	2.500	12.50	2.899	11.80	3.279	11.11	3.846
16.66	2.667	15.62	3.077	14.70	3.448	14.70	4.000
20.00	3.175	18.25	3.571	17.70	3.922	16.65	4.444
26.66	3.226	25.00	3.636	23.60	4.082	22.20	4.651
40.00	3.571	37.50	3.922	35.40	4.348	33.30	4.878
66.50	4.000	62.50	4.444	59.00	4.762	55.50	5.555
100.00	4.878	93.75	5.263	88.00	5.556	83.33	6.061
Fig.93		Fig.94		Fig.95		Fig.96	

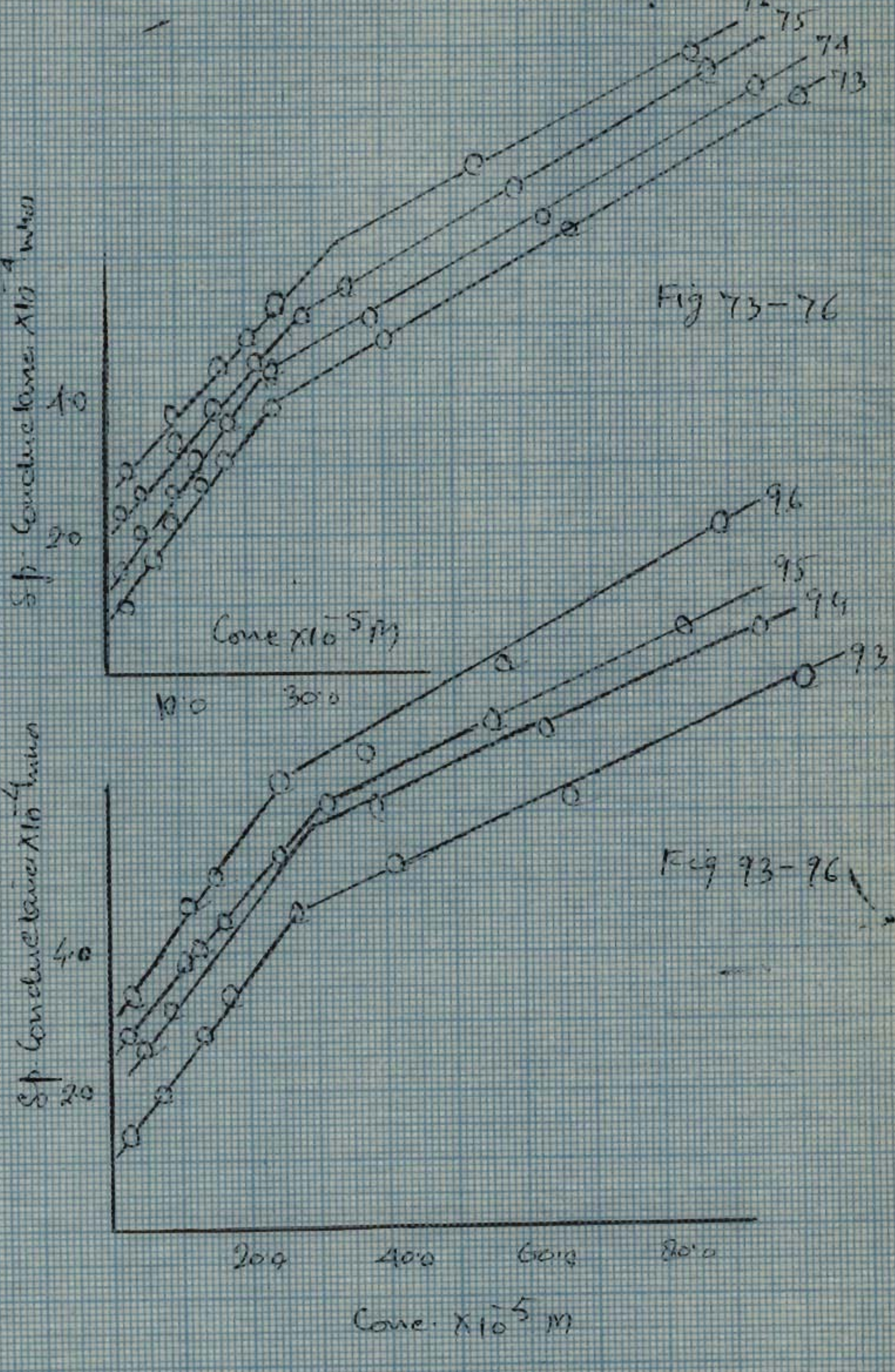


Fig 73-76

Fig 93-96

TABLE 25

Effect of formamide on the behaviour of cetyl pyridinium bromide.

Formamide 0.2M		Formamide 0.4M		Formamide 0.5M		Formamide 0.75M	
Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos	Conc.soap $\times 10^{-4}$M	Sp.Cond. $\times 10^{-3}$mhos.
2.66	0.894	2.50	1.729	2.36	2.400	2.22	2.931
6.65	1.294	6.25	2.100	5.90	2.734	5.55	3.010
9.31	1.524	8.75	2.328	8.26	2.931	7.77	3.234
13.33	1.934	12.50	2.719	11.80	3.213	11.11	3.628
16.66	2.309	15.62	3.013	14.70	3.429	14.70	3.871
20.00	2.631	18.75	3.294	17.70	3.782	16.65	4.000
26.66	3.436	25.00	3.821	23.60	4.100	22.20	4.435
40.00	4.807	37.50	4.926	35.40	5.032	33.30	5.238
66.50	6.536	62.50	6.724	59.00	6.831	55.50	6.931
100.00	7.246	93.75	7.462	88.00	7.751	83.33	8.000

Fig.97 Fig.98 Fig.99 Fig.100

Effect of lauryl diethanol amine condensate (LDC) on the behaviour of soaps.

TABLE 26

Effect of LDC on the behaviour of sulphonated phenyl stearic acid

mole ratio of LDC/ SPSA: A-1:49; B - 1:9; C - 1:4.

Conc.soap ($\times 10^{-5}$ M)	pH		
	A	B	C
2.4	4.22	4.70	4.62
4.8	3.88	4.24	4.18
7.0	3.78	4.02	4.02
9.0	3.69	3.89	3.89
11.1	3.58	3.79	3.78
13.0	3.54	3.73	3.69
16.7	3.45	3.61	3.60
20.0	3.37	3.52	3.52
23.0	3.32	3.44	3.45
28.6	3.25	3.38	3.37
33.3	3.20	3.31	3.31
37.5	3.14	3.26	3.27
44.4	3.08	3.19	3.19
50.0	3.05	3.13	3.13
60.0	3.00	3.07	3.06
66.7	2.95	3.02	3.00
	Fig.101	Fig.102	Fig.103

Fig 101-103

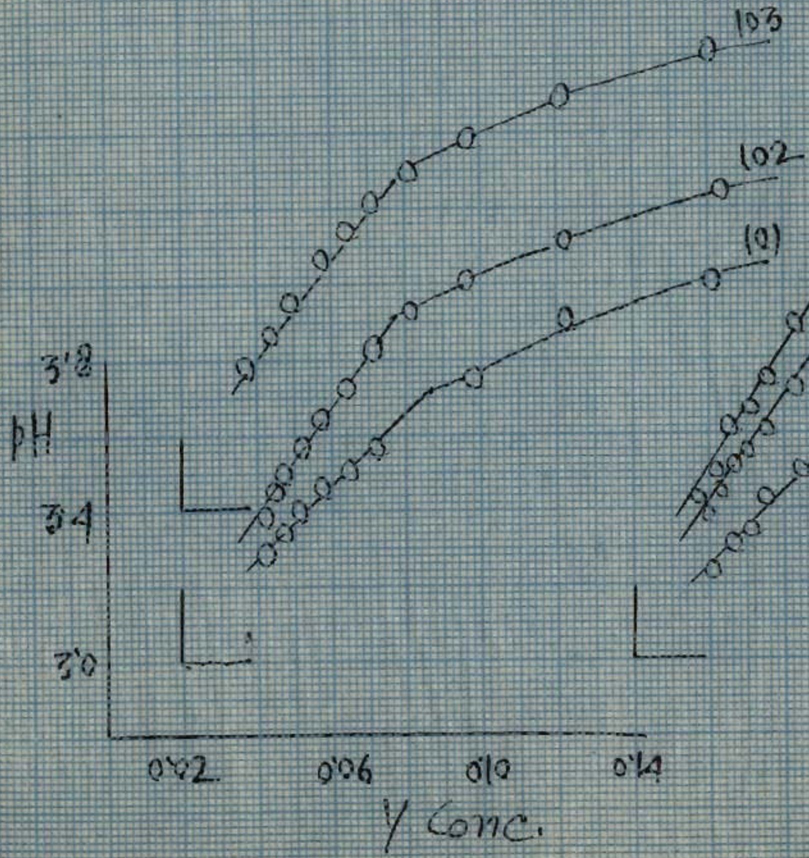


Fig 104-106

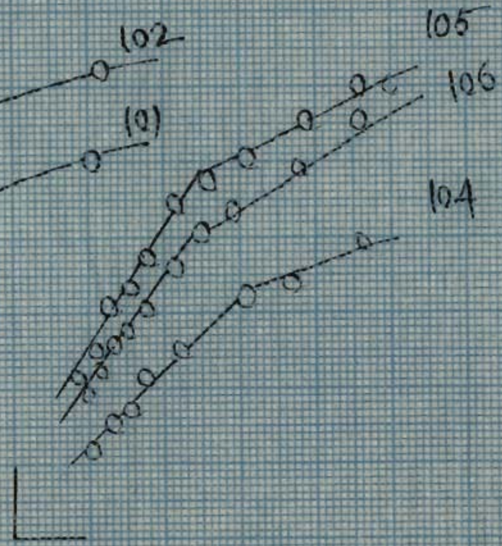


Fig 107-109

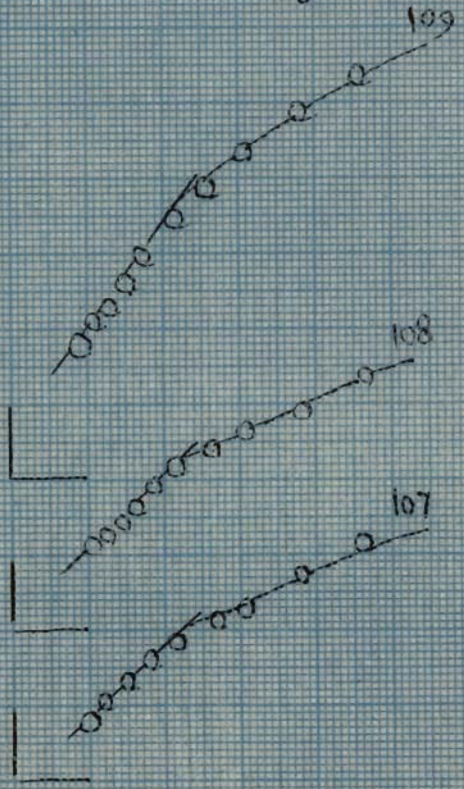


TABLE 27

Effect of LDC on the behaviour of sulphonated tolyl stearic acid mole ratio of LDC/STSA: A-1:49; B - 1:9; C - 1:4.

Conc.soap($\times10^{-5}$M)	pH		
	A	B	C
2.4	4.37	4.60	4.60
4.8	4.00	4.26	4.24
7.0	3.82	4.16	4.10
9.0	3.69	4.06	3.98
11.1	3.58	3.98	3.90
13.0	3.45	3.88	3.77
16.7	3.41	3.78	3.65
20.0	3.35	3.74	3.58
23.0	3.28	3.69	3.50
28.6	3.20	3.54	3.40
33.3	3.14	3.44	3.34
37.5	3.08	3.38	3.28
44.4	3.00	3.27	3.22
50.0	2.90	3.19	3.17
60.0	2.90	3.14	3.06
66.7	2.86	3.10	3.01
	Fig.104	Fig.105	Fig.106

TABLE 28

Effect of LDC on the behaviour of sulphonated xylyl stearic acid mole ratio LDC/SXSA A-1:49; B - 1:9; C - 1:4.

Conc.soap (x 10^{-5}M)	pH		
	A	B	C
2.4	4.48	4.65	4.68
4.8	4.10	4.20	4.20
7.0	3.95	4.00	4.10
9.0	3.65	3.85	3.90
11.1	3.42	3.50	3.80
13.0	3.32	3.40	3.70
16.7	3.25	3.30	3.65
20.0	3.20	3.25	3.40
23.0	3.15	3.20	3.30
28.6	3.10	3.15	3.25
33.3	3.06	3.10	3.20
37.5	3.00	3.07	3.15
44.4	2.96	3.04	3.08
50.0	2.94	3.00	3.00
60.0	2.90	2.98	3.00
66.7	2.68	2.96	2.95
	Fig.107	Fig.108	Fig.109

TABLE 29

Effect of LDC on the behaviour of cetyl trimethyl ammonium bromide: mole ratio of LDC/CTMAB A 1:49; B 1:9 ; C 1:4.

Conc.soap x 10^{-5}M	Sp.conductivity($\times 10^{-4}$ mhos)		
	A	B	C
2.66	1.294	1.638	2.100
6.65	1.842	2.318	2.542
9.31	2.500	2.983	3.211
13.33	3.308	3.732	4.000
16.66	3.934	4.430	4.628
20.00	4.700	5.215	5.500
26.66	6.315	6.537	5.833
40.00	7.081	7.500	7.941
66.50	8.130	8.549	8.967
100.00	9.436	9.450	9.900
Fig.	110	111	112

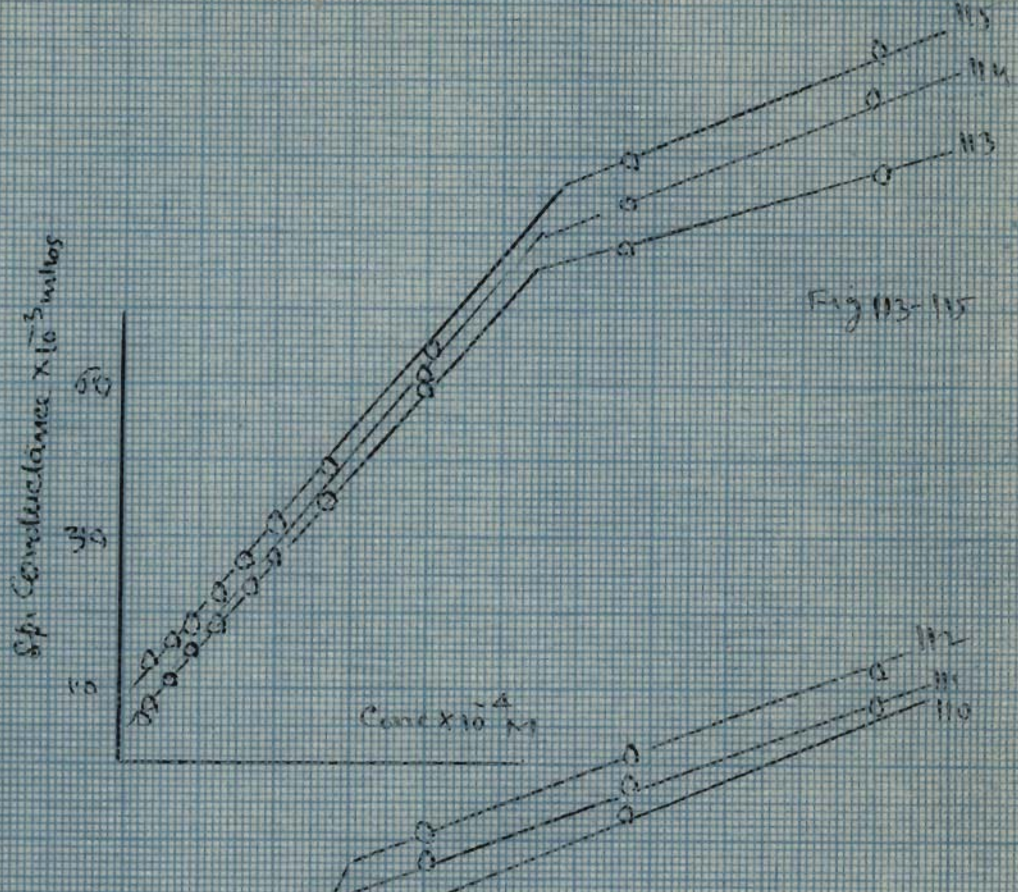


Fig 113-115

Fig 110-112

T_A_B_L_E 30

Effect of LDC on the behaviour of cetyl pyridinium bromide: mole ratio of LDC/CPB: A. 1:49; B.1:9;C.1:4

Conc.soap x 10^{-4}M	Sp. conductivity (x 10^{-3} mhos)		
	A	B	C
2.66	0.893	0.653	1.328
6.65	1.051	1.100	1.500
9.31	1.438	1.500	1.850
13.33	1.790	1.810	2.153
16.66	2.362	2.411	2.732
20.00	2.732	2.983	3.211
26.66	3.308	3.500	3.732
40.00	4.700	5.000	5.215
66.50	6.728	7.201	7.941
100.00	7.750	8.638	9.125
Fig.	113	114	115

RESULTS AND DISCUSSION

Effect of alcohols.

The effect of methyl and ethyl alcohols on the anionic and cationic soaps has been studied pH and conductometrically respectively. The c.m.c. values have been calculated for the anionic soaps from the plots between the inverse of soap concentration and pH and for cationic soaps from the plots between soap concentration and specific conductivity. The values so obtained are given in Table I and II.

TABLE I.

Critical micelle concentration of anionic and cationic soaps in presence of different amounts of methyl alcohol.

Soap	Critical micelle concentration			
	Methyl alcohol			
	6%	12%	17%	25%
SPSA x 10^{-5}M	13.8	13.0	16.4	21.0
STSA "	15.0	14.7	18.5	20.0
SXSA "	20.0	19.2	23.5	25.0
CTMAB "	25.0	19.0	26.0	30.0
CPB x 10^{-4}M	40.0	33.0	50.0	63.0

TABLE II.

Critical micelle concentration of anionic and cationic soaps in presence of different amounts of ethyl alcohol.

Soap	Critical micelle concentration			
	Ethyl alcohol			
	6%	12%	17%	25%
SPSA $\times 10^{-5}$M	13.6	12.3	17.8	21.7
STSA "	15.4	14.3	17.0	20.0
SXSA "	20.0	19.2	23.0	25.0
CTMAB "	27.0	26.0	33.0	35.0
CPB $\times 10^{-4}$M	42.0	40.0	50.0	61.0

From the above results it is evident that the critical point for micelle formation is shifted towards higher concentration with the increase in the alcoholic content of the solution. An initial lowering in the c.m.c. is,however,observed in all cases.

According to Lawrence and Stenson(14) if the soap is represented by R_1 (s) and the added alcohol as R_2 (a),the over all solubility S in the ternary system (soap solution-alcohol mixture) may be represented by

$S = S_s + S_a + S_1 - (R_1 + R_2)$, where S_s,S_a and S_1 are the tendencies leading to solubility of the two polar groups(soap and alcohol) plus the "Interaction addition" of soap,alcohol and water(S_1); R_1 and R_2 are the terms representing reducing solubility. Obviously, if S_1 is greater than R_2 , the addition of $R_2(a)$ will peptize the soap solution and hence raise the c.m.c. ; if S_1 is smallar,solubility is reduced and the c.m.c. is lowered.

In our case,when the alcohol is less than 12 %, a decrease in the critical concentration is observed. This according to the above equation, means that the solubilisation tendency of the " Interaction addition " that is soap + water + alcohol, is smallar than that of the added alcohol in the system and hence the lowering in c.m.c. observed. It appears that in mixtures with lower alcohol content large number of ions are made available for aggregation, resulting the formation of the micelle at lower concentration of the soap. This also evident from the variation in pH of anionic soaps in presence of alcohols where a decrease in pH is observed upto 12 % of alcohol.

On the other hand for alcohol concentration beyond 12% the ionisation of the soap is markedly retarded since very little change in pH is then observed. The tendency to the solubility of the " Interaction addition " is higher then that of added alcohol itself and, therefore, addition of the alcohol more than 12% peptizes the soap solution, leading to an increase in the c.m.c. value.

The conductivity variations in cationic soap in presence of alcohols is worth mentioning. It is that although the sp.conductivity-concentration curves with and without alcohol overlap each other before association, large deviations towards higher conductivity side are observed with increasing concentration of the alcohol after the micelle formation has taken place.

Effect of urea.

The c.m.c. values in presence of varying amounts of the reagent as determined from the plots of 1/Conc. vs. pH(anionic soaps)and concentration vs. sp.conductance (cationic soaps) are summarized in table III.

TABLE III.

Critical micelle concentration in presence of different amounts of urea.

Soap	Critical micelle concentration			
	Urea			
	0.5M	1.0M	3.0M	6.0M
SPSA x 10^{-5}M	17.2	17.8	20.0	23.7
STSA "	18.5	20.0	23.8	25.0
SXSA "	20.0	20.8	25.0	27.5
CTMAB "	26.0	29.5	32.5	40.5
CPB x 10^{-4}M	56.0	59.0	64.0	68.0

From the above results it is evident that the addition of urea invariably increases the c.m.c. of both anionic and cationic soaps. Small concentrations of urea(less than 1.0 M) has little influence on the micelle formation of anionic soaps. The maximum effect is observed with 6.0 M urea. The presence of urea in the soap solutions breaks the hydrogen-hydrogen bonds, thereby weakening the cohesive forces existing between the water molecules. The pushing out tendency for the hydrophobic portion is thus lessened with the result that a large proportion of a single soap molecules can remain in solution. Micelle formation would, therefore, take place at a higher soap concentration. Another factor, viz., the increase in dielectric constant of water by the addition of urea as considered by some authors may also be responsible for the inhibition of aggregation.

TABLE IV

The values of c.m.c. (u) (in presence of urea)/c.m.c.(o) (without the presence of urea)

Soap	c.m.c.(u) / c.m.c. (o)			
	Urea			
	0.5M	1.0M	3.0M	6.0 M
SPSA	1.24	1.29	1.45	1.71
STSA	1.18	1.28	1.46	1.60
SXSA	1.00	1.04	1.25	1.37
CTMAB	1.04	1.18	1.30	1.62
CPB	1.05	1.11	1.20	1.28

From the table IV, it is evident that urea influences the aggregation of the alkyl-aryl sulphonates in the order SPSA > STSA > SXSA. In the case of cationic soaps, the order is CTMAB > CPB. It is, therefore, obvious that a uniform decrease in effectiveness is observed with the increase in the molecular weights of the soaps.

The inductive effect in these soaps is in the order SXSA > STSA > SPSA. Therefore, this would also be the order of solubilising power of the hydrophilic group(SO_3^-) of these soaps. Since aggregation of the soap molecules would result as a compromise between the solubilising power of the hydrophilic portion of the surfactant and the cohesive force (responsible for pushing out the hydrophobic portion) of the water molecules, and therefore, the soaps with a higher solubilising power will be least effected by the addition of substances responsible for weakening the cohesive force. It is for this reason that the lowest value of c.m.c.(u)/c.m.c. (0) (Table IV) is obtained in the case of sulphonated xylyl stearic acid.

<u>Effect of acetamide and formamide</u>.

In the presence of acetamide and formamide the c.m.c. increases with the increase in amide concentration. However, when higher concentrations of amides (more than one molar) are used, irregular variations are observed.

TABLE V.

Critical micelle concentration in presence of different amount of acetamide.

Soap	Critical micelle concentration			
	Acetamide			
	0.1 M	0.5 M	0.75 M	1.0 M
SPSA $\times 10^{-5}$M	19.2	20.0	22.0	23.0
STSA "	20.0	21.7	22.7	23.7
SXSA "	20.0	21.7	24.4	26.5
CTMAB "	25.0	25.5	29.0	32.0
CPB $\times 10^{-4}$M	54.0	56.0	59.0	62.0

TABLE VI.

Critical micelle concentration in presence of different amount of formamide.

Soap	Critical micelle concentration			
	Formamide			
	0.1 M	0.5 M	0.75 M	1.0 M
SPSA $\times 10^{-5}$M	18.5	19.2	21.7	22.5
STSA "	16.7	17.5	19.0	20.0
SXSA "	20.0	20.8	21.5	25.0
CTMAB "	25.0	25.2	28.0	30.0
CPB $\times 10^{-4}$M	53.5	55.0	58.0	60.0

TABLE VII

The values of c.m.c. (a) (in presence of acetamide)/ c.m.c.(0) (without the presence of acetamide).

Soap	c.m.c(a) / c.m.c.(0)			
	Acetamide			
	0.1 M	0.5 M	0.75 M	1.0 M
SPSA	1.39	1.45	1.59	1.66
STSA	1.28	1.39	1.45	1.51
SXSA	1.00	1.08	1.22	1.32
CTMAB	1.00	1.02	1.16	1.28
CPB	1.02	1.05	1.11	1.17

TABLE VIII.

The values of c.m.c.(f) (in presence of formamide)/ c.m.c.(0) (without the presence of formamide.

Soap	c.m.c.(f) / c.m.c.(0)			
	Formamide			
	0.1 M	0.5 M	0.75 M	1.0 M
SPSA	1.34	1.40	1.57	1.63
STSA	1.07	1.12	1.22	1.28
SXSA	1.00	1.04	1.07	1.25
CTMAB	1.00	1.01	1.12	1.20
CPB	1.00	1.03	1.09	1.13

Rupley(15) reported low viscosities of aqueous solutions of acetamide and formamide,suggesting that these amides break the hydrogen-hydrogen bonds in the water structure. This observation of Rupley gets support by our findings. Acetamide and formamide in their lower concentrations disorder the water structure with the result that it increases the micelle formation of anionic and cationic soaps.

Both acetamide and formamide effect the micellisation of anionic soaps in the same way as urea does. The same order,viz., SPSA > STSA > SXSA is realised here also. The behaviour towards cationic soaps is,however,different. Unlike urea,lower concentrations of these additives influence the c.m.c. of cetyl pyridinium bromide to a greater extent than that of cetyl trimethyl ammonium bromide. The striking difference between the effect of urea and the amides, however,is that higher concentrations of the latter cannot be used to bring about the change in the c.m.c. of the soaps. This may ascribed due to the difference in their polymerisation,the amides getting polymerised at a much lower concentration than the urea. Klotz(16) reached the same conclusion on the basis of the infra-red studies with solutions of N-methyl acetamide and urea at different concentrations.

Effect of lauric acid di-ethanol amine condensate(LDC).

For the sake of comparision the effect of a non-ionic soap(LDC) was also studied. The values of c.m.c. of anionic and cationic soaps in presence of this additive are given in Table IX.

TABLE IX

Critical micelle concentration in presence of different amount of LDC.

Soap	Critical micelle concentration.		
	LDC/ anionic or cationic soap		
	1:49	1:9	1:4
SPSA x 10^{-5}M	15.2	17.7	18.2
STSA "	16.1	18.1	18.7
SXSA "	20.6	23.2	24.0
CTMAB "	27.2	30.0	31.5
CPB x 10^{-4}M	53.5	55.6	60.0

TABLE X

The values of c.m.c.(1) (in presence of LDC) / c.m.c.(0) (without the presence of LDC).

Soap	c.m.c. (1) / c.m.c.(0)		
	LDC/ anionic or cationic soap		
	1:49	1:9	1:4
SPSA	1.10	1.28	1.32
STSA	1.03	1.16	1.20
SXSA	1.01	1.14	1.17
CTMAB	1.09	1.20	1.26
CPB	1.01	1.05	1.13

From Table IX and X it is evident that LDC increases the critical concentration for micelle formation of anionic and cationic soaps like urea and amides. It can be said here also that LDC breaks the water structure like urea and amides. The c.m.c. of the anionic soaps are influenced in the same order SPSA > STSA > SXSA by the addition of LDC, and same order exist in the case of cationic soaps(CTMAB > CPB).

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CHAPTER IV.

Polarography of soap-dye mixtures.

INTRODUCTION

The interaction of surface active agents with dyes,proteins etc. is a well established fact. The choice of the methods that have been employed to study the interaction is very limited. Usually spectrophotometric studies have been carried out in studying the interaction.

Mukerjee and Mysels(1) isolated the insoluble dye-detergent salts of methylene blue-lauryl sulphate,cetyl trimethyl ammonium-brom phenol blue and dicetyl trimethyl ammonium bromphenol blue and confirmed the interaction by microanalysis of C,H,N,S; C,H,Br; C,H,Br respectively for the above salts. Hiskey and Downey(2) studied the interaction of methyl orange and octadecyl trimethyl ammonium chloride spectrophotometrically and found independently that ionic dyes interact with oppositely charged detergents. Since the formation of a dye-detergent salt requires the presence of opposite charges on the dye and the soap,it explains the noted corresponding requirement for the success of the spectral change method(3) and Hartley's (4) "Sign Rule" for the indicator effect.

The reaction between long chain quaternary ammonium salts and brom phenol blue dye has been studied by Colichman(5) spectrophotometrically and explained the spectral absorption results in terms of quaternary-dye micellar phenomenon. Other empirical analytical methods (6-8) for quantitative analysis of surface active agents are also there to study the long chain quaternary ammonium salts with brom phenol blue. The nature of this reaction has been investigated by conductance(9) and surface and interfacial tension methods(10). These studies reveal that ion-pair compound are formed between quaternary cations and divalent dye anions.

It is worth mentioning that the polarographic technique has not so far been employed to study these interactions. In the literature references are available in which polarography of dyes as such (11) or influence of surface active agents on the total current of the dye(which generally decreases with increase in soap concentration) has been reported. The latter(12) has been utilized to know the concentration of surface active agents. The presence of soaps,even if they are in small quantities,exert a marked effect on the electrode processes. Generally, the adsorption of soaps at the dropping mercury electrode,may decrease the limiting current and some-times shift the half wave potential. At the d.m.e. - solution interface the soaps behave in a similar fashion as they do at solution-air interfaces. Due to the influence of cohesive force,existing between the water molecules,the hydrophobic portion of the soap will reach at air-water interface and the hydrophobic portion is directed towards the interface. Similarly at the electrode-solution interface the hydrophobic portion of the soap is directed towards the electrode surface and generally, monolayers are built up. Such films may interact with the interchange of electric charges. In the saturated capillary active material, polymolecular layers, unlike at the air-water interface, may be built up(13). The nature of the layer which is immediately adjacent to the electrode surface significantly controls the electrode machanism.

There are different methods to study the surface coverage due to the surface active agents. The electrocapillary curves depends upon the nature of the solution and provides the information regarding adsorption. The applicability of Gibb's adsorption equation in this connection has been extensively discussed by many workers(14-19). Laitinen and Moiser(20), using a simple Langmuir adsorption isotherm determined in this way, the adsorption coefficient for many soaps. The different methods of determining the surface coverage as a function of potential have been done by Breiter and Delahay(21).

The oscillographic current-time curves during the life of a single mercury drop give considerably more information than other methods employed and the study of such curve allows an interpretation of the various types of surface phenomena encountered(22,23). Polarographic current-voltage curves may also give some valuable information on this point. We have restricted the explaination of the behaviour of soap-dye mixture at the d.m.e. by simple polarographic curves.

Preliminary experiments revealed many interesting facts which merited comprehensive and detailed study. For example,it was observed that the behaviour of the adsorption and reduction wave of the dyes under investigation was different in the acetate and the phosphate buffers. Sometimes the addition of soaps to the dye, instead of suppressing the maximum,resulted in the emergence of a pronounced maximum. In certain cases the dye showed the unusual tendency to colour the mercury drops.

In this chapter a critical study of some of the aspects,mentioned above using malachite green,methylene blue and rhodamine 6G as the typical dyes and sulphonated phenyl,tolyl and xylyl stearic acids,have been studied. The proof of the fact that the soaps interact with the dyes in the micellar units has also been provided on the basis of these studies.

EXPERIMENTAL

Reagents:- The surface active agents sulphonated phenyl,tolyl and xylyl (SPSA,STSA and SXSA) were prepared in the laboratory(Chapter I).

The dyes,malachite green and rhodamine 6G were B.D.H. and methylene blue was an E.Merk product. The phosphate and acetate buffers were prepared having the following compositions.

0.2 M solution of disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$; mol.wt.178.16) of guarantted reagent supplied by Sarabhi Merk Ltd.Baroda(India),in double distilled water was used for phosphate buffer.

0.2 M sodium acetate and 0.02 M acetic acid (both A.R.reagents) in double distilled water were used for the acetate buffer. The pH was adjusted to 4.7. All pH measurements were carried out by Cambridge Bench Type pH meter.

Apparatus. Heyrovsky polarograph(model Lp 55 A) was operated manually in conjuction with Pye Scalamp galvanometer(Model 7903/5). Triple distilled mercury was used for the dropping mercury electrode. The solutions were dearated by passing purified nitrogen for about 20 to 30 minutes in the polarographic cell. All measurements were carried out at 25° ± 0.1°C in the water thermostat .

The capillary used had the following characteristics in the open circuit.

Phosphate buffer $t = 3.50$ sec.;$m = 5.54$ mg/sec.: $m^{2/3}t^{1/6} = 3.88$.

Acetate buffer $t = 3.55$ sec.;$m = 5.54$ mg/sec.: $m^{2/3}t^{1/6} = 3.89$.

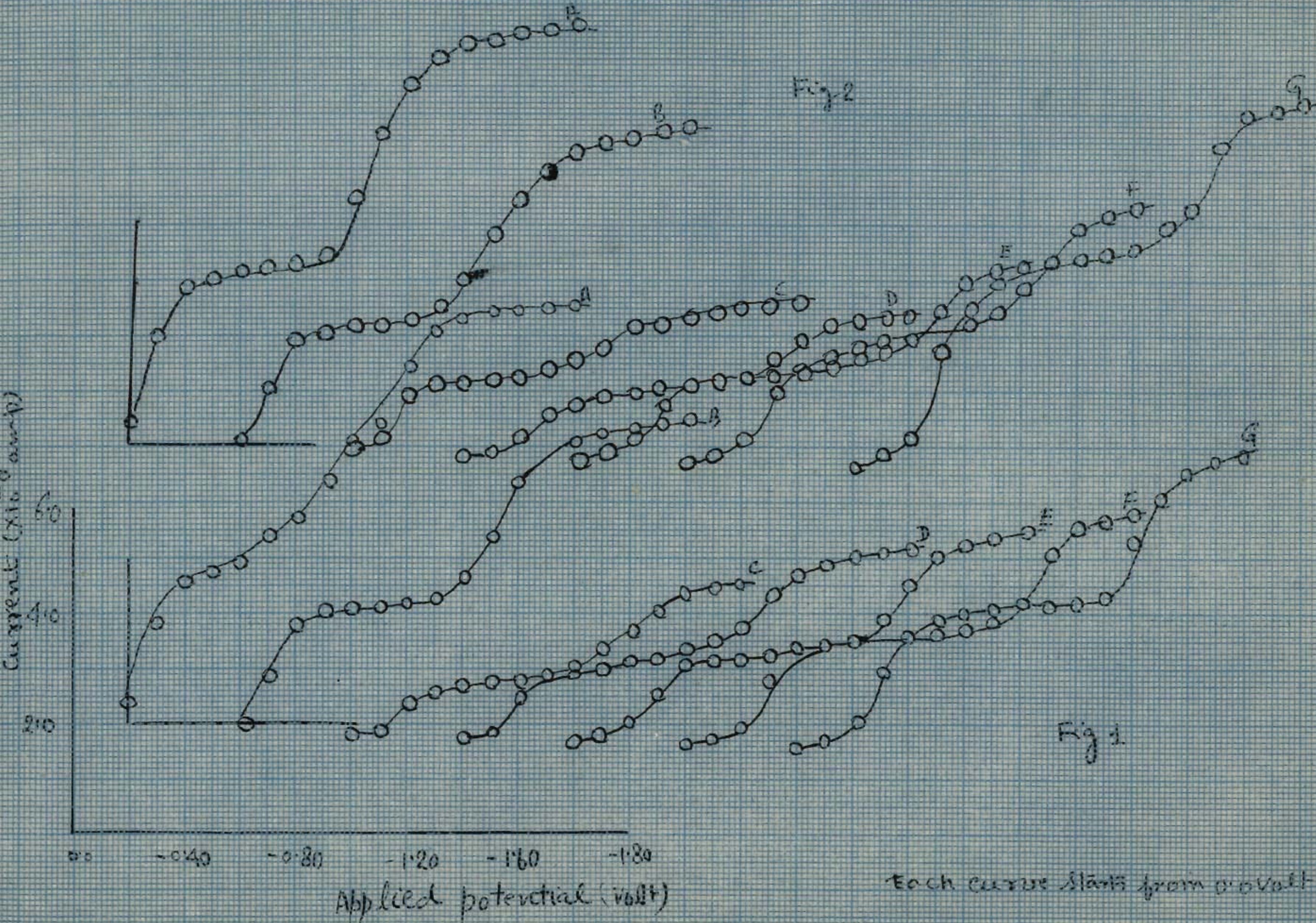
The dye-soap mixtures in well buffered solutions were kept for about an hour before taking the polarograms The results are given in the following tables.

Polarography in phosphate buffer (pH 8.40) of malachite green in presence of different concentrationsof soap.

TABLE 1

Polarograms of 6.7 x 10^{-5}M malachite green in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.40	0.10	-0.05	-0.10	-0.20	-0.25	-0.25
0.1	1.95	1.00	0.00	-0.05	-0.05	-0.10	-0.15
0.2	2.65	1.95	0.50	0.70	0.20	0.20	0.25
0.3	2.85	2.15	0.70	0.90	0.80	1.00	1.25
0.4	2.95	2.20	0.80	1.00	1.20	1.50	1.80
0.5	3.50	2.25	0.85	1.15	1.25	1.65	2.00
0.6	3.85	2.30	0.90	1.25	1.30	1.70	2.15
0.7	4.50	2.40	1.00	1.35	1.40	1.75	2.20
0.8	5.20	2.80	1.15	1.50	1.50	1.80	2.25
0.9	5.50	3.50	1.50	1.65	1.60	1.90	2.30
1.0	6.50	4.50	1.80	1.90	1.70	2.10	2.40
1.1	7.20	4.80	2.20	2.50	2.00	2.45	2.50
1.2	7.40	5.20	2.50	2.85	2.65	3.30	3.50
1.3	7.55	5.35	2.65	3.00	3.20	3.80	4.30
1.4	7.50	5.45	2.70	3.15	3.40	3.85	4.80
1.5	7.55	5.50	2.80	3.20	3.55	3.95	5.00
1.6	7.60	5.60	2.90	3.30	3.60	4.00	5.15
Fig.1	A	B	C	D	E	F	G



Each curve starts from 0·0 volt

Scale for Fig 1 & 2.

TABLE 2

Polarograms of 6.7 x 10^{-5} M malachite green in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8}amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.35	0.05	-0.05	-0.15	-0.20	-0.25	-0.25
0.1	1.95	0.95	0.10	-0.05	-0.05	-0.15	-0.15
0.2	2.85	1.95	0.95	0.20	0.22	0.20	0.20
0.3	3.00	2.00	1.10	0.65	0.85	1.00	1.80
0.4	3.15	2.15	1.15	0.85	1.20	1.45	2.50
0.5	3.20	2.20	1.20	0.95	1.30	1.65	3.00
0.6	3.25	2.25	1.25	1.00	1.35	1.85	3.25
0.7	3.40	2.50	1.40	1.15	1.45	1.95	3.35
0.8	4.40	3.00	1.60	1.20	1.60	2.00	3.45
0.9	5.58	3.80	1.80	1.25	1.65	2.15	3.50
1.0	6.50	4.50	2.20	1.40	1.80	2.30	3.65
1.1	7.00	5.00	2.25	1.65	2.00	2.50	4.00
1.2	7.25	5.35	2.35	1.95	2.50	2.95	4.35
1.3	7.30	5.55	2.40	2.25	3.00	3.45	5.55
1.4	7.45	5.60	2.50	2.30	3.25	4.00	6.00
1.5	7.50	5.70	2.55	2.40	2.35	4.25	6.15
1.6	7.60	5.90	2.65	2.45	3.40	4.15	6.15
Fig.2	A	B	C	D	E	F	G

TABLE 3

Polarograms of 6.7 x 10^{-5} M malachite green in presence of different concentrations of SXSA (order 10^{-5} M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.45	0.00	-0.15	-0.25	-0.30	-0.30	-0.15
0.1	2.05	0.95	-0.05	-0.05	-0.05	-0.15	-0.05
0.2	3.15	2.00	0.95	0.25	0.30	0.90	0.20
0.3	3.55	2.25	1.10	0.75	1.05	1.40	1.35
0.4	3.70	2.30	1.15	1.10	1.55	1.65	2.50
0.5	3.80	2.35	1.20	1.20	1.80	1.75	3.15
0.6	3.85	2.40	1.25	1.30	1.90	1.80	3.35
0.7	4.15	2.50	1.40	1.40	1.95	1.90	3.45
0.8	5.10	3.30	1.70	1.50	2.00	2.95	3.50
0.9	6.15	4.35	2.00	1.55	2.10	3.00	3.50
1.0	6.75	4.55	2.50	1.65	2.25	3.20	3.65
1.1	7.35	4.80	3.00	1.95	2.53	3.70	3.80
1.2	7.55	5.00	3.25	2.30	3.30	4.10	4.35
1.3	7.70	5.20	3.45	2.80	4.45	5.25	6.00
1.4	7.65	5.20	3.50	3.15	4.95	4.85	8.10
1.5	7.70	5.30	3.60	3.20	4.85	5.00	7.60
1.6	7.75	5.35	3.70	3.35	5.15	5.15	7.70
Fig.3	A	B	C	D	E	F	G

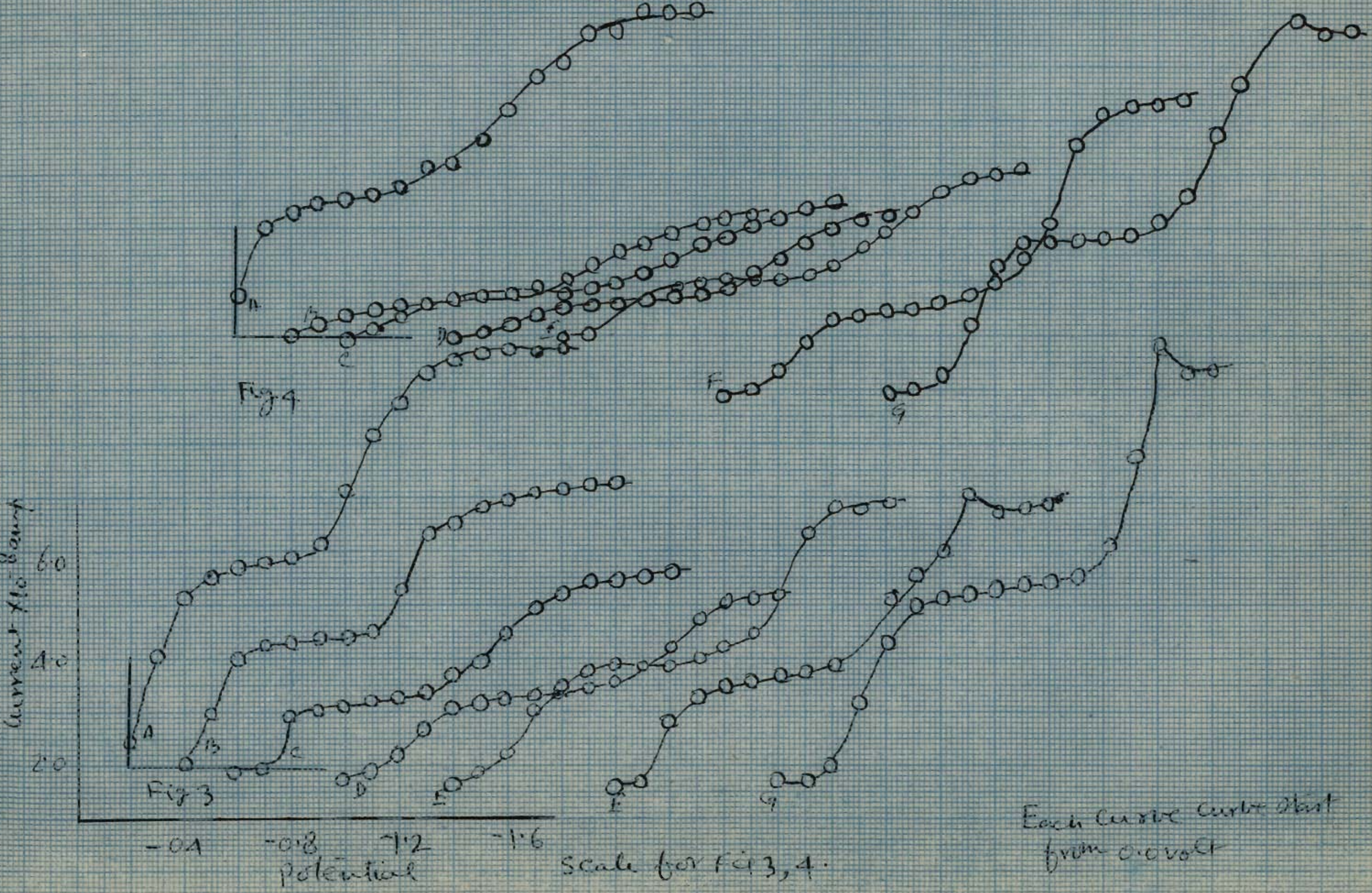


Fig 4

Fig 3

Scale for Fig 3, 4.

Each curve curve start from 0.0 volt

Polarography in phosphate buffer(pH 8.40) of rhodamine 6G in presence of different concentrations of soap.

TABLE 4.

Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of SPSA(order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentration of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.6	-0.10	-0.15	-0.15	-0.20	-0.25	-0.25
0.1	1.95	0.10	0.05	-0.05	-0.05	-0.05	-0.05
0.2	2.20	0.25	0.25	0.15	0.20	0.20	0.15
0.3	2.35	0.35	0.50	0.35	0.55	0.80	1.05
0.4	2.40	0.40	0.55	0.40	0.70	1.20	2.05
0.5	2.50	0.45	0.55	0.45	0.80	1.30	2.50
0.6	2.65	0.55	0.65	0.45	0.90	1.40	2.60
0.7	3.00	0.60	0.70	0.55	0.90	1.40	2.60
0.8	3.05	0.65	0.75	0.60	0.95	1.50	2.65
0.9	3.50	0.75	0.85	0.65	1.05	1.60	2.75
1.0	4.05	0.90	1.05	0.80	1.25	1.85	3.00
1.1	4.70	1.20	1.35	1.10	1.60	2.35	3.45
1.2	5.00	1.40	1.55	1.35	2.00	2.95	4.60
1.3	5.50	1.60	1.75	1.70	2.30	3.40	5.50
1.4	5.55	1.80	2.00	1.90	2.55	4.00	6.40
1.5	5.90	1.90	2.10	2.00	2.80	4.10	6.65
1.6	5.85	2.00	2.30	2.10	2.80	4.15	6.45
Fig.4	A	B	C	D	E	F	G

TABLE 5

Polarograms of 6.7×10^{-5}M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.50	0.05	-0.16	-0.15	-0.15	-0.30	-0.30
0.1	1.90	1.20	0.05	0.05	-0.05	-0.15	-0.15
0.2	2.15	1.30	0.45	0.30	0.15	0.05	0.10
0.3	2.25	1.35	0.80	0.55	0.40	0.50	0.65
0.4	2.35	1.40	0.90	0.65	0.55	0.90	1.25
0.5	2.40	1.45	1.00	0.70	0.70	0.95	1.60
0.6	2.50	1.50	1.10	0.75	0.75	1.00	1.65
0.7	2.65	1.60	1.15	0.80	0.75	1.00	1.70
0.8	2.85	2.00	1.20	0.85	0.80	1.10	1.80
0.9	3.25	2.40	1.35	1.05	0.90	1.20	1.80
1.0	3.90	3.00	1.60	1.30	1.20	1.40	2.00
1.1	4.40	3.60	2.15	1.80	1.60	1.70	2.25
1.2	4.90	4.20	2.85	2.30	2.00	2.45	2.00
1.3	5.20	4.40	3.10	2.60	2.50	2.90	4.10
1.4	5.40	4.45	3.20	2.70	2.60	3.70	5.45
1.5	5.55	4.50	3.30	2.70	2.00	3.65	5.60
1.6	5.50	4.60	3.40	2.75	3.00	3.65	5.25
Fig.5	A	B	C	D	E	F	G

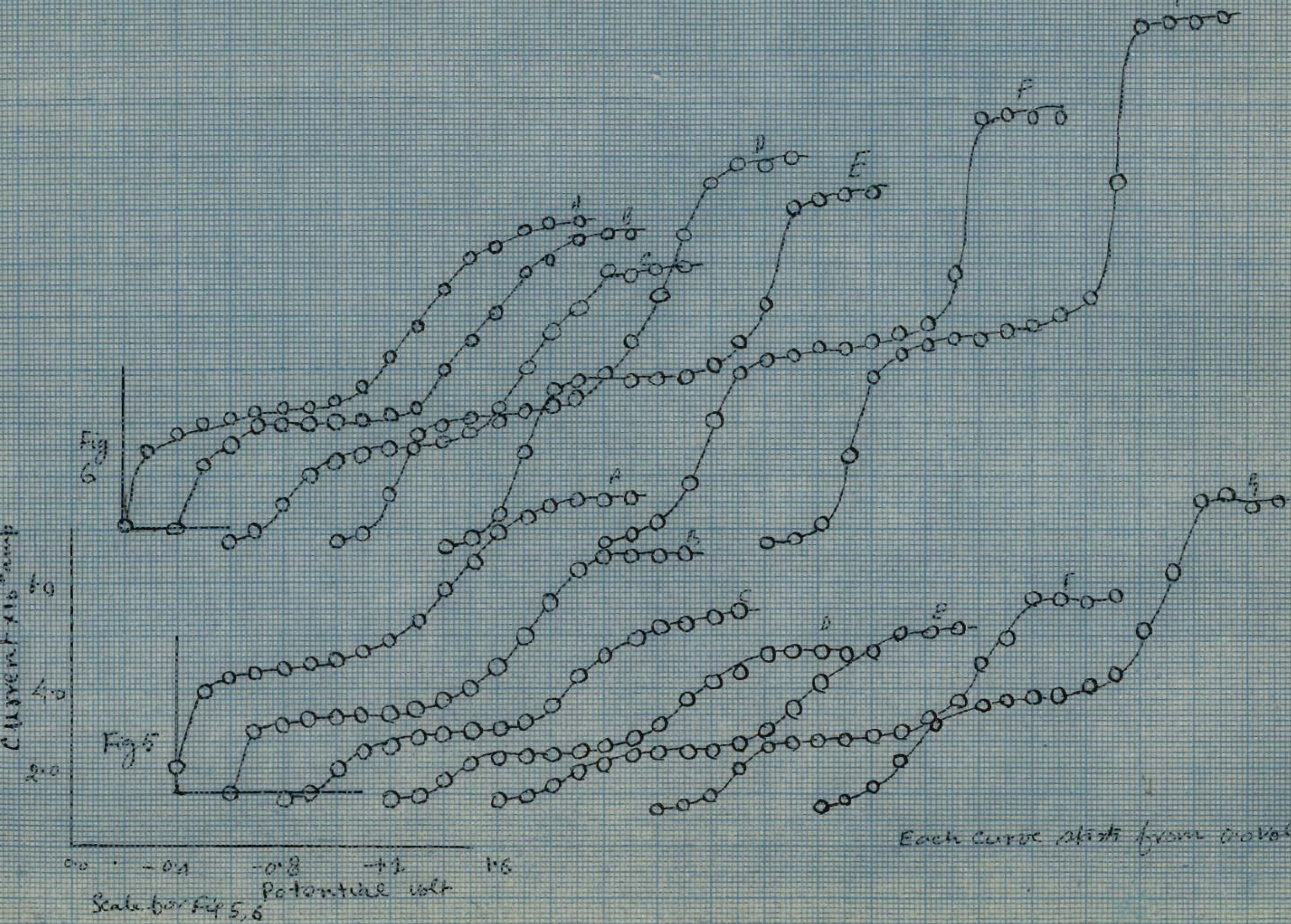

G
F
D
E
A
B
C
Fig 6
A
B
C
D
E
F
G
6.0
4.0
2.0
Current x10⁻⁶ amp
Fig 5
0.0
-0.4
-0.8
-1.2
1.6
Potential volt
Scale for Fig 5, 6
Each curve starts from 0.0 Volt

TABLE 6

Polarograms of 6.7 x 10^{-5} M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5} M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.00	-0.05	-0.20	-0.20	-0.25	-0.25	-0.35
0.1	1.95	1.20	0.00	-0.05	-0.15	-0.15	-0.15
0.2	1.75	1.60	0.50	0.60	0.25	0.10	0.05
0.3	2.05	2.00	1.10	1.85	1.45	1.30	0.80
0.4	2.15	2.00	1.30	1.90	2.55	2.85	2.05
0.5	2.20	2.00	1.45	1.95	2.70	3.25	2.90
0.6	2.25	2.05	1.55	2.00	2.70	3.40	3.10
0.7	2.25	2.15	1.60	2.20	2.75	3.50	3.20
0.8	2.40	2.20	1.65	2.30	2.75	3.50	3.30
0.9	2.70	2.22	1.80	2.40	2.75	3.65	3.30
1.0	3.20	3.00	2.20	2.90	3.00	3.75	3.45
1.1	3.75	3.50	2.95	3.50	3.50	4.95	3.60
1.2	4.40	4.00	3.65	4.30	4.20	4.55	3.75
1.3	5.05	4.85	1.10	5.50	6.00	6.40	4.75
1.4	5.25	5.00	4.80	6.40	6.10	8.30	7.70
1.5	6.65	4.95	4.75	6.80	6.15	8.35	7.75
1.6	5.75	5.50	4.80	6.80	6.25	8.40	7.60
Fig. 6	A	B	C	D	E	F	G

Polarography in phosphate buffer(pH 8.40) of methylene blue in presence of different concentrations of soap.

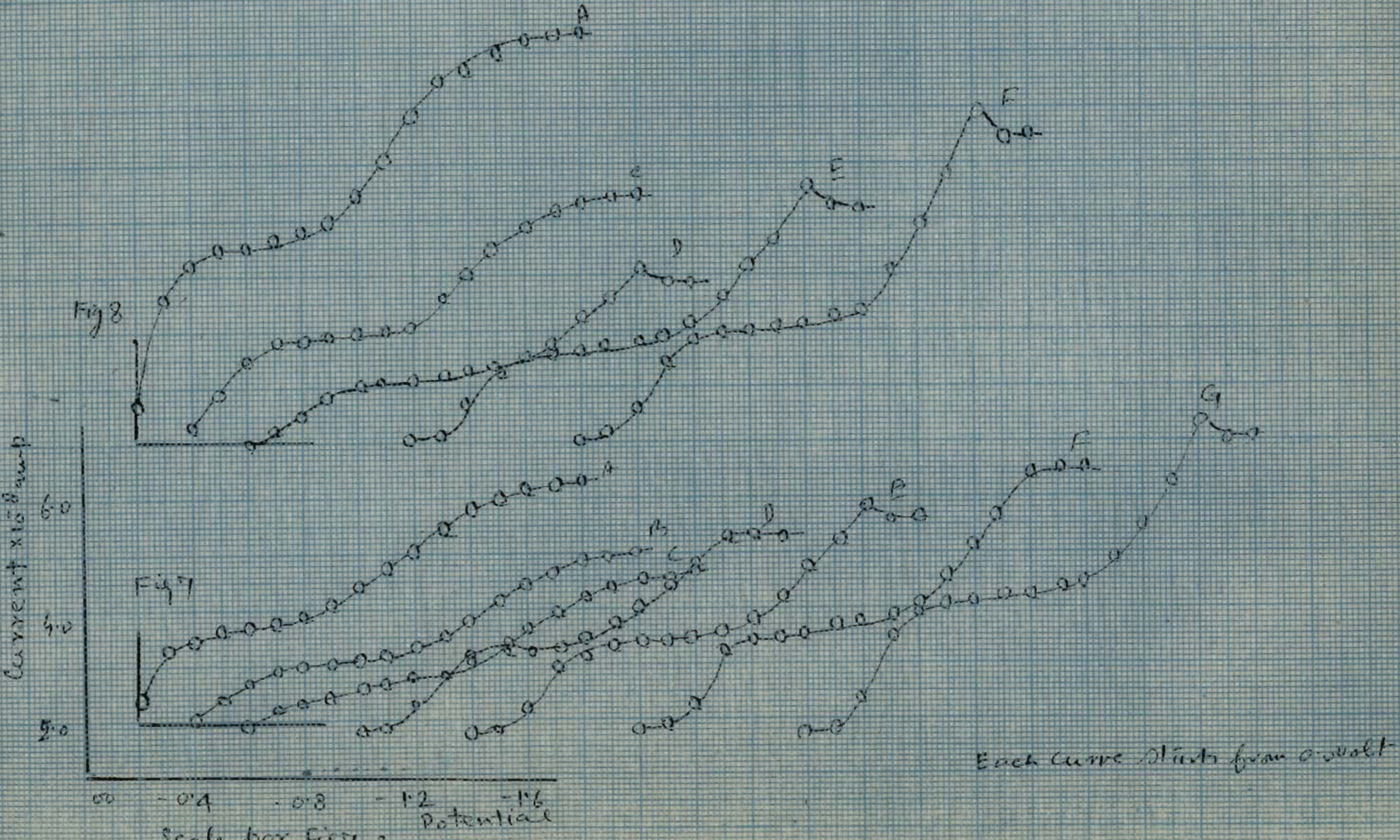
TABLE 7

Polarograms of 6.7 x 10^{-5}M methylene blue in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.35	-0.15	-0.20	-0.20	-0.25	-0.25	-0.25
0.1	1.25	0.30	0.15	-0.05	-0.10	-0.15	-0.15
0.2	1.35	0.60	0.30	0.40	0.30	0.35	0.50
0.3	1.55	0.80	0.40	0.95	1.00	1.20	1.50
0.4	1.65	0.90	0.50	1.15	1.20	1.40	2.00
0.5	1.75	0.90	0.60	1.20	1.30	1.45	2.15
0.6	1.85	1.10	0.65	1.25	1.40	1.55	2.20
0.7	2.05	1.20	0.90	1.30	1.45	1.70	2.30
0.8	2.35	1.40	1.10	1.60	1.55	1.75	2.40
0.9	2.75	1.70	1.30	1.80	1.65	1.80	2.50
1.0	3.00	2.05	1.70	2.25	1.90	2.10	2.06
1.1	3.40	2.30	2.00	2.60	2.35	2.65	3.00
1.2	3.70	2.50	2.30	2.95	2.85	3.25	3.50
1.3	3.90	2.80	2.00	3.55	3.30	3.70	4.20
1.4	4.10	2.80	2.55	3.35	4.10	4.50	5.50
1.5	4.15	2.85	2.60	3.45	3.70	4.45	5.00
1.6	4.20	3.05	2.70	3.55	3.75	4.45	5.10
Fig.7	A	B	C	D	E	F	G

Fig 8

Fig 7



Scale for Fig 7, 8

Each curve starts from 0 volt

TABLE 8.

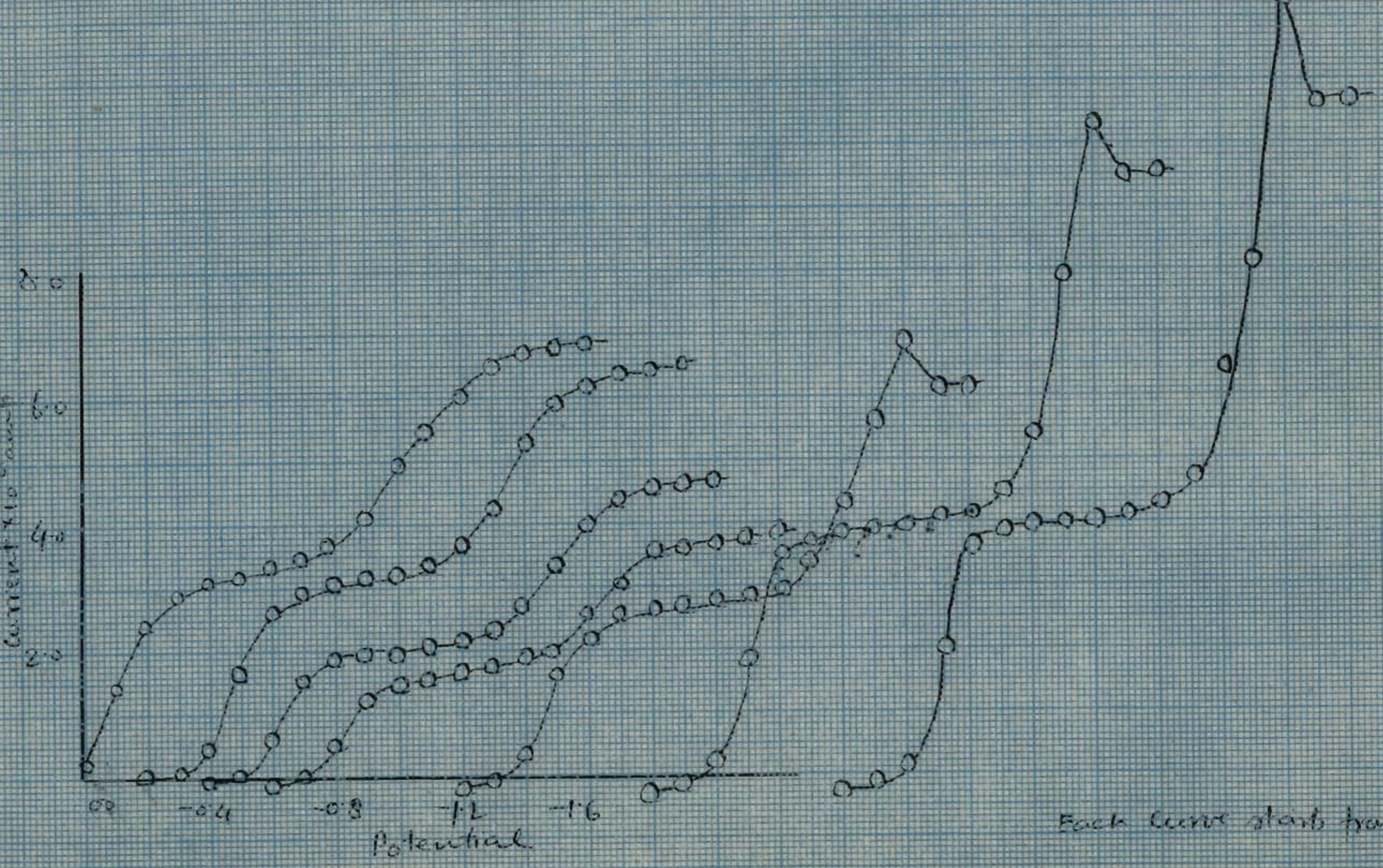
Polarograms of 6.7×10^{-5} M methylene blue in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current ($\times 10^{-8}$ amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.40	-0.10	-0.15	-0.20	-0.20	-0.25	-0.25
0.1	2.30	0.55	0.30	0.00	-0.05	-0.05	-0.10
0.2	2.90	1.20	1.30	0.25	0.45	0.40	0.55
0.3	3.20	1.50	2.05	0.70	1.10	1.25	2.55
0.4	3.30	1.55	2.25	0.80	1.40	1.60	3.95
0.5	0.40	1.65	2.35	0.85	1.55	1.75	4.65
0.6	3.55	1.70	2.45	0.90	1.55	1.85	4.80
0.7	3.65	1.75	2.60	0.95	1.65	1.84	4.90
0.8	4.20	1.90	2.60	1.05	1.65	1.90	0.55
0.9	4.85	2.40	3.10	1.10	1.70	2.10	5.15
1.0	5.65	2.80	3.45	1.25	2.00	2.15	5.40
1.1	6.30	3.30	4.45	1.60	2.55	2.85	6.55
1.2	6.45	3.60	5.00	2.00	3.05	2.90	8.70
1.30	6.85	3.90	5.40	2.40	3.60	4.60	10.30
1.4	7.10	4.10	5.60	2.95	4.50	6.10	12.40
1.5	7.10	4.15	5.70	2.60	4.05	5.10	12.00
1.6	6.80	4.20	5.80	2.70	4.10	5.30	12.20
Fig.8	A	B	C	D	E	F	G

TABLE 9.

Polarograms of 6.7 x 10^{-5}M methylene blue in presence of different concentrations of SXSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	0.05	-0.15	-0.20	-0.20	-0.25	-0.25	-0.25
0.1	1.30	0.30	0.00	-0.05	-0.10	-0.15	-0.15
0.2	2.40	1.55	0.60	0.50	0.30	0.20	0.05
0.3	2.80	2.55	1.50	1.20	1.60	1.85	1.90
0.4	3.05	2.85	1.85	1.50	2.35	3.45	3.65
0.5	3.20	2.95	1.95	1.55	2.55	3.70	3.85
0.6	3.30	3.05	1.95	1.65	2.65	3.90	3.95
0.7	3.45	3.15	2.10	1.75	2.70	3.95	3.95
0.8	3.65	3.30	2.20	1.90	2.75	4.00	4.00
0.9	4.05	3.65	2.30	2.00	2.80	4.10	4.10
1.0	4.85	4.25	2.70	2.30	2.95	4.15	4.20
1.1	5.40	5.25	3.35	2.95	3.40	4.50	4.70
1.2	6.00	5.90	4.00	3.60	4.30	4.50	6.42
1.3	6.40	6.10	4.40	3.65	5.60	7.85	8.00
1.4	6.70	6.40	4.60	3.70	7.00	7.30	11.20
1.5	6.80	6.40	4.65	3.80	6.10	9.45	9.60
1.6	6.75	6.50	4.70	3.90	6.25	9.55	9.70
Fig.9	A	B	C	D	E	F	G



Each curve starts from 0·0 volt

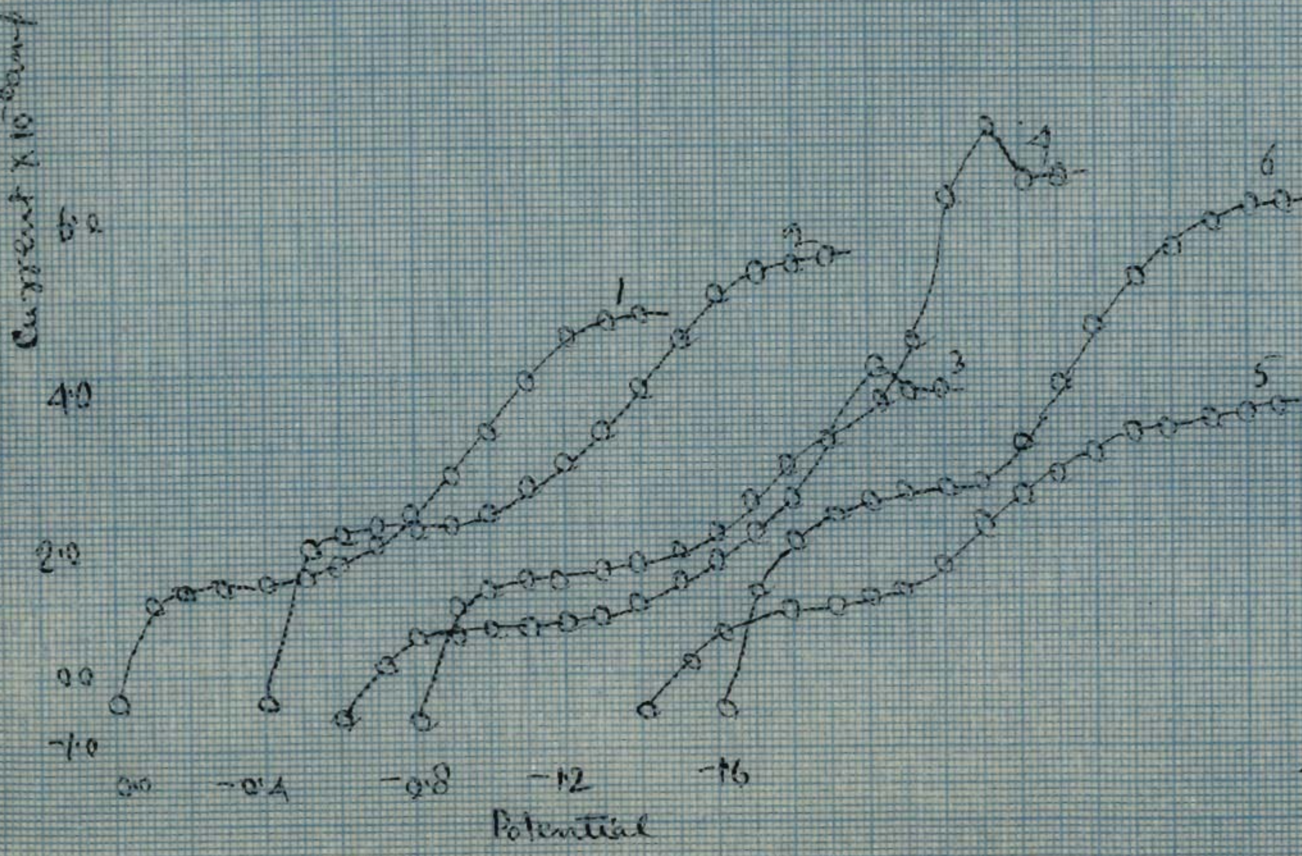
Fig 9.

TABLE 10

Polarograms of different concentrations(order 10^{-5}M) of malachite green, rhodamine 6G and methylene blue in phosphate buffer(pH 8.40).

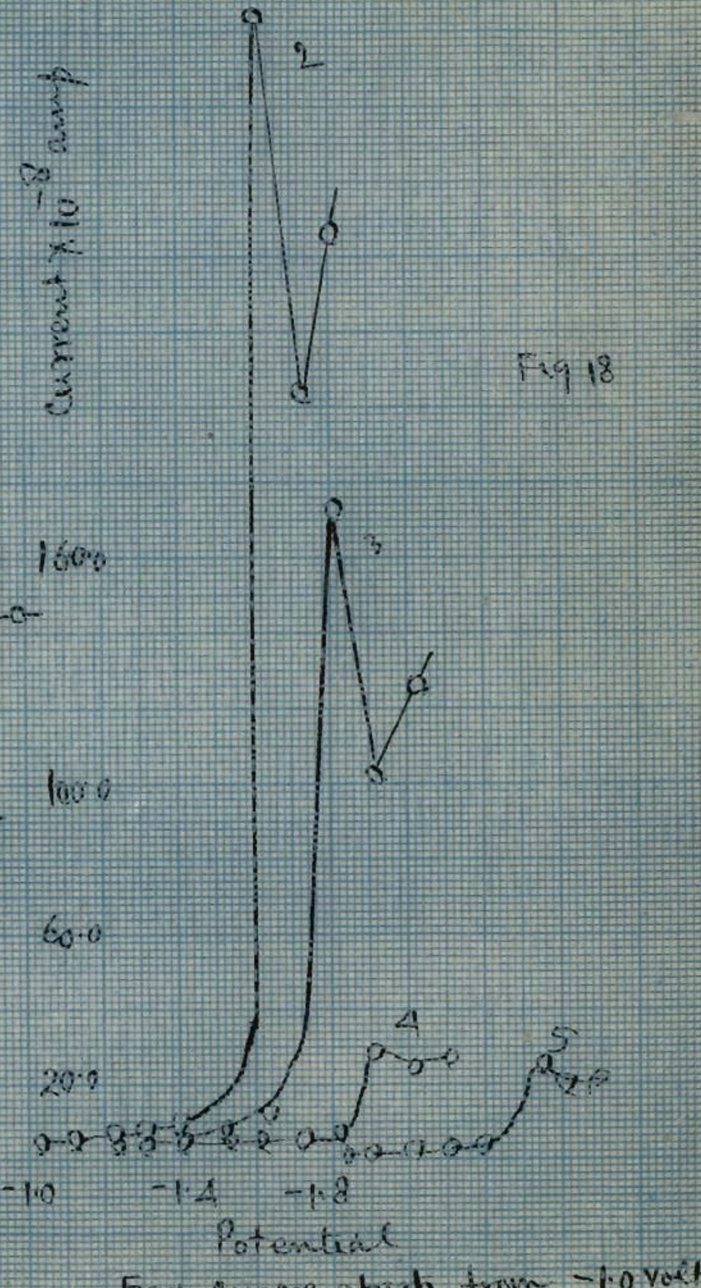
Applied potential in volts.	CURRENT (x 10^{-8} amp.)					
	Malachite green		Rhodamine 6G		Methylene blue	
	6.7	13.3	6.7	13.3	6.7	13.3
0.0	0.55	0.50	0.20	0.20	0.40	0.40
0.1	1.90	2.50	1.20	1.80	1.20	2.10
0.2	2.10	2.70	1.40	2.10	1.50	2.90
0.3	2.20	2.80	1.50	2.20	1.70	3.20
0.4	2.30	2.85	1.55	2.30	1.80	3.35
0.5	2.45	3.00	1.60	2.40	1.85	3.40
0.6	2.60	3.10	1.65	2.50	2.00	2.50
0.7	2.70	3.50	1.70	2.50	2.20	3.60
0.8	3.10	3.70	1.80	2.80	2.50	4.20
0.9	3.70	4.20	2.10	3.40	3.00	4.85
1.0	4.20	4.80	2.30	3.80	3.40	5.70
1.1	4.80	5.50	2.70	4.20	3.60	6.30
1.2	5.55	5.60	2.90	2.60	3.90	6.40
1.3	5.70	6.20	3.40	5.50	4.10	6.85
1.4	5.90	6.20	4.40	7.40	4.20	7.10
1.5	6.00	6.25	5.20	8.30	4.30	7.20
1.6	6.05	6.30	4.80	7.50	4.50	7.30
1.7	6.10	6.40	4.80	7.50	4.60	7.50
Fig.10	1	2	3	4	5	6

Fig 10



Each curve starts from 0.0 Volt

Fig 18



Each curve starts from -1.0 Volt

Polarography in acetate buffer(pH 4.70) of malachite green in presence of different concentrations of soap.

TABLE 11

Polarograms of 6.7×10^{-5}M malachite green in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current($\times 10^{-8}$ amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	0.30	-0.05	-0.15	-0.20	-0.15	-0.30	-0.20
0.10	0.70	0.30	0.15	0.05	-0.05	-0.15	-0.15
0.20	0.90	0.60	0.60	0.35	0.25	0.25	0.20
0.30	0.95	0.75	1.00	0.70	0.75	0.95	0.40
0.40	0.95	0.90	1.15	0.80	0.95	1.40	0.50
0.50	1.00	1.00	1.30	0.90	1.05	1.60	0.60
0.60	1.10	1.15	1.45	1.05	1.15	1.75	0.70
0.70	1.45	1.35	1.55	1.15	1.30	1.85	0.80
0.80	1.65	1.60	1.65	1.30	1.40	1.95	0.90
0.90	2.00	1.95	2.00	1.45	1.60	2.20	1.20
1.00	2.10	2.45	2.50	1.80	2.00	2.22	1.60
1.10	2.45	2.85	3.30	2.40	2.70	2.50	2.15
1.20	2.85	3.20	3.60	3.45	3.10	3.15	3.00
1.30	3.75	7.50	7.50	5.00	5.00	3.75	7.50
1.40	27.50	62.50	60.00	55.00	33.50	22.50	21.25
1.50	152.00	200.00	197.50	180.00	120.00	72.50	20.00
1.55	203.75	262.50	255.00	232.50	147.50	81.25	26.25
1.60	86.25	130.00	95.00	105.00	65.00	94.50	-
1.65	96.00	117.50	105.00	102.00	70.00	59.75	-
1.70	136.25	155.00	135.00	135.00	90.00	78.75	-

Fig. 11

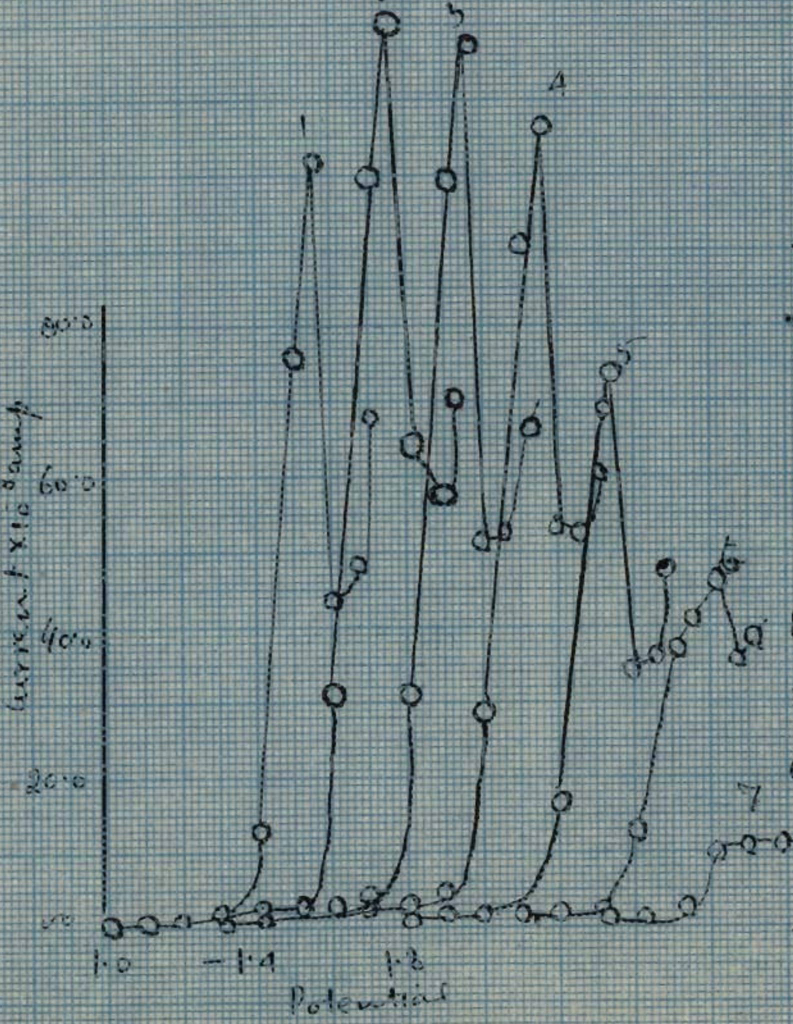


Fig 11

Each curve starts from 1 volt

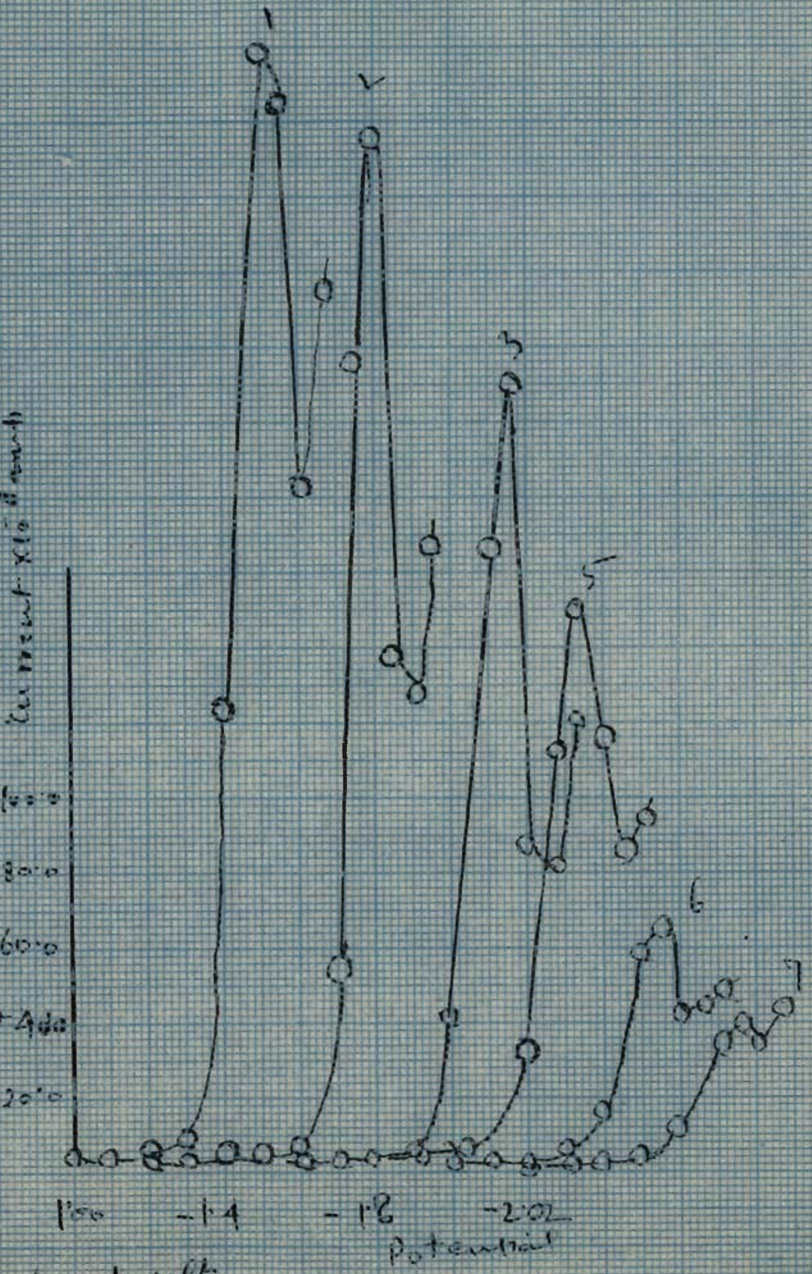


Fig 12

TABLE 12

Polarograms of 6.7 x 10^{-5}M malachite green in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8}amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	0.75	-0.10	-0.15	-0.15	-0.20	-0.25	-0.25
0.10	2.00	0.15	-0.05	0.05	-0.05	-0.10	-0.05
0.20	2.35	0.40	0.15	0.25	0.30	0.05	0.15
0.30	2.55	0.60	0.30	0.30	0.70	0.20	0.60
0.40	2.65	0.60	0.35	0.35	0.95	0.35	1.00
0.50	2.75	0.70	0.45	0.35	1.05	0.35	1.20
0.60	2.85	0.75	0.45	0.45	1.15	0.35	1.30
0.70	3.35	0.90	0.50	0.50	1.25	0.50	1.45
0.80	3.60	1.00	0.60	0.70	1.30	0.70	1.50
0.90	4.05	1.15	0.75	0.80	1.70	0.80	1.55
1.00	5.00	2.00	1.00	0.90	3.35	1.20	1.60
1.10	5.05	3.00	2.00	2.00	4.95	2.00	1.70
1.20	7.50	5.00	3.00	3.00	5.50	2.25	3.00
1.30	10.00	7.50	5.00	5.00	7.50	2.50	5.00
1.40	12.50	55.00	42.50	16.50	33.75	18.75	13.75
1.50	44.50	215.00	165.00	50.00	111.25	58.75	37.50
1.55	222.50	270.00	210.00	56.25	150.00	68.75	40.00
1.60	310.00	137.00	87.50	27.50	117.50	41.25	36.25
1.65	285.00	125.00	80.00	32.50	83.75	46.25	46.25
1.70	180.00	175.00	120.00	40.00	90.00	50.00	-

Fig. 12

TABLE 13

Polarograms of 6.7 x 10^{-5}M malachite green in presence of different concentrations of SXSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8}amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	-0.20	-0.20	-0.10	-0.15	-0.15	-0.15	-0.20
0.10	-0.05	-0.05	0.05	0.00	-0.05	-0.05	-0.05
0.20	0.05	0.05	0.15	0.25	0.05	0.10	0.05
0.30	0.15	0.15	0.25	0.50	0.25	0.35	0.15
0.40	0.30	0.20	0.30	0.55	0.30	0.45	0.25
0.50	0.40	0.30	0.35	0.55	0.35	0.55	0.30
0.60	0.50	0.40	0.40	0.60	0.45	0.60	0.35
0.70	0.70	0.60	0.55	0.70	0.55	0.65	0.45
0.80	0.90	0.70	0.60	0.75	0.60	0.75	0.50
0.90	0.95	0.85	0.70	0.95	0.65	0.75	0.55
1.00	1.35	1.40	1.20	1.15	0.85	1.20	1.20
1.10	2.40	2.50	2.20	1.85	1.25	2.40	2.35
1.20	2.70	2.80	2.80	2.20	1.50	2.75	2.65
1.30	10.00	4.60	10.00	3.75	2.70	3.95	3.65
1.40	42.50	22.50	97.50	52.50	37.50	30.00	15.00
1.50	245.00	127.00	32.00	217.50	170.00	127.50	67.50
1.60	165.00	100.00	440.00	300.00	222.50	195.00	67.50
1.65	-	-	-	120.00	92.50	95.00	57.50
1.70	260.00	177.50	217.50	135.00	107.50	105.00	77.50

Fig. 13

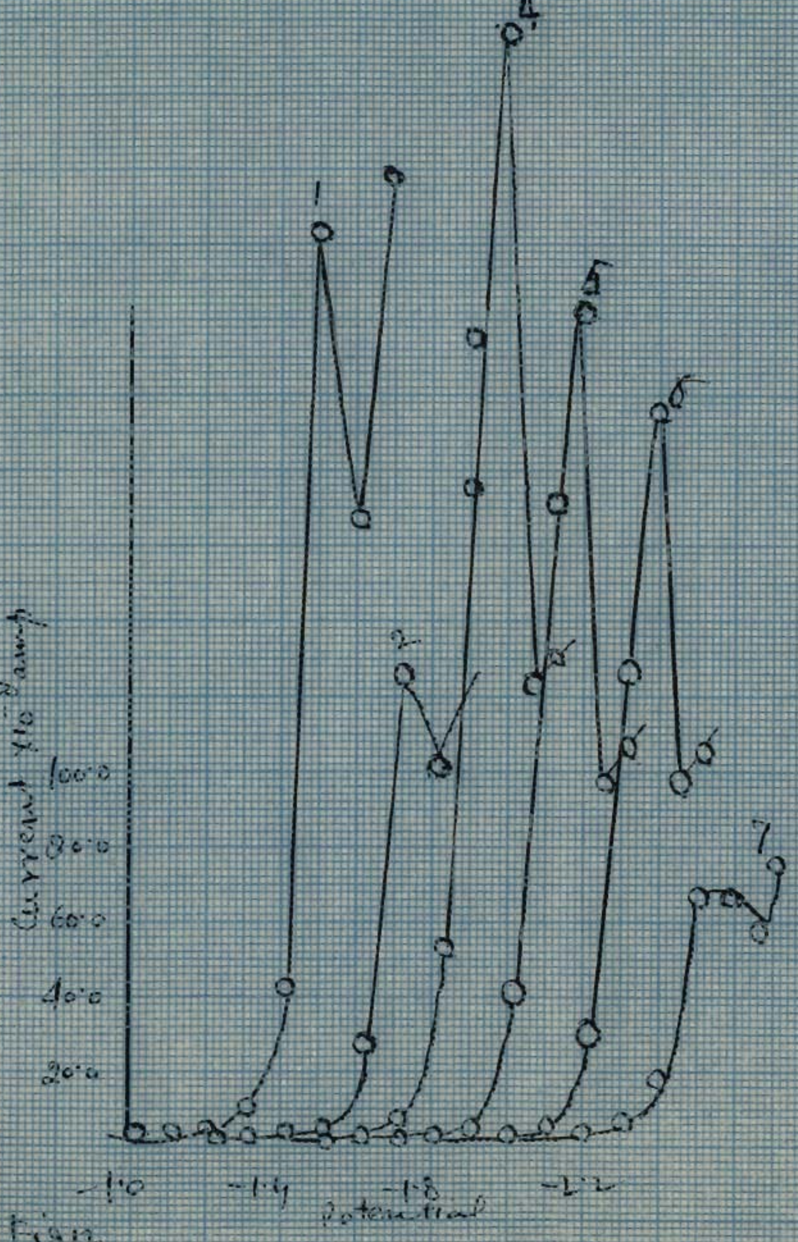
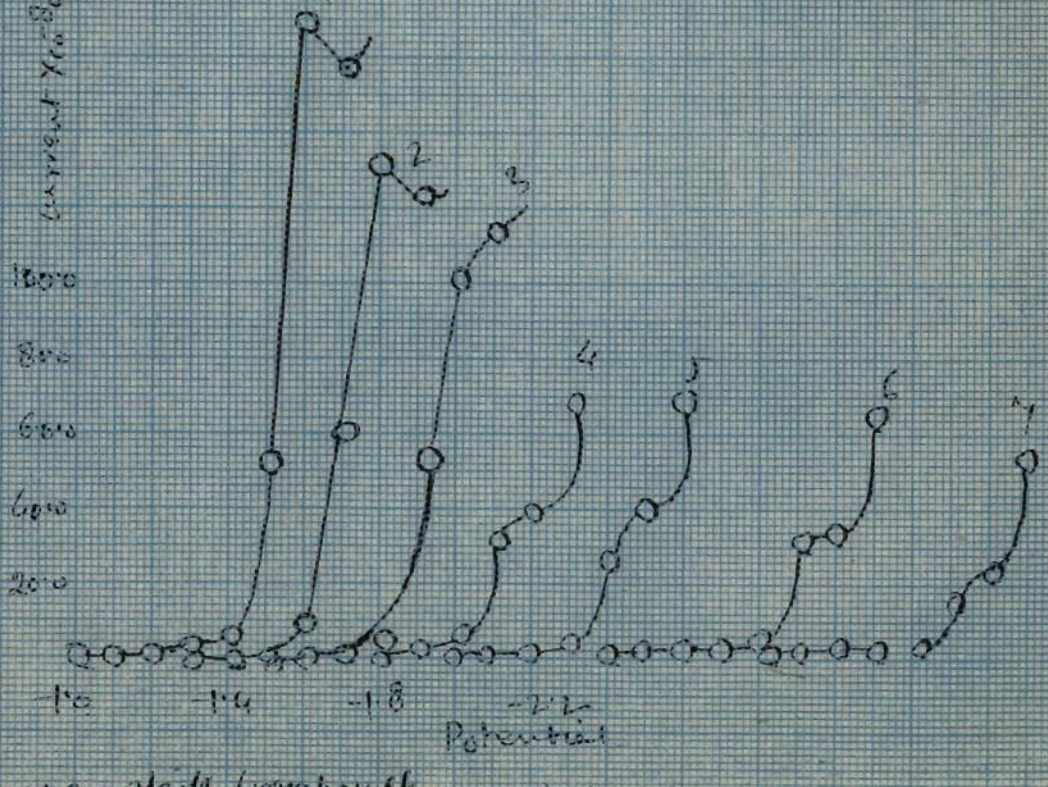


Fig 13



Each curve start from zero volt

Fig 14

Polarography in acetate buffer(pH 4.70) of rhodamine 6G in presence of different concentrations of soap.

TABLE 14.

Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of SPSA(order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8}amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	-0.25	-0.25	-0.15	-0.15	-0.20	-0.20	-0.25
0.10	-0.05	-0.10	0.05	-0.10	-0.15	-0.15	-0.15
0.20	0.00	-0.05	0.30	0.40	0.40	0.30	0.30
0.30	0.05	0.20	0.60	0.65	0.40	0.40	0.50
0.40	0.20	0.20	0.55	0.70	0.75	0.50	0.60
0.50	0.30	0.30	0.60	0.75	0.80	0.55	0.65
0.60	0.35	0.35	0.65	0.80	0.90	0.60	0.75
0.70	0.40	0.40	0.75	0.90	0.95	0.65	0.80
0.80	0.45	0.55	0.85	1.00	1.10	0.90	0.90
0.90	0.50	0.60	0.95	1.50	1.60	1.20	1.10
1.00	0.60	0.70	1.00	2.00	2.20	1.50	1.20
1.10	0.00	1.10	1.20	2.50	2.80	2.00	1.30
1.20	3.10	2.00	1.80	2.90	3.20	2.20	1.50
1.30	4.20	3.00	2.60	3.50	5.00	2.70	1.70
1.40	6.50	10.00	6.50	5.00	27.50	3.80	2.50
1.50	52.50	62.50	65.00	32.50	40.00	22.50	15.00
1.60	170.00	130.00	107.50	40.00	70.00	32.50	22.50
1.70	157.50	125.00	120.00	70.00	-	65.00	52.50

Fig. 14

TABLE 15

Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of STSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{8} amp) for different concentrations of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	1.50	-0.05	-0.10	-0.10	-0.15	-0.20	-0.25
0.10	3.90	0.10	0.05	0.05	-0.05	-0.05	-0.05
0.20	4.70	0.20	0.15	0.20	0.20	0.05	0.10
0.30	4.85	0.25	0.25	0.25	0.35	0.20	0.25
0.40	5.05	0.30	0.25	0.30	0.40	0.25	0.30
0.50	5.15	0.35	0.35	0.35	0.45	0.30	0.35
0.60	5.25	0.40	0.40	0.40	0.45	0.35	0.40
0.70	5.30	0.45	0.50	0.45	0.50	0.40	0.45
0.80	5.40	0.85	0.55	0.75	0.60	0.50	0.50
0.90	6.00	1.50	0.70	0.85	0.70	0.55	0.60
1.00	7.50	2.00	1.00	0.90	1.00	0.90	0.80
1.10	8.75	2.50	1.50	1.10	1.50	1.20	1.20
1.20	8.75	3.00	2.00	1.30	2.00	1.50	1.50
1.30	11.25	5.00	2.50	1.80	2.50	2.50	1.80
1.40	15.00	11.25	10.00	7.50	5.00	6.25	2.50
1.50	48.75	65.00	56.25	50.00	18.75	27.50	5.00
1.55	115.00	131.25	110.00	82.00	40.00	46.25	20.50
1.60	119.00	153.75	128.75	90.00	53.75	46.25	40.50
1.65	235.00	137.50	116.25	90.00	53.75	51.25	41.25
1.70	240.00	148.75	125.00	120.00	62.50	67.50	52.00

Fig. 15

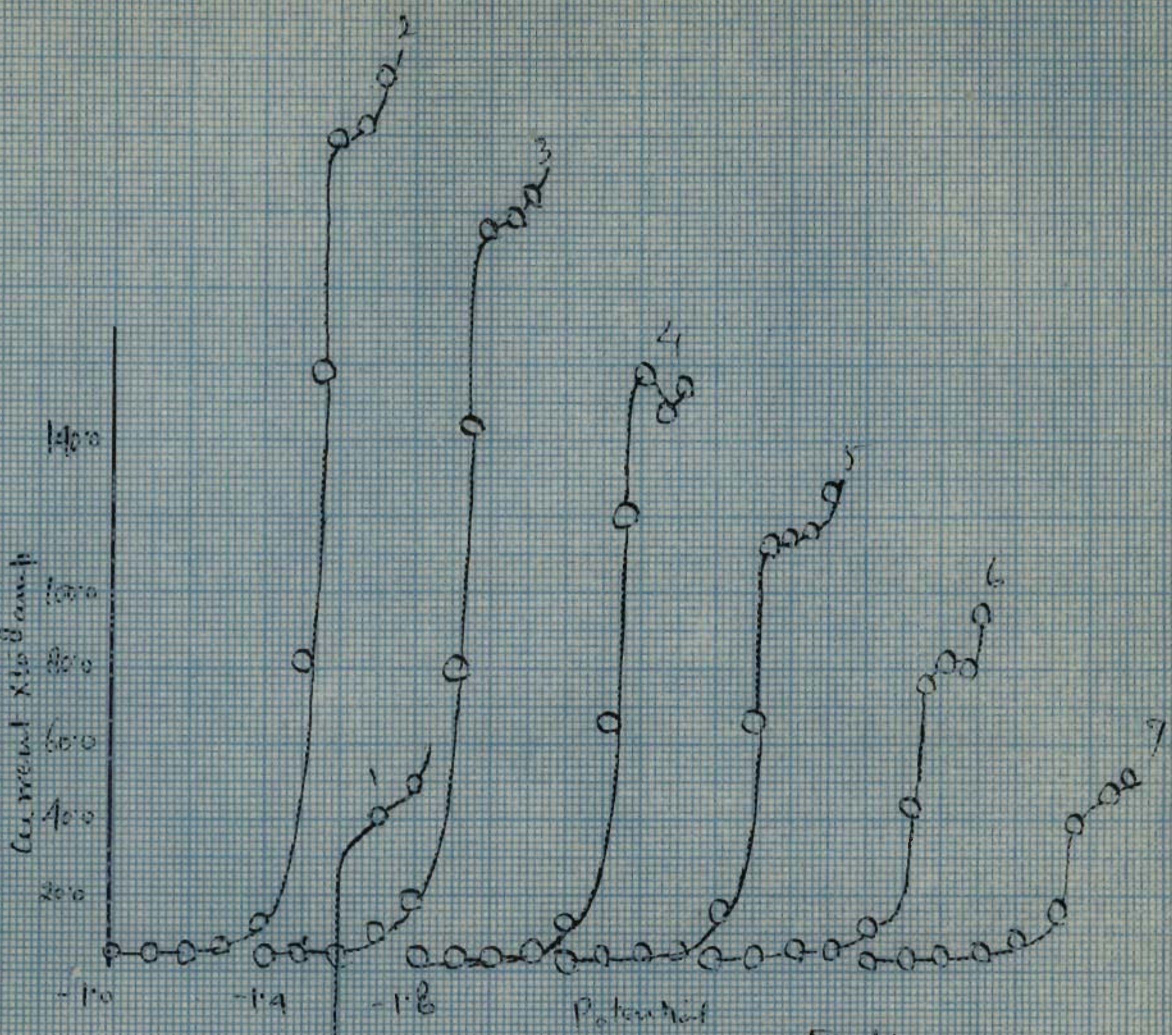


Fig 16

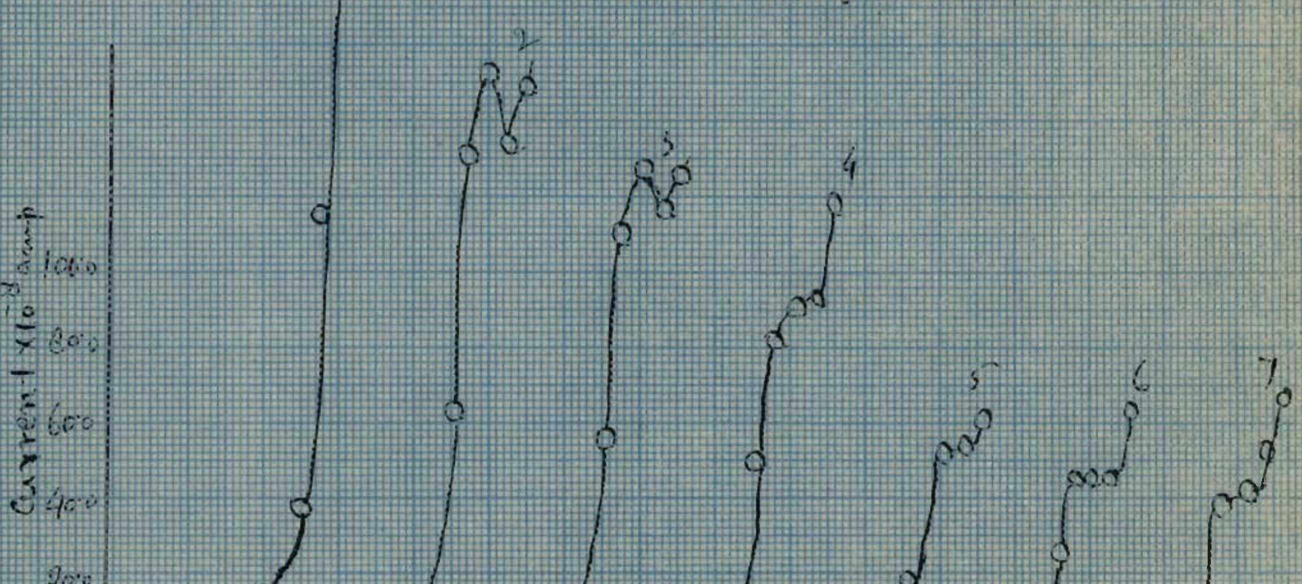


Fig 15

Each curve starts from -1.0 volt

TABLE 16

Polarograms of 6.7 x 10^{-5}M rhodamine 6G in presence of different concentrations of SXSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	0.10	-0.15	0.15	-0.25	-0.25	-0.25	-0.35
0.10	0.60	0.20	0.20	-0.15	-0.15	-0.15	-0.25
0.20	0.75	0.75	0.80	0.00	0.05	-0.05	-0.15
0.30	0.80	1.20	1.10	0.40	0.55	0.25	0.05
0.40	0.90	1.30	1.20	0.60	0.90	0.40	0.40
0.50	0.95	1.55	1.45	0.70	1.10	0.55	0.60
0.60	1.10	1.65	1.55	0.70	1.20	0.65	0.60
0.70	1.15	1.75	1.70	0.75	1.25	0.75	0.65
0.80	1.30	1.95	1.85	0.80	1.35	0.80	0.70
0.90	1.60	2.10	2.00	0.95	1.45	0.90	0.80
1.00	2.00	2.75	2.65	1.20	1.55	1.10	1.25
1.10	2.50	3.00	3.00	1.60	2.00	1.50	1.50
1.20	3.00	3.50	3.50	2.00	2.50	2.50	1.75
1.30	15.00	4.00	8.75	3.75	5.00	3.75	2.50
1.40	87.50	10.00	15.00	10.00	13.75	10.00	6.25
1.50	177.50	80.00	76.25	63.75	65.00	41.25	13.75
1.55	275.00	157.00	140.00	116.00	110.00	75.00	36.25
1.60	355.00	217.50	192.50	155.00	112.50	80.00	33.75
1.65	360.00	220.00	195.00	142.50	115.00	77.50	46.25
1.70	-	232.50	203.50	151.25	125.00	91.25	50.00

Fig. 16

Polarography in acetate buffer(pH 4.70) of methylene blue in presence of different concentrations of soap.

TABLE 17

Polarograms of 6.7 x 10^{-5}M methylene blue in presence of different concentrations of SPSA (order 10^{-5}M).

Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SPSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	-0.25	0.00	-0.20	-0.45	-0.35	-0.25	-0.25
0.10	-0.05	0.15	0.10	-0.20	-0.15	-0.05	-0.10
0.20	0.10	0.20	0.30	0.10	0.10	0.10	0.10
0.30	0.25	0.30	0.40	0.25	0.20	0.20	0.15
0.40	0.35	0.40	0.45	0.35	0.35	0.30	0.25
0.50	0.70	0.35	0.60	0.45	0.55	0.40	0.30
0.60	0.70	0.40	0.70	0.55	0.60	0.45	0.35
0.70	0.80	0.50	0.75	0.60	0.70	0.55	0.35
0.80	0.90	0.55	0.90	0.65	0.85	0.65	0.45
0.90	2.70	0.65	1.00	0.70	0.85	0.65	0.55
1.00	7.50	0.80	5.00	0.80	0.95	0.85	0.65
1.10	10.00	1.10	7.50	1.10	1.00	1.00	0.85
1.20	15.00	2.50	7.50	2.00	1.95	1.30	1.00
1.30	22.50	7.50	10.00	5.00	4.00	1.50	2.00
1.40	170.00	37.50	32.50	25.00	27.50	20.00	10.00
1.50	400.00	200.00	160.00	120.00	110.00	75.00	22.50
1.60	300.00	403.00	362.00	240.00	190.00	120.00	30.00
1.70	-	290.00	300.00	205.00	155.00	102.00	60.00
1.80	-	-	-	222.50	215.00	147.50	90.00

Fig. 17

TABLE 18

Polarograms of 6.7 x10^{-5}M methylene blue in presence of different concentrations of STSA(order 10^{-5}M)

Applied potential in volts.	CURRENT (10^{-8} amp) for diff.conc.of STSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.0	-0.10	- 0.15	- 0.20	- 0.15	-0.15	- 0.20	- 0.20
0.1	0.00	0.05	0.10	0.05	0.00	0.05	0.10
0.2	0.20	0.35	0.35	0.40	0.45	0.40	0.50
0.3	0.70	0.40	0.40	0.45	0.50	0.55	0.60
0.4	0.85	0.60	0.55	0.60	0.60	0.65	0.70
0.5	0.90	0.60	0.60	0.65	0.65	0.70	0.80
0.6	1.10	0.60	0.70	0.75	0.70	0.75	0.90
0.7	1.20	0.70	0.75	0.80	0.80	0.80	0.95
0.8	1.30	0.75	0.85	0.85	0.90	0.85	1.00
0.9	1.35	0.80	0.90	0.90	0.95	0.70	1.10
1.0	1.45	0.90	1.00	0.95	1.00	0.95	1.20
1.1	2.70	2.50	2.50	2.40	2.40	2.00	1.80
1.2	7.50	7.00	6.65	5.00	4.00	3.35	2.00
1.3	10.00	9.00	8.85	6.00	4.55	4.00	3.85
1.4	15.00	12.00	10.00	8.00	5.00	6.00	7.00
1.5	20.00	18.00	15.00	30.00	27.00	20.00	15.00
1.6	360.60	300.00	180.00	23.00	20.00	22.00	17.00
1.7	200.00	200.00	100.00	27.05	25.00	26.00	20.00
1.8	250.00	245.00	125.00	40.00	30.00	30.05	25.00

Fig. 18

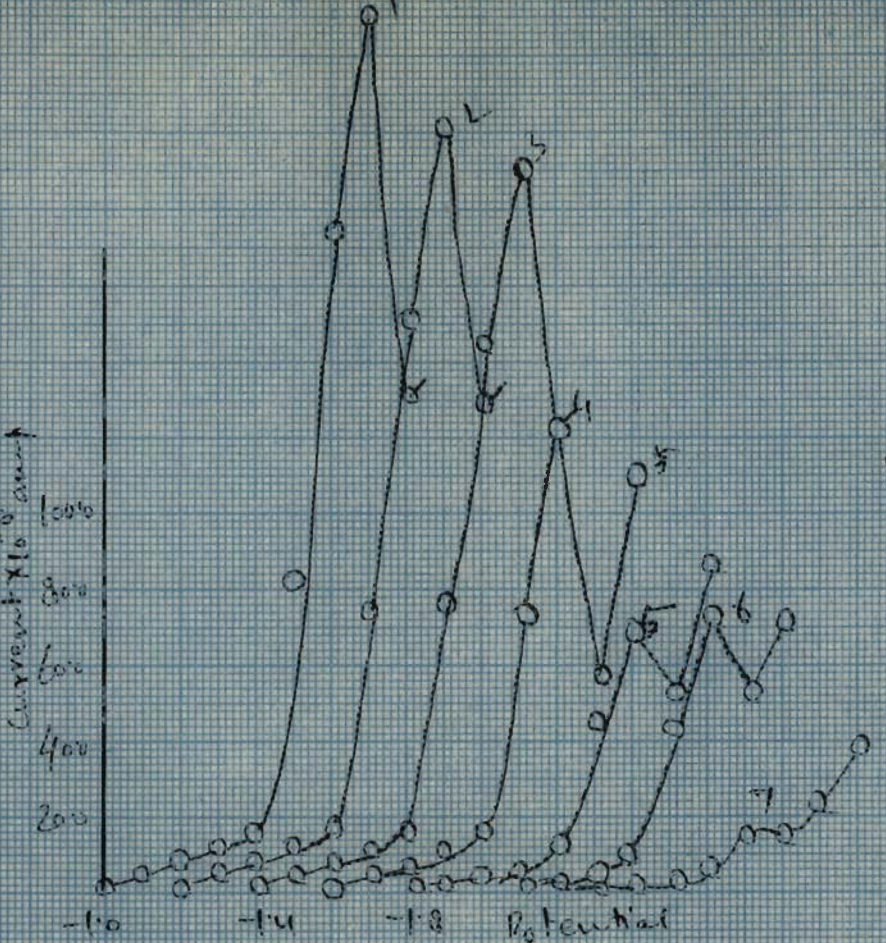


Fig 19

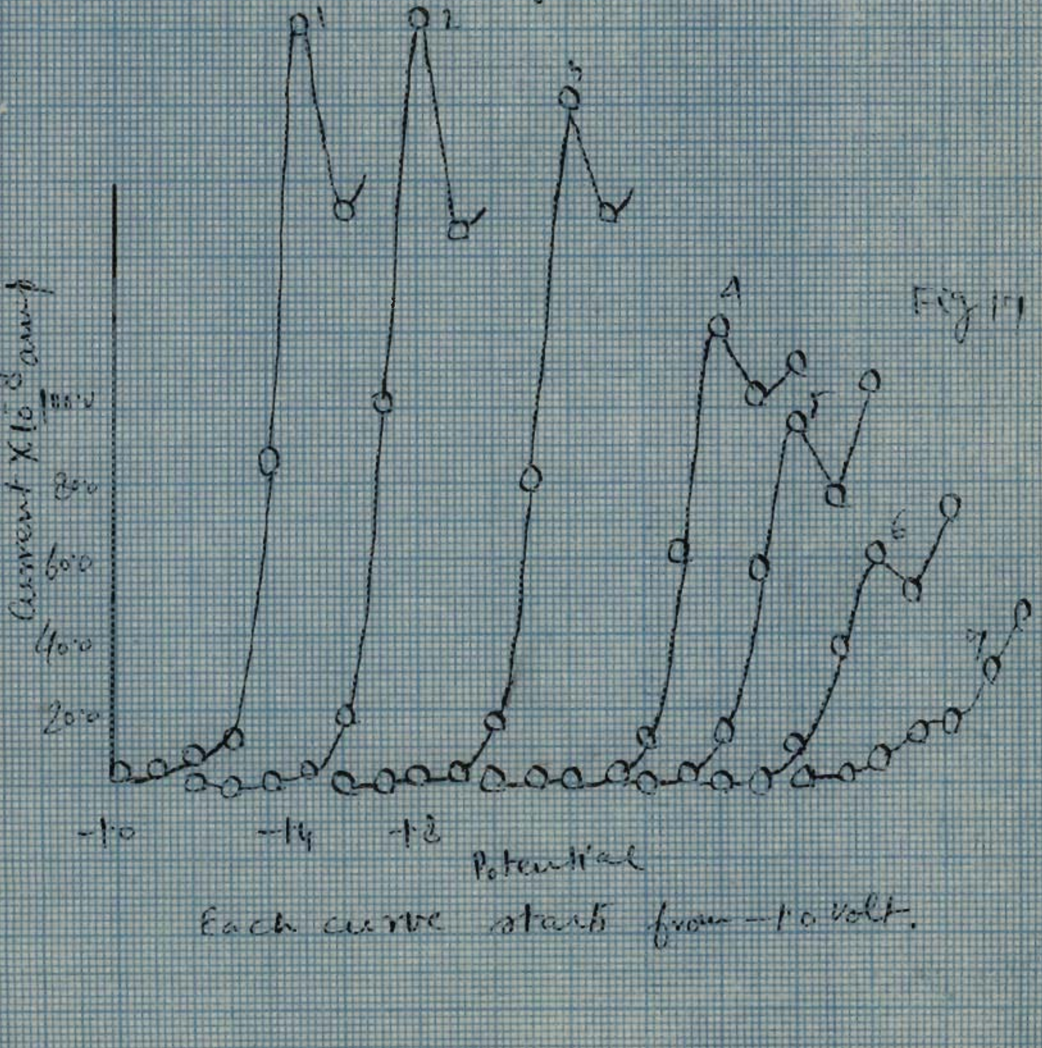


Fig 17

Each curve start from -1.0 volt.

TABLE 19

Polarograms of 6.7 x 10^{-5} M methylene blue in presence of different concentrations of SXSA (order 10^{-5}M).

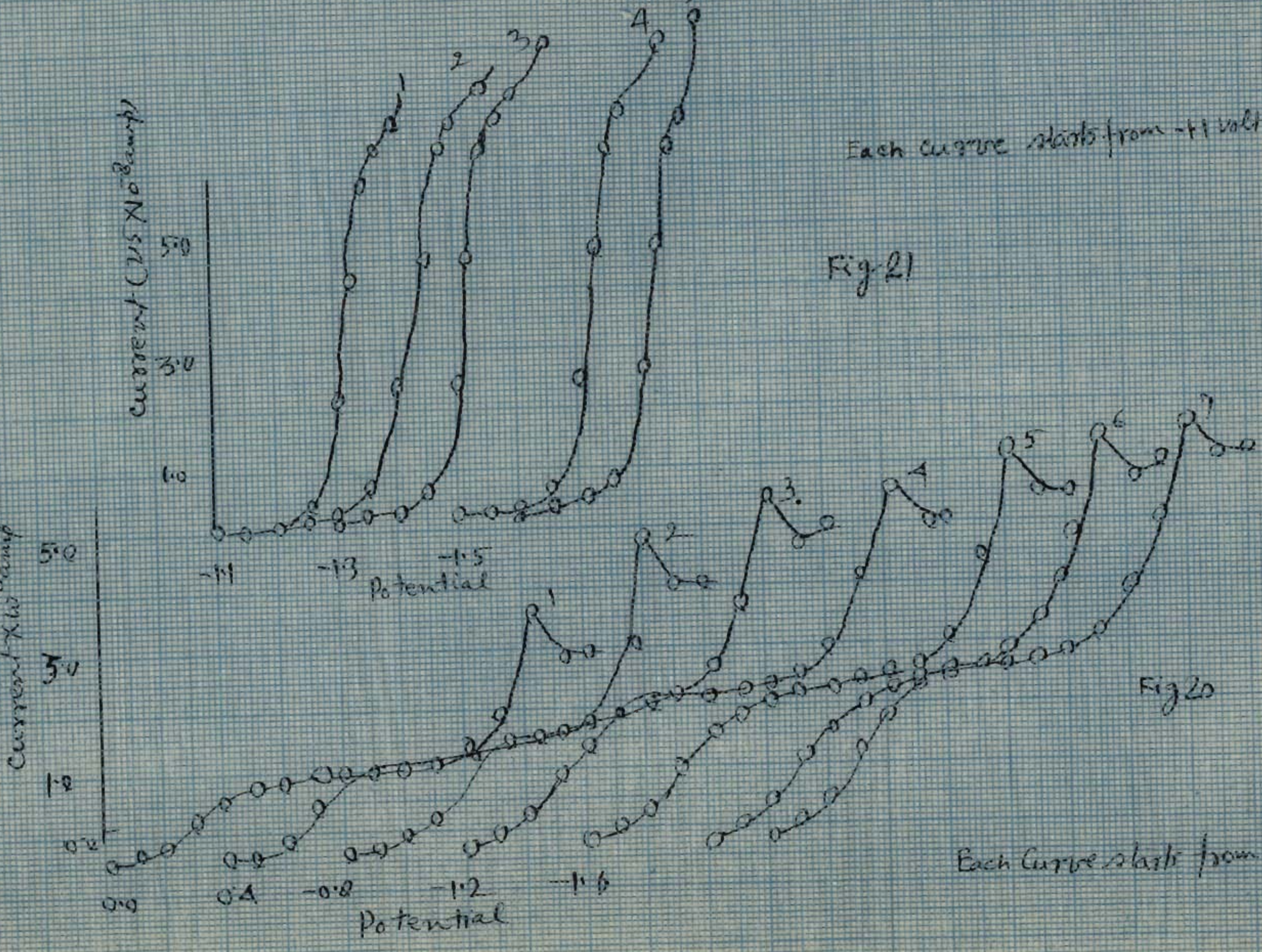
Applied potential in volts.	Current (x 10^{-8} amp) for different concentrations of SXSA						
	1	2	3	4	5	6	7
	6.7	13.3	20.0	26.7	40.0	53.3	80.0
0.00	-0.10	-0.15	-0.15	-0.15	-0.20	-0.20	-0.20
0.10	0.20	0.00	0.00	-0.05	-0.05	-0.05	-0.05
0.20	0.60	0.20	0.20	0.15	0.10	0.15	0.10
0.30	0.85	0.30	0.30	0.25	0.20	0.25	0.25
0.40	0.95	0.40	0.45	0.35	0.30	0.35	0.35
0.50	1.15	0.50	0.55	0.45	0.35	0.40	0.45
0.60	1.20	0.55	0.65	0.50	0.45	0.50	0.50
0.70	1.30	0.55	0.70	0.55	0.50	0.55	0.55
0.80	1.40	0.65	0.75	0.65	0.60	0.60	0.60
0.90	1.50	0.70	0.80	0.70	1.80	0.65	0.60
1.00	5.00	2.50	1.30	0.90	2.55	1.70	1.50
1.10	10.00	10.50	5.00	4.50	3.00	2.50	2.50
1.20	12.00	9.00	9.00	8.50	5.00	3.00	2.80
1.30	15.00	11.50	10.00	10.00	7.00	4.00	3.50
1.40	82.50	15.00	17.50	15.00	12.50	10.00	7.50
1.50	172.50	72.50	75.00	72.50	45.00	42.50	15.00
1.60	237.50	150.00	145.00	120.00	70.00	72.50	15.00
1.70	130.00	200.00	190.00	55.00	52.50	52.50	25.00
1.80	180.00	127.00	122.50	90.00	87.50	77.50	40.00

Fig. 19.

TABLE 20

Effect of mercury height on the post-wave and normal reduction wave malachite green (6.7×10^{-5}M) + sulphonated xylyl stearic acid(6.0×10^{-4}M) in phosphate buffer.

Applied potential in volt.	Current ($\times 10^{-8}$ amp.) at different heights(in cm.)						
	40	45	50	55	60	65	70
0.0	-0.4	-0.35	-0.30	-0.20	-0.20	-0.20	-0.20
0.1	-0.25	-0.25	-0.10	0.00	0.10	0.10	0.10
0.2	-0.05	0.05	0.15	0.30	0.40	0.40	0.50
0.3	0.40	0.55	0.30	1.00	1.10	1.20	1.30
0.4	0.70	1.00	1.25	1.55	1.65	1.75	1.95
0.5	0.90	1.15	1.55	1.85	1.95	2.05	2.30
0.6	1.00	1.20	1.70	2.00	2.15	2.25	2.45
0.7	1.10	1.45	1.85	2.15	2.25	2.40	2.60
0.8	1.10	1.50	1.90	2.25	2.35	2.50	2.70
0.9	1.15	1.60	2.00	2.30	2.45	2.60	2.80
1.0	1.15	1.65	2.15	2.35	2.50	2.65	2.90
1.1	1.25	1.75	2.25	2.60	2.75	2.95	3.20
1.2	1.45	1.10	2.70	3.00	3.20	3.50	3.90
1.3	2.10	3.10	3.90	4.20	4.45	4.85	5.15
1.4	3.85	4.95	5.50	5.75	6.10	6.40	6.65
1.5	2.85	4.00	4.65	4.90	5.50	5.60	5.95
1.6	3.00	4.10	5.00	5.10	5.50	5.85	6.20
1.7	3.10	4.80	5.45	5.75	6.25	6.50	7.00
Fig.20	1	2	3	4	5	6	7



Each curve starts from -1.1 volt

Fig. 21

Fig 20

Each Curve starts from 0.0 volt

T_A_B_L_E 21

Effect mercury height on the normal reduction wave of rhodamine 6G (6.7 x10^{-5}M) + sulphonated phenyl stearic acid (6.0 x10^{-4}M) in acetate buffer.

Applied potential involt.	Current (2.5 x 10^{-7} amp.) at different heights(in cm.)				
	40	45	50	55	65
1.10	0.10	0.25	0.30	0.25	0.35
1.20	0.15	0.30	0.35	0.30	0.35
1.30	0.25	0.40	0.39	0.35	0.45
1.40	0.60	0.65	0.70	0.65	0.70
1.50	2.30	2.45	2.50	2.50	2.55
1.55	4.25	4.50	4.55	4.55	4.65
1.60	5.90	6.25	6.40	6.25	6.30
1.65	6.35	6.95	7.05	6.85	6.80
1.70	6.90	7.70	8.15	8.10	8.40
Fig.21	1	2	3	4	5

T A B L E 22.

Effect of temperature on the adsorption and reduction wave of rhodamine 6G(6.7×10^{-5}M) + SXSA(6.0×10^{-4}M) in phosphate buffer.

Applied potential in volt.	Current ($\times 10^{-8}$ amp.) at diff.heights. (cm.)			
	40	50	60	70
		25°C		
0.50	2.10	2.10	2.25	2.50
1.40	5.45	5.60	6.40	7.25
1.50	5.40	5.90	6.55	7.45
		35°C		
0.50	3.10	3.40	3.75	4.00
1.40	7.75	8.75	9.60	10.50
1.50	7.75	8.60	9.60	10.55
		45°C		
0.50	1.30	1.40	1.65	1.50
1.40	4.60	4.85	5.50	5.65
1.50	4.10	4.60	4.90	5.35

T A B L E 23

Effect of temperature on the reduction wave of rhodamine 6G (6.7×10^{-5}M) +SXSA(6.0×10^{-4}M) in acetate buffer at -1.65 V.

Temp.in °C	Current (2.5×10^{-7} amp.) at diff.heights(cm.)			
	40	50	60	70
30	4.75	4.15	4.05	4.00
35	2.80	3.90	3.85	3.70
40	5.00	4.50	3.90	3.70

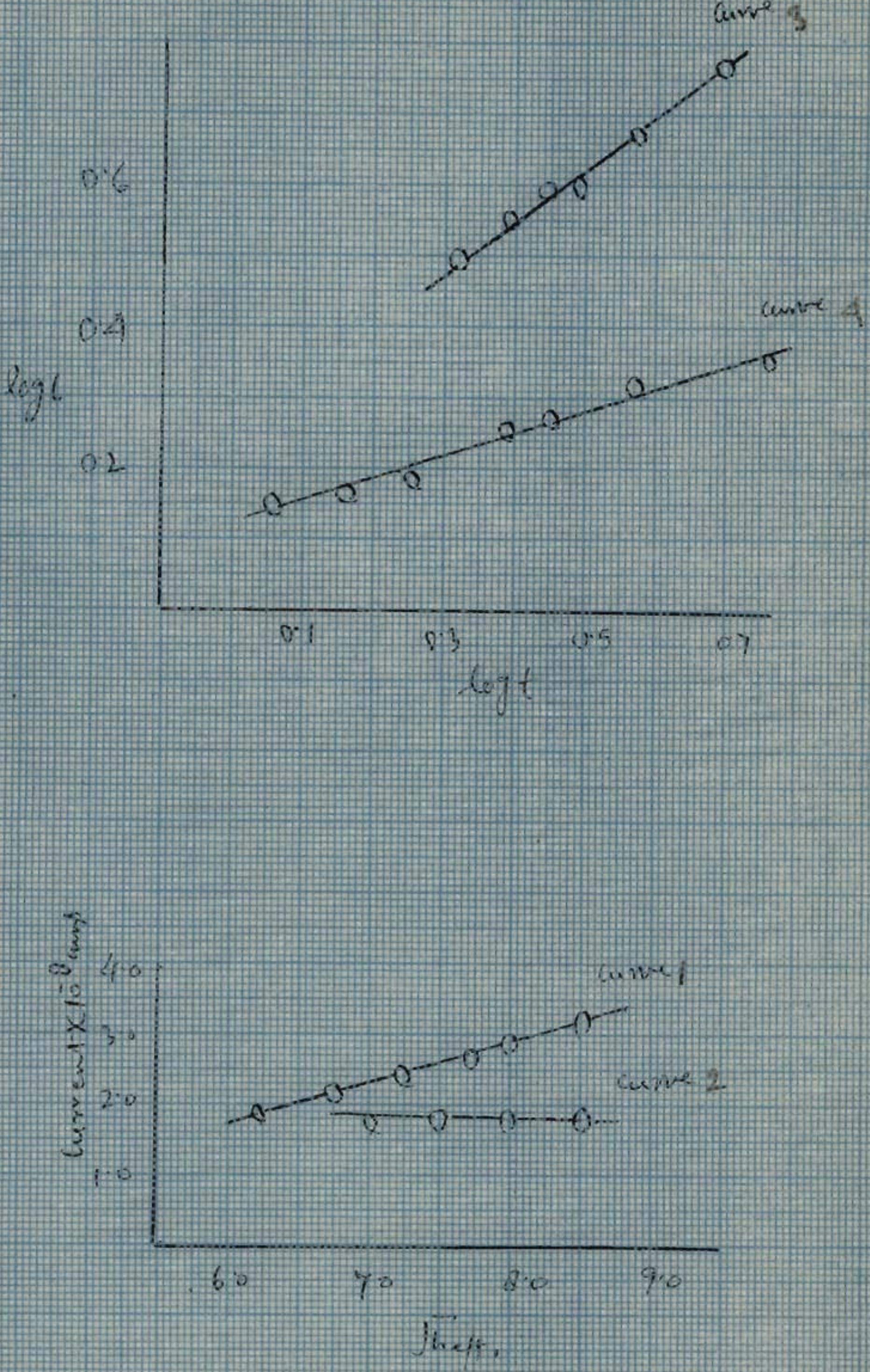

curve 3
0.6
0.4
curve 4
log i
0.2
0.1
0.3
0.5
0.7
log t
current × 10⁻⁸ amps
4.0
curve 1
3.0
curve 2
2.0
1.0
6.0
7.0
8.0
9.0
√heff.

Fig 22.

TABLE 24

Current-time measurements of rhodamine 6G (6.7 x10^{-5}M) + SPSA (6.0 x10^{-4}M) in acetate buffer at 1.65 volts.

	Height of the mercury column (cm.)					
	40	45	50	55	60	65
Drop time in sec.(t)	4.01	3.75	3.35	3.05	2.78	2.53
Current (2.5x10^{-7}amp.) i_d	4.90	4.90	4.50	3.70	3.70	3.20

Fig.22 curve 3

TABLE 25

Current-time measurements of malachite green (6.7 x10^{-5}M) + SXSA (6.0 x10^{-4}M) in phosphate buffer at 1.00 volt.

	Height of mercury column(cm.)					
	40	45	50	55	60	65
Drop time in sec.(t)	3.54	2.80	2.40	1.74	1.42	1.30
Current (x10^{-8} amp.) i_d	2.10	1.80	1.70	1.40	1.40	1.30

Fig.22 curve 4.

RESULTS AND DISCUSSION

The current-voltage curves of different concentration of dyes were noted in phosphate and acetate buffers(Fig.10). At very small concentrations(1.0×10^{-5}M) no reduction wave was realised but at higher concentrations than this reduction was possible.

Results in phosphate buffer.

Two waves were obtained: the post wave and normal reduction wave. The name post wave was preferred to prewave since the dyes in the oxidised form was used and it is the oxidised form which is eventually adsorbed at dropping mercury electrode.

The reversibility was tested by Tome's method(24) and by logarthimic analysis (25). Both the waves were found to be irreversible.

Effect of soap:- The polarograms of the set: 1 ml.dye (1×10^{-3}M) + 0.5, 1 , ...8 ml. of the soap(1×10^{-3}M) total volume made upto 15 ml.by buffer. From the polarograms in phosphate buffer) it would be seen that the adsorption wave disappeared after a certain concentration and a new wave at a more negative potential appeared. The height of the wave increased with increase in the concentration of the added soap. The concentration of the soap influence the normal reduction wave in the manner that(i) its position was shifted to more negative potential,(ii) wave height first decreased with increasing concentration of the soap but after crossing ~~and~~ optimum concentration(c.m.c.),the wave height again increased with the increase in the soap concentration.

In absence of the soap the normal waves were flat but steep waves were obtained in their presence. The order of changing the flat waves to steeper ones was SXSA > STSA > SPSA. The change in half wave potentials are reported in Table I.

TABLE I.

Variatioh in $E_{1/2}$ of the dyes on the addition of the soap: concentration of dye $=6.7 \times 10^{-5}$M: Concentration of soap varying ($6.7 - 80.0 \times 10^{-5}$M).

Dye-soap	Post wave	Normal wave	$E_{3/4}-E_{1/4}$
Malachite green			
SPSA	0.10 - 0.30	0.90 - 1.20	0.12
STSA	0.10 - 0.30	0.90 - 1.26	0.08
SXSA	0.10 - 0.34	0.90 - 1.30	0.04
Rhodamine 6G			
SPSA	0.04 - 0.36	1.02 - 1.22	0.14
STSA	0.04 - 0.34	1.12 - 1.28	0.08
SXSA	0.06 - 0.32	1.12 - 1.32	0.06
Methylene blue			
SPSA	0.06 - 0.24	1.00 - 1.28	0.16
STSA	0.05 - 0.30	1.00 - 1.24	0.10
SXSA	0.06 - 0.32	1.02 - 1.28	0.05

Effect of mercury height:- The results for a typical case, malachite green and SXSA mixture are given in Table 20. The height of the post wave increased with the mercury pressure but after a certain height (50 cm.; t = 3.15 sec. and m = 0.0551 mg/sec. measured in the closed circuit at -0.5 volt), the current became independent of the mercury height. The reduction wave, however, remained dependent on the mercury height throughout. A linear relation between limiting current and $\sqrt{h}_{eff.}$ was also found to exist in this case (Fig.22 curve 1).

Effect of temperature:- The temperature coefficient of the two waves for different heights of mercury column was determined employing Kolthoff's (26) method. The results are given in Table II.

TABLE II.

Temp.coefficient in phosphate buffer: Rhodamine 6G (6.7×10^{-5}M) + SXSA (6.0×10^{-4}M).

Height of mercury column in cm.	40	50	60	70
Temp.coeff.of post wave (%).	3.99	5.40	5.20	4.70
Temp.coeff.of reduction wave(%).	3.50	3.99	3.90	2.90

Results in acetate buffer.

Like the phosphate buffer here too two waves, although more steeper, were realised. In case of rhodamine 6G a red coloured precipitate was formed at the mercury surface. This behaviour was not observed in the case of the other dyes.

Effect of soap:- Unlike the phosphate buffer the emergence of the new wave after the disappearance of the first wave was not observed. Such dissimilarity was also observed for normal wave where a pronounced maximum appeared from the very beginning. Moreover, the potential of the wave started shifting towards more positive values and a continuous reduction in the wave height with increasing soap concentration was observed. The shifts in the $E_{1/2}$ are given in the Table III.

TABLE III.

Variation in $E_{1/2}$ of the dyes with varying conc.soap ($6.7 \times 10^{-5}M$ - $8.0 \times 10^{-4}M$).

Dye-soap	post wave	Normal wave
Malachite green		
SPSA	No clear wave	1.44 - 1.46
STSA	"	1.46 - 1.46
SXSA	"	1.44 - 1.48
Rhodamine 6G		
SPSA	"	1.50 - 1.46
STSA	"	1.58 - 1.46
SXSA	"	1.58 - 1.48
Methylene blue		
SPSA	"	1.50 - 1.46
STSA	"	1.50 - 1.46
SXSA	"	1.46 - 1.42

Effect of mercury height:- The effect of mercury height on the limiting current was also different in the case of acetate buffer. Unlike the phosphate buffer, the limiting current was independent on the height of the mercury column (Fig.22 curve 2).

Temperature coefficient:- The temperature coefficient in the acetate buffer for different heights of the mercury was markedly lower than that in the phosphate buffer. The values are given in Table IV.

TABLE IV.

Temperature coefficient at different mercury heights: Rhodamine 6G (6.7×10^{-5}M) + SXSA(6.0×10^{-4}M).

Height of mercury column in cm.	40	50	60	70
Temp.coeff.of reduction wave(%).	0.50	0.70	-	2.09

The surface active agents are known to exert a marked influence on the electrode processes. In the case of polarographic reduction a film of the surfactant is formed on the mercury drop,leaving little space for the actual electrode process to take place. The extent of film formation,however,depends on many factors like adsorption coefficient,diffusion coefficient,the concentration of the surfactant and the possible interaction of the latter with the substance whose reduction being studied. The behaviour of the soap-dye mixture at the dropping mercury electrode can form the basis of an interesting study provided one of the constituent possesses for less surface active properties than the other.

Let us first consider the case when the dye does not react with the soap. Under this condition the mechanism will be quite simple involving the diffusion of the soap from the bulk of the mixture towards the mercury drop and its subsequent adsorption. With mixtures of low soap content, the reduction of the dye will not be appreciably retarded but with the gradual increase in soap concentration a sizable reduction in the current should take place. This behaviour is realised upto the concentrations (below c.m.c.) of the soap, after which the current uniformly increases with the increase in the concentration of the soap solution.

Assuming that factors controlling the adsorption of the soap at the mercury drop have ceased to be operative after a certain optimum concentration of the soap, the subsequent variations in current may be attributed to the reduction of a new product formed by the interaction of the dye and the soap. The new product, in all probability, is a dye-soap complex as has already been shown on the basis of our spectrophotometric studies on alkyl aryl sulphonates and basic dyes mixtures (Chapter I). A polarographic evidence of complex formation, although purely qualitative,also obtained from the fact that the $E_{1/2}$ of the waves contineously changes with the change in soap concentration of the mixture(Table I and III).

The nature of the electrode process has been explained in the light of Delahay's equation(27). He gave an equation for polarographic current controlled by rate of reaction and diffusion as:

$$i = 1255\ nm^{2/3}t^{2/3}\ C_0K\ \left[1-\phi\ (K\sqrt{t}/D)\right]\ \text{exp.}\ \frac{k^2t}{D} \quad \text{-(1)}$$

where m is in mg/sec., t is in sec., C_0 in mili moles/lit. K in cm./sec., D in cm./sec., $\phi\ (K\sqrt{t}/D)$ is error integral. The average current is given by

$$i_{average} = 1255\ n\ m^{2/3}\ C_0\ K\frac{1}{\tau}\int_0^{\tau}\ t^{2/3}\left[1-0(K\sqrt{t}/D)\right]\text{exp.}\ \frac{k^2t}{D} \quad \text{-(2)}$$

The equation shows that the current is a function of time during the life of a mercury drop~~s~~. He plotted the ratio γ of the average value of the current to the maximum value vs. the drop time. He showed that γ is practically equal to 0.60 when $KD^{-1/2}$ is smaller than 0.05 and if $KD^{-1/2}$ is larger than 5, γ is practically equal to 0.857 or 6/7 which is corresponds to the value of the constant in the Ilkovic equation. In the former case the limiting current is proportional to $t^{2/3}$, whereas it is proportional to $t^{1/6}$ in the latter case.

With other mathematical derivation he further showed that if the valuq of $KD^{-1/2}$ is 0.05, current is purely kinetic while for values betweem 0.05 and 5, both diffusion and kinetic currents determine the magnitude of the limiting current.

The analysis of our results in the light of Delahay's equation suggest that the value of γ (obtained by dividing average current by maximum current) in acetate buffer was 0.7 which corresponds to $KD^{-1/2} = 0.4$. This shows that the nature of the reduction wave is more kinetic than diffusion controlled. Further confirmation to this view point is obtained from the facts that the limiting current is independent of mercury height and the temperature coefficient(Table IV),although low is not constant. Another anamolous behaviour,viz.,the appearance of a well pronounced maximum in presence of soap,may also be taken as an indication of the complex nature of the reduction wave.

<u>i-t curves and drop time</u>:- The current time curves of individual drops obtained at the potential of the peak current were investigated to determine whether the electrod process is diffusion or kinetic controlled. The plots of log i vs. log t gave a value of the slope as 0.5. This value is very close to the value of 0.67 expected for a purely kinetic controlled electrode process and is far beyond the value of 0.167 expected for a diffusion controlled process.

Application of Delahay's equation in the case of phosphate buffer gave a value of γ equal to 0.8 which is quite near to the value of 0.857 expected for a diffusion. controlled process. Any how it is not a purely diffusion controlled inspite of the fact that the limiting current is linearly related to $\sqrt{h}_{eff.}$, because the temperature coefficient is much above 2%. The current time curves gave a slope of 0.25 which is far different from that for a purely kinetic current but is nearer to the value for a diffusion controlled wave.

Although it is difficult to throw some light on the quantitative aspect of the binding of the dye to the soap on the basis of the polarographic data discussed above, the results do indicate that the binding between the dye and the soap does take place. Preliminary experiments on the polarograms of soaps in presence of increasing concentration of the dyes also lend support to this view.

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REVIEW

REVIEW

The physico-chemical properties of surface active agents have been studied by several eminent workers from time to time. Much has been said about their fundamental properties i.e. critical micelle concentration(c.m.c.), shape and size of micelles, solubilisation etc., but even some of them especially the synthetic ones, deserve a more comprehensive and systematic study. This has become~~s~~ all the more important with the development of the new instrumental techniques and the useful data available in the recent years on the influence of the addition of foreign substance on the properties of soap solution. One such case is the problem of the interaction of surface active substances with dyes, which have not been fully investigated even quantitatively and qualitatively studies on the problem have yet to be taken up. This therein deals with investigation on the following aspects, using Twichell's reagents and quaternary salts, are:

(i) physico-chemical studies on the interaction of surface active agents with dyes, using anionic soaps (Twichell's reagents i.e. sulphonated phenyl, tolyl and xylyl stearic acid) and basic dyes (malachite green and rhodamine 6G) and cationic soaps (cetyl trimethyl ammonium bromide and cetyl pyridinium bromide) and acid dye(alizarin red S) combinations, (ii) determination of the c.m.c. of anionic soaps by pH metric, conductometric and spectrophotometric methods and that of cationic soaps by potentiometric, conductometric and spectrophotometric methods,(iii) effect of methyl and ethyl alcohols, urea,acetamide, formamide and lauric acid diethanol amine condensate on behaviour of the anionic and cationic soaps,and (iv) polarography of soap-dye mixtures. The experimental results are reviewed in the following pages:

The anionic soaps, viz., sulphonated phenyl, tolyl and xylyl stearic acids were prepared in the laboratory. The cationic soaps, viz., cetyl trimethyl ammonium bromide and cetyl pyridinium bromide used were of B.D.H. products and they were recrystalised from acetone.

1. <u>Soap-dye interaction</u>:- The quantitative studies on the interaction of anionic soaps with basic dyes (malachite green and rhodamine 6G) and that of cationic soaps with acid dye (alizarin red S) were studied spectrophotometrically. The spectral shift in the dye (both acidic and basic) maximum on the addition of either anionic or cationic soaps have been explained in terms of the formation of the soap-dye complex (page 66) after giving due consideration to factors like pH change of the medium, the disturbance in the monomer-polymer equilibrium etc.. The extent of binding was calculated by Klotz's method employed for protein-dye interaction(J.Amer.Chem.Soc. 68 ,2299,1946). From the results so obtained,it is concluded that the nature of the dye as well as the pH greatly influenced the

extent of binding. Rhodamine 6G combined with the anionic soaps to a greater extent than malachite green, the relative binding capacity being 4:3. The binding was larger in the basic than the acidic range.

The plots between concentration of free dye and moles of bound dye/moles total soap gave straight lines in all the three pH ranges(Fig.10-15). The low values were observed in contrast to Klotz's values which were always higher than one. These low values have been explained in the light of the fact that the dye molecules interact with the ionic micelles and not with single soap molecules(Page 88). These values could be higher if calculations were made simply on the basis of micellar weights.

The micellar size or aggregation number was calculated by dividing total soap molecules with bound dye molecules. Although these data do not provide information on true aggregation number but it can be said that the aggregation number would be an integral part of these values. The values at one particular concentration are given in Table I.

TABLE I.

Aggregation number of anionic and cationic soaps.

Soap + dye	Aggregation number		
		pH	
	2.72	7.00	9.12
Malachite green (2.0×10^{-5}M)			
SPSA (8.4×10^{-4}M)	118	70	70
STSA "	70	70	63
SXSA "	100	78	70
Rhodamine 6G (1.8×10^{-5}M)			
SPSA (8.0×10^{-4}M)	57	88	70
STSA "	104	195	146
SXSA "	90	195	195
Alizarin red S (6.66×10^{-5}M)	(2.00)	(7.00)	(9.12)
CTMAB (8.0×10^{-4}M)	80	11	11
CPB (8.0×10^{-3}M)	31	13	13

In the case of cationic soaps and acid dye exceedingly small shift in dye maximum is observed at 2.00 pH, However, large shift in maximum is observed at pH 7.00 (515 mµ - 550 mµ) and at pH 9.12 (445 mµ - 550 mµ). At pH 7.00 precipitate occured in lower soap concentration(below c.m.c.) but the precipitate redissolve with further addition of the soap (Table 22, Page 90). The influence of pH on the extent of binding is slightly complicated here. It is observed that the binding is greater both in the neutral and the alkaline ranges than in the acidic range, such a behaviour is possible since at pHs 7.00 and 9.12 the ionisation of the phenolic groups side by side with that of the sulphonate group take place providing more negative sites for interaction with the positively charged micelles of the cationic soaps. The micellar size of cationic soaps, calculated in presence of alizarin red S tends to be larger at pH 2.00 and about constant at pHs 7.00 and 9.12 and also increases with the increase in dye and soap concentration(Table 29 and page 98).

2. <u>Determination of c.m.c.</u>:- Besides the other methods like conductivity,surface tension,viscosity,solubility, transport number, osmotic pressure etc. used for determining the c.m.c., the pH metric method, which had attracted very little attention,was used to determine the c.m.c. of anionic soaps. The plots of 1/c (reciprocal of soap concentration) against pH give sharp break corresponding to the formation of micelle.

In the initial concentrations of these soaps they behave as an ordinary electrolytes upto a certain concentration. On further addition of the soaps,more or less a constant value of pH is reached which shows that the charged micelles so formed contain an appreciable amount of negative charge and the hydrogen ions present there get attracted electrostatically by these negatively charged micelles, resulting in the formation of a diffused double layer around the negatively charged micelles. ~~The~~

The break in pH-concentration curve was taken to give the c.m.c. of the soap. Further experiments were performed in presence of foreign electrolytes to make a comparative study with the results of polarography on the c.m.c. values of alkyl aryl sulphonates determined earlier(papers of Malik and Co-workers, Ind.J. Chem. 2 ,35,1964). The comparative studies has shown that although the same order(10^{-5}M) of c.m.c. is realised by both pH metric and polarographic methods, the specific values slightly differ from each other. Thus it is found that the c.m.c. values determined pH metrically are high in presence of KCl and KNO_3 (Table 10,page 114).

The results of pH metry were further confirmed from the conductivity and spectrophotometric measurements. The values obtained by different methods show the same order of c.m.c. that is, 10^{-5}M. Further it is observed that a certain regularity existed in the c.m.c. values of the anionic soaps viz., SXSA > STSA > SPSA. The values obtained spectrophotometrically show that micelles are formed earlier in the lower pH ranges than in the alkaline and the neutral medium. Both pH metric and spectrophotometric methods give higher values of c.m.c. when the soap solution is added to a solution of pH about 7.00 or above.

The c.m.c. values of the cationic soaps were determined potentiometrically and spectrophotometrically and the results were compared from conductometric measurements. For potentiometric measurements the e.m.f. of the cell,

Ag - AgBr/$\underset{C_1}{\text{Cationic}}$ soap / KNO_3 Agar Bridge/KCl(sat.),

Hg_2Cl_2 , Hg.

was measured. The c.m.c. values were calculated from the plots of 1/c vs. e.m.f.. The plots between soap concentration and activity coefficient give a break corresponding to the c.m.c. value. A comparision of these data with the c.m.c. values determined by conductometry show that the conductivity results are a little higher than those of e.m.f. but the order of the c.m.c. values is the same(Table III, page 127).

The other method which was used for determining the c.m.c. of the cationic soaps was the spectral changes of alizarin red S dye by the addition of cationic soaps. This dye is found to be more sensitive than the other dyes so far employed to study the c.m.c. of cationic soaps. The spectra of alizarin red S solutions changed very markedly with increasing concentration of cationic soaps. pH 9.12 was found to be most suitable for the measurements, since at this pH larger shift in the dye maximum is observed(445 mµ to 550 mµ). At pH 7.00 precipitation occured below the c.m.c. but the precipitate redissolves in the micellar soap solution. However,at pH 2.00 no appreciable shift in the dye maximum is observed (415 mµ to 425 mµ). It has been shown in Chapter I that the cationic soaps in their lower concentration form a

1:1 dye-soap complex and this ratio changed at higher soap concentrations due to micelle formation(Table 29, page 98). Due to this fact two shifts in dye maximum are observed (445 - 525 mμ and 525 - 550 mμ) at pH 9.12. The first shift is claimed due to the dye soap complex formation and second due to the micelle formation of the cationic soaps. At pH 7.00 the complex is, however, insoluble but get redissolved when the micelles are formed and we get the same maximum for the dissolved precipitate as obtained at pH 9.12.

3. Effect of alcohols,urea and amides:- The effect of methyl and ethyl alcohols on the c.m.c. of anionic and cationic soaps was studied pH metrically and conductometrically. It is realized that the c.m.c. values shift towards higher concentration with the increase in the alcoholic content of the solution. When the alcoholic content is less than 12% a decrease in the critical concentration is realised (Table I and II, page 165,166). This has been attributed to the fact that in such mixtures a large number of ions are made available for the aggregation,resulting in the formation of micelles at lower concentration of the soap. This is also evident from the variations in pH of anionic soaps in presence of alcohols where a decrease in pH is observed upto 12% alcohol.

On the other hand, the c.m.c. value increases when the alcohol concentration is beyond 12%,which is due to the fact that the ionisation of the soap is markedly retarded(since as is evident from little change in pH). The results have been explained quantitatively on the basis of Lowrence and Stenson (Ref.14,Chapter III) equation,taking into consideration the tendency of the solubility of the "Interaction addition" product,added alcohol and the remaining soap(Page 166).

The effect of urea and amides on the micelle formation of anionic and cationic soaps was also studied by the above two techniques. From the results it is concluded that the addition of urea increases the c.m.c. of both anionic and cationic soaps(Table III,Page 168). The presence of urea breaks the hydrogen-hydrogen bonds and thereby weakens the cohesive forces existing between the water molecules. The pushing out tendency for the hydrophobic portion is thus lessened, with the result that a large proportion of a single soap molecule can remain in solution. The micelle formation takes place at a higher concentration owing to the above mechanism. The other factor, viz., the increase in the dielectric constant of water by the addition of urea may also be responsible for bringing about an increase in the c.m.c. value.

Urea influences the aggregation of the alkyl-aryl sulphonates in the order SPSA > STSA > SXSA(Table IV,Page 169). In the case of cationic soaps the order is CTMAB > CPB. It is obvious that a uniform decrease in the effectiveness is observed with the:increase in the molecular weights of the soaps. Among the anionic soap SXSA is the least effected due to the fact that the inductive effect is more pronounced in this soap owing to the presence of two CH_3 groups in its molecule. With the result of it the solubilising power of hydrophilic group(SO_3^-) increased. Since aggregation of the soap molecules would result as a compromise between the solubilising power of the hydrophilic portion of the soap and the cohesive force of water molecules,with the result that the soaps with a high solubilising power will be least effected by the addition of the substances responsible for weakening the cohesive force. It is for this reason that the SXSA is comparatively least effected.

The presence of acetamide and formamide increase the c.m.c. with the increase in amide concentration. Higher concentration(more than 1 molar) of these amide was not used since the amides themselves started to aggregate. Both acetamide and formamide effect the micellisation of the anionic soaps in the same way as urea does. The order SPSA > STSA > SXSA is also realised here(Tables VII & VIII, Page 172). In the case of cationic soaps the CPB is more easily effected at lower amide concentration than CTMAB.

For the sake of comparision the effect of a non ionic soap, namely lauric acid diethanol amine condensate was also studied. The addition of this compound also increases the c.m.c. of anionic as well as of cationic soaps (Table IX and X, Page 174). It appears that the non-ionic soap break the water structure when present in small concentration.

4. Polarography of soap-dye mixtures:- The soap-dye interaction was also studied polarographically. The results are explained in terms of the adsorption of the soaps at the d.m.e.. The soaps form a film around the mercury drop and the film formation of the soap depends upon the adsorption coefficient, diffusion coefficient, concentration of the surfactant and the extent of interaction between soap and dye. If the soap does not react with the dye than the soap would leave very little space for the reduction of the dye due to its adsorption. This should result in the reduction of the total current in the concentration range where micelles are not formed. The total current reduced contineously with increasing the soap concentration(below c.m.c.) but after crossing the critical concentration, the current increases contineously with increasing soap concentration. The latter behaviour of the soap-dye mixture at d.m.e. is attributed to complex formation, this is also supported by our earlier results on spectrophotometric investigations. Other salient features about the reduction of soap dye mixture in the phosphate buffer are: (i) the wave position is shifted to more negative potential,(ii) the flat waves of dyes become steep in presence of the soaps.

In acetate buffer, unlike phosphate buffer,(i) a pronounced maxima appeared from the very begining ,(ii)the position of the reduction waves start shifting towards more positive potentials, and (iii) a continuous reduction in the wave height with increasing soap concentration is observed.

The nature of these limiting current was tested in the light of Delahay's equation (Page 210) for polarographic current controlled by rate of reaction and by diffusion. If the values of γ ,which is equal to average current divided by maximum current, is equal to 0.6 for $KD^{-1/2}$ then the current will be purely kinetic while if $\gamma = 0.87$ or 6/7 as required by Ilkovic equation, the current will be diffusion controlled.

In acetate buffer(i) the value of γ was 0.7, (ii) slope of the log i vs. log t (current-time curve) is 0.6 which is nearer to 0.67, the value expected for a pure kinetic current, (iii) the limiting current is independent on mercury pressure, (iv) temperature coefficient is not fairly constant at different heights. These results point towards the fact that in acetate buffer the current is more kinetic than diffusion controlled.

In phosphate buffer, the limiting current has the following properties, (i) the value of γ is 0.8, (ii) the slope of log i vs. log t = 0.25, which is more nearer to the diffusion controlled wave(0.167), (iii) temperature coefficient = 3.5% and (iv) $i_d/\sqrt{\bar{h}_{eff.}}$ = constant.

All these values indicated that the current in phosphate buffer is more diffusion controlled than in the acetate buffer.

Hence it has been concluded that in the electroreduction of dye-soap mixtures at d.m.e. is neither purely kinetic nor purely diffusion controlled. A comparative study in acetate and phosphate buffers showed that in acetate buffers the process is more kinetic and less diffusion controlled. The behaviour is almost reverse in case of the phosphate buffer.

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