PHYSICO-CHEMICAL STUDIES ON THE MICELLAR PROPERTIES OF SURFACTANTS AND THEIR INTERACTION WITH DYES

Thesis submitted for the
award of the degree of
Doctor of Philosophy
in
Chemistry

by
PURAN CHAND

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ROORKEE
ROORKEE
September. 1967

CERTIFICATE

Certified that the thesis entitled ''PHYSICO-CHEMICAL STUDIES ON THE MICELLAR PROPERTIES OF SURFACTANTS AND THEIR INTERACTION WITH DYES'' which is being submitted by Mr. Puran Chand for the award of Doctor of Philosophy in Chemistry of University of Roorkee, Roorkee, is a record of his own work under my supervision and guidance. The matter embodied in the thesis has not been submitted for the award of any other degree of any University.

This is further to certify that he has worked from August, 1964 to September, 1967 at this University to prepare this thesis.

Wahid U. Malik
(Wahid U. Malik)
Ph.D., D.Sc.,
F.R.I.C. (London), F.N.A.Sc.,
Professor and Head of the
Chemistry Department,
University of Roorkee,
Roorkee.

September 28, 1967

ACKNOWLEDGEMENT

I feel great pleasure in expressing my deep sense of gratitude to my teacher Dr. Wahid U. Malik, Ph.D., D.Sc., F.R.I.C. (London), F.N.A.Sc., Professor and Head, Department of Chemistry, University of Roorkee, Roorkee, under whose guidance this work has been carried out. I am also thankful to Dr. S. P. Srivastava, Reader in Chemistry for his kind help and encouragement.

I am also grateful to Dr. S. P. Verma, Lecturer in Chemistry Department, Regional Engg. College Krukshetra, for his valuable help. My thanks are also due to Mr. A. K. Jain and Mr. S. M. Saleem from whom I got help, co-operation and encouragement during the course of the work.

Puran Chand.
Puran Chand

CONTENTS

--oo--

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Surface active agents,well known for their specific behaviour of altering the surface energy of their solvents, have been obtained from natural products by extraction or modification since prehistoric times. These products have, however,always found limited applicability due to their instability in the acid solution or their tendency to undergo hydrolysis in the aqueous medium. The industrial and technical developments which came in the wake of the first world war,focussed attention on the disadvantages of these soaps and a vigorous search was made to have soaps or surfactants which besides being free from these disadvantages may be more effective and industrially useful. The discovery of synthetic surface active agents is thus of recent origin as compared to those obtained from natural products.

Most of the interest in surface chemistry has centered about the behaviour of surfactants in water although examples depicting the use of organic solvents for bringing them into solution are not wanting. Generally speaking the water soluble surface active agents can be classed under two heads, the ionic and non-ionic soaps. Of the two,the former have undergone further subdivision into anionic and cationic soaps, depending upon the charge which the large hydrophobic part attains when brought into the solution. On the other hand non-ionic soaps,although not ionizable,possess a sufficient number of ionizing polar groups,e.g., -O-,-OH, - CONH -,- COO, which make them soluble in water. And yet there is another class of compounds named amphoteric surfactants which ionize in solution with the long chain carrying either positive or negative charge,depending upon the pH of the solution. Besides there are surfactants which fall under polymers and fluorocarbons.

Non-ionic surface active agents have greatly attracted the attention of industry with the result that they are finding increasing applications and appreciation in many fields. The advantages of non-ionic agents are based on such fundamental concepts of surface chemistry as the modification of the property of each compound by simply changing the length of polyoxyethylene group, the ease with which they can be mixed and formulated,their stability towards pH and chemical inertness and their non-vulnerability towards high concentrations of electrolytes.

Surfactants have been put to use in industry, technology and allied fields. They are finding increasingly great use in medicine and hygeine as powerful bactericides, as agents for preparing skin lotions,ointments and emulsions of the sex harmones (1). A very large proportion of the total surfactant production is used in textile industry. The importance of surfactants in the field of cosmetics, metal and mineral technology,in paper,leather,synthetic rubber, polymer,plastic,paint,petroleum industries is now well established. Although the building and construction industries seldom claim the use of surfactants for soil stabilization,the possibility of their being used as soil stabilizers can be explored (2). Their usefulness in agriculture to improve physical properties of fertilizers and soils (3) and in bringing about quick germination of seeds is also being gradually recognised.

The selection of surfactants for specific application is governed by some of the distinction features like adsorption and orientation of molecules at the interfaces,micelle formation above a certain concentration known as critical micelle concentration (c.m.c.), solubilization of water insoluble substances by micelles etc.. Truly speaking amongst colloids it is the surfactants which possess the unique distinction of exhibiting reversible thermodynamical equilibrium between colloidal aggregates and surrounding environments.

Many physical properties of the surfactants exhibit more or less an abrupt change over a narrow concentration range. This abruptness in property has been utilised in the determination of c.m.c.. A number of methods based on electrical conductance (4-8), osmotic pressure (9),vapour pressure (10),viscosity (11),e.m.f. (12),diffusion (13,14), freezing point (15),solubility (16,17),surface tension (18-20), refractive index (21), polarography (22),light scattering (23) measurements have been employed from time to time by various workers to study the micellar properties of surfactant solutions. Of these the light scattering method is of special importance since it affords the determination of both the aggregation number and c.m.c. of the surface active substances (ionic and non-ionic). Spectral dye method for the determination of c.m.c.,first initiated by Hartley (24), has met with great success (25-27). This method has now been extended to non-ionic surfactants also (28-29). Another method,although an indirect one,has been used to provide evidence for micelle formation. It is based on the ability of the surfactant solution to dissolve or solubilize water insoluble dyes at the c.m.c. (30,31). This method can be equally well employed in the case of both aqueous (32) and non-aqueous solutions (33-35) of surfactants.

All surface chemists subscribe to the existence of micelles in solution of surface active agents but opinions differ as to their kinds,shapes and mechanism of formation (36-39). McBain considers two kinds of micelles,one a highly conducting,spherical one revealing its existence before c.m.c. while the other, a non-conducting lameller micelle making its appearance beyond c.m.c.. Contrary to McBain's views Hartley (40,41) acknowledges only one kind of micelle, namely the spherical one. On the other hand Debye (42) has proposed a cylinderical micelle while others (43,44) have indicated the presence of rod like micelle giving impression of a stack of coins.

Light scattering technique is probably the most powerful tool which can be employed to fathom the mysteries of micelles. It affords the determination of micellar molecular weight (45-49), amount of charge on the micelle (50), and dissymmetry (51). This method singly provides such a hoard of information which other methods like diffusion (52-54), X-ray (55,56), ultracentrifuge measurements (57) and sedimentation data (58) may not be able to give when used collectively. Recently Schott (59) calculated the micellar molecular weight and aggregation number of some ionic and non-ionic agents by solubilization. Such effects as the decrease in c.m.c. and increase in micellar size (60,61) on the addition of salts to surfactant solutions can be studied by this technique.

Thermodynamical considerations of Debye (45) based on the free energy of the micelle rather than of the entire system aroused great controversy (62,63). Reich (62) pointed out that Debye's treatment was not conclusive and could not provide explanation for such simple facts as the formation of micelles by non-ionic surfactants. Other workers like Philips (64) made simple assumptions that the micelles are mono-dispersed, with all of the micelles having essentially the same size and charge while Hoeve and Benson (65) criticized the simplicity of such statements. Later on, Nakagawa et.al., (66) put forward a theory which envisaged such factors as heat of hydration and configurational entropy terms of the hydrophobic chains in discussing the formation of associated colloids. This theory could give the quantitative prediction for c.m.c.,micellar weights,and other properties but could not reasonably explain temperaure effects and clouding phenomenon. Stainsby and Alexander (67) have calculated the change in heat content and also in entropy at micellization from the temperature dependence of the c.m.c. of surfactant. Recently,the heat of micellizatio in aqueous solutions of various ionic detergents has been determined by direct calorimetric measurements of heats of dilution (68-71).

Attempts have been made to discuss micelle formation in terms of phase separation.But the aggregation number of micelles,30 2000,is not large enough to treat the micelle as a phase,though it seems adequate to call it a pseuodophase (72). It is,however,convenient to use the model based on the law of mass action for micelles with smal aggregation number while phase separation model is preferre to when dealing with large aggregation number.Critical micelle concentration in terms of phase theory would then mean as the saturation solubility of single species,which if exceeded,leads to the production of a new phase.

Dependence of c.m.c.is not limited to the chain length but factors like the position of the ionic group in the alkyl-chain(73),presence of double bond and also the substitution of polar group for hydrogen in the hydrocarbon chain influences the c.m.c. of the surface active agents. The difference in c.m.c. of various surfactants having the same hydrocarbon chain has been found mainly due to the kinds of hydrophilic group, the number of charges on geggenions, molecular shape and so on (66,74,75). Lottermoser and Püschel (5) have reported correspondingly smaller c.m.cs. for bivalent Zn, Cu, and Mg-salts than for univalent Na, K, and Ag-salts of the alkyl sulphates. The c.m.c. is not markedly dependent on the nature of geggenions (76).

The effect of additives and salts on the c.m.c. of surface active agents has been studied by a number of investigators (21,26,76-80). It has been found that the concentration, number of charges on geggenions are the important factors. The addition of salts to the solution of non-ionic agents has a relatively small effect (81).

The physico-chemical properties, such as surface tension (82), c.m.c. (7,78,83,84), foaminess (85), foam stability (78), and solubilization of hydrocarbon (86,87) change considerably in presence of a very small amount of paraffin chain alcohols. The c.m.c. change due to the added alcohols is very important both academically and industrially to elucidate the phenomena. Hutchinson et.al., (83) have measured the effect of cyclohexane, n-heptane and toluene on the c.m.c. of dodecyl pyridinium chloride by electrical conductivity, resulting a decrease in the c.m.c.. The effect of added dioxane, glycol, methanol, etc. on the c.m.c.

has been reported by Harkins et.al.(88).

INTERACTIONS:

Interactions of soaps with other materials offer an entirely new field of study of both fundamental and applied importance. The materials with which the soaps or surfactants would interact, include soaps (89), dyes (90), high polymers (91), proteins (92), metal ions (93), clays (94), simple organic compounds etc..

Soap and soap:- Interaction between one soap and the other leads to the formation of mixed micelles (95). A typical case is a mixture (96) of ionic (e.g. sodium dodecyl sulphate) and non-ionic (e.g. polyoxyethylene dodecyl ether) agents in the aqueous medium. It has been observed that the presence of an ionic agent obstructs the increase in micellar weight of the non-ionic agent and enhances the cloud point. Investigations on the c.m.cs. and the micellar properties of the mixture of ionic (97-100) and non-ionic surface active agents (101,102) have proved of immense value in clarifying our ideas of micelle formation and preferential micelle forming tendency. The study is also very useful from the industrial viewpoint because commercial surface active substances almost always contain some higher or lesser homologes as an impurity.

Soap and protein:- These interactions have been extensively studied from both biochemical and industrial point of views (103-109). Kuhn et.al.(103) showed in their study on cationic surfactants that disinfecting action of these agents on bacteria can be attributed to the combining power of these compounds with cell proteins. The effect of chain length of surfactant ions on complex formation with gelatin has been recently observed. Jerchel and coworkers (110) studied the reaction of cationic surfactants with a wide variety of proteins. Equilibrium dialysis and electrophoresis techniques (111,112) have been usually employed in these studies but other methods like turbidimetry,fluorimetry,surface tension and viscosity can be employed for these studies. Even polarographic waves other than the diffusion controlled ones can prove to be of immense value in such studies.

Soap-metal interaction:- Soaps of metals like copper, nickel,mercury,zinc,cobalt etc. have been prepared by metathesis (113). Besides their industrial and technical importance (114),these soaps can be fruitfully investigated from the point of view of their solubility in organic solvents and the nature of the micelles vis-a-vis those formed in the aqueous medium. Their studies in organic solvents in close gel forming effects of the system with some other causative properties like X-ray structure,dipole moment,viscosity,temperature,solubility coefficients etc.(115,116). Techniques like polarography (117-119), spectrophotometry (120,121),e.m.f. measurements using metal-metal soap and membrane electrodes (122),viscometry (123) measurements and radio-isotopy (124) have recently been used to study the physico-chemical behaviour of soaps.

Schulman (93) has studied the reactions of copper with dodecyl sulphate while Walton (125) and Von Voorst (126) have prepared the mercury salts of anionic surfactants. Interaction of soaps with complex compounds like zinc amine (127) has formed the basis for the recovery of the surfactant from the solution. Potassium dichromate (128) forms an insoluble compound with cetyl trimethyl ammonium compound.

Oleophilic colloids like metals and metal hydroxide sols would also react with soaps (129-134). Recently Ottewill (135) examined the effect of non-ionic agents on the stability of Ag sols.

Soap-clay interactions:- Until recently the effective utilization of clays in conjunction with various surfactants was largely a matter of art and empirical knowledge. Because of the differences in the polarity of charge on edge and face surfaces of clay minerals(94),one can expect that organic cations will be adsorbed on the negative surfaces and organic anions at the positive edges. In analogy with water,polar organic compounds will be adsorbed on both hydrophilic surfaces. Long chain aliphatic amines can be anchored on clay minerals(136) like bentonite,imparting to them strongly organophilic properties.

Cashen (137) has used cetyl trimethyl ammonium bromide to distinguish planer and edge functions of clays. Clays have also been used to sorb the normally liquid non-ionic detergents when they are used in powdered household detergent formulations (138).

Soap-dye interaction:- Interaction between dye-stuff and surface active agent is a complicated phenomenon and not much has been achieved in this direction. This is not surprising since the behaviour of the dye in water is not yet satisfactorily elucidated. Some dyes associate even at a fairly low concentration giving aggregates which remain in equilibrium with the monomer. Pinacyanol chloride belongs to this type (25). Inspite of all these limitations, this interaction can be usefully applied to determine the c.m.c. of the surfactants. The method is named as a spectral dye method and was first developed by Hartley (24) and was later on extended by many workers (25-27). Mukerjee and Mysels (139) has used this method in determining the c.m.c. of sodium lauryl sulphate. The colour change accompanying this reaction was attributed to the formation of dye detergent complex. Hiskey and Downey (140) confirmed the existence of a complex of methyl orange with octadecyl trimethyl ammonium chloride at different pH values while Colichman (141) investigated the complex formed by the interaction of bromophenol blue with quaternary ammonium compounds. A colorimetric method based on determining the quantity of bromocresol purple liberated from a protein complex with dye on addition of the anionic detergent,has recently been proposed.

In recent years,the interaction of non-ionic surfactants with dyes has been investigated (29). Nakagawa (142) has calculated the partition coefficient of the dye and from that the partition is very favourable to the incorporation into the micelle. The importance of this reaction in dyeing process (143) is well recognised now. For example,dyeing with Rhodamine B is improved by using a mixture of the dye and sodium alkyl sulphate.

SOLUBILIZATION.

Organic water insoluble compounds becomes soluble when brought in contact with the aqueous solution of the detergents. This phenomenon has been named as solubilization. Direct evidence of the fact that the solubilized material is present in the micelle is provided by X-ray measurements.

Many interesting aspects of the phenomenon have been investigated. For example,McBain and McBain (144) found that the components in solubilized systems are in thermodynamical equilibrium. Mclay (145) has studied the effect of added solubilizates on the cloud point. Stearns et.al.,(30) ,Kolthoff and Graydon (146) , Kolthoff and Stricks

(147) , Klvens (148) and Richards and McBain (149) think that the addition of electrolytes increases the extent of solubilization greatly. Green (150) has studied the increasing effect of solubilization of Orange OT by the addition of hydrocarbons. The introduction of a polar group in the molecule and also the presence of a double bond increases the extent of solubilization (30).

Palit and McBain (151) have shown that soap greatly increases the mutual solubility of benzene and ethylene glycol. Further Palit and coworkers (152-155) have pointed out that the mixtures of surfactants are frequently far better solubilizers for water than the same surfactants taken individually. They have presented the data for a large number of the systems in which water is the solubilizate, with both the solubilizers and the solvents representing a wide range of chemical structures. Solubilizing effect of some basic organic compounds on the metallic soaps has been studied extensively by Palit et.al. (156). They pointed out that glycols are strong solubilizers for heavy metal soaps (157).

EFFECT OF SURFACTANTS ON ELECTRO-CHEMICAL PROCESSES.

The influence of surfactants on electro-chemical processes of industrial and metallurgical importance is fairly well known. From the viewpoint of fundamental study, the effect of surfactant at the solution mercury interface is of special interest. This subject has not been fully investigated and offers a fresh avenues for further work.

Proskurnin and Frumkin (158), for the first time made use of differential capacity measurements at the solution mercury interface in order to investigate the adsorption of colloidal surfactants at the solution interface. Their work was further extended and improved by Grahme (159) who applied it in an extensive study of the structure of double layers. Eda (160) carried out investigations on the adsorption of paraffin chain electrolytes on the solution-mercury interface,but little information (161) is available concerning the effect of compounds of high molecular weight such as polyoxyethylene lauryl ether.

Surface active agents influence the reduction at the dropping mercury electrode (d.m.e.) in more than one way. The adsorption of the surfactants at the d.m.e. may decrease the limiting current, shift the half wave potentials and in some cases oblitrate the entire wave. In some cases, the presence of surfactants results in the appearance of adsorption or catalytic waves (162) while in others,instead of suppressing the maxima,enhanced current in the form of kinks (163) appear.

Colichman (22) and Tamamushi et.al. (164) have studied the effect of some ionic and non-ionic surfactants on the polarographic reduction of simple metal and complex ions while Meits (165) and Zuman (166) have studied the suppressive action of a number of these compounds. Kolthoff

(167) has recommended the use of polyacryl-amide as a maximum suppressor in the case of rotating platinum electrode. Reilley (168) and Smoler (169) had studied the effect of surfactants on polarographic currents.

Holleck and Exner (170) have observed the effect of these compounds on the reduction mechanism of nitro-compounds at the d.m.e.. Stromberg (171) has studied the effect of camphor on the electrode process of cadmium-amalgum electrode, while Silvestroni (172) has shown that the half wave potential of oxygen shifted to more negative potential by the presence of these compounds. Kemulla (173,174), Schwab (175), and Kolthoff (176) have studied the reduction waves of copper in presence of surface active agents.

Recently,new fields have been covered. These include the polarographic behaviour of fatty acids (177) and quaternary ammonium salts (178), the effect of surfactants on the maxima of anions (179), inorganic ions (180), behaviour of some substances at the d.m.e. at different frequencies (181) and the researches of Doss and coworkers (182) on the effect of gelatin,acetone,thymol blue,etc., on the capacity of double layer. The latter author has also studied (183) the behaviour of bromo-cresol purple blue,bromo-thymol blue and cetyl pyridinium bromide at the d.m.e. in order to see their effect on the capacity of the double layer. More recently, Chaki (184) studied the effect of these compounds in oscillopolarography while Hagi (185) observed the effect on the chronopotentiograms of Cu^{++},Pb^{++},Cd^{++} and Bi^{+++} in various supporting electrolytes.

ANALYSIS AND ESTIMATION OF SURFACTANTS.

The surfactants are generally identified by surface tension and elemental analysis. Dyes and certain other indicators (186,187) are used to estimate the ionic surfactants in the mixture. Preston(188)escribed a tensiometric titration for the estimation of surfactants while Wilson (189) described a gravimetric method for quaternaries. Recently Gorden and Urner (190) have described a polarographic method for the determination of sulphite and sulphates in petroleum sulphonates.

Despite the great commercial importance of the non-ionics,relatively few quantitative analytical procedures for these substances have yet been developed. Harada and Kimura (191)studied the precipitation reaction of bismuth nitrate and potassium iodide with non-ionics. The precipitate does not have a definite stoichiometric composition,but the inorganic components included in it have a definite compositions.In order to remove the interfering substances the use of a suitable solvent (192) and ion exchangers(193) have been carried out. Surface active agents form an inclusion compound with amylose in which the hydrocarbon chain penetrates into the amylose helix(194).The inhibition of iodine-starch colour reaction in the presence of non-ionics has been utilized to determine the concentration of non-ionics.

The impurity or heterogenity of a non-ionic surface active agent includes many complications in its physico-chemical properties. The molecular distillation method, chromatography especially paper partition chromatography (195) have been employed for the purification of non-ionics.

Recently, selective adsorptivity has been determined for several pairs of detergents by radio-tracer technique (196) in order to analyse the action of a mixture of surface active agents and to clarify the effect of highly surface active impurities.

--oo--

THE PROBLEM

The work described in the thesis deals with the following aspects of the chemistry of non-ionic and ionic surfactants:

(i) The behaviour of non-ionic surfactants as polarographic maxima suppressors and their relative superiority to ionic surfactants.

(ii) C.M.C. determination of non-ionic surfactants by polarography and spectrophotometry (iodine solubilization and spectral dye methods) and with the help of electrocapillary curves-a method which has not so far been used for c.m.c. determination and offer a new approach for extensive studies.

(iii) Quantitative studies on the binding of dyes with ionic surfactants carried out spectrophotometrically.

(iv) Polarographic estimation of ionic surfactants by determining the decrease in wave-height of dyes.

(v) Polarographic determination of aggregation number of dyes and the effect of additives known for breaking the water structure the aggregation of dyes.

—

REFERENCES

1. Nakagawa,T. and Maneyuki,R.; J.Pharm.Soc. Japan,73 , 1106 (1953).

2. Clare,K.E.,Nature, 160,829 (1947).

   Davidson,D.T., High way Research Board,Proc.,29,537 (1949).

3. Kumagai, R. and Hardesty, J.O.; J.Agr.Food Chem., 3 , 34 (1955).

4. McBain,M.E.L., Dye,W.B., and Johnston,S.A., J.Am.Chem. Soc. 61 ,3210 (1939).

5. Lottermoser, A. and Puschel,F.Kolloid-Z. 63 ,175 (1933).

6. Wright, K.A.; Abbott, A.D.; Sivertz, V. and Tartar,H.V. J.Am.Chem.Soc. 61 ,549 (1939).

7. Ralston,A.W.; and Hoerr, C.W. J.Am.Chem.Soc. 64 ,772 (1942).

8. Williams,R.J., Phillips,J.N.; and Mysels,K.J., Trans. Faraday Soc. 51 ,728 (1955).

9. Hess,L.,and Suranyi, L.A., Z.Physik. Chem. (Leipzig) A 184 ,321 (1939).

10. McBain,J.W., and Salmon, C.S., J.Am.Chem.Soc. 43 , 426 (1920).

11. Hess, L.,Phillippoff,W.; and Kiessig, H.; Kolloid -Z, 88 ,40 (1939).

12. Walton, H.F.; J.Am.Chem.Soc. 68 ,1180 (1946).

13. Mysels, K.J.; and Stigter, D., J.Phys.Chem. 57 ,104 (1953).

14. Stigter,D.; Williams, R.J. and Mysels, K.J.,ibid. 59 , 330 (1955).

15. Johnston,S.A.; and McBain, J.W.; Proc.Roy.Soc. A 181 , 119 (1942).

16. Tartar, H.V. and Wright, K.A.; J.Am.Chem.Soc. 61 ,539 (1939).

17. Adam,N.K.; and Pankhurst, K.G.A.,Trans.Faraday Soc.42 , 523 (1946).

18. Powney, J. and Addison,C.C.; ibid., 33 ,1243 (1937).

19. Kushner, L.M. and Hubbard,W.D.; J.Phys.Chem. 57 , 898 (1953).

20. Bury,C.R. and Browning, J.Trans.Faraday Soc. 49 ,209 (1953).

21. Klevens, H.B.; J. Phys. and Colloid Chem. 52 , 130 (1948).

22. Colichman,E.L.; J.Am.Chem. Soc. 72 ,4036 (1950).

23. Debye, P. ; J.Phys. and Colloid Chem. 53 ,1 (1949).

24. Hartley,G.S.; Trans.Faraday Soc. 30 ,444 (1934).

25. Sheppard, S.E. and Geddes, A.L.; J.Chem.Phys. 13 , 63 (1945).

26. Corrin,M.L.; and Harkins,W.D.; J.Am.Chem. Soc. 69 , 679 (1947).

27. Kolthoff,I.M. and Stricks,W.; J.Phys. and Colloid Chem. 52 ,915 (1948).

28. Ross,S. and Olivier, J.P.; J.Phys.Chem. 63 ,1671 (1959).

29. Martin,J.T. and Standing,H.A.,; J.Textile. Inst.,Trans. 40 ,689 (1949).

30. Stearns,R.S. Oppenheimer, H.Simon,E., and Harkins,W.D.; J.Chem.Phys. 15,496 (1947).

31. McBain,J.W. and Richards,P.H.; Ind.Engg.Chem. 38 , 642 (1946).

32. Goto,R.,Sugano,T.; and Koizumi,N.; J.Chem.Soc.Japan, 75 ,73 (1954).

33. McBain,J.W.,Merrill,R.C.; Jr. and Vinograd,J.R.; J. Am.Chem.Soc. 62 ,2880 (1940).

34. Arkin,L. and Singleterry,C.R.; J.Colloid Sci.4 ,537 (1949).

35. Kaufman,S.and Singleterry,C.R.; J.Colloid Sci. 7 ,453 (1952).

36. McBain,M.E.L. and Hutchinson,E.; ''Solubilization and Related Phenomena'' Academic Press,New York,1955.

37. Hartley,G.S.; ''State of solution of colloidal electrolytes,Quast.Rev.Chem.Soc.2 ,152 (1948).

38. Hartley,G.S.; Ann.Repts.Chem.Soc. 43 ,33 (1949).

39. Moilliet,J.L. and Collie,B.; ''Surface Activity'' Van Nostrand,New York (1951).

40. Hartley,G.S.; ''Aqueous solutions of paraffin chain salts'',Hermann,Paris (1936).

41. Hartley,G.S.; Kolloid-Z, 88 ,22 (1939).

42. Debye,P. and Anacker,E.W.; J.Phys.Chem. 51 ,18 (1947).

43. Debye,P. and Anacker,E.W.; J.Phys. and Colloid Chem. 55 ,644 (1951).

44. Halsey, G.D.; Jr.J.Phys.Chem. 57 ,87 (1953).

45. Debye,P.; Ann.N.Y. Acad.Sci. 51 ,575 (1949).

46. Hutchinson,E.; J.Colloid Sci. 9 ,191 (1954).

47. Mysels,K.J.; J.Phys.Chem. 58 ,303 (1954).

48. Mysels,K.J.; J.Colloid Sci. 10 ,507 (1955).

49. Prins,W., and Hermans,J.J.; J.Phys.Chem. 59,576 (1955).

50. Mysels,K.J.; J.Phys.Chem. 58 ,303 (1954).

51. Zimm,B.H.; J.Chem.Phys. 16 ,1093 (1948).

52. Hartley,G.S. and Runnicles,D.F.; Proc.Roy.Soc. (London) 168A ,420 (1938).

53. Miller,G.L. and Anderson,K.J.; J.Biol.Chem. 144 , 475 (1942).

54. Vetter,R.J.; J.Phys.Chem. 51 ,262 (1947).

55. McBain,J.W. and Hoffman,O.A.; J.Phys.and Colloid Chem. 53 ,39 (1949).

56. Mattoon,R.W.,Stearns,R.S. and Harkins,W.D.; J.Chem. Phys. 16 ,644 (1948).

57. Granath,C.; Acta Chemica Scand, 4 ,103 (1954).

58. Kucher,R.V. and Yurzhenko,A.I.; Kolloid -Z,15 ,442 (1953).

59. Schott,H.; J.Phys.Chem. 70 ,2966 (1966).

60. Stigter,D. and Mysels,K.J.; J.Phys.Chem.59,45 (1955).

61. Monkawich,A.M.,; J.Phys.Chem. 58 ,1027 (1954).

62. Reich,I.; J.Phys.Chem. 60,257 (1956).

63. Ooshika,Y.; J.Colloid Sci. 9 ,254 (1954).

64. Phillips,J.N.; Trans.Faraday Soc. 51 ,561 (1955).

65. Hoeve,C.A.J. and Benson,G.C.; J.Phys.Chem. 61 , 1149 (1957).

66. Nakagawa,T.and Kuriyama,K.; J.Chem.Soc.Japan Pure Chem.Sect. 78 ,1568 (1957) in Japanese.

67. Stainsby, G. and Alexander,A.E.; Trans.Faraday Soc. 46 ,587 (1950).

68. Hutchinson,E.,Manchester,K.E., Winsolow,L.; J.Phys. Chem. 58 ,1124 (1954).

69. Goddard,E.D., Hoeve,C.A.J. and Benson,G.C.;ibid.61, 593 (1957).

70. White,P. and Benson,G.C.; J.Colloid Sci. 13 ,584 (1958).

71. White,P. and Benson,G.C.; Trans.Faraday Soc. 55, 1025 (1959).

72. Hutchinson,E.,Inaba,A. and Baieley,L.G.; Z.Physik. Chem. (Frankfurt) 5 ,344 (1955).

73. Winsor, P.A.; Trans.Faraday Soc. 44 ,463 (1948).

74. Shinoda,K.,Yamanaka, T.,and Kinoshita, K.; J.Phys. Chem. 63 ,648 (1959).

75. Hsiao,L.,Dunning,H.N. and Lorenz,P.B.; ibid. 60 , 657 (1956).

76. Goddard,E.D., Harva,O. and Jones,T.G.; Trans.Faraday Soc. 49,980 (1953).

77. Lange,H.; Kolloid -Z, 117,48 (1950).

78. Shick,M.J. and Fowkes,F.M.; J.Phys.Chem.61 ,1062 (1957).

79. Shinoda,K., J.Phys.Chem. 59 ,432 (1955).

80. Herzfeld,S.H., ibid. 56 ,953 (1952).

81. Shinoda,K., Yamaguchi, T., and Hori,R.,Bull.Chem. Soc. Japan.,34 ,237 (1961).

82. Harva,O.,Rec.Trav. Chim. 75 ,101 (1956).

83. Hutchinson,E., Inaba,A., and Bailey,L.G.,Z.Physik. Chem. (Frankfurt) 5 ,344 (1955).

84. Evers,E.C. and Krans,C.A., J.Am.Chem.Soc. 70 ,3049 (1948).

85. Nakagaki, M. and Shinoda,K., Bull.Chem.Soc. Japan. 27,367 (1954).

86. Shinoda,K. and Akamatu,H., ibid, 31 ,497 (1958).

87. Klevens,H.B., J.Am.Chem.Soc. 72 ,3581 (1950).

88. Harkins,W.D., Mittelemann,R. and Corrin,M.L., J. Phys.and Colloid Chem. 53 ,1350 (1949).

89. Yoda,O.,Meguro, K., Kondo,T. and Ino,K., J.Chem.Soc. Japan, Pure Chem. Sect.,77, 905 (1956) (In Japanese).

90. Levine,A. and Schubart,M., J.Amer.Chem.Soc. 74 , 91 (1952).

91. Saito,S., J.Colloid Sci., 15 ,283 (1960).

92. Putnam,F.W.,''Advances in Protein Chemistry''. Academic Press Inc. Pub.New York (1948).

93. Schulman,J.H., Austral.J.Chem.,13 ,236 (1960).

94. H.van Olphen,''An Introduction to Clay Colloid Chemistry''. Inter Science.Publishers New York, Page 157 (1963).

95. Nakagawa, T. and Inoue,H.,J.Chem.Soc.Japan.Pure.Chem. Soc. Japan. Pure Chem. Sect. 78 ,636 (1957),(In Japanese).

96. Biswas,A.K. and Mukerjee,B.K., J.Phys.Chem. 64 ,1 (1960).

97. Shinoda,K., ibid.58 ,541 (1954).

98. Lange,H., Kolloid-Z, 131 ,96 (1953); 132 ,45 (1953).

99. Corrin,M.L. and Harkins,W.D., J.Colloid Sci., 1 , 469 (1946).

100. Klevens,H.B., J.Chem.Phys., 14,742 (1946).

101. Shinoda,K.,Yamaguchi,T. and Hori,R.,Bull.Chem.Soc. Japan, 34 ,237 (1961).

102. Nakagawa,T., Ann.Repts., Shinogi Research Lab.,8 , 835 (1958) (In Japanese).

103. Kuhn,R. and Bielig,H.J., Ber.deut.Chem.Ges.73 , 1080 (1940);74 ,941 (1941); 75 ,1942 (1942).

104. Putnam,F.W. and Neurath,H., J.Am.Chem.Soc. 66 , 692 (1944).

105. Pankhurst,K.G.A. and Smith,R.C.M., Trans.Faraday Soc.40 ,565 (1944).

106. Pankhurst,K.G.A. ''Surface Chemistry''Butter-Worths,London,Page 109 (1949).

107. Elkes,J. and Finean, J.B. '' Surface Chemistry'' Butterworths,Page 231 (1949).

108. Aoki,K., Hori,J.,Sakurai,K., and Suzuki,Y.,Bull.Chem. Soc. Japan,29,104 (1956); 29 ,369 (1956).

109. Tamamushi,B. and Tamaki,K., Bull.Chem.Soc.Japan, 28 ,555 (1955); 29 ,731 (1956).

110. Jerchel,D., Becker,H. and Schmeiser,K., Z. Naturforsch, 9b ,169 (1954); 8b, 541 (1953).

111. Foster,J.F., J.Phys.and Colloid Chem. 53,175 (1949).

112. Yang,J.T. and Foster,J.F., J.Am.Chem.Soc. 75 ,5560 (1953) ; 76 ,1015 (1954).

113. Koening,A.E.,ibid. 36 ,951 (1914).

114. Palit,S.R. and McBain,J.W.,J.Amer.Oil.Chemist's Soc. 24 ,193 (1947).

115. Banerjee,B.C. and Palit,S.R., J.Ind.Chem.Soc. 27 , 385 (1950) ; 29 ,175-82 (1952).

116. McRoberts,T.S. and Schulman,J.H., Nature,163 ,101 (1948).

117. Malik,W.U. and Haque,R., Nature 194 ,863 (1962).

118. Malik,W.U.,Haque,R. and Verma,S.P., Bull.Chem.Soc. Japan, 30 ,746 (1963).

119. Malik,W.U. and Ahmad,S.I., Ind.J.Chem. 2 ,168,247 (1964).

120. Malik,W.U. and Haque,R., Z.Analyst.Chem. 189 ,179 (1962).

121. Malik,W.U. and Ahmad,S.I., J.Amer.Oil. Chemist's Soc. 42 ,451 (1965).

122. Malik,W.U. and Jain,A.K., J.Electro,Chem. Soc.14, 37 (1967).

123. Malik,W.U. and Ahmad,S.I., J.Amer.Oil.Chemist's Soc. 42 ,454 (1965).

124. Malik,W.U. and Jain,A.K., Experentia, 23 ,346 (1967).

125. Walton,H.F., J.Am.Chem.Soc. 68 ,1130 (1946).

126. Van Voorst,F.,Trans.Faraday Soc. 57,110 (1961).

127. Frantisck Erben Czech 89046 March 15,(1959).

128. Fenard,I., J.Pharm.Belg., 7 ,403 (1952).

129. Lottermoser,A. and Steudel,R.,Kolloid-Z, 82 ,319 (1938) ; 83 ,37 (1938).

130. Tamamushi,B. and Tamaki,K.,Kolloid-Z, 163,122 (1959)

131. Ottewill,R.H., Rastogi,M.C. and Watanabe,A.,Trans. Faraday Soc. 56 ,854,866,880 (1960).

132. Horne,R.W.,Matijevie, E.,Ottewill,R.H.,and Weymonth, J.W., Kolloid-Z, 161 ,50 (1958).

133. Matijevic,E., and Ottewill,R.H., J.Colloid.Sci. 13, 242 (1958).

134. Hazel,J.F. and Strange,H.O., J.Colloid Sci.12 ,529 (1957); J.Phys.Chem. 61,1281 (1957).

135. Ottewill,R.H. and Mathai,K.G., Trans.Faraday Soc., 61 , (1965).

136. Strong,M.W., Nature 169,756 (1952).

137. Cashen,G.H., Trans.Faraday Soc. 55 ,477 (1959).

138. U.S.Pat. 2,594,257-8,C.B.Durgin to Monsanto Chemical Co.

139. Mukerjee, P. and Mysels,K.J., J.Am.Chem.Soc., 77 ,2937 (1955).

140. Hiskey,C.F. and Downey,T.A., J.Phys.Chem. 58 ,835 (1954).

141. Colichman,E.L., J.Am.Chem.Soc. 67 ,1212 (1945).

142. Nakagawa,T., Ann.Repts. Shionogi Research Lab. 8 , 326 (1958) (In Japanese).

143. Lenher and du Pant. USP2,052,716.

144. McBain,J.W. and McBain,M.E.L., J.Am.Chem.Soc. 58 , 2610 (1936).

145. Maclay,W.N., J.Colloid Sci. 11,272 (1956).

146. Kolthoff,I.M. and Graydon,W.F., J.Phys. and Colloid Chem. 55 ,699 (1951).

147. Kolthoff,I.M. and Stricks,W., ibid. 53 ,424 (1949).

148. Klevens,H.B., J.Am.Chem.Soc. 72 ,3780 (1950).

149. Richards,P.H. and McBain,J.W.,ibid. 70,1338 (1948).

150. Green,A.A. and McBain,J.W., J.Phys. and Colloid Chem. 51 ,286 (1947).

151. Palit,S.R. and McBain,J.W., Ind.Eng.Chem. 38 ,741 (1946).

152. Palit,S.R. and McBain,J.W., J.Soc. Chem.Ind. 66 , 3-5 (1947).

153. Palit,S.R., J.Colloid Sci. 4 ,523-4 (1949).

154. Palit,S.R. and Venkaterswarlu,V.,Proc.Roy.Soc. (London) ; A 208,542-51 (1951).

155. Palit,S.R. and Venkaterswarlu,V., J.Chem.Soc. (London) 2129 (1954).

156. Chaterjee,B.K. and Palit,S.R., J.Ind.Chem.Soc. 31, 421 (1954); 39 ,571 (1962).

157. Palit,S.R., et.al., J.Ind.Chem. Soc. 19 ,271 (1942), 26 ,577 (1949).

158. Proskurnin,M.A. and Frumkin,A.N.,Trans.Faraday Soc. 31 ,110 (1935).

159. Grahame,D.C., J.Am.Chem.Soc. 68 ,301 (1946); 71, 2975 (1949).

160. Eda,K., J.Chem.Soc. Japan. 80 ,343,347,349,461, 465,708 (1959); 81, 689,875 (1960) (In Japanese).

161. Jamamushi,R., Yamamoto,S., Takaheshi,A., and Tanaka,N., Anal.Chim.Acta. 20 ,436 (1959).

162. Malik,W.U. and Ahmad,S.I., J.Polarographic. Soc. 12 ,50(1966)

163. Malik,W.U. and Gupta,G.C. Talenta (In Press).

164. Tamamushi,R. and Yamanaka,T.,Bull.Chem.Soc.Japan. 28 ,673 (1955).

165. Meits,L. and Meits, T., J.Am.Chem.Soc. 73 ,177 (1951).

166. Zuman,P., Chem. Listy, 48 ,1020 (1954).

167. Kolthoff,I.M., Okinaka,Y. and Fujinaga,T., Anal. Chim. Acta. 18 ,295 (1958).

168. Schmidt,R.W. and Reilley,C.N., J.Am.Chem.Soc. 80, 2087 (1958).

169. Kuta,J. and Smoler, I.,Z. Elektro, Chem. 64 ,285 (1960).

170. Holleck,L. and Exner,J., ibid. 56 ,46 (1952).

171. Stromberg,A.G. and Zagainova,L.S.,Doklady.Akad. Nauk. U.S.S.R., 97 ,107 (1954).

172. Silvestroni,P., Ricerace Sci., 26 ,166 (1956).

173. Kemula,W., Roc. Chem. 30 ,1725 (1956).

174. Kemula,W. and Weronski, E., Roc. Chem. 34 ,1023 (1960).

175. Schwab,K. and Mai, U., J.Electro.Anal.Chem. 1 , 54 (1959).

176. Kolthoff,I.M. and Okinaka,Y., J.Am.Chem. Soc. 81 , 2296 (1959).

177. Ashara,T. and Hayano,S., Abura Kagaku, 5 ,352 (1956).

178. Mairanovskii,S.G.,Doklady Akad.Nank. U.S.S.R.,110, 593 (1956).

179. Nikolajeva,N.V., Damskin,B.B. and Petry,O.A.Coll. Czechslov. Chem. Communs. 25 ,2982 (1960).

180. Tanaka,N.,Tamamushi,R. and Takatashi,A.,Coll. Czechslov.Chem.Communs. 25 ,3016 (1960).

181. Gupta,S.L., Proc.Ind.Acad.Sci., 39A ,282 (1954).

182. Doss,K.S.G. and Kolyonasundram,A., ibid. 35A ,27 (1952).

183. Doss,K.S.G. and Gupta,S.L., ibid. 36A ,493 (1952).

184. Imai,G. and Chaki,S.Bull.Chem. Sec. Japan. 29 ,496 (1956).

185. Nagi,T., J.Chem.Soc. Japan 81 ,93 (1960).

186. Salton,M.R.J. and Alexander,A.E.Research (London) 2 ,247 (1949).

187. Glazer,J., Smith,T.D. Nature, 169 ,497 (1952).

188. Preston,J.M., J.Soc. Dyers. and Colorists 61,165 (1945).

189. Wilson, J.B., J.Assoc.Office, Agr. Chemist's 35 ,455 (1952).

190. Gordon,B.E., Urner,R.S.,Anal.Chem. 25 ,897 (1953).

191. Harada,T. and Kimura,W.,Abura Kagaku 8 ,523 (1959) (In Japanese).

192. Kortland,C. and Dammers.,H.F., J.Am.Oil.Chemists Soc. 32 ,58 (1955).

193. Barber,A.,Chinnick,C.C.T., and Lincolon, P.A., Analyst, 81 ,18 (1956).

194. Takagi,T. and Isemura,T., Bull.Chem.Soc.Japan. 33, 437 (1960).

195. Nakagawa,T. and Nakata,I., J.Chem.Soc. Japan, Ind. Chem.Sect. 59,710 (1956).

196. Shinoda,K. and Mashio,K., J.Phys.Chem. 64 ,54 (1960)

—

CHAPTER I.

Non-ionic and cationic surfactants as maxima suppressors.

INTRODUCTION

The appearance of maxima in polarographic waves is a well known phenomena. Although conflicting views exist regarding their origin (1-2),many experimental facts like, the existence of positive and negative maxima (3),their non-reproducibility (4),dependence of their shapes on the composition of electrolyte solutions (5),height of the mercury column (6),emergence of the maxima of the second kind (7),appearance of kinks in presence of suspensoids (8) etc.,offer several new fields of investigation,both of fundamental and applied importance.

A simple consideration of the phenomenon of the maximum suppression would reveal that investigations in this direction are not limited to the discovery of new maximum suppressors but various factors affecting the equilibrium at the mercury-solution interface can be studied by carrying out polarographic determinations in presence of surface active compounds. Attention to some such points will be drawn in the following paragraphs.

The maximum suppressors cited in the literature, include substances like,proteins,carbohydrates,dyes,soaps, surfactants,etc.,but only a few of them like gelatin, methyl red and Triton x-100 are generally used for this purpose. Even then a substained effort in this direction is being made so that new suppressors which would prove useful for difficultly suppressable maxima without producing insidious effect at the electrode surface may be discovered. The use of material like Triton X-100 (9),polyacrylamide (10),thiobarbitrates (11),separan (12) as maximum suppressors in a few difficult cases may be cited as examples in support of the above viewpoint. Investigation by Malik et.al. (13-14) with alkyl aryl sulphonates, quaternary ammonium salts as maximum suppressors for a number of difficulty suppressable simple and complex metal ions over a wide range of hydrogen ion concentrations is another example of the discovery of new surfactants for polarographic work.

Other interesting aspects connected with the discovery of new maximum suppressors and their influence on polarographic reduction are the work of Reilley (15) and Smoler (16) on the effect of surface active agents on polarographic current,that of Badinand and Boucherle (17) on the inhibiting power of polyethylene glycols and of Capitanio and Pittoni (18-19) on the suppression coefficient of sulphonated naphthyl stearic acid. Holleck and Exner (20) investigated the effect of surfactants on the mechanism of reduction of organic compounds while Kryukova and Campbell (21) studied the effect of these compounds on the rate of mercury flow. The work of Kolthoff (10), Kemulla (22) and Schwab (23) on the effect of surfactants on copper waves is also an interesting study worth mentioning.

The presence of surfactants in trace quantities not only bring about a suppression of the maximum (sometimes accompained by decrease in the limiting current) but also bring about the shifts in the half wave potentials, appearance of minima or deceiving split waves, kinks, obliteration of the entire wave etc.. These effects are usually discussed in terms of adsorption of the surface active substances at the interface of the electrode and the depolarizer and can be well demonstrated from the study of electrocapillary curves.

Gouy (24), for the first time demonstrated that if small quantity of surface active substance like octanol is added to the solution, the electrocapillary curve changes its form resulting in the displacement of the electrocapillary zero (e.c.z.) downward as well as sideward.

The shape of the electrocapillary curves depends on the nature of the solution and provides useful information on the capillary activity of dissolved substances and the structure of the double layer. A close relationship exists between the electrode potential and interfacial tension, and symmetrical parabolic curves are obtained if the adsorption of ions takes place at the mercury surface.

Colichman (25) and Tammaushi et.al. (26) have studied the formation of micelles of surface active agents and discussed their effect on the current-voltage and electrocapillary curves. Several Russian investigators (27) has confirmed the finding that the inhibiting action of the paraffin chain compound on the current-voltage and electrocapillary curves is essentially connected to the coverage on the electrode surface by adsorbed molecules or ions. Meibur (28) used the electrocapillary curves to determine the extent of adsorption of organic substances. Recently Barradas and Kamerlle (29) studied the adsorption of highly surface active agents such as Triton X-100, Triton X-35 and Triton X-305 on d.m.e. by plotting electrocapillary curves in 0.1 N KCl.

The studies on adsorption of highly surface active agents by conventional polarographic drop-time measurements is of special interest in investigating the electrochemical processes such as the mitigation of corr~~i~~osion by inhibitors and the attainment of smooth deposits and polished metal surfaces in electroplating. Some studies along this line are reported in the literature (30-32). Heyrovsky (33) mentioned the effects of the films of adsorbed molecules such as pyridine in the discussion on the mechanism of electro deposition of metals. Randles (34) demonstrated that rate of some electro-chemical processes at the mercury cathode is changed by the addition of a small amount of gelatin and methyl red to the electrolyte solutions.

The polarographic maxima have been found useful in both analytical and applied fields. Their study provides a rapid method for determining the surface activity (35) and also the concentration of the compound

(36). It can even be employed in determining the c.m.c. of surfactants (25). In the applied field, polarographic maximum has found use in biology and medicine (37-38), in testing the synthetic and natural products (39), the purity of water (40), in the estimation of refined and also in determining the wetting power of surfactants (42). Striking similarities have been reported between the processes involved in polarographic maximum suppression on one hand and the metallic corr~~i~~osion and its inhibition on the other (43).

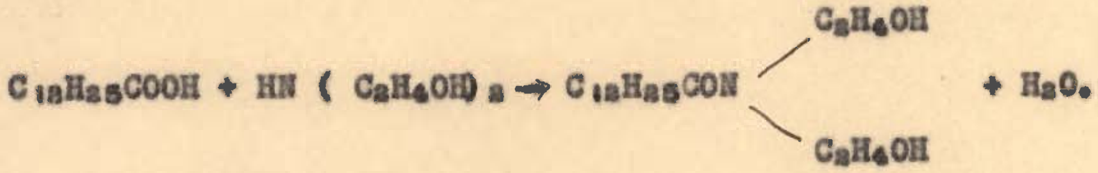
The problem of polarographic maxima and electrocapillary curves reviewed above has been investigated mostly in presence of surface active substances like dyes, proteins, or ionic surfactants. Very few references, mentioning the use of non-ionic surfactants in these studies have so far been reported. Probably the only exception is Triton X-100, mentioned by Meits (9) and Colichman (25). In this chapter, the use and relative merits of some new non-ionic surfactants as maximum suppressors for simple and complex metal ions and their effect on the electrocapillary curves in potassium chloride as the extraneous electrolyte is described. The results obtained from these studies have been compared with one or two typical ionic surfactants.

EXPERIMENTAL

PREPARATION OF LAURIC ACID DIETHANOLAMINE CONDENSATE(LDC).

Lauric acid diethanolamine condensate (LDC) was prepared in the laboratory by the method recommended by Kritchevsky (44). The conditions used for obtaining it were briefly as follows.

One mole of lauric acid (B.D.H.) and two moles of diethanol amine were mixed in a porcelain disc. The mixture was heated to about 150-170°C on an oil bath for about one hour. At this temperature, water got slowly distilled off. The formation of the lauric acid diethanolamine condensate or lauryl diethanolamide took place according to the equation:



$$C_{12}H_{25}COOH + HN(C_2H_4OH)_2 \rightarrow C_{12}H_{25}CON(C_2H_4OH)_2 + H_2O.$$

The fuel product obtained was a clear yellowish brown liquid of high viscosity. It was readily soluble to a clear solution in water and had a pH of about 9.00.

REAGENTS.

Non-ionic surface active substances viz; Nonidet P40 (100% poly ethylene oxide condensate), Nonidet P42 (condensation product of dioctyl phenol and ethylene oxide), and Nonex 501 (methoxy poly ethylene glycol laurate) and cationic surface active substances viz., cetyltrimethyl ammonium bromide (CTMAB) and cetyl pyridinium bromide

(CPB) were all BDH products. All were used without further purification.

Lauric acid diethanolamine condensate was prepared in the laboratory. Their solutions were prepared in double distilled water (all glass).

Solutions of lead nitrate,nickel chloride,cobalt chloride,copper sulphate and cadmium iodide were prepared by dissolving A.R.samples in double distilled water. The strength of the solutions were determined by usual methods. Solutions of potassium nitrate,potassium chloride and potassium iodide were also prepared with A.R.samples.

Pyridine used in studying the polarograms of Ni^{++}-Co^{++} mixture was obtained by distilling A.R.sample. A.R. glycine was used while biuret was prepared in the laboratory (45).

APPARATUS.

Polarographic measurements were made using Heyrovsky polarograph (No.Lp 55A) operated manually in conjuction with a pye scalamp galvanometer (No.7903/5) in the external circuit. Dropping mercury electrode was used as the cathode whereas saturated calomel electrode as the reference electrode. Triple distilled pure mercury was used throughout the measurements. Nitrogen (purified by passing through alkaline solution of pyrogallol and chromous chloride) was passed in the polarographic cell

(S-type) to keep an inert atmosphere. The height of mercury reservoir was kept at a constant height (60.0 cms.). Polarographic capillary (Gallen Kamp) with drop time 4.30 second was used. All the measurements were carried out at 25 ± 0.1°C using a thermostatic water bath. All the pH measurements were made with the help of a Beckman pH meter Model H.

PROCEDURE.

Polarographic measurements were carried out after putting a known volume of the metal salt or the complex metal ion solution in the polarographic cell,making up the total volume 20.0 ml. after adding the supporting electrolyte. The solutions were deaerated by bubbling purified nitrogen gas through them for about 10 minutes. The polarogram was taken and the same procedure was then repeated in the presence of surface active agents. Increasing amounts of the surfactant solutions were added by microburette until the maximum was completely eliminated. The results are depicted in the figs.1-44.

ELECTROCAPILLARY CURVES METHOD.

The solutions of concentration 0.1M KCl were deaerated by bubbling nitrogen in the polarographic cell (H-type) . At least 20 drops were counted and drop time measured by means of a stop watch. Each set of measurements at a constant potential were repeated three times. The electrocapillary data were obtained from 0.0 to -1.2 volt (S.C.E.). The electrocapillary data were repeated in the presence of different concentrations of the surfactant. The results are shown in the figs.45-49.

—

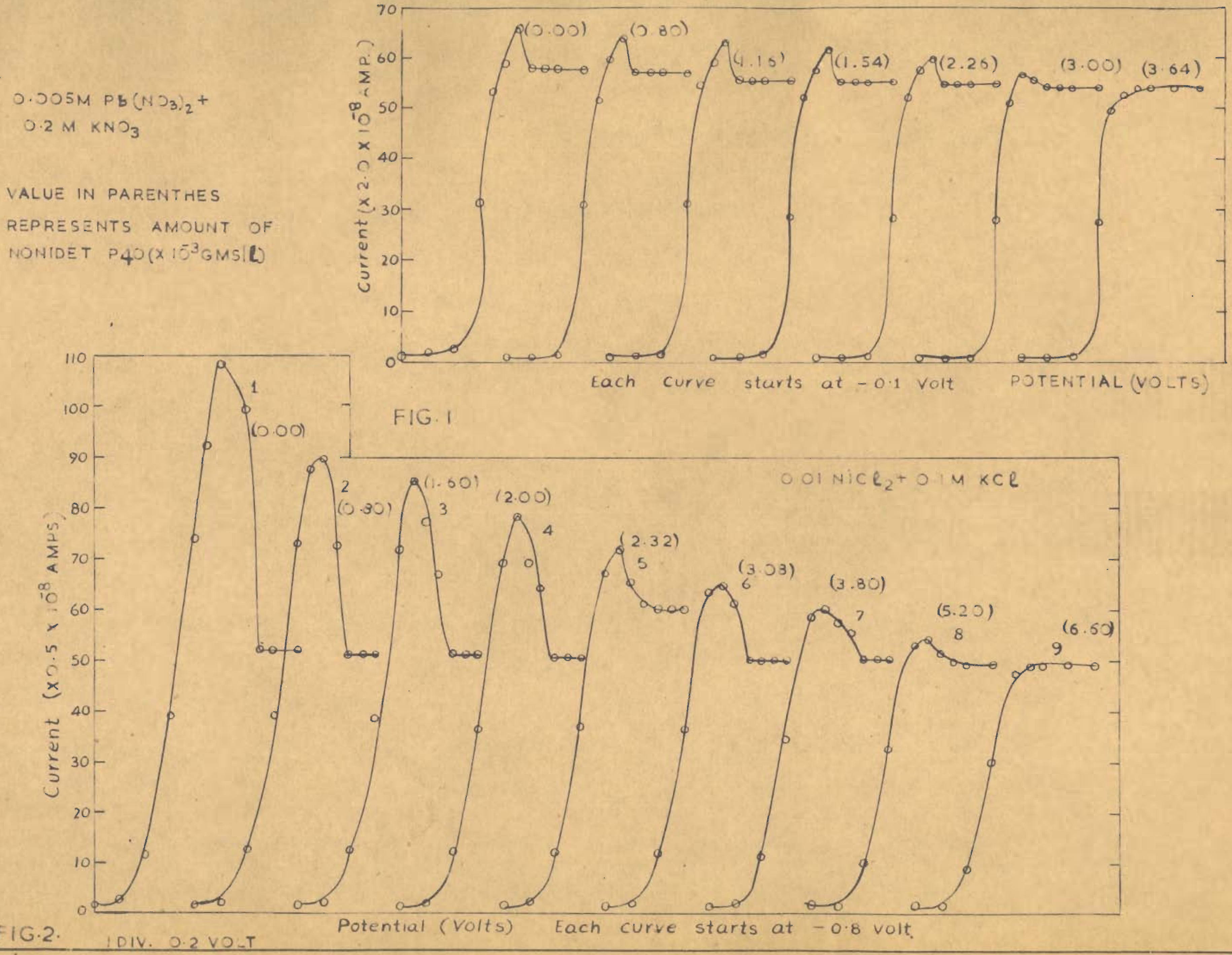
0·005M Pb(NO3)2 +
0·2 M KNO3
VALUE IN PARENTHES
REPRESENTS AMOUNT OF
NONIDET P40(x 10⁻³GMS/L)
Current (x 2·0 x 10⁻⁸ AMP.)
70
60
50
40
30
20
10
0
(0.00)
(0.80)
(1.16)
(1.54)
(2.26)
(3.00)
(3.64)
Each curve starts at -0·1 Volt
POTENTIAL (VOLTS)
Current (x 0·5 x 10⁻⁸ AMPS)
110
100
90
80
70
60
50
40
30
20
10
0
1
(0.00)
2
(0.80)
3
(1.60)
4
(2.00)
5
(2.32)
6
(3.08)
7
(3.80)
8
(5.20)
9
(6.60)
0.01 NiCl2 + 0.1 M KCl
Potential (Volts)
Each curve starts at -0·8 volt
1 DIV. 0·2 VOLT

FIG. 1

FIG-2.

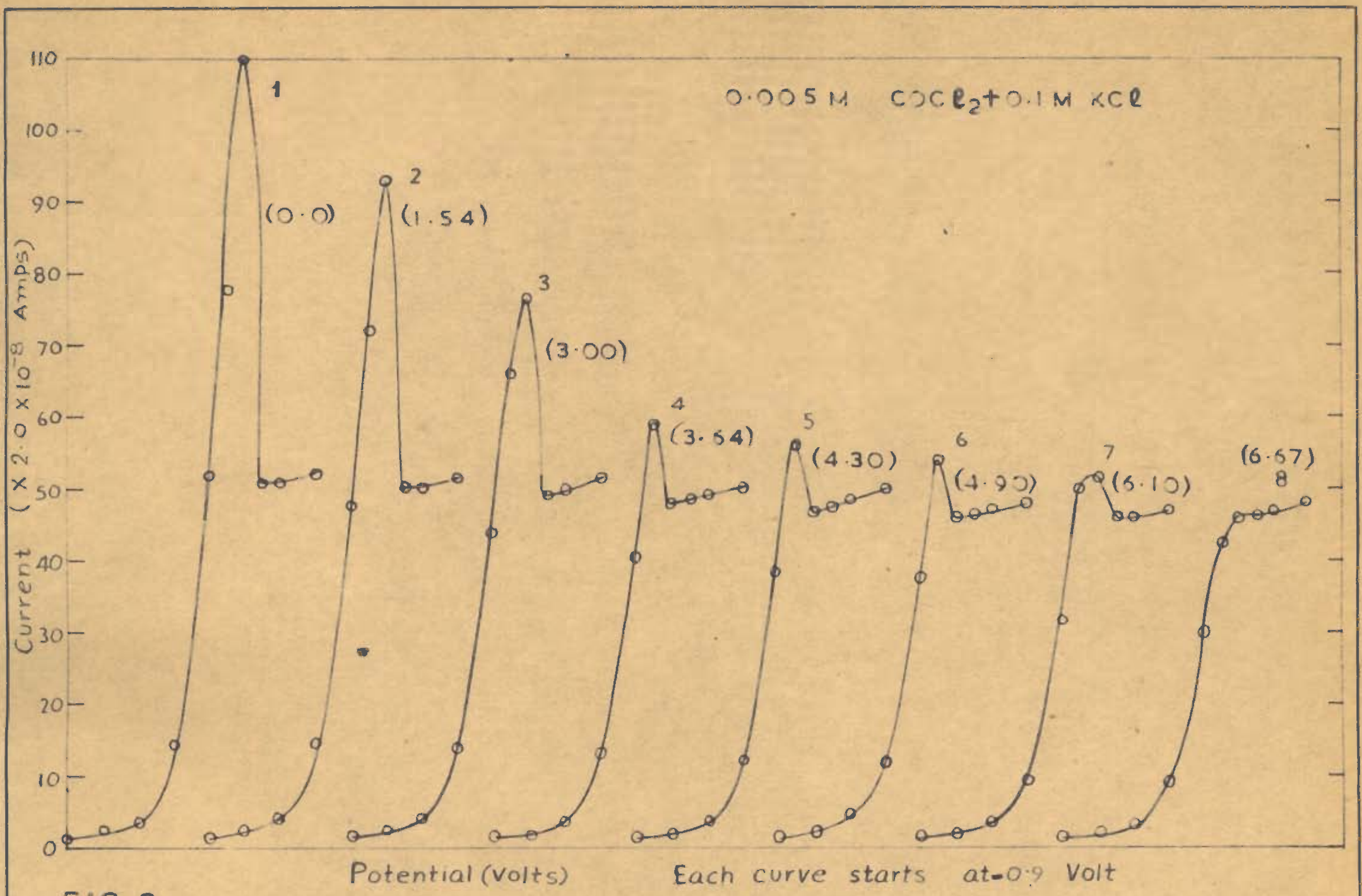


FIG. 3

VALUE IN PARENTHES REPRESENTS AMOUNT OF NONIDET P 40=(x 10^{-3} GMS/L)

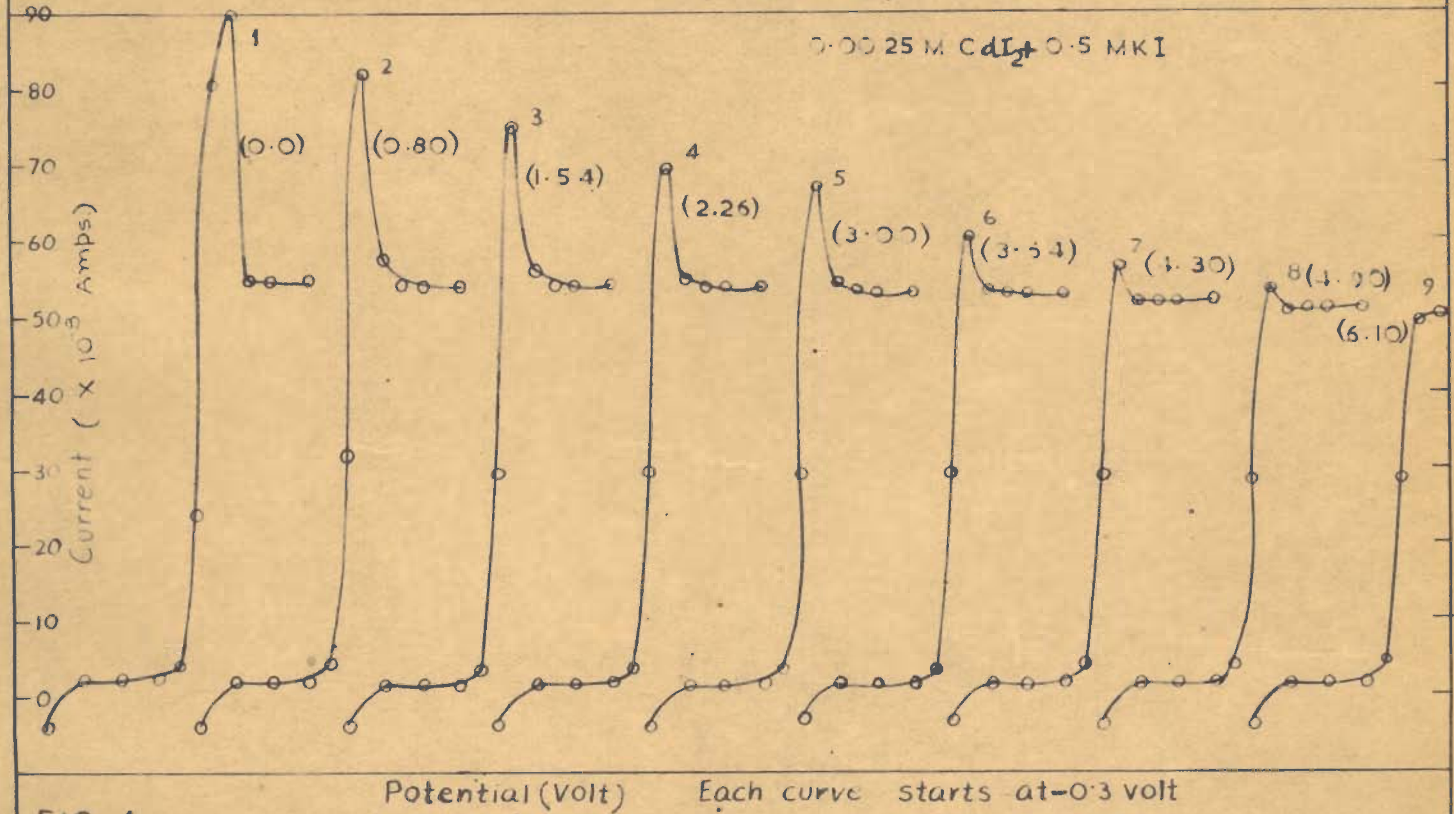


FIG. 4

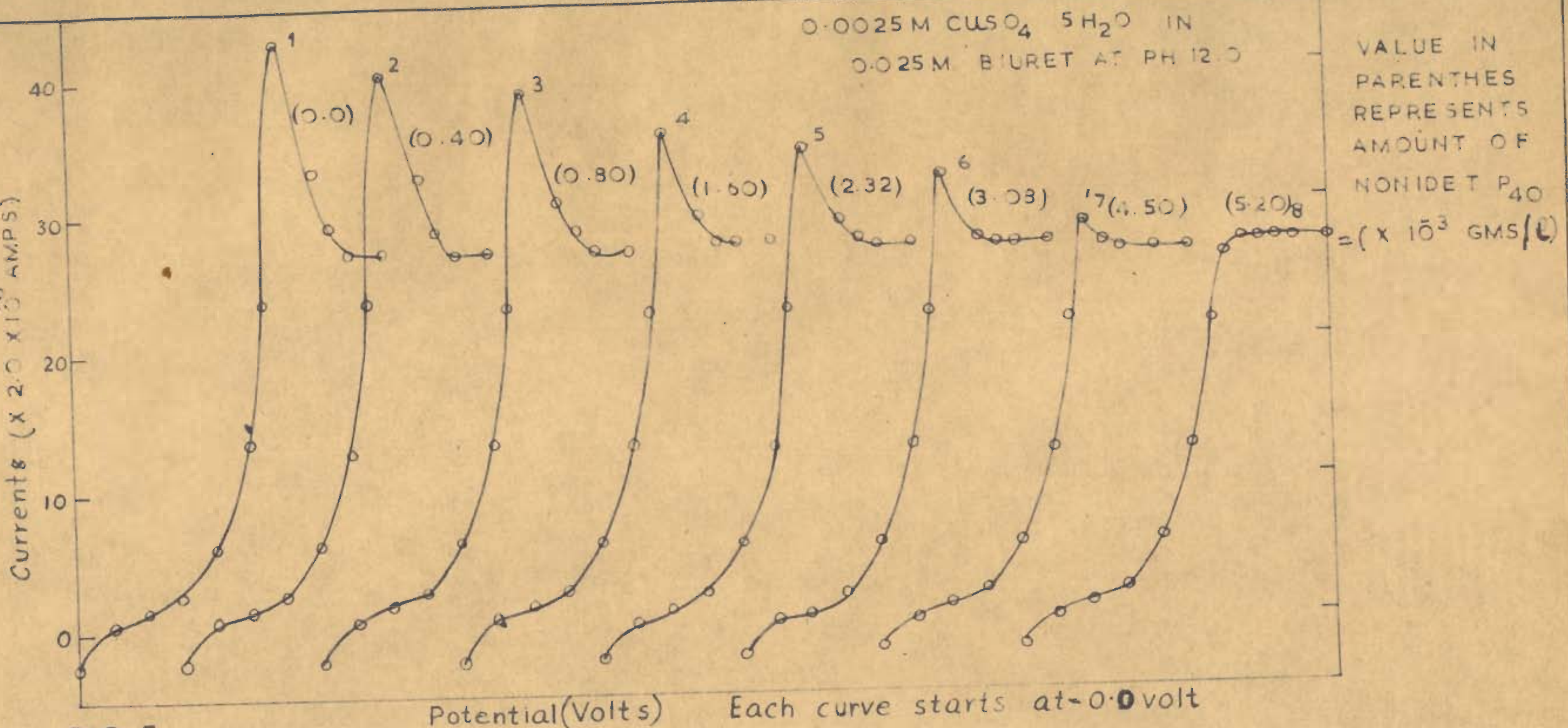
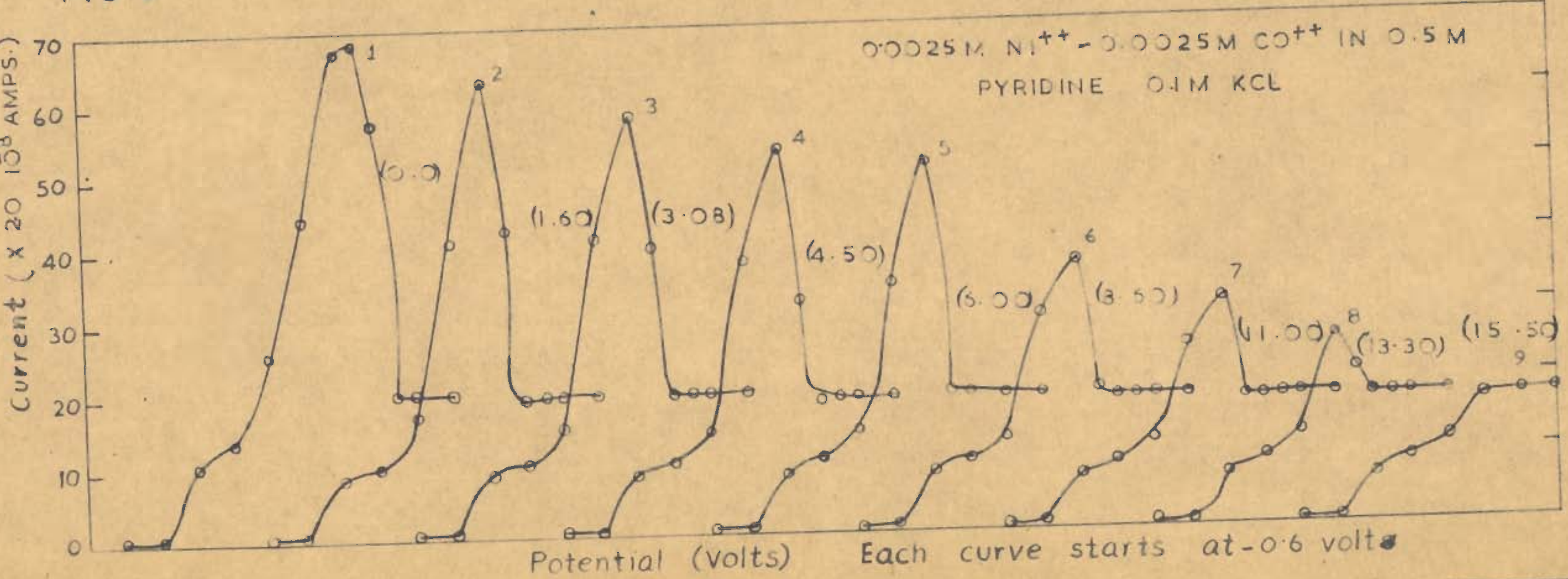


FIG.5



FIG·6 1 DIV.=0.2 VOLT

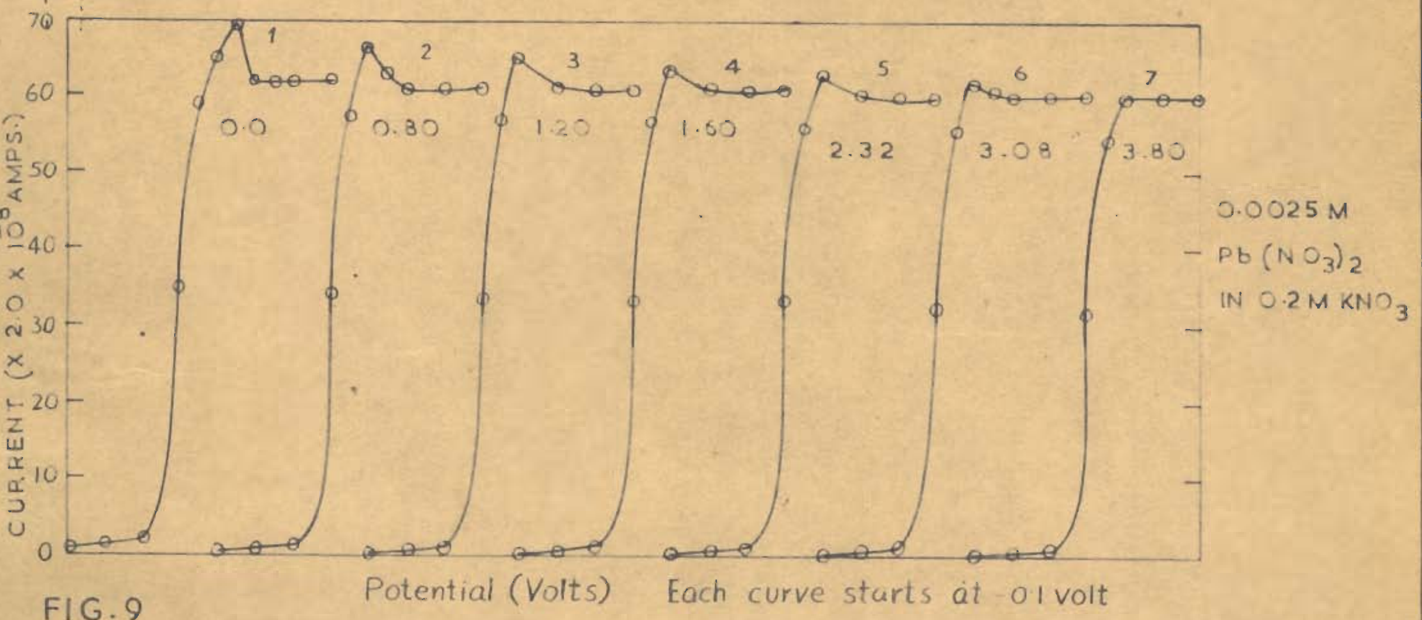


FIG. 9

VALUE IN PARENTHES REPRESENTS AMOUNT OF NONEX 501=(X 10^{-3} GMS/ℓ)

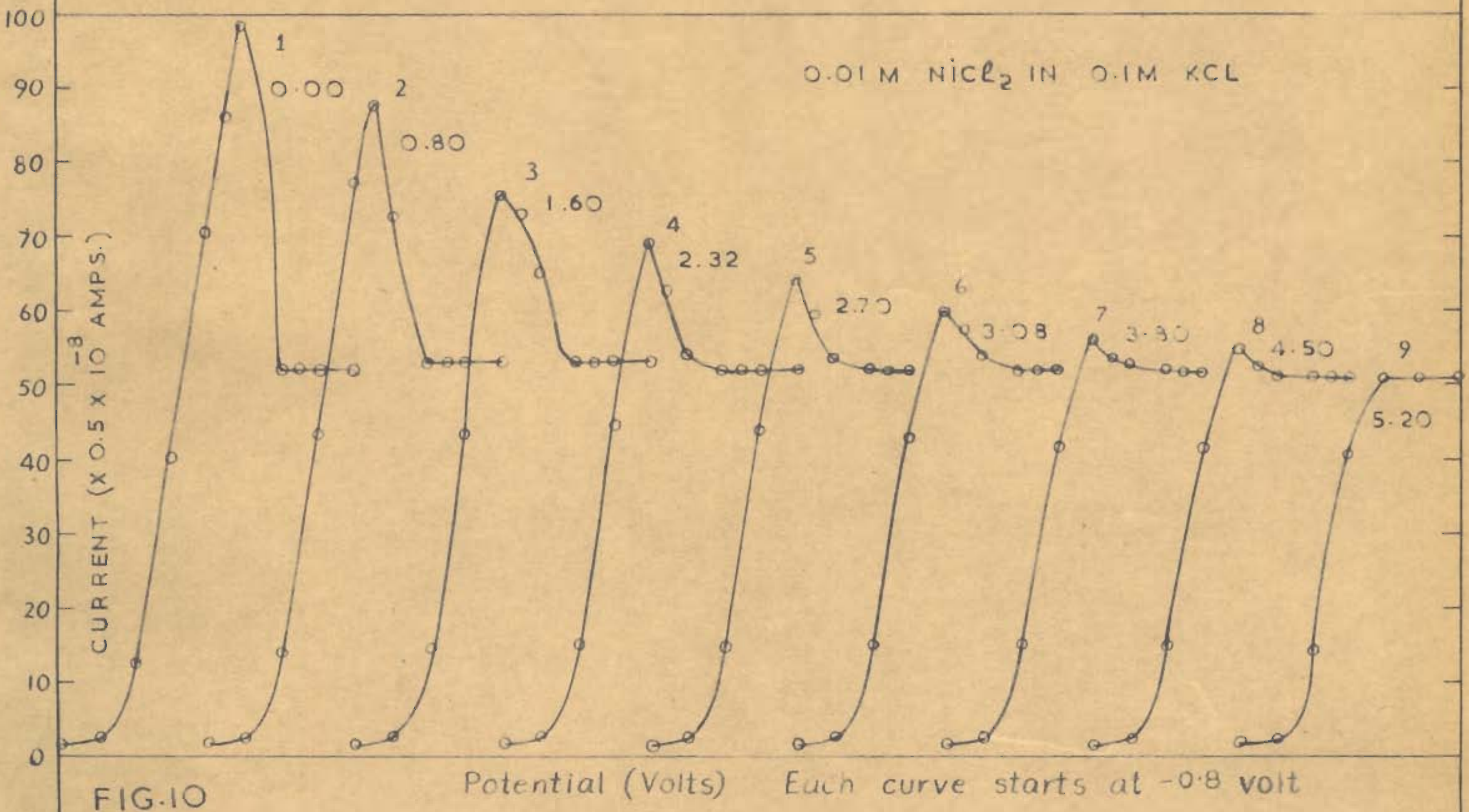


FIG. 10

1 DIV=0.2 VOLT

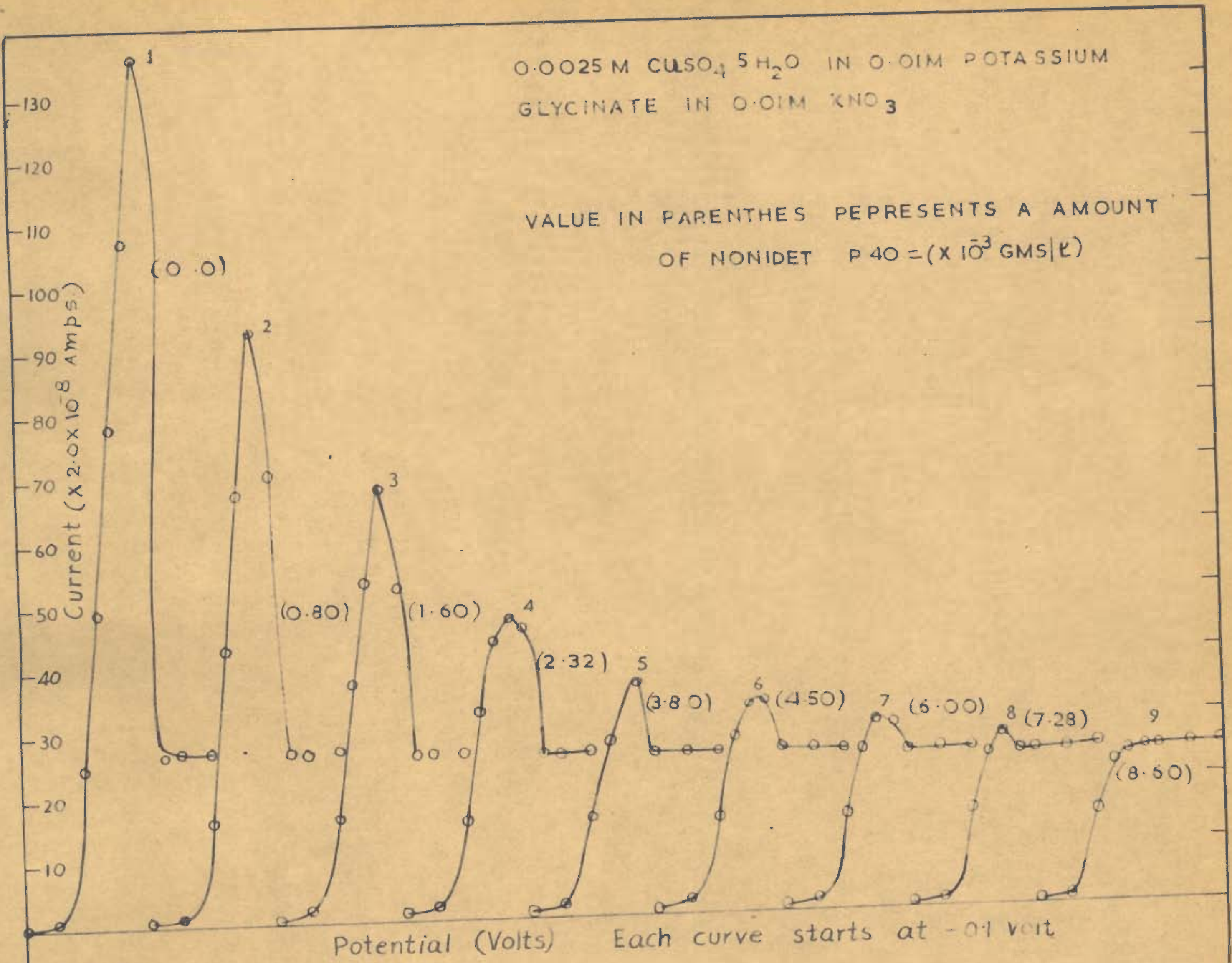


FIG.7

1 DIV = 0· 2 VOLT

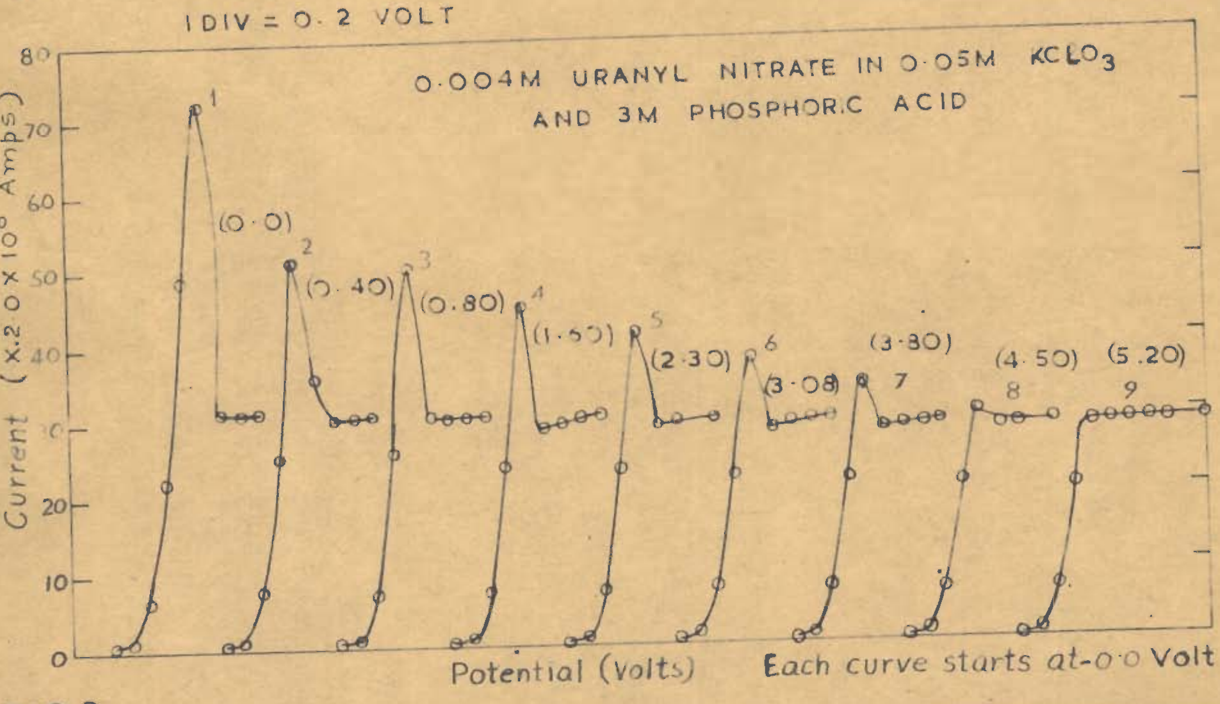
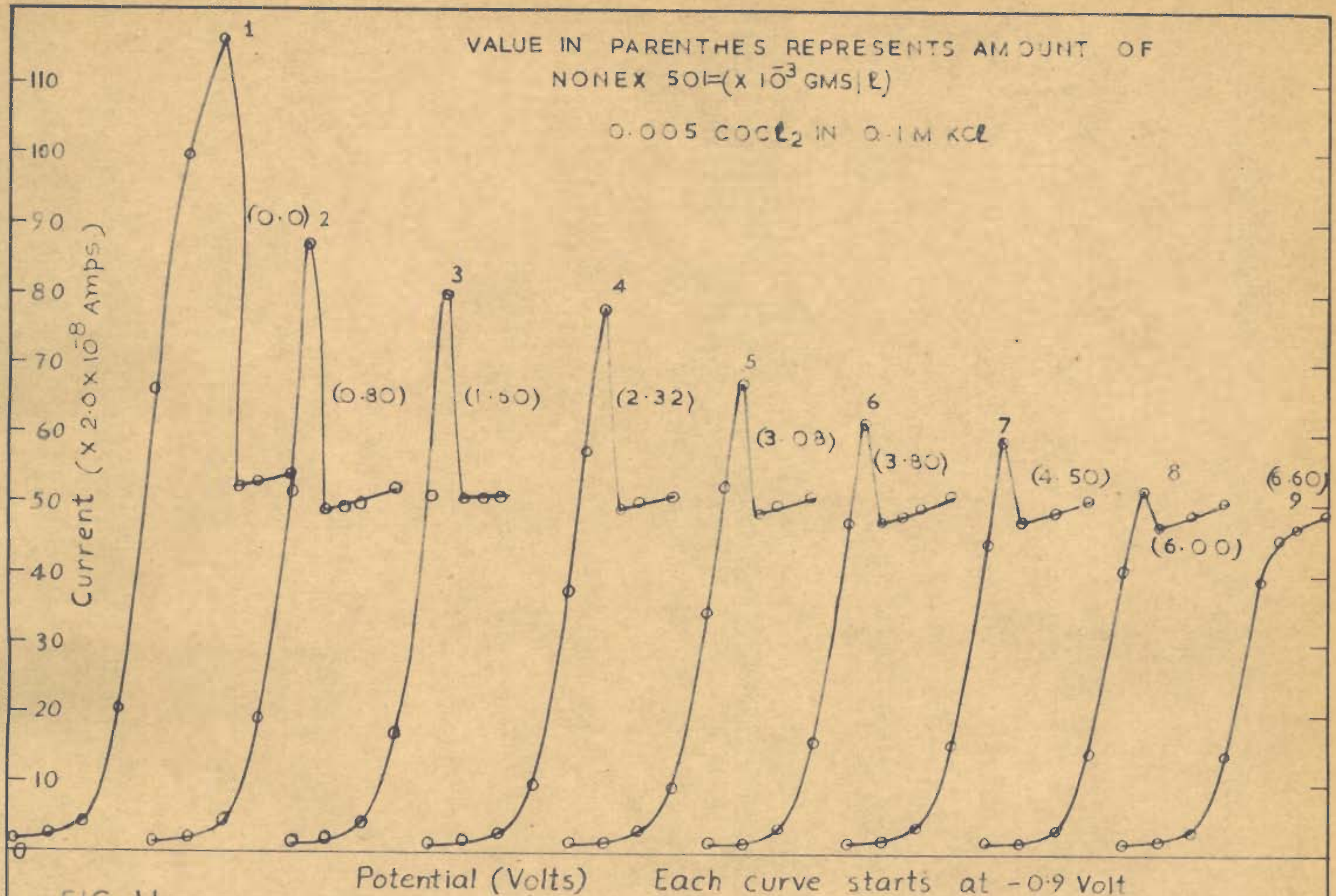
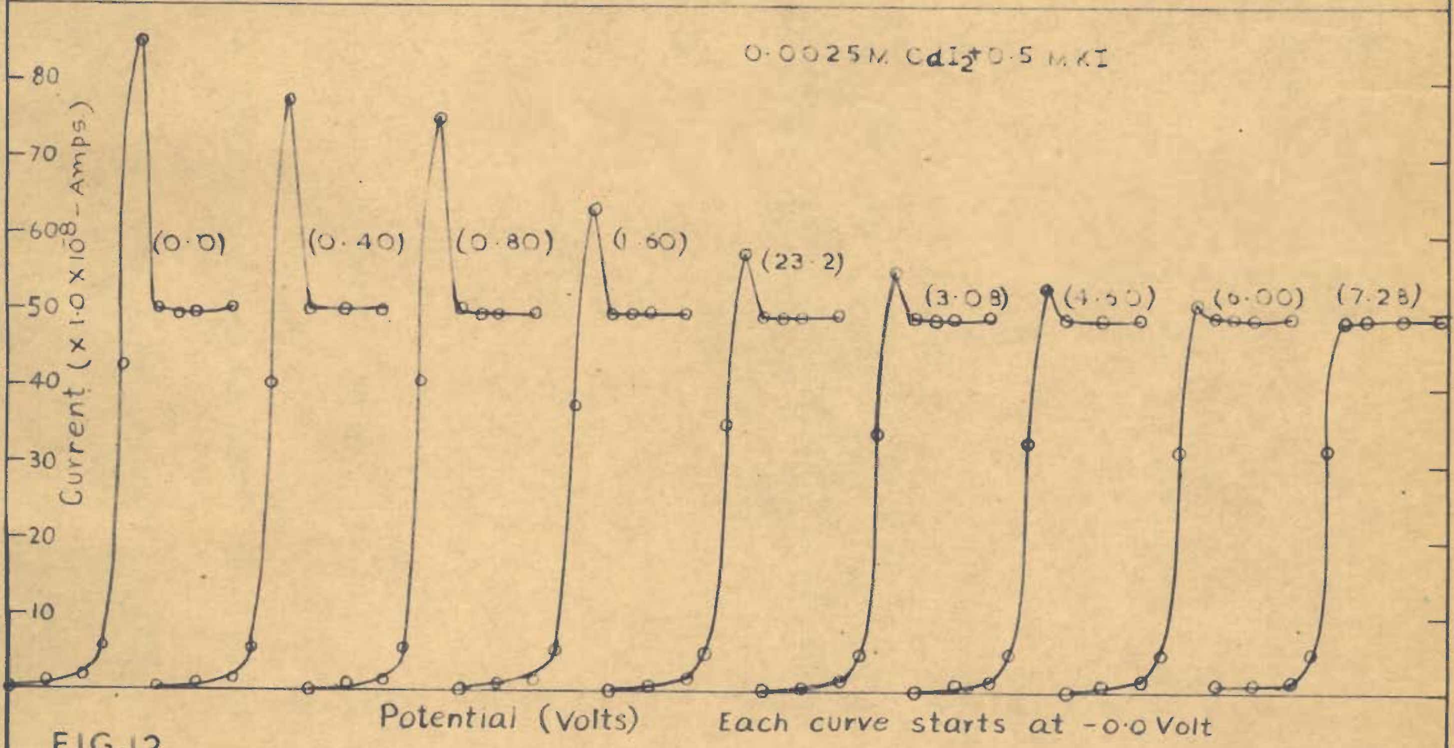


FIG.8

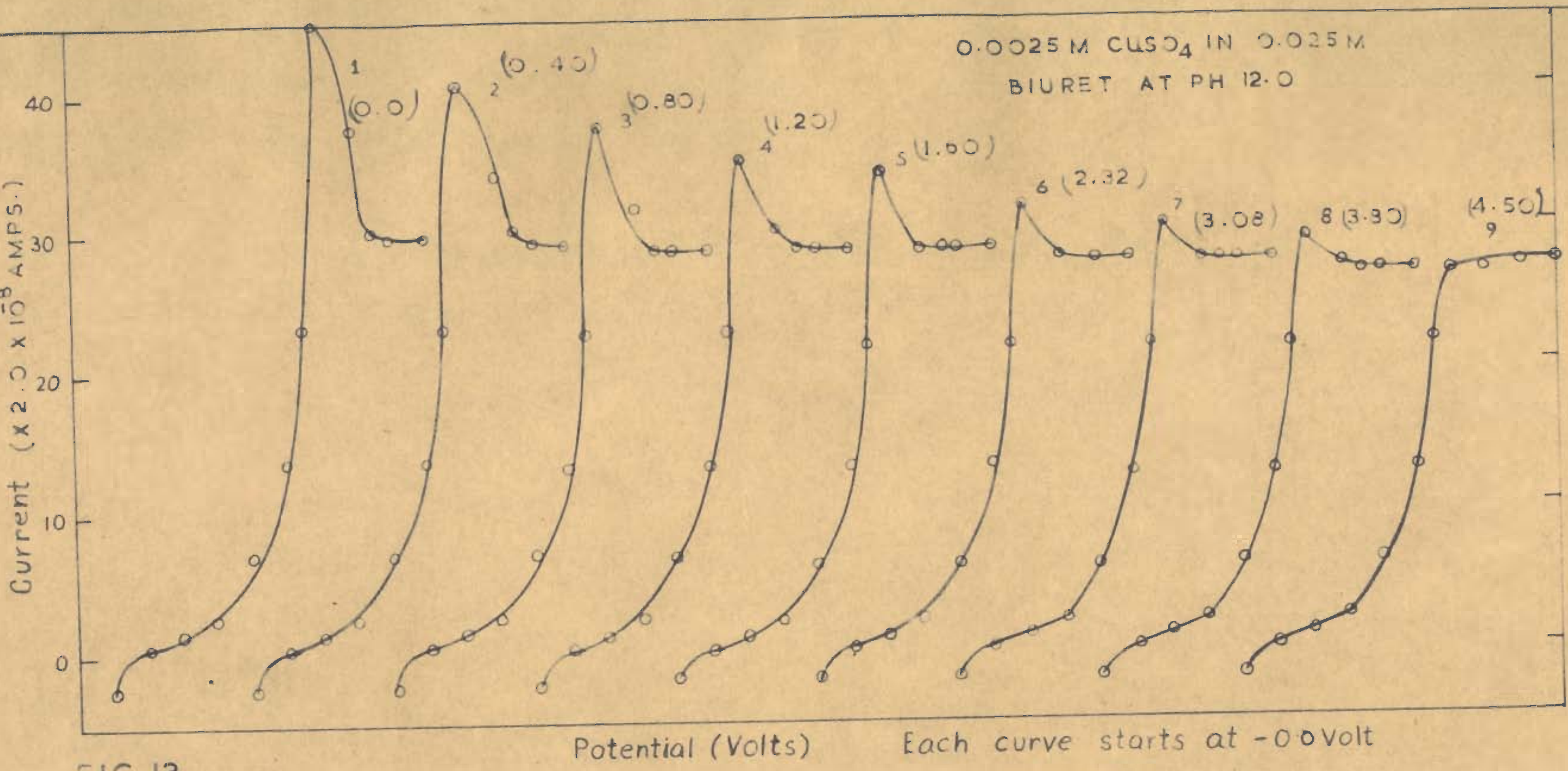


FIG·11



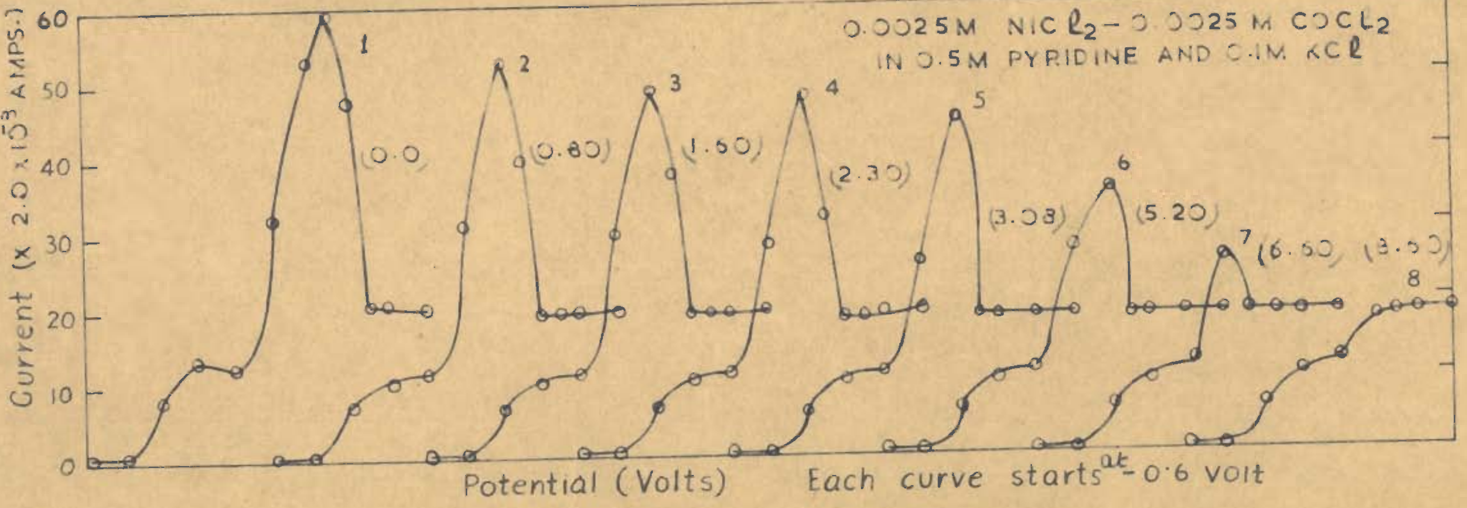
FIG·12

1 DIV. = 0·2 VOLT



FIG·13

VALUE IN PARENTHES REPRENTS AMOUNT OF NONEX 501(x 10^{-3} GMS/l)



FIG·14 1 DIV. = 0.2 VOLT

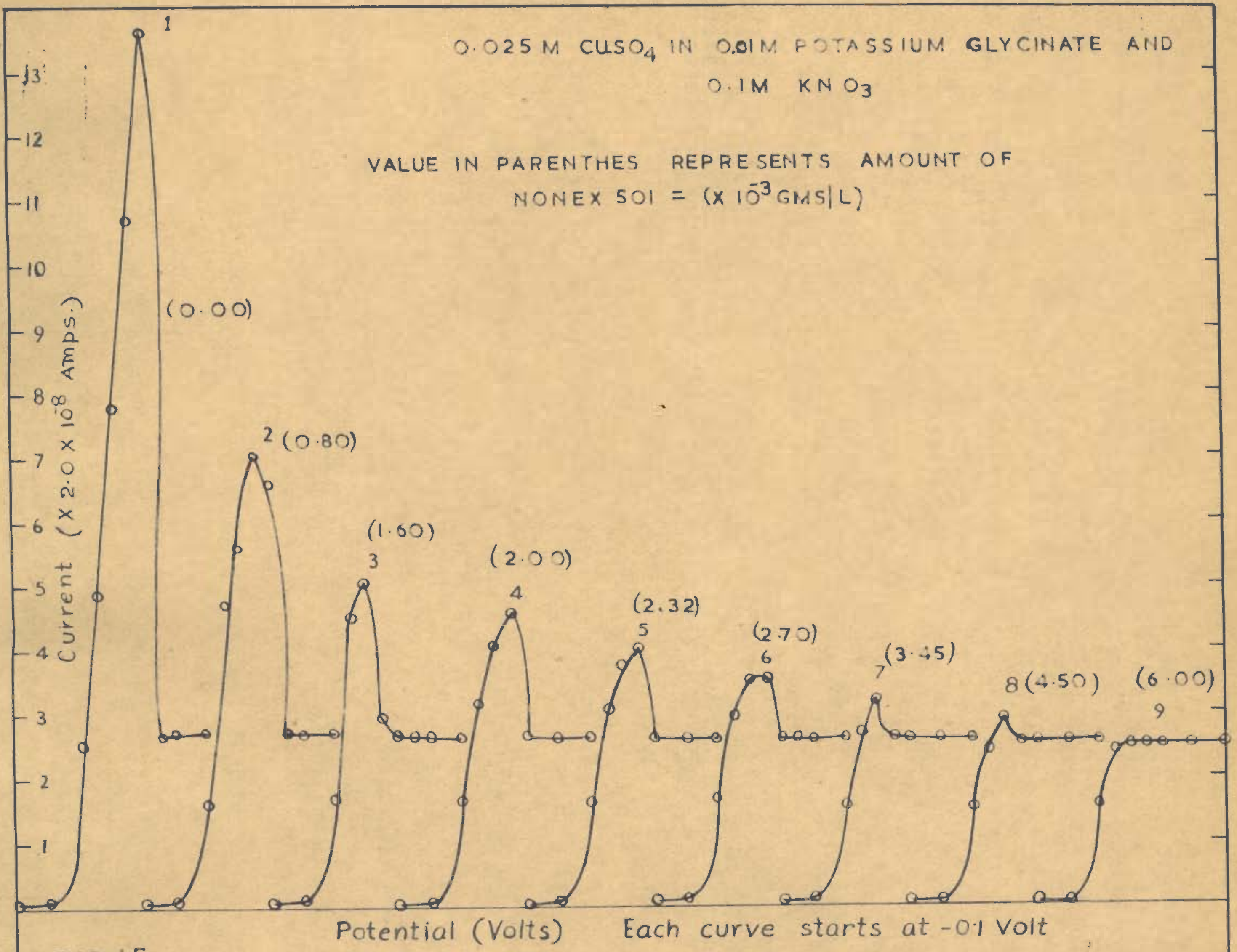

0·025 M CuSO4 IN 0.01 M POTASSIUM GLYCINATE AND
0·1 M KNO3
VALUE IN PARENTHES REPRESENTS AMOUNT OF
NONEX 501 = (X 10-3 GMS/L)
Current (X 2·0 X 10-8 Amps.)
13
12
11
10
9
8
7
6
5
4
3
2
1
1 (0·00)
2 (0·80)
3 (1·60)
4 (2·00)
5 (2.32)
6 (2·70)
7 (3·45)
8 (4·50)
9 (6·00)
Potential (Volts) Each curve starts at -0·1 Volt

FIG. 15

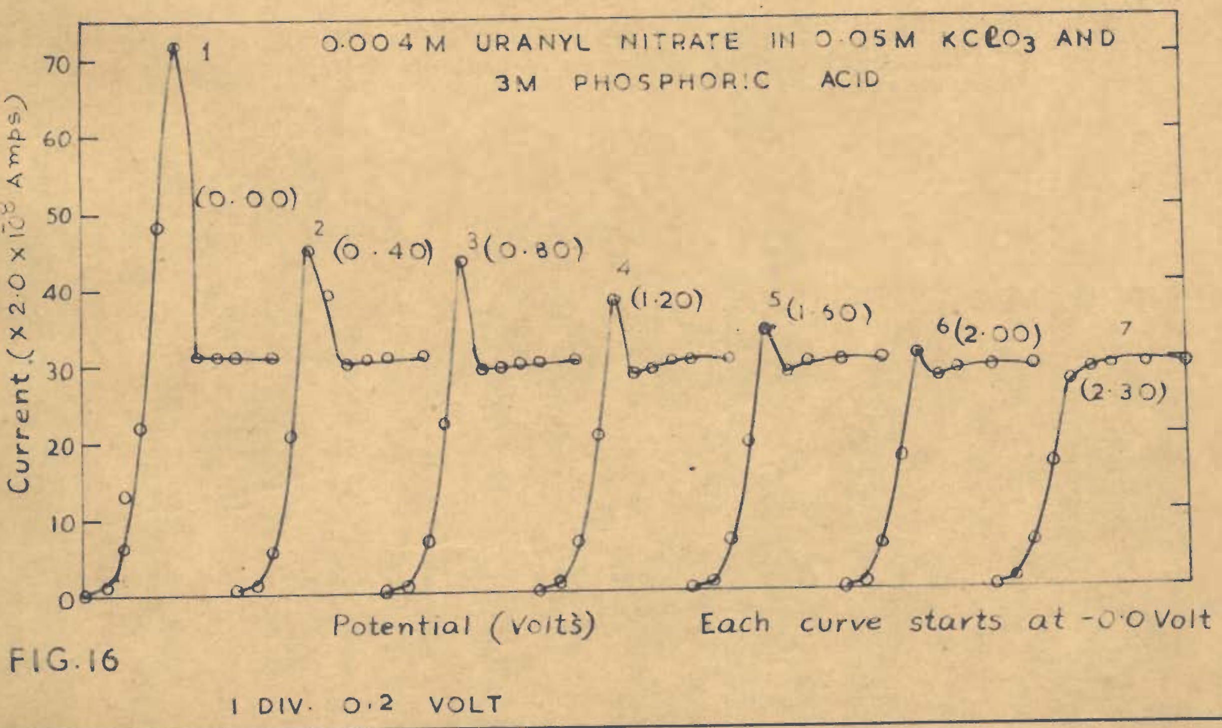

0·004 M URANYL NITRATE IN 0·05 M KClO3 AND
3 M PHOSPHORIC ACID
Current (X 2·0 X 10-8 Amps)
70
60
50
40
30
20
10
0
1 (0·00)
2 (0·40)
3 (0·80)
4 (1·20)
5 (1·60)
6 (2·00)
7 (2·30)
Potential (Volts) Each curve starts at -0·0 Volt
1 DIV. 0·2 VOLT

FIG. 16

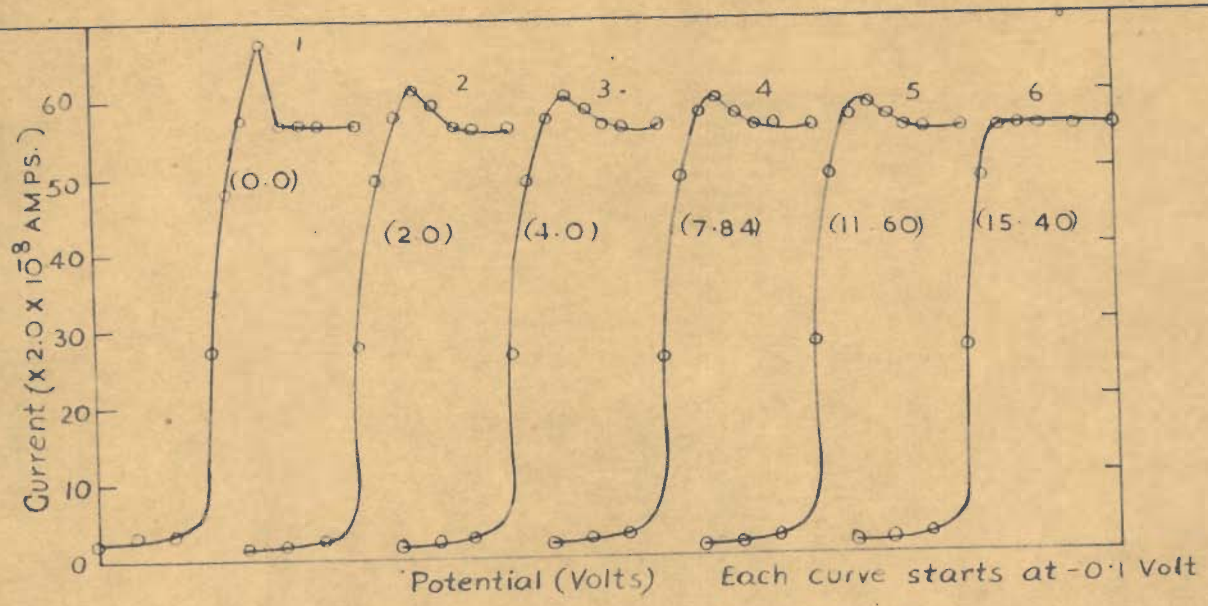
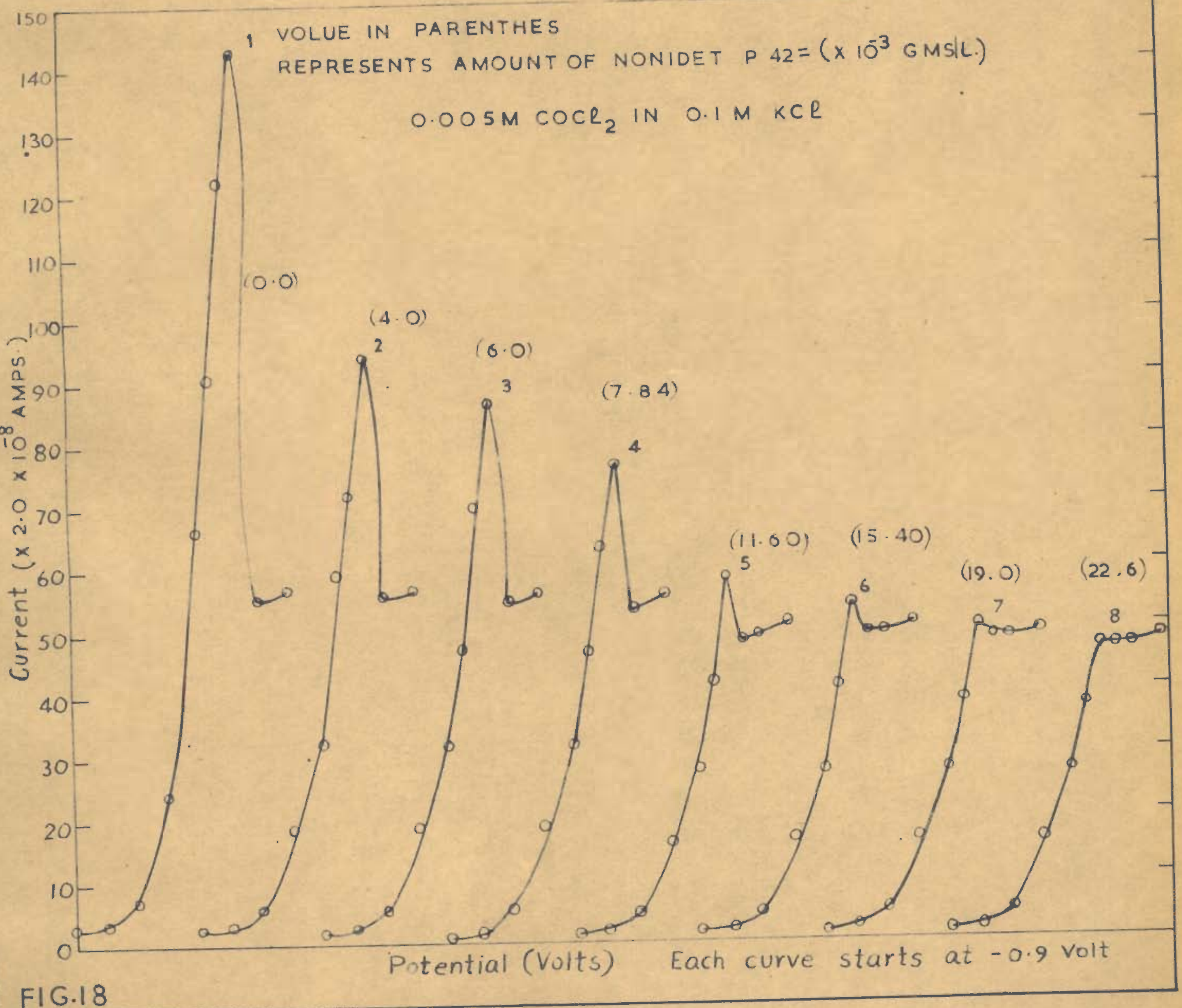


FIG 17

1 DIV. 0.2 VOLT

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



VOLUE IN PARENTHES
REPRESENTS AMOUNT OF NONIDET P 42 = (x 10^{-3} GMS/L.)

0.005M $CoCl_2$ IN 0.1 M KCl

FIG.18

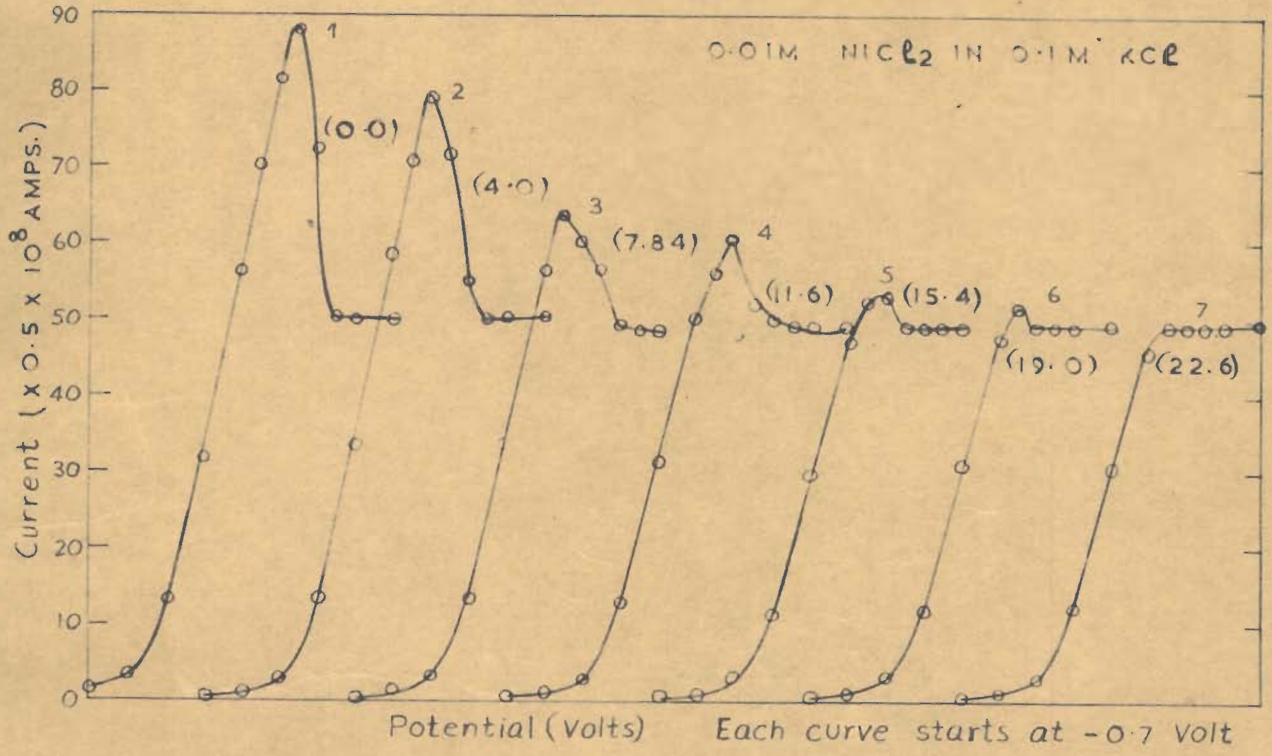


FIG.19 VALUE IN PARENTHES REPRESENTS THE AMOUNT OF NONIDET P 42 = (X 10^{-3} GMS/L)

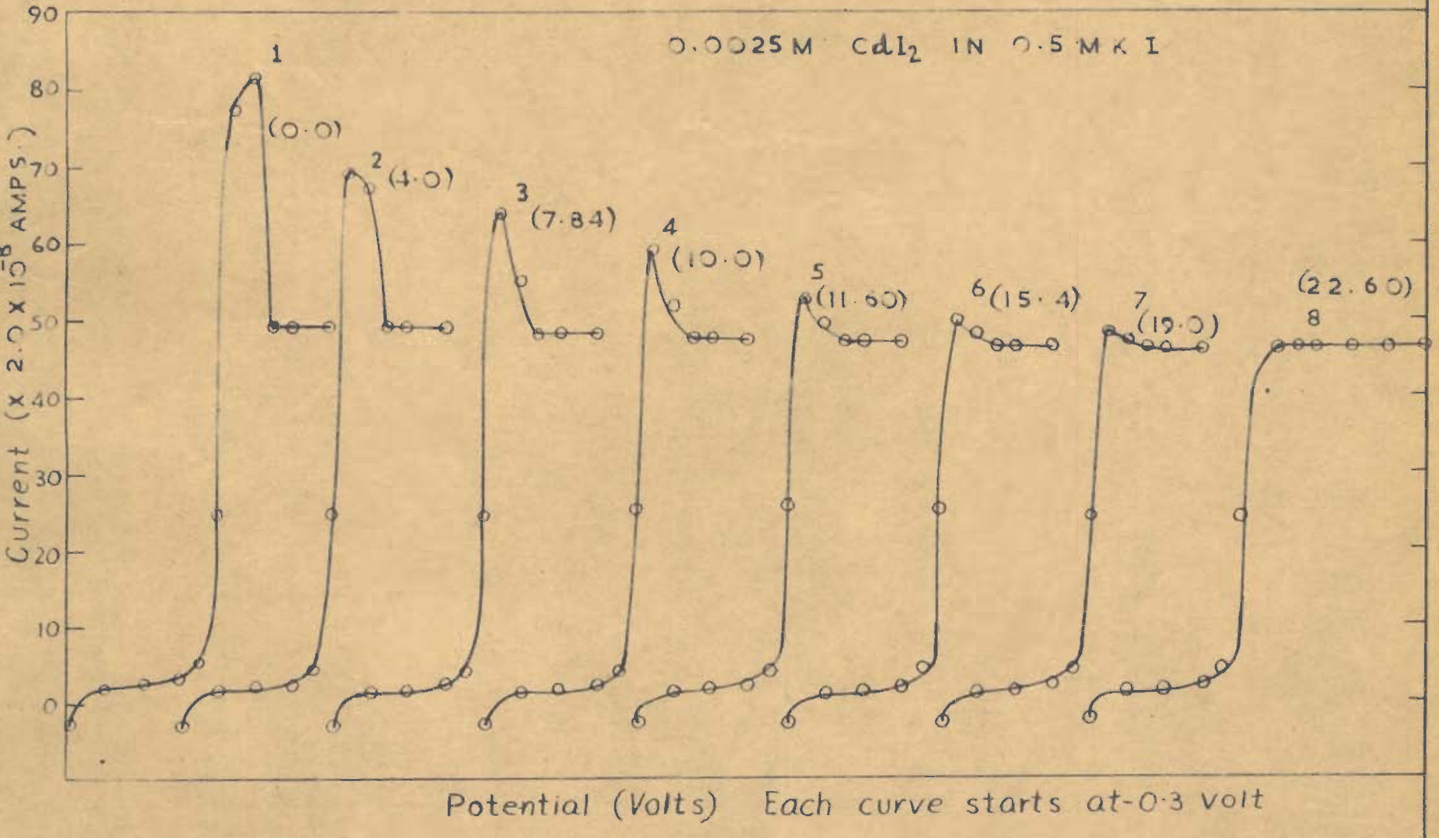
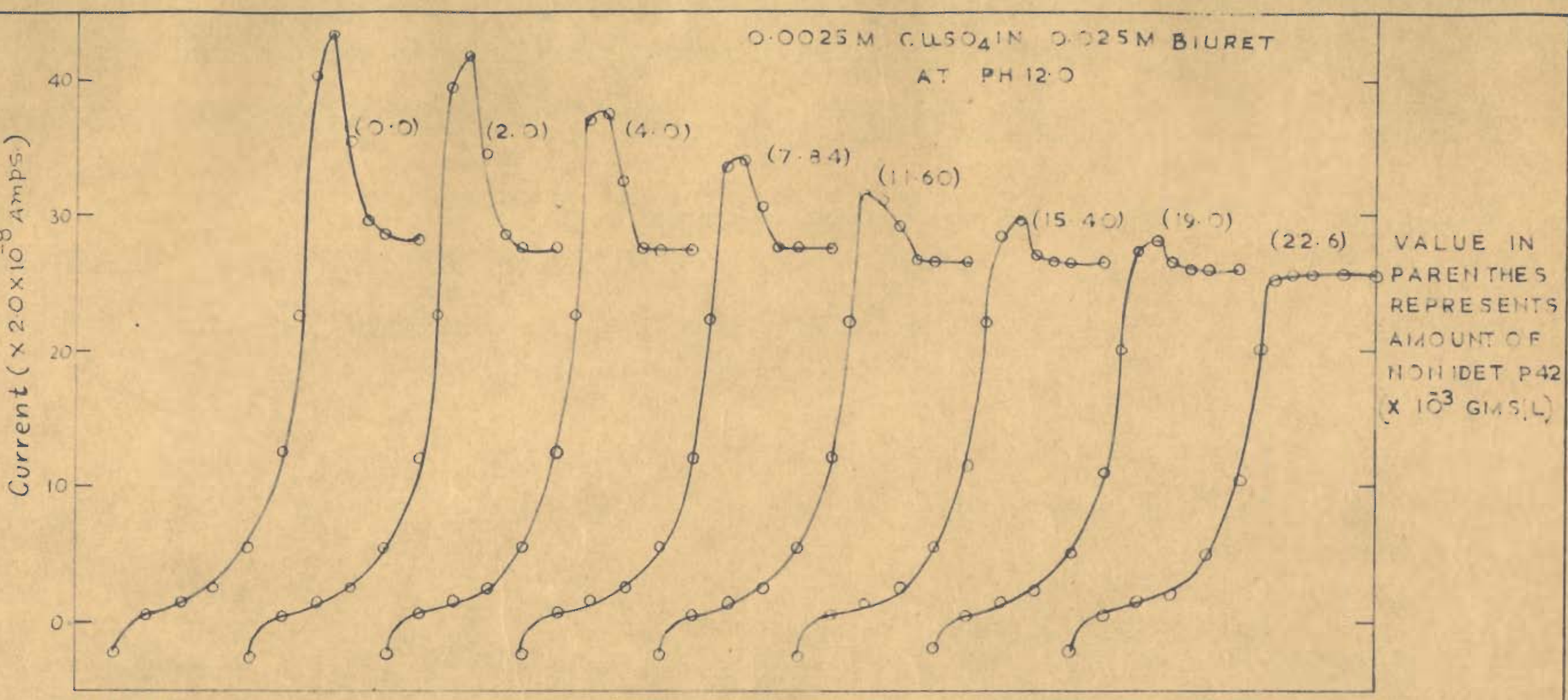


FIG.20

1 DIV. 0·2 VOLT



FIG·21

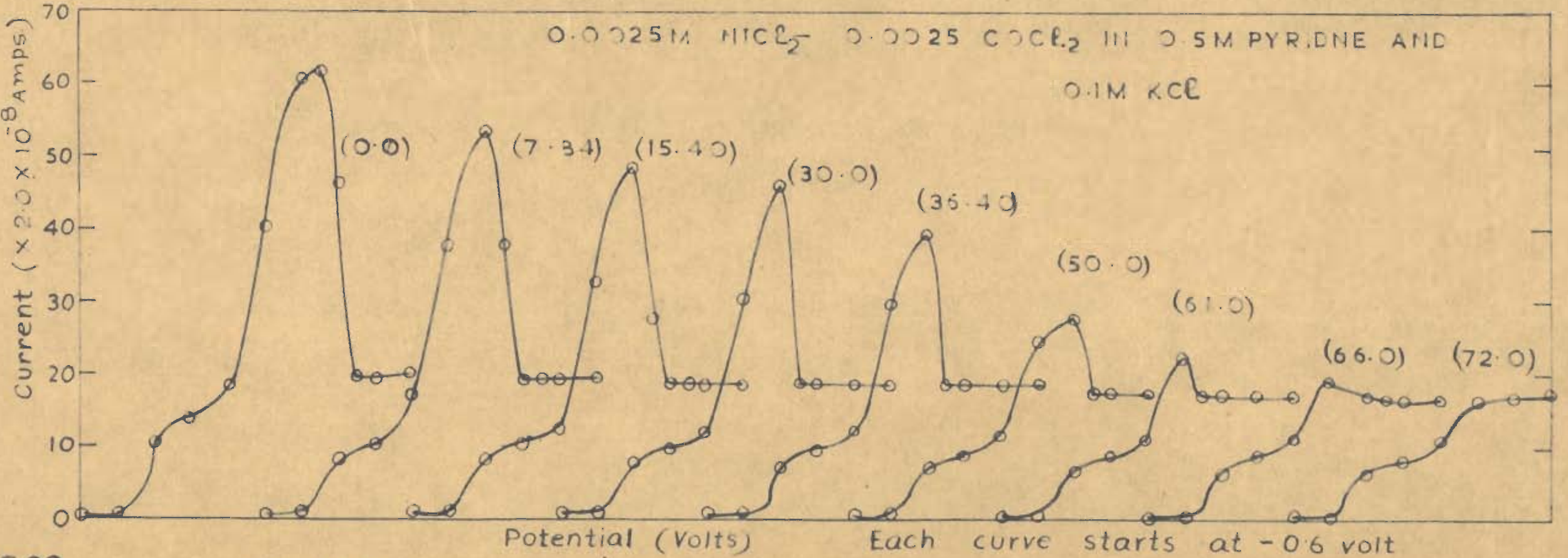


FIG 22

1 DIV 0·2 VOLT

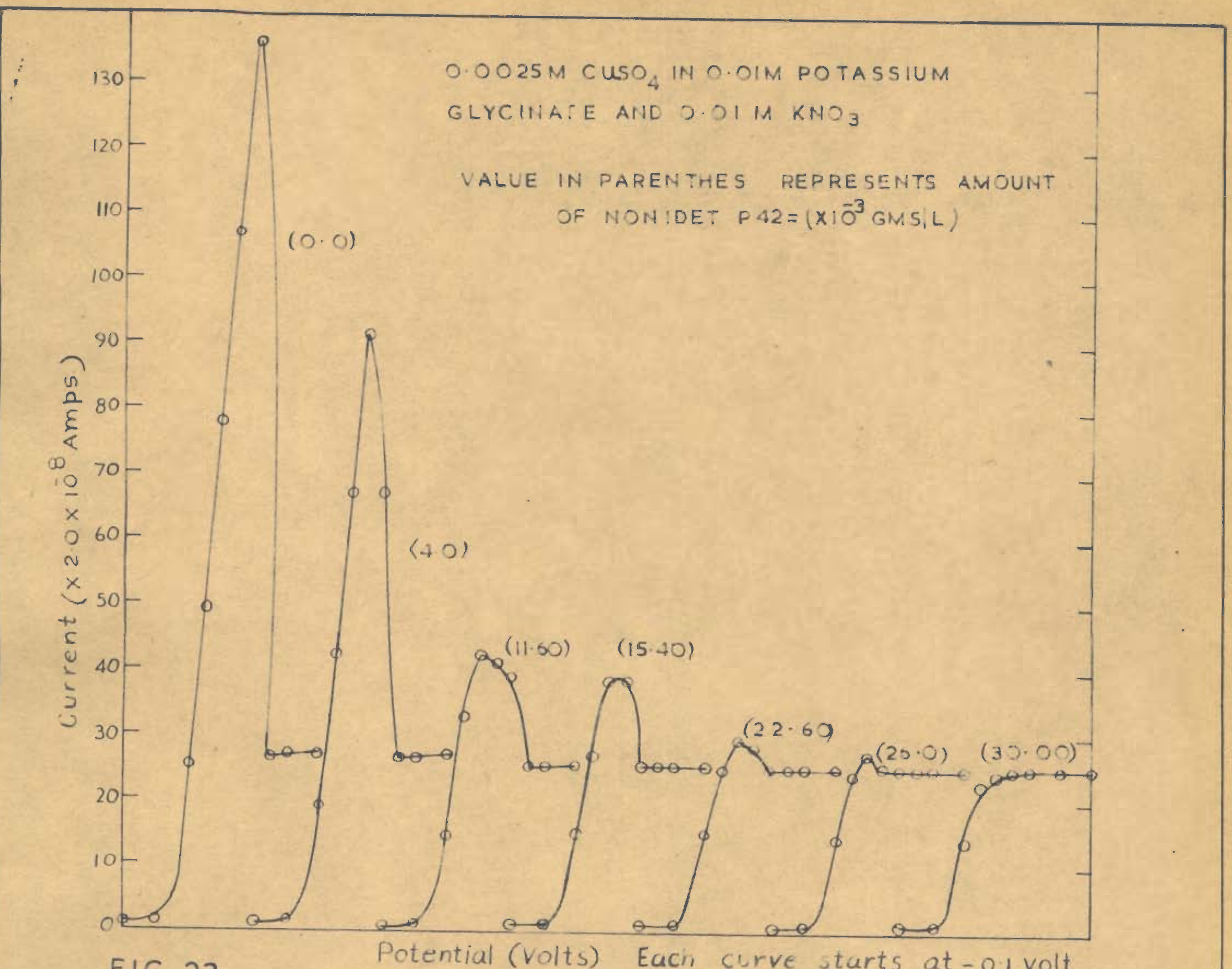


FIG. 23

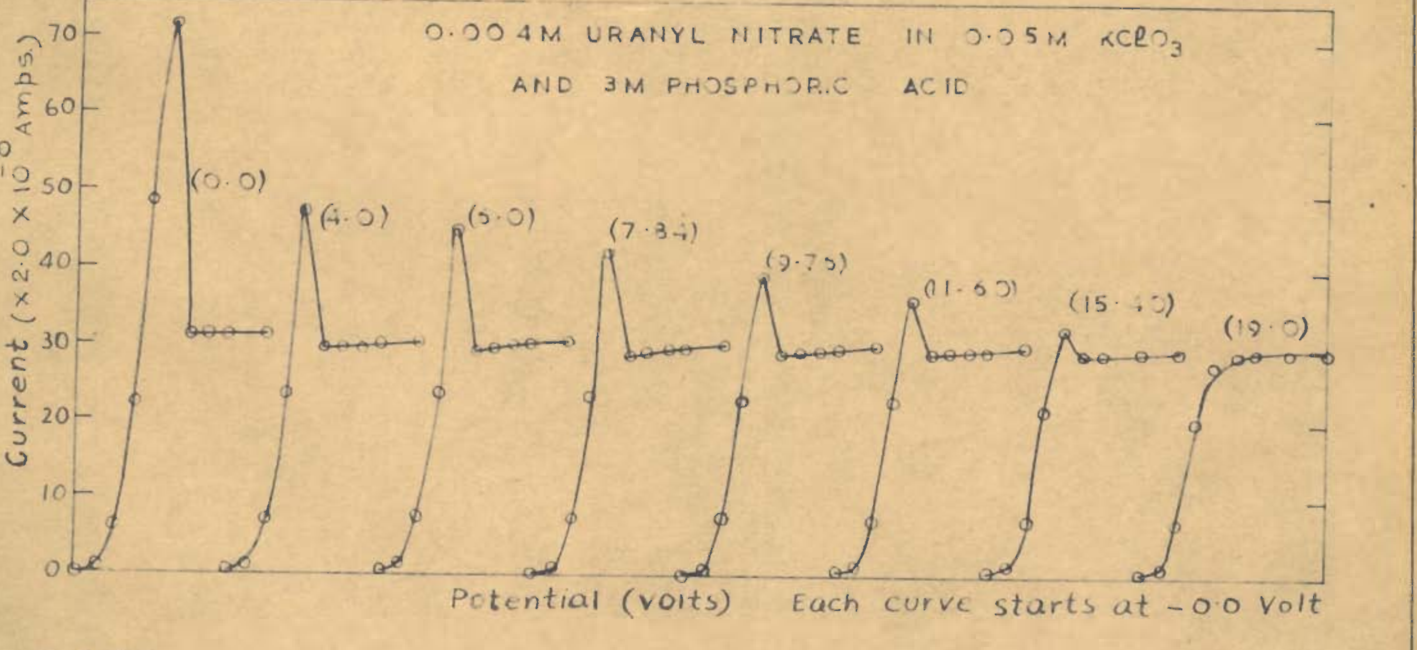


FIG. 24

1 DIV. = 0·2 VOLT

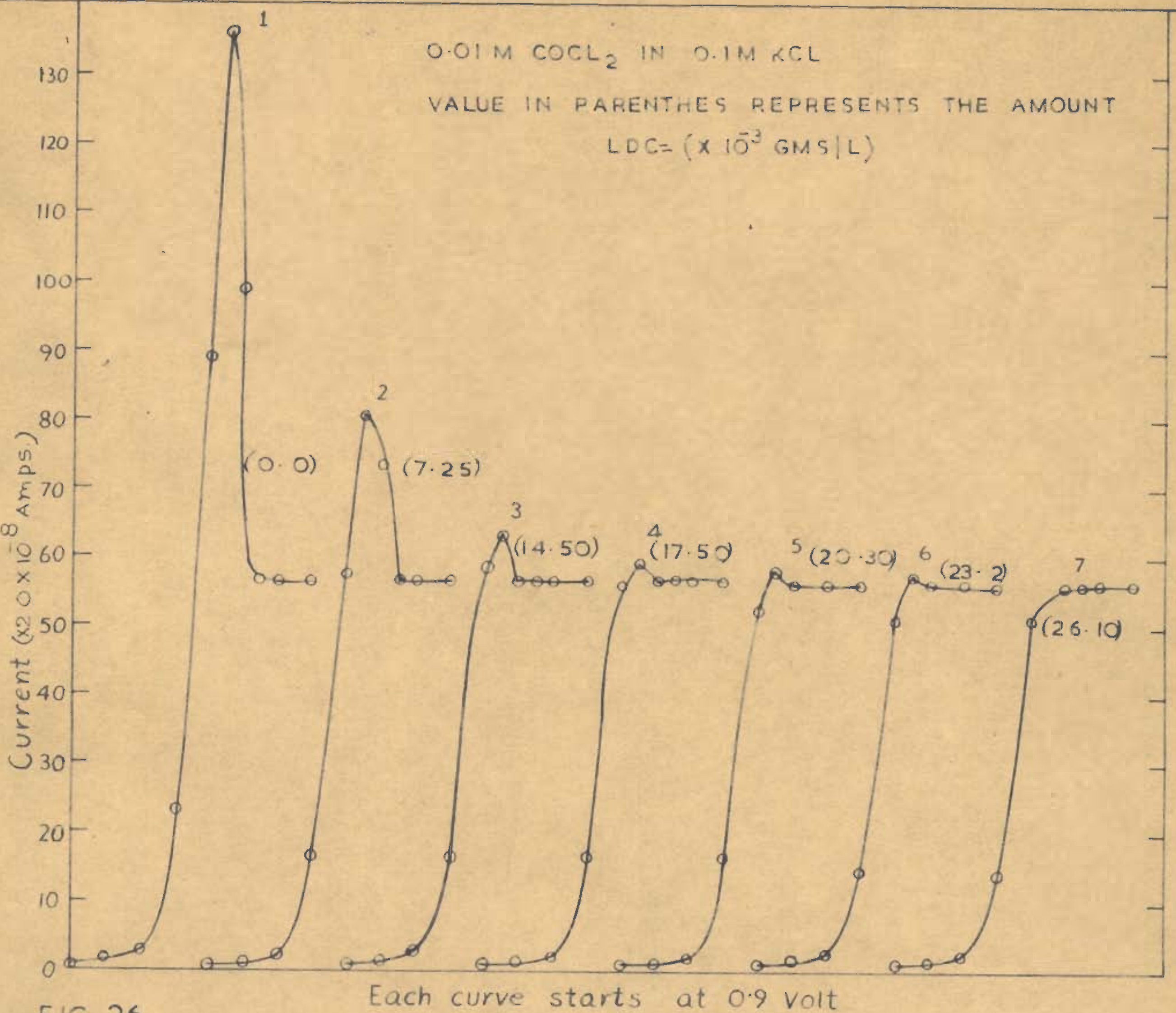

0·01 M COCL$_2$ IN 0·1M KCL
VALUE IN PARENTHES REPRESENTS THE AMOUNT
LDC= (x 10^{-3} GMS/L)
Current (x2·0 x 10^{-8} Amps)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
1
(0·0)
2
(7·25)
3
(14·50)
4
(17·50)
5
(20·30)
6
(23·2)
7
(26·10)
Each curve starts at 0·9 Volt

FIG. 26

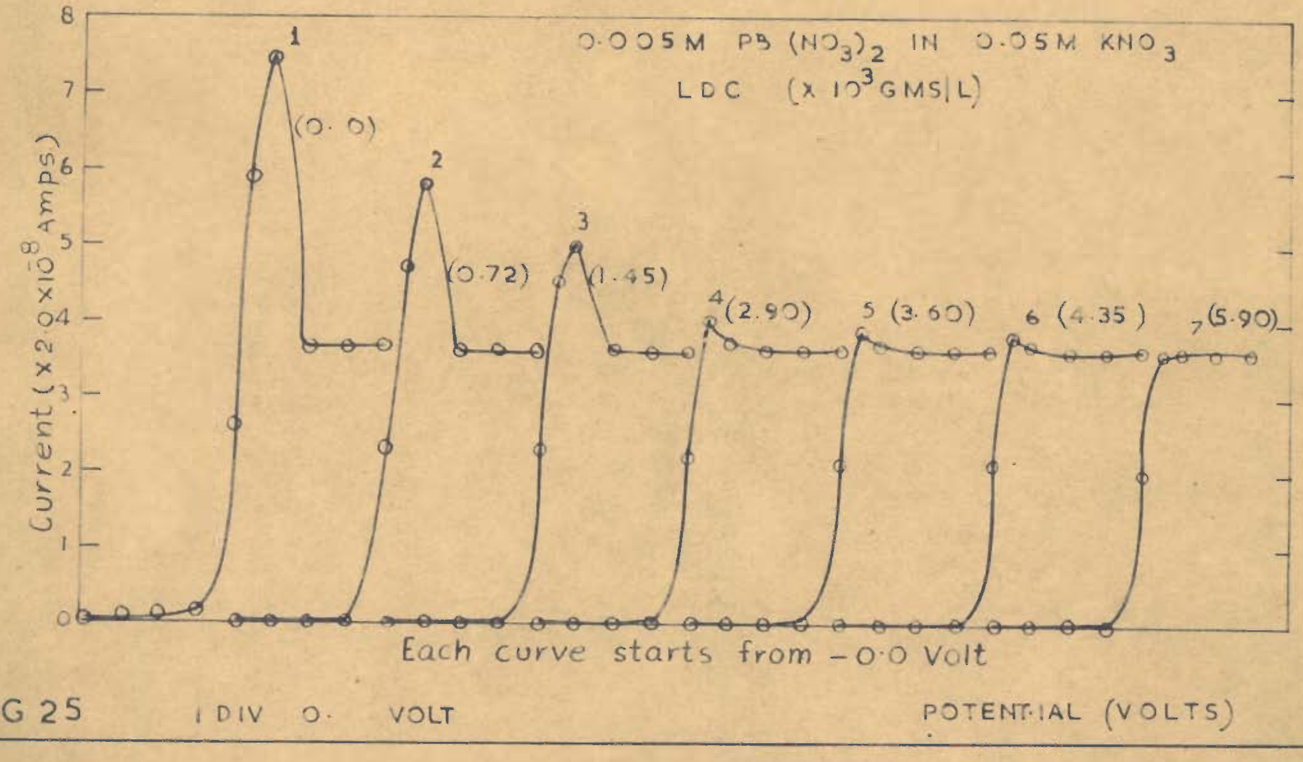
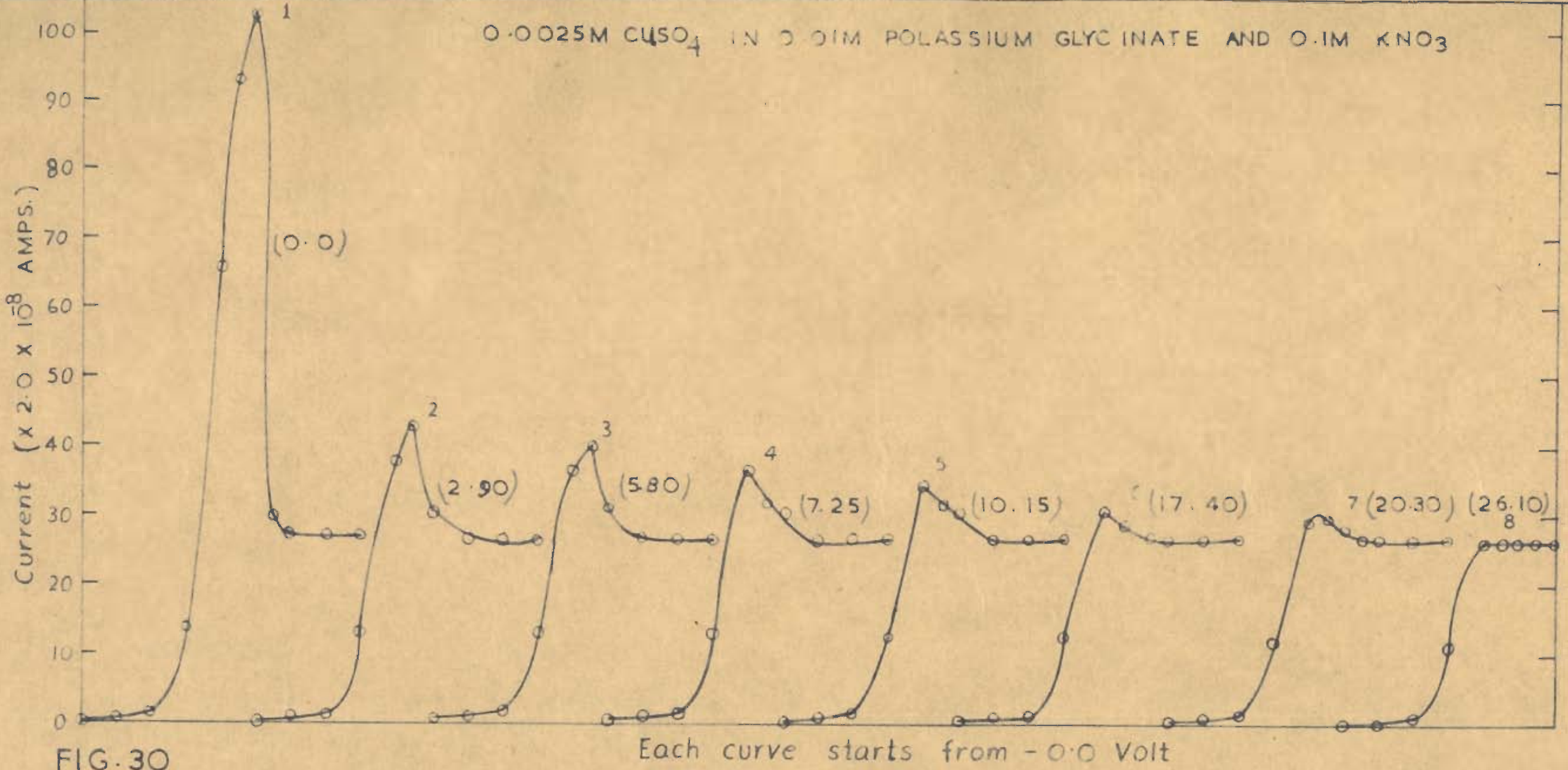
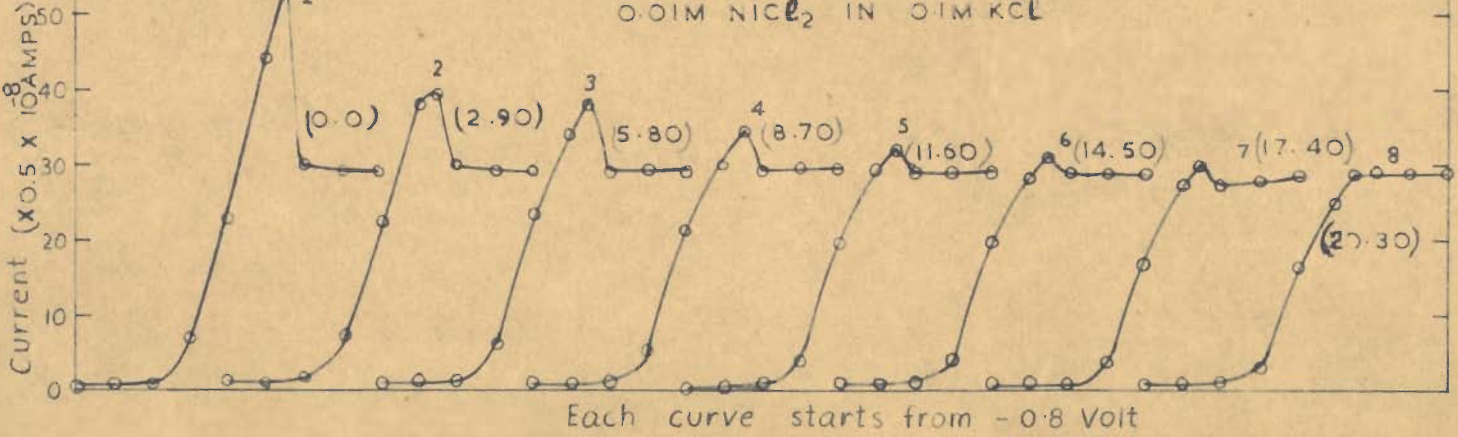

0·005M PB (NO$_3$)$_2$ IN 0·05M KNO$_3$
LDC (x 10^3 GMS/L)
Current (x 2·0 x 10^{-8} Amps)
8
7
6
5
4
3
2
1
0
1
(0·0)
2
(0·72)
3
(1·45)
4
(2·90)
5
(3·60)
6
(4·35)
7
(5·90)
Each curve starts from –0·0 Volt
1 DIV 0· VOLT
POTENTIAL (VOLTS)

FIG 25


0·0025M CuSO$_4$ IN 0·01M POLASSIUM GLYCINATE AND 0·1M KNO$_3$

FIG·30

VALUE IN PARENTHES REPRESENTS AMOUNT OF LDC = (x 10^{-3}GMS/l)


0·01M NiCl$_2$ IN 0·1M KCl

FIG·29

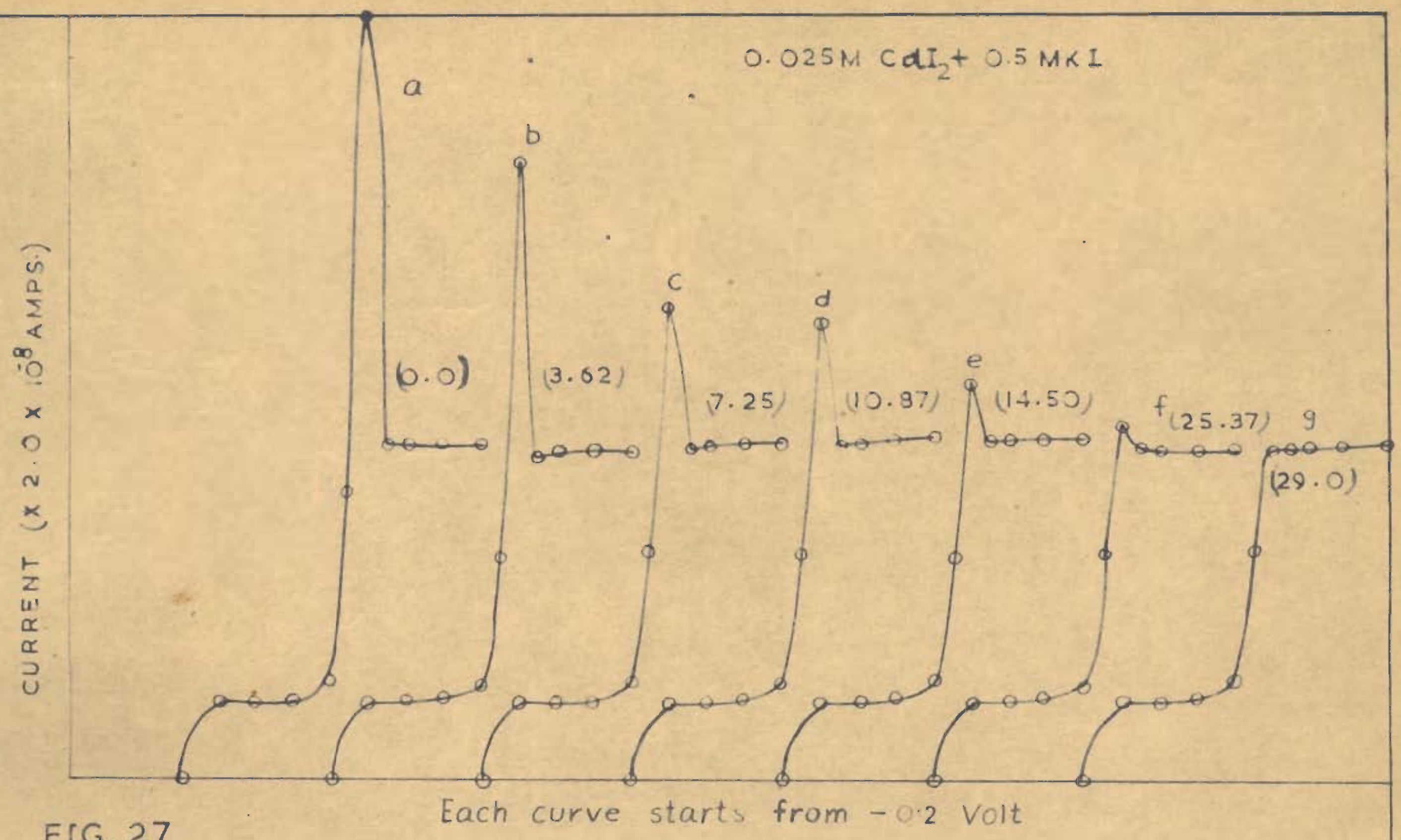


FIG. 27

VALUE IN PAPENTHES REPRESENTS

LDC ($\times 10^{-3}$ GMS|L)

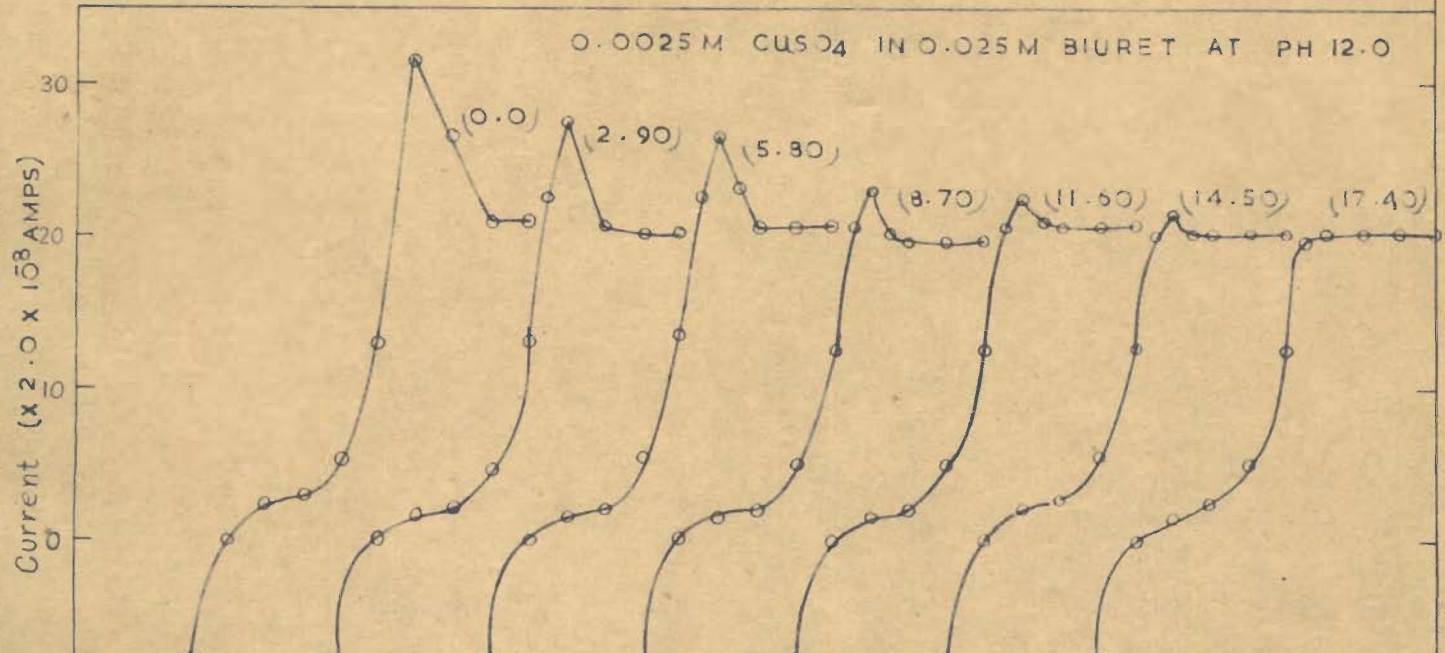


FIG. 28

1DIV 0.2 VOLT

POTENTIAL (VOLTS)

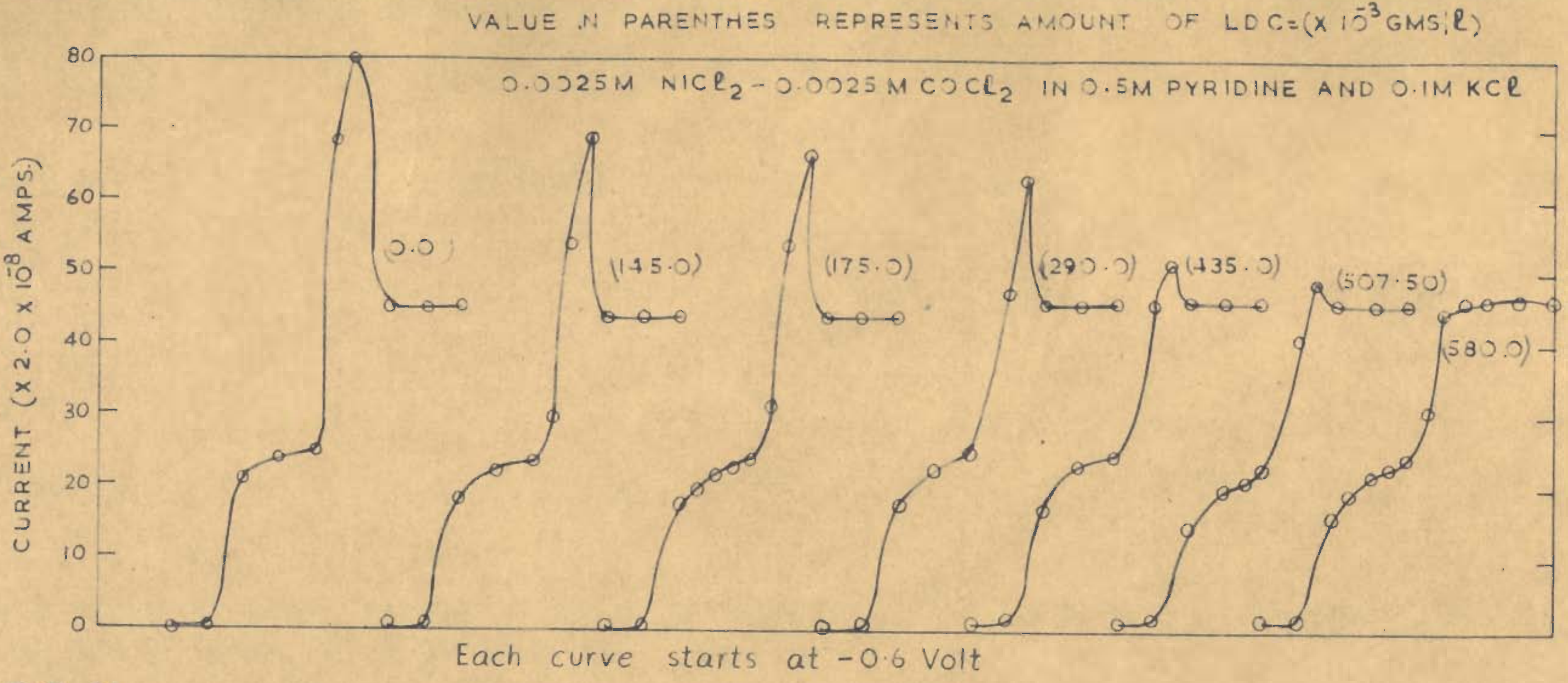
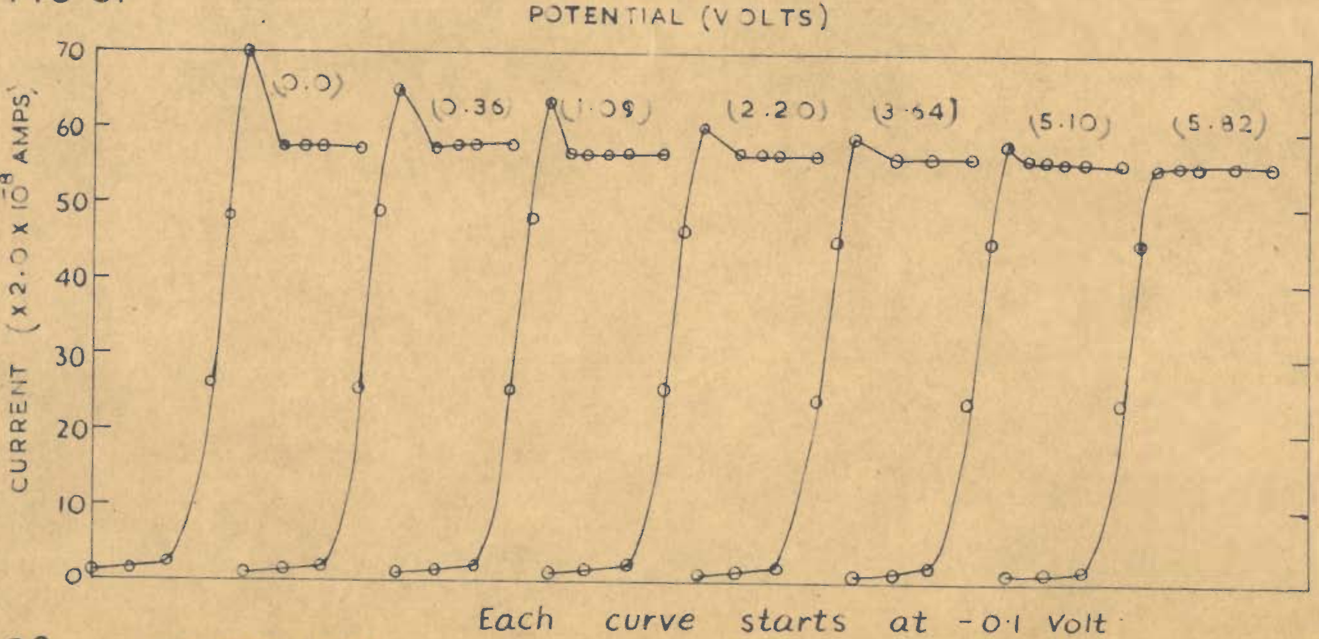


FIG.31



0.0025 M Pb(NO$_3$)$_2$
IN 0.2 M KNO$_3$

VALUE IN PARENTHES
REPRESENTS AMOUNT
OF CTMAB (x 10^{-3} GMS/L)

FIG.32 1 DIV.=0.2 VOLT

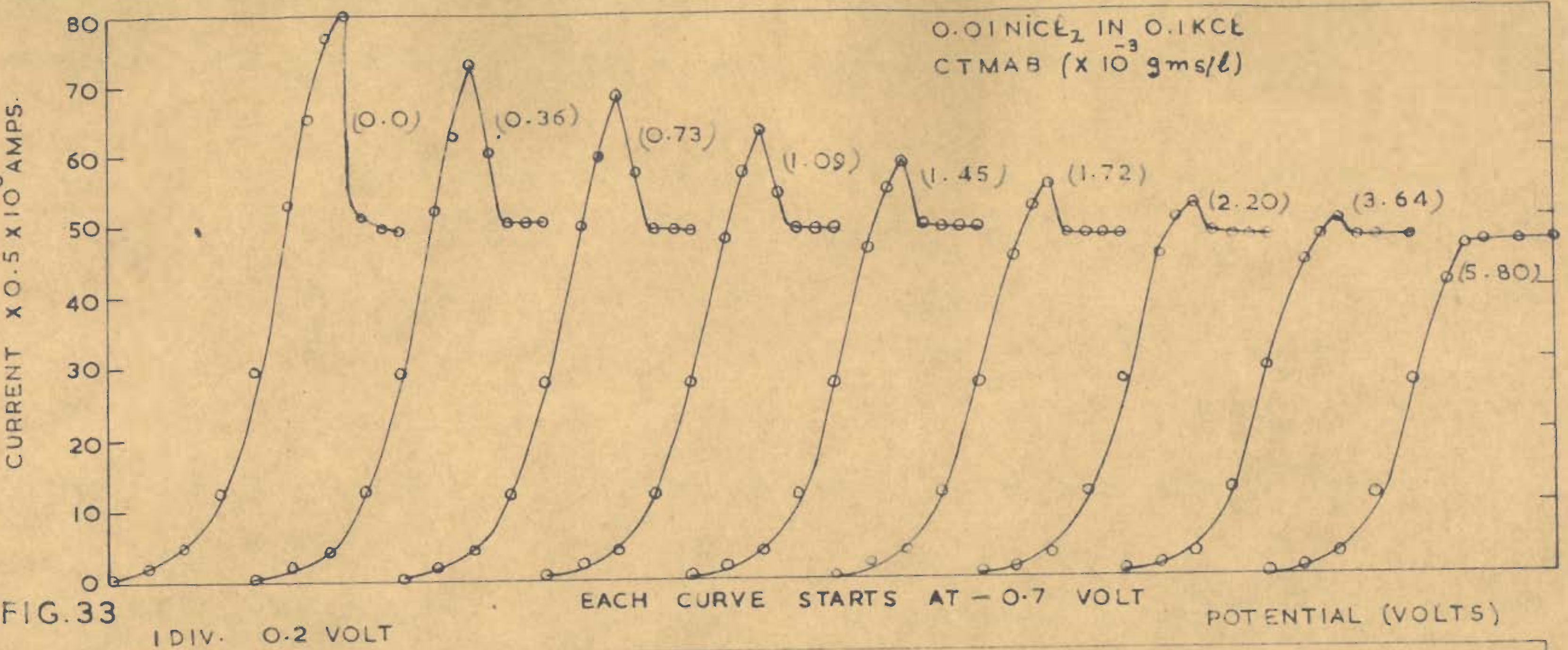

0.01 NiCl2 IN 0.1 KCl
CTMAB (x 10-3 gms/l)
CURRENT x 0.5 x 10-8 AMPS.
0
10
20
30
40
50
60
70
80
(0.0)
(0.36)
(0.73)
(1.09)
(1.45)
(1.72)
(2.20)
(3.64)
(5.80)
EACH CURVE STARTS AT – 0.7 VOLT
POTENTIAL (VOLTS)
1 DIV. 0.2 VOLT

FIG.33

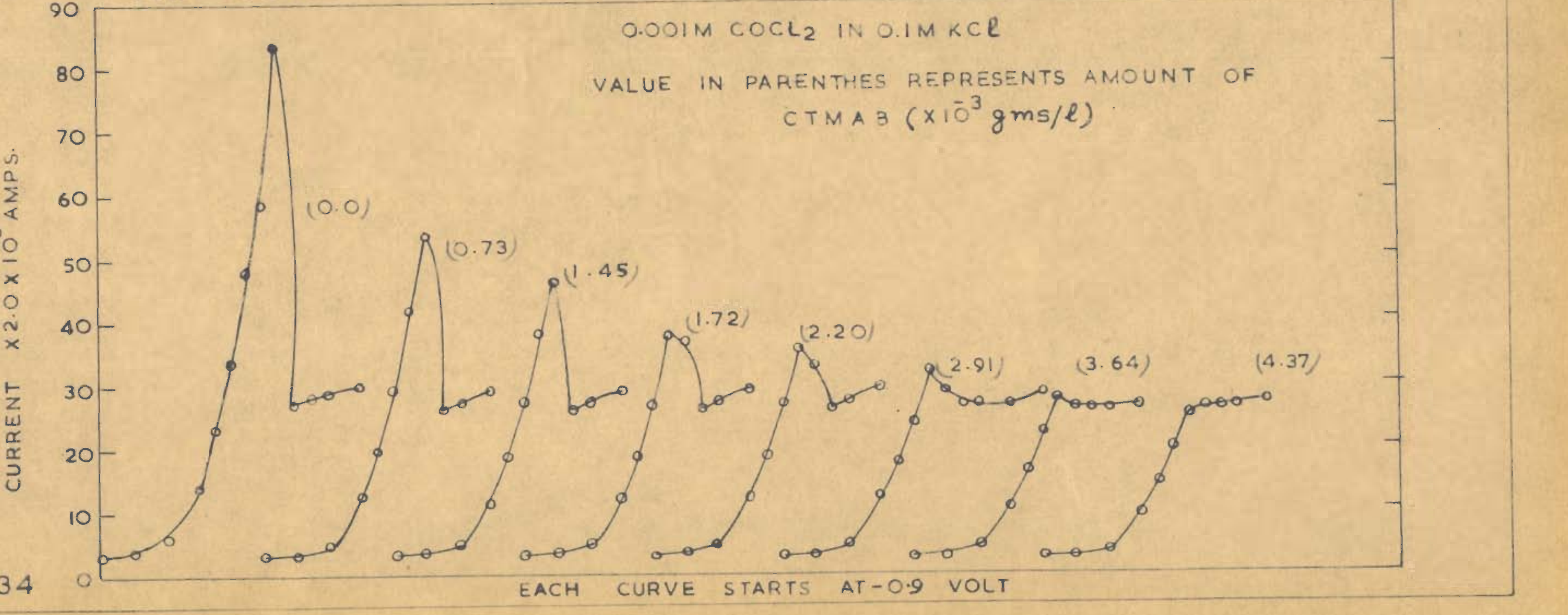
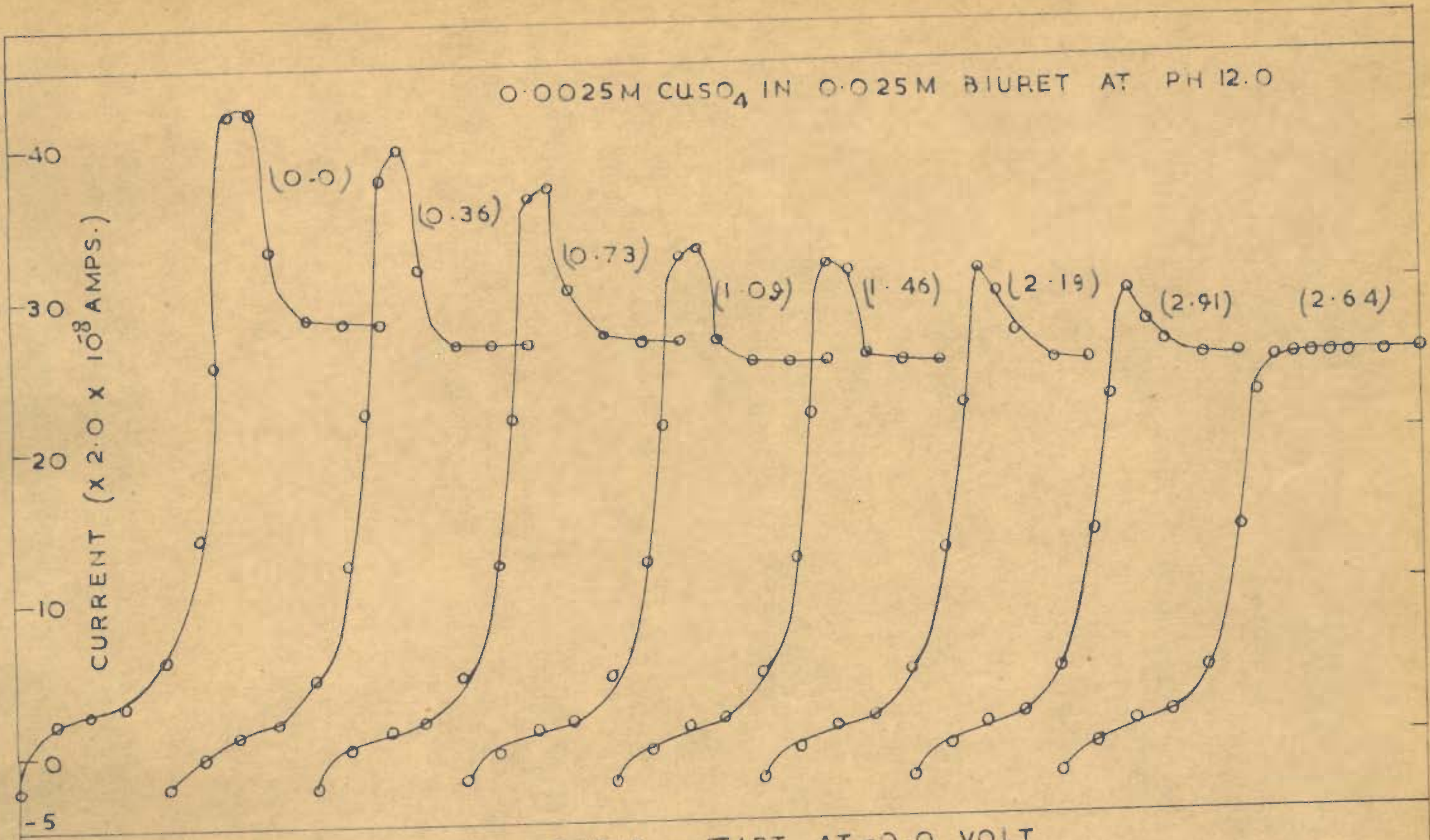

0.001M CoCl2 IN 0.1M KCl
VALUE IN PARENTHES REPRESENTS AMOUNT OF CTMAB (x10-3 gms/l)
CURRENT x 2.0 x 10-8 AMPS.
0
10
20
30
40
50
60
70
80
90
(0.0)
(0.73)
(1.45)
(1.72)
(2.20)
(2.91)
(3.64)
(4.37)
EACH CURVE STARTS AT – 0.9 VOLT

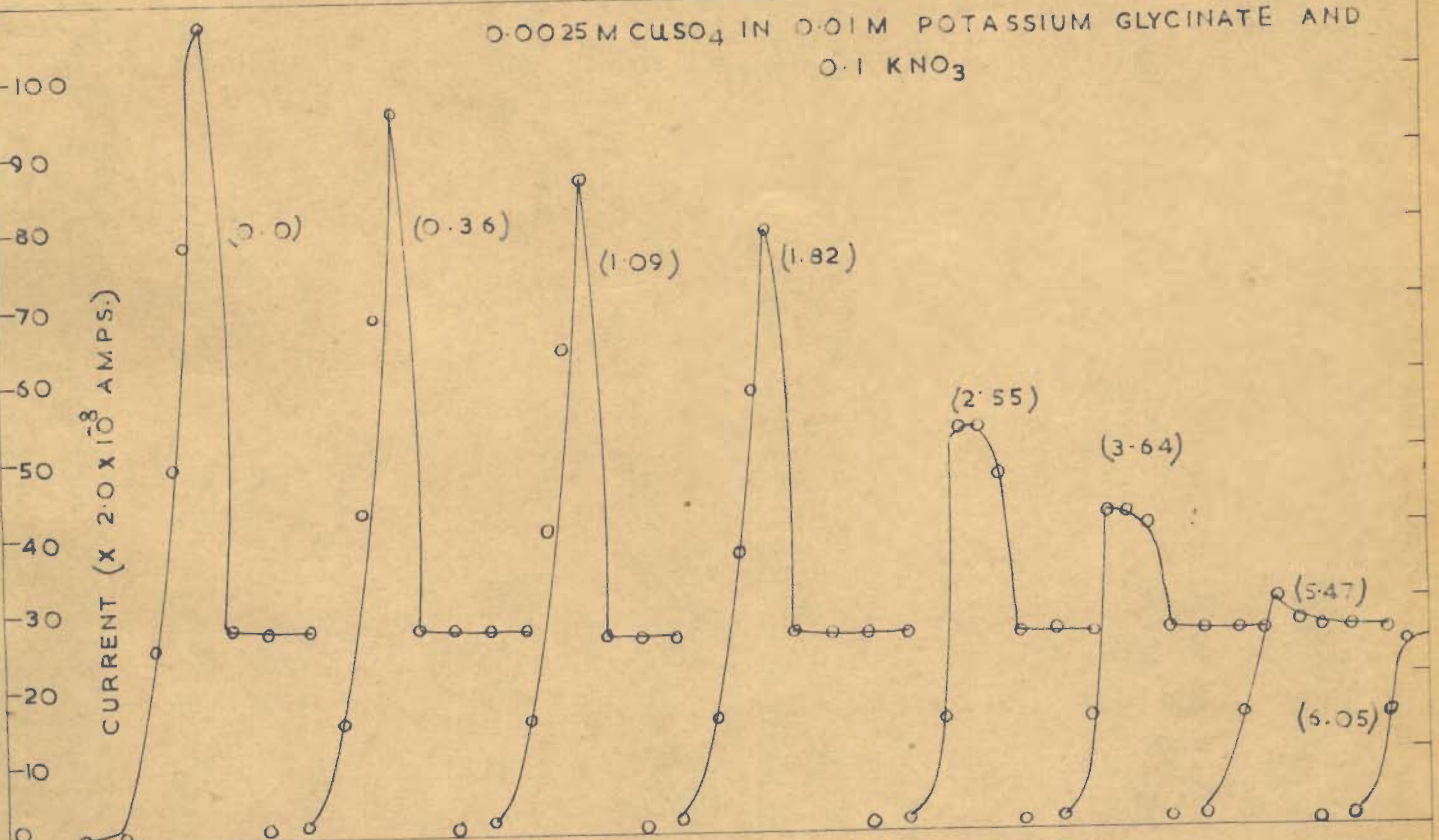
FIG.34



EACH CURVE START AT -0·0 VOLT

FIG. 35

VALUE IN PARENTHES REPRESENTS C_{TMABr} (X 10^{-3} GMS/l)

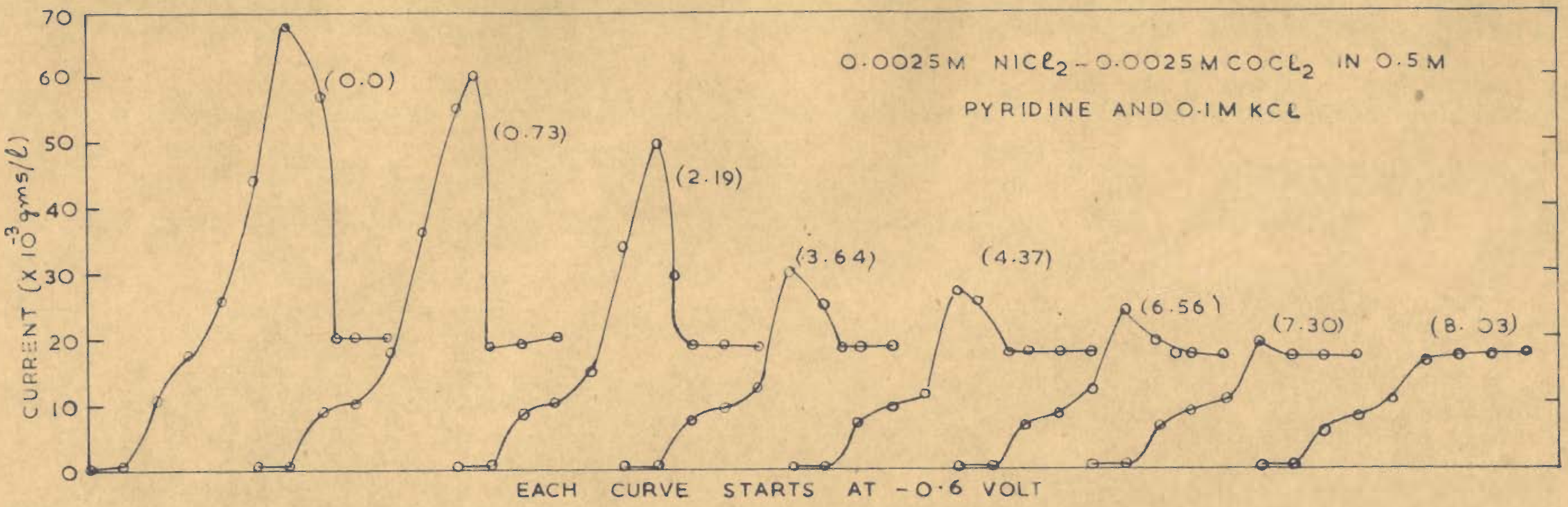


EACH CURVE STARTS AT 0·1 VOLT

FIG.37

1 DIV = 0·2 VOLT

POTENTIAL (VOLTS)



FIG·36

VALUE IN PARENTHES REPRESENTS CTMAB = ($\times 10^{-3}$ gms/ℓ)

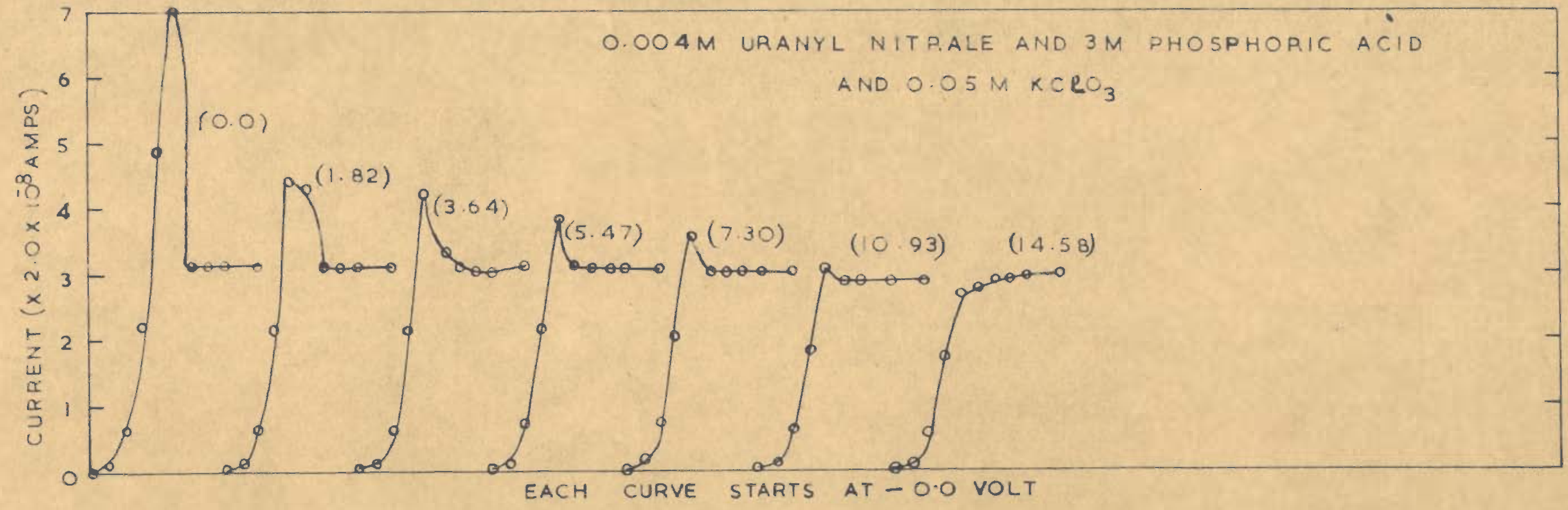


FIG. 38

1 DIV = 0.2 VOLT

POTENTIAL (VOLTS)

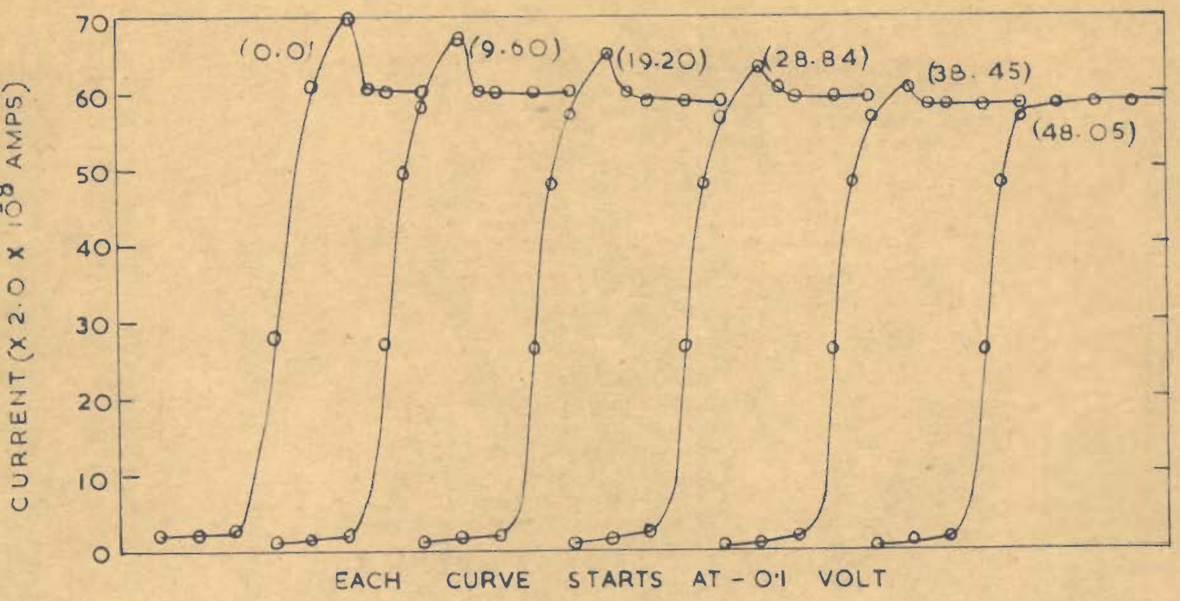


FIG. 39

0·005 M $Pb(NO_3)_2$ IN 0·1 M KNO_3

VALUE IN PARENTHES REPRESENTS AMOUNT OF CPB=(x 10^{-3} gms/l)

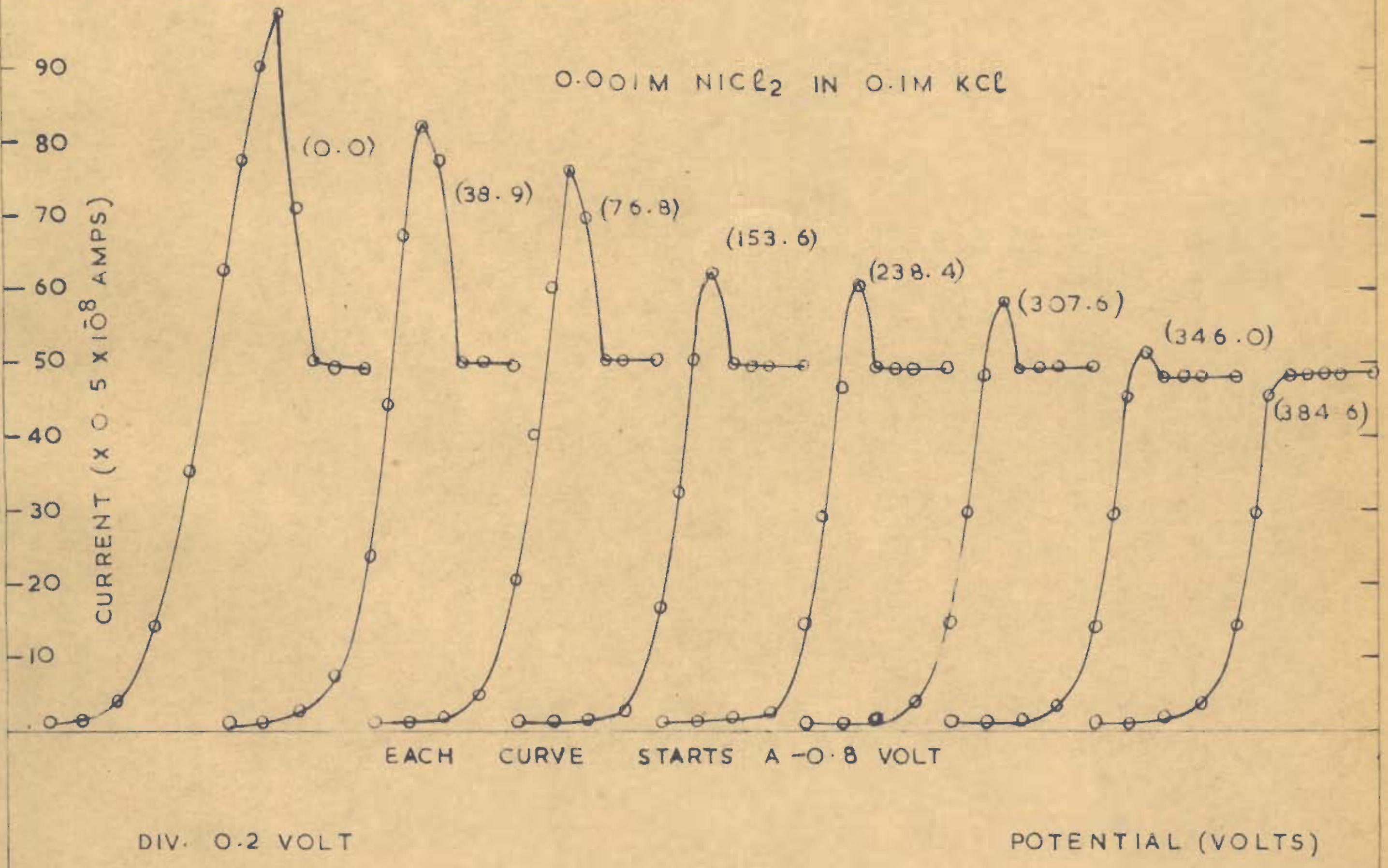


FIG. 40

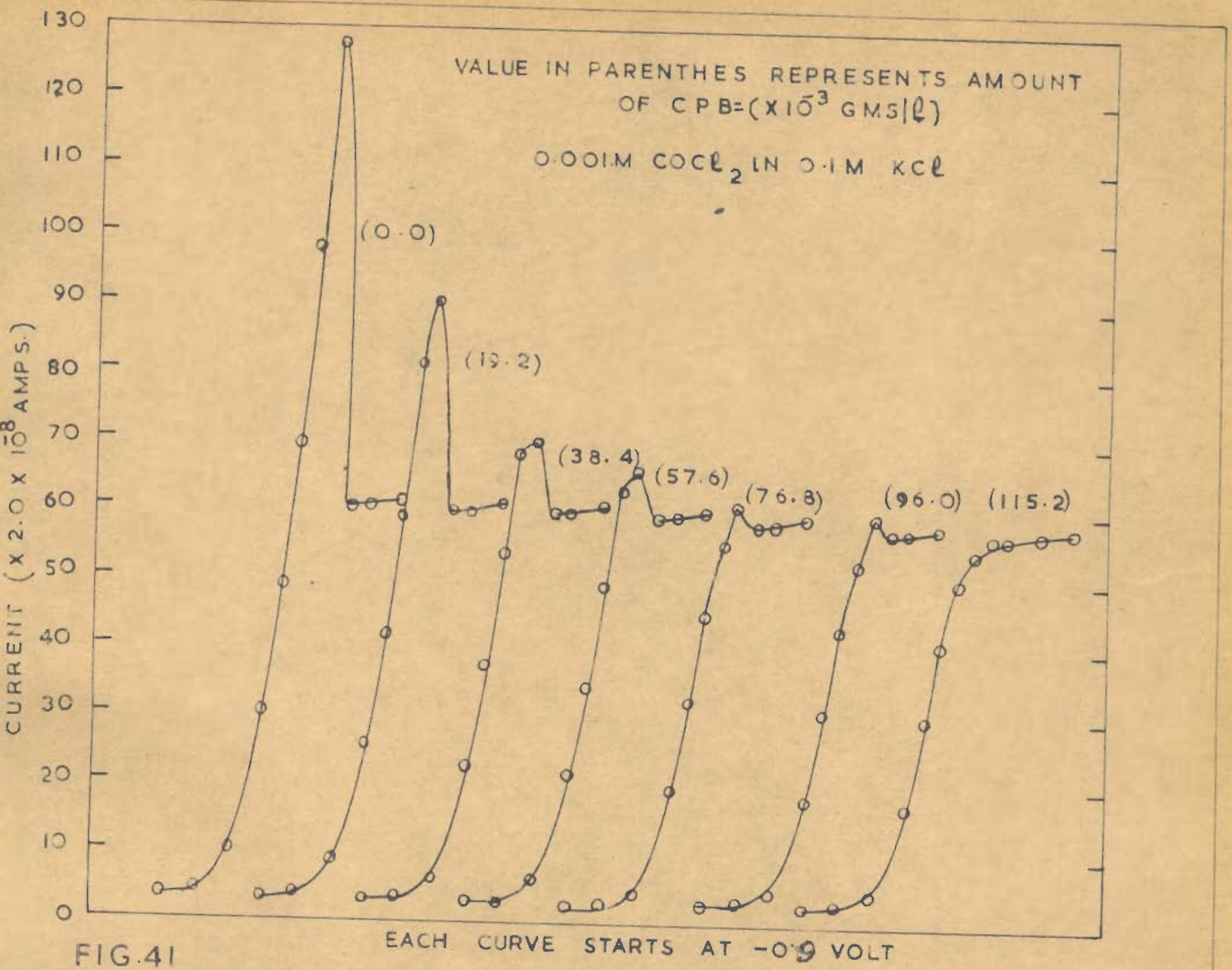

VALUE IN PARENTHES REPRESENTS AMOUNT OF CPB=(X10^{-3} GMS/ℓ)
0·001M COCℓ$_2$ IN 0·1M KCℓ
(0·0)
(19·2)
(38.4)
(57·6)
(76·8)
(96·0)
(115·2)
CURRENT (x 2.0 x 10^{-8} AMPS.)
130
120
110
100
90
80
70
60
50
40
30
20
10
0
EACH CURVE STARTS AT −0·9 VOLT

FIG.41

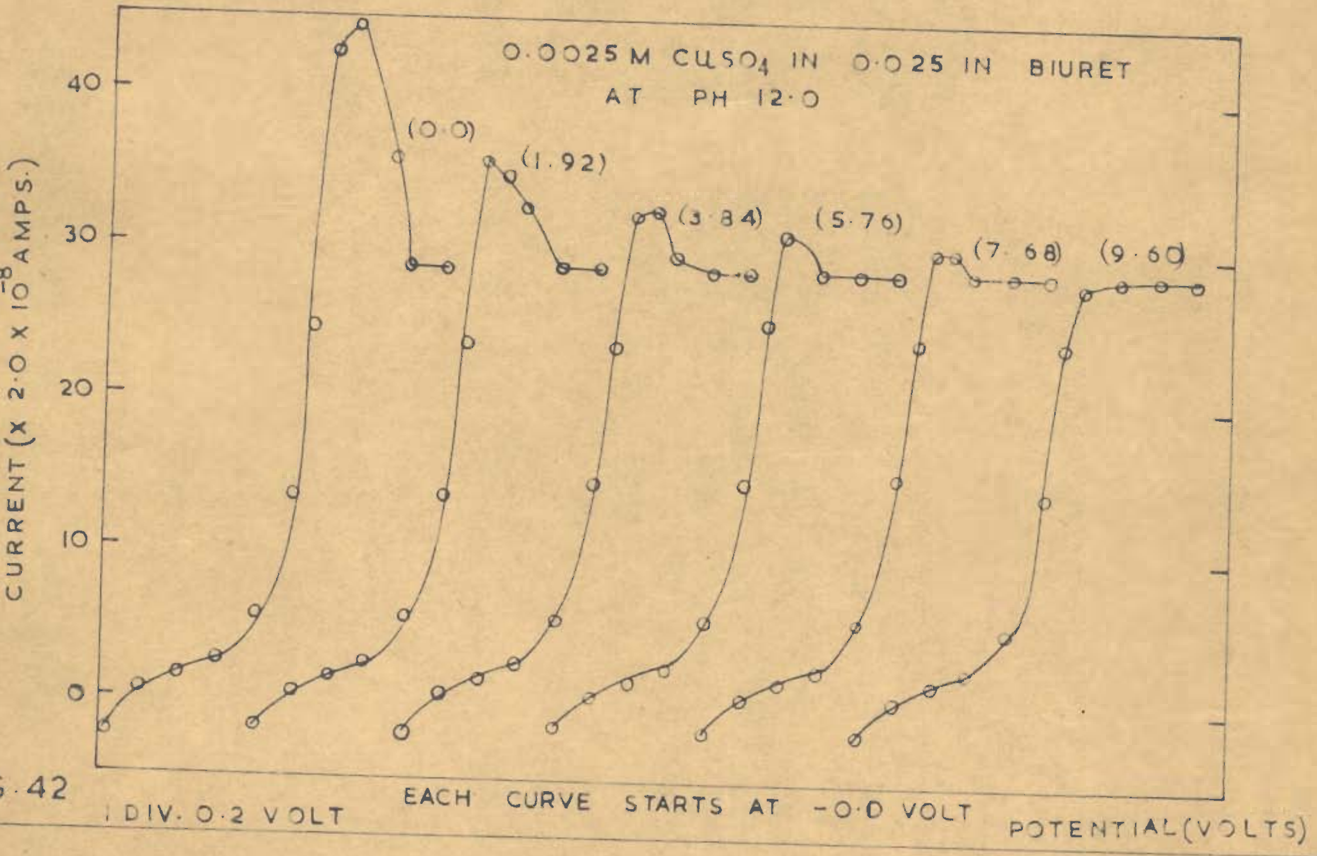

0·0025 M CuSO$_4$ IN 0·025 IN BIURET AT PH 12·0
(0·0)
(1·92)
(3·84)
(5·76)
(7·68)
(9·60)
CURRENT (x 2·0 x 10^{-8} AMPS.)
40
30
20
10
0
1 DIV. 0·2 VOLT
EACH CURVE STARTS AT −0·0 VOLT
POTENTIAL (VOLTS)

FIG.42

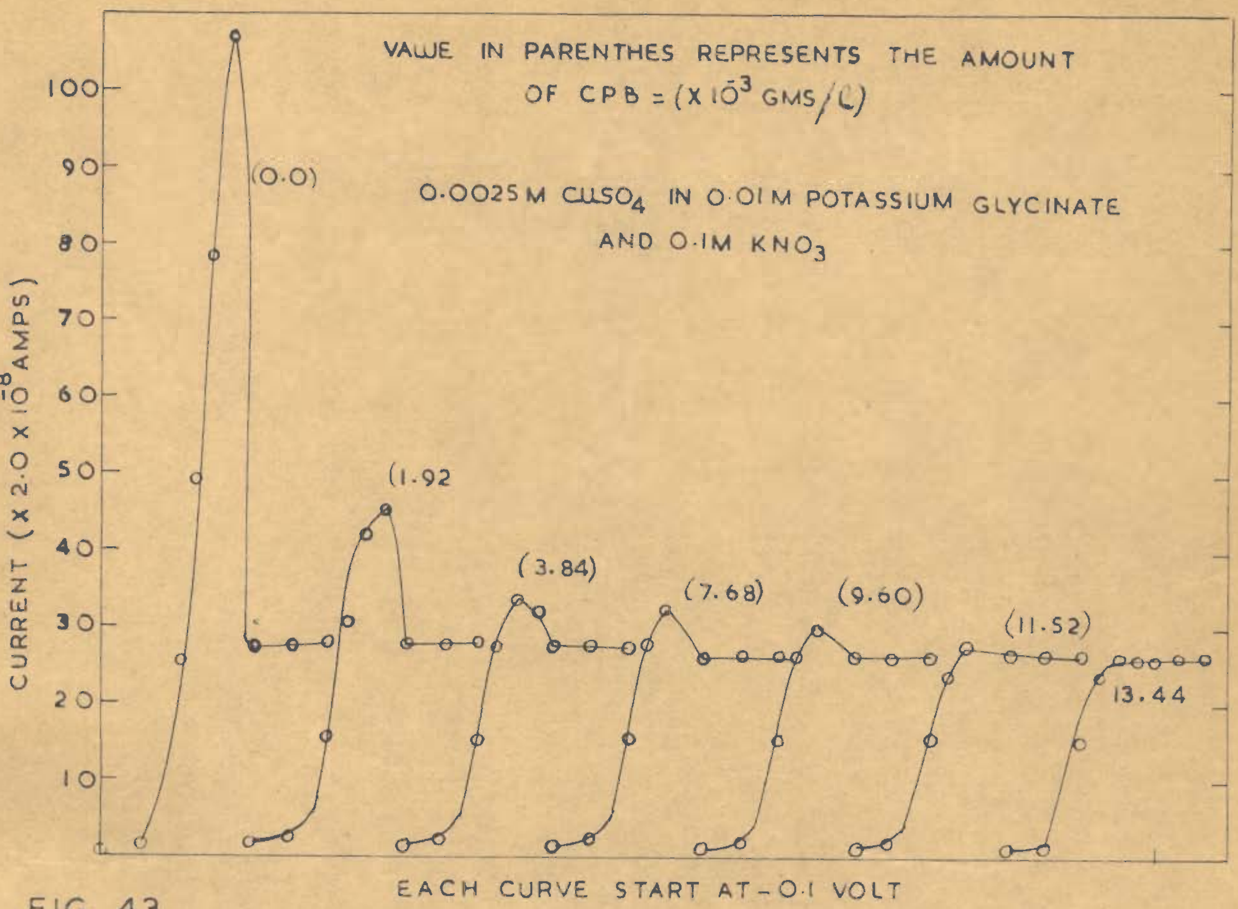


FIG. 43

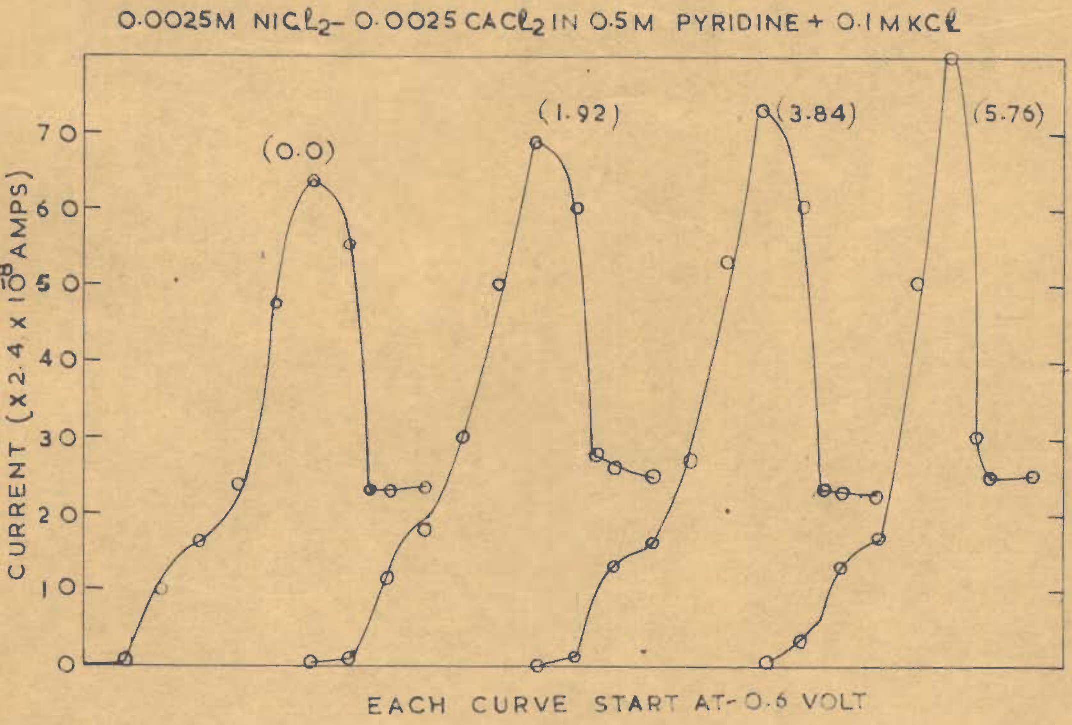


FIG. 44

1 DIV:: 0.2 VOLT

POTENTIAL (VOLTS)

EFFECT OF NONIDET P42 AND NONEX 501 ON ELECTRO-CAPILLARY CURVES.

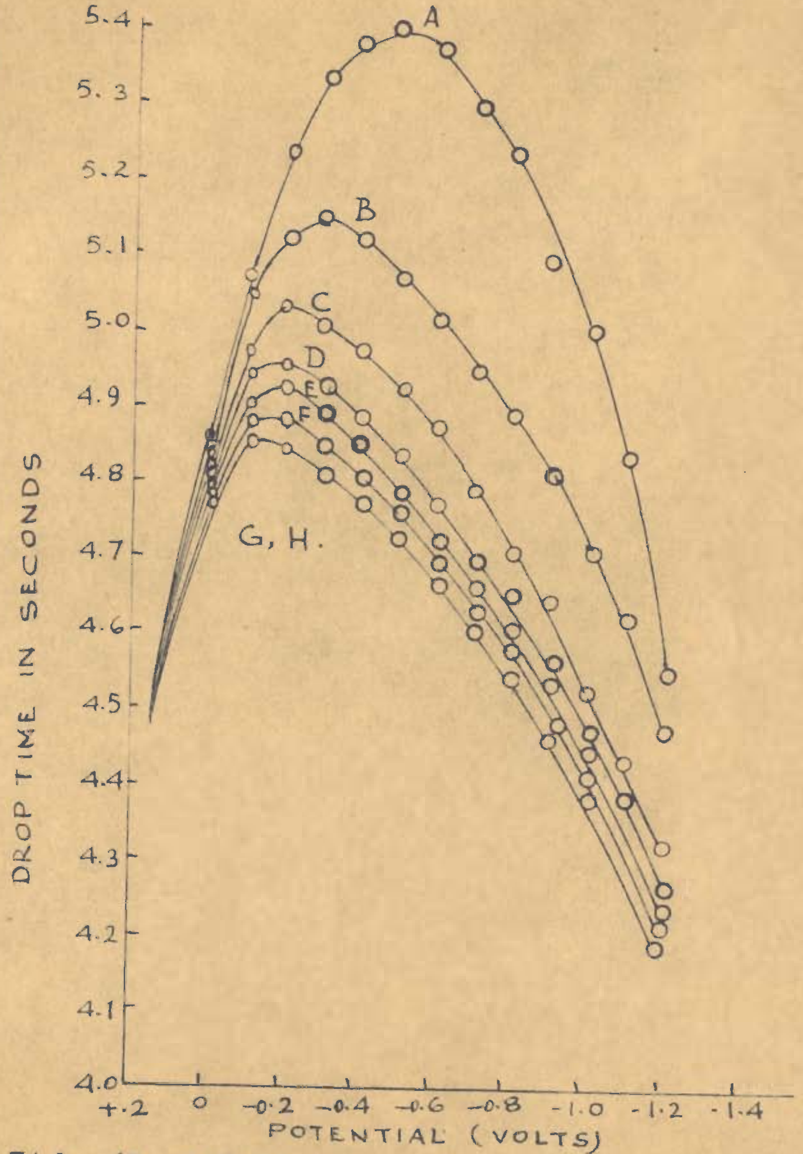


FIG. 45. CURVE A = 0.0; B = 2.0; C = 6.0; D = 8.0
E = 11.25; F = 14.5; G = 16.0; H = 25.0 $(\times 10^{-2}$ gms/l)
OF NONIDET P 42.

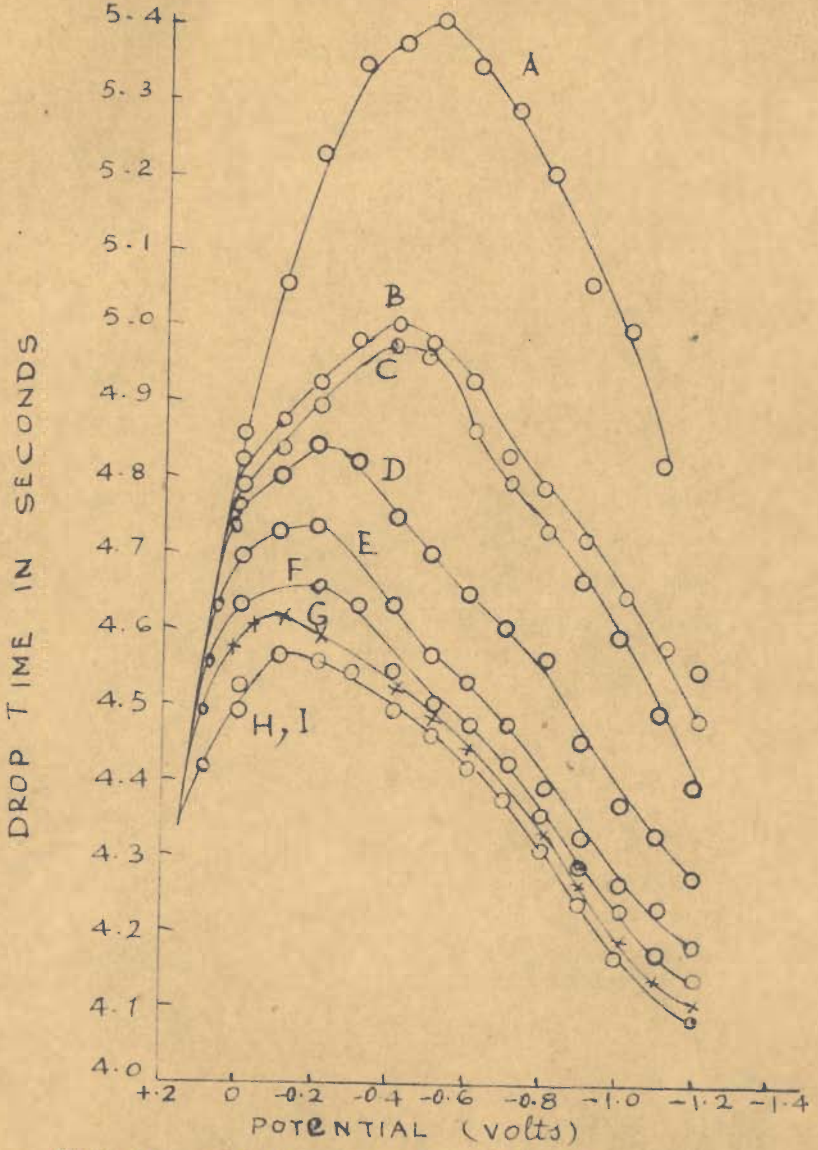


FIG 46. CURVE A = 0.0; B = 0.5, C = 1.0; D = 2.0;
E = 3.0; F = 4.0; G = 5.0; H = 6.0; I = 8.0 $(\times 10^{-2}$ gm/l)
OF NONEX501

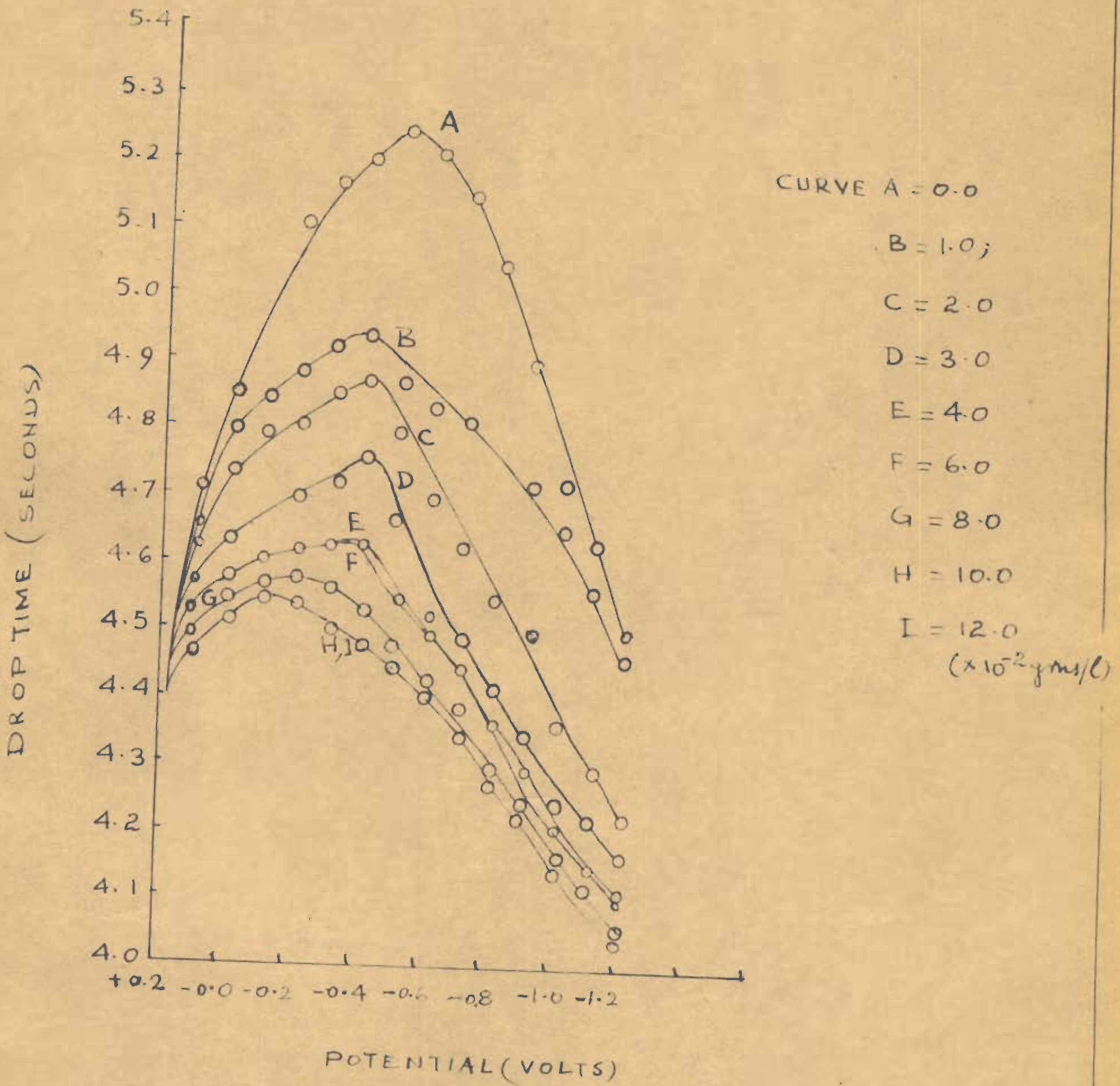


FIG. 47 EFFECT OF NONIDET P40 ON ELECTRO CAPILLARY CURVES IN 0.1 M KCl

EFFECT OF LDC ON ELECTRO CAPILLARY CURVES

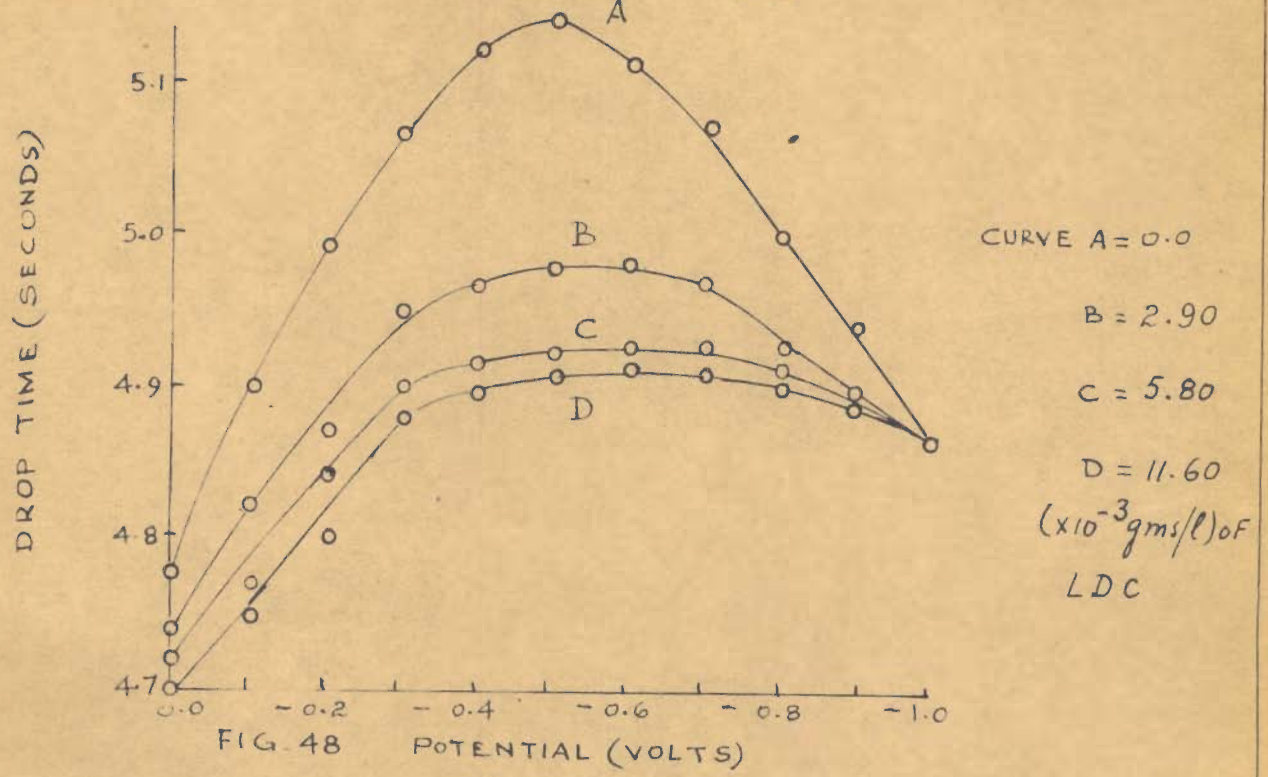


FIG. 48

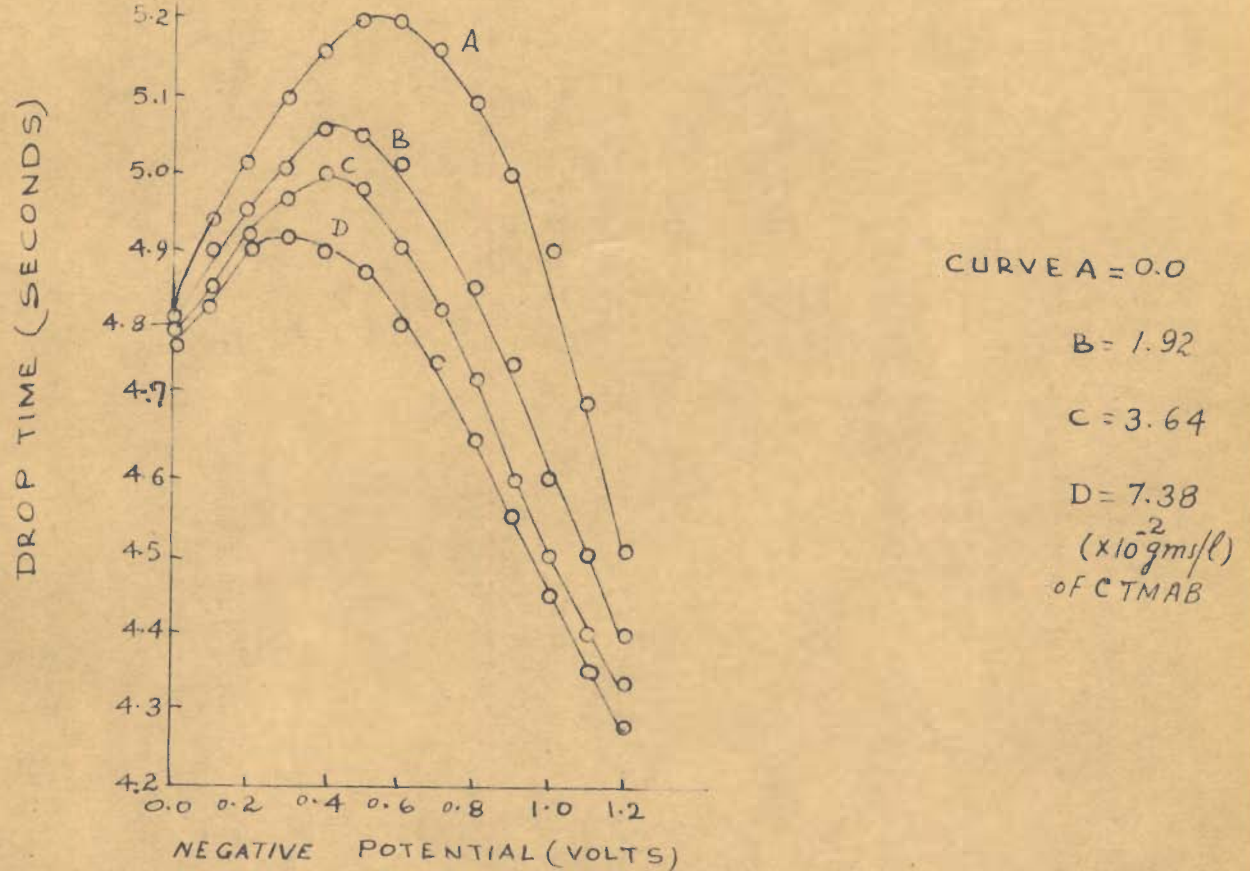


FIG. 49 EFFECT OF CTMAB ON ELECTRO-CAPILLARY CURVES IN 0.1 M KCl.

RESULTS AND DISCUSSION

EFFICACY OF NEW SURFACTANTS AS MAXIMUM SUPPRESSORS.

The effectiveness of synthetic surface active agents in suppressing the polarographic maxima of different simple and complex metal ions is very well borne out on the basis of experimental results given in the preceding pages.

The data on the suppression of maxima of both the types,positive and negative,observed during the reduction of simple and complex metal ions are given in the following tables.

Table 1.

Relative effectiveness of ionic and non-ionic surfactants in suppressing the positive maxima.

Surfactants	Ion or complexes.			
($\times 10^{-3}$ gms/l.)	Pb^{++}-KNO_3	U^{6+}-$KClO_3$ and phosphoric acid.	Cu-glycine	Cu-biuret
Non-ionic:				
Nonidet P40	3.64	5.20	8.60	5.20
Nonidet P42	15.40	19.00	30.00	22.60
Nonex 501	3.80	2.32	6.00	4.50
LDC.	5.80	-	26.10	17.40
Cationic:				
CTMAB	5.80	14.50	5.90	3.60
CPB	38.50	-	13.00	11.50
*DPB	19.00	-	19.70	16.40
*IDEH	16.00	-	22.50	54.00
**Anionic:				
SPSA	76.60	-	73.00	345.76
STSA	25.40	-	23.10	54.40
SXSA	17.70	-	23.76	13.05

M.S.P.values ($\times 10^{-5}$M) given in ref.13 and 14 were converted in ($\times 10^{-3}$ gms/l.).

* from ref.13; ** from ref.14.

Table 2.

Relative effectiveness of ionic and non-ionic surfactants in suppressing the negative maxima.

Surfactants	Ion or complexes			
(x10^{-3}gms/l.)	Ni^{++}-KCl	Co^{++}-KCl	Ni^{++}-Co^{++}mixture in pyridine and KCl.	CdI$_2$-KI complex.
Non-ionic:				
Nonidet P40	6.60	8.25	15.50	6.10
Nonidet P42	22.60	22.60	72.00	22.60
Nonex 501	5.20	6.60	8.60	8.60
LDC	20.30	26.10	580.00	29.00
Cationic:				
CTMAB	5.80	4.35	6.50	pptn.
CPB	385.00	115.00	Not suppressed	pptn.
*DPB	20.00	78.70	16.40	47.50
*IDEH	19.00	19.50	-	26.00
**Anionic:				
SPSA	191.30	76.60	1597.00	748.00
STSA	226.50	543.60	94.70	71.60
SXSA	233.00	368.8	97.80	73.60

M.S.P. values (x10^{-5} M) given in ref.13 and 14 were converted in (x10^{-3} gms/l.).

* from ref.13; ** from ref.14.

DPB = Dodecyl pyridinium bromide.
IDEH = Isothiourea dodecyl ether hydrobromide.
SPSA = Sulfonated phenylstearic acid.
STSA = Sulfonated tolylstearic acid.
SXSA = Sulfonated xylyl stearic acid.

The following conclusions may be drawn:

(i) By and large, the anionic surface active agents, viz., SPSA, STSA and SXSA are more effective in suppressing the positive maxima than the negative ones. Heyrovsky and Dullinger's rule (46), that is, negatively charged colloids are effective in suppressing the positive maxima and vice versa, is followed.

(ii) Cationic surfactants suppress both the positive and negative maxima with equal case. The cationic surfactants are superior to the anionic surfactants in another respect The amount of surfactant required to suppress the maxima is much lower than in the case of anionic surfactants. Even polarographic maxima suppressable with difficulty like those of Ni^{++}-Co^{++} mixture in pyridine and KCl; and CdI_2-KI complex etc. can be easily suppressed and that too with small quantity of CTMAB (Table 2).

(iii) The behaviour of non-ionic surfactants as maximum suppressors is not different from that of cationic surfactants although in a few cases (e.g. the maxima of Ni^{++}, Co^{++} and Pb^{++}) lesser quantity of the surfactant is required. Furthermore, the non-ionic surfactants have an extra advantage of not undergoing chemical interaction with the depolarizer. It has been observed that CdI_2-KI complex-maximum is easily suppressed with non-ionic surfactants whereas precipitation of the depolarizer takes place on adding CTMAB and CPB.

The non-ionic surfactants differ among themselves in their suppressive action. For example, the maximum suppression point (M.S.P.) values of Nonidet P40 and Nonex 501 are much lower (order 10^{-3} gms/l.) than LDC and Nonidet P42 (order 10^{-2} gms/l.). The non-ionic surfactants, as far as their efficacy as maximum suppressors is concerned, follow the order:

Nonex 501 $\geq$ Nonidet P40 $\gg$ Nonidet P42 $>$ LDC.

This specificity is also shown by cationic surfactants. It may thus be seen that small amount of CTMAB can suppress the maximum of Ni^{++}- Co^{++} mixture in pyridine and KCl while CPB is quite in-effective in this case. On the other hand, the maximum increases progressively with the gradual addition of the CPB (Fig.44).

The anionic surfactants (13,26) show little capability to suppress the negative maxima which are easily suppressed by non-ionic and cationic surfactants. It may be due to the fact that adsorption of anionic surfactants on the d.m.e. is almost absent at such negative potentials.

AMOUNT OF MAXIMUM SUPPRESSOR VIS-A-VIS THE E.C.Z. AND pH OF THE SOLUTION.

The amount of the non-ionic and cationic surfactants required to suppress the maximum follow the normal behaviour with respect to $E_{1/2}$ and the e.c.z.. In cases, like the reduction of the copper biuret complex, the amount of either of the surfactants required for suppressing the maximum is very small since the $E_{1/2}$, -0.50 volt, is very close to the e.c.z. value of -0.55 volt in KOH. In a similar manner, for ions showing positive maxima, the M.S.P. values are smaller, higher the half wave potential. Thus for Pb^{++}, Cu-glycinate and U^{6+} ions, with $E_{1/2}$ values equal to -0.40, -0.30 and -0.15 volts respectively, the order of the quantity of the maximum suppressor required is $U^{6+} >$ Cu glycinate $> Pb^{++}$.

Non-ionic surfactants and cationic surfactants are not influenced by the pH of the solution. The amount of these surfactants required to suppress the maximum at pH 12.0 (Cu-biuret complex) is almost the same as at pH 5.15 (Pb^{++}). On the other hand, the anionic surfactant required with Cu-biuret is larger than Pb^{++} in KNO_3, although both show a positive maxima.

REDUCTION OF U^{6+} IN $KClO_3$ AND PHOSPHORIC ACID.

U^{6+} gives reduction waves with pronounced maximum in phosphoric acid and $KClO_3$. Gelatin, even in small quantity, (0.001%) distorts the polarographic wave and even changes its character from the reversible to the irreversible one. Higher concentration of the supporting electrolyte (>1M $KClO_3$) no doubt helps in suppressing the maximum but the appearance of second maximum in its place makes the polarographic analysis all the more difficult. On the other hand the non-ionic and cationic surfactants, not only suppress the maximum of U^{6+} completely but do so with dilute solutions (0.05M) of the supporting electrolyte. It is observed that addition of 0.005% of

Nonidet P40 is enough to suppress the maximum without bringing any distortion or irreversibility in the polarographic wave. The $E_{1/2}$ and i_d values also do not change.

EFFECT OF SURFACTANTS ON $E_{1/2}$ AND Id.

Addition of maxima suppressors in excess to the requisite amount brings about either a decrease of i_d or shift in $E_{1/2}$ or both. The surfactants employed here have got the extra advantage over the existing one that such insidious effect are not observed with them. The only exception is LDC which changes the $E_{1/2}$ and shape of current-voltage curves greatly when used to suppress the maximum of Ni^{++}. Very high concentrations of CTMAB were found to decrease the limiting current of most of the depolarizers.

ELECTROCAPILLARY CURVES.

Fig.(45) gives the result of the variation of drop time concentration of Nonidet P42 from +0.1 to -1.2 volt (with reference to calomel electrode). Curve A in Fig.(45) shows the relationship between the electrode potential and the drop time in 0.1 N KCl solution. The curve is symmetrical and parabolic, showing specifically no adsorption on the mercury surface. However, with the gradual addition of Nonidet P42 (and so also with the other two non-ionic surfactants), electro-capillary zero shifts towards the more positive potential (Fig.45, Curve A to H). Curves B to H show the effect of gradual addition of Nonidet P42 on drop time within the potential range +0.1 to -1.2 volt. The curve no more remains symmetrical and the electrocapillary zero shifts towards more positive potential. The shape of these curves also points towards the desorption in the region where the curves merge with the normal one (Curve A). Similar behaviour is observed with the other two surfactants Nonex 501 and Nonidet P40.

The shift in the electrocapillary zero towards the positive potential by the addition of non-ionic surfactants needs a little elaboration since ionic surfactants are only known to effect such a change. The peculiar behaviour shown by the non-ionic surfactants under investigation can be explained in the light of the model proposed by Barradas and Kimmerle (29) for multilayer adsorption of Triton X-100, Triton X-305 and similar compounds.

According to them the first adsorbed layer of the non-ionic surfactant extends its contracted ''zig zag'' hydrophilic portions towards the solution. A second layer is then assumed to form by intramolecular hydrogen bonding between another perpendicular array of surfactant molecules, and a third layer is formed by Vander Waal's attractive forces between similar non-polar ends of the molecules. Besides each compact array of the surfactant molecules may hydrogen bond with some water molecules. The latter behaviour is not unlikely since the micellar structures of these surfactant molecules are hydrated (10).

Fig.49 shows the variation of drop time with the increasing concentration of CTMAB in the potential range +0.1 to -1.2 volt. Here too a shift in potential towards the more positive side accompained by the merger with the original symmetrical curve is observed. The shift in potential is, however, not so marked as in the case of non-ionic surfactants. From this it may be concluded that the non-ionic surfactants are more strongly adsorbed at the mercury-solution interface than the cationic surfactants.

An altogether different behaviour is observed in the case of LDC where a marked decrease in drop time takes place on both the sides of electrocapillary zero and the top of the electrocapillary curve starts gradually flattening with the addition of the surfactant without bringing about a shift in e.c.z.. The merger with the normal curve (desorption), however, takes place at the negative side of the e.c.z.. The behaviour is similar to that observed for non-electrolytes e.g., amyl alcohol, by Frumkin (47), and for anionic surfactants by Tammakashi (26).

The electrocapillary curves in presence of different surfactants discussed above explain the effectiveness of non-ionic and cationic surfactants as maximum suppressors. With anionic surfactants and LDC, the amount of surfactant, required to suppress the maximum is much larger than the non-ionic and cationic surfactants. This is evident from the fact that portions without shift in e.c.z.,indicating small adsorption of the surfactant are realised with LDC while in the case of non-ionic and cationic surfactants marked shifts in e.c.z. are observed due to large adsorption of the surfactant.

The experimental observation that lesser amount of the non-ionic surfactants is required in comparision to cationic surfactants also finds support from the electrocapillary curves. With non-ionic surfactants the shift in e.c.z. is from -0.55 volt to -0.10 volt while in cationic surfactant the shift is relatively small,that is,from -0.55 volt to -0.25 volt. This provides an indirect proof of the fact that non-ionic surfactants are adsorbed more than the cationic ones. The former would thus be required in a lesser quantity than the latter in suppressing the polarographic maximum.

The shape of the electrocapillary curves besides giving information of fundamental importance regarding the interfacial forces acting at the d.m.e.,also explain why non-ionic and cationic surfactants are better maximum suppressors than anionic soaps.

Both the surfactants bring about a marked lowering in the drop time(and so also the interfacial tension). This lowering,however,is greater with non-ionic surfactants in the entire potential range (0.1 to -1.2 volt). Since the lowering in interfacial tension results in adsorption,it may be safely concluded that the non-ionic surfactants are adsorbed more than the cationic ones. This explains the efficacy of these surfactants as maximum suppressors provided we assume that this phenomena takes place by allowing the adsorption of the surfactant in preference to the depolarizer. Since non-ionic surfactants are adsorbed more,these surfactants can be used with greater advantage than the cationic ones in eliminating the maxima. The relative merits of the two types of surfactants as maximum suppressors is thus self explanatory.

To conclude it may be said that although no forthright mechanism regarding the influence of the surface active agents on the electrode processes at the d.m.e.can be put forward,a few interesting facts emerged out on the basis of the experimental results discussed above.

Firstly,a close relationship exists between the electrode process and the adsorption phenomena of the surfactants. Secondly,the structure of the electrical double layer formed immediately adjacent to the electrode surface is of great significance in controlling the mechanism ofelectrode reaction. The polarographic maxima is suppressed with the concentration of surfactants about 20 or 100 times smaller than that just sufficient to impair the kinetics of electrode process. However,factors like the drop time and the activity and diffusion coefficient of the surfactants cannot be overlooked while discussing the influence of the surfactants as the maximum suppressors or as agents influencing shape and position of electrocapillary curve.

—

REFERENCES

1. Heyrovsky,J., 'Polarographie' 174, Wein,Springer-verlag (1941).

2. Ilkovic,D., Collection Czechoslov, Chem. Communs., 8 ,13 (1936).

3. Emilianova,N.V. and Heyrovsky,J., Trans.Faraday Soc., 24 ,257 (1928).

4. Herasymenko,P., Heyrovsky,J. and Tancakivsky,K.,Trans. Faraday Soc., 25 ,152 (1929).

5. Varasova,E., Collection Czechoslov. Chem. Communs., 2 ,8 (1930).

6. Kolthoff,I.M. and Miller,C.S., J.Amer. Chem.Soc. 63 , 1013 (1941).

7. Krjukowa,T.,Acta Physicochim. U.R.S.S., 22 ,381 (1947).

8. Malik,W.U. and Gupta,G.C., Talenta (In Press).

9. Meits,L. and Meits,T., J.Amer.Chem.Soc. 73 ,177 (1951).

10. Kolthoff,I.M. and Okinaka,Y., J.Amer.Chem. Soc. 81 , 2296 (1959).

11. Zuman,P., Chem.Listy, 48 ,1020 (1954).

12. Abro,A., Institute de Engeria Atomica Rept.IEA-66(1962).

13. Malik,W.U. and Haque,R., Anal.Chemistry 32 ,1528 (1960).

Malik,W.U. and Haque,R., Z.Analyt.Chem. 180 ,425 (1961)

14. Malik,W.U. and Haque,R.,Naturwiss, 15 ,346 (1962).

15. Schmidt,R.W. and Reilley,C.N., J.Amer.Chem.Soc. 80 , 2087 (1958).

16. Kuta,J. and Smoler,I.,Z.Elektrochem. 64 ,285 (1960).

17. Badinand,A. and Boucherle,A.,Bull.Soc.Chim.France.Lo21 (1957).

18. Capitanio,V. and Pittoni,A., Chem.Zentr., II,1332 (1942).

19. Capitanio,V. and Pittoni,A., Arri.ist.Venetosci,100, 290 (1941).

20. Holleck,I. and Exner, J.Z. Elektrochem., 56 ,46 (1952).

21. Kryukova, T.A., J.Phys.Chem. (U.S.S.R.) 20 ,1179 (1946).

22. Kemula,W., Roc.Chem. 30 ,1725 (1956).

23. Schwab,K. and Mai,U., J.Electroanal.Chem. I, 54 (1959).

24. Gouy,L., Ann.Chim. Phys. (7) ,29,149 (1903).

25. Colichman,E.L., J.Amer.Chem.Soc. 72 ,4036 (1950).

26. Tamamushi,R. and Yamanaka,T.,Bull.Chem.Soc. Japan, 28 ,673 (1955).

27. Frumkin,A.N., In '' Surface activity'': Proceedings of the second International Congress,London, 1957 Vol.III.p.578, Academic Press,New York, 1958.

28. Meibuhr,S.G.,Electrochim.Acta. 10 ,215 (1965).

29. Barradar,R.G., and Kimmerle,F.M., J.Electroanal.Chem. 9 ,483 (1965).

30. Tanaka,N. and Kobayashi,M. Bull.Chem.Soc. Japan, 24 , 132 (1951).

31. Dratovsky, M. and Ebert,M., Chem. Listy, 45 ,88 (1956).

32. Strassner,J.E. and Delhay, P., J.Amer.Chem.Soc. 24 , 6232 (1952).

33. Heyrovsky,J., Disscussions of Faraday Soc. 212 (1947).

34. Randles,J.E.B., ibid. 11 (1947).

35. Veldstra,H., Bull.Soc. Chim.biol, 31,594 (1949), Chem.Abstr.44 ,179 (1950).

36. Heyrovsky,J., Polarography, Springer-verlag, Berlin (1941) p. 408 H.

37. Gawalowski,K. and Gosman,B.A., Bull.inst.Acad.Sci. Boeheme 33 ,88 (1932).

38. Talafant,E., Collection Czechoslov.Chem.Communs., 15 , 232 (1950).

39. Heyrovsky,J. and Smoler,I.,Collection Czechoslov Chem.Communs.,4 ,521 (1932).

40. Schwarz,K.,Z.Anal.Chem. 115 ,161 (1939).

41. Vauruch,I., Collection Czechoslov.Chem. Communs. 15 ,217 (1950); Anal.Chem. 22 ,930 (1950).

42. Thiesse,X. and Belon,S.,Compt.rend, 223 ,794 (1946).

43. Gatos,H.C.,J.Electrochem.Soc.101 ,433 (1954).

44. Schwartz,A.M. and Perry,J.W., Interscience Publishers, INC., New York,Vol.I,pp.212 (1949).

45. Haworth,R.C. and Mann,F.G.,J.Chem.Soc.(London) 603 (1943).

46. Heyrovsky,J. and Dullinger,M., Collection Czechoslov Chem.Communs., 2 ,626 (1930).

47. Frumkin,A.,''Polarography'',Kolthoff, 9.M.,ed.,Vol.I, p.143, Interscience,Newyork,1952.

—

CHAPTER II.

c.m.c.of non-ionic surfactants by polarographic,electrocapillary and spectrophotometric measurements.

INTRODUCTION

A knowledge of the critical micelle concentration of surfactants is essential in order to understand their physico-chemical behaviour. Many properties like the change in thermodynamic functions at the micellization point; the nature of surface tension vs. concentration curve; the partition equilibrium between the bulk and the surface; the effect of additives on the surface activity of surfactants etc. can be explained satisfactorily on the basis of c.m.c. data.

Although evidence regarding the formation of aggregates or micelles through association of amphipathic molecules is available from different sources, controversy exists about the size and shape of these micelles. According to McBain (1), any combination of molecules or ions that causes a reduction in the free energy of the system can exist in a stable form. Stauff (2) has also discussed quantitatively the possibility of the existence of thermodynamically stable associated colloids. Other workers who have put forward plausible mechanism of micelle formation are, Debye, Reich, Kushner (3-5).

Abrupt change in a particular property of the surfactant over a narrow range of concentration is observed during micelle formation. This change can be followed by a number of experimental techniques thereby providing means for determining the c.m.c.. The techniques or physico-chemical methods employed are:electrical conductance (6,7),transference number (8), dialysis (12),electrophoretic mobility (13),freezing point (14),solubility (15),e.m.f. (16), light scattering (17-18) etc..

From the existing literature it is seen that above methods have not found general applicability for non-ionic surfactants. It may be due to the following reasons (i) the hydrophilic portion of non-ionics is much larger than the hydrophobic portion in comparision to the ionic surfactants; (ii) unlike the ionic surfactants,non-ionics have negative solubility coefficients,known as clouding phenomena and (iii) the absence of electric charge on the micelle. An attempt was,therefore,made to find suitable methods for determining the c.m.c. of non-ionic surfactants with fairly high accuracy.

Before introducing the subject matter of this aspect of the problem, it will be worthwhile to survey briefly the literature on the c.m.c. of non-ionic surfactants. Not only that a clear understanding about the micelles of non-ionic surfactants is lacking,the convenient determination of c.m.c. of these surfactants is a problem by itself. Commonly used methods are surface tension (19-20), viscosity (21) measurements. According to Moilliet and Collie (22) ''no suitable dyestuffs have as yet been found which show sufficient alteration in spectrum by non-ionic surface active agents to render them suitable indicators''. Ross and Olivier (23) selected iodine as a good indicator for this purpose while benzopurpurin 4B was used by Martin and Standing (24). This method was applied with considerable success by Becher (25) in determining the c.m.c. of polyoxyethylene -23- lauryl alcohol. Kushner and Hubbard (26) failed to get evidence for micelle formation in Triton X-100 by light scattering measurements. The only reference worth-mentioning is the work of Colichman (27) and Tamamushi et.al (28) on polarographic maximum suppression method to determine the polarographic micelle point (PMP) of the above surfactants. The polarographic method has also not been extensively employed to determine the c.m.c.of surfactants. Recently Malik and coworkers (29) have employed this method in determining the c.m.c. values of a number of ionic agents viz.,alkyl aryl sulphonates,dodecyl pyridinium bromide and isothiourea dodecyl hydrobromide. Little attempt has been made to apply this method to non-ionic surfactants.

The present chapter described with the use of polarographic method in determining the c.m.c.values of some non-ionic surfactants,like,lauric acid diethanolamine condensate (LDC),Nonex 501,Nonidet P40 and Nonidet P42. The method besides offering a new electro-chemical approach to the c.m.c. determination of non-ionic surfactants has the extra advantage of being used to study the effect of different electrolytes on the c.m.c.. The c.m.c.values thus obtained are compared with those obtained by iodine solubilization, spectral dye and electrocapillary curves methods.

—

EXPERIMENTAL

PREPARATION OF SOLUTIONS.

Solutions of surface active agents (LDC, Nonidet P40, Nonidet P42 and Nonex 501) and metal salts were prepared as described in Chapter I.

APPARATUS AND TECHNIQUE.

Polarographic measurements were also carried out as given in Chapter I.

PROCEDURE.

The determination of polarographic micelle concentrations was made from the ratio $i_{maximum}/i_{diffusion}$ for the non-ionic surfactants under reference. The data of Chapter I were used to know the above ratio. The results in presence of different supporting electrolytes are summarized in the following tables:

Table 1.

NONIDET P40		
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Pb^{++} (KNO_3).
0.80	-3.0969	1.17
1.16	-2.9355	1.14
1.54	-2.8125	1.12
1.90	-2.7215	1.10
2.26	-2.6459	1.07
3.00	-2.5229	1.03
3.64	-2.4389	1.00

Fig.1(a).

Table 2.

NONIDET P40		
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Ni^{++} (KCl)
0.80	-3.0969	1.75
1.60	-2.7959	1.67
2.00	-2.6990	1.52
2.32	-2.6345	1.41
3.08	-2.5115	1.29
3.80	-2.4202	1.19
5.20	-2.2840	1.07
6.60	-2.1805	1.00

Fig.2(a)

Table 3.

NONIDET P40		
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for $(CdI_4)^{--}$
0.80	-3.0969	1.46
1.54	-2.8125	1.37
2.26	-2.6459	1.29
3.00	-2.5229	1.25
3.64	-2.4389	1.14
4.30	-2.3665	1.10
4.91	-2.3090	1.05
5.50	-2.2597	1.01
6.10	-2.2147	1.00

Fig.4(a)

Table 4.

NONIDET P40

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Co^{++} (KCl).
1.54	-2.8125	1.86
3.00	-2.5229	1.36
3.64	-2.4389	1.21
4.30	-2.3665	1.18
4.91	-2.3090	1.12
6.10	-2.2147	1.09
6.67	-2.1759	1.05
8.25	-2.0835	1.00

Fig.5 (a)

Table 5.

NONIDET P40

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Ni^{++} - Co^{++} (KCl - pyridine)
1.60	-2.7959	3.12
3.08	-2.5115	3.01
4.50	-2.3468	2.76
6.00	-2.2219	2.66
8.60	-2.0655	2.45
11.00	-1.9586	1.63
13.30	-1.8762	1.42
15.5	-1.8097	1.00

Fig.7 (b)

Table 6.

NONIDET P40

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Cu-biuret(pH 12.0)
0.40	-3.3980	1.50
0.80	-3.0969	1.41
1.60	-2.7959	1.31
2.32	-2.6345	1.26
3.08	-2.5115	1.18
4.50	-2.3468	1.08
5.20	-2.2840	1.00

Fig.9(a)

Table 7.

	NONIDET P40	
Concentration (x 10^{-3} gms/1.)	log concentration	i_m/i_d for Cu-glycinate(KNO_3)
0.80	-3.0969	3.51
1.60	-2.7959	2.52
2.32	-2.6345	1.81
3.80	-2.4202	1.38
4.50	-2.3468	1.32
6.00	-2.2219	1.16
7.28	-2.1379	1.08
8.60	-2.0655	1.00

Fig.6 (a)

Table 8.

	NONIDET P40	
Concentration (x 10^{-3} gms/1.)	log concentration	i_m/i_d for U^{6+} ($KClO_3$-phosphoric acid).
0.40	-3.3980	1.70
0.80	-3.0969	1.68
1.60	-2.7959	1.48
2.32	-2.6345	1.36
3.08	-2.5115	1.24
3.80	-2.4202	1.19
4.50	-2.3468	1.07
5.20	-2.2840	1.00

Fig.2 (b)

Table 9.

	NONEX 501	
Concentration (x 10^{-3} gms/1.)	log concentration	i_m/i_d for Pb^{++} (KNO_3)
0.80	-3.0969	1.09
1.20	-2.9208	1.07
1.60	-2.7959	1.06
2.32	-2.6345	1.04
3.08	-2.5115	1.02
3.80	-2.4202	1.00

Fig.1 (b)

Table 10.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Ni^{++} (KCl)
0.80	-3.0969	1.70
1.60	-2.7959	1.46
2.32	-2.6345	1.33
2.70	-2.5686	1.23
3.08	-2.5115	1.18
3.80	-2.4202	1.08
4.50	-2.3468	1.01
5.20	-2.2840	1.00

Fig.3 (a)

Table 11.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Co^{++} (KCl)
0.80	-3.0969	1.80
1.60	-2.7959	1.60
2.32	-2.6345	1.51
3.08	-2.5115	1.36
3.80	-2.4202	1.24
4.50	-2.3468	1.17
6.00	-2.2219	1.06
6.60	-3.1805	1.00

Fig.8 (b)

Table 12.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for $(CdI_4)^{--}$
0.40	-3.3980	1.55
0.80	-3.0969	1.50
1.60	-2.7959	1.30
2.32	-2.6345	1.18
3.08	-2.5115	1.12
4.50	-2.3468	1.08
6.00	-2.2219	1.04
7.28	-2.1379	1.00

Fig.8 (a)

Table 13.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Cu-biuret(pH 12.0)
0.40	-3.3980	1.41
0.80	-3.0969	1.34
1.20	-2.9208	1.30
1.60	-2.7959	1.23
2.32	-2.6345	1.17
3.08	-2.5115	1.11
3.80	-2.4202	1.05
4.50	-2.3468	1.00

Fig.9 (b)

Table 14.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Cu-glycinate(KNO_3)
0.80	-3.0969	2.70
1.60	-2.7959	1.90
2.00	-2.6990	1.72
2.32	-2.6345	1.54
2.70	-2.5686	1.39
3.45	-2.4622	1.26
4.50	-2.3468	1.16
6.00	-2.2219	1.00

Fig. 6 (b)

Table 15.

	NONEX 501	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for U^{6+} ($KClO_3$-phosphoric acid).
0.40	-3.3980	1.50
0.80	-3.0969	1.45
1.60	-2.7959	1.15
2.00	-2.6990	1.03
2.32	-2.6345	1.00

Fig. 10 (a).

Table 16.

NONEX 501

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Ni^{++}-Co^{++} (KCl-pyridine).
0.80	-3.0969	2.76
1.60	-2.7959	2.55
2.32	-2.6345	2.47
3.08	-2.5115	2.34
5.20	-2.2840	1.84
6.60	-2.1805	1.34
8.60	-2.0655	1.00

Fig. 7 (a)

Table 17.

NONIDET P42

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Pb^{++} (KNO_3)
2.0	-2.6990	1.09
4.0	-2.3980	1.08
7.84	-2.1057	1.07
11.6	-1.9355	1.03
15.4	-1.8125	1.00

Fig.1 (c)

Table 18.

NONIDET P42

Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for CO^{++}(KCl)
4.0	-2.3980	1.88
6.0	-2.2219	1.72
7.84	-2.1057	1.52
11.60	-1.9355	1.17
15.40	-1.8125	1.10
19.00	-1.7215	1.04
22.60	-1.6459	1.00

Fig. 5 (b)

Table 19.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for CO^{++}(KCl)
4.0	-2.3980	1.88
6.0	-2.2219	1.72
7.84	-2.1057	1.52
11.60	-1.9355	1.17
15.40	-1.8125	1.10
19.00	-1.7215	1.04
22.60	-1.6459	1.00

Fig. 5 (b)

Table 20.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d $(CdI_4)^{=}$
4.00	-2.39800	1.45
7.84	-2.2219	1.32
10.00	-2.0000	1.20
11.60	-1.9355	1.13
15.40	-1.8125	1.07
19.00	-1.7215	1.03
22.00	-1.6459	1.00

Fig. 4 (b).

Table 21.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Cu-biuret (pH 12.00).
2.00	-2.6990	1.55
4.00	-2.3980	1.40
7.84	-2.1057	1.26
11.60	-1.9355	1.18
15.40	-1.8125	1.11
19.00	-1.7215	1.04
22.60	-1.6459	1.00

Fig.9 (c).

Table 22.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Cu-glycinate(KNO$_3$)
4.00	-2.3980	3.41
11.60	-1.9355	1.67
15.40	-1.8125	1.38
22.60	-1.6459	1.18
26.00	-1.5850	1.10
30.00	-1.5229	1.00

Fig. 6 (c)

Table 23.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for U^{6+}(KCl$_3$-phosphoric acid.
4.00	-2.3980	1.60
6.00	-2.2210	1.48
7.84	-2.1057	1.42
9.76	-2.0156	1.32
11.60	-1.9355	1.22
15.40	-1.8125	1.05
19.00	-1.7215	1.00

Fig.10 (b)

Table 24.

	NONIDET P42	
Concentration (x 10^{-3} gms/l.)	log concentration	i_m/i_d for Ni^{++}-Co^{++} (KCl-pyridine)
7.84	-2.1057	2.65
15.40	-1.8125	2.59
22.60	-1.6459	2.56
30.00	-1.5229	2.55
36.40	-1.4389	2.16
50.00	-1.3010	1.40
61.00	-1.2147	1.30
66.00	-1.1805	1.15
72.00	-1.1427	1.00

Fig.11

Table 25.

Concentration (x 10^{-3} gms/l.)	L.D.C. log concentration	i_m/i_d for Pb^{++} (KNO_3)
0.72	-3.1397	1.61
1.45	-2.8386	1.40
2.90	-2.5376	1.11
3.62	-2.4413	1.08
4.35	-2.3615	1.05
5.80	-2.2366	1.00

Fig.12.

Table 26.

Concentration (x 10^{-3} gms/l.)	L.D.C. log concentration	i_m/i_d for Ni^{++} (KCl)
2.90	-2.5376	1.36
5.80	-2.2366	1.31
8.70	-2.0605	1.19
11.60	-1.9355	1.10
14.50	-1.8386	1.07
17.40	-1.7595	1.03
20.30	-1.6925	1.00

Fig.13 (a)

Table 27.

Concentration (x 10^{-3} gms/l.)	L.D.C. log concentration	i_m/i_d for CO^{++} (KCl)
7.25	-2.1397	1.43
14.50	-1.8386	1.11
17.40	-1.7595	1.05
20.30	-1.6925	1.03
23.20	-1.6345	1.02
26.10	-1.5834	1.00

Fig.13 (b).

Table 28.

Concentration (x 10^{-2} gms/l.)	L.D.C. log concentration	i_m/i_d for Ni^{++}-Co^{++} mixture in pyridine.
14.50	-0.8386	1.53
21.75	-0.6635	1.48
29.00	-0.5376	1.41
43.50	-0.3615	1.14
50.75	-0.2946	1.03
58.00	-0.2366	1.00

Fig.16.

Table 29.

Concentration (x 10^{-3} gms/l.)	L.D.C. log concentration	i_m/i_d for CdI_4^{--}
3.62	-2.4413	2.12
7.25	-2.1397	1.54
10.87	-1.9636	1.37
14.50	-1.8386	1.27
25.37	-1.5960	1.09
29.00	-1.5376	1.00

Fig.14 (a)

Table 30.

Concentration (x 10^{-3} gms/l.)	L.D.C. log concentration	i_m/i_d for Cu-biuret.
2.90	-2.5376	1.36
5.80	-2.2366	1.32
8.70	-2.0605	1.17
11.60	-1.9355	1.12
14.50	-1.8386	1.07
17.40	-1.7595	1.00

Fig.15.

Table 31.

LDC		
Conc. (x10^{-3} gms/l.)	log conc.	i_m/i_d for Cu-glycinate (KNO_3)
2.90	-2.5376	1.60
5.80	-2.2366	1.43
7.25	-2.1397	1.37
10.15	-1.9936	1.28
17.40	-1.7595	1.15
20.30	-1.6925	1.11
26.10	-1.5834	1.00

Fig. 14 b.

C.M.C. DETERMINATION BY IODINE SOLUBILIZATION METHOD.

PREPARATION OF THE SOLUTION.

The solutions of non-ionic surface active agents under investigation were prepared as already described.

The stock solution of iodine (A) was prepared by dissolving 100 mg. in one litre.

APPARATUS.

Absorption measurements were made by Bausch and Lomb 'spectronic 20'.

PROCEDURE.

The stock solution of non-ionic surfactant (B) whose c.m.c. was to be determined, contained a known concentration of the surfactant well above its c.m.c.. By diluting the fixed amount of iodine solution (A) with the different amounts of surfactant (B) a wide range of concentrations of surfactant for carrying out spectral studies was made available. This procedure helped in fixing an appropriate range of concentration to work with. The spectrophotometer readings were best made with solution A as the standard for 100% transmittance.

The spectrophotometric measurements were made at a 360 mμ (iodine micelle complex maximum). It was always found advisable to record the readings within an hour of the preparation of solution, because of a slow fading of colour of iodine-micelle complex.

Table 32.

Differential absorbence measurements of Nonidet P40, Nonex 501 and Nonidet P42 at different concentrations in presence of iodine solution at 360 mμ.

Conc. of surfactant solution ($\times 10^{-2}$ gms/l.)	Differential absorbence		
	Nonidet P40	Nonex 501	Nonidet P42
2.0	0.000	0.000	-
3.0	0.000	0.000	-
4.0	0.000	0.010	0.010
6.0	0.010	0.080	0.000
8.0	0.010	0.150	0.010
10.0	0.010	0.230	0.020
14.0	0.075	0.350	0.030
18.0	0.180	0.480	0.040
20.0	0.280	0.600	0.050
25.0	0.470	0.750	0.070
30.0	0.640	0.800	0.080
35.0	-	-	0.085
40.0	0.850	-	0.150
50.0	-	-	0.320
60.0	-	-	0.450
75.0	-	-	0.700
Fig.17	Curve a.	b.	c.

Table 33.

Differential absorbence measurements of LDC at different concentrations in presence of iodine solution at 360 mμ.

Conc.of surfactant solution (x 10^{-2} gms/l.)	Differential absorbence. LDC
0.380	0.010
0.580	0.010
0.770	0.015
0.970	0.020
1.160	0.025
1.550	0.040
2.300	0.105
2.900	0.120
3.500	0.150
3.920	0.170
4.200	0.190
4.70	0.210

Fig. 18

c.m.c. DETERMINATION BY SPECTRAL DYE METHOD.

PREPARATION OF SOLUTIONS

The solutions of non-ionic surface active agents were prepared as described previously.

Benzopurpurin 4B was a BDH product. The stock solution of the dye was prepared of the concentration 10^{-5}M by dissolving 0.0072 gm. in 100 ml..

APPARATUS.

Absorption measurements were carried out by a Bausch and Lomb 'Spectronic 20'.

PROCEDURE.

The fixed amount of the dye (10^{-5}M) was mixed with the different amounts of the non-ionic surfactant solution whose c.m.c. was to be determined and the total volume (10 ml.) was made up with water. A series of the solutions having a fixed concentration of the dye and different concentrations of surface active agent above and below the c.m.c. were obtained.

The spectrophotometric measurements were made at a wavelength of 510 mμ, using one centimeter cell, after half an hour of the mixing of the mixture.

Table 34.

Differential absorption measurements of Nonidet P40 and Nonex 501 at different concentrations in presence of benzopurpurin 4B solution at 510 mμ.

Conc. of surfactant solution (x 10^{-2} gms/l.)	Differential absorbence	
	Nonidet P40	Nonex 501
1.0	-	0.000
2.0	0.000	0.000
3.0	-	0.000
4.0	0.000	0.010
6.0	0.000	0.016
8.0	0.010	0.028
10.0	0.020	0.040
14.0	0.035	0.060
16.0	0.050	0.070
18.0	-	0.082
20.0	0.065	0.086
24.0	0.080	0.104
28.0	0.100	0.130
Fig. 19 Curve	a	b.

Table 35.

Differential absorbence measurements of Nonidet P42 at different concentrations in presence of benzopurpurin 4B at 510 mμ.

Conc.of surfactant solution (x 10^{-2} gms/l.)	Differential absorbence Nonidet P42
8.0	0.000
16.0	0.000
20.0	0.000
28.0	0.005
32.0	0.010
36.0	0.010
40.0	0.030
50.0	0.045
60.0	0.050
80.0	0.070
100.0	0.100

Fig. 20

C.M.C.DETERMINATION BY ELECTROCAPILLARY CURVES METHOD.

APPARATUS AND PROCEDURE.

The apparatus and procedure used in drop time measurements were the same as described in Chapter I.

The drop time was plotted against log.concentration of the surfactants at various potentials. In order to locate the c.m.c. point, the portion of the curves (Figs.21-23) showing sharp fall in drop time with the increase in surfactant concentration was extrapolated downwards while the flat portion was extrapolated backwards. The concentration of the surfactants corresponding to the point of intersection of the extrapolated portions of the curve was taken as c.m.c.value.

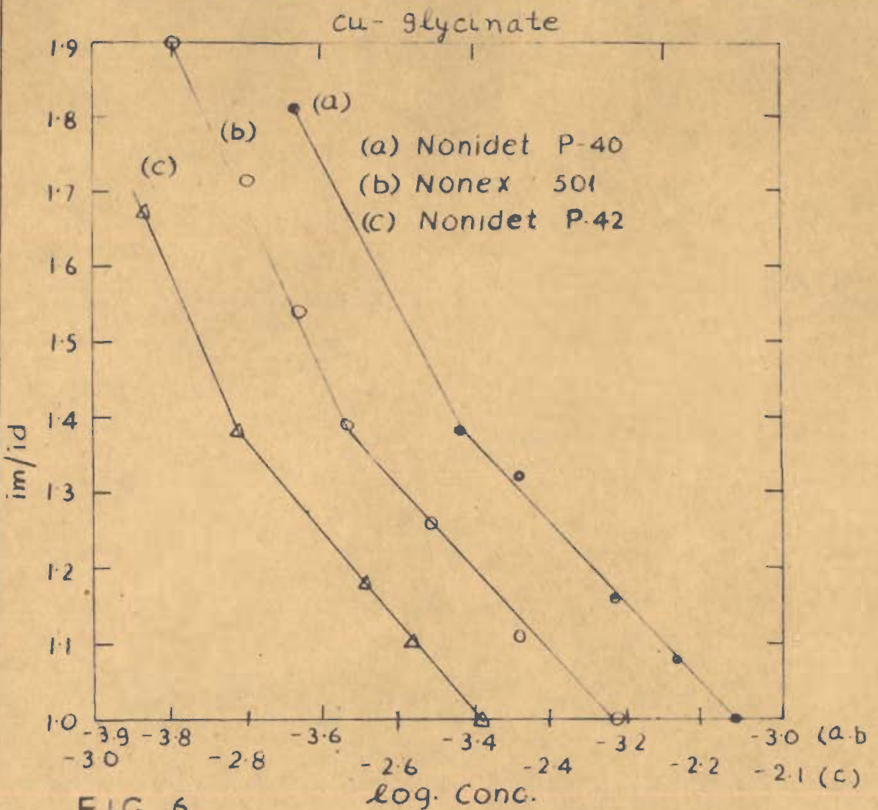


FIG 6

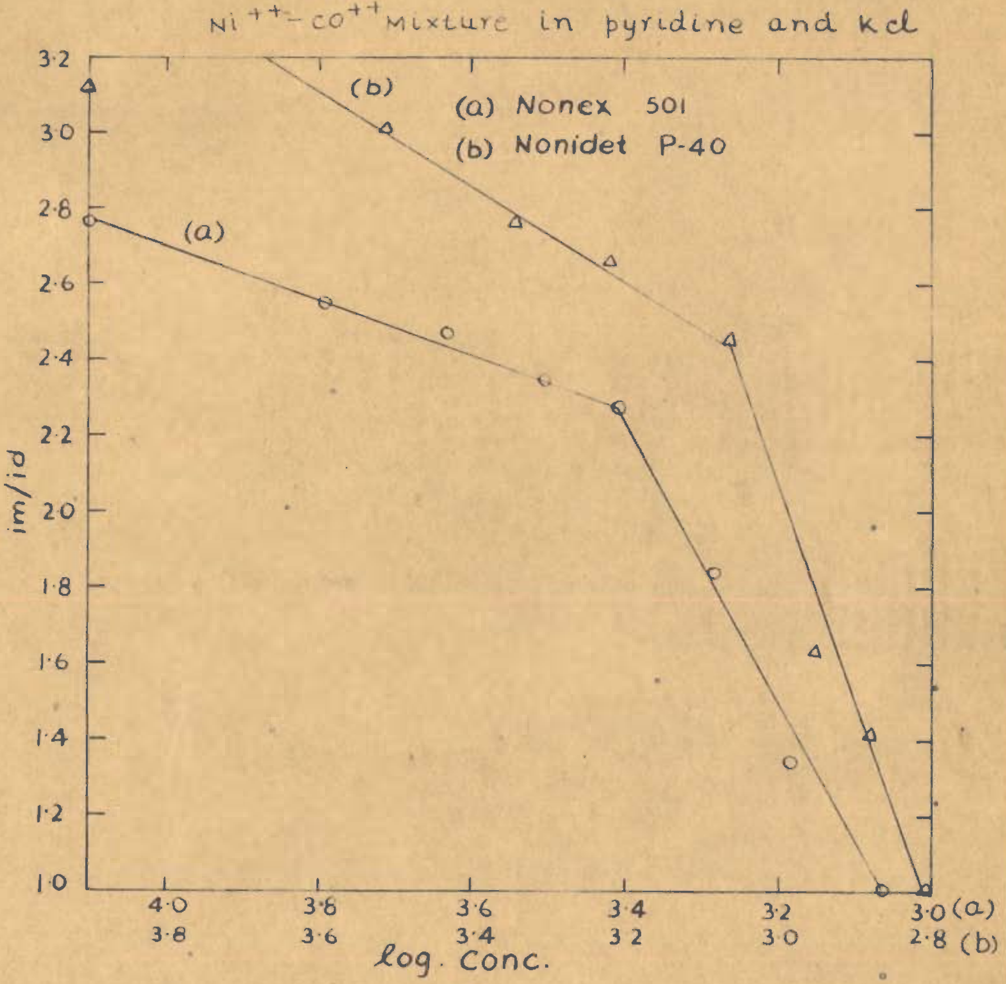


FIG.7

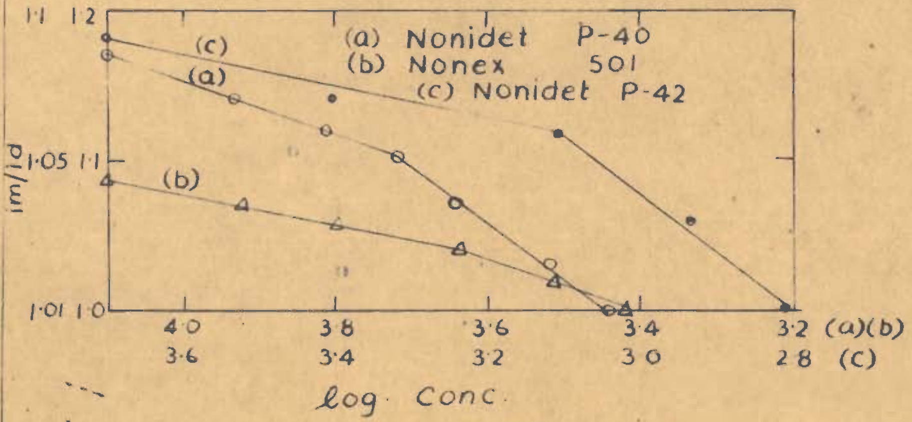


FIG. 1

Pb^{++} – KNO_3

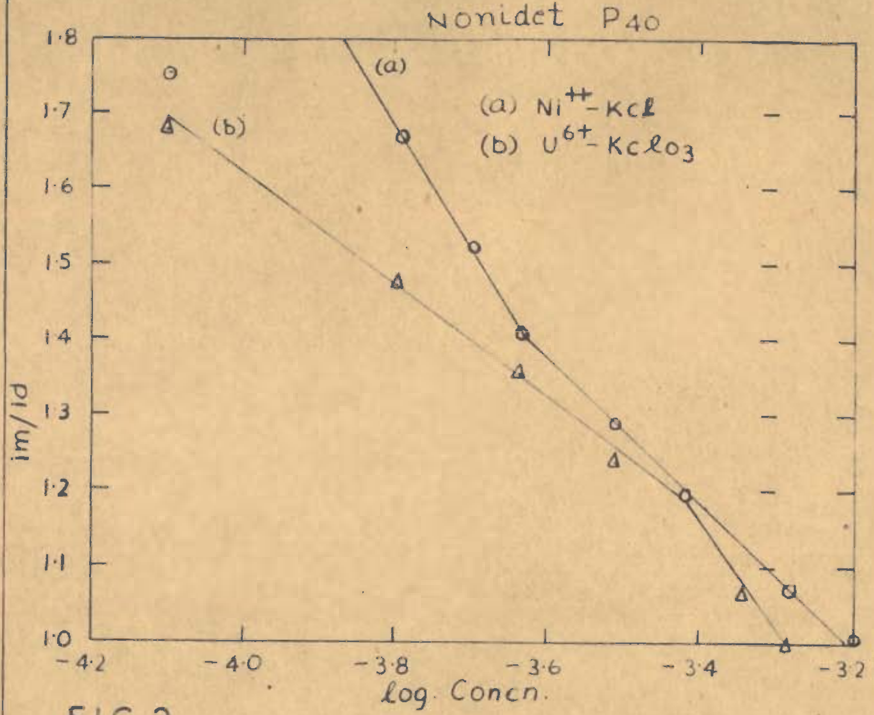
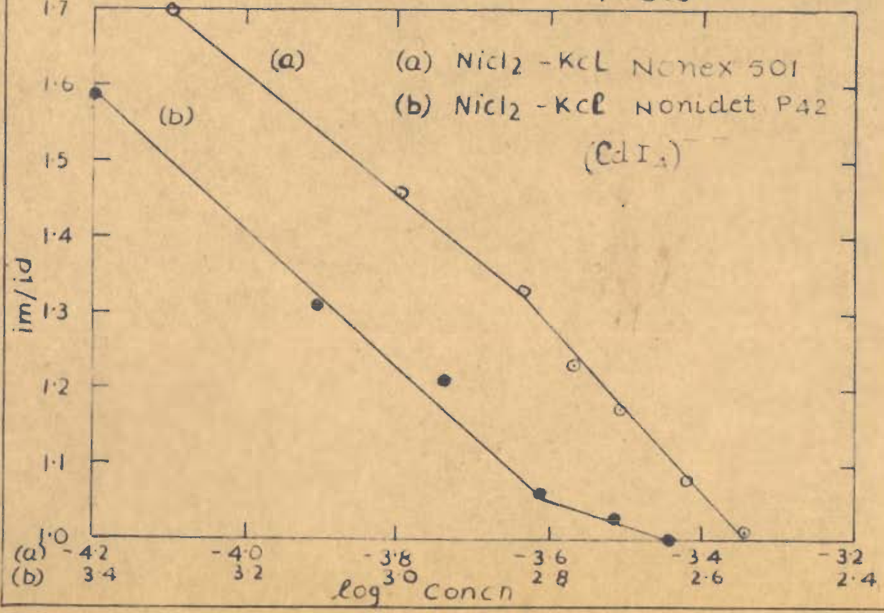


FIG. 2

FIG. 3



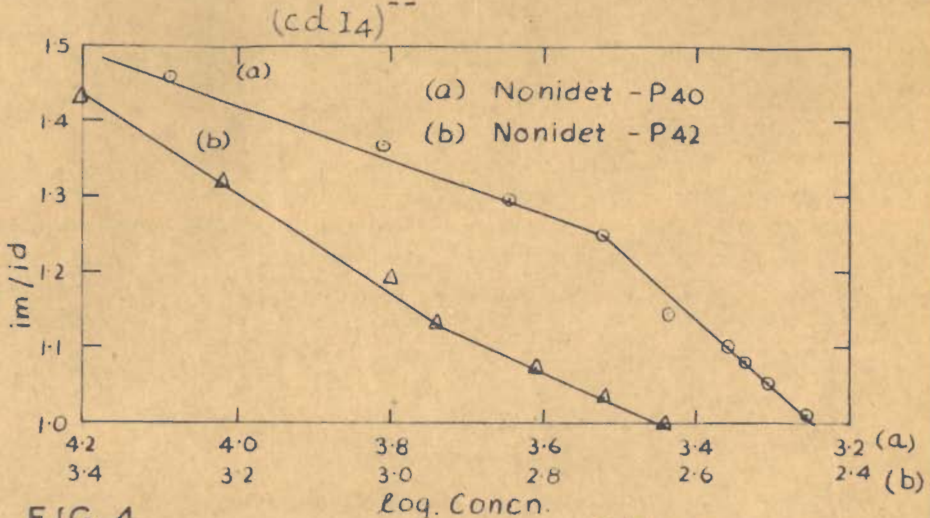
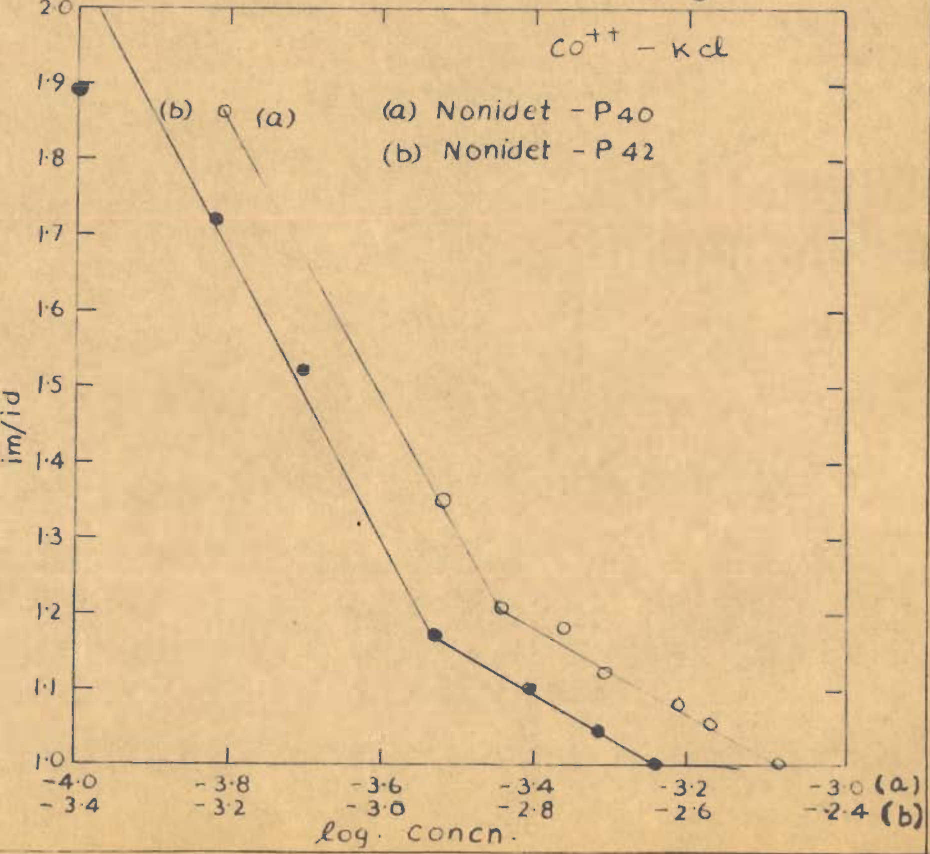


FIG. 4

FIG. 5



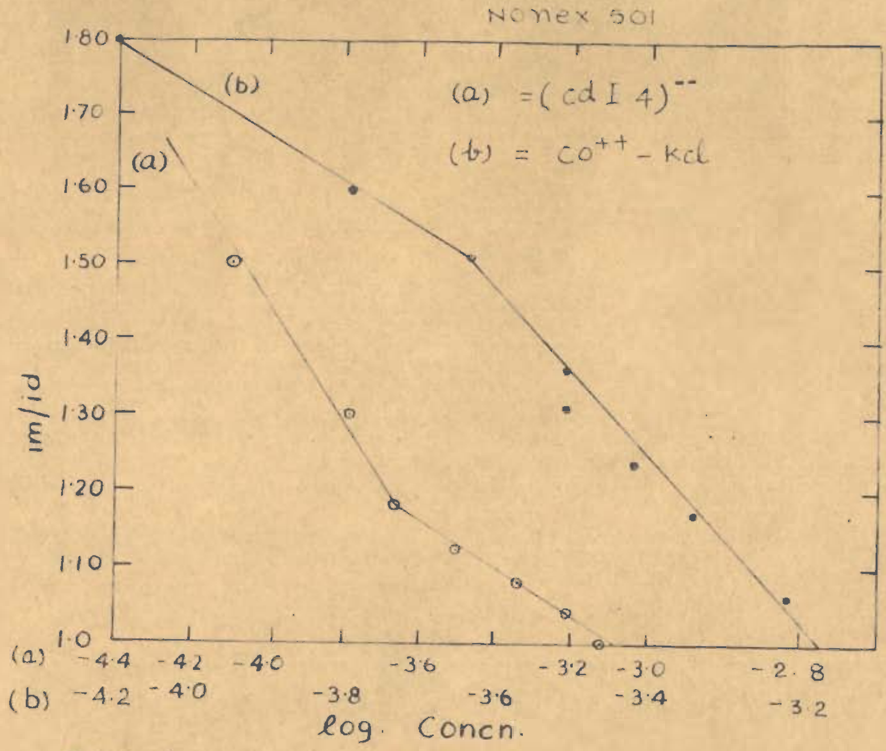


FIG. 8

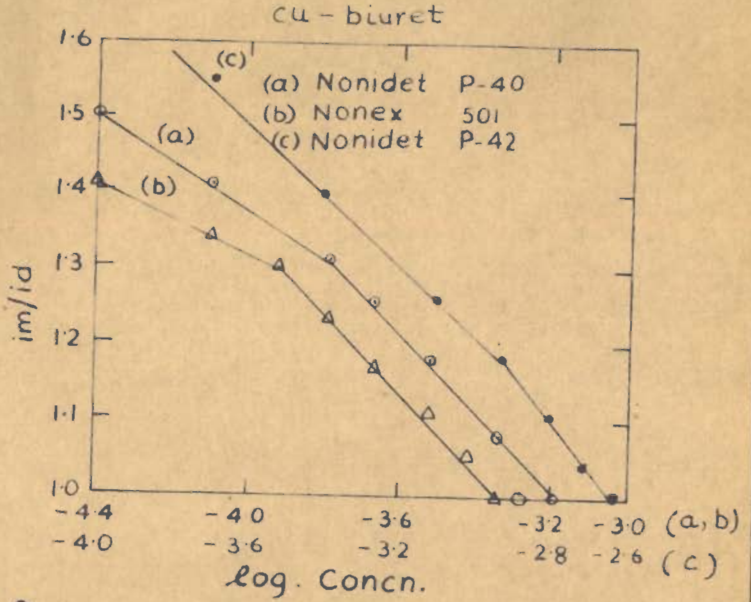


FIG. 9

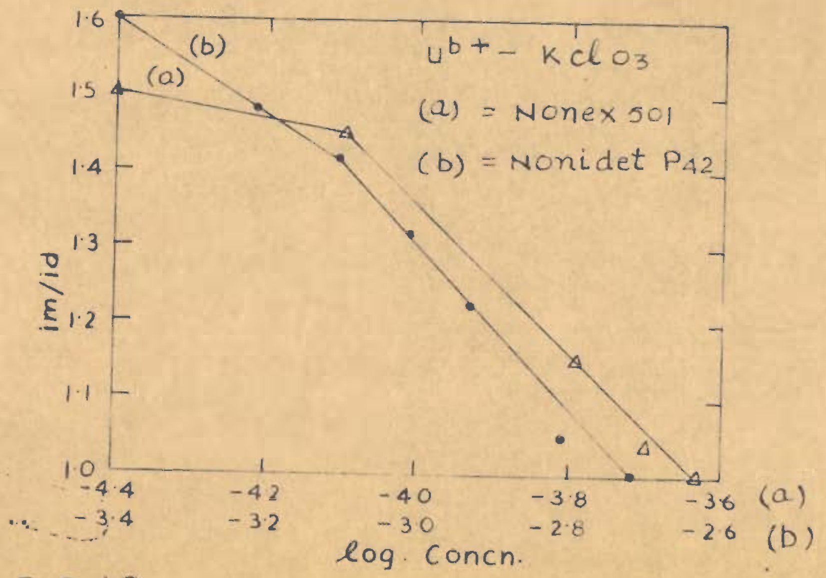


FIG. 10

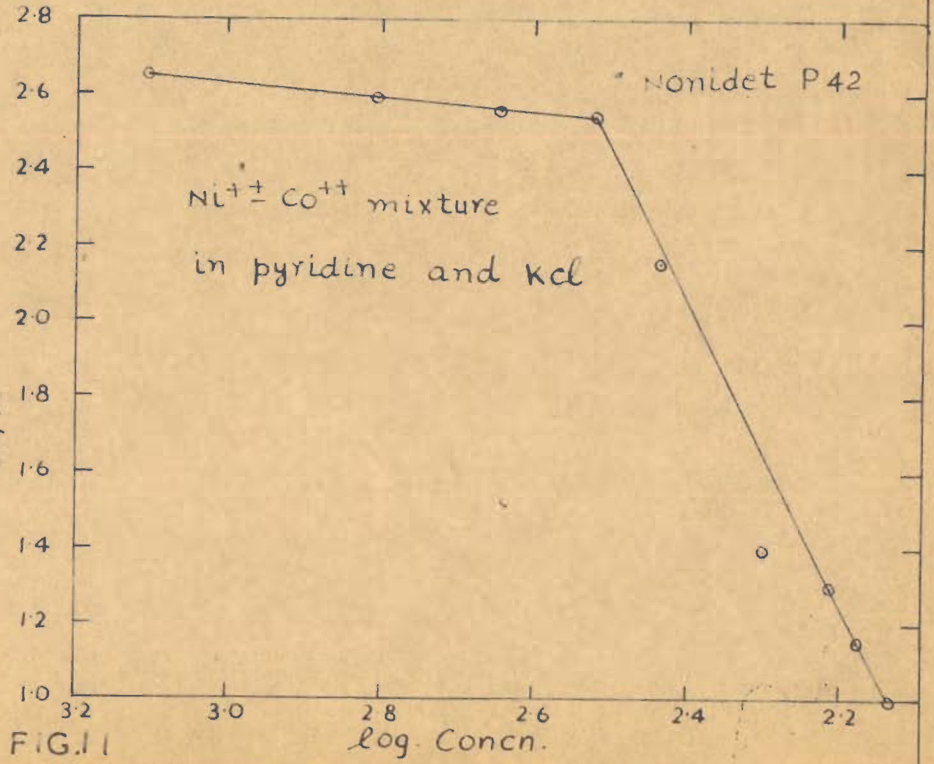


FIG.11

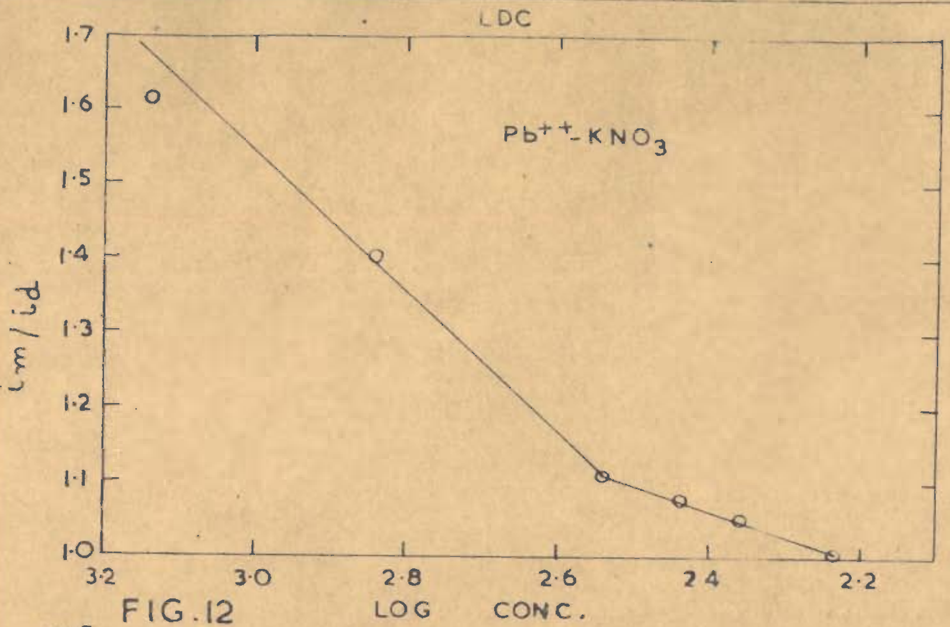


FIG. 12

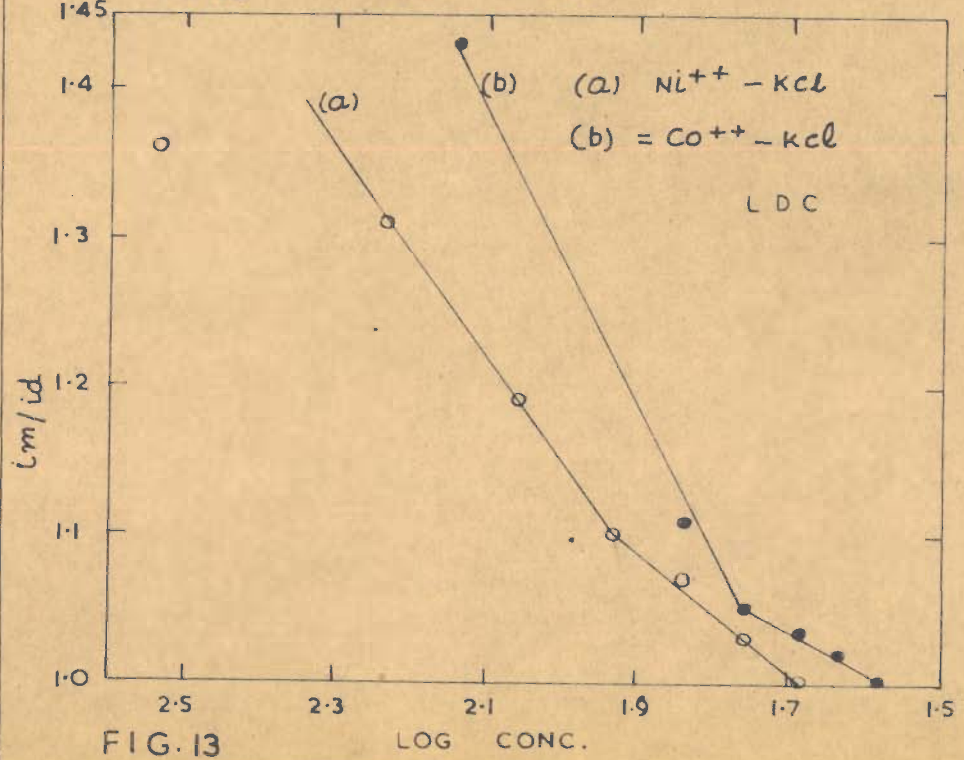


FIG. 13

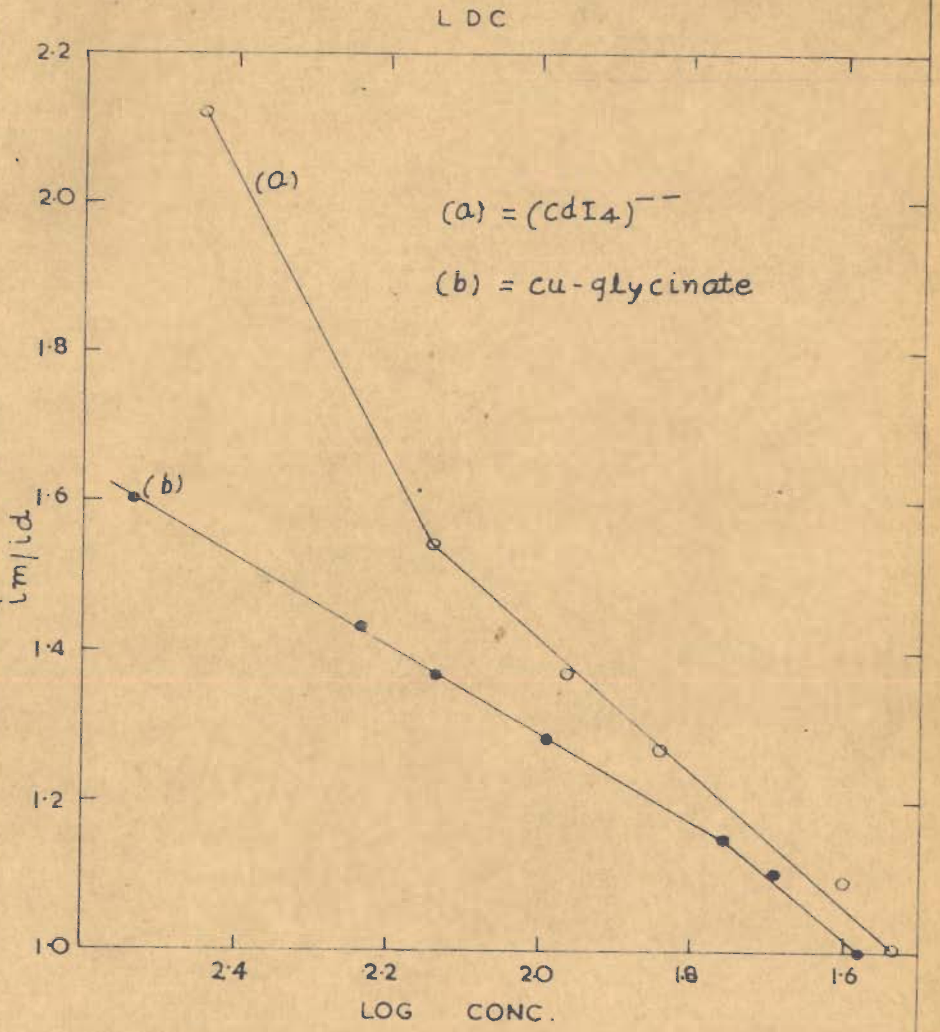


FIG. 14

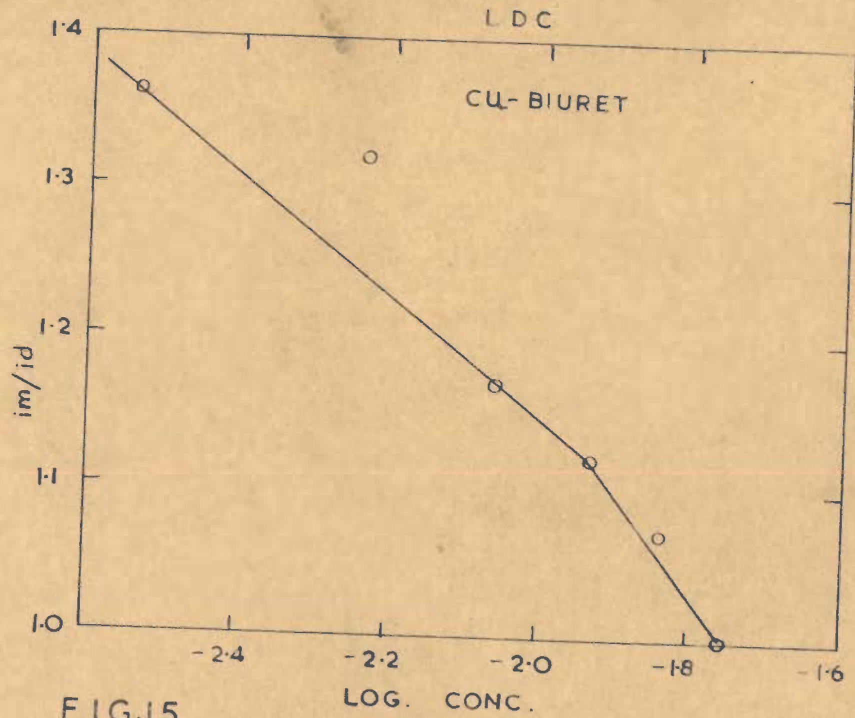

LDC
CU-BIURET
1·4
1·3
1·2
1·1
1·0
im/id
- 2·4
- 2·2
- 2·0
-1·8
- 1·6
LOG. CONC.

FIG.15

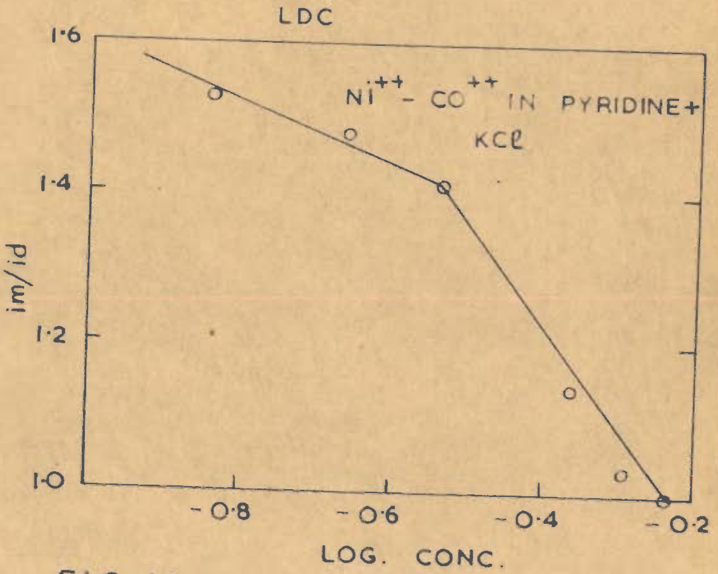

LDC
Ni^{++} - CO^{++} IN PYRIDINE+ KCl
1·6
1·4
1·2
1·0
im/id
- 0·8
- 0·6
- 0·4
- 0·2
LOG. CONC.

FIG.16

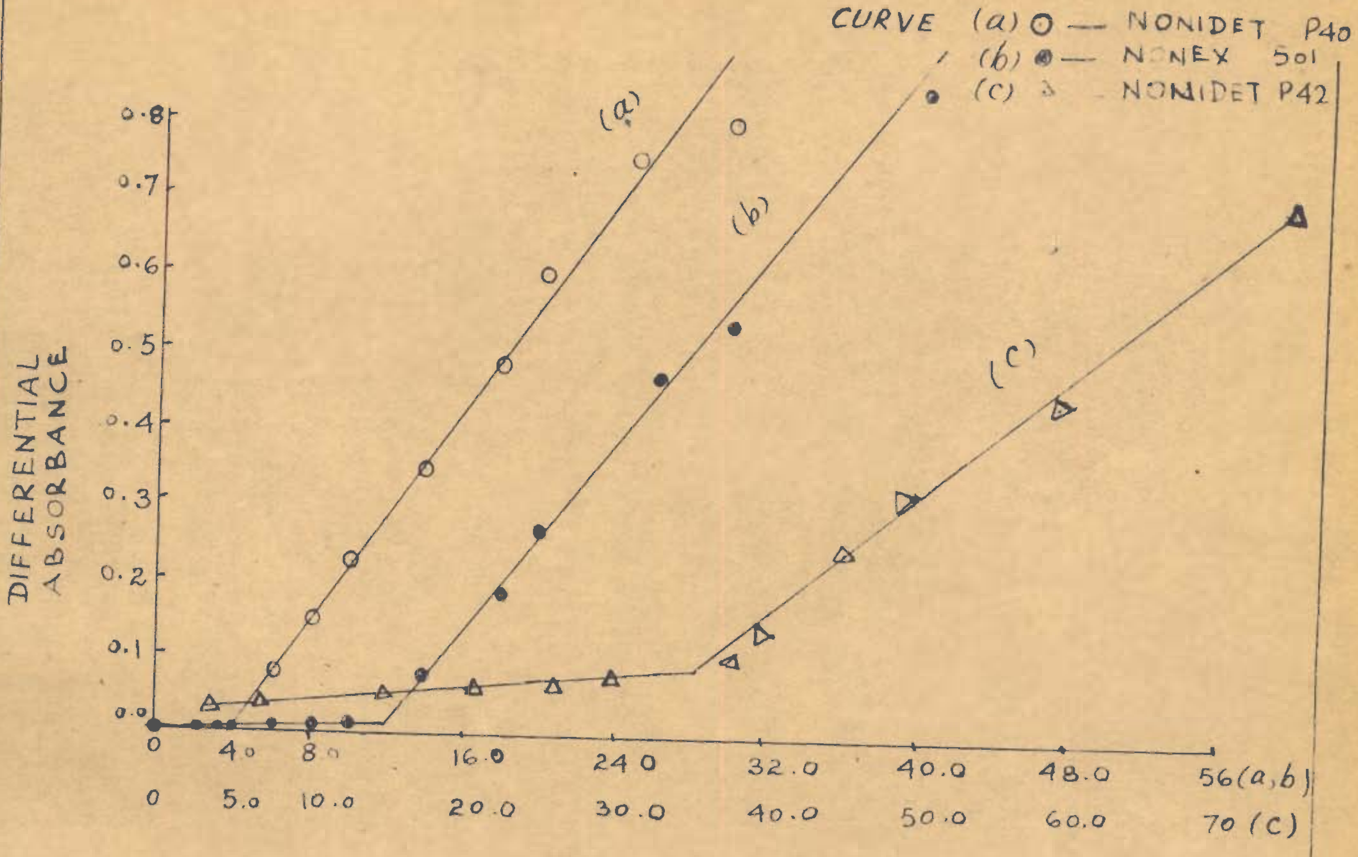


FIG. 17 SURFACTANT CONC.(x10^{-2} gms/l)

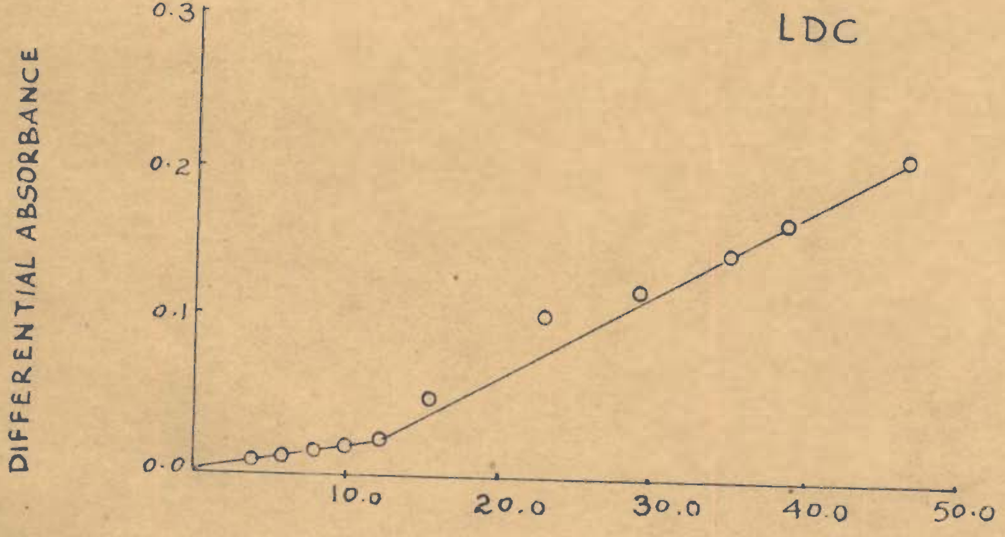


FIG. 18 SURFACTANT CONC.(x10^{-2} gms/l)

C.M.C. DETN. BY IODINE SOLUBILIZATION METHOD.

C.m.c. DETN. BY SPECTRAL DYE METHOD.

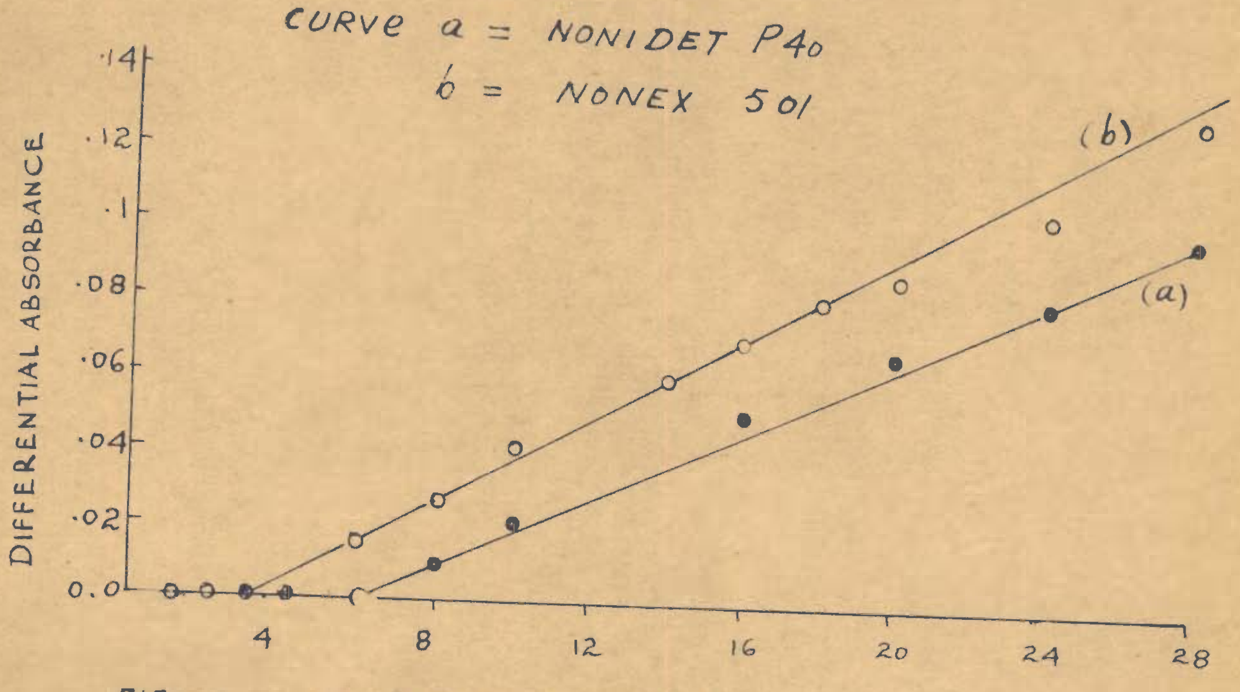


FIG. 19 SURFACTANT CONC. ($\times 10^{-2}$ gms/l)

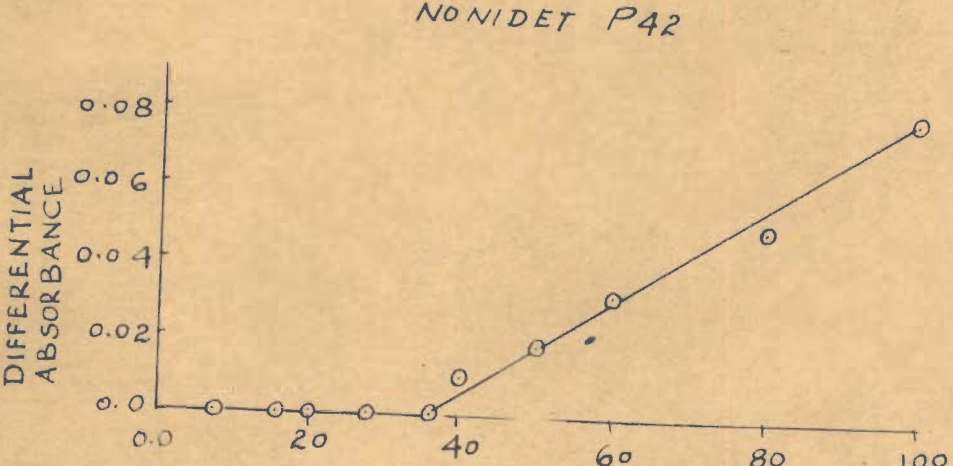


FIG. 20 SURFACTANT CONC. ($\times 10^{-2}$ gms/l)

C.m.C DETERMINATION OF NONIDET P40, NONEX501

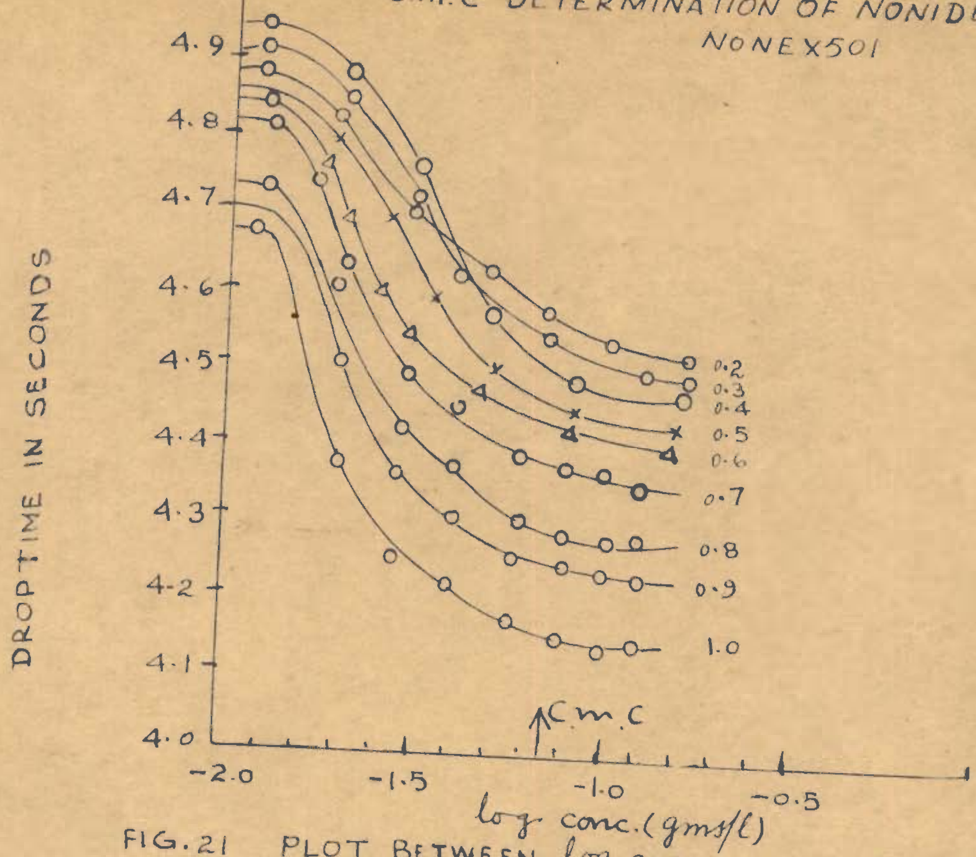


FIG. 21 PLOT BETWEEN log conc. OF NONIDET P40 AND DROP TIME AT DIFFERENT POTENTIALS

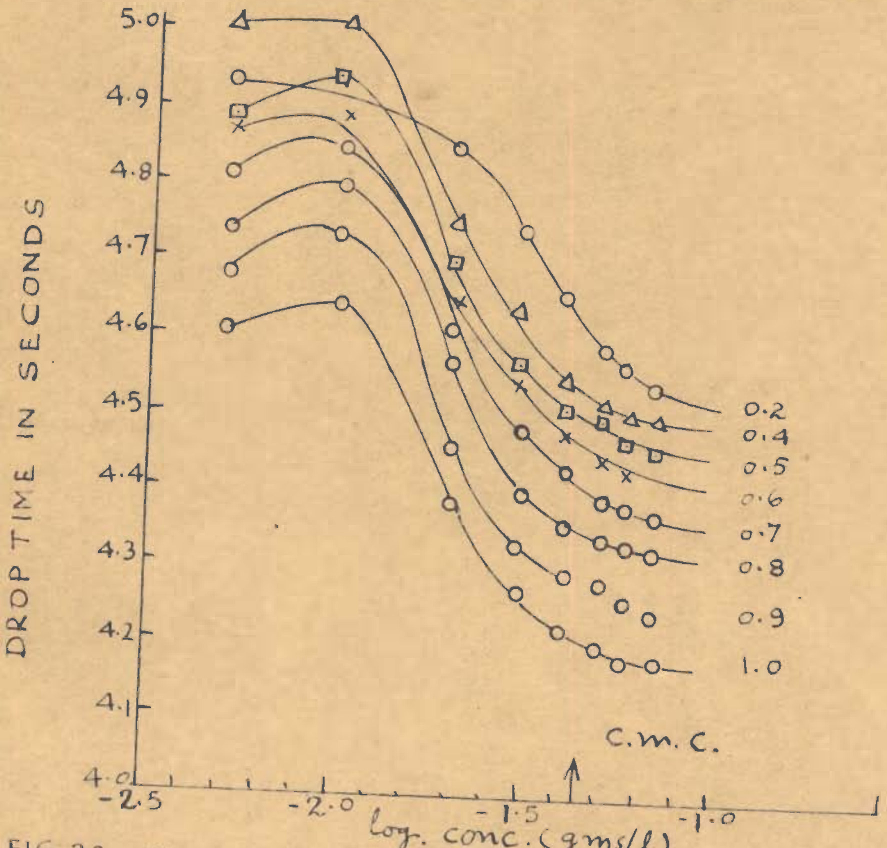


FIG. 22 PLOT BETWEEN log. conc. OF NONEX501 AND DROP TIME (SECONDS) AT DIFFERENT POTENTIALS.

C.m.C. DETERMINATION OF NONIDET P42

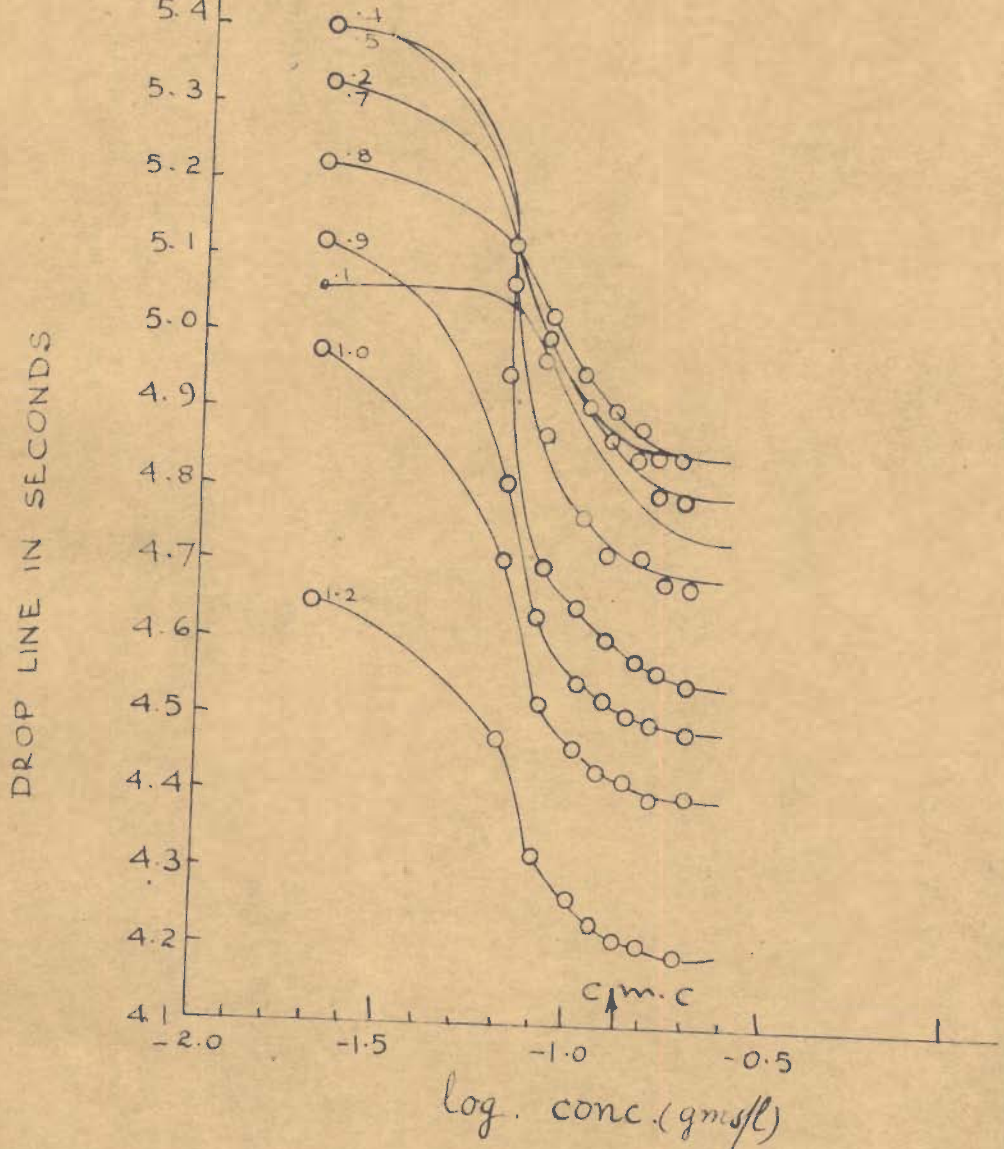


FIG. 23 PLOT BETWEEN log conc. OF NONIDET P42 AND DROP TIME (SECONDS) AT DIFFERENT POTENTIALS.

RESULTS AND DISCUSSION

The plots between $i_{maximum}/i_{diffusion}$ and log concentration of the surfactant can be used to determine the two polarographic characterstics of the surfactants, viz.,polarographic micelle point (P.M.P.) and maximum suppression point (M.S.P.). The former is obtained from the point where the first discontinuity appears in the curve while the latter is determined by extrapolating the curve to $i_{maximum}/i_{diffusion} = 1$. The data on the M.S.P. and P.M.P. values obtained from the respective curves of the surfactants,are summarized in the following tables:

Table 1.

Polarographic micelle point (P.M.P.) values of Nonidet P40, Nonex 501, Nonidet P40 and LDC in presence of different supporting electrolytes.

Ion or complex studied.	(order 10^{-3} gms/l.) Nonex 501	Nonidet P40	Nonidet P42	LDC
Pb^{++}-KNO_3	2.32	1.90	7.84	2.90
Ni^{++}-KCl	2.32	2.32	15.40	11.54
Co^{++}-KCl	2.32	3.64	11.60	17.37
Ni^{++}-Co^{++} mixture in pyridine acid KCl.	3.39	8.60	30.00	290.00
CdI_2-KI complex.	2.32	3.00	11.60	7.25
Cu-biuret complex.	3.08	1.60	11.60	8.70
Cu-glycine complex in KNO_3.	2.70	3.80	15.40	5.80
U^{6+}-$KClO_3$ and phosphoric acid.	0.80	3.80	7.84	-

Table 2.

Maximum suppression point (M.S.P.) values of Nonidet P40, Nonex 501, Nonidet P42 and LDC in presence of different supporting electrolytes.

Ion or complex	Nonex 501 ($x10^{-3}$gms/l)	Nonidet P40 ($x10^{-3}$gms/l)	Nonidet P42 ($x10^{-3}$gms/l)	LDC ($x10^{-3}$gms/l)
Pb^{++}-KNO_3	3.80	3.64	15.40	5.80
Ni^{++}-KCl	5.20	6.60	22.60	20.30
Co^{++}-KCl	6.60	8.25	22.60	26.10
CdI_2-KI complex.	8.60	6.10	22.60	29.00
Cu-biuret	4.50	5.20	22.60	17.40
Cu-glycine in KNO_3	6.00	8.60	30.00	26.10
Ni^{++}-Co^{++} mixture	8.60	15.50	72.00	580.00
U^{6+}-$KClO_3$	2.32	5.20	19.00	-

From the foregoing tables, it may be seen that the P.M.P. values differ very little from each other irrespective of the cations used. With the exception of Ni^{++}- Co^{++} mixture in pyridine and KCl, where a large amount of the surfactants is required to suppress the maximum, the P.M.P. values range within narrow limits. The values range between 0.8 to 3.08 x 10^{-3} gms/l.; 1.60 to 3.80 x 10^{-3} gms/l. and 7.84 to 15.4 x 10^{-3} gms/l. for Nonex 501, Nonidet P40 and Nonidet P42 respectively. Similar behaviour is observed with LDC, inspite of the fact that LDC is not so effective surfactant for the maximum suppression as the other three. Like the cations of the depolarizer, the anions of the supporting electrolytes do not affect the P.M.P. values of the non-ionic surfactants. The pH of the medium also does not markedly influence the P.M.P. values. It is thus seen that the P.M.P. values obtained in the higher pH ranges, pH 10.0 and 12.0 for Cu-glycine, Cu-biuret complexes are not far removed from the values obtained with metals in the lower pH range.

The P.M.P. values of anionic surfactants are, however, greatly influenced by pH as observed by Malik et.al. (30) in the case of alkyl aryl sulphonates.

The P.M.P. and M.S.P. values can both be correlated to the c.m.c. of the surfactants although it is usual to donate it with the former. In either case, however, the values are much lower than those obtained by the iodine solubilization, spectral dye and surface tension methods (31) which incidently, compare favourably with each other and give concentration values in the same range. Such a discrepency is likely to occur since the ions of the depolarizer and the supporting electrolytes influence the water structure.

A comparision of the c.m.c. values of non-ionic surfactants with those of the ionic ones (Table 3) found previously (32) reveal that the former has got smaller c.m.c.values than the latter. This difference may be attributed to the several factors,viz.,(i) greater hydration of the non-ionized polar groups,(ii) greater tendency of non-ionic groups to associate because of lack of electrical charge,(iii) absence of geggenions in non-ionic surfactants.

Table 3.*

Comparative c.m.c. values of anionic surfactants from different electro-chemical methods.

Method	(x 10^{-2} gms/l.)		
	SPSA	STSA	SXSA
Polarographic method (Ni^{++} in 0.1N KCl).	3.60	21.20	17.00
pH-metric method (without electrolyte)	6.10	7.10	9.40
Conductometric method (without electrolyte)	13.90	22.68	25.10

C.m.c.values (x 10^{-5}M) given in ref.32 were converted in (x 10^{-2} gms/l.).

* from ref.32.

The low c.m.c. values for non-ionic surfactants find support in the words of Fowkes (33) who said ''one might also note that for micelles of equal aggregation number,twice as many ionic particles are required to make up a micelle and the tendency to form micelles is proportional to the square of the concentration of ionic detergents but only to the first power of the concentration of non-ionic agent''.

As already stated another new approach can be made to determine the c.m.c. of surfactants in presence of salts of alkali metals (used as supporting electrolytes in polarographic work) by studying their electrocapillary curves.

Figs. (21-23) depict the drop time log concentration curves in the potential range (-0.2 to -1.0 volt). These curves show an initial slow change followed by a sharp decrease in drop time until a concentration of 10^{-2} gms/l. is reached, when the curves show the signs of flattening out. Since flattening sets in at the same concentration irrespective of the potential applied, this concentration can be taken as the point of incipient micelle formation. The results for the three surfactants are given in Table (4).

Table 4.

Comparative c.m.c. values of non-ionic surfactants from different electro-chemical methods.

Method	(x 10^{-2} gms/l.)			
	Nonidet P40	Nonex 501	Nonidet P42	LDC
Electrocapillary curves method in 0.1N KCl.	7.60	4.70	13.80	-
Iodine solubilization method in water.	12.00	4.80	35.00	0.116
*Surface tension.	12.50	6.20	39.80	1.160
Spectral dye method.	6.00	3.00	36.00	-
Polarographic method. (Ni^{++} in 0.1N KCl)	0.36	0.23	1.16	1.54

* from ref. 31.

Unlike the polarographic method,the c.m.c.values determined by this method compare favourably with those obtained by iodine solubilization,spectral dye and surface tension methods. The small discrepency may be attributed to the presence of the electrolytes.

The importance of electrocapillary curves method is all the more realised when dealing with non-ionic surfactants which have low c.m.c.values. With ionic surfactants,other methods can be applied,since their c.m.c.values are quite high and small deviation would not effect the accuracy of the results. The polarographic method may,therefore, be quite useful in determining the c.m.c.of ionic surfactants but fail to give reliable data in the case of non-ionic surfactants. In such cases the electrocapillary curves method will prove to be the most suitable one.

--OO--

REFERENCES

1. McBain,J.W., '' Frontiers in Colloid Chemistry'',p.144, New York, Inter Science Publishers, 1949.

2. Stauff,J., Kolloid-Z, 125 ,79 (1952).

3. Debye,P., J.Phys.Chem. 53 ,1 (1949).

4. Reich,I., J.Phys. Chem. 60 ,257 (1956).

5. Kushner, L.M., Hubbard,W.D. and Doan, A.S.,J.Phys. Chem. 61 ,371 (1957).

6. Walton,H.F., Hiebert,E.N. and Scholtes, E.H., J.Colloid Sci. 1 ,385 (1946).

7. Lin,W., Bull.Chem.Soc. Japan. 28 ,227 (1955).

8. Hartley,G.S., Callie,B. and Samis,C.S., Trans.Faraday Soc. 32 ,795 (1936).

9. Addison,C.C. and Elliott,T.A., J.Chem.Soc. p.3103 (1950).

10. Thiele, H., Kolloid-Z. 113 ,155 (1949).

11. Wright,K.A. and Tartar, H.V., J.Amer.Chem.Soc. 61 , 544 (1939).

12. Yang, J.T. and Foster, J.F., Phys.Chem. 57 ,628 (1953)

13. Stigter,D. and Mysels, K.J., J.Phys.Chem. 59 ,45 (1955).

14. Gonick,E. and McBain, J.W., J.Amer.Chem.Soc. 69 ,334 (1947).

15. Murray,R.C. and Hartley,G.S. Trans.Faraday Soc. 31 , 183 (1935).

16. McBain,J.W. and Willians,R.C., J.Am.Chem. Soc. 55 , 2250 (1933).

17. Phillips,J.N. and Mysels, K.J., J.Phys.Chem. 59 , 325 (1955).

18. Nakagawa,T., Kuriyama, K., Inoue,H. and Oyama,T., Chem. Soc. Japan. 79 ,348 (1958) (In Papanese).

19. Shinoda,K., Yamanaka,T. and Kinoshita,K., J.Phys.Chem. 63 ,648 (1959).

20. Bury,C.R. and Browning,J., Trans.Faraday Soc. 49 , 209 (1953).

21. Greenwald, H.L. and Brown,G.L., J.Phys.Chem. 58 ,825 (1954).

22. Moilliet,J.L. and Collie,B., '' Surface Activity'' D.Van Nostrand Co., Inc., New York, N.Y. p.50 (1951).

23. Ross,S. and Oilliver, J.P., J.Phys.Chem. 63 ,1671 (1959).

24. Martin, J.T. and Standing,H.A., J.Textile Inst. 40 , T 689 (1949).

25. Becher,P., J.Phys.Chem. 66,374 (1962).

26. Kushner,L.N. and Hubbard,W.D., J.Phys.Chem. 58 ,1163 (1954).

27. Colichman,E.L., J.Amer.Chem.Soc. 72 ,4036 (1950).

28. Tamamushi,R. and Yamanaka,T.Bull.Chem.Soc. Japan,28 , 673 (1955).

29. Malik,W.U. and Haque,R., Ind.J.Chem.Soc. 2 ,35 (1964).

30. Malik,W.U., Haque,R., Z.fur Anal.Chem. 425 (1961).

31. Malik,W.U., and Saleem,S.M. (Unpublished data).

32. Malik,W.U. and Verma,S.P., J.I.C.S., 41 ,317 (1964).

33. Fowkes, F.M.,Discussion in J.Phys.Chem. 63 ,1674 (1959).

CHAPTER III.

Spectrophotometry of dye-surfactant mixtures.

INTRODUCTION

The interaction of surface active agents with other substances, both colloidal and non-colloidal in nature, has been studied to establish certain characteristics peculiar to the surface active agents and to extend the domain of their applications. Proteins (1-4), nucleic acid (5), polymers (6-7), organic dyes (8), hydrophobic sols (9,10), metals in their simple (11) and complex forms (12) have been employed in such studies but the approach has been mostly of qualitative nature.

From the list of the substances mentioned above, the reactions with dye stuffs need special mention since investigations on them would pose aggregational problems of great complexity. Nevertheless, the researches carried out by Hartley (13) and few others (14-17) have proved to be quite useful in determining the c.m.c. of the surfactants and in ascertaining the structural changes taking place in the dyes due to their association with surface active substances.

Another interesting feature of the interation of surfactants and dyes is the existence of 'metachromacy', a term introduced by Lison (18) and Holmes (19) to explain the changes in colour of dilute solutions of dyes caused by the addition of substances of high molecular weight. This phenomena is useful both from the fundamental and the applied point of views. Solutions of dyes not obeying Beer's law can be very well studied on the basis of this property. Recently Colichman (20) had carried out investigations on the variations in the optical density of the acidic and basic forms of bromophenol blue on the addition of long chain quaternary ammonium compounds. Mehrotra (21) studied the influence of surface active substances like Igepon T, and Nekol BX on the colorimetric determination of pH.

Attention to another interesting aspect of surfactant-dye interaction,viz.,formation of surfactant-dye complex,was drawn by Hiskey and Downey (22) ,Mysels and others. They observed that the change in absorption spectrum of dyes in the presence of surface active agents may be attributed to this property. Mukerjee and Mysels (17) also tried to establish the composition of methylene blue-lauryl sulphate,cetyl trimethyl ammonium-bromophenol blue complexes. Hiskey and Downey (22) studied spectrophotometrically the existence of a complex of methyl orange with octadecyl trimethyl ammonium chloride at different pH values. They had interpreted the spectral data in terms of association reaction between the quaternary ammonium salt and the basic form of methyl orange. Hayashi (23) has studied the interaction of congo red with Tween-80 and cetyl pyridinium chloride and interpreted the metachromatic effect produced in dye solution due to complex formation.

Inspite of the fact that the indications of the existence of the surfactant-dye complexes were forthcoming in a few cases, the investigations have been more or less of preliminary nature. So far little has been said about the mechanism of interaction or mode of binding. Efforts in this direction were done by Malik and coworkers. Although, their earlier work (24,25) could only throw light on the mechanism of interaction, their latter approach was quantitative and dealt with the binding of the various surfactants with acid and basic dyes. To increase the domain of our knowledge on the quantitative aspect of surfactant-dye interaction, it was considered worthwhile to carry out investigations with several surfactant-dye combinations. The investigations described in this chapter giving the extent of binding, also throw some light on the structural changes accompanying surfactant-dye interaction.

The investigations described in the chapter deal with the following interactions:

(i) Rosaniline hydrochloride and dodecane sulphonic acid.

(ii) Rosaniline hydrochloride and dioctyl sodium sulpho succinate.

(iii) Malachite green and dodecane sulphonic acid.

(iv) Malachite green and dioctyl sodium sulpho succinate.

(v) Rhodamine 6G and dodecane sulphonic acid.

(vi) Rhodamine 6G and dioctyl sodium sulpho succinate.

(vii) Congo red and cetyl trimethyl ammonium bromide.

(viii) Congo red and cetyl pyridinium bromide.

—

EXPERIMENTAL

PREPARATION OF DODECANE SULPHONIC ACID: ($C_{12}H_{25}SO_3H$).

Dodecane sulphonic acid was prepared by the method recommended by Noller and Gordon (26) in the laboratory.

A solution of 0.2 mole of dodecane mercapton in 200 ml. of 95% alcohol was added slowly, with rapid stirring to a solution of 150 gm. lead acetate in 200 ml. of 50% alcohol. The mercaptide precipitated out as a light canary yellow salt. This was filtered with suction and washed twice with water and once with acetone and dried. The dry powdered salt was added in small proportions, to 50% nitric acid. A white salt settled to the bottom of the flask. After all the mercaptide has been added to the mixture, it was allowed to stand for an hour, diluted with cold water and filtered with suction. The salt was filtered and washed twice with water and then extracted with hot acetone.

On cooling the acetone extracts of the lead lauryl sulphonate, a white crystalline product was separated out.

Dry HCl gas was introduced into the suspension of lead lauryl sulphonate in isopropyl alcohol. After complete decomposition, the lead chloride was filtered on to a sintered glass filter.

The solvent was further evaporated under vacuum distillation. Viscous solution was dissolved in the freshly distilled ether (150 ml.) and mixed with water and thoroughly shaken. The aqueous solution was then drawn from the separating funnel and evaporated at reduced pressure over anhydrous $CaCl_2$ and then finally over P_2O_5. The final product was a white crystalline solid (m.p. 40°C).

REAGENTS:

Rosaniline hydrochloride, malachite green, rhodamine 6G, congo red used in these investigations were BDH products.

Other surfactants, viz., dioctyl sodium sulpho succinate (Manoxl OT), cetyl trimethyl ammonium bromide (CTMAB) and cetyl pyridinium bromide (CPB) were BDH products and were used without further purification. Stock solutions of anionic surfactants were prepared of the concentration 1.0×10^{-2}M while those of cationic surfactants and dyes were of the concentrations 1.0×10^{-3}M, in doubly distilled water.

Walpole (pH 2.0, 4.6), McIlvaine (pH 7.0) and borax buffers (pH 9.12) were prepared in the laboratory (27) to carry out the experiments.

PRELIMINARY EXPERIMENTS:

On carrying out the preliminary experiments the following changes in the colour of the dye, in presence of surface active agents were observed:

(i) in acedic and neutral media, the colour of rosaniline hydrochloride changed from red to redish violet in presence of dodecane sulphonic acid and Manoxol OT;(ii) the colour of malachite green changed from bluish green to dark green in presence of dodecane sulphonic acid and Manoxol OT irrespective of the pH of the medium;(iii) the colour of rhodamine 6G changed from yellowish red to red in presence of dodecane sulphonic acid and Manoxol OT irrespective of the pH of the medium; (iv) the colour of congo red changed from bluish violet to orange in acidic medium (pH 2.0) ,red to orange in neutral (pH 7.0) and redish orange to orange in alkaline media (pH 9.12) in presence of CPB and CTMAB.

In the vicinity of pH 7.0,an orange coloured precipitate was observed at the low concentrations of the CTMAB and CPB which got dispersed by further addition of surfactant.

APPARATUS.

A Bausch and Lomb 'Spectronic 20' was used for the absorption measurements. The molar extinction coefficients were calculated from the relationship

$$\epsilon = (1/cd) \log_{10} I_o/I$$

pH-measurements were made with a Cambridge Bench-Type pH meter.

FORMULA USED.

Klotz (28) studied spectrophotometrically the interaction of proteins with organic anions. The

The concentrations of the unbound dye were calculated using the formula

$$\alpha = \frac{\epsilon_{app.} - \epsilon_b}{\epsilon_f - \epsilon_b}$$

where $\epsilon_{app.}$ is the apparent molar extinction coefficient, ϵ_b molar extinction coefficient of the bound dye, ϵ_f molar extinction coefficient of the free dye and α is the fraction of the free dye.

The validity of this equation was extended to surfactant-dye interaction.

<u>PROCEDURE</u>.

The absorption of the following sets of the mixtures was measured in order to determine the binding of dyes with surfactants.

(i) Solutions of varying concentrations of the dyes (0.1,0.2,...... 0.6 ml.of 10^{-3}M); made up to 15.0 ml. with the buffers alone.

(ii) A known and constant amount of the dye + 8.0 ml.of buffer solution of requisite pH + varying amount of surfactant solution (0.0,0.2,0.3,0.4,0.6,0.8,1.0 .... 5.0 ml.of 10^{-2} M); total volume made up to 15.0 ml. with water.

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 surfactants combinations.

Set I and Set II were employed to determine ϵ_f and $\epsilon_{app.}$ respectively in Klotz's equation. The method used by Malik and Verma (25) to determine ϵ_b was considered to give dubious results on the binding of dye with surfactants since it was based on the tentative assumption that a small quantity of the dye would completely bound with excess of the surfactant. For example, they assumed that 1.0 x 10^{-5}M of malachite green or rhodamine 6G was completely bound with 5.0 x 10^{-4}M of alkyl aryl sulphonates (SPSA, STSA, SXSA). Their results on binding determined by substituting the value of ϵ_b in the Klotz's equation, however, showed a sufficient amount of the free dye left in the solution in the high concentration of the surfactants (10^{-4}M). The following modified procedure was, therefore, employed in determining the extent of binding of the dye with surfactants.

From our absorption data, it appeared that beyond a certain concentration of the surfactant solutions say, 20.0 x 10^{-4}M of Manoxl OT or dodecane sulphonic acid (DS) the absorbence did not increase further by the addition of further amount of the surfactant. The plots between absorbence and surfactant concentration give curves (Figs. 2-19) in which the absorbence first increases and then becomes constant giving the flat portion of the curve. Extrapolating the flat portion of the curve to the zero surfactant concentration,the absorbence of the bound dye can be found out. Dividing the absorbence by the dye concentration the value of ϵ_b can be determined.

—

Dodecane sulphonic acid (DS)-malachite green.

Table 1.

Absorption spectra of 2.00 x 10^{-5}M malachite green in presence of different concentrations of DS (order 10^{-4}M) at pH 2.00

Wavelength in mμ	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	5.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
610	0.31	0.40	0.47	0.54	0.65	0.72	0.74	0.75	0.75
620	0.30	0.39	0.52	0.57	0.72	0.84	0.83	0.86	0.85
625	0.28	0.35	0.52	0.64	0.75	0.85	0.87	0.87	0.86
630	0.26	0.32	0.48	0.56	0.71	0.82	0.84	0.85	0.81

Table 2.

Absorption spectra of 2.67 x 10^{-5}M malachite green in presence of different concentrations of DS (order 10^{-4}M) at pH 7.00.

Wavelength in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	5.34	6.67	10.00	13.34	16.67	20.00	26.67	33.34
610	0.58	0.75	0.82	0.97	1.04	1.09	1.08	1.11	1.12
620	0.60	0.81	0.91	1.12	1.22	1.26	1.30	1.30	1.30
625	0.57	0.82	0.92	1.11	1.22	1.28	1.32	1.30	1.32
630	0.53	0.69	0.88	1.02	1.15	1.23	1.24	1.24	1.23

Table 3.

Absorption spectra of 2.00 x 10^{-5}M malachite green in presence of different concentration of DS (order 10^{-4}M) at pH 9.12.

Wavelength in mμ	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	6.67	10.00	13.34	16.67	20.00	26.67	33.34	40.00
610	0.18	0.26	0.30	0.37	0.43	0.45	0.48	0.50	0.50
620	0.17	0.29	0.36	0.43	0.47	0.52	0.54	0.60	0.60
625	0.16	0.29	0.37	0.44	0.49	0.53	0.57	0.61	0.61
630	0.13	0.27	0.33	0.42	0.47	0.52	0.52	0.58	0.58

Dioctyl sodium sulpho succinate(Manoxl OT)-malachite green.

Table 4.

Absorption spectra of 4.00 x 10^{-5}M malachite green in presence of different concentrations of Manoxl OT (order 10^{-4}M) at pH 2.00.

Wave-length in mμ.	ABSORBENCE 1 1.34	2 3.34	3 6.67	4 10.00	5 13.34	6 20.00	7 26.67	8 33.34	9 40.00
610	0.290	0.410	0.660	0.750	0.800	0.850	0.865	0.875	0.885
620	0.320	0.420	0.705	0.810	0.855	0.920	0.920	0.930	0.960
625	0.260	0.430	0.730	0.850	0.890	0.960	0.960	0.965	0.990
630	0.240	0.365	0.670	0.720	0.830	0.890	0.905	0.925	0.950

Table 5.

Absorption spectra of 4.00 x 10^{-5}M malachite green in presence of different concentrations of Manoxl OT (order 10^{-4}M) at pH 7.00

Wave-length in mμ.	ABSORBENCE 1 1.34	2 3.34	3 5.34	4 6.67	5 10.00	6 13.34	7 16.67	8 20.00
610	0.850	1.000	1.250	1.350	1.470	1.510	1.515	1.515
620	0.830	1.015	1.335	1.375	1.555	1.585	1.590	1.600
625	0.830	1.030	1.410	1.455	1.570	1.630	1.630	1.635
630	0.620	0.630	0.880	0.980	1.040	1.070	1.095	1.075

Table 6.

Absorption spectra of 3.34 x 10^{-5}M malachite green in presence of different concentrations of Manoxl OT (order 10^{-4}M) at pH 9.12.

Wave-length in mμ.	ABSORBENCE 1 1.34	2 3.34	3 6.67	4 10.00	5 13.34	6 20.00	7 26.67	8 33.34	9 40.00
610	0.280	0.355	0.520	0.600	0.640	0.670	0.680	0.695	0.70
620	0.235	0.310	0.485	0.640	0.670	0.725	0.750	0.780	0.78
625	0.200	0.285	0.450	0.615	0.695	0.745	0.785	0.810	0.82
630	0.170	0.250	0.370	0.570	0.625	0.650	0.705	0.735	0.74

Dodecane sulphonic acid (DS)-rhodamine 6G.

Table 7.

Absorption spectra of 1.34 x 10^{-5}M rhodamine 6G in presence of different concentrations of DS (order 10^{-4}M) at pH 2.00.

Wave-length in mμ.	ABSORBENCE							
	1	2	3	4	5	6	7	8
	3.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
510	0.660	0.530	0.550	0.580	0.715	0.710	0.685	0.665
520	0.745	0.645	0.670	0.690	0.770	0.780	0.785	0.780
530	0.640	0.695	0.740	0.765	0.820	0.880	0.895	0.900
540	0.340	0.450	0.520	0.560	0.590	0.630	0.595	0.550

Table 8.

Absorption spectra of 1.34 x 10^{-5}M rhodamine 6G in presence of different concentrations of DS (order 10^{-4}M) at pH 7.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	5.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
510	0.630	0.640	0.650	0.670	0.680	0.690	0.705	0.725	0.725
520	0.670	0.700	0.725	0.750	0.765	0.790	0.800	0.820	0.820
530	0.630	0.710	0.765	0.800	0.820	0.840	0.845	0.850	0.850
540	0.565	0.630	0.695	0.720	0.740	0.760	0.765	0.765	0.780

Table 9.

Absorption spectra of 2.00 x 10^{-5}M rhodamine 6G in presence of different concentrations of DS(order 10^{-4}M) at pH 9.12.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	4.00	6.00	8.00	10.00	12.00	14.00	16.00	20.00	24.00
510	0.975	0.930	0.900	0.880	0.860	0.890	0.900	0.875	0.875
520	1.150	1.115	1.100	1.140	1.205	1.300	1.350	1.350	1.350
530	0.900	1.020	1.100	1.250	1.350	1.410	1.430	1.450	1.450
540	0.560	0.625	0.765	0.790	0.810	0.875	0.900	0.820	0.830

Dioctyl sodium sulpho-succinate(Manoxl OT)-rhodamine 6G.

Table 10.

Absorption spectra of 1.34 x 10^{-5}M rhodamine 6G in presence of different concentrations of Manoxl OT (order 10^{-4}M) at pH 2.00.

Wave-length in mµ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	5.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
510	0.33	0.47	0.515	0.500	0.495	0.510	0.510	0.505	0.490
520	0.50	0.58	0.630	0.645	0.650	0.655	0.650	0.660	0.675
530	0.43	0.70	0.770	0.780	0.800	0.820	0.835	0.850	0.855
540	0.42	0.64	0.680	0.740	0.750	0.780	0.790	0.800	0.820

Table 11.

Absorption spectra of 2.00 x 10^{-5}M rhodamine 6G in presence of different concentrations of Manoxl OT(order 10^{-4}M) at pH 7.00.

Wave-length in mµ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	5.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
510	0.720	0.765	0.800	0.855	0.895	0.94	0.93	0.92	0.915
520	0.875	0.930	0.965	1.025	1.070	1.14	1.14	1.15	1.150
530	0.750	0.870	0.990	1.060	1.130	1.19	1.21	1.22	1.220
540	0.525	0.660	0.705	0.785	0.795	0.80	0.82	0.83	0.825

Table 12.

Absorption spectra of 1.34 x 10^{-5}M rhodamine 6G in presence of different concentrations of Manoxl OT(order 10^{-4}M) at pH 9.12.

Wave-length in mµ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67	33.34
510	0.425	0.485	0.565	0.59	0.620	0.630	0.640	0.640	0.640
520	0.430	0.485	0.580	0.65	0.725	0.750	0.760	0.765	0.760
530	0.400	0.570	0.640	0.69	0.770	0.780	0.790	0.820	0.830
540	0.360	0.425	0.545	0.56	0.545	0.580	0.560	0.575	0.580

Dodecane sulphonic acid(DS)-rosaniline hydrochloride.

Table 13.

Absorption spectra of 2.00 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of DS(order 10^{-4}M) at pH 2.00

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	3.34	5.34	6.67	10.00	13.34	16.67	20.00	26.67
535	0.360	0.380	0.470	0.565	0.730	0.800	0.825	0.790	0.790
545	0.395	0.410	0.500	0.600	0.800	0.920	0.940	0.965	0.970
560	0.320	0.350	0.460	0.560	0.850	0.935	1.055	1.060	1.060
575	0.280	0.250	0.340	0.460	0.765	0.900	1.025	1.030	1.020

Table 14.

Absorption spectra of 1.34 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of DS(order 10^{-4}M) at pH 4.60.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	6.67	10.00	13.34	16.67	20.00	26.67	33.34	40.00
525	0.90	0.82	1.05	1.35	1.36	1.35	1.34	1.33	1.35
535	0.97	0.82	1.15	1.25	1.31	1.36	1.39	1.40	1.41
545	0.84	0.74	1.19	1.29	1.36	1.42	1.46	1.48	1.49
560	0.72	0.68	1.05	1.22	1.30	1.33	1.36	1.38	1.38

Table 15.

Absorption spectra of 1.34 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of DS(order 10^{-4}M) at pH 7.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	6.67	8.00	10.00	12.00	13.34	16.67	20.00	26.67
525	0.620	0.920	0.970	1.025	1.015	1.000	0.990	1.000	1.025
535	0.695	0.940	1.010	1.120	1.140	1.185	1.195	1.205	1.210
545	0.650	0.960	1.050	1.150	1.220	1.240	1.250	1.250	1.260
560	0.590	0.740	0.790	0.800	0.830	0.845	0.850	0.845	0.850

Dioctyl sodium sulpho succinate (Manoxl OT)-rosaniline hydrochloride.

Table 16.

Absorption spectra of 2.67 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of Manoxl OT(order 10^{-4}M) at pH 2.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	3.34	6.67	10.00	13.34	20.00	26.67	33.34	40.00
535	0.700	1.040	1.105	1.115	1.140	1.200	1.220	1.230	1.240
545	0.780	1.055	1.200	1.240	1.290	1.355	1.360	1.360	1.360
560	0.650	1.000	1.110	1.225	1.270	1.340	1.385	1.440	1.450
575	0.580	0.830	0.870	0.980	1.010	1.075	1.090	1.130	1.130

Table 17.

Absorption spectra of 1.34 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of Manoxl OT(order 10^{-4}M) at pH 4.60.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	2.67	5.34	6.67	8.00	10.00	13.34	16.67	20.00	26.67
525	0.600	0.765	1.045	1.100	1.155	1.220	1.255	1.255	1.255
535	0.660	0.820	1.110	1.220	1.330	1.430	1.460	1.470	1.480
545	0.610	0.780	1.140	1.280	1.390	1.505	1.550	1.550	1.560
560	0.550	0.650	0.810	0.940	1.000	0.990	0.990	0.980	1.020

Table 18.

Absorption spectra of 1.34 x 10^{-5}M rosaniline hydrochloride in presence of different concentrations of Manoxl OT(order 10^{-4}M) at pH 7.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	3.34	6.67	10.00	13.34	16.67	20.00	26.67	33.34	40.00
525	0.950	0.995	1.040	1.090	1.140	1.240	1.270	1.275	1.275
535	0.960	1.035	1.150	1.210	1.290	1.420	1.450	1.450	1.460
545	0.890	1.015	1.150	1.235	1.355	1.475	1.520	1.540	1.540
560	0.700	0.810	0.880	0.920	0.950	0.970	1.000	1.000	1.010

Cetyl trimethyl ammonium bromide (CTMAB) -congo red.

Table 19.

Absorption spectra of 3.34 x 10^{-5}M congo red in presence of different concentrations of CTMAB (order 10^{-5}M) at pH 2.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	2.67	3.34	5.34	6.67	10.00	13.34	16.67	20.00
425	0.40	0.42	0.43	0.46	0.45	0.49	0.46	0.50	0.51
450	0.46	0.51	0.56	0.65	0.64	0.67	0.62	0.70	0.70
460	0.48	0.57	0.60	0.71	0.69	0.70	0.65	0.72	0.72
480	0.53	0.57	0.68	0.79	0.76	0.68	0.63	0.70	0.71
500	0.58	0.56	0.68	0.78	0.73	0.67	0.57	0.63	0.64
525	0.61	0.56	0.62	0.64	0.58	0.58	0.50	0.55	0.56
550	0.62	0.55	0.54	0.45	0.39	0.36	0.29	0.31	0.31
560	0.63	0.54	0.50	0.36	0.29	0.22	0.19	0.17	0.17
580	0.60	0.50	0.43	0.24	0.16	0.10	0.06	0.05	0.06
600	0.54	0.43	0.38	0.18	0.10	0.07	0.04	0.03	0.03

Table 20.

Absorption spectra of 3.34 x 10^{-5}M congo red in presence of different concentrations of CTMAB (order 10^{-5}M) at pH 7.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	2.67	3.34	4.67	5.34	6.67	10.00	13.34	20.00
425	0.69	0.60	0.55	0.52	0.50	pptn.	0.51	0.54	0.55
450	0.96	0.88	0.80	0.76	0.72		0.69	0.72	0.74
460	1.05	1.02	0.93	0.85	0.80		0.74	0.76	0.77
470	1.11	1.07	0.99	0.91	0.84		0.76	0.77	0.79
480	1.12	1.09	1.00	0.92	0.84		0.75	0.76	0.77
490	1.07	1.00	0.91	0.84	0.80		0.74	0.75	0.75
500	0.96	0.87	0.77	0.76	0.70		0.72	0.72	0.70
525	0.66	0.58	0.54	0.52	0.51		0.60	0.64	0.63

Fig.22.

Table 21.

Absorption spectra of 3.34 x 10^{-5}M congo red in presence of different concentrations of CTMAB (order 10^{-5}M) at pH 9.12.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	2.00	2.67	3.34	5.34	6.67	10.00	20.00	26.67
425	0.58	0.53	0.45	0.45	pptn.	pptn.	0.40	0.43	0.47
450	0.82	0.77	0.70	0.70			0.63	0.66	0.68
460	0.92	0.83	0.80	0.78			0.72	0.73	0.73
470	0.99	0.89	0.84	0.82			0.76	0.77	0.76
480	1.00	0.91	0.85	0.82			0.74	0.76	0.75
490	0.98	0.90	0.83	0.74			0.68	0.74	0.70
500	0.89	0.85	0.75	0.63			0.66	0.68	0.65
525	0.63	0.60	0.53	0.41			0.50	0.50	0.49

Fig. 23.

Cetyl pyridinium bromide (CPB) -congo red.

Table 22.

Absorption spectra of 2.00 x 10^{-5}M in presence of different concentrations of CPB (order 10^{-5}M) at pH 2.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	0.67	1.34	2.01	2.67	3.34	4.02	5.34	6.67	10.00
450	0.24	0.26	0.30	0.33	0.36	0.37	0.38	0.38	0.38
460	0.25	0.27	0.32	0.37	0.38	0.38	0.39	0.40	0.41
480	0.26	0.28	0.31	0.33	0.36	0.35	0.35	0.36	0.36
500	0.30	0.29	0.29	0.31	0.29	0.26	0.27	0.28	0.26
520	0.34	0.30	0.28	0.27	0.23	0.21	0.19	0.19	0.18
540	0.37	0.31	0.26	0.23	0.19	0.17	0.14	0.14	0.14
560	0.39	0.32	0.25	0.18	0.13	0.10	0.08	0.07	0.07
580	0.37	0.30	0.22	0.13	0.09	0.05	0.04	0.03	0.03
600	0.33	0.28	0.17	0.09	0.07	0.04	0.02	0.02	0.02

Table 23.

Absorption spectra of 2.67 x 10^{-}M congo red in presence of different concentrations of CPB (order 10^{-5}M) at pH 7.00.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	2.67	3.34	4.67	5.34	6.67	10.00	13.34	20.00
425	0.50	0.47	0.43	0.40	pptn.	pptn.	0.36	0.33	0.33
450	0.66	0.63	0.60	0.56			0.53	0.52	0.52
460	0.74	0.70	0.67	0.63			0.56	0.55	0.55
470	0.79	0.74	0.72	0.66			0.54	0.53	0.53
480	0.81	0.77	0.73	0.66			0.51	0.50	0.50
490	0.79	0.74	0.72	0.61			0.47	0.45	0.45
500	0.75	0.72	0.67	0.54			0.41	0.38	0.38
525	0.48	0.42	0.40	0.35			0.27	0.23	0.23

Fig. 24.

Table 24.

Absorption spectra of 2.67 x 10^{-5}M congo red in presence of different concentrations of CPB (order 10^{-5}M) at pH 9.12.

Wave-length in mμ.	ABSORBENCE								
	1	2	3	4	5	6	7	8	9
	1.34	2.67	3.34	4.67	5.34	6.67	10.00	13.34	20.00
425	0.42	0.41	0.38	0.27	pptn.	pptn.	0.33	0.36	0.40
450	0.62	0.61	0.53	0.40			0.50	0.51	0.55
460	0.69	0.66	0.56	0.41			0.52	0.54	0.58
470	0.74	0.72	0.59	0.42			0.50	0.52	0.57
480	0.76	0.72	0.61	0.43			0.45	0.47	0.51
490	0.75	0.69	0.57	0.35			0.40	0.42	0.45
500	0.72	0.62	0.52	0.31			0.34	0.38	0.39
525	0.54	0.43	0.38	0.20			0.26	0.23	0.23

Fig.25.

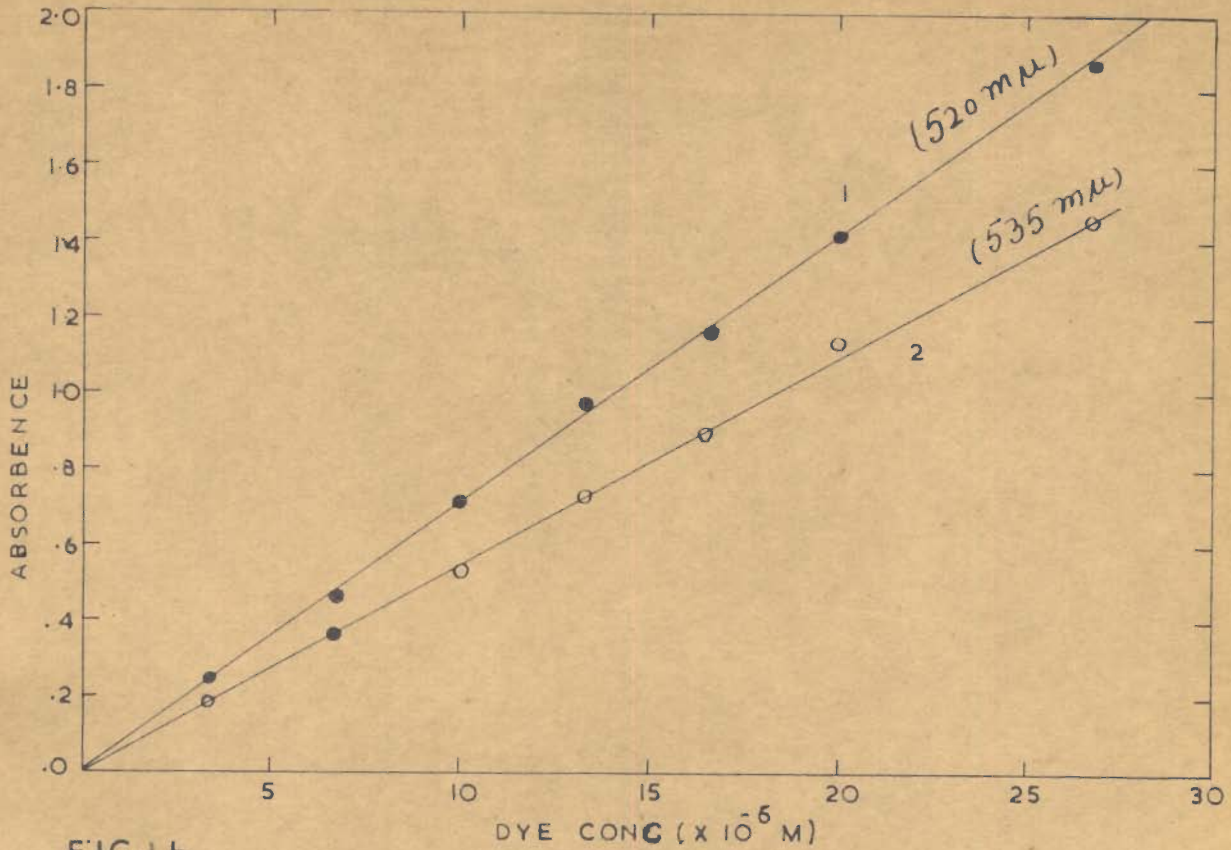


FIG.1b

CURVE 1 ROHDAMINE 6G (520 mμ)

CURVE 2 ROSANILINE HYDRO CHLORIDE (535 mμ)

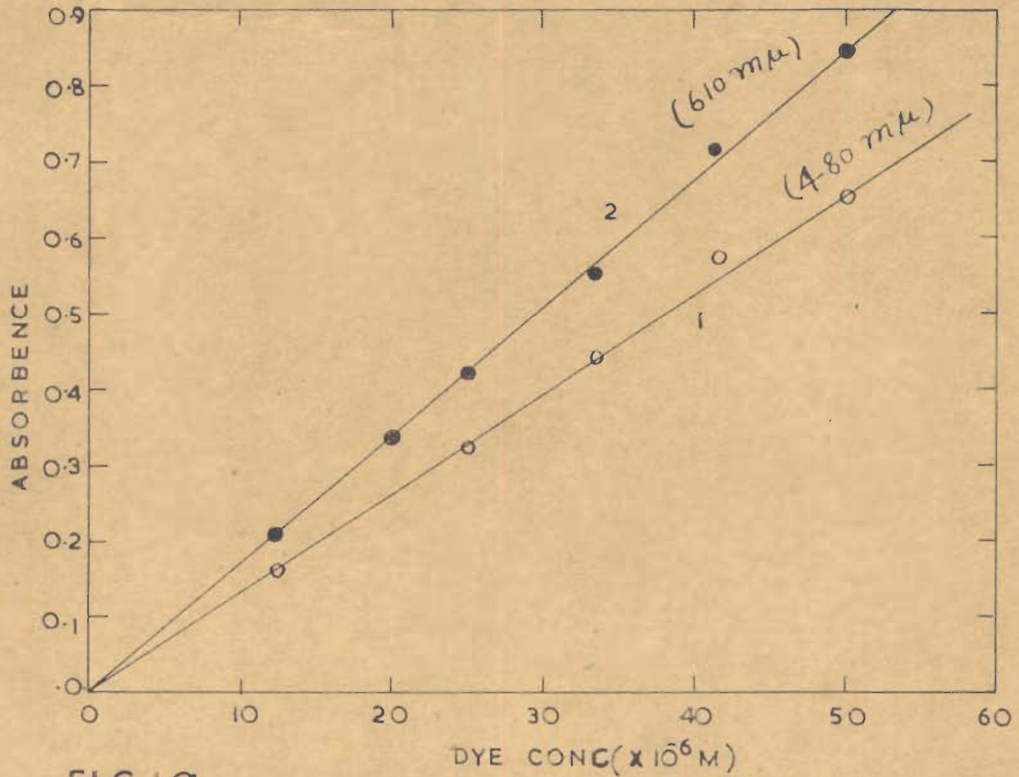


FIG.1a

CURVE 1 CONGORED (480 mμ)

CURVE 2 MALACHITE GREEN (610 mμ).

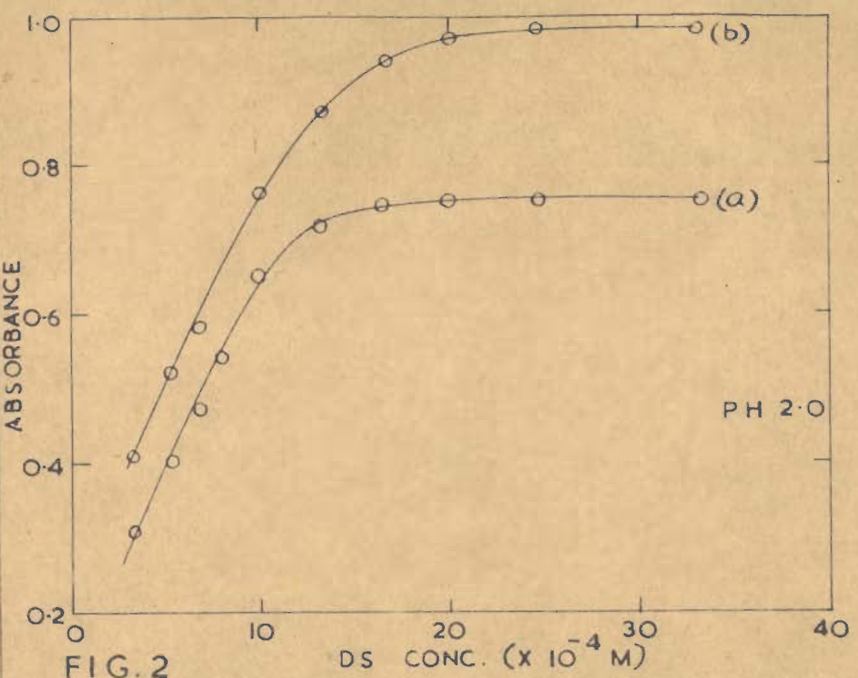


FIG. 2

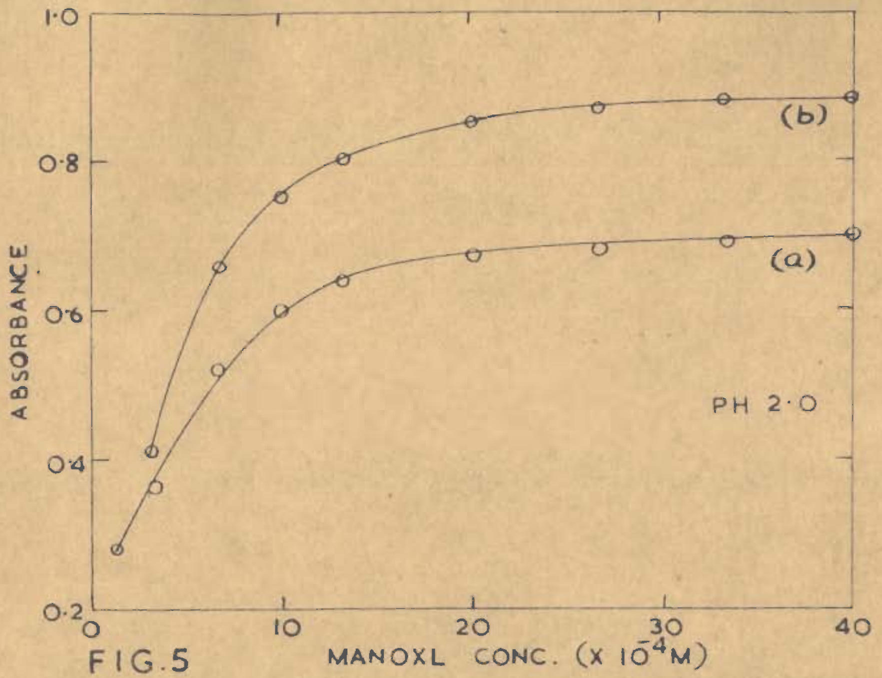


FIG. 5

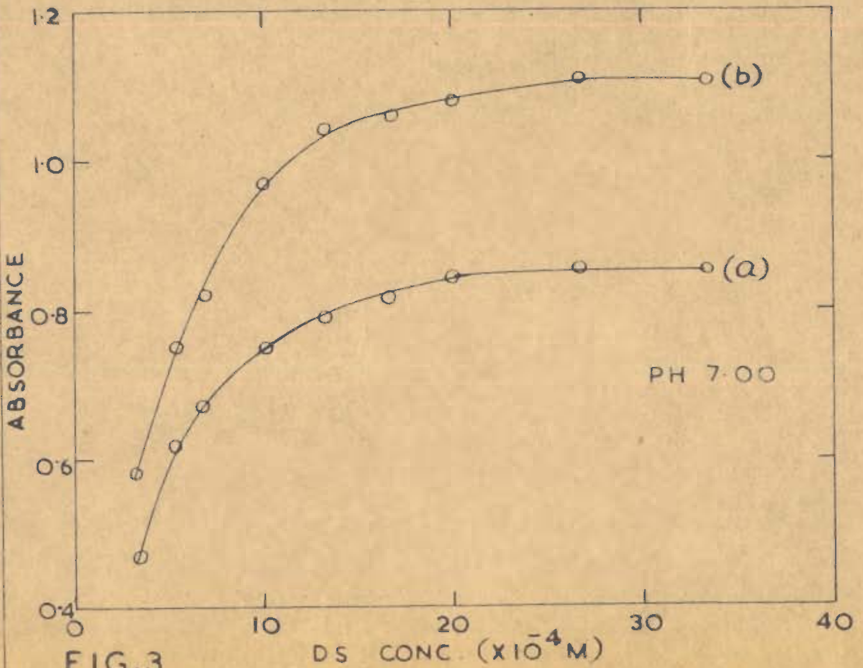


FIG. 3

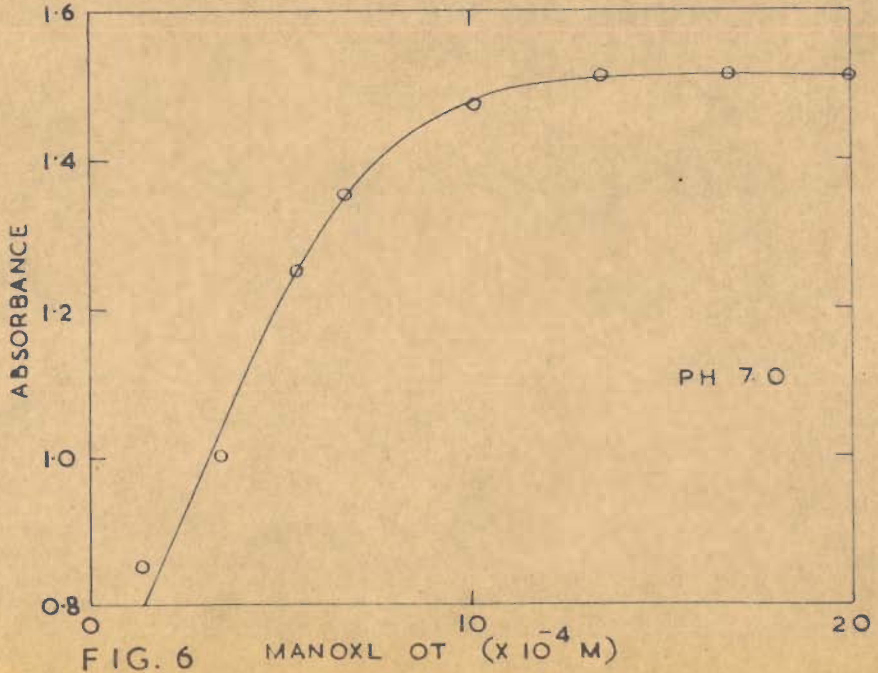


FIG. 6

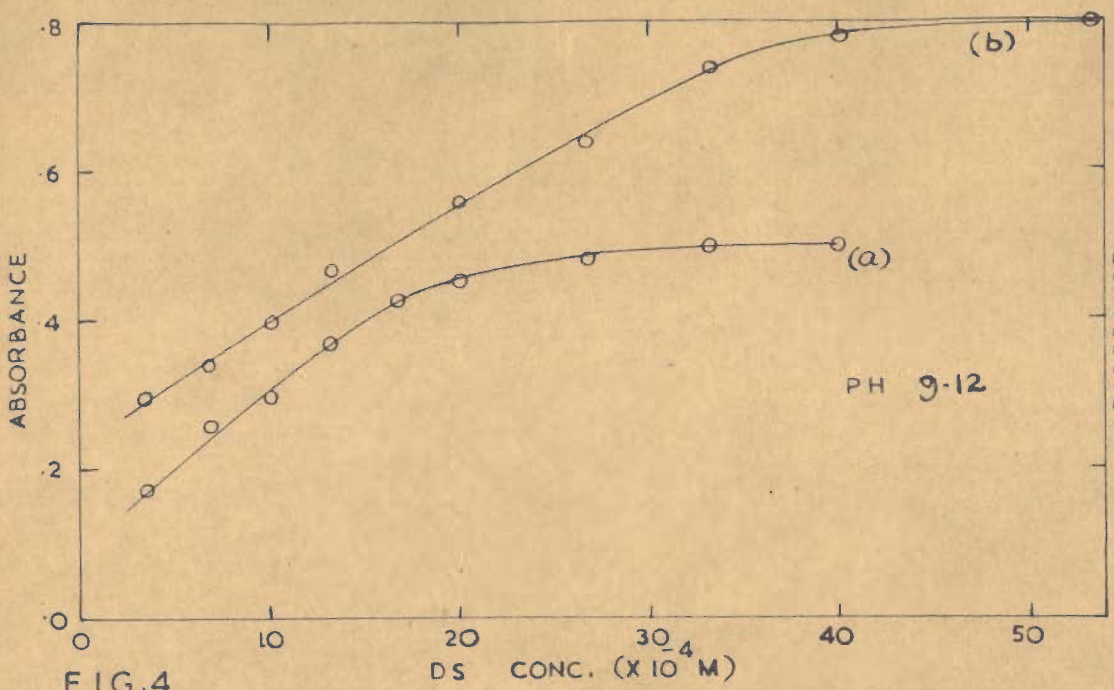


FIG.4

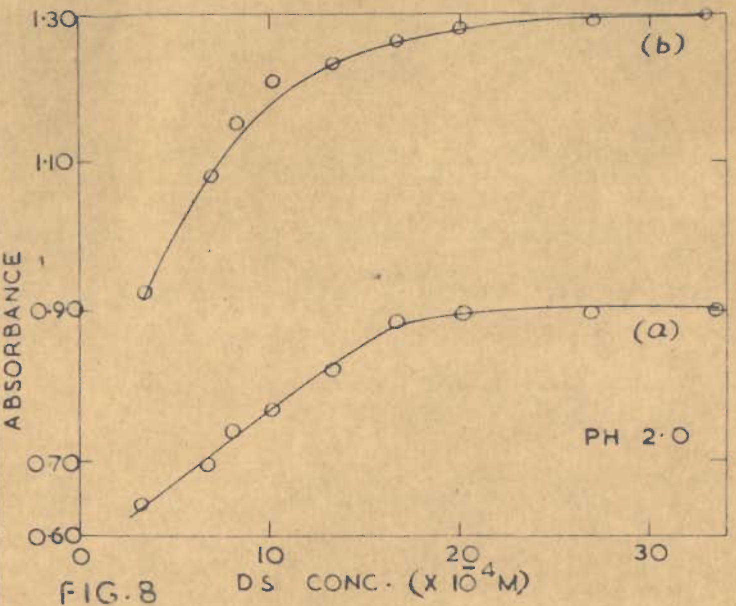


FIG.8

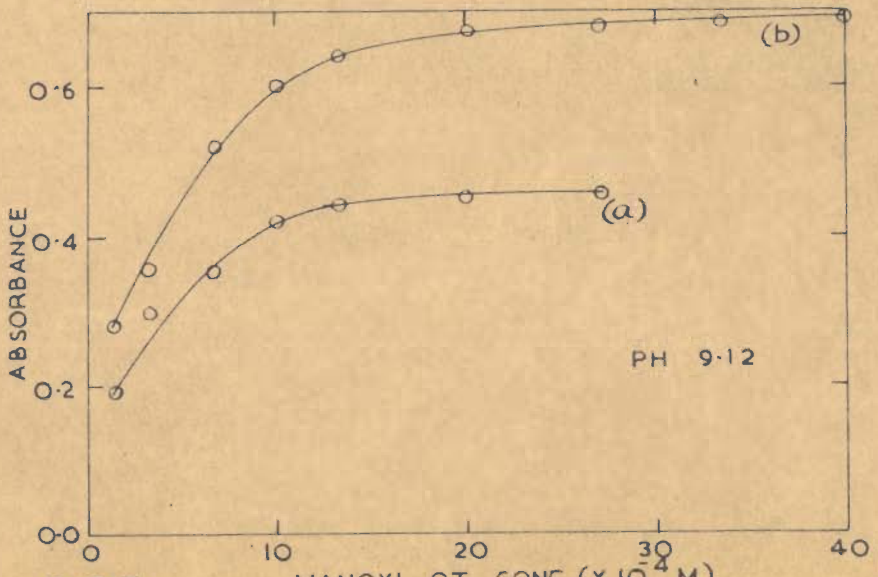


FIG.7

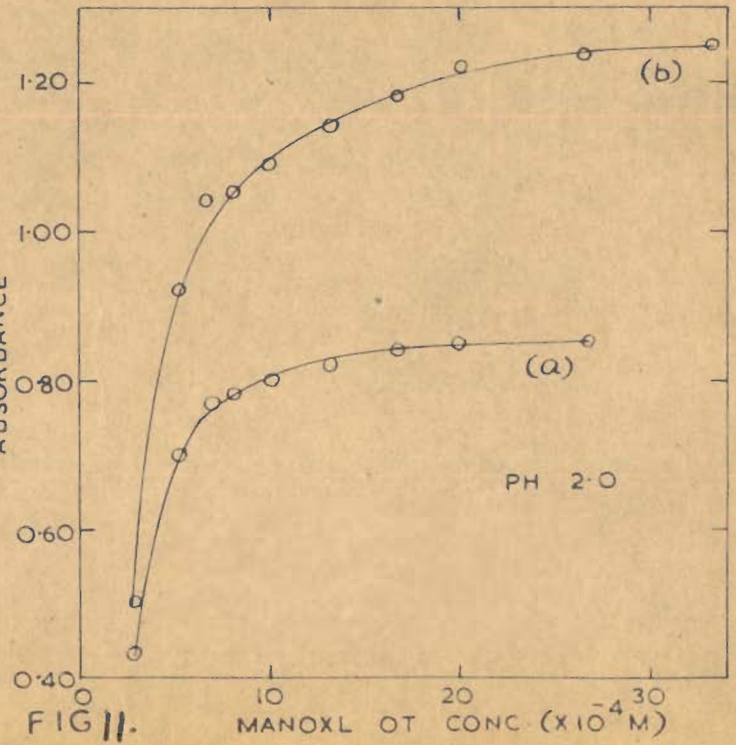


FIG 11.

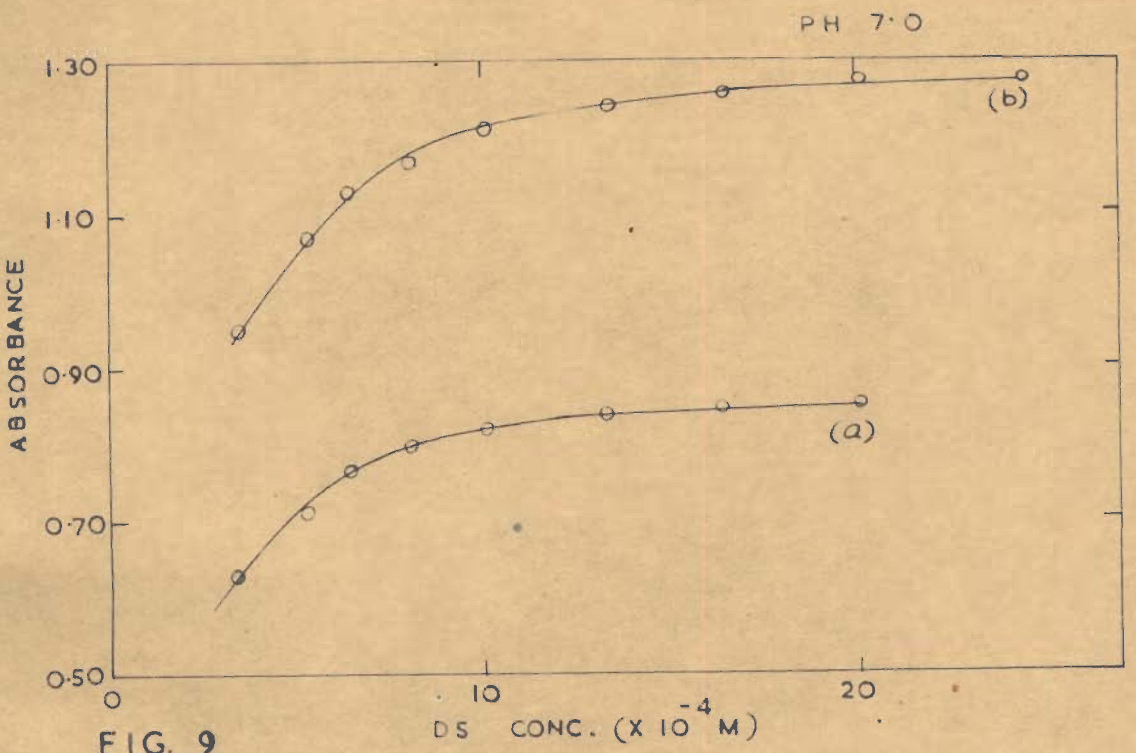

PH 7·0
1·30
1·10
0·90
0·70
0·50
ABSORBANCE
(b)
(a)
0
10
20
DS CONC. (X 10^{-4} M)

FIG. 9

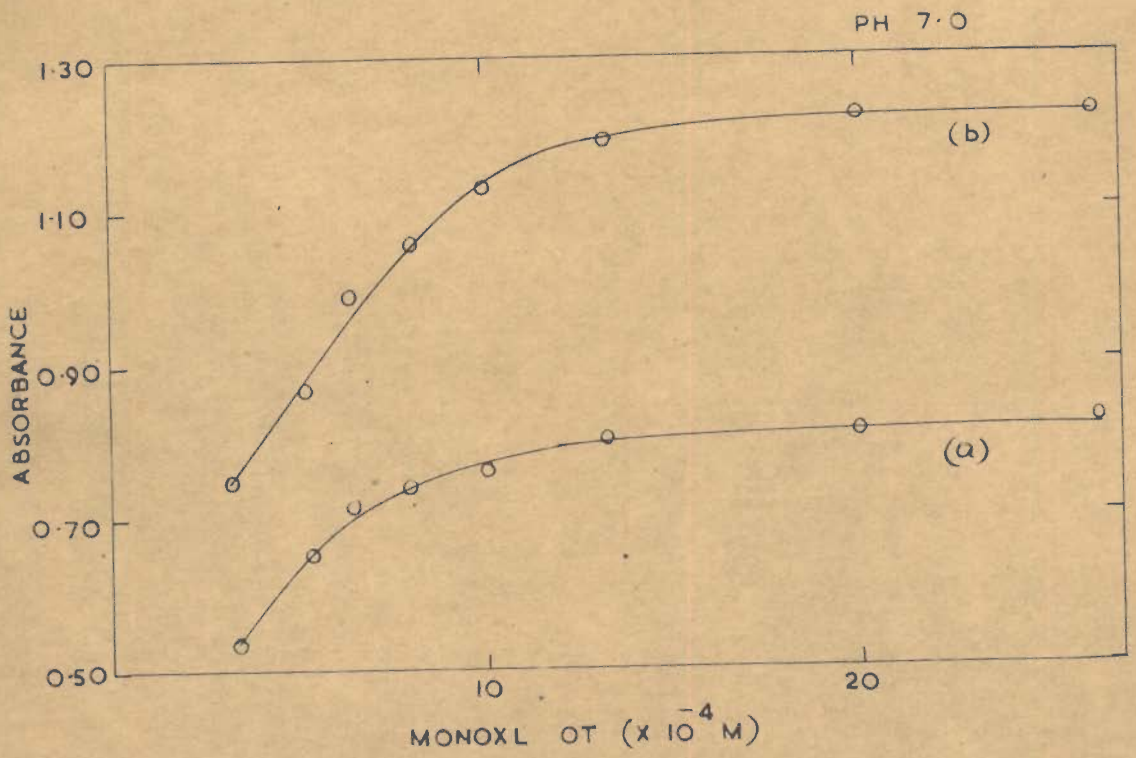

PH 7·0
1·30
1·10
0·90
0·70
0·50
ABSORBANCE
(b)
(a)
10
20
MONOXL OT (X 10^{-4} M)

FIG. 12

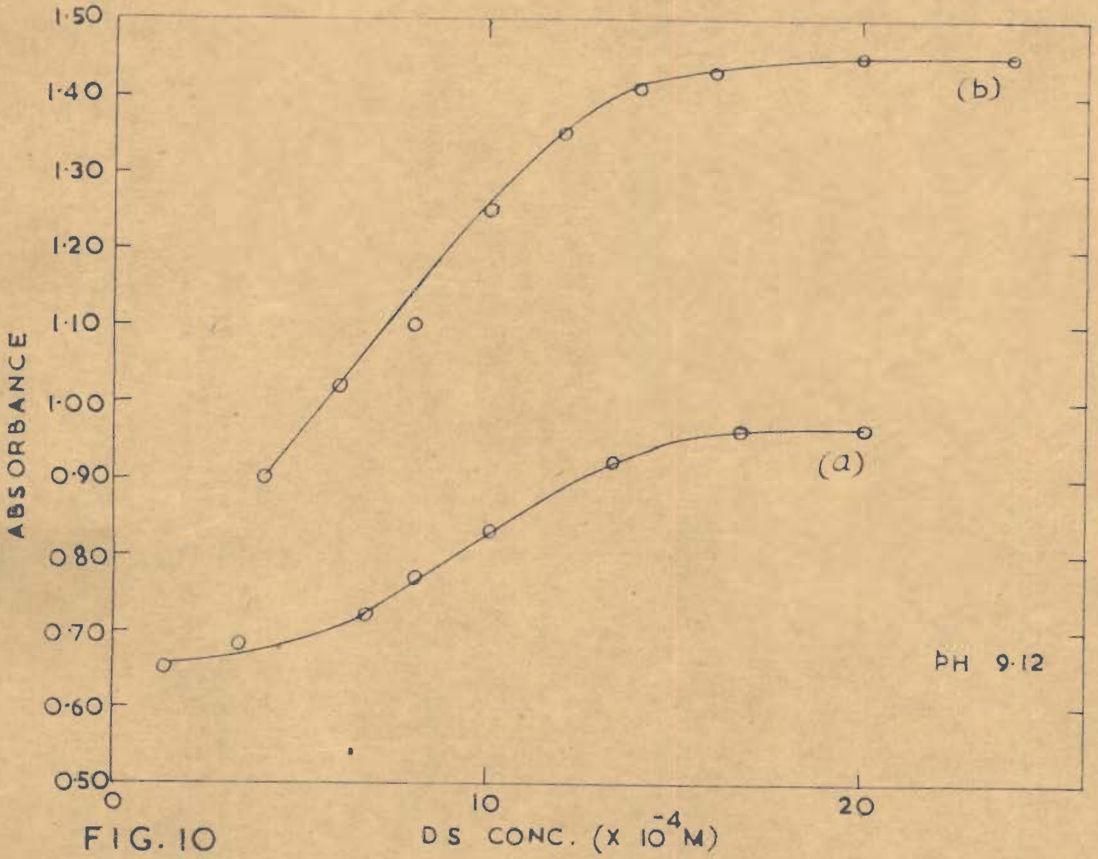

1·50
1·40
1·30
1·20
1·10
1·00
0·90
0 80
0·70
0·60
0·50
ABSORBANCE
(b)
(a)
ÞH 9·12
0
10
20
D S CONC. (X 10^{-4} M)

FIG. 10

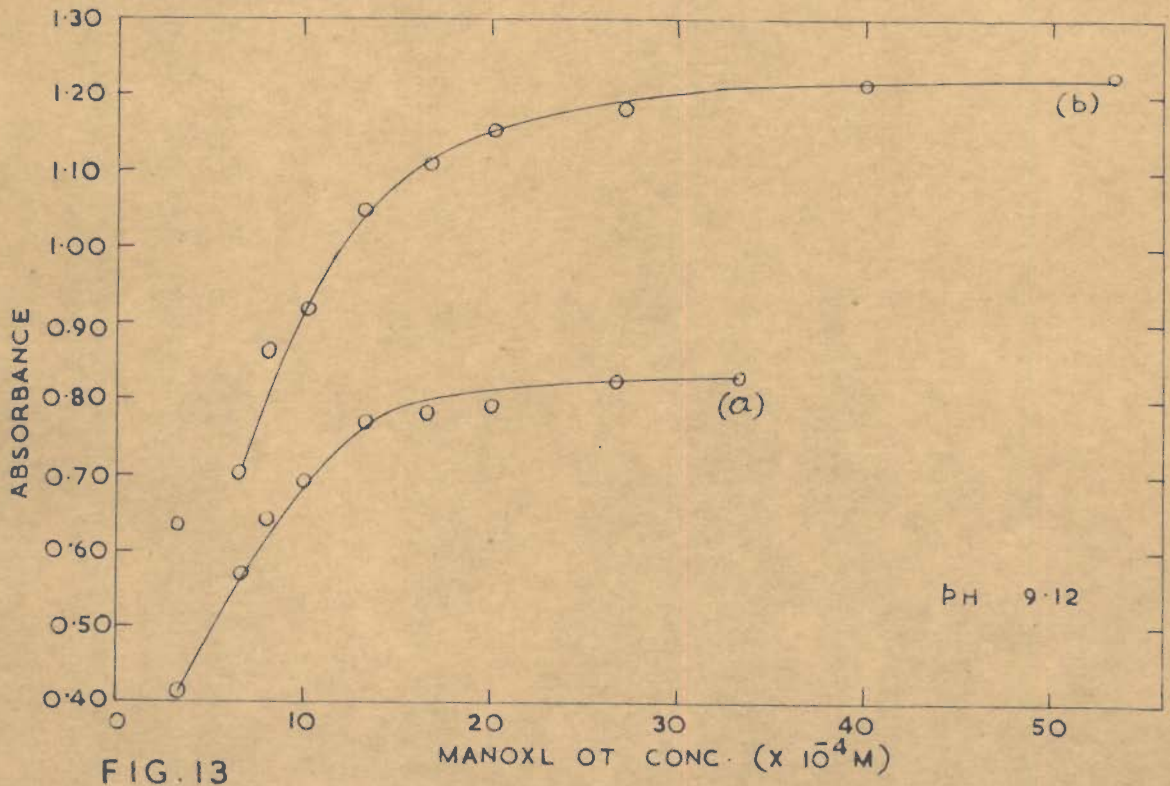

1·30
1·20
1·10
1·00
0·90
0·80
0·70
0·60
0·50
0·40
ABSORBANCE
(b)
(a)
ÞH 9·12
0
10
20
30
40
50
MANOXL OT CONC. (X 10^{-4} M)

FIG. 13

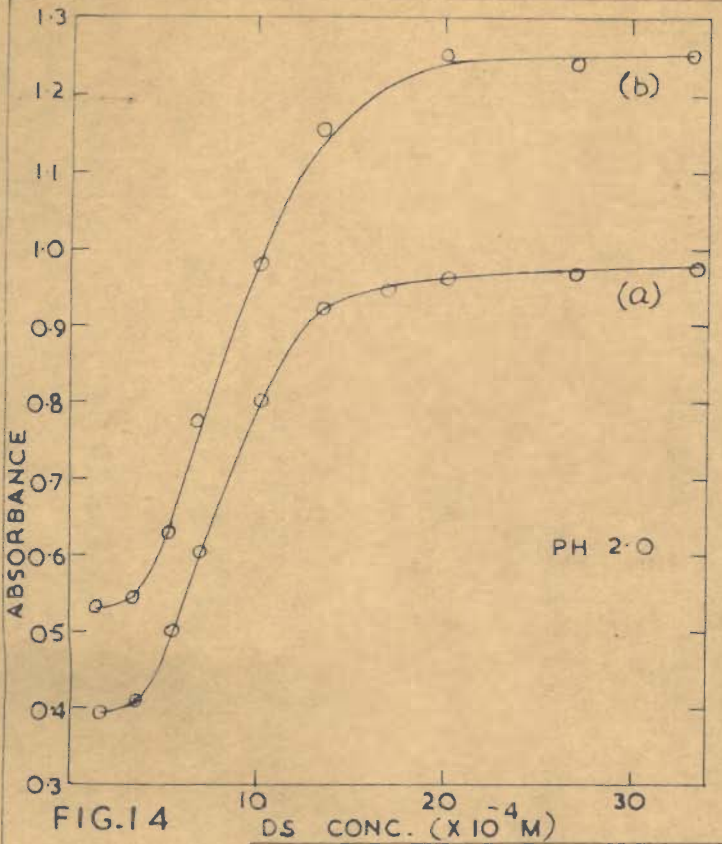
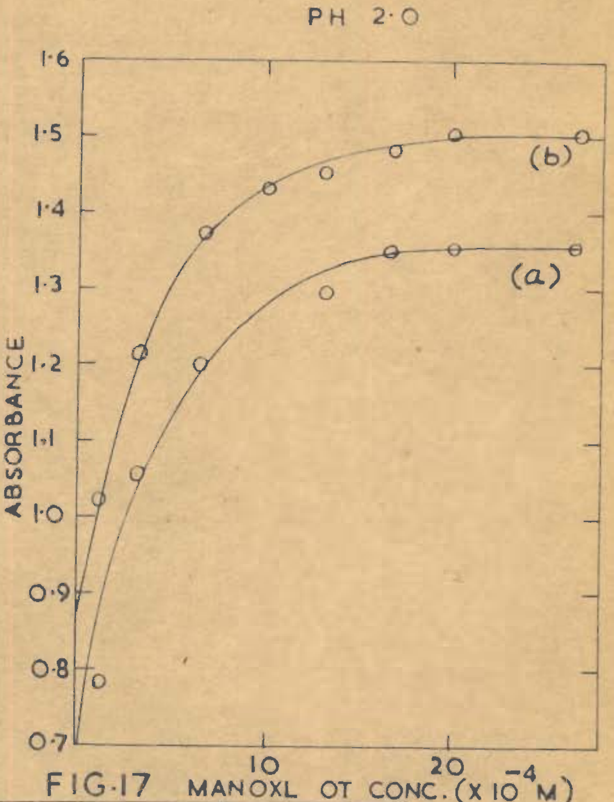


FIG.14



FIG·17

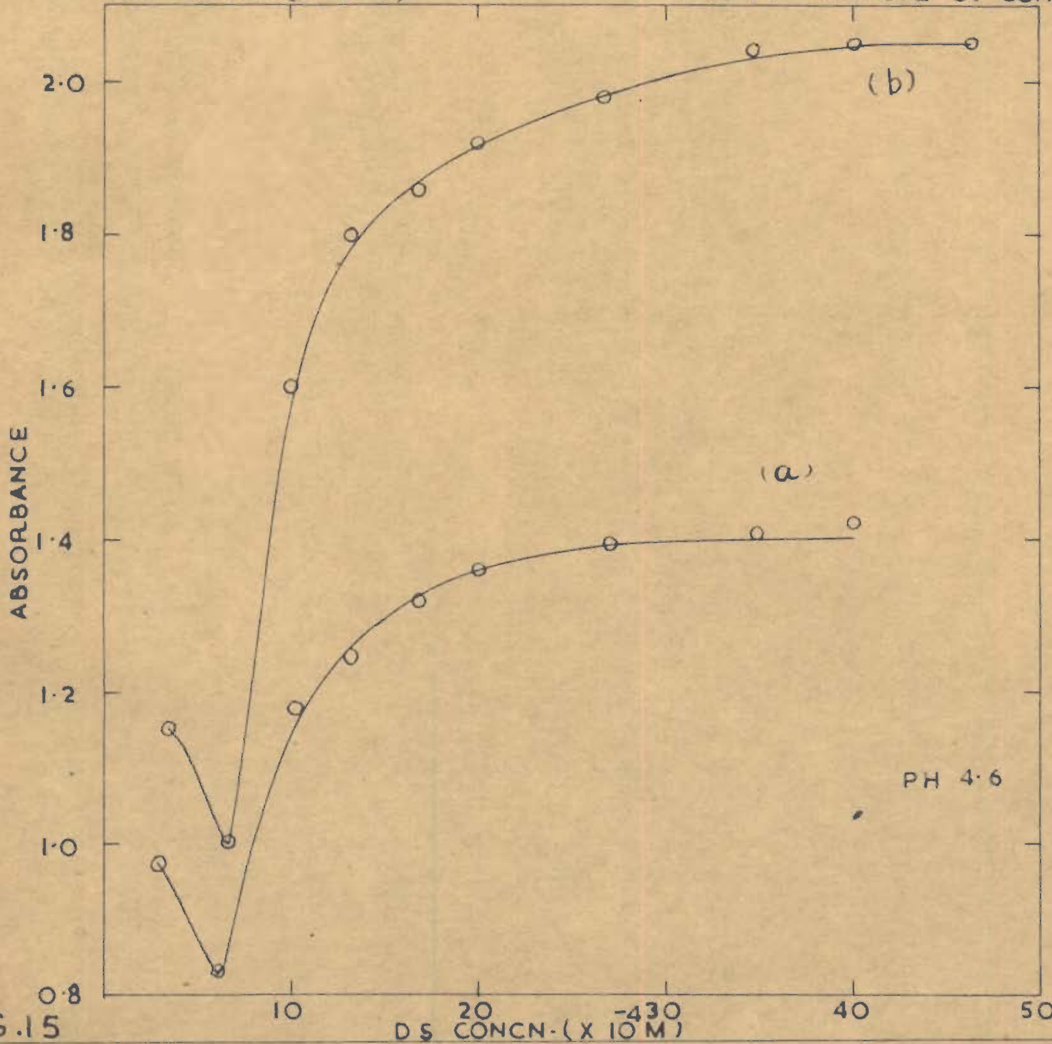


FIG.15

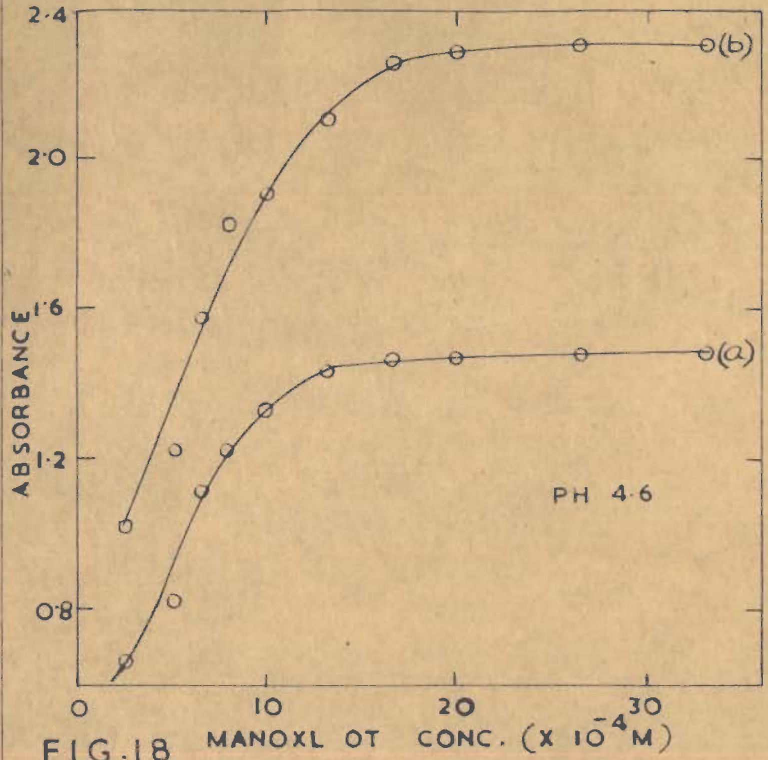


FIG.18

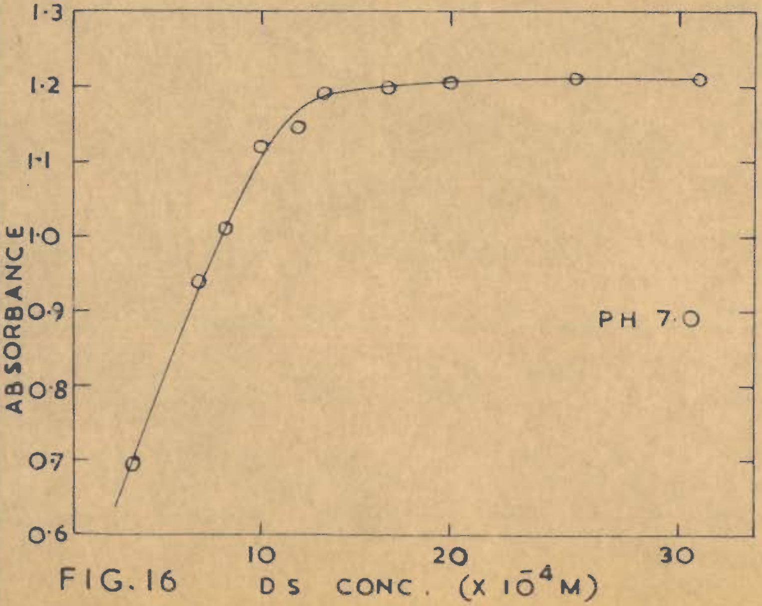
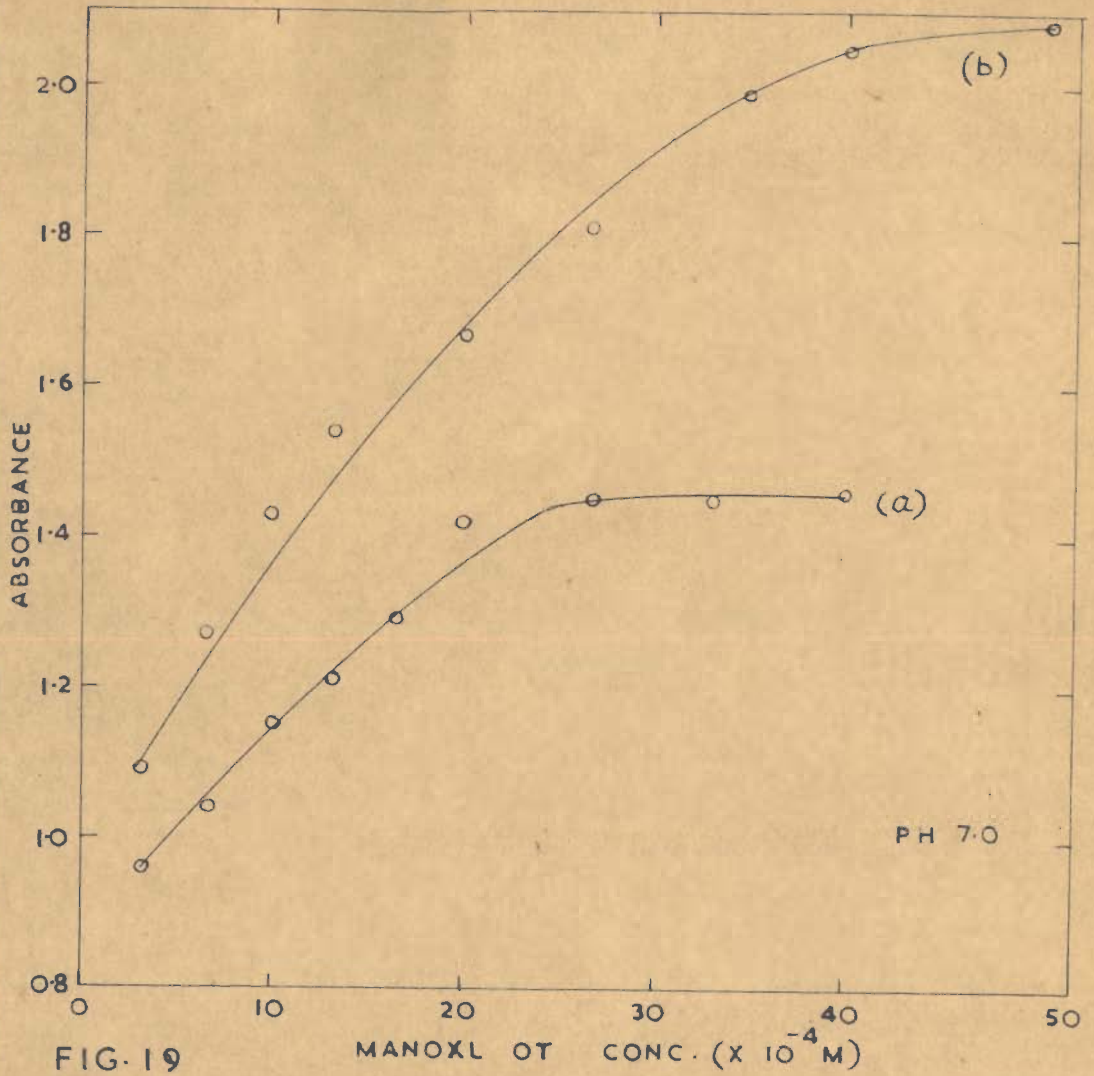


FIG.16



FIG·19

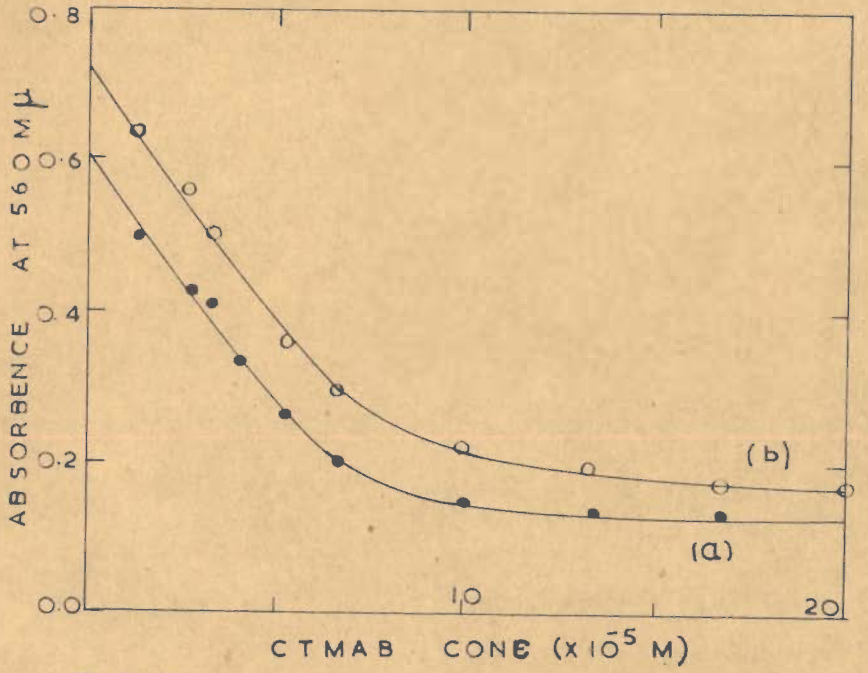


FIG.20

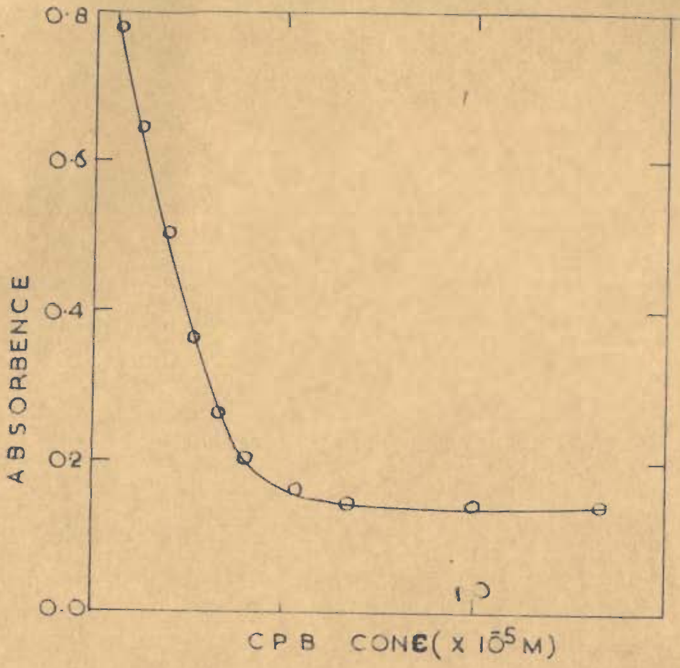


FIG.21a

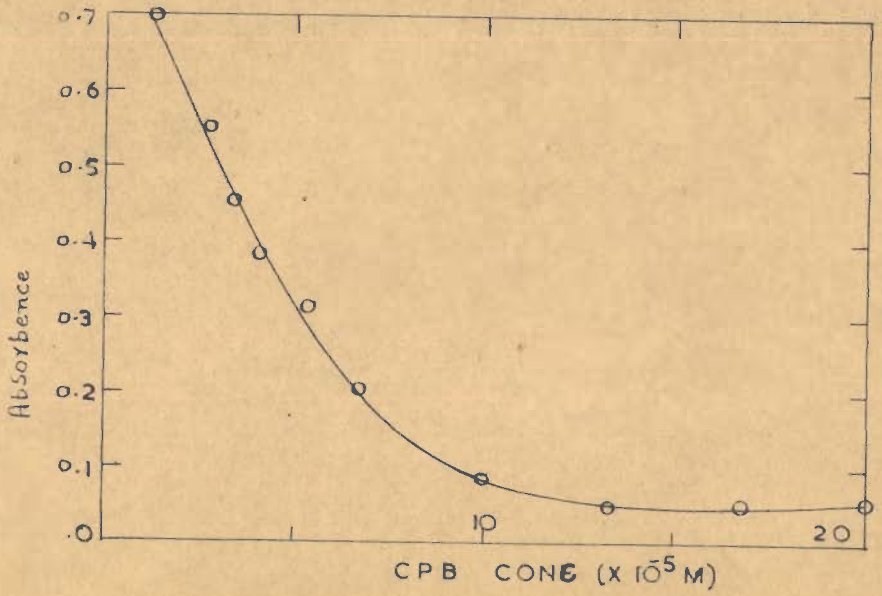


FIG.21b

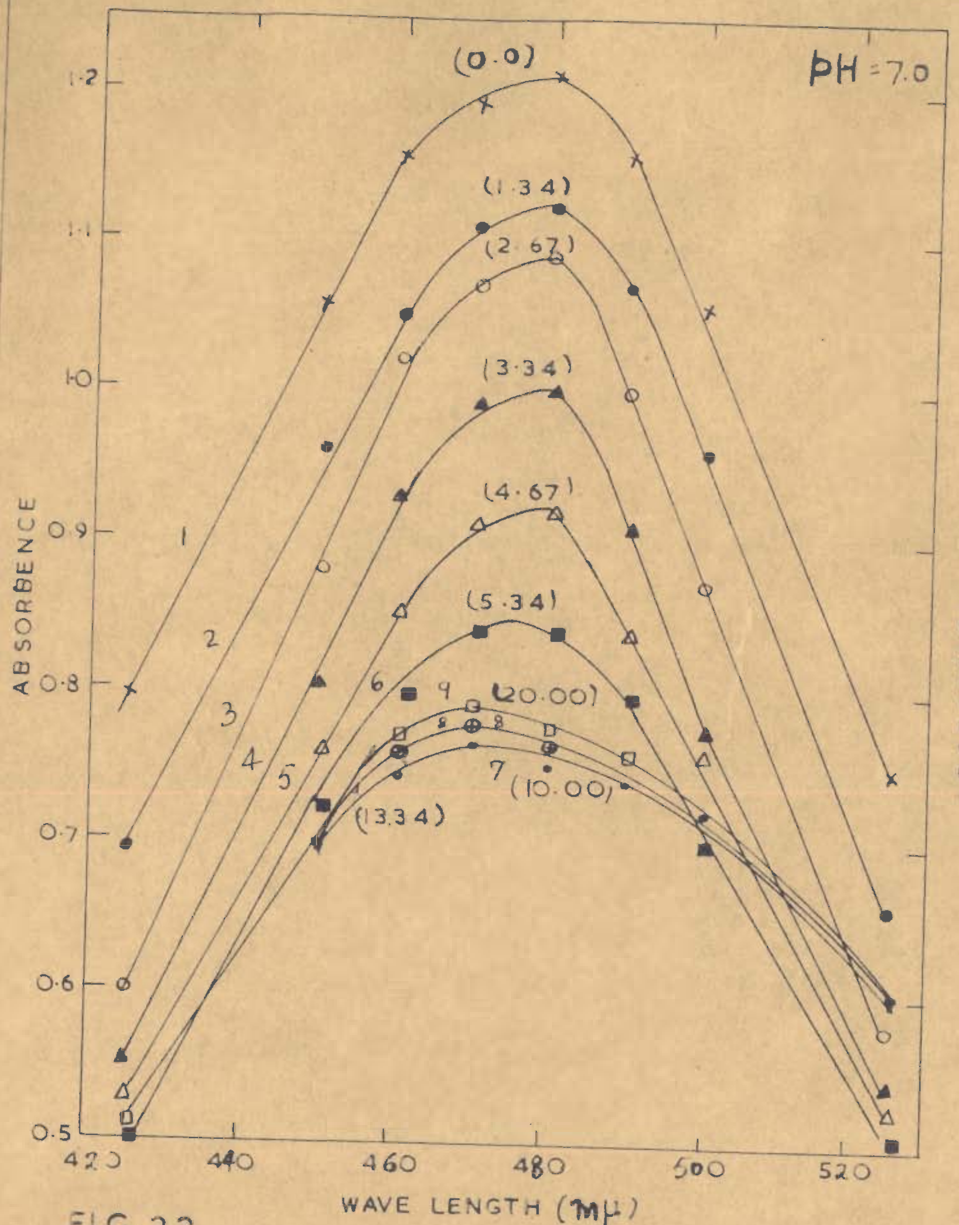


FIG. 22

CONC. OF CONGORED = (3.34×10^{-5} M)

CONC. OF CTMAB ($\times 10^{-5}$ M)

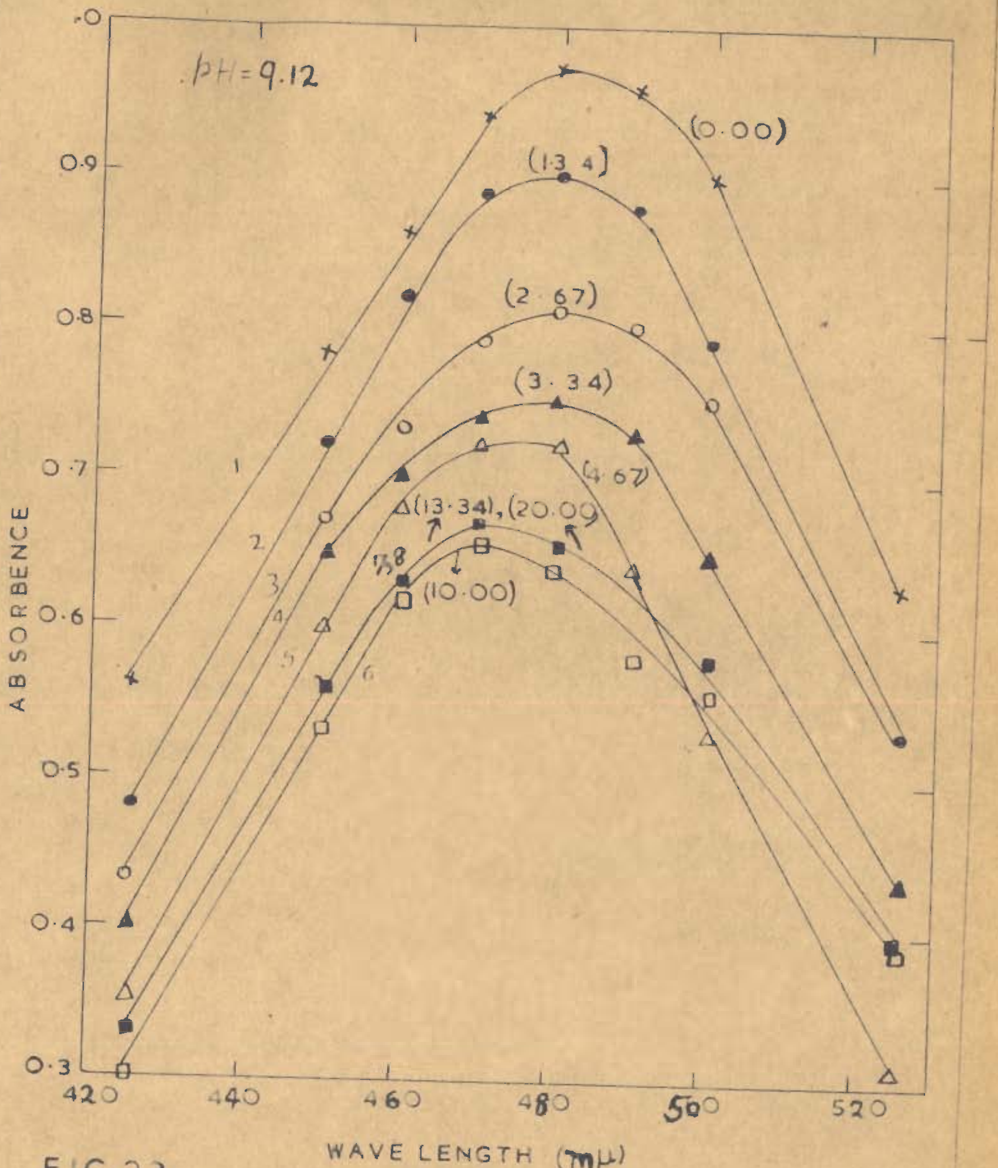


FIG. 23

CONC. OF CONGORED = (3.34×10^{-5} M)

CONC. OF CTMAB ($\times 10^{-5}$ M)

Value in parenthes represents the amount of CTMAB

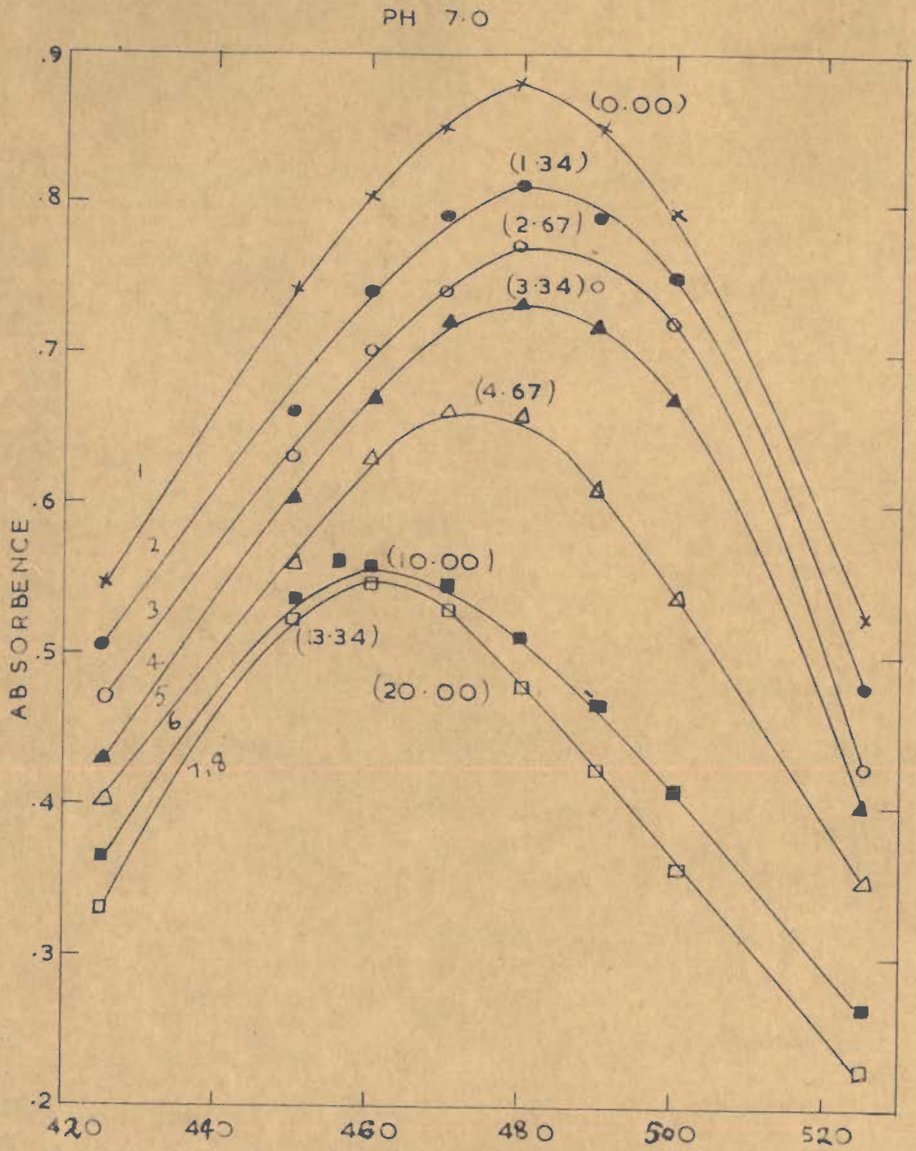


FIG. 24

CONC. OF CONGORED $(2.67 \times 10^{-5} M)$

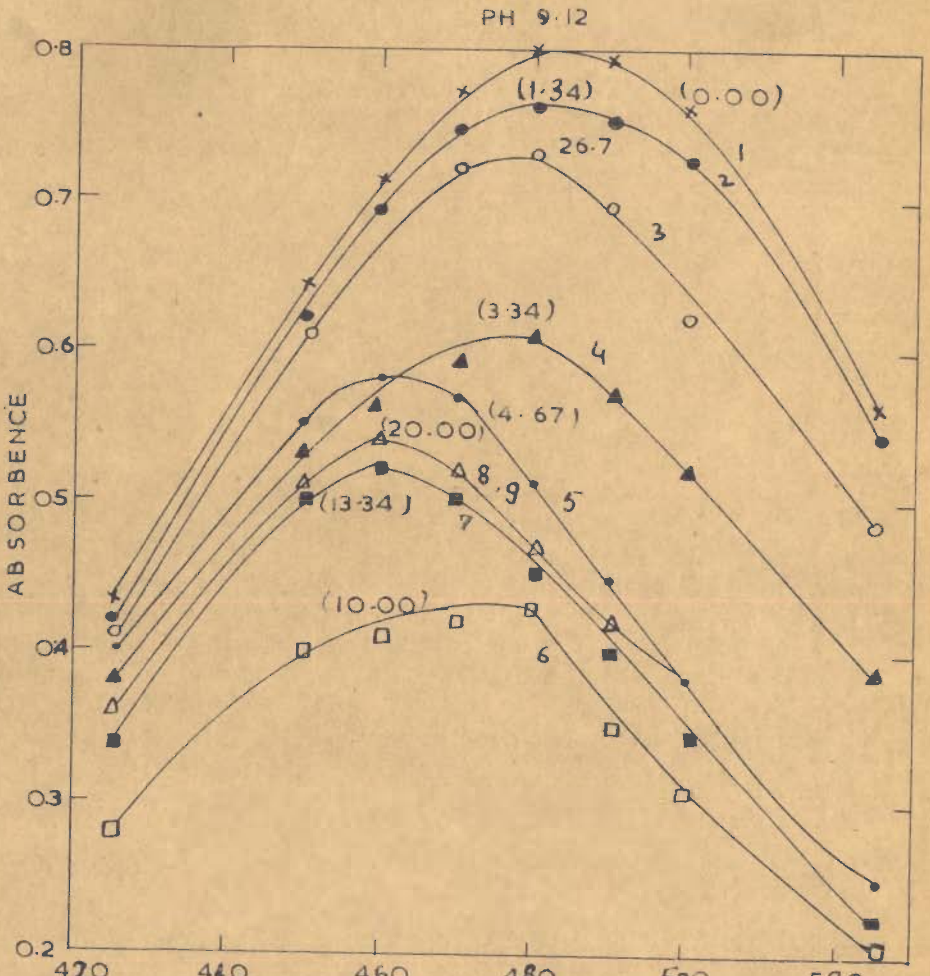


FIG.25

CONC. OF CONGORED $(2 \cdot 67 \times 10^{-5} M)$

CONC. OF CPB $(\times 10^{-5} M)$

Value in parenthes represents the amount of CPB $(\times 10^{-5} M)$

RESULT AND DISCUSSIONS

The results of the absorption studies on surfactant-dye mixtures carried out at different pHs are summarized in Tables (1-18). From the data, it can be seen that the absorbence peak is shifted towards the higher wavelength in presence of as low as 6.67×10^{-4}M of the surfactant, the shifts being from 610 to 625 mμ for malachite green, 520 to 530 mμ for rhodamine 6G and 535 to 545 mu for rosaniline hydrochloride. In all cases, the shift was independent of pH, except for rosaniline hydrochloride where a shift from 545 to 560 mμ was observed at pH 2.0 while it was 535 to 545 mμ at pH 4.6 and 7.0. It was further observed that the absorbence value got increased in presence of surfactants irrespective of the fact whether measurements were carried out at dye maxima or the shifted wavelength.

Another interesting observation was that a larger quantities of these surfactants in comparision to the alkyl aryl sulphonates (25) were required to shift the dye maxima (Table 1). This may be due to the lower c.m.c. values of the latter (order 10^{-5}M) than for the former where it was found to be of the order 10^{-4}M(Table 46).

The spectral shift in the dye maxima offers the following possibilities of intermolecular and intramolecular changes:

(i) Molecular rearrangement of the dye molecule owing to the change in the pH of the solution.

(ii) Disturbance in the monomer-polymer equilibrium of the dye.

(iii) Interaction of the dye molecules with surface active substances.

Each of the above possibilities can be resolved as follows:

1. In order to know the molecular state of the dye in the solution, the absorption of the dyes was studied over a concentration range (0.0 to 4.0 x 10^{-5}M) in which the interaction with the surfactants was to be studied (Fig. 1 a, 1 b). Beer Lambert's law was obeyed in this concentration range thereby providing evidence of the fact that aggregated dye molecules do not exist in highly dilute solutions.

2. In order to find out whether intramolecular rearrangement in the dye molecules takes place, absorption were carried out in different buffer media (pH 2.0, 4.6, 7.0, 9.12). No shift in maxima was observed confirming thereby that pH variation did not bring about molecular rearrangement in the dyes under investigation.

3. Absorption measurements carried out in presence of surfactants at the shifted wave lengths (625 mu, 530mu and 545 mu for malachite green, rhodamine 6G and rosaniline

Table 1.

Amount of dodecane sulphonic acid (DS) and Manoxl OT required to shift the maxima of malachite green, rhodamine 6G and rosaniline hydrochloride at different pHs.

Dye	Shift in maxima mu.	pH	DS		Manoxl OT	
			Dye conc. ($x10^{-5}M$)	Surfactant conc. ($x10^{-4}M$)	Dye conc. ($x10^{-5}M$)	Surfactant conc. ($x10^{-4}M$)
Malachite green.	610-625	2.00	2.00	6.67	4.00	1.34
		7.00	2.67	5.34	4.00	3.34
		9.12	2.00	6.67	3.34	10.00
Rhodamine 6G.	520-530	2.00	1.34	6.67	1.34	3.34
		7.00	1.34	5.34	2.00	6.67
		9.12	2.00	10.00	1.34	10.00
Rosaniline hydrochloride.	545-560	2.00	2.00	10.00	2.67	40.00
	535-545	4.60	1.34	6.67	1.34	6.67
	535-545	7.00	1.34	6.67	1.34	13.34

hydrochloride respectively) showed larger increase in absorbence in the initial stages (Figs.26-43) . The increase in absorbence was more marked in the case of rosaniline hydrochloride and malachite green than in the case of rhodamine 6G.

The above data could,therefore,indicate a possible interaction of the dyes with the surfactant molecules, probably in the form of soluble complexes. At higher concentrations of the surfactant,no further increase in absorbence or a new shift in maxima was observed. These results went to show that the complete binding of the dye molecule with the surfactant took place after a certain concentration of the latter was reached. The levelling off points in the plots between absorbence and surfactant concentration would correspond to the complete extraction of the dye into the surfactant micelle (Figs.2-19). It was further observed that the varying concentration of the surfactants shifted the dye maxima to the same extent provided the experiments were performed at a fixed pH. However,the amount of the surfactant required to bring about these shifts depended upon the pH of the solution. For example, it was observed that a lesser quantity of the anionic surfactants was required to shift the dye maxima of malachite green and rhodamine 6G in the acedic medium than that required in alkaline media. This behaviour was, however, reversed in the case of rosaniline hydrochloride where large quantity of the surfactant was required at low pH values.

The experimental results of the spectrophotometric studies thus provide evidence for the formation of a dye-surfactant complex. These observations are in quite agreement with the earlier reported investigations (25) where the formation of such complexes was shown on the basis of shift in dye maxima and enhanced absorbence in presence of surfactants. These observations also go to show that other factors like pH of the dye solution, monomer-polymer equilibrium etc. exert a very little influence on the surfactant-dye interaction.

The absorption data besides providing evidence for surfactant-dye interaction can be profitably employed to calculate the extent of binding. Applying Klotz's formula, the following results were obtained.

Dodecane sulphonic acid-malachite green.

Table 2.

Calculation of binding at pH 2.00

Dye concentration=2.00 x 10^{-5}M ϵ_f=14500 ϵ_b=37500

Conc.of DS (x 10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	0.305	15250	0.97	1.94	0.06
5.34	0.400	20000	0.76	1.52	0.48
6.67	0.470	23500	0.69	1.38	0.62
8.00	0.540	27000	0.46	0.92	1.08
10.00	0.650	22500	0.22	0.44	1.56
13.34	0.720	36000	0.07	0.14	1.86
16.67	0.745	37200	0.01	0.02	1.98
20.00	0.750	37500	0.00	0.00	2.00
26.67	0.755	37750	0.00	0.00	2.00

Fig.2 (a)

Table 3.

ϵ_f = 14500 ϵ_b = 36890

Dye concentration 2.67 x 10^{-5}M

Conc.of DS (x10^{-4}M)	Absorbence	ϵ_{app}	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	0.41	15350	0.96	2.56	0.11
5.34	0.52	19470	0.78	2.08	0.59
6.67	0.58	21720	0.68	1.82	0.85
10.00	0.76	28460	0.38	1.01	1.66
13.34	0.87	32580	0.20	0.53	2.14
16.67	0.94	35210	0.08	0.21	2.46
20.00	0.97	36330	0.02	0.05	2.62
26.67	0.985	36890	0.00	0.00	2.67
33.34	0.985	36890	0.00	0.00	2.67

Fig. 2 (b).

Table 4.

Calculation of binding at pH 7.00

Dye concentration = 2.00 x 10^{-5} M ϵ_f=21000 ϵ_b= 42500

Conc.of DS ($x10^{-4}M$)	Absorbence	ϵ_{app}	α	Conc.of free dye ($x10^{-5}M$)	Conc.of bound dye ($x10^{-5}M$)
3.34	0.465	23250	0.90	1.80	0.20
5.34	0.620	31000	0.54	1.08	0.92
6.67	0.670	33500	0.42	0.84	1.16
10.00	0.750	37500	0.23	0.46	1.54
13.34	0.790	39500	0.14	0.28	1.72
16.67	0.810	40500	0.10	0.20	1.80
20.00	0.840	42000	0.02	0.04	1.96
26.67	0.850	42500	0.00	0.00	2.00
33.34	0.850	42500	0.00	0.00	2.00

Fig.3 (a).

Table 5.

Dye concentration = 2.67 x 10^{-5}M ϵ_f=21000 ϵ_b= 41570

Conc.of DS ($x10^{-4}M$)	Absorbence	ϵ_{app}	α	Conc.of free dye ($x10^{-5}M$)	Conc.of bound dye ($x10^{-5}M$)
3.34	0.580	21720	0.96	2.56	0.11
5.34	0.750	28090	0.65	1.74	0.93
6.67	0.820	30710	0.53	1.41	1.26
10.00	0.970	36330	0.25	0.67	2.00
13.34	1.040	39140	0.17	0.45	2.22
16.67	1.060	39700	0.12	0.32	2.35
20.00	1.080	40450	0.05	0.13	2.54
26.67	1.110	41570	0.00	0.00	2.67
33.34	1.110	41570	0.00	0.00	2.67

Fig.3 (b).

Table 6.

Calculation of binding at pH 9.12

Dye concentration = 2.00 x 10^{-5}M ϵ_f=8250 ϵ_b= 25000

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.180	9000	0.95	1.90	0.10
6.67	0.260	13000	0.72	1.44	0.56
10.00	0.300	15000	0.60	1.20	0.80
13.34	0.375	17750	0.43	0.86	1.14
16.67	0.430	21500	0.21	0.42	1.58
20.00	0.450	22500	0.15	0.30	1.70
26.67	0.480	24000	0.06	0.12	1.88
33.34	0.500	25000	0.00	0.00	2.00
40.00	0.500	25000	0.00	0.00	2.00

Fig.4 (a)

Table 7.

Dye concentration = 3.34 x 10^{-5}M ϵ_f=8250 ϵ_b= 23950

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.300	9000	0.95	3.17	0.17
6.67	0.340	10180	0.88	2.94	0.40
10.00	0.400	11980	0.76	2.54	0.80
13.34	0.470	14070	0.63	2.10	1.24
20.00	0.560	16770	0.46	1.54	1.80
26.67	0.640	19160	0.24	0.80	2.54
33.34	0.740	22160	0.11	0.37	2.97
40.00	0.780	23350	0.01	0.03	3.31
53.34	0.800	23950	0.00	0.00	3.34

Fig.4 (b)

Dioctyl sodium sulpho succinate(Manoxl OT) -malachite green.

Table 8.

Calculation of binding at pH 2.00

Dye concentration = 3.34 x 10^{-5}M ϵ_f=14500 ϵ_b=20960

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.280	8680	-	-	-
3.34	0.360	10620	-	-	-
6.67	0.520	15660	0.82	2.74	0.60
10.00	0.600	17660	0.51	1.70	1.64
13.34	0.640	19160	0.29	0.97	2.37
20.00	0.670	20290	0.10	0.33	3.01
26.67	0.680	20360	0.09	0.30	3.04
33.34	0.690	20810	0.02	0.07	3.27
40.00	0.700	20960	0.00	0.00	3.34

Fig.5 (a)

Table 9.

Dye concentration = 4.00 x 10^{-5}M ϵ_f= 14500 ϵ_b= 22000

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.410	10250	-	-	-
6.67	0.660	16500	0.73	2.92	1.08
10.00	0.750	18750	0.43	1.72	2.28
13.34	0.800	20000	0.30	1.20	2.80
20.00	0.850	21250	0.10	0.40	3.60
26.67	0.865	21620	0.05	0.20	3.80
33.34	0.875	21880	0.02	0.08	3.92
40.00	0.885	22120	0.00	0.00	4.00

Fig.5 (b).

Table 10.

Calculation of binding at pH 7.00.

Dye concentration = 4.0 x 10^{-5}M ϵ_f= 21000 ϵ_b= 37750

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	ϵapp.	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.850	21250	0.98	3.92	0.08
3.34	1.000	25000	0.76	3.04	0.96
5.34	1.250	31250	0.39	1.56	2.44
6.67	1.350	33750	0.24	0.96	3.04
10.00	1.470	36750	0.06	0.24	3.76
13.34	1.510	37800	0.00	0.00	4.00
16.67	1.515	37900	0.00	0.00	4.00
20.00	1.515	37900	0.00	0.00	4.00

Fig. 6.

Table 11.

Calculation of binding at pH 9.12.

Dye concentration = 2.67 x 10^{-5}M ϵ_f=6660 ϵ_b= 21720

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.190	7120	0.97	2.59	0.08
3.34	0.300	11100	0.71	2.00	0.67
6.67	0.455	17030	0.31	0.83	1.84
10.00	0.520	19480	0.15	0.40	2.27
13.34	0.540	20130	0.10	0.27	2.40
20.00	0.550	20700	0.07	0.19	2.48
26.67	0.570	21290	0.03	0.08	2.55
33.34	0.580	21790	0.00	0.00	2.67
40.00	0.580	21790	0.00	0.00	2.67

Fig. 7 (a)

Table 12.

Dye concentration = 3.34 x 10^{-5}M ϵ_f= 6660 ϵ_b= 21000

Conc.of Manoxyl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.280	8680	0.86	2.87	0.47
3.34	0.355	10620	0.72	2.40	0.94
6.67	0.520	15660	0.37	1.04	2.30
10.00	0.600	17660	0.23	0.77	2.57
13.34	0.640	19160	0.11	0.37	2.97
20.00	0.670	20290	0.05	0.17	3.17
26.67	0.680	20360	0.04	0.13	3.21
33.34	0.695	20810	0.01	0.03	3.31
40.00	0.700	20960	0.00	0.00	3.34

Fig.7 (b).

Dodecane sulphonic acid (DS) - rhodamine 6G.

Table 13.

Calculation of binding at pH 2.00

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 51120 ϵ_b= 67160

Conc.of DS (x10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	0.640	48000	-	-	-
6.67	0.695	51870	0.95	1.17	0.17
8.00	0.740	55220	0.75	1.00	0.34
10.00	0.765	57830	0.58	0.78	0.56
13.34	0.820	61190	0.37	0.50	0.84
16.67	0.880	65670	0.09	0.11	1.23
20.00	0.895	66800	0.02	0.03	1.31
26.67	0.900	67160	0.00	0.00	1.34
33.34	0.900	67160	0.00	0.00	1.34

Fig.8 (a)

Table 14.

Dye concentration = 2.00 x 10^{-5} M ϵ_f= 51120 ϵ_b= 64500

Conc.of DS (x10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	0.920	46000	-	-	-
6.67	1.080	54000	0.80	1.60	0.40
8.00	1.150	57500	0.53	1.06	0.94
10.00	1.210	60500	0.31	0.62	1.38
13.34	1.230	61500	0.24	0.48	1.52
16.67	1.260	63000	0.11	0.22	1.78
20.00	1.280	64000	0.05	0.10	1.90
26.67	1.290	64500	0.02	0.04	1.96
33.34	1.295	64750	0.00	0.00	2.00
40.00	1.295	64750	0.00	0.00	2.00

Fig.8 (b).

Table 15.

Calculation of binding at pH 7.00

Dye concentration = 1.34×10^{-5}M $\epsilon_f = 42500$ $\epsilon_b = 63430$

Conc. of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc. of free dye ($\times 10^{-5}$M)	Conc. of bound dy ($\times 10^{-5}$M)
3.34	0.630	47000	0.80	0.11	1.23
5.34	0.710	53000	0.50	0.67	0.67
6.67	0.765	57090	0.33	0.44	0.90
8.00	0.800	60000	0.16	0.21	1.13
10.00	0.820	61200	0.11	0.15	1.19
13.34	0.840	62690	0.04	0.05	1.29
16.67	0.845	63050	0.02	0.03	1.31
20.00	0.850	63430	0.00	0.00	1.34
26.67	0.850	63430	0.00	0.00	1.34

Fig.9 (a).

Table 16.

Dye concentration = 2.00×10^{-5}M $\epsilon_f = 42500$ $\epsilon_b = 64000$

Conc. of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc. of free dye ($\times 10^{-5}$M)	Conc. of bound dy ($\times 10^{-5}$M)
3.34	0.950	47500	0.77	1.54	0.46
5.34	1.070	53500	0.49	0.98	1.02
6.67	1.130	56500	0.35	0.70	1.30
8.00	1.165	58250	0.27	0.54	1.46
10.00	1.210	60500	0.17	0.34	1.66
13.34	1.250	62500	0.08	0.16	1.84
16.67	1.260	63000	0.04	0.08	1.92
20.00	1.275	63750	0.02	0.04	1.96
26.67	1.280	64000	0.00	0.00	2.00
33.34	1.280	64000	0.00	0.00	2.00

Fig.9 (b).

Table 17.

Calculation of binding at pH 9.12

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 42000 ϵ_b= 71640

Conc.of DS ($\times 10^{-4}$M)	Absorbence	ϵ app.	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.65	48510	0.78	1.05	0.29
3.34	0.68	50750	0.70	0.94	0.40
6.67	0.72	53730	0.60	0.80	0.54
8.00	0.77	57500	0.48	0.64	0.70
10.00	0.83	61946	0.33	1.10	0.24
13.34	0.92	68660	0.10	0.13	0.21
16.67	0.96	71640	0.00	0.00	1.34
20.00	0.96	71640	0.00	0.00	1.34

Fig.10 (a)

Table 18.

Dye concentration = 2.00 x 10^{-5}M ϵ_f=42000 ϵ_b= 72500

Conc.of DS ($\times 10^{-4}$M)	Absorbence	ϵ app.	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
4.00	0.90	45000	0.90	1.80	0.20
6.00	1.02	51000	0.70	1.40	0.60
8.00	1.10	55000	0.57	1.14	0.86
10.00	1.25	62500	0.33	0.66	1.34
12.00	1.35	67500	0.16	0.32	1.68
14.00	1.41	70500	0.06	0.12	1.88
16.00	1.43	71500	0.03	0.06	1.94
20.00	1.45	72500	0.00	0.00	2.00
24.00	1.45	72500	0.00	0.00	2.00

Fig.10 (b)

Dioctyl sodium sulpho succinate(Manoxl OT) -rhodamine 6G.

Table 19.

Calculation of binding at pH 2.00

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 51120 ϵ_b= 64500

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.430	32100	-	-	-
5.34	0.700	52240	0.92	1.13	0.21
6.67	0.770	57460	0.53	0.71	0.63
8.00	0.780	58210	0.47	0.63	0.71
10.00	0.800	60000	0.34	0.45	0.89
13.34	0.820	61200	0.25	0.33	1.01
16.67	0.835	62310	0.16	0.21	1.13
20.00	0.850	63430	0.08	0.11	1.23
26.67	0.855	64500	0.00	0.00	1.34
33.34	0.855	64500	0.00	0.00	1.34

Fig.11 (a)

Table 20.

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 51120 ϵ_b= 62500

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.500	25000	-	-	-
5.34	0.920	46000	-	-	-
6.67	1.040	52000	0.94	1.88	0.12
8.00	1.050	52500	0.90	1.80	0.20
10.00	1.090	54500	0.70	1.40	0.60
13.34	1.140	57000	0.48	0.96	1.04
16.67	1.180	59000	0.37	0.74	1.26
20.00	1.220	61000	0.13	0.26	1.74
26.67	1.240	62000	0.05	0.10	1.90
33.34	1.250	62500	0.00	0.00	2.00
40.00	1.250	62500	0.00	0.00	2.00

Fig. 11 (b)

Table 21.

Calculation of binding at pH 7.00.

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 42500 ϵ_b= 61200

Conc.of Manoxl OT ($x10^{-4}$M)	Absorbence	ϵ app.	α	Conc.of free dye ($x10^{-4}$M)	Conc.of bound dye ($x10^{-4}$M)
3.34	0.535	39930	-	-	-
5.34	0.650	48500	0.68	1.01	0.33
6.67	0.715	53360	0.41	0.55	0.79
8.00	0.740	53220	0.32	0.43	0.91
10.00	0.760	56720	0.24	0.32	1.02
13.34	0.780	58210	0.16	0.21	1.13
16.67	0.800	59700	0.08	0.11	1.23
20.00	0.810	60500	0.04	0.05	1.29
26.67	0.820	61200	0.00	0.00	1.34

Fig.12 (a).

Table 22.

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 42500 ϵ_b= 61000

Conc.of Manoxl OT ($x10^{-4}$M)	Absorbence	ϵ app.	α	Conc.of free dye ($x10^{-5}$M)	Conc.of bound dye ($x10^{-5}$M)
3.34	0.75	37500	-	-	-
5.34	0.87	43500	0.95	1.90	0.10
6.67	0.99	49500	0.62	1.24	0.76
8.00	1.06	53000	0.43	0.86	1.14
10.00	1.13	56500	0.24	0.48	1.52
13.34	1.19	59500	0.06	0.12	1.88
16.67	1.21	60500	0.03	0.06	1.94
20.00	1.22	61000	0.00	0.00	2.00
26.67	1.22	61000	0.00	0.00	2.00

Fig.12 (b).

Table 23.

Calculation of binding at pH 9.12.

Dye concentration = 1.34 x 10^{-5}M ϵ_f = 42000 ϵ_b = 62000

Conc. of Manoxl OT (x10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc. of free dye (x10^{-5}M)	Conc. of bound dye (x10^{-5}M)
3.34	0.405	30220	-	-	-
6.67	0.570	42540	0.97	1.20	0.14
8.00	0.640	47760	0.76	1.02	0.32
10.00	0.690	51500	0.50	0.67	0.67
13.34	0.770	57460	0.23	0.31	1.03
16.67	0.780	58210	0.19	0.25	1.09
20.00	0.790	59000	0.15	0.21	1.13
26.67	0.820	61200	0.04	0.05	1.29
33.34	0.830	62000	0.00	0.00	1.34
40.00	0.830	62000	0.00	0.00	1.34

Fig. 13 (a).

Table 24.

Dye concentration = 2.00 x 10^{-5} M ϵ_f = 42000 ϵ_b = 61500

Conc. of Manoxl OT (x10^{-4}M)	Absorbence	ϵ_{app}	α	Conc. of free dye	Conc. of bound dye.
3.34	0.63	31500	-	-	-
6.67	0.70	35000	-	-	-
8.00	0.86	43000	0.95	1.90	0.10
10.00	0.92	46000	0.80	1.60	0.40
13.34	1.05	52500	0.46	0.92	1.08
16.67	1.11	55500	0.33	0.66	1.34
20.00	1.15	57500	0.21	0.42	1.58
26.67	1.18	58500	0.15	0.30	1.70
33.34	1.20	60000	0.08	0.16	1.84
40.00	1.22	61000	0.03	0.06	1.94
53.34	1.23	61500	0.00	0.00	2.00

Fig.13 (b)

Dodecane sulphonic acid(DS)-rosaniline hydrochloride.

Table 25.

Calculation of binding at pH 2.00.

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 18500 ϵ_b= 48500

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.395	19750	0.96	1.92	0.08
3.34	0.410	20500	0.93	1.86	0.14
5.34	0.500	25000	0.78	1.56	0.44
6.67	0.600	30000	0.62	1.24	0.76
10.00	0.800	40000	0.28	0.56	1.44
13.34	0.920	46000	0.08	0.16	1.84
16.67	0.945	47250	0.04	0.08	1.92
20.00	0.965	48250	0.00	0.00	2.00
26.67	0.965	48250	0.00	0.00	2.00

Fig.14 (a).

Table 26.

Dye concentration = 2.67 x 10^{-5}M ϵ_f= 18500 ϵ_b= 46630

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
1.34	0.530	19800	0.94	2.51	0.16
3.34	0.540	20400	0.91	2.43	0.24
5.34	0.630	23595	0.80	2.14	0.53
6.67	0.770	28090	0.64	1.71	0.96
10.00	0.980	36700	0.34	0.91	1.76
13.34	1.155	43260	0.10	0.27	2.40
16.67	1.200	44940	0.06	0.16	2.51
20.00	1.255	46630	0.00	0.00	2.67
26.67	1.230	46080	-	-	-

Fig.14 (b).

Table 27.

Calculation of binding at pH 4.60.

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 87000 ϵ_b= 105220

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.97	72400	-	-	-
6.67	0.82	61200	-	-	-
10.00	1.15	98040	0.94	1.26	0.08
13.34	1.25	93250	0.64	0.86	0.48
16.67	1.31	97740	0.38	0.51	0.83
20.00	1.36	101570	0.16	0.21	1.13
26.00	1.39	103730	0.04	0.05	1.29
33.34	1.40	104480	0.00	0.00	1.34
40.00	1.41	105220	0.00	0.00	1.34

Fig.15 (a)

Table 28.

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 87500 ϵ_b= 102750

Conc.of DS ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	1.150	57500	-	-	-
6.67	1.000	50000	-	-	-
10.00	1.600	80000	-	-	-
13.34	1.800	90000	0.84	1.68	0.32
16.67	1.860	93000	0.64	1.28	0.72
20.00	1.920	96000	0.44	0.88	1.12
26.67	1.980	99000	0.25	0.50	1.50
33.34	2.040	102000	0.05	0.10	1.90
40.00	2.050	102500	0.00	0.00	2.00
46.67	2.055	102750	0.00	0.00	2.00

Fig.15 (b).

Table 29.

Calculation of binding at pH 7.00.

Dye concentration = 1.34×10^{-5}M ϵ_f= 71000 ϵ_b= 90250

Conc.of DS ($\times 10^{-4}$M)	Absorbence	ϵ app.	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
3.34	0.695	51870	-	-	-
6.67	0.940	71000	-	-	-
8.00	1.010	75230	0.78	1.04	0.30
10.00	1.120	83610	0.35	0.47	0.87
12.00	1.140	85210	o.26	0.35	0.99
13.34	1.185	88580	0.09	0.12	1.22
16.67	1.195	89190	0.06	0.08	1.26
20.00	1.205	90080	0.01	0.01	1.33
26.67	1.210	90250	0.00	0.00	1.34
33.34	1.210	90250	0.00	0.00	1.34

Fig. 16.

Dioctyl sodium sulpho succinate(Manoxl OT)-rosaniline hydrochloride.

Table 30.

Calculation of binding at pH = 2.00.

Dye concentration = 2.67×10^{-5}M ϵ_f = 18500 ϵ_b = 50930

Conc. of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc. of free dye ($\times 10^{-5}$M)	Conc. of bound dye ($\times 10^{-5}$M)
1.34	0.780	29250	0.66	1.76	0.91
3.34	1.055	29520	0.35	0.93	1.74
6.67	1.200	44850	0.19	0.51	2.16
10.00	1.240	46720	0.14	0.37	2.30
13.34	1.290	48400	0.10	0.27	2.40
20.00	1.355	50790	0.00	0.00	2.67
26.67	1.360	50930	0.00	0.00	2.67

Fig.17 (a).

Table 31.

Dye concentration = 3.34×10^{-5}M ϵ_f = 18500 ϵ_b = 45090

Conc. of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc. of free dye ($\times 10^{-5}$M)	Conc. of bound dye ($\times 10^{-5}$M)
1.34	1.020	30540	0.55	1.84	1.40
3.34	1.210	36220	0.33	1.10	2.24
6.67	1.370	41050	0.15	0.50	2.84
10.00	1.430	42810	0.08	0.27	3.07
13.34	1.450	43410	0.06	0.24	3.14
16.67	1.470	44000	0.04	0.13	3.21
20.00	1.505	45090	0.00	0.00	3.34
26.67	1.510	45090	0.00	0.00	3.34

Fig.17 (b).

Table 32.

Calculation of binding at pH 4.6.

Dye concentration = 1.34×10^{-5}M ϵ_f= 87310 ϵ_b= 110460

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
2.67	0.66	49250	-	-	-
5.34	0.82	61500	-	-	-
6.67	1.11	82830	-	-	-
8.00	1.22	91040	0.83	1.11	0.23
10.00	1.33	100000	0.45	0.60	0.74
13.34	1.43	103600	0.29	0.39	0.95
16.67	1.46	108800	0.07	0.10	1.24
20.00	1.47	109400	0.04	0.05	1.29
26.67	1.48	110460	0.00	0.00	1.34
33.34	1.48	110460	0.00	0.00	1.34

Fig.18 (a).

Table 33.

Dye concentration = 2.0×10^{-5}M ϵ_f= 87500 ϵ_b= 115000

Conc.of Manoxl OT ($\times 10^{-4}$M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye ($\times 10^{-5}$M)	Conc.of bound dye ($\times 10^{-5}$M)
2.67	1.01	50500	-	-	-
5.34	1.22	61000	-	-	-
6.67	1.57	78500	-	-	-
8.00	1.82	91000	0.80	1.60	0.40
10.00	1.90	95000	0.73	1.46	0.54
13.34	2.10	105000	0.37	0.74	1.26
16.67	2.25	112500	0.15	0.30	1.70
20.00	2.29	114500	0.02	0.04	1.96
26.67	2.30	115000	0.00	0.00	2.00
33.34	2.30	115000	0.00	0.00	2.00

Fig.18 (b).

Table 34.

Calculation of binding at pH 7.00.

Dye concentration = 1.34 x 10^{-5}M ϵ_f= 71000 ϵ_b= 108900

Conc.of Manoxl OT (x10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	0.960	71640	0.99	1.33	0.01
6.67	1.035	77600	0.83	1.11	0.23
10.00	1.150	85820	0.6L	0.82	0.52
13.34	1.210	90000	0.50	0.67	0.67
16.67	1.290	96530	0.33	0.44	0.90
20.00	1.420	105750	0.08	0.11	1.23
26.67	1.450	108200	0.01	0.01	1.33
33.34	1.450	108200	0.01	0.01	1.33
40.00	1.460	108900	0.00	0.00	1.34

Fig.19 (a).

Table 35.

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 71000 ϵ_b= 105000

Conc.of Manoxl OT (x10^{-4}M)	Absorbence	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
3.34	1.090	54500	-	-	-
6.67	1.270	63500	-	-	-
10.00	1.430	71500	0.99	1.98	0.02
13.34	1.540	76950	0.82	1.64	0.36
20.00	1.665	83200	0.64	1.28	0.72
26.67	1.810	90350	0.43	0.86	1.14
33.34	1.990	99000	0.18	0.36	1.64
40.00	2.040	102000	0.09	0.18	1.82
53.34	2.100	105000	0.00	0.00	2.00

Fig. 19 (b).

From the tables (2-12), it could be seen that at pH 7.0, a very small amount of the Manoxl OT (13.34 x 10^{-4}M) was needed for the complete binding of the malachite green (4.0 x 10^{-5} M), whereas relatively larger amount of dodecane sulphonic acid was required under similar conditions. However, larger amount of the dodecane sulphonic acid was needed at the higher pH. Similar behaviour was observed in the case of rhodamine 6G (Tables 13-24).

With rosaniline hydrochloride the behaviour was altogether different. Small amount of dodecane sulphonic acid and Manoxl OT was sufficient for the complete incorporation of the dye into the surfactant micelle at pH 2.0 while a larger amount of the two surfactants was required at pHs 4.6 and 7.0 (Tables 25-35).

The plots between absorbence and surfactant concentration could be used to determine the amount of surfactant bound per molecule of dye assuming that all the dye got bound with the surfactant at the inflexion point. These ratios at two different concentrations of the dye and different pHs are given below.

Table 36.

Combining ratios of anionic surfactants to the bound dye obtained from the inflexion points at different pHs.

Dye	pH	DS Conc. of max. bound dye ($\times 10^{-5}$M)	DS Surf. conc. ($\times 10^{-4}$M)	DS Surf. conc./bound dye	Manoxl OT Conc. of max. bound dye ($\times 10^{-5}$M)	Manoxl OT Surf. conc. ($\times 10^{-4}$M)	Manoxl OT Surf. conc./bound dye
Malachite green.	2.00	2.00	16.67	83.	3.34	28.00	84
		2.67	20.00	76	4.00	33.34	83
	7.00	2.00	20.00	100	4.00	13.34	34
		2.67	26.67	100	-	-	-
	9.12	2.00	26.67	133	2.67	14.00	60
		3.34	40.00	122	3.34	20.00	60
Rhodamine 6G.	2.00	1.34	16.67	125	1.34	16.67	125
		2.00	24.00	120	2.00	24.00	120
	7.00	1.34	12.00	90	1.34	12.00	90
		2.00	16.67	83	2.00	16.67	83
	9.12	1.34	14.50	108	1.34	20.00	150
		2.00	20.00	100	2.00	40.00	200
Rosaniline hydrochloride.	2.00	2.00	16.67	83	2.67	16.67	62
		2.67	20.00	77	3.34	20.00	60
	4.60	1.34	26.67	200	1.34	13.34	100
		2.00	40.00	200	2.00	20.00	100
	7.00	1.34	26.67	200	1.34	26.67	200
		2.00	-	-	2.00	40.00	200

Mysels had reported that micellization occurs markedly at low concentrations of the surfactant in the presence of the dye and that throughout the transition region, the amount of micellized detergent was greatly increased by the presence of the dye. According to them the curves between the absorbence and surfactant concentrations (Figs.2-19) would report the change from dye rich induced micelles to the more normal type ordinarily containing no more than one dye cation per micelle.

As these levelling off points were at concentrations higher than the c.m.c., it could be concluded that the surfactants interact with the dye only in the form of micelle. The results in table (36) give number of surfactant molecules micellized per dye ion. Assuming that 1:1 interaction (the assumption is justified since rhodamine 6G and malachite green ionize to give only one cation) between dodecane sulphonic acid and rhodamine 6G or malachite green is favoured at pH 7.0, it may be inferred that the surfactant micelle interacting with the dye is made up of 100 surfactant anions (vide Mukerjee,P., and Mysels, K.J.,J.Amer. Chem.Soc., 77 , 2937 (1955) work on methylene blue-lauryl sulphate interaction).

On the other hand,the interaction between rosaniline hydrochloride would involve three surfactant molecules (vide Malik,W.U. and Haque,R.,J.Phys.Chem.67 , 2082 (1963)). Hence at pH 7.0, where 200 surfactant anions are found to be bound with the dye molecule, it can be concluded that there are three surfactant micelles, each having about 66 surfactant anions, which combine with rosaniline hydrochloride to give the surfactant-dye complex. Similar results were obtained by Mukerjee and Mysels (17) who studied the complex formed between pinacyanol chloride and sodium lauryl sulphate and found that three ordinary micelles having about 80 lauryl sulphate anions per dye cation were formed in the very dilute solution of the dye (4.0×10^{-5}M).

The effect of pH on the number of surfactant anions forming the micelle could also be seen on the basis of these investigations.

It was found that there was no effect of pH on the number of dodecane sulphonate anions forming the micelle. The number of surfactant anions in Manoxl OT was affected by pH. The number was smaller in the acidic range (pH 2.0) than that in the alkaline range (dye: rhodamine 6G, 2.0×10^{-5}M), and were least in the neutral medium.

No such uniformity was observed with malachite green. The number of both dodecane sulphonic acid and Manoxl OT surfactant anions (forming the three ordinary micelles) per dye cation are smaller at pH 2.0 in rosaniline hydrochloride (2.0×10^{-5}M) but as the pH increases, the number of anions per micelle increases. A marked effect of pH on the number of micellized surfactant anions in the solution of rosaniline hydrochloride was thus observed.

The above mentioned observations may be attributed to the fact that in the acedic medium, the dissociation of dodecane sulphonic acid is very much suppressed thereby making available a small number of surfactant anions to form micelle for dye interaction. Similar behaviour cannot be expected in the case of Manoxl OT since this surfactant is an ester (dioctyl sodium sulpho succinate) and is likely to ionise more in acidic medium.

CATIONIC SURFACTANTS-ACID DYE.

Unlike the basic dyes,viz.,malachite green, rhodamine 6G and rosaniline hydrochloride, the absorption maximum of congo red shifts with the pH of the solution (tables 19-24).

The absorption measurements for determining the extent of binding were,therefore,performed in buffered systems.

Table 37.

Influence of CTMAB and CPB on the absorption maximum of congo red at different pHs.

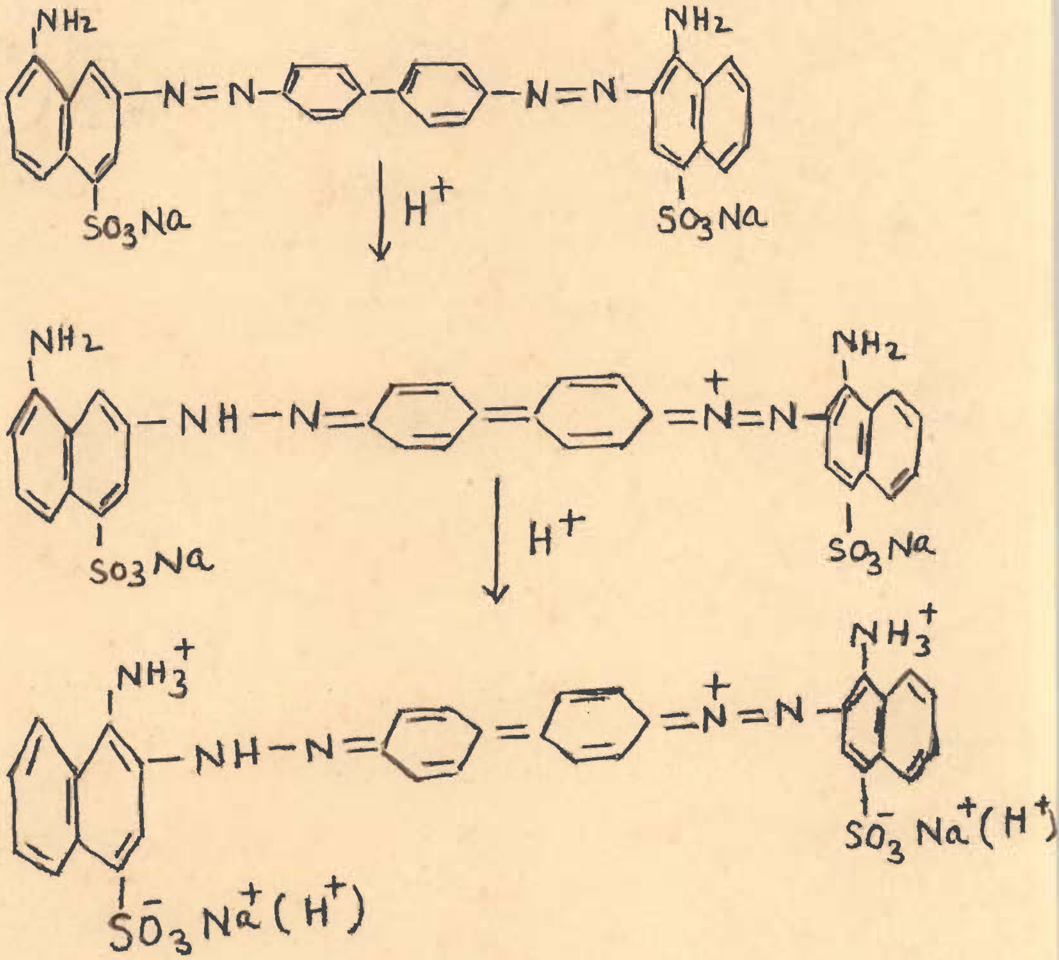
Conc. of CTMAB or CPB (x 10^{-5}M)	Absorption maximum of congo red.					
	Shift with CTMAB pH			Shift with CPB pH		
	2.00 mμ	7.00 mμ	9.12 mμ	2.00 mμ	7.00 mμ	9.12 mμ
0.00	560	480	480	560	480	480
0.67	560	480	480	560	480	480
1.34	560	480	480	560	480	480
3.34	500	480	480	460	480	480
5.34	480	pptn.	pptn.	460	pptn.	pptn.
6.67	480	pptn.	pptn.	460	pptn.	pptn.
10.00	460	470	470	460	460	460
13.34	460	470	470	460	460	460
20.00	460	470	470	460	460	460

To rule out the possibility of the shift in dye maximum due to disturbance in the monomer-polymer equilibrium of the dye, absorption measurements were carried out over a wide concentration range. Beer Lambert's law was found to hold good in the concentration range (0.0 to 4.0 x 10^{-5}M) (Fig.1 b). Our polarographic studies (Chapter V) also confirm the non-existence of aggregates in congo red.

From the absorption data, the following conclusions were arrieved at:

In the lower pH range, very large shift in the dye maximum (560 mμ to 460 mμ) was observed even with very small amount of either of the surfactants (6.67 x 10^{-5}M), while in neutral and basic media, a precipitate of the insoluble surfactant-dye salt was formed. This compound was found to form a coarse suspension in the presence of a little more than the stoichiometric amounts of CTMAB or CPB. Further addition of the surfactant resulted in the dispersion of insoluble dye-surfactant complex, accompained by a spectral shift in the maximum (480 mμ to 470 mμ with CTMAB and 480 mμ to 460 mμ with CPB) was observed. The complete dispersion of the insoluble salt was dependent upon the concentration of the dye and the absolute value of c.m.c. of the surfactant.

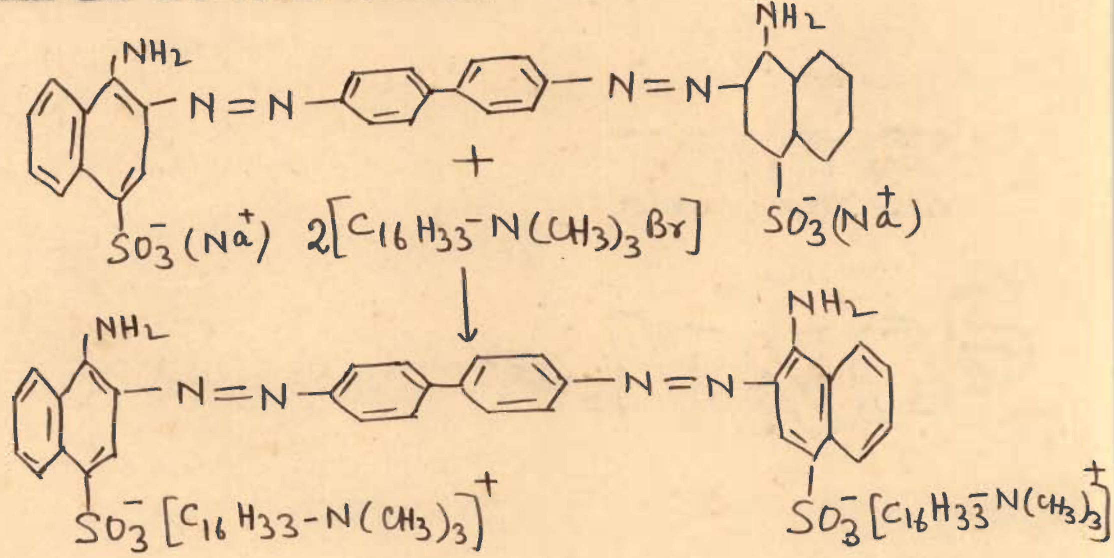
The dye structure offered possibilities for the existence of zwitter ions or resonance structure due to the protonation of azo nitrogen. It may be the reason why large amount of cationic surfactants was required in the low pH range. The structural equilibrium existing in the congo red dye may be represented as follows: (vide Malik and Haque loc.cit.)



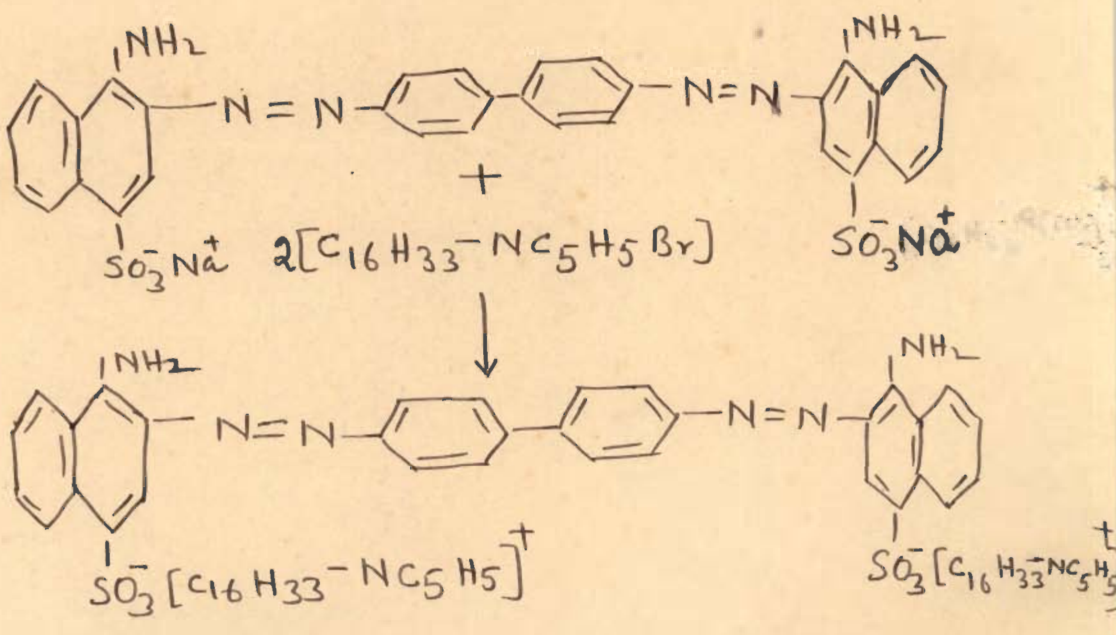
The formation of cationic surfactant-dye complex would take place in the higher pH range. The probable mechanism for this reaction would involve deprotonation of the dye by the surfactant and its subsequent interaction with excess of the surfactant to give the complex. It is, however, difficult to predict the amount of the surfactant required to deprotonise the NH_3^+ and $= N^+$ of the protonated dye and that required for complex ion formation.

The possible reaction between the congo red and CTMAB and CPB would then be:

1.



2.



From the absorbence data in the lower pH range (pH 2.0) the extent of binding of the dye with CTMAB and CPB can be calculated by Klotz's formula. The results are given in the following tables:

Cetyl trimethyl ammonium bromide (CTMAB) - congo red.

Table 38.

Calculation of binding at pH 2.00

Dye concentration = 2.67 x 10^{-5}M ϵ_f = 22470 ϵ_b= 5240

Conc. of CTMAB (x 10^{-5}M)	Absorbence at 560 mμ	$\epsilon_{app.}$	α	Conc. of free dye (x10^{-5}M)	Conc. of bound dye (x10^{-5}M)
1.34	0.50	18725	0.78	2.08	0.59
2.67	0.43	16105	0.63	1.68	0.99
3.34	0.41	15350	0.59	1.57	1.10
4.00	0.33	12360	0.41	1.10	1.57
5.34	0.26	9725	0.26	0.69	1.98
6.67	0.20	7680	0.14	0.37	2.30
10.00	0.15	5620	0.02	0.05	2.62
13.34	0.14	5240	0.00	0.00	2.67
16.67	0.14	5240	0.00	0.00	2.67

Fig. 20 a.

Table 39.

Calculation of binding at pH 2.00

Dye concentration = 3.34 x 10^{-5}M ϵ_f= 22400 ϵ_b= 5240

Conc.of CTHAB (x 10^{-5}M)	Absorbence at 560 mμ.	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
1.34	0.63	18860	0.79	2.64	0.70
2.67	0.56	16760	0.67	2.24	1.10
3.34	0.50	15000	0.56	1.87	1.47
5.34	0.36	10930	0.33	1.10	2.24
6.67	0.29	8680	0.21	0.70	2.64
10.00	0.22	6590	0.08	0.27	3.07
13.34	0.19	5690	0.03	0.10	3.24
16.67	0.17	5240	0.00	0.00	3.34
20.00	0.17	5240	0.00	0.00	3.34

Fig. 20 b.

Cetyl pyridinium bromide (CPB) - congo red.

Table 40.

Calculation of binding at pH 2.00

Dye concentration = 2.00 x 10^{-5}M ϵ_f= 22500 ϵ_b= 3700

Conc.of CPB (x 10^{-5}M)	Absorbence at 560 mμ	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
0.67	0.39	19500	0.84	1.68	0.32
1.34	0.32	16000	0.65	1.30	0.70
2.01	0.25	12500	0.47	0.94	1.06
2.67	0.18	9000	0.30	0.60	1.40
3.34	0.13	6500	0.14	0.28	1.72
4.02	0.10	5000	0.06	0.12	1.88
5.34	0.08	4000	0.02	0.04	1.96
6.67	0.07	3700	0.00	0.00	2.00
10.00	0.07	3700	0.00	0.00	2.00

Fig.21 a.

Table 41.

Calculation of binding at pH 2.00

Dye concentration = 4.00 x 10^{-5}M ϵ_f= 22500 ϵ_b= 3750

Conc.of CPB (x 10^{-5}M)	Absorbence at 560 mμ.	$\epsilon_{app.}$	α	Conc.of free dye (x10^{-5}M)	Conc.of bound dye (x10^{-5}M)
1.34	0.80	20000	0.80	3.44	0.56
2.67	0.65	16250	0.67	2.68	1.32
3.34	0.55	13750	0.53	2.12	1.88
4.02	0.48	12000	0.44	1.76	2.24
5.34	0.41	10250	0.35	1.40	2.60
6.67	0.30	7500	0.20	0.80	3.20
10.00	0.18	4500	0.04	0.16	3.84
13.34	0.15	3750	0.00	0.00	4.00
16.67	0.15	3750	0.00	0.00	4.00

Fig. 21 b.

The levelling off points in the curves plotted between absorbence and concentration of the surfactants were used to give the amounts of CTMAB and CPB required to incorporate whole of the dye into the surfactant micelle. These results go to show that two quaternary ammonium cations combine with one dye anion to form a micelle in the acedic medium (pH 2.0). On the other hand, 1:2 dye-surfactant complex is formed in the neutral and alkaline media. As already stated, the latter complex got dispersed in excess of CTMAB and CPB.

Table 42.

Number of CTMAB and CPB molecules required to solubilize the dye-surfactant complex at different pHs.

pH	Dye conc. ($\times 10^{-5}$M)	CTMAB conc. ($\times 10^{-5}$M)	$\frac{\text{CTMAB conc.}}{\text{Dye conc.}}$
7.00	3.34	10.0	3.0
9.12	3.34	10.0	3.0
	CPB		
7.00	2.67	10.00	4.0
9.12	2.67	10.00	4.0

It can be seen from the above table that three molecules of CTMAB and four molecules of CPB are required to solubilize the single dye anion.

C.M.C. DETERMINATION.

The above mentioned data can also be employed to determine the c.m.c. values of anionic (Table 1-18) and cationic (Tables 19,22) surfactants. The concentration of the surfactant, required to cause an abrupt change in the spectrum of the dye, was considered to give the c.m.c.. The exact values were obtained by plotting the absorbence of the surfactant-dye mixtures vs. the surfactant concentration, at both the original and shifted dye maxima. The point of intersection of the two curves gave the c.m.c. value (Figs. 26-43).

Another fundamental property worth considering in the case of surfactant-dye mixture is the stable micelle point (S.M.P.). This point corresponds to the minimum concentration of the surface active agent which would yield a constant value of the absorbence. The levelling off point corresponding to the S.M.P. value indicates complete incorporation of the dye into the surfactant micelle (Figs. 26-43).

The c.m.c. and S.M.P. values determined by the above method are given in the following tables. Table 46 gives the data on the c.m.c. of the pure surfactant (without dye) found by conductivity method for the sake of comparision.

Table 43.

Results on c.m.c. values of dodecane sulphonic acid.

Dye	pH	Dye conc. ($x10^{-5}M$)	c.m.c. ($x10^{-4}M$)	S.M.P. ($x10^{-4}M$)
Malachite green	2.00	2.00	6.67	16.67
	7.00	2.67	5.34	26.67
	9.12	2.00	-	-
Rhodamine 6G.	2.00	1.34	5.34	16.67
	7.00	1.34	5.34	12.00
	9.12	2.00	8.00	20.00
Rosaniline hydrochloride.	2.00	2.00	8.00	16.67
	4.60	1.34	8.00	26.67
	7.00	1.34	5.00	26.67

Table 44

Results on c.m.c.values of dioctyl sodium sulpho succinate

Dye	pH	Dye conc. ($x10^{-5}M$)	c.m.c. ($x10^{-4}M$)	S.M.P. ($x10^{-4}M$)
Malachite green.	2.00	4.00	3.34	33.34
	7.00	4.00	3.34	13.34
	9.12	3.34	10.00	20.00
Rhodamine 6G.	2.00	1.34	4.00	16.67
	7.00	2.00	6.00	16.67
	9.12	1.34	4.00	20.00
Rosaniline hydrochloride.	2.00	2.67	-	-
	4.60	1.34	6.00	13.34
	7.00	1.34	10.00	26.67

Table 45.

Results on c.m.c. values of CTMAB and CPB.

pH	Dye conc. ($x10^{-5}M$)	c.m.c. ($x10^{-5}M$)	S.M.P. ($x10^{-5}M$)
		CTMAB	
2.0	3.34	2.67	6.67
		CPB	
2.0	2.00	1.34	3.34

Table 46*

Results on c.m.c. values of anionic and cationic surfactants.

Conductivity method (without dye)	c.m.c.			
	DS ($x10^{-4}M$)	Manoxl OT ($x10^{-4}M$)	CTMAB ($x10^{-4}M$)	CPB ($x10^{-4}M$)
	30.0	6.80	2.50	53.00

* Carried out separately.

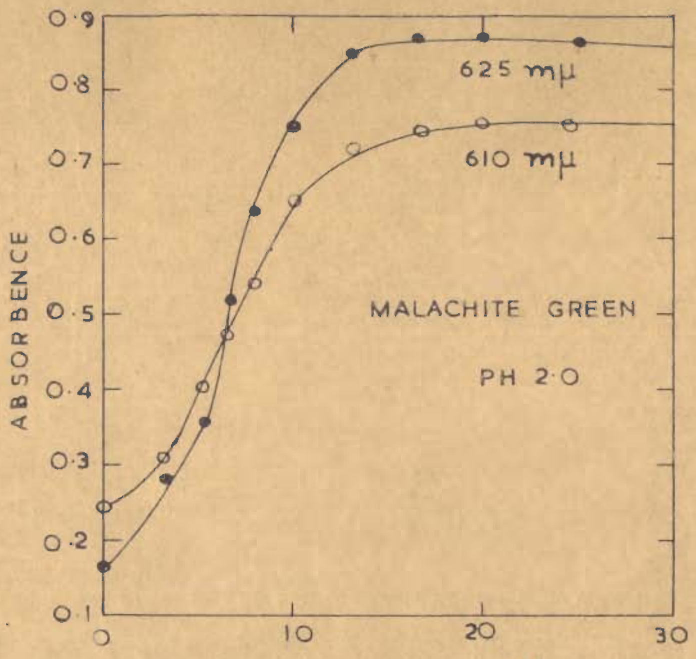


FIG.26

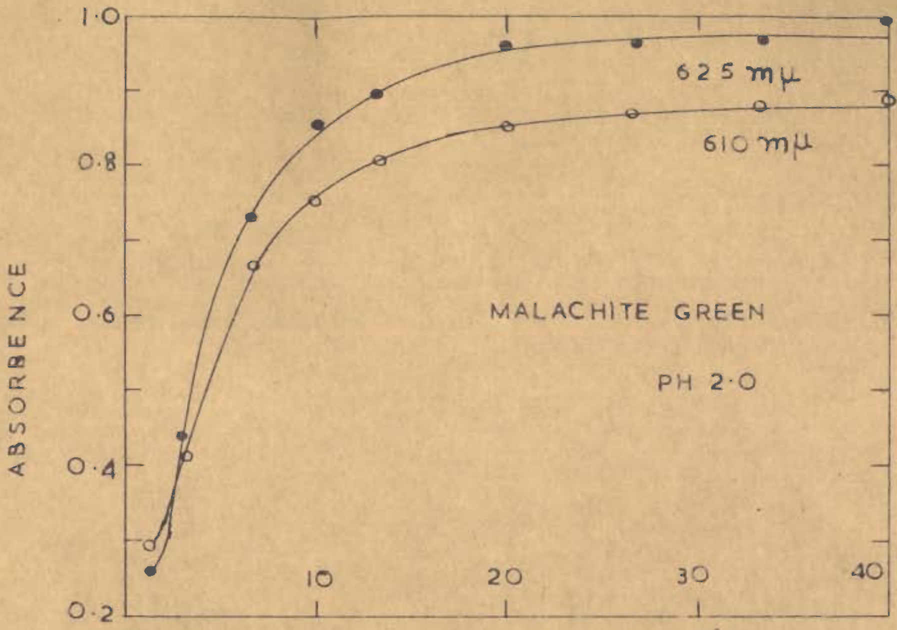


FIG.28

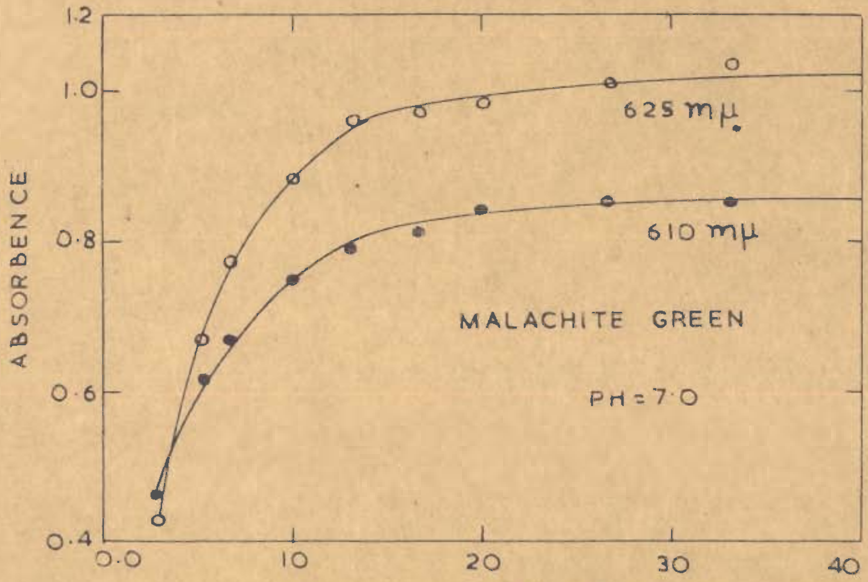


FIG.27

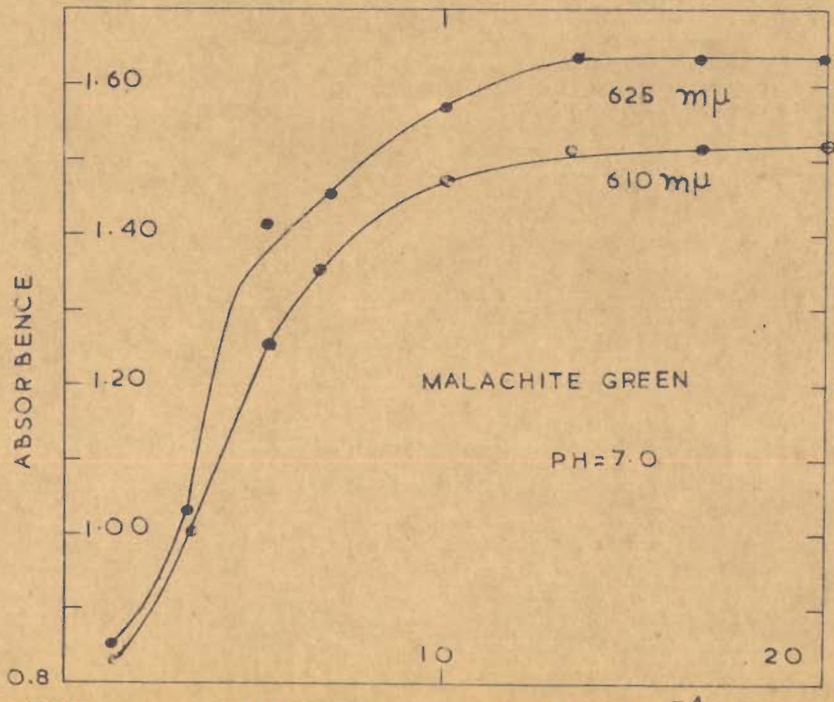


FIG.29

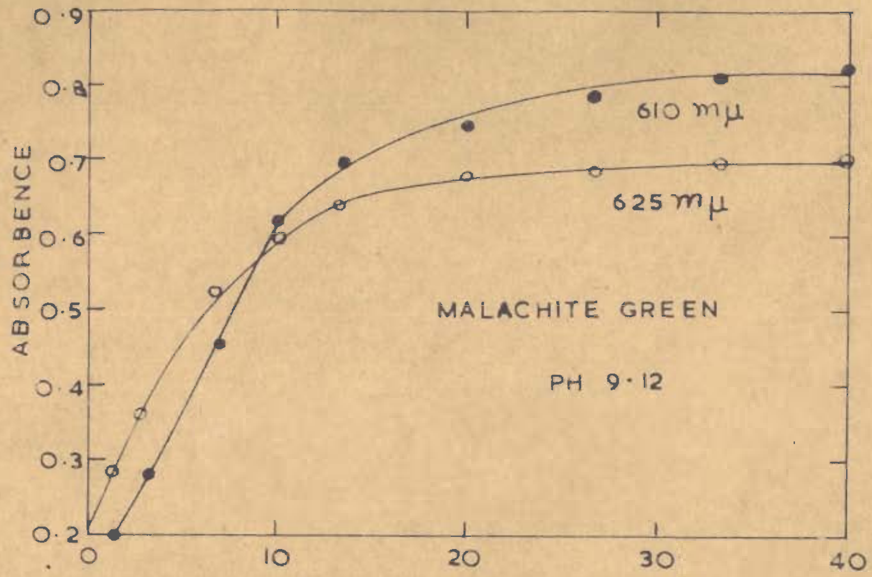


FIG.30

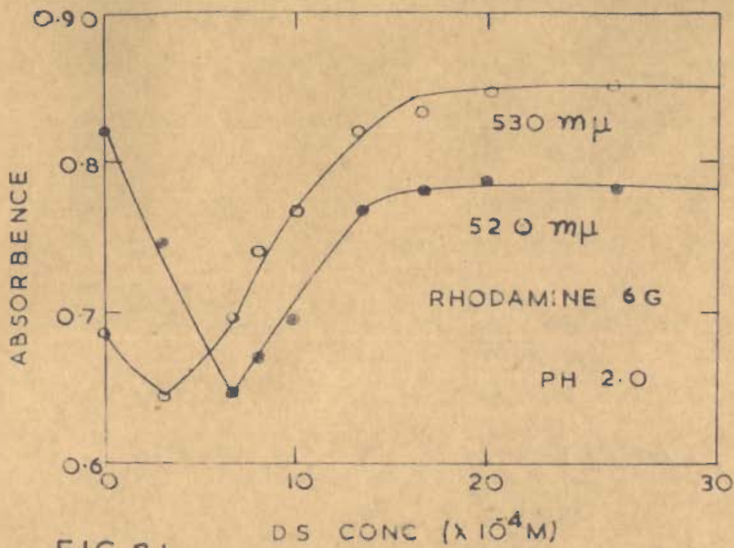


FIG.31

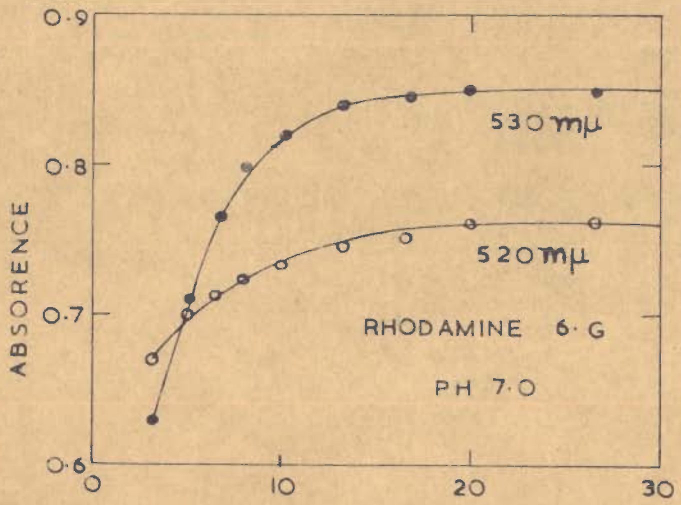


FIG 32

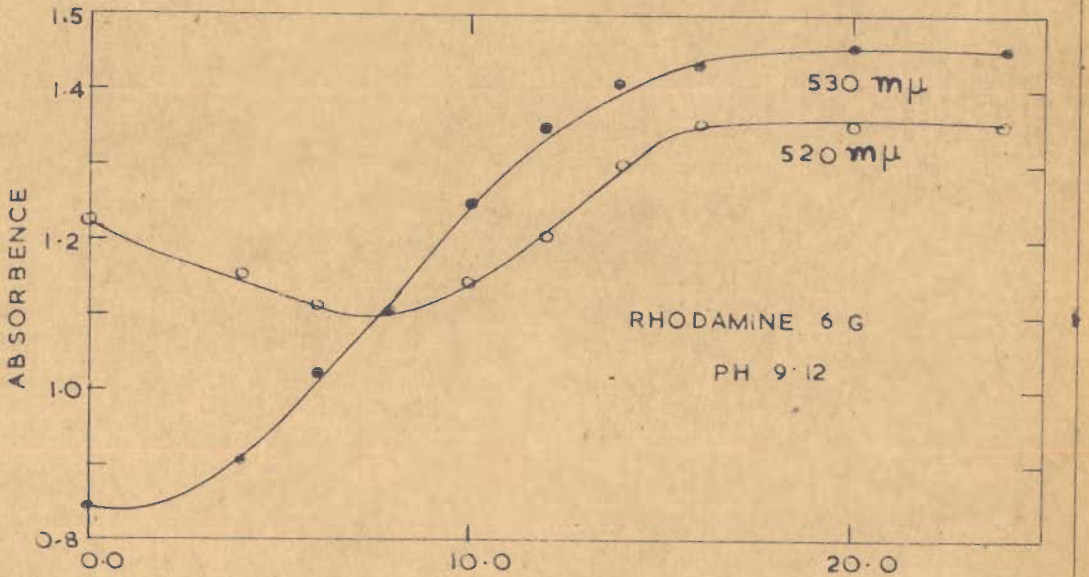


FIG 33

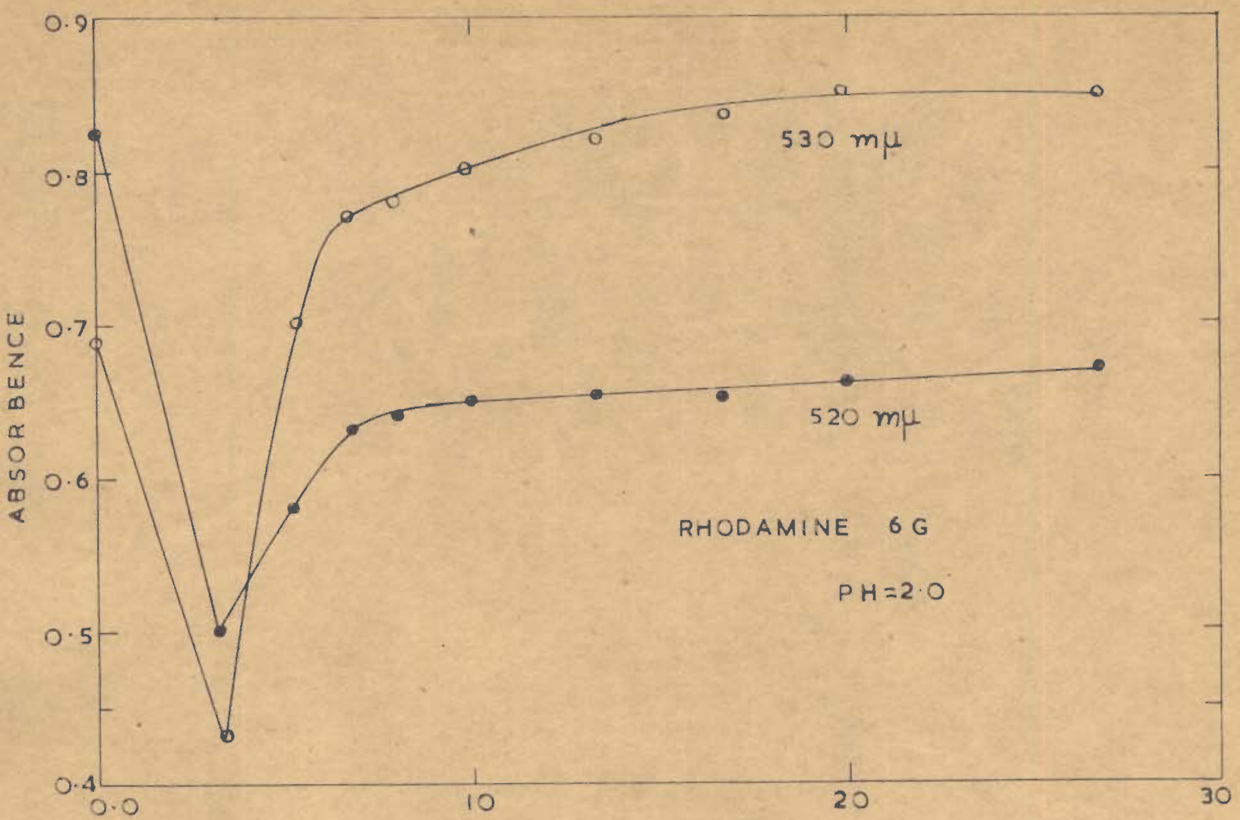


FIG. 34

MANOXL OT CONC. ($\times 10^{-4}$ M)

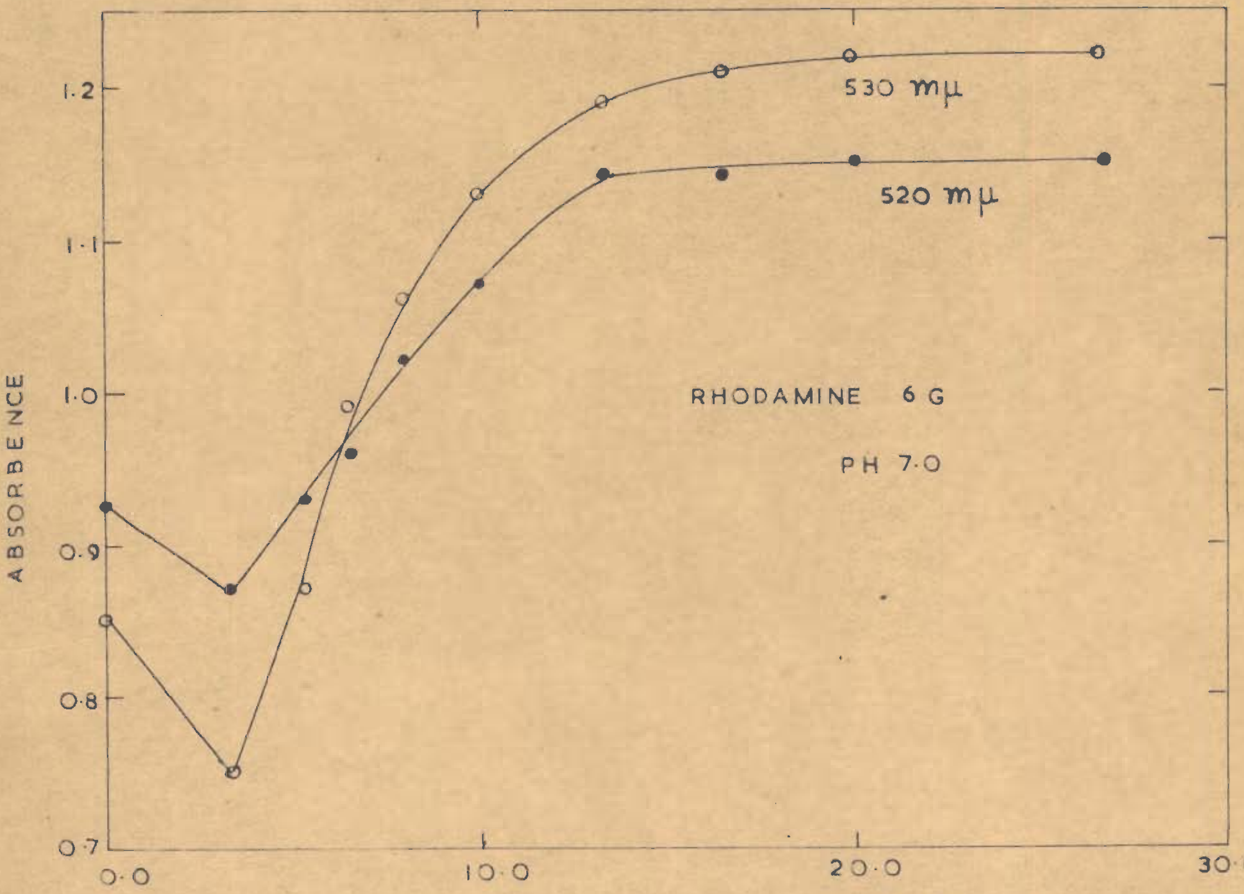


FIG. 35

MANOXL OT CONC. ($\times 10^{-4}$ M)

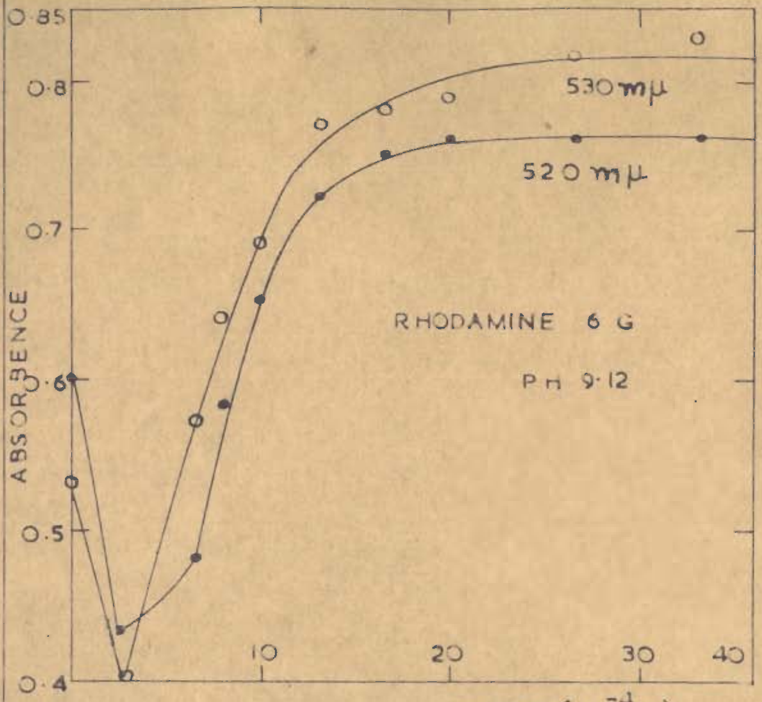


FIG. 36

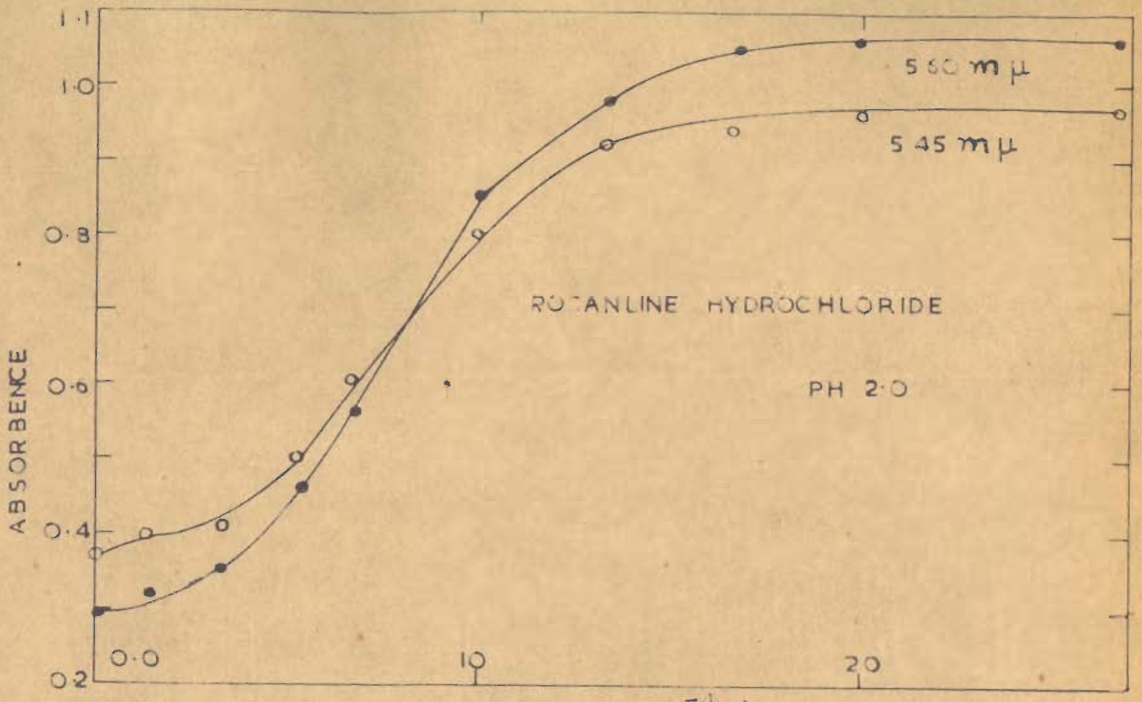


FIG.37

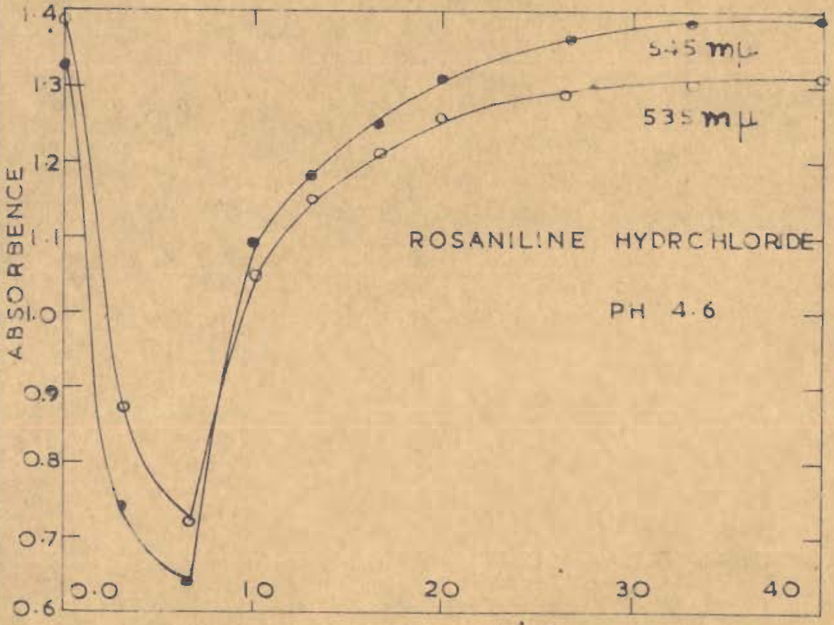


FIG.38

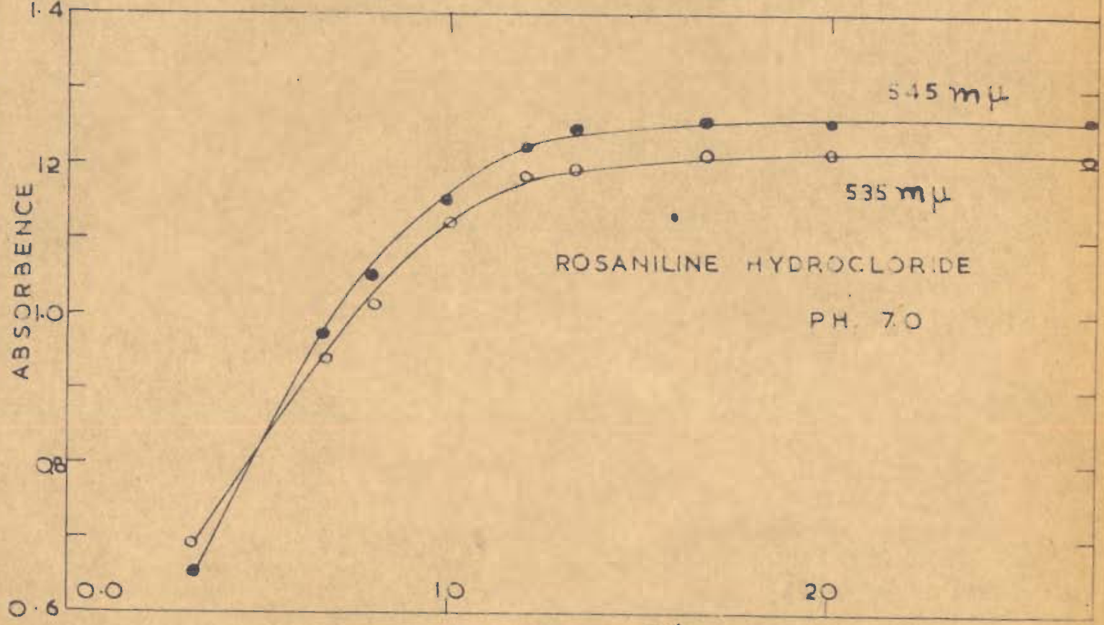


FIG.39

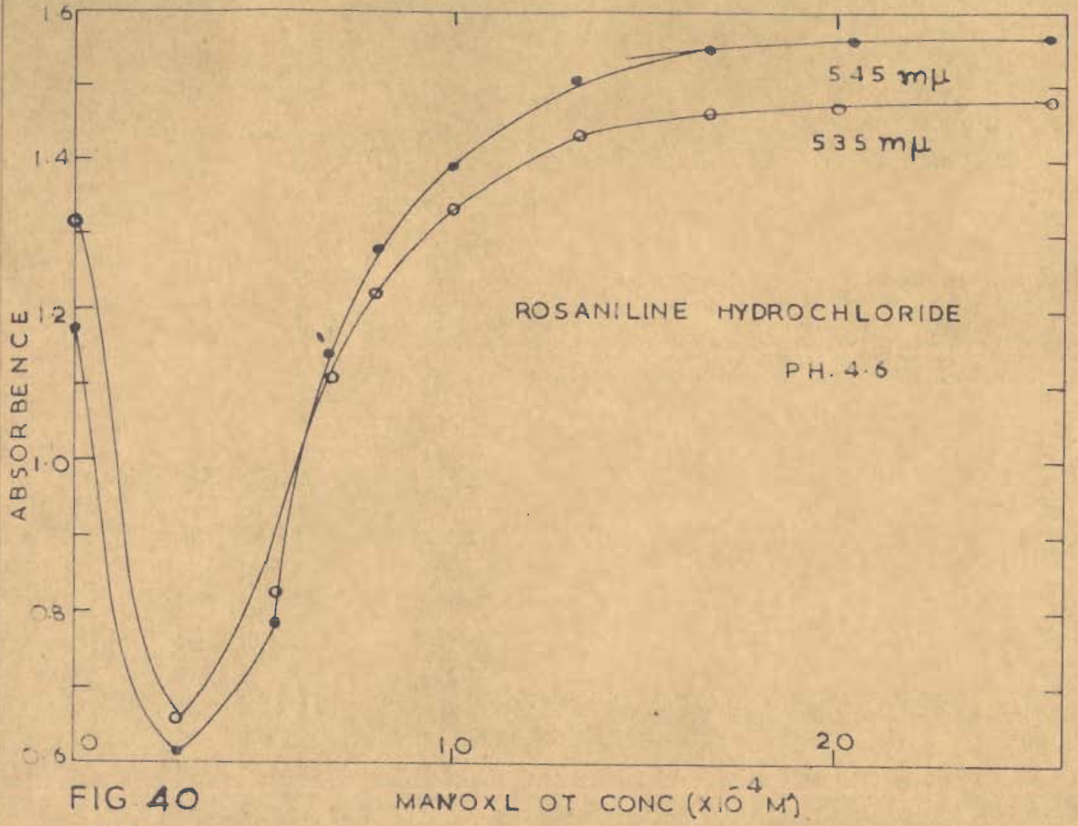


FIG 40

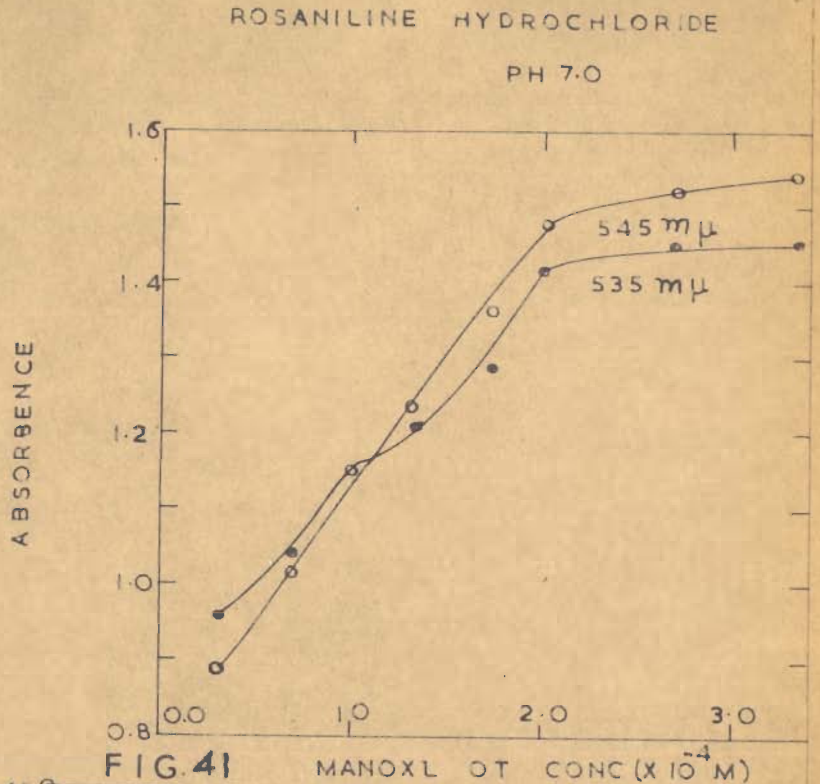


FIG. 41

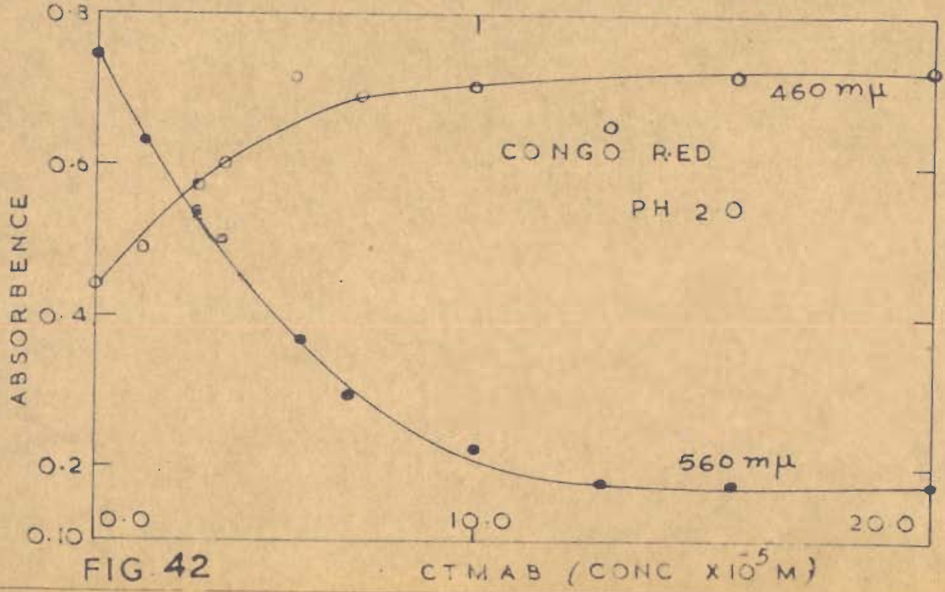


FIG 42

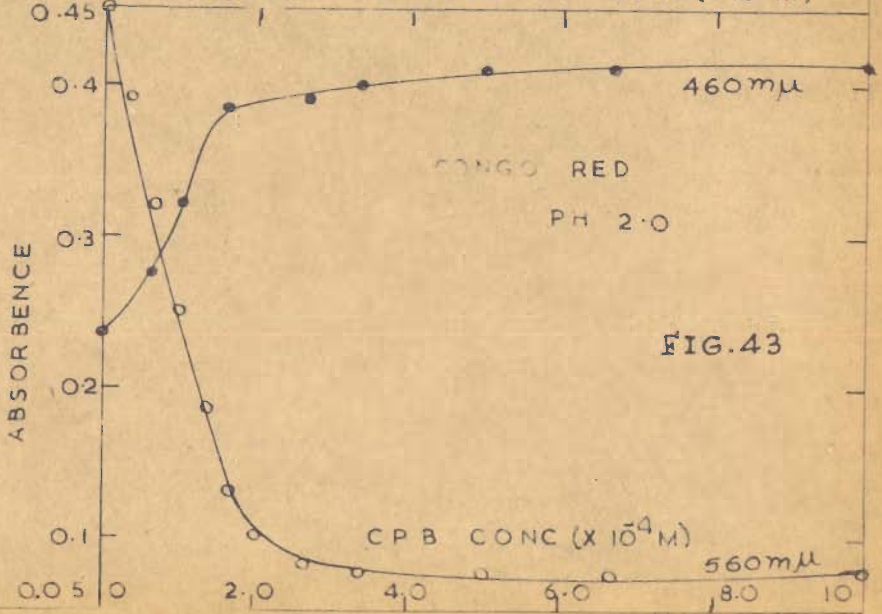


FIG. 43

DISCUSSION

The c.m.c.values both of anionic and cationic surfactants obtained in presence of dyes are lower than those of the pure surfactants. Already stated the lowering in c.m.c. of the surfactant by the dyes can be explained in terms of induced micelle formation. This concept involves the formation of a surfactant-dye complex whose micelles would be formed at lower concentration.

Although parallelism exists between the effect of dyes and electrolytes on c.m.c.,the mechanism proposed in the latter case takes into consideration breaking of water structure instead of induced micelle formation.

--00--

REFERENCES

1. Putnam,F.W., 'Advances in Protein Chemistry' Vol.IV, 80 (1948), Academic Press Inc., Pub.New York.

2. Cockbain,E.G., Trans.Faraday Soc. 49 ,104 (1953).

3. Harrap,B.S. and Schulman,J.H., Diss.Faraday Soc. 13 ,177 (1953).

4. Aoki,K. and Hori,J., J.Amer. Chem.Soc. 81 ,1885 (1959).

5. Guerritore,D. and Belleli,L., Nature, 184 ,Suppl., 21 , 1638 (1959).

6. Saito,S., J.Colloid Sci., 15 ,283 (1960).

7. Saito,S., Kolloid-Z, 168 ,128 (1960).

8. Hartley,G.S., Trans.Faraday Soc. 30 ,44 (1934).

9. Ottewill,R.H., Rastogi,M.C. and Watanabe,A.,Trans. Faraday Soc. 56 ,854 (1960).

10. Ottewill,R.H. and Watanabe,A., Kolloid-Z 170 ,38, 132 (1960).

11. Schulman, J.H., Austral.J.Chem. 13,236 (1960).

12. Frantisck Erben Czech 89,046 (1959).

13. Hartley,G.S. and Samis,C.S., Trans.Faraday 34 ,1288 (1938).

14. Corrin,M.L. and Harkins, W.D.,J.Amer.Chem.Soc. 69 , 679 (1947).

15. Kolthoff,I.Am. and Stricks,W., J.Phys.and Colloid Chem. 52 ,915 (1948).

16. Arkin,L. and Singbettery,C.R., J.Amer.Chem. Soc. 70 , 3965 (1948).

17. Mukerjee,P. and Mysels,K.J., ibid. 77 ,2937 (1955).

18. Lison,L. Arch.Biol., 46 ,599 (1935).

19. Holmes,W.C. Strain,Technol., 1 , 116 (1926).

20. $\overset{o}{\underset{\lambda}{\text{C}}}$lichman,E.L., J.Amer.Chem.Soc., 73 ,3385 (1951).

21. Mehrotra,R.C., J. Ind.Chem.Soc. 25 ,541 (1948).

22. Hiskey,C.F. and Downey,T.A., J.Phys.Chem. 58 ,835 (1954).

23. Hayashi,M., Bull.Chem.Soc. Japan ,34 ,119 (1961).

24. Malik,W.U. and Haque,R., J.Phys.Chem. 67 ,2082 (1963).

25. Malik,W.U. and Verma,S.P., J.Phys.Chem. 70 ,26 (1966).

26. Noller,C.R. and Gordon, J.J., J.Amer.Chem.Soc. 55 ,1090 (1933).

27. ''Hydrogen ions'' by Britton,H.S.,Vol. 1,D.Nostrand Company, Inc. Princeton New Jersey (1956).

28. Klotz,L.M., J.Amer. Chem. Soc. 68 ,2299 (1946).

CHAPTER IV

Polarographic estimation of ionic surfactants.

INTRODUCTION

The various problems of analysis which confront the chemist who deals with the surfactants do not differ greatly from analytical problems in other fields of chemistry and chemical technology. A list of various methods for the analysis and the estimation of water-soluble synthetic surface active agents (1) is reviewed in the literature.

Probably the most widely used method for estimating the anionic surfactants is by titration with long chain quaternary ammonium salts,using methylene blue in chloroform as an indicator (2-3). Another general method for determining the ionic surfactants (4,5) is the formation of a water insoluble dye-surfactant salt which is dissolved in non-aqueous solvent and is estimated colorimetrically. The method has been employed in modified and unmodified form, to determine the quaternaries in milk,various food stuffs,sanitizing solutions and other compositions (6) as well as to the laboratory analysis of relatively pure surfactants. Other analytical methods like potentiometry (7) and conductometry methods have also been employed for the determination of surfactants and their auxilaries.

Polarographic method as already mentioned,has been used to measure the extent to which surfactants suppress the maximum on the current voltage curve (8-10).The technique was,however,put to indirect use for determining the soap concentration by precipitating it with a standard cadmium solution and measuring the effect on the cadmium wave (11). Gorden and Urner (12) had recently described a polarographic method for the otherwise difficult determination of sulphite and sulphate in peteroleum sulphonates.

A new approach,based on polarography for determining the concentration of surfactant solutions,can be by making use of the surfactant dye interaction. The existing literature showed that this method has not been fully exploited. Investigation in this direction would not only provide a quick and sensitive method for determining the concentration of the surfactants but may throw some light on the surfactant-dye binding.

The investigations described in this chapter deal with the determination of cationic surfactant,viz., cetyl trimethyl ammonium bromide (CTMAB),cetyl pyridinium bromide (CPB) using congo red and alizarin Red S and that of anionic surfactants,viz.,dodecane sulphonic acid (DS) and dioctyl sodium sulpho succinate with methylene blue.

This method is based on the observation that marked decrease in the diffusion current of the reducible dye takes place in presence of ionic surface active agents, owing to the formation of water-insoluble compound. The decreased wave height was found to be a linear function of the surfactant concentration. The concentration of an unknown sample can then be determined from appropriate calibration curves.

—

EXPERIMENTAL

REAGENTS.

Dodecane sulphonic acid (DS) was prepared in the laboratory (vide Chapter III). Dioctyl sodium sulpho succinate (Manoxl OT), cetyl trimethyl ammonium bromide (CTMAB), cetyl pyridinium bromide (CPB) were all BDH products and used without further purification. Methylene blue, congo red and alizarin Red S were BDH products and were purified by further recrystallization. All other reagents were Analar grade.

All solutions were prepared in doubly distilled water. Glycine and acetate buffers of the following compositions were prepared.

i) Glycine = 0.0025M and KCl = 0.025M (pH 6.00).

ii) 0.2M acetic acid and 0.2M sodium acetate.

pH-measurements were made by Beckman pH meter Model H.

APPARATUS.

Polarographic measurements were carried out using Heyrovsky polarograph model (Lp 55A) operated manually using scalamp Pye galvanometer. All the measurements were made at 25 ± 0.1°C using thermostatic water bath.

PROCEDURE.

Working solutions were made by taking a known amount of dye solution (10^{-3}M) and mixing with a constant amount of the appropriate buffer solution (4.0 ml.), varying amounts of the surfactant solution (10^{-2}M) and then making the total volume to 10 ml. with water. The solutions were allowed to stand over night for complete reaction. The polarograms of the supernant solutions were taken after passing the purified hydrogen for about ten minutes.

—

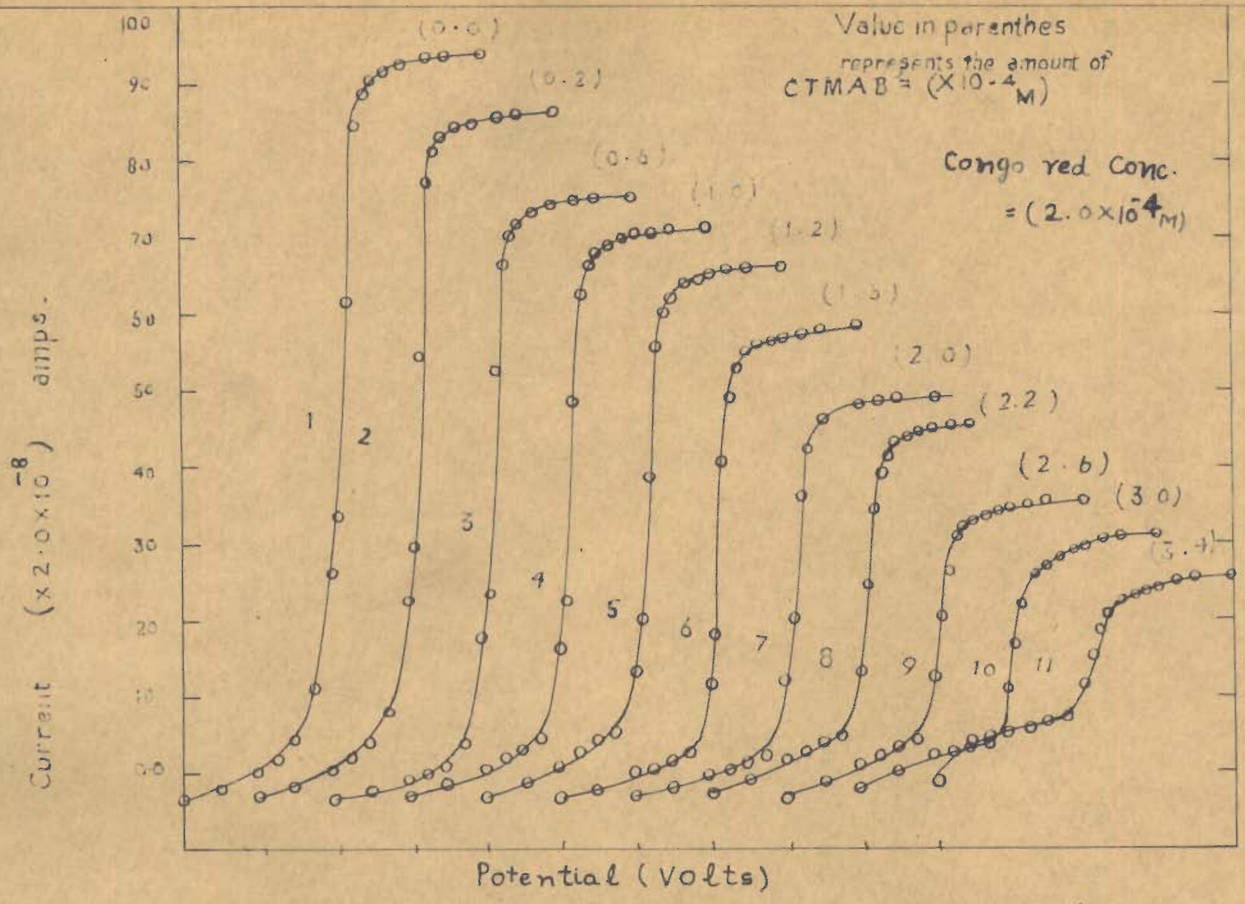


FIG.1 Value in parenthes represents the amount of CTMAB=(X10^{-4}M)

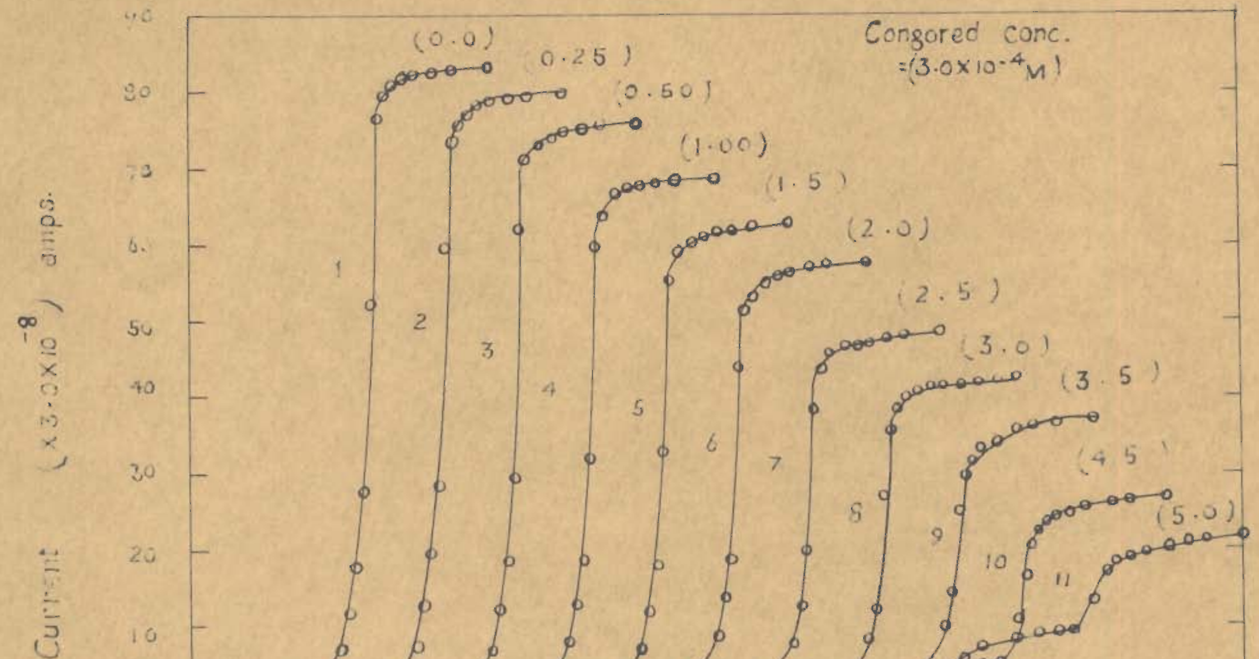


FIG. 2

1 div. 0.2 volt

Each curve starts at 0.1 volt

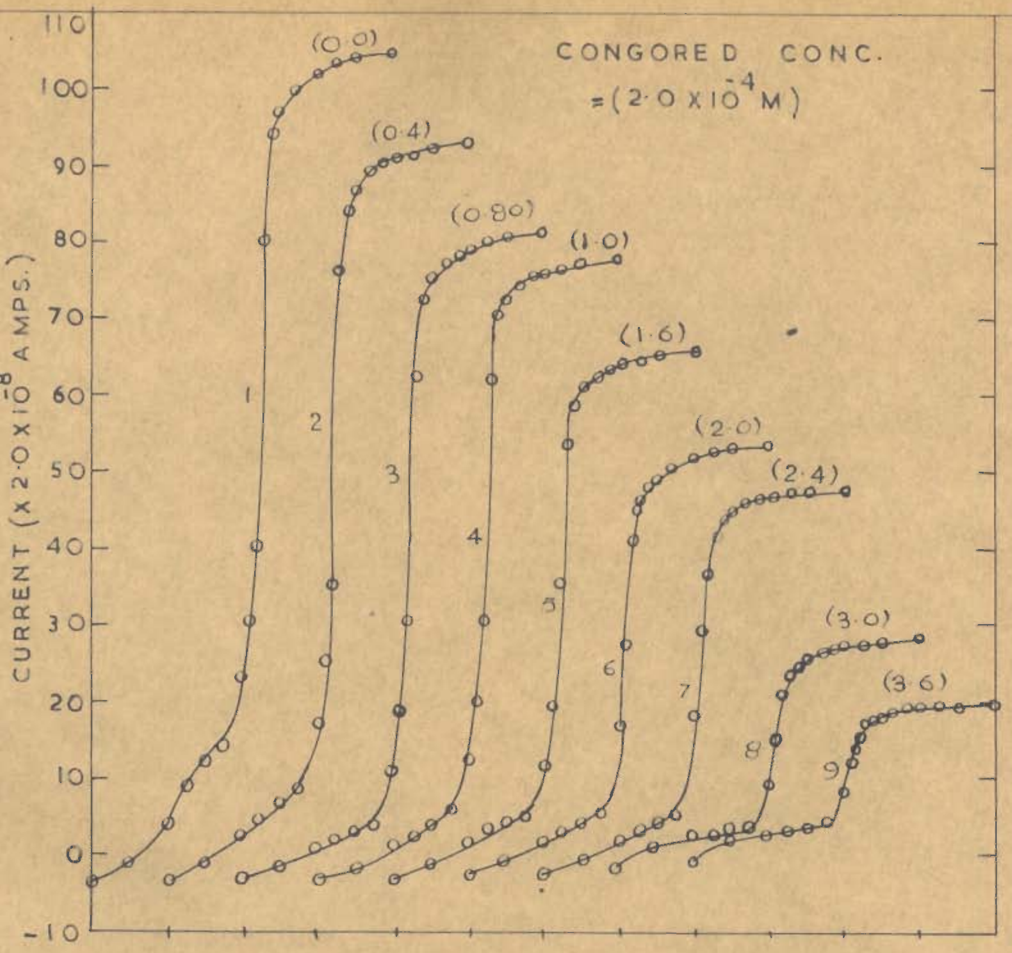


FIG.3

VALUE IN PARENTHES REPRESENT THE AMOUNT OF CPB =(X 10^{-4} M)

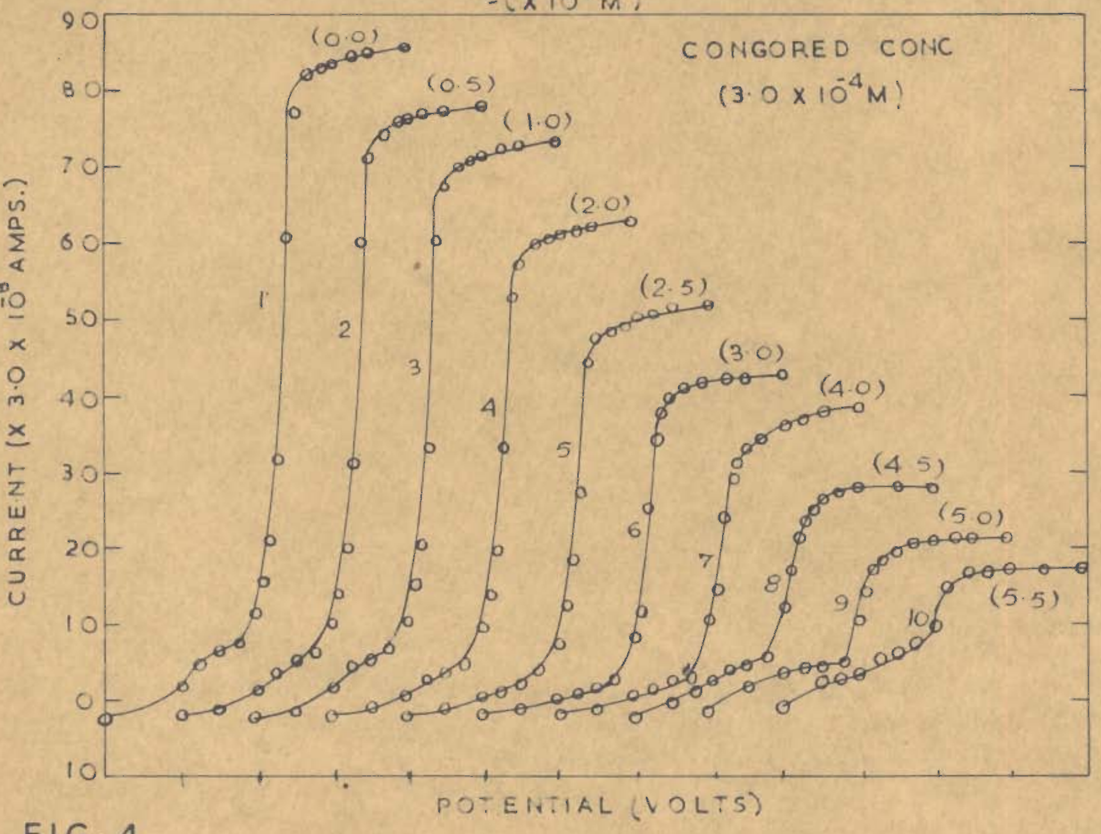


FIG. 4

1 DIV. 0·2 VOLT

EACH CURVE STARTS AT 0·1 VOLT

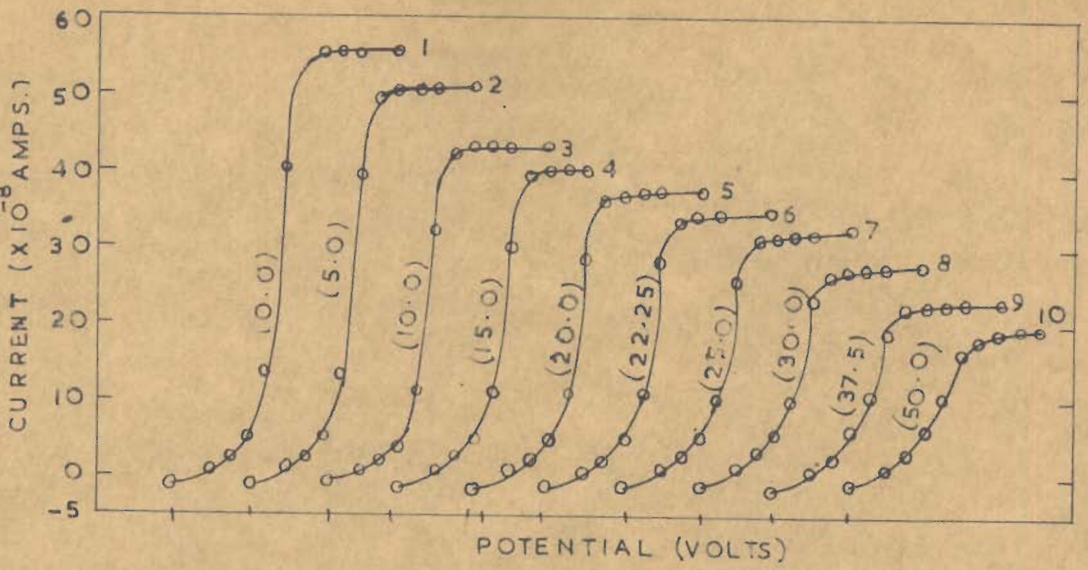


FIG. 5 ALIZARIN REDS CONC. = $(10\cdot0 \times 10^{-4}$ M) AT PH 3·09

VALUE IN PARENTHE REPRESENTS THE AMOUNT OF CTMAB = $(\times 10^{-5}$ M)

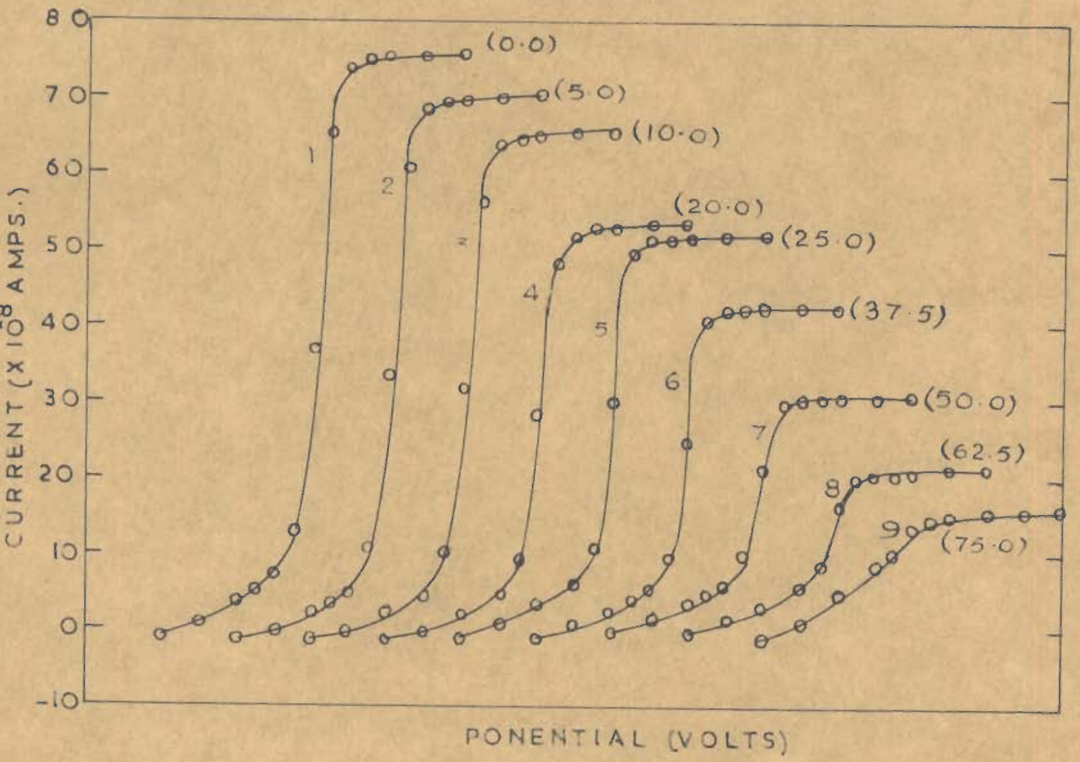
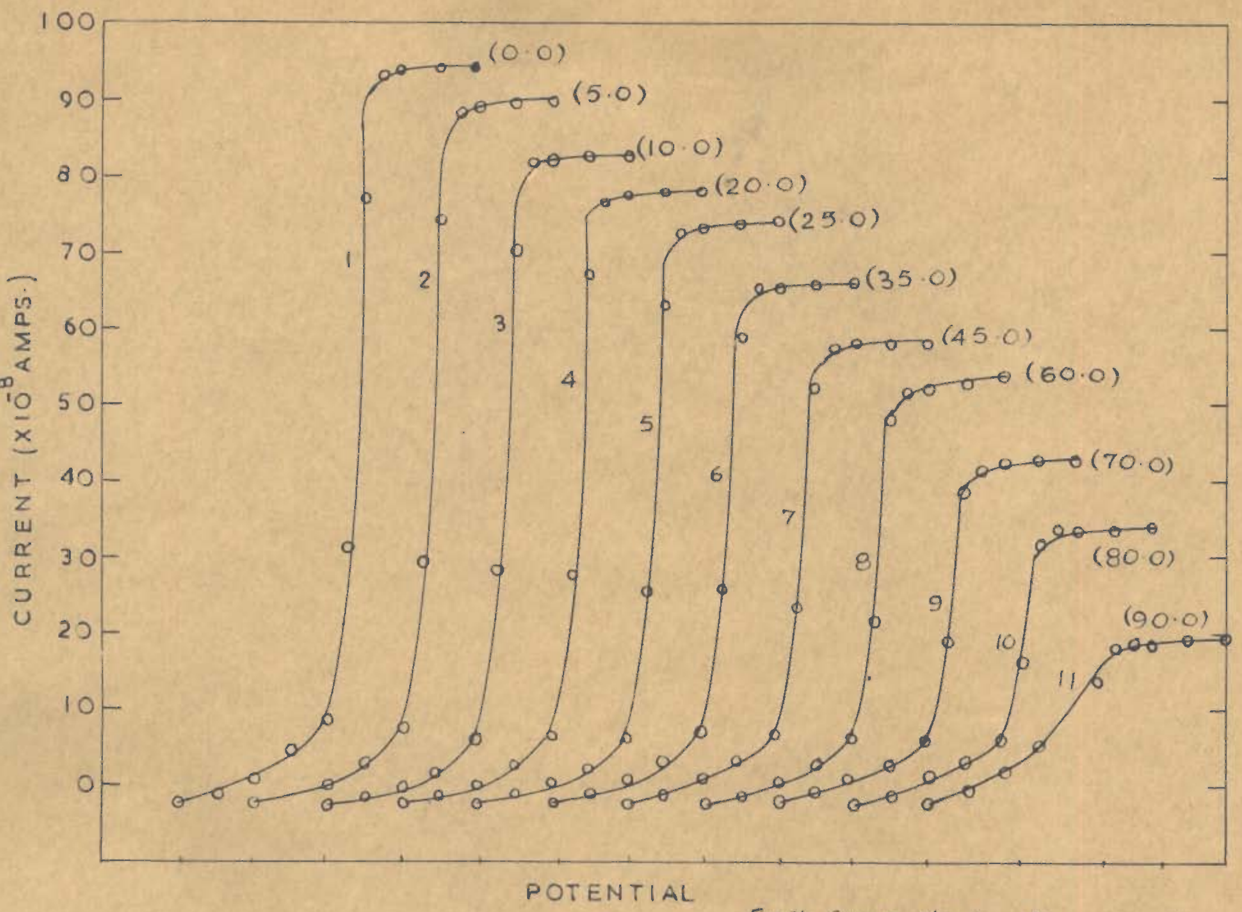


FIG. 6 ALIZARIN REDS CONC = $(10\cdot0 \times 10^{-4}$ M) AT PH 4·0

1 DIV. 0·2 VOLT EACH CURVE STARTS AT - 0·0 VOLT



Each Curve starts at -0.0 Volt.

FIG. 7 ALIZARIN REDS CONC.=(20·0 X10^{-4}M) AT PH 5.0

VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CTMAB=(X10^{-5}M)

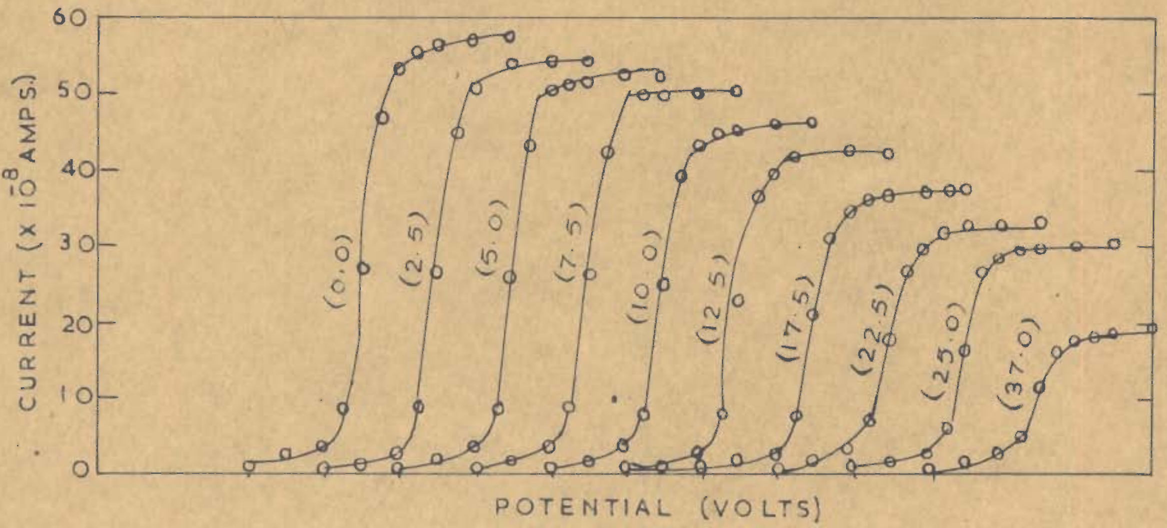


FIG. 8 ALIZARIN REDS CONC (10·0 X 10^{4}M) AT PH 7·0

1 DIV.= 0.2 VOLT EACH CURVE STARTS AT - 0·2 VOLT

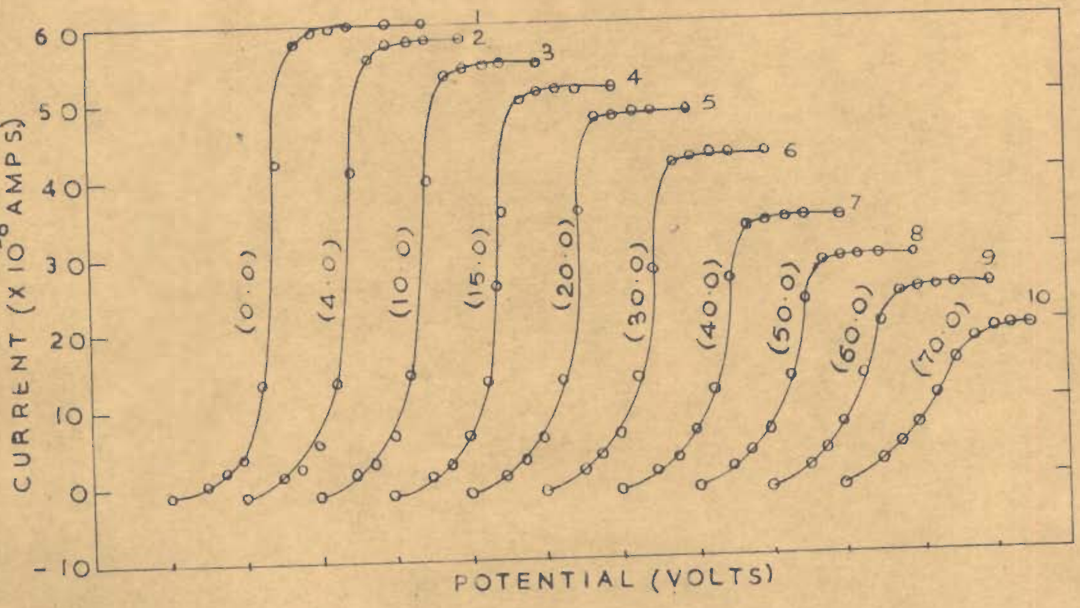


FIG. 9 ALIZARIN REDS CONC=(10·0 X 10^{-4}M) AT PH 3 09

VALUE IN PARENTHES REPRESENT THE AMOUNT OF CPB = (X 10^{-4}M)

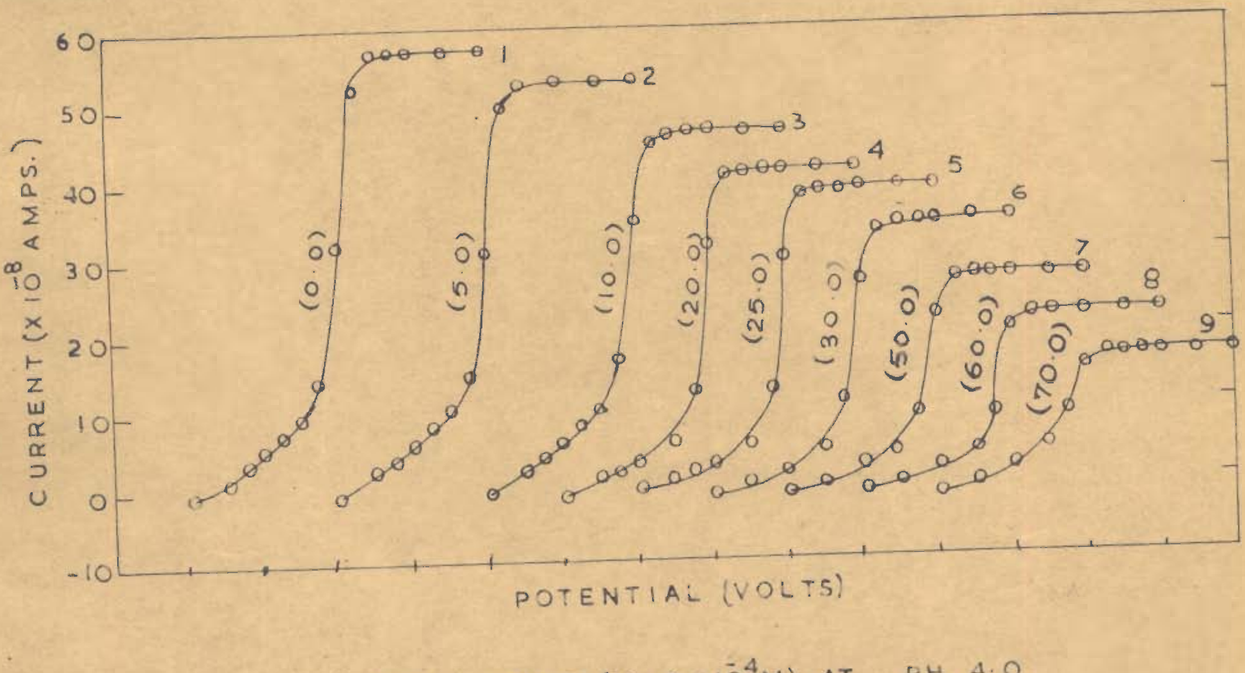
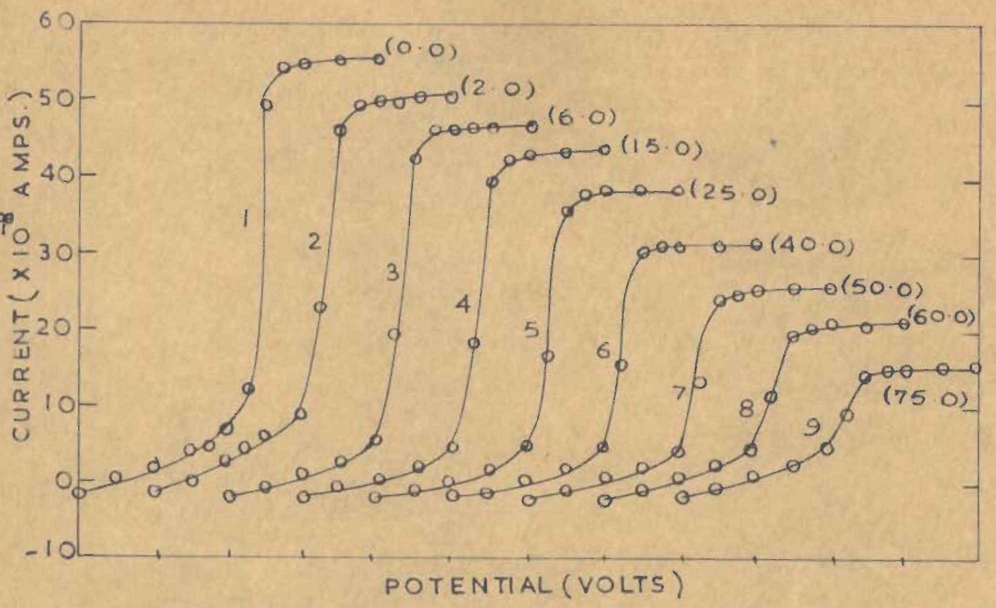


FIG. 10 ALIZARIN REDS CONC=(10·0 X 10^{-4}M) AT PH 4·0

1 DIV. 0·2 VOLT

EACH CURVE STARTS AT - 0·0 VOLT



EACH CURVE STARTS AT - 0.0 VOLT

FIG. 11 ALIZARIN RED CONC.= (10.0 X 10^{-4} M) AT PH 5.0

VALUE IN PARENTHES REPRESENT THE AMOUNT OF CPB = (X10^{-4}M)

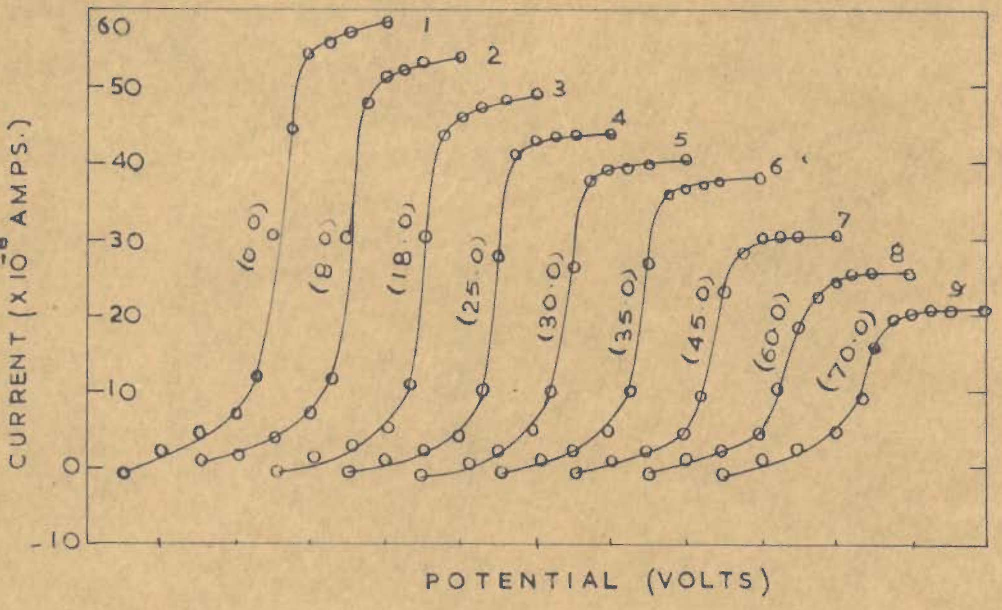
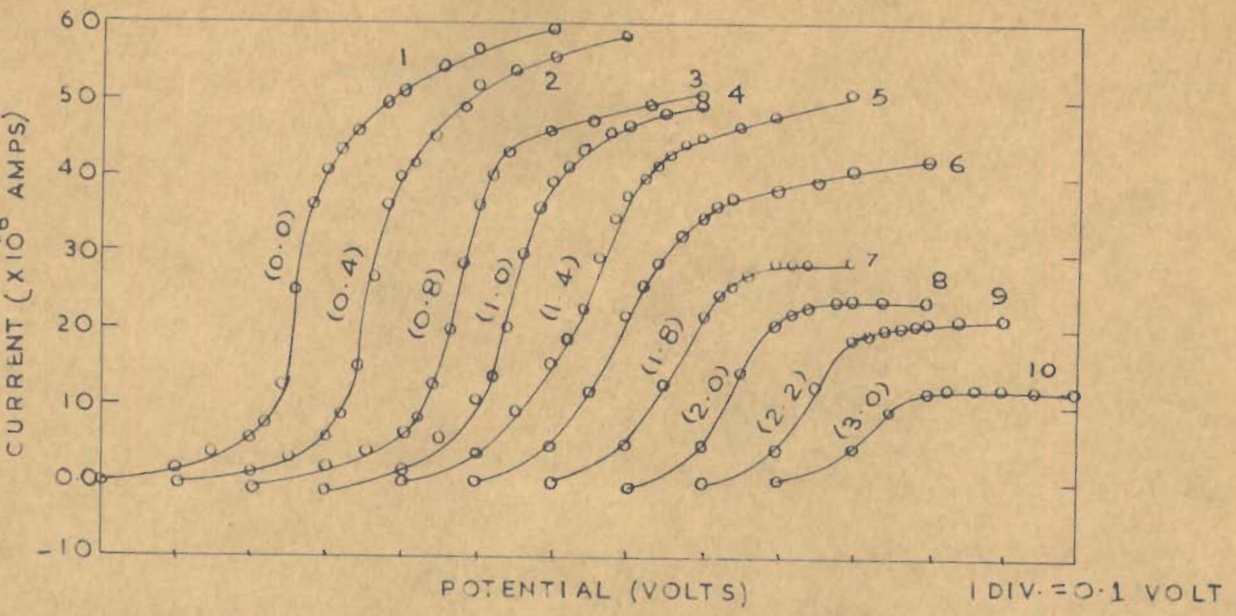


FIG. 12 ALIZARIN RED S CONC. = (10.0 X10^{-4}M) AT PH 7.00

1 DIV. = 0.2 VOLT   EACH CURVE STARTS AT - 0.1 VOLT



Each Curve starts at -0.0 volt

FIG. 13 METHYLENE BLUE CONC = ($2{\cdot}0 \times 10^{-3}$ M) AT PH 6·6

VALUE IN PARENTHES REPRESENTS THE AMOUNT

MANOXL OT = ($\times 10^{-3}$ M)

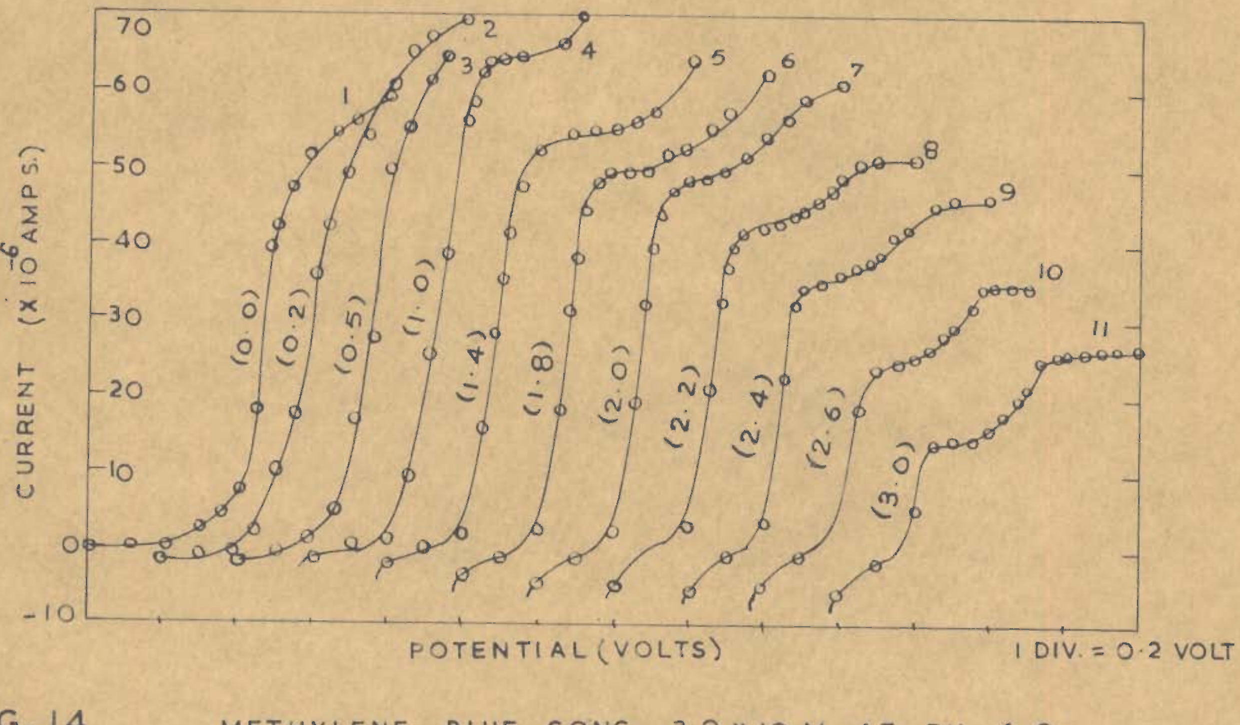


FIG. 14 METHYLENE BLUE CONC. 3·0 X 10 M AT PH 6·0

VALUE IN PARENTHES REPRESENTS THE AMOUNT OF DS ($\times 10^{-3}$ M)

EACH CURVE STARTS AT + 0·2 VOLT

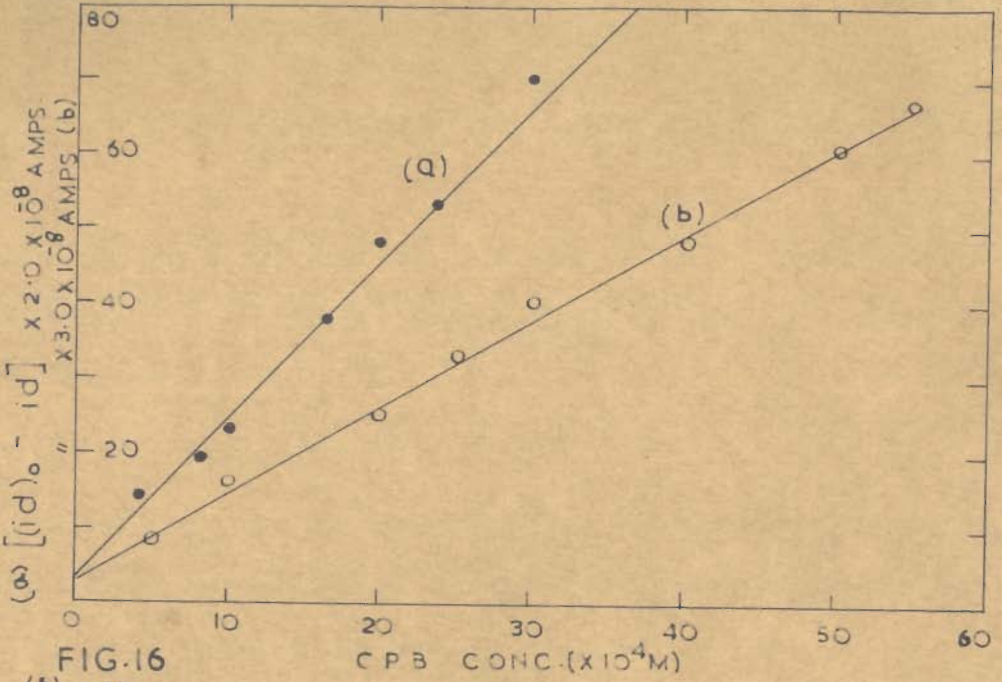


FIG.16

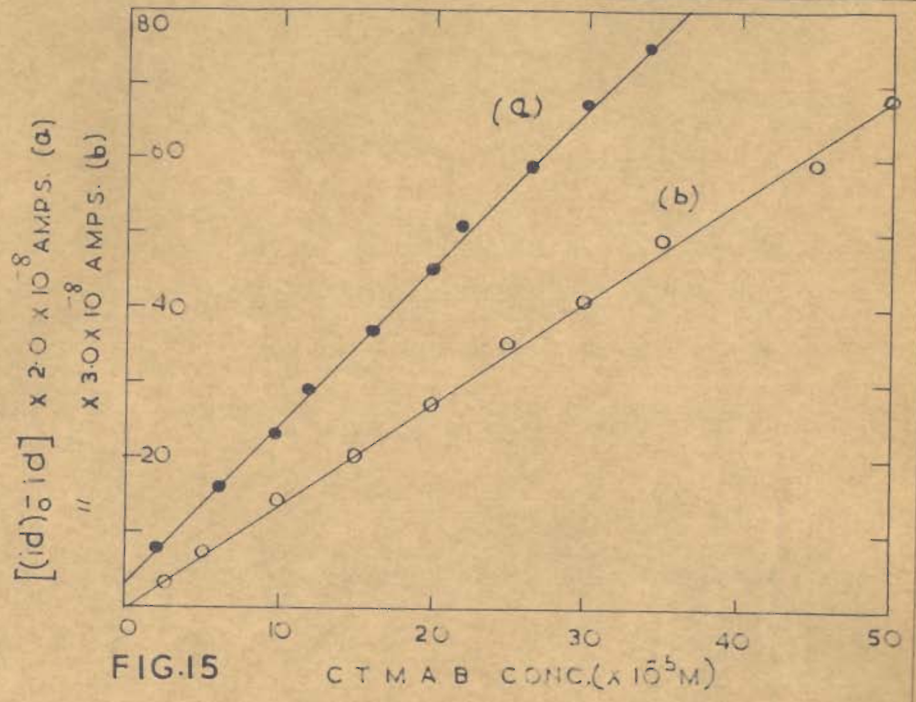


FIG.15

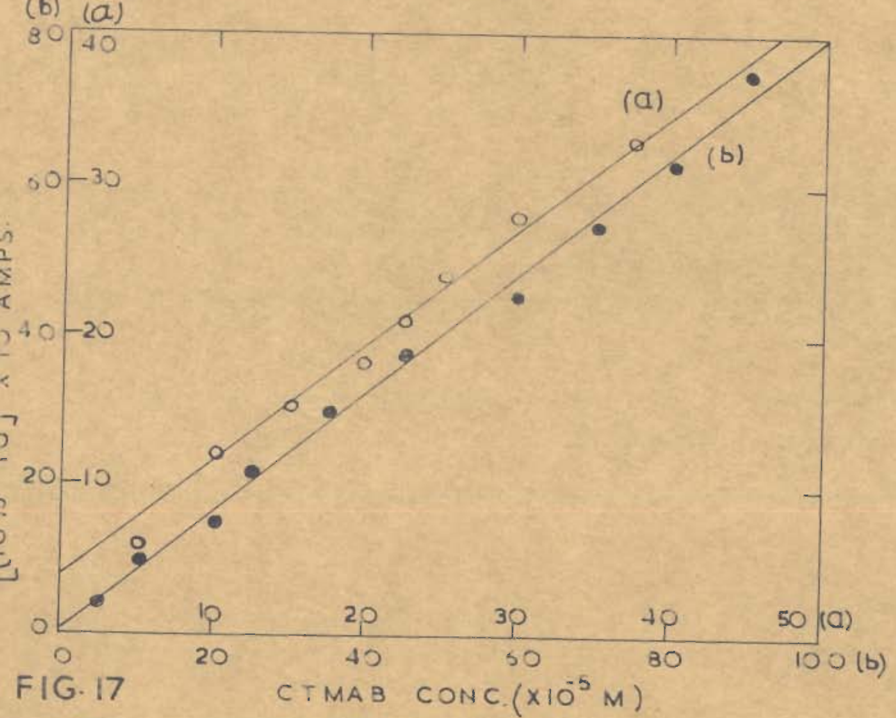


FIG. 17

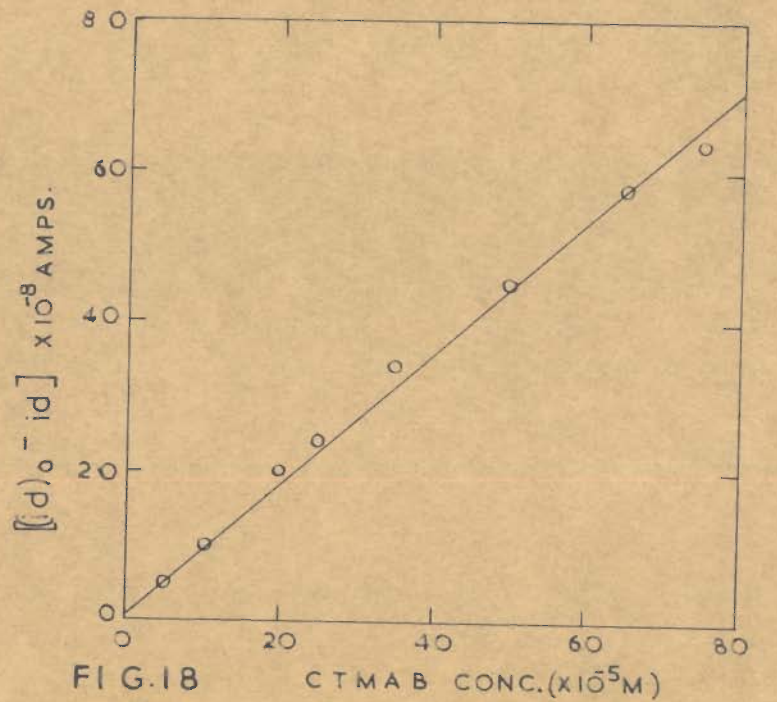


FIG.18

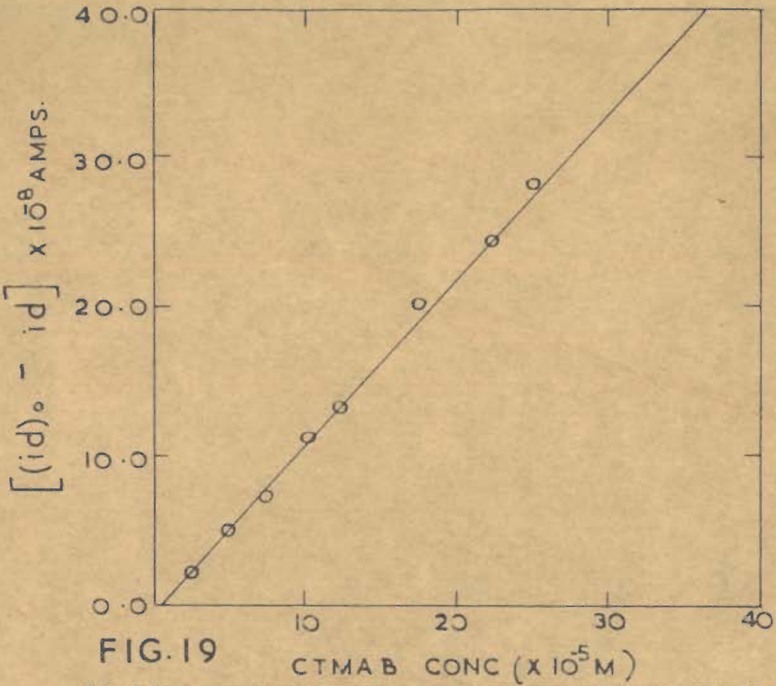


FIG.19

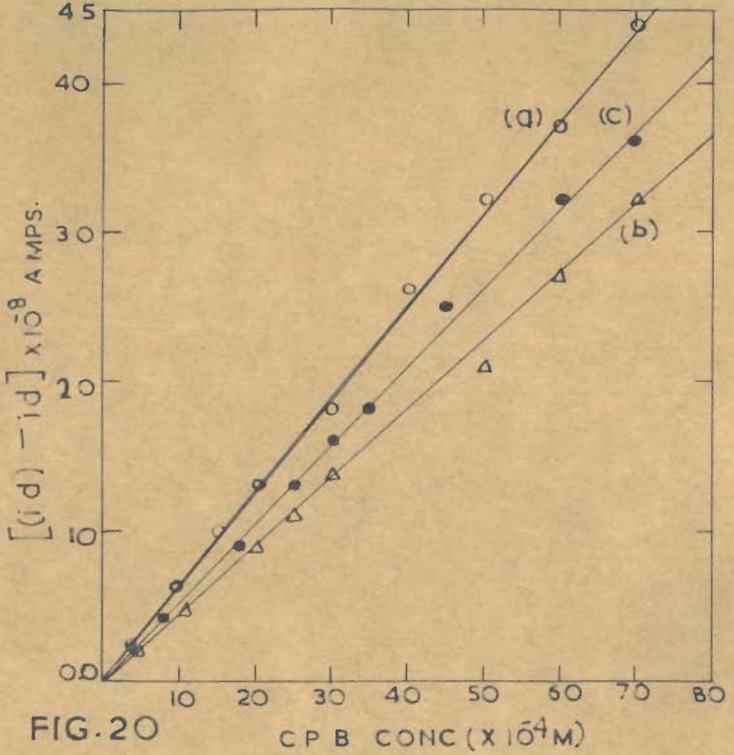


FIG.20

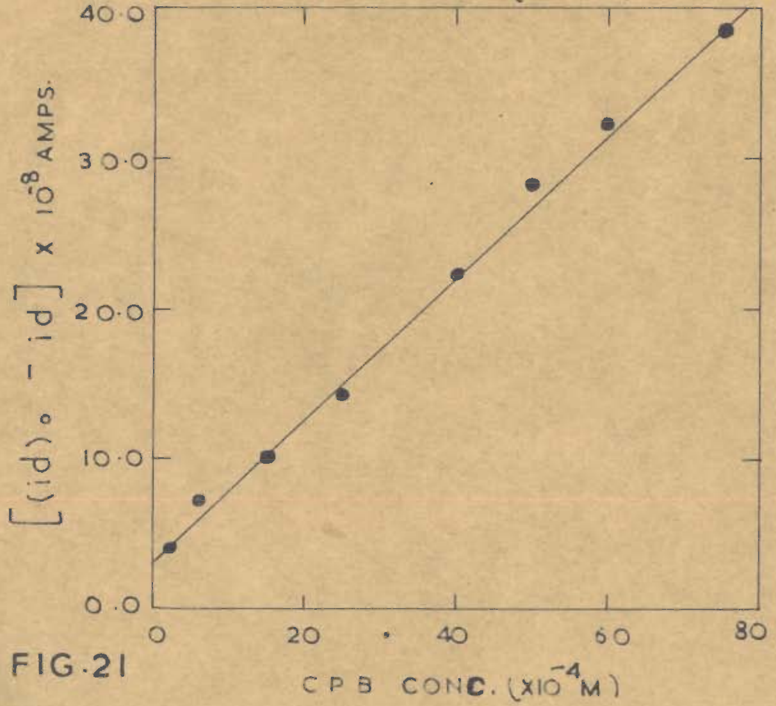


FIG.21

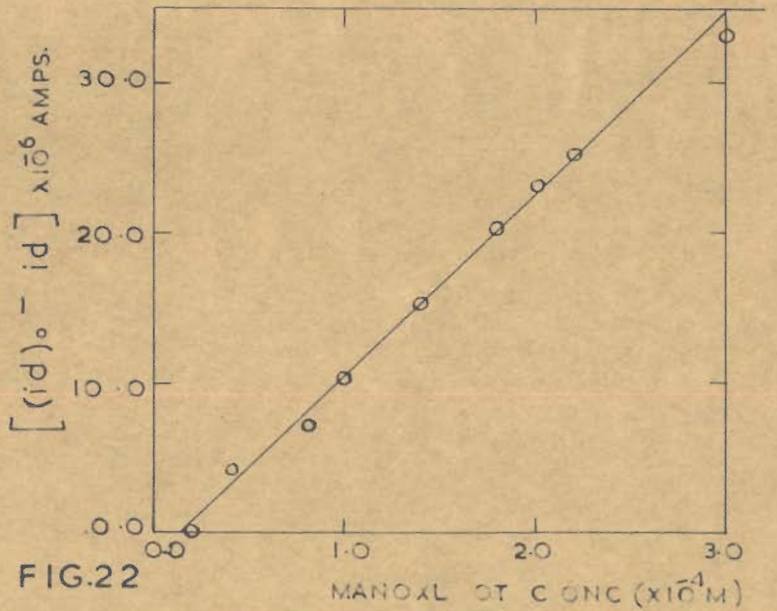


FIG.22

RESULTS AND DISCUSSION

The polarographic reduction of dyes, viz., congo red, alizarin Red S provided the following information:

(i) Congo red gave a reversible polarographic wave with a half wave potential ($E_{1/2}$) = - 0.50 volt in glycine buffer of pH 6.00. The reduction of the dye could not be studied at low pH values because of change in colour (blue) in the acidic medium due to the attainment of the quionid structure (Fig.1, Curve 1).

(ii) The reduction of alizarin Red S was made in various buffers at different pHs. The wave was found to be reversible (Figs.8-12, Curve 1). The half wave potentials at different pH were as follows:

Table 1.

	Acetate buffer			Robinson-Briton buffer
pH	3.09	4.00	5.00	7.00
$E_{1/2}$ (volts)	-0.28	-0.40	-0.48	-0.50

(iii) A well defined reversible polarographic wave was obtained in the case of methylene blue ($E_{1/2}$ = -0.26 volt) in the glycine buffer at pH 6.00. No anodic step was realized in this buffer (Figs.13,14, Curve 1).

The reversibility of the polarographic waves was tested by Tomme's method, i.e., $E_{3/4} - E_{1/4} = 0.056/n$ where n is the number of electrons transfered in the reaction. Congo red was found to be reduced by four electron transfer reaction while alizarin Red S and methylene blue by two electron transfer reaction.

Polarographic measurements of congo red and alizarin Red S with CTMAB and CPB, and of methylene blue with DS and Manoxl OT were carried out. The polarograms are shown in Figs. 1-14.

CATIONIC SURFACTANTS-ACIDIC DYES.

Polarograms of congo red (2.0, and 3.0 x 10^{-4}M) in the presence of varying concentrations of CTMAB or CPB are depicted in Figs. 1-4. It is seen from the curves that there is a gradual decrease in the limiting current by the addition of increasing concentration of surfactants due to the removal of a portion of the dye in the form of the precipitate.

Similar results were obtained with alizarin Red S in presence of varying amounts of CTMAB and CPB at different pHs (3.09, 4.00, 5.00 and 7.00). The results are depicted in Figs. 5-12.

On plotting the decrease in wave heights ($(i_d)_o - i_d$ against the surfactant concentration, a linear relationship was obtained (Figs. 15-21). A slight deviation from linearity was observed at low concentrations of the surfactant. It appears that the flocculation zone was not reached at low concentration of the surfactant.

The concentration of the dye used initially was found to be dependent upon the concentration range of the surfactant which it was desired to cover. Above the highest concentration of the surfactants studied,the complete precipitation of the dye-surfactant complex took place and no dye was found to be unreacted. When stoichiometric amounts or excess of the dye was present, a fine precipitate settled out slowly. Excess of the surfactant reduced the flocculation so that a stable suspension which is non-reducible at d.m.e.,was formed.

The results on the binding of congo red and alizarin Red S with CTMAB and CPB are summarized in the following tables;

Cetyl trimethyl ammonium bromide (CTMAB)-congo red.

Table 2.

Calculation of binding.

Dye concentration = 2.0 x 10^{-4}M, $(i_d)_o$=90.0 x 2.0x10^{-8}amp.

Conc.of CTMAB (x10^{-4}M)	(x2.0x10^{-8}amp.) i_d	 $(i_d)_o - i_d$	$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M) Free dye conc.	 Bound dye conc.	$\frac{\text{CTMAB conc.}}{\text{Bound dye conc.}}$
0.20	82.0	8.0	0.92	1.84	0.16	1.25
0.60	74.0	16.0	0.82	1.64	0.36	1.70
1.00	77.0	23.0	0.74	1.48	0.52	1.92
1.20	71.0	29.0	0.68	1.36	0.64	1.90
1.60	53.0	37.0	0.59	1.18	0.82	1.95
2.00	45.0	45.0	0.50	1.00	1.00	2.00
2.20	39.0	51.0	0.43	0.86	1.14	1.93
2.60	31.0	59.0	0.34	0.68	1.32	2.00
3.00	23.0	57.0	0.25	0.50	1.50	2.00
3.40	15.0	75.0	0.17	0.34	1.66	2.00

Fig.15 a.

Table 3.

Calculation of binding.

Dye concentration= 3.0 x 10^{-4}M, $(i_d)_o$= 78.0 x 3.0x10^{-8} amp.

Conc.of CTMAB (x10^{-4}M)	(x3.0x10^{-8}amp.) i_d	 $(i_d)_o - i_d$	$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M) Free dye conc.	 Bound dye conc.	$\frac{\text{CTMAB conc.}}{\text{Bound dye conc.}}$
0.25	75.0	3.0	0.96	2.88	0.12	2.08
0.50	71.0	7.0	0.91	2.73	0.27	1.85
1.00	64.0	14.0	0.82	2.46	0.54	1.85
1.50	58.0	20.0	0.74	2.00	0.78	1.92
2.00	51.0	27.0	0.66	1.98	1.02	1.96
2.50	42.0	36.0	0.55	1.65	1.35	1.85
3.00	37.0	41.0	0.47	1.41	1.59	1.89
3.50	29.0	49.0	0.38	1.14	1.86	1.95
4.50	19.0	59.0	0.25	0.75	2.25	2.00
5.00	10.0	68.0	0.14	0.42	2.58	1.96

Fig.15 b.

Cetyl pyridinium bromide (CPB) - congo red.

Table 4.

Calculation of binding.

Dye concentration = 2.0 x 10^{-4}M, $(i_d)_o$ = 93.0 x 2.0 x10^{-8}amp

Conc.of CPB ($\times 10^{-4}$M)	($\times 2.0\times 10^{-8}$amp.)		$\frac{i_d}{(i_d)_o}$	($\times 10^{-4}$M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dye conc.	
0.40	79.0	14.0	0.85	1.70	0.30	1.30
0.80	74.0	19.0	0.80	1.60	0.40	2.00
1.00	70.0	23.0	0.75	1.50	0.50	2.00
1.60	56.0	37.0	0.60	1.20	0.80	2.00
2.00	45.0	48.0	0.48	0.96	1.04	1.95
2.40	40.0	53.0	0.43	0.86	1.14	2.10
3.00	23.0	70.0	0.25	0.50	1.50	2.00
3.60	14.0	79.0	0.15	0.30	1.70	2.10

Fig.16 a.

Table 5.

Calculation of binding.

Dye concentration= 3.0 x 10^{-4}M, $(i_d)_o$=78.0 x 3.0 x10^{-8}amp.

Conc.of CPB ($\times 10^{-4}$M)	($\times 3.0\times 10^{-8}$amp.)		$\frac{i_d}{(i_d)_o}$	($\times 10^{-4}$M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dye conc.	
0.50	70.0	8.0	0.90	2.70	0.30	1.68
1.00	62.0	16.0	0.80	2.40	0.60	1.68
2.00	53.0	25.0	0.68	2.04	0.96	2.08
2.50	46.0	32.0	0.59	1.77	1.23	2.03
3.00	37.0	41.0	0.48	1.44	1.56	1.60
4.00	30.0	48.0	0.40	1.20	1.80	1.70
4.50	20.0	58.0	0.27	0.81	2.19	1.83
5.00	15.0	63.0	0.20	0.60	2.40	1.90
5.50	8.0	70.0	0.11	0.33	2.67	2.06

Fig.16 b.

Cetyl trimethyl ammonium bromide (CTMAB)-alizarin Red S.

Table 6.

Calculation of binding at pH 3.09

Dye concentration = 10.0 x 10^{-4}M $(i_d)_o$=53.0 x10^{-8}amp.

Conc.of CTMAB (x10^{-5}M)	(x 10^{-8}amp.) i_d	$(i_d)_o-i_d$	$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M) Free dye conc.	Bound dye conc.	CTMAB conc / Bound dye conc.
5.0	47.0	6.0	0.90	9.0	1.0	0.50
10.0	41.0	12.0	0.78	7.8	2.2	0.45
15.0	38.0	15.0	0.72	7.2	2.8	0.53
20.0	35.0	18.0	0.66	6.6	3.4	0.60
22.5	32.0	21.0	0.60	6.0	4.0	0.55
25.0	29.0	24.0	0.55	5.5	4.5	0.55
30.0	25.0	28.0	0.47	4.7	5.3	0.57
37.5	20.0	33.0	0.34	3.4	6.6	0.57
50.0	10.0	43.0	0.19	1.9	8.1	0.62

Fig.17 a.

Table 7.

Calculation of binding at pH 4.00.

Dye concentration = 15.0 x 10^{-4}M $(i_d)_o$ =70.0x10^{-8} amp.

Conc.of CTMAB (x10^{-5}M)	(x 10^{-8} amp.) i_d	$(i_d)_o-i_d$	$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M) Free dye conc.	Bound dye conc.	CTMAB conc / Bound dye conc.
5.0	65.0	5.0	0.93	13.95	1.05	0.50
10.0	60.0	10.0	0.86	12.90	2.10	0.50
20.0	50.0	20.0	0.71	10.65	4.35	0.46
25.0	46.0	24.0	0.66	9.90	5.10	0.50
37.5	36.0	34.0	0.50	7.50	7.50	0.50
50.0	25.0	45.0	0.36	5.40	9.60	0.52
62.5	13.0	57.0	0.19	2.85	12.15	0.50
75.0	8.0	63.0	0.11	1.65	13.35	0.56

Fig.18

Table 8.

Calculation of binding at pH 5.00.

Dye concentration = 20.0 x 10^{-4}M $(i_d)_o$ = 90.0x10^{-8} amp.

Conc.of CTMAB ($\times10^{-5}$M)	(x 10^{-8} amp.)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M)		$\frac{\text{CTMAB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dye conc.	
5.0	86.0	4.0	0.95	19.0	1.0	0.50
10.0	80.0	10.0	0.89	17.8	2.2	0.46
20.0	75.0	15.0	0.83	16.6	3.4	0.60
25.0	68.0	22.0	0.76	15.2	4.8	0.52
35.0	60.0	30.0	0.67	13.4	6.6	0.53
45.0	52.0	38.0	0.58	11.6	8.4	0.54
60.0	45.0	45.0	0.52	10.4	9.6	0.62
70.0	35.0	55.0	0.45	9.0	11.0	0.63
80.0	28.0	62.0	0.31	6.2	13.8	0.57
90.0	15.0	75.0	0.17	3.4	16.6	0.54

Fig.17 b.

Table 9.

Calculation of bonding at pH 7.00

Dye concentration = 10.0 x 10^{-4}M $(i_d)_o$ = 53.0 x10^{-8}amp.

Conc.of CTMAB ($\times10^{-5}$M)	(x 10^{-8} amp.)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M)		$\frac{\text{CTMAB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dye conc.	
2.50	51.0	2.0	0.96	9.6	0.4	0.60
5.00	48.0	5.0	0.90	9.0	1.0	0.50
7.50	46.0	7.0	0.87	8.7	1.3	0.58
10.00	42.0	11.0	0.80	8.0	2.0	0.50
12.50	40.0	13.0	0.75	7.5	2.5	0.50
17.50	33.0	20.0	0.62	6.2	3.8	0.46
22.50	29.0	24.0	0.55	5.5	4.5	0.50
25.00	25.0	28.0	0.47	4.7	5.3	0.47
37.50	12.0	41.0	0.23	2.3	7.7	0.49

Fig.19

Cetyl pyridinium bromide (CPB) - alizarin Red S.

Table 10

Calculation of binding at pH 3.09.

Dye concentration = 10.0 x 10^{-4}M $(i_d)_o$=57.0x10^{-8} amp.

Conc.of CPB (x10^{-4}M)	(x 10^{-8} amp.)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o-i_d$		Free dye conc.	Bound dye conc.	
4.0	55.0	2.0	0.96	9.6	0.4	10.0
10.0	51.0	6.0	0.90	9.0	1.0	10.0
15.0	47.0	10.0	0.84	8.4	1.6	8.8
20.0	44.0	13.0	0.77	7.7	2.3	8.7
30.0	39.0	18.0	0.70	7.0	3.0	10.0
40.0	31.0	26.0	0.54	5.4	4.6	8.7
50.0	25.0	32.0	0.44	4.4	5.6	8.9
60.0	20.0	37.0	0.35	3.5	6.5	9.2
70.0	13.0	44.0	0.23	2.3	7.7	9.1

Fig. 20. a

Table 11.

Calculation of binding at pH 4.00.

Dye concentration = 10.0 x 10^{-4}M $(i_d)_o$ =44.0x10^{-8} amp.

Conc.of CPB (x10^{-4}M)	(x 10^{-8}amp)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4}M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o-i_d$		Free dye conc.	Bound dye conc.	
5.0	42.0	2.0	0.95	9.5	0.5	10.0
10.0	39.0	5.0	0.89	8.9	1.1	9.1
20.0	35.0	9.0	0.80	8.0	2.0	10.0
25.0	33.0	11.0	0.75	7.5	2.5	10.0
30.0	30.0	14.0	0.68	6.8	3.2	9.4
50.0	23.0	21.0	0.52	5.2	4.8	9.6
60.0	17.0	27.0	0.40	4.0	6.0	10.0
70.0	12.0	32.0	0.27	2.7	7.3	9.6

Fig.20 b.

Table 12.

Calculation of binding at pH 5.00.

Dye concentration = 10.0 x 10^{-4}M $(i_d)_o$ = 48.0x10^{-8} amp.

Conc.of CPB. (x10^{-4}M)	(x 10^{-8}amp.)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4} M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dye conc.	
2.0	44.0	4.0	0.92	9.2	0.8	4.0
6.0	41.0	7.0	0.85	8.5	1.5	4.0
15.0	38.0	10.0	0.80	8.0	2.0	6.5
25.0	34.0	14.0	0.75	7.5	2.5	10.0
40.0	26.0	22.0	0.54	5.4	4.6	8.7
50.0	20.0	28.0	0.42	4.2	5.8	8.5
60.0	16.0	32.0	0.33	3.3	6.7	8.9
75.0	10.0	38.0	0.21	2.1	7.9	9.5

Fig.21.

Table 13.

Calculation of binding at pH 7.00

Dye concentration= 10.0 x 10^{-4}M $(i_d)_o$= 50.0x10^{-8}amp.

Conc.of CPB (x10^{-4}M)	(x 10^{-8} amp.)		$\frac{i_d}{(i_d)_o}$	(x 10^{-4} M)		$\frac{\text{CPB conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o - i_d$		Free dye conc.	Bound dys conc.	
8.0	46.0	4.0	0.92	9.2	0.8	10.0
18.0	41.0	9.0	0.82	8.2	1.8	10.0
25.0	37.0	13.0	0.74	7.4	2.6	9.6
30.0	34.0	16.0	0.68	6.8	3.2	9.4
35.0	32.0	18.0	0.64	6.4	3.6	9.7
45.0	25.0	25.0	0.50	5.0	5.0	9.0
60.0	18.0	32.0	0.36	3.6	6.4	9.4
70.0	14.0	36.0	0.28	2.8	7.2	9.8

Fig.20. c.

The surfactant-bound dye ratio was found to be independent of the concentration of the surfactants and a binding ratio of 1:2 dye-surfactant complex was obtained in almost all dye-surfactant mixtures. The data on the binding of congo red with CTMAB and CPB confirm the results of the spectrophotometric studies (vide Chapter III).

With alizarin Red S, the binding ratio is entirely different from that obtained in the case of congo red. Here instead of 1:2 dye-surfactant ratio, a 1:10 binding ratio is obtained in the case of CPB while a 2:1 ratio is realised for CTMAB. The results further reveal that alizarin Red S has got a greater affinity for the CTMAB than CPB.

EFFECT OF pH.

Just like the concentration of the surfactant, the pH of the reaction mixture does not influence the combining ratio. This effect could not be measured in the case of congo red since the dye attained a quionoid structure at low pH values thereby making the reduction non-feasible.

ANIONIC SURFACTANTS-BASIC DYE.

Polarograms of methylene blue in presence of DS and Manoxol OT in glycine buffer of pH 6.00 were recorded and are depicted in Figs.(13,14). The following conclusions have been drawn:

1. From the Figs.(13,14),it is seen that like cationic surfactant,there was a gradual decrease in limiting current of the dye by increasing concentrations of the surfactant due to the removal of the dye from the reaction mixture in the form of an insoluble dye-surfactant complex.

On plotting the decrease in wave height vs. concentration of Manoxl OT, a linear behaviour was observed (Fig.22).

The binding of the dye with Manoxl OT was determined and the results are summarized in the following table:

Table 14.

Results on the binding of methylene blue with Manoxl OT.

Dye concentration = 2.00 x 10^{-5}M

($i_d)_o$ = 46.0 x 10^{-6} amp.

Conc.of Manoxl OT (x10^{-4}M)	(x10^{-6}amp.)		$\frac{i_d}{(i_d)_o}$	(x10^{-5}M)		Manoxl OT $\frac{\text{Conc.}}{\text{Bound dye conc.}}$
	i_d	$(i_d)_o-i_d$		Free dye	Bound dye	
0.4	42.0	4.0	0.91	1.82	0.18	0.22
0.8	39.0	7.0	0.85	1.70	0.30	0.26
1.0	36.0	10.0	0.78	1.56	0.44	0.25
1.40	31.0	15.0	0.67	1.34	0.66	0.21
1.80	26.0	20.0	0.57	1.14	0.86	0.21
2.00	23.0	23.0	0.50	1.00	1.00	0.20
2.20	21.0	25.0	0.46	0.92	1.08	0.20
3.00	13.0	33.0	0.28	0.56	1.44	0.17

Fig. 22.

It is clear from the above table that the combining ratio is same in all the cases. 0.2 mole of Manoxl OT is bound with one mole of the dye.

An altogether different behaviour was observed in the reduction of methylene blue at higher concentrations of DS when a second wave of constant height appeared after the normal reduction wave (Fig.14). The appearence of the second wave may be explained on the assumption that the dye-surfactant complex of methylene blue and dodecane sulphonic acid gets adsorbed on d.m.e. in excess of the latter resulting in the emergence of the second wave of constant height.

2. The limiting current of the reaction mixture was found to increase to a very small extent than the original current (without surfactant) by the presence of small concentration of surfactant (Fig.14,Curves 2-4). This may be attributed to the fact that the insoluble compound is soluble in the excess of the dye and thus the limiting current of the solution is increased.

3. The $E_{1/2}$ of the reaction mixture was found to be shifted towards the more positive potentials in presence of surfactants. It is more marked in the case of dodecane sulphonic acid than Manoxl OT. For example,the shift is from -0.2 volt to -0.04 volt in the case of DS while it is from - 0.26 volt to -0.14 volt with Manoxl OT. The presence

of surfactants made the polarographic waves irreversible.

The shift in the half wave potential towards the positive side may be explained on the basis that the dissociation of DS is favourable at pH 6.00 releasing a large number of H^+ ions which lower the pH of the solution and therefore, the $E_{1/2}$ of the unreacted dye is lowered. The little shift in $E_{1/2}$ by the addition of Manoxol OT (pH 4.5) is because of small lowering in the pH of the medium as it is an ester (dioctyl sodium sulpho succinate) releasing no hydrogen ions in the solution.

4. A small anodic step was observed in the reduction of methylene blue in the presence of higher concentrations of DS while it was not found with Manoxol OT.

It is clear from the above observations that the anodic step is obtained in the lower pH region. Our study is supported by the work of Muller (13) who reported the disappearence of the anodic step in the phosphate buffer at pH 6.8 while ho observed it in the acetate buffer of low pH value.

Although, many analytical methods are available for the determination of ionic surfactants, the polarographic method has the advantage over the others in the sense that it can be used at higher concentrations above the critical micelle concentrations and for small volumes e.g. less than 1.0 ml. The polarographic measurements can be made by the direct addition of varying quantities of the surfactant solution to the polarographic cell. Besides the above advantages there are few difficulties in the above methods: (i) the corrections in the current due to the dilution of the solution are to be made, (ii) the settling of the insoluble dye-surfactant compound requires a large time before measurements can be made, (iii) the insoluble dye-surfactant compound formed by the interaction of methylene blue and anionic surfactants sticks on the wall of the container and also on the tip of polarographic capillary and hence this method cannot be used for determining the concentration of anionic surfactants with the help of methylene blue, (iv) the method cannot be successfully employed to estimate small amounts ($< 1.0 \times 10^{-3}$ M) of the alkyl sulphonated type surfactant

--OO--

REFERENCES

1. Tschoegl,N.W., Rev.Pure.Appl.Chem. 4 ,No.3,171-206 (1954).

2. Glazer,J. and Smith,T.D., Nature,169,497 (1952).

3. Hillenbrand,E.F.Jr.Sutherland,W.W. and Hogsett,J.N.,Anal. Chem. 23 ,626-9 (1951).

4. Edwards,G.R.,Ewers,W.E. and Mansfield,W.W.,Analyst,77, 205-7 (1952).

5. Few,A.V. and Ottewill,R.H., J.Colloid Sci.11 ,34-8 (1956).

6. Harris,T.H., J.Assoc.Official Agr.Chem. 29,310-11 (1946).

7. Benkenkamp,J.,Rieman,W. and Lindenbaum,S., Anal.Chem., 26 ,505-12 (1954).

8. Heyrovsky,J.,Polarography,Springer-Verlag, Berlin 1941,p. 408ff.

9. Schwartz,K.E.,Schroder,H.J. and Stackelberg,M.V., Z.Electrochem. 48 ,6 (1942).

10. Stackelbeg,M.V. and Schutz,H.,Kolloid-Z 105 ,20 (1948).

11. Fiala,S. and Jancik,Collection Czechoslov. Chem.Communs., 13 ,30-6 (1948).

12. Gordon,B.E. and Urner,R.S., Anal.Chem. 25 ,897 (1953).

13. Muller,O.H., J.Biol.Chem. 145 ,425 (1942) and Trans. Electrochem.Soc. 87 ,441 (1945).

CHAPTER V.

Polarographic determination of aggregation number of dyes and effect of additives on the aggregation.

INTRODUCTION

Dyes, like other surfactants, are also known to undergo aggregation in aqueous solutions (1-4), various mechanisms, based on vander Waal's forces (5,6), intermolecular hydrogen bonding (7), bonding by sandwitched water molecules (6-8) etc. have been put forward from time to time to explain the aggregation of dye molecules. However, a more convenient and straight forward approach to the problem can be made if their aggregation is discussed in the light of water structure.

The role of water structure in the aggregation of surface active substances (9-11) and dyes (12) has been discussed by many authors. Thermodynamical data (13) has shown that the mutual ordering of water molecules around the solute is enhanced with non-polar solutes. This results in the formation of iceberg structures. Urea, well known for its denaturation capacity, and ability to undergo hydrogen bonding with water (and also its small effect (14) on the polarity of water) brings about the destruction of 'iceberg' structures. Physico-chemical investigations on surfactants in presence of urea can thus be employed to determine the water structure contribution to micelle formation and hydrophobic bonding (14-16). A similar approach can be made in the case of dyes provided a suitable method, sensitive enough to register variations in the properties of dye as a result of the breaking of the water molecules,is found.

The polarographic method very recently proposed by Hilson and Mckay (17) for studying the aggregation of dyes was extented to determine the effect of urea, formamide and methyl alcohol on the aggregation concentration.

EXPERIMENTAL

REAGENTS.

All the chemicals,except the dyes,were of Analar grade. Congo red ($C_{32}H_{22}N_6Na_2O_6.6H_2O$) and crystal violet ($C_{25}H_{30}ClN_3.2H_2O$) were the BDH products and purified by recrystallization. The solutions were prepared in double distilled water (all glass).

Urea (A.R.) and formamide (Riedel) were used while methyl alcohol was the BDH product which was further purified by redistillation. Urea and formamide were used in moles/l., while methyl alcohol by precentage.

Glycine and citrate buffer used in the reduction of dyes were of the following compositions:

glycine buffer:	Potassium chloride 0.025M; glycine 0.0025M,pH 6.00.
citrate buffer:	Potassium chloride 0.01M; trisodium citrate 0.005M; citric acid 0.005M, pH 4.40.

APPARATUS.

The polarographic measurements were carried out using Heyrovsky polarograph (No. Lp 55A) operated manually in conjuction with a scalamp Pye galvanometer. A normal polarographic capillary (Gallenkamp) having the drop time 4.30 sec. was used and the mercury reserviour was kept at a constant height (60 cm) throughout the measurements. Saturated calomel electrode was used as a reference electrode. All the measurements were made at a constant temperature 25 ± 0.1°C using a thermostatic water bath.

PROCEDURE.

Working solutions were prepared by mixing different amounts of the concentrated solution of the dye in water with a fixed amount of the appropriate buffer (4.0 ml.) and then, making up the total volume (10.0 ml.) by more water. The solutions were allowed to keep overnight after adding the substance the effect of which was to be studied. Polarograms were taken by passing purified nitrogen through the solution for about 10 minutes. One set of observations for each dye was taken without the presence of the additive. The additives, urea (1M, 3M, 6M) ; formamide (0.6M, 1.2M, 2.4M), and methyl alcohol (10%, 20% v/v) were used at three different concentrations.

The under lying principle of this method is described as follows:

For a non-aggregating species, such as cadmium ions, the diffusion current i_d, is proportional to the molarity of the species in solution c, i.e., the plot of $\log_{10} i_d$ against $\log_{10} c$ is linear and of unit gradient. Aggregating species such as dye ions, would deviate from this ideal behaviour.

In actual experiments the difference in the logarithms of the diffusion currents of equimolar solutions of dye ions and cadmium ions $-\Delta \log_{10} i_d$, is plotted as a function of $\log_{10} c$. These plots are linear and horizontal for a non-aggregating species while aggregation causes the upward deviation from this line. Since the limiting current is proportional to the square-root of the diffusion coefficient D, ($i_d \propto D^{1/2}$), the plot of $-\Delta \log_{10} i_d$ against $\log_{10} c$ is also, the plot of $-\Delta \log_{10} D$ (the difference between the logarithms of the diffusion coefficients of cadmium ions and the dye ions) against $\log_{10} c$.

Furthermore, D is related to the molecular weight since the plots of $\log_{10} D$ against $\log_{10}$ (molecular weight also gives a linear relationship (vide ref.17). Thus the values of $-\Delta \log_{10} i_d$ can be converted both in terms of $-\Delta \log_{10} D$ and $\log_{10}$ (molecular weight).

The above method may be exemplified by considering the polarograms of congo red.

The dye was reduced at the d.m.e. by four electron transfer reaction in glycine buffer at pH 6.00 (Fig.3). To make the use of calibration curve of Cd^{++}(which is reduced by two electron transfer reaction), the limiting current of Cd^{++} ions obtained from their polarograms (Fig.1) was multiplied by two. The logarithms of twice the diffusion current of Cd^{++} ions and that of the dye was then plotted against $\log_{10}$ (molarity). The two curves are shown in Fig.20. A linear curve is obtained with Cd^{++} ions while that of the dye shows a deviation from linearity after a certain concentration of the dye (1.0×10^{-4}M).

The difference of logarithms of diffusion currents of Cd^{++} ions and dye as found from the above curves (Table 2) was further plotted against dye concentration, $\log_{10} c$ (Fig. 23). From the plot a horizontal line (parallel to the concentration axis) was obtained up to the concentration 1.0×10^{-4} M. Beyond this concentration, an upward deviation from the horizontal line was observed. It was thus concluded that the dye remained in the molecular state upto the concentration 1.0×10^{-4}M and thereafter got aggregated rapidly.

The aggregation number can be found if the molecular weight of the dye can be related to the i_d or D. Since a linear relationship is found to exist between D and molecular weight, the aggregation number (N) can be found by reading the molecular weight on the second scale of the fig.23, on which the plot of $-\Delta \log_{10} D$ against $\log_{10} c$ are shown. Fig. 23 depicts the plots of $-\Delta \log_{10} i_d$ (or $-\Delta \log_{10} D$) against $\log_{10} c$ along with the scales of aggregation number and $\log_{10}$ (molecular weight) on the right hand side. Assuming that the horizontal portion cuts the $\log_{10}$ (molecular wt.) axis at unit aggregation number, the dye concentration corresponding to different aggregation number can be found from the part of the curve showing upward deviation. In the calculation of aggregation number, it was further assumed that the diffusing species was the dye ion while aggregates contain both dye ions and counter ions.

The data for crystal violet were similarly calculated. The results are summarized in the following tables.

Table 1.

Results on i_d values obtained from the polarograms of $CdCl_2$ at different concentrations in 0.1M KCl for the calibration of congo red and crystal violet.

Conc.of $CdCl_2$ ($\times 10^{-4}$M)	$\log_{10} c$	For the calibration of congo red			Conc.of $CdCl_2$ ($\times 10^{-4}$M)	$\log_{10} c$	For the calibration of crystal violet.	
		i_d µA	$2 \times i_d$ µA	$\log_{10} 2i_d$			i_d µA	$\log_{10} i_d$
2.00	-3.6990	0.80	1.6	0.2041	2.00	-3.6990	1.30	0.1139
5.00	-3.3110	2.10	4.2	0.6232	3.34	-3.4763	2.00	0.3010
10.00	-3.0000	4.75	9.5	0.9777	6.67	-3.1769	3.90	0.5910
15.00	-2.8239	7.25	14.5	1.1614	13.34	-2.8860	7.00	0.8451
20.00	-2.6990	10.00	20.0	1.3010	20.00	-2.6980	10.50	1.0212
25.00	-2.6021	13.00	26.0	1.4150	33.34	-2.4763	16.40	1.2184
30.00	-2.5229	16.50	31.0	1.4913	46.67	-2.3307	22.60	1.3541
40.00	-2.3980	21.50	43.0	1.6335	-	-	-	-
Fig.		1					2	

Table 2.

Results on the i_d values of congo red at different concentrations.

Dye conc. ($\times 10^{-4}$M)	$\log_{10} c$	i_d μA	$\log_{10} i_d$	$-\Delta_{10} \log_{10} i_d$
0.40	-4.3980	0.20	-0.6990	0.10
0.80	-4.0969	0.42	-0.3768	0.11
1.00	-4.0000	0.56	-0.2518	0.10
2.00	-3.6990	1.12	+0.0492	0.14
4.00	-3.3980	1.75	0.2430	0.28
6.00	-3.2219	2.10	0.3222	0.40
8.00	-3.0969	2.80	0.4472	0.41
10.00	-3.0000	3.50	0.5441	0.43
20.00	-2.6990	3.60	0.5563	0.74
40.00	-2.3980	3.60	0.5563	1.08
Fig.		3	20 a.	23 a.

Table 3.

Results on the i_d values of congo red in presence of different concentrations of urea.

Dye Conc. ($\times 10^{-4}$M)	$\log_{10} c$	Urea (1.0 M) i_d µA	Urea (1.0 M) $\log_{10} i_d$ µA	Urea (1.0 M) $-\Delta \log_{10} i_d$ µA	Urea (3.0 M) i_d µA	Urea (3.0 M) $\log_{10} i_d$ µA	Urea (3.0 M) $-\Delta \log_{10} i_d$ µA	Urea (6.0 M) i_d µA	Urea (6.0 M) $\log_{10} i_d$ µA	Urea (6.0 M) $-\Delta \log_{10} i_d$ µA
0.2	-4.6990	0.18	-0.7447	0.08	0.18	-0.7447	0.08	-	-	-
0.4	-4.3980	0.36	-0.4437	0.08	0.34	-0.4685	0.09	0.30	-0.5229	0.10
0.6	-4.2219	0.54	-0.2776	0.06	0.50	-0.3010	0.09	0.40	-0.3979	0.12
0.8	-4.0969	-	-	-	0.62	-0.2076	0.10	0.54	-0.2676	0.11
1.0	-4.0000	0.76	-0.1192	0.11	0.70	-0.1549	0.10	0.64	-0.1939	0.12
2.0	-3.6990	1.52	+0.1818	0.09	-	-	-	1.25	+0.1004	0.09
4.0	-3.3980	2.90	0.4624	0.09	2.12	0.3264	0.11	2.30	0.3617	0.09
6.0	-3.2219	3.70	0.5682	0.15	3.65	0.5623	0.12	3.35	0.5250	0.10
8.0	-3.0969	4.25	0.6284	0.20	4.20	0.6232	0.17	4.20	0.6232	0.10
10.0	-3.0000	3.60	0.5563	0.37	4.90	0.6902	0.24	4.70	0.6721	0.15
40.0	-2.3980	4.00	0.6020	0.89	5.60	0.7482	0.74	5.30	0.7243	0.61
80.0	-2.0969	2.90	0.4624	1.31	3.90	0.5910	1.18	4.80	0.6812	0.92
Fig.		4	20 b.	23 b.	5	20 c.	23 c.	6	20 d.	23 d.

Table 4.

Results on the i_d values of congo red in presence of different concentrations of formamide.

Dye Conc. ($\times 10^{-4}$M)	$\log_{10} c$	Formamide (0.6 M). i_d µA	Formamide (0.6 M). $\log_{10} i_d$	Formamide (0.6 M). $-\Delta\log_{10} i_d$	Formamide (1.2 M). i_d µA	Formamide (1.2 M). $\log_{10} i_d$	Formamide (1.2 M). $-\Delta\log_{10} i_d$	Formamide (2.4 M). i_d µA	Formamide (2.4 M). $\log_{10} i_d$	Formamide (2.4 M). $-\Delta\log_{10} i_d$
0.2	-4.6990	0.18	-0.7447	0.08	0.20	-0.6990	0.09	-	-	-
0.4	-4.3980	-	-	-	0.40	-0.3980	0.09	0.30	-0.5229	0.10
0.6	-4.2219	0.50	-0.3010	0.09	0.56	-0.2518	0.10	-	-	-
0.8	-4.0969	0.64	-0.1938	0.09	-	-	-	0.54	-0.2676	0.10
1.0	-4.0000	0.76	-0.1192	0.11	0.86	-0.0655	0.11	0.78	-0.1675	0.10
2.0	-3.6990	1.50	+0.1761	0.09	1.65	+0.2175	0.10	1.44	+0.1583	0.11
4.0	-3.3980	2.70	0.4316	0.12	3.35	0.5250	0.10	-	-	-
6.0	-3.2219	3.70	0.5682	0.14	4.50	0.6532	0.14	4.20	0.6232	0.09
8.0	-3.0969	4.20	0.6232	0.21	5.50	0.7404	0.16	5.30	0.7243	0.10
10.0	-3.0000	-	-	-	-	-	-	6.80	0.8325	0.09
20.0	-2.6990	4.60	0.6628	0.54	6.50	0.8129	0.46	-	-	-
30.0	-2.5229	-	-	-	-	-	-	7.00	0.8451	0.51
40.0	-2.3980	4.70	0.6721	0.81	5.90	0.7708	0.78	-	-	-
50.0	-2.3010	-	-	-	-	-	-	7.10	0.8513	0.71
60.0	-2.2219	4.20	0.6230	1.03	5.20	0.7160	0.99	7.00	0.8451	0.79
Fig.		7	21 a.	24 a.	8	21 b.	24 b.	9	21 c.	24 c.

Table 5.

Results on the i_d values of congo red in presence of different concentrations of methyl alcohol.

Dye conc. ($\times 10^{-4}$M)	$\log_{10} c$	10% methyl alcohol			20% methyl alcohol		
		i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$	i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$
0.40	-4.3980	0.20	-0.6990	0.10	0.22	-0.6576	0.10
0.80	-4.0969	0.40	-0.3980	0.12	0.46	-0.3372	0.11
1.00	-4.0000	0.52	-0.2840	0.12	0.56	-0.2518	0.13
2.00	-3.6990	1.04	+0.0170	0.17	1.10	+0.0414	0.17
4.00	-3.3980	1.74	0.2405	0.27	1.72	0.2355	0.30
6.00	-3.2219	2.25	0.3522	0.36	2.50	0.3979	0.34
8.00	-3.0969	3.10	0.4914	0.36	2.55	0.4065	0.46
10.00	-3.0000	-	-	-	2.60	0.4149	0.53
20.00	-2.6990	4.30	0.6335	0.66	-	-	-
Fig.		10	22 a.	25	11	22 b.	26

Table 6.

Results on the i_d values of crystal violet at different concentrations.

Dye conc. ($\times 10^{-4}$M)	$\log_{10} c$	i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$
0.20	-4.6990	0.14	-0.8539	0.09
0.30	-4.5229	0.20	-0.6990	0.09
0.40	-4.3980	0.24	-0.6198	0.11
0.60	-4.2219	0.33	-0.4815	0.13
1.00	-4.0000	0.48	-0.3188	0.17
2.00	-3.6990	0.86	-0.0658	0.18
3.00	-3.5229	1.25	+0.0655	0.18
4.00	-3.3980	1.60	0.2041	0.19
6.00	-3.2219	2.35	0.3710	0.19
8.00	-3.0969	3.00	0.4771	0.19
16.00	-2.7959	3.20	0.5051	0.43
Fig.		12	27 a.	30

Table 7.

Results on the i_d values of crystal violet in presence of different concentrations of urea.

Dye conc. ($\times 10^{-4}$ M)	$\log_{10} c$	Urea (1.0 M)			Urea (3.0 M)			Urea (6.0 M)		
		i_d µA	$\log_{10} i_d$	$-\Delta\log_{10} i_d$	i_d µA	$\log_{10} i_d$	$-\Delta\log_{10} i_d$	i_d µA	$\log_{10} i_d$	$-\Delta\log_{10} i_d$
0.40	-4.3980	0.22	-0.6576	0.10	0.18	-0.7447	0.09	0.16	-0.7959	0.09
0.60	-4.2219	0.30	-0.5230	0.11	-	-	-	-	-	-
0.80	-4.0969	0.42	-0.3768	0.09	0.32	-0.4949	0.10	0.26	-0.5950	0.10
1.00	-4.0000	0.48	-0.3188	0.11	0.38	-0.4202	0.11	0.34	-0.4685	0.11
1.40	-3.8539	0.66	-0.1805	0.14	-	-	-	-	-	-
1.60	-3.7959	-	-	-	0.60	-0.2219	0.10	0.52	-0.2840	0.11
1.80	-3.7747	0.74	-0.1308	0.14	-	-	-	-	-	-
2.00	-3.6990	-	-	-	0.78	-0.1079	0.10	0.64	-0.1938	0.11
2.40	-3.6198	0.98	-0.0088	0.17	-	-	-	-	-	-
3.00	-3.5229	-	-	-	1.02	+0.0040	0.13	0.88	-0.0516	0.13
4.00	-3.3980	1.04	+0.0170	0.32	1.26	0.1044	0.15	1.08	+0.0334	0.16
6.00	-3.2219	-	-	-	1.15	0.0607	0.34	1.00	0.0000	0.35
Fig.		13	27 b.	31	14	27 c.	32	15	27 d.	33

Table 8.

Results on the i_d values of crystal violet in presence of different concentrations of formamide.

Dye conc. (x10^{-4}M)	$\log_{10} c$	Formamide (0.6M)			Formamide (1.2M)		
		i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$	i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$
0.40	-4.3980	0.20	-0.6576	0.10	0.32	-0.4949	0.06
0.60	-4.2219	0.30	-0.5229	0.12	-	-	-
0.80	-4.0969	0.38	-0.4222	0.12	0.35	-0.4600	0.10
1.00	-4.0000	0.42	-0.3768	0.17	0.42	-0.3768	0.10
1.60	-3.7959	0.62	-0.2079	0.18	0.76	-0.1192	0.09
2.00	-3.6990	0.80	-0.0862	0.17	0.82	-0.0862	0.09
3.00	-3.5229	1.12	+0.0492	0.18	1.04	+0.0170	0.14
4.00	-3.3980	1.44	0.1584	0.18	1.30	0.1139	0.16
6.00	-3.2219	2.10	0.3222	0.18	1.50	0.1760	0.25
Fig.		16	28 a.	34	17	28 b.	35

Table 9.

Results on the i_d values of crystal violet in presence of different concentrations of methyl alcohol.

Dye conc. (x10^{-4}M)	$\log_{10} c$	10% methyl alcohol			20% methyl alcohol		
		i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$	i_d µA	$\log_{10} i_d$	$-\Delta \log_{10} i_d$
0.40	-4.3930	0.14	-0.8539	0.13	0.16	-0.7959	0.11
0.60	-4.2219	0.22	-0.6576	0.10	0.24	-0.6198	0.10
1.00	-4.0000	0.34	-0.4685	0.11	0.36	-0.4437	0.12
1.60	-3.7959	0.50	-0.3019	0.12	0.56	-0.2518	0.11
2.00	-3.6990	0.64	-0.1938	0.10	0.72	-0.1427	0.09
3.00	-3.5229	0.82	-0.0862	0.16	0.98	-0.0088	0.12
4.00	-3.3930	1.02	+0.0086	0.17	1.25	+0.0969	0.11
6.00	-3.2219	1.40	0.1461	0.19	1.50	0.1760	0.20
8.00	-3.0969	1.85	0.2672	0.18	1.95	0.2900	0.20
Fig.		18	29 a.	36	19	29 b.	37

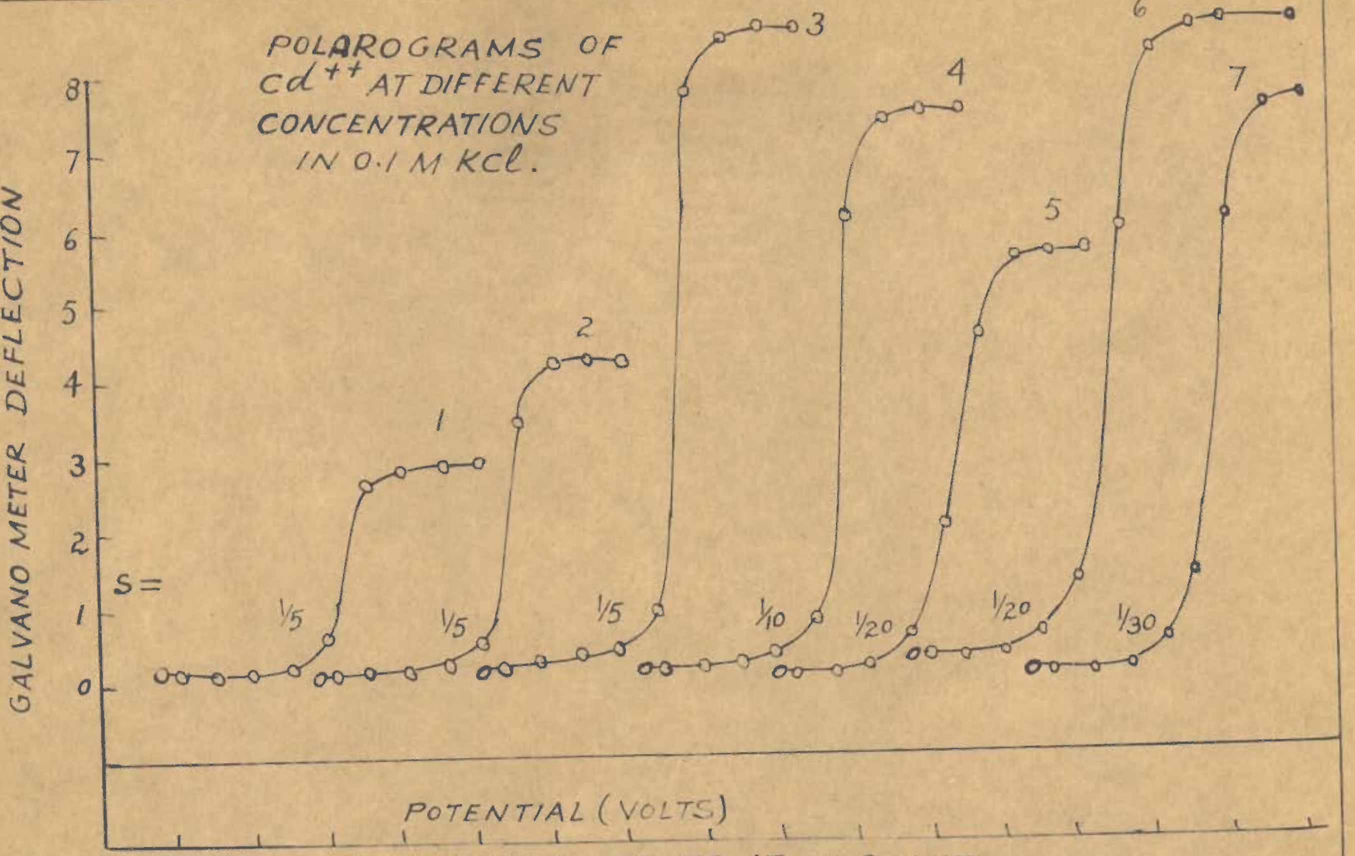


FIG-2 EACH CURVE STARTS AT -0.3 VOLT

S = SENSITIVITY

(1 DIV = 0.2 VOLTS)

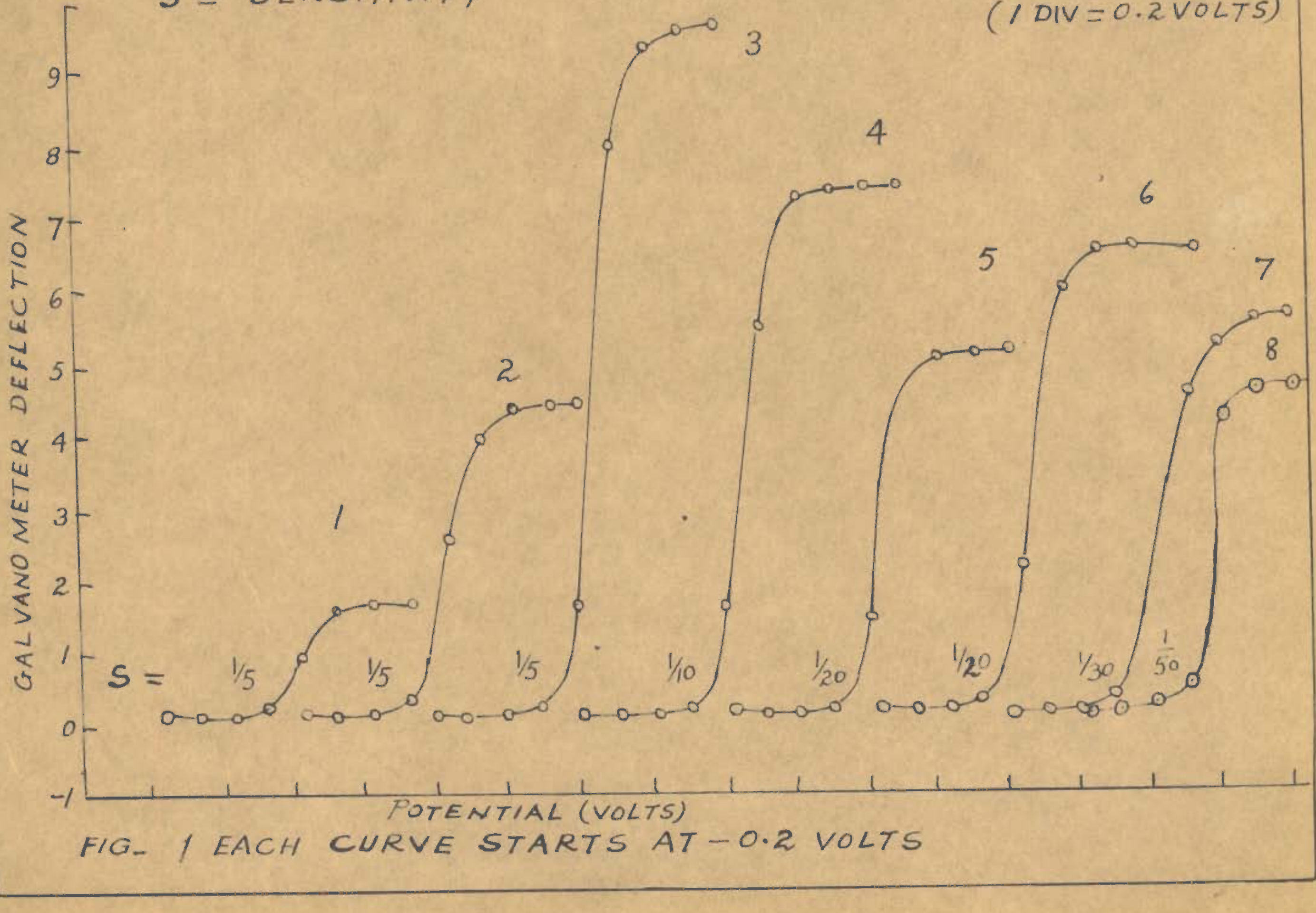


FIG_ 1 EACH CURVE STARTS AT -0.2 VOLTS

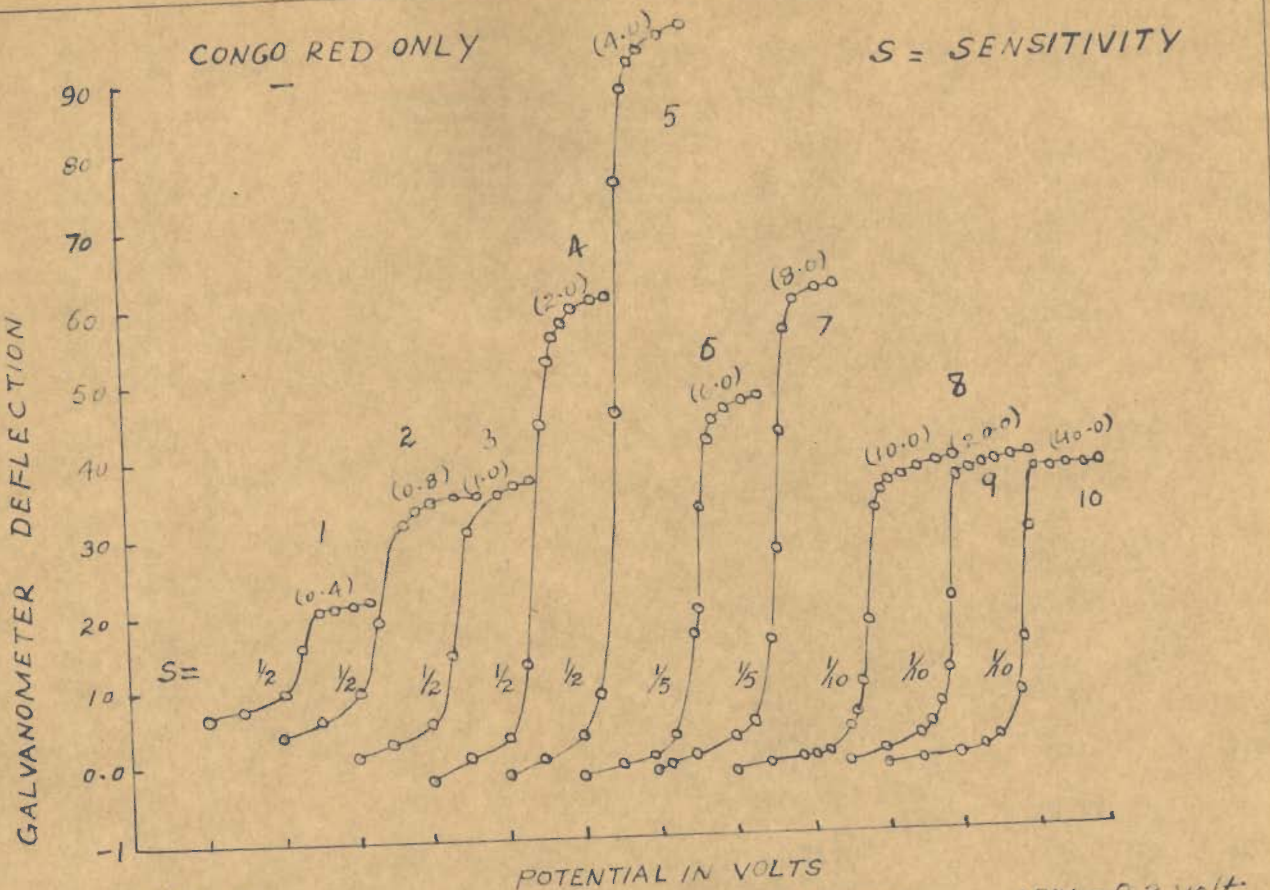


FIG-3

EACH CURVE STARTS AT -0.2 VOLTS

1 DIV. = 0.2 volt.

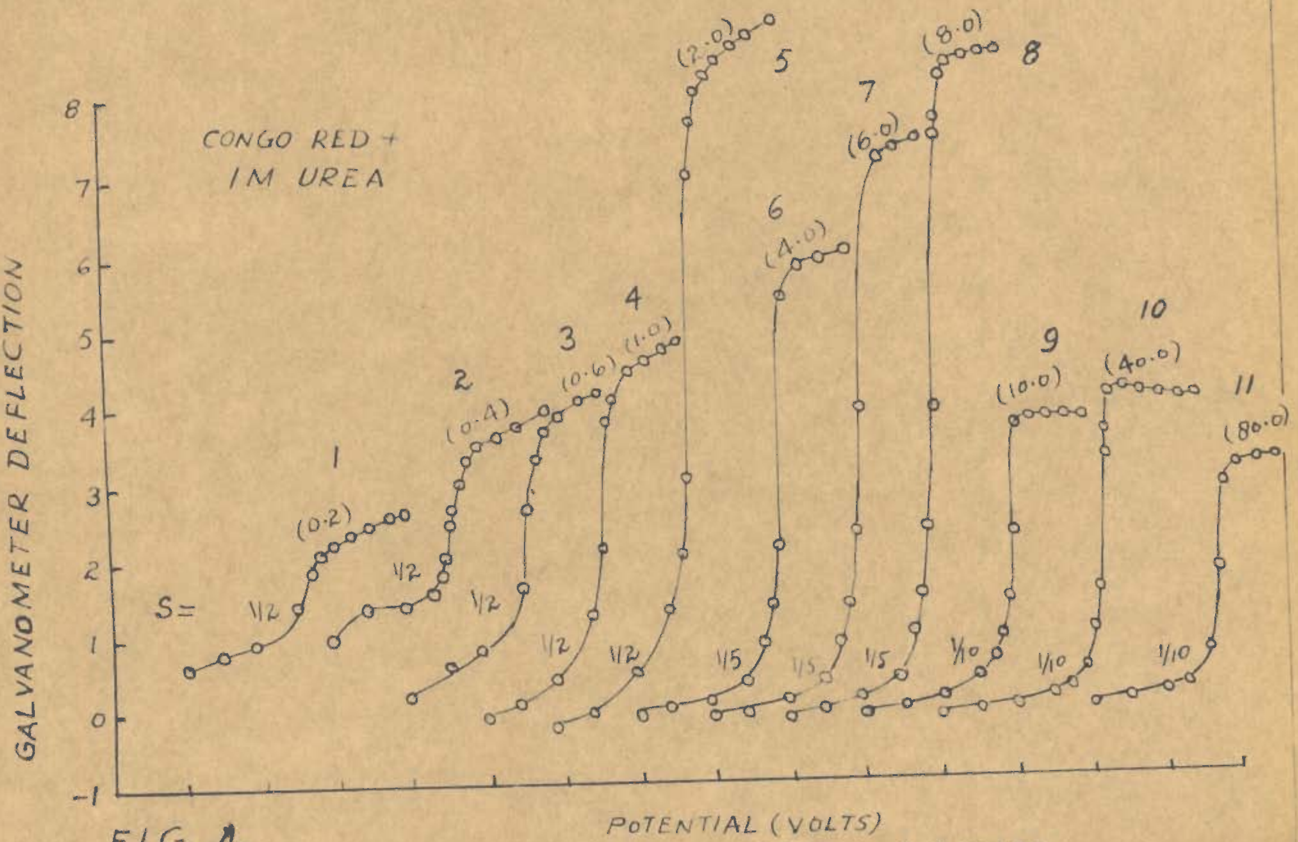


FIG. 4

EACH CURVE STARTS AT - 0.2 VOLTS.

VALUE IN PARENTHES REPRESENTS THE AMOUNT CONGO-RED($\times 10^{-4}$M)

POLAROGRAMS OF CONGORED + UREA

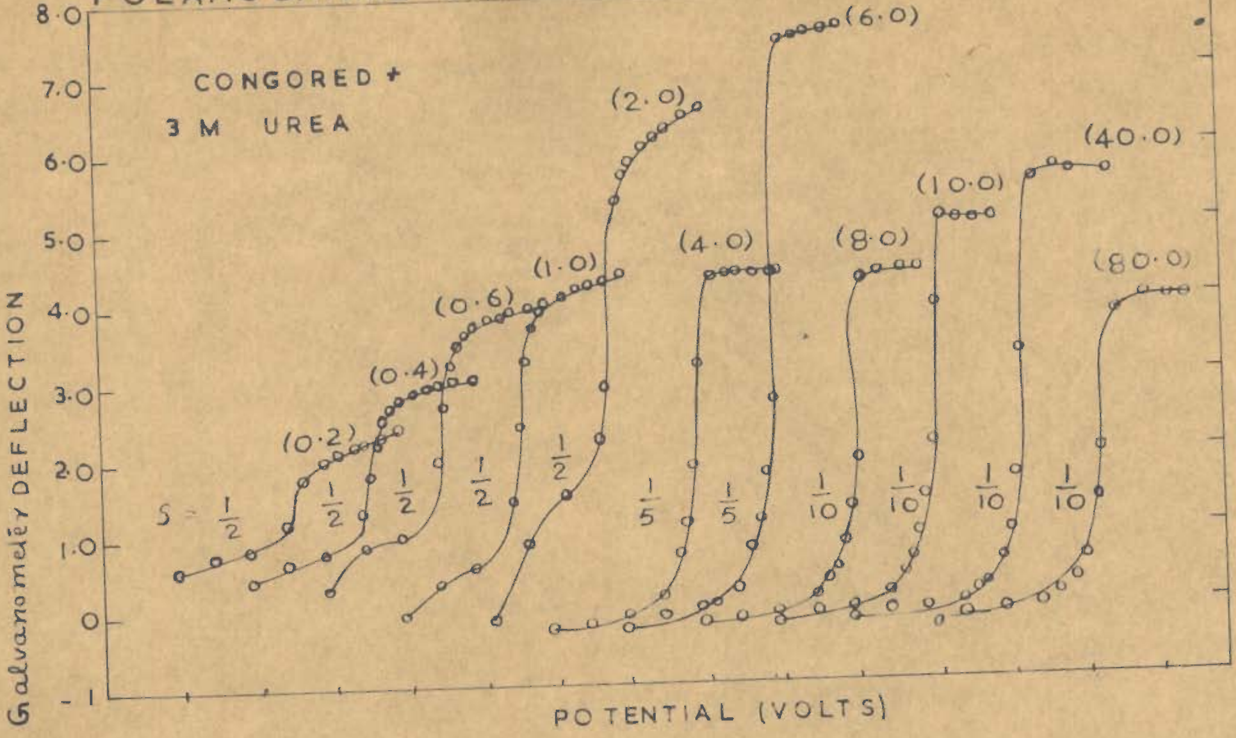


FIG. 5 VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CONGORED $(\times 10^{-4}$ M$)$

S SENSITIVITY

EACH CURVE STARTS AT - 0.2 VOLT

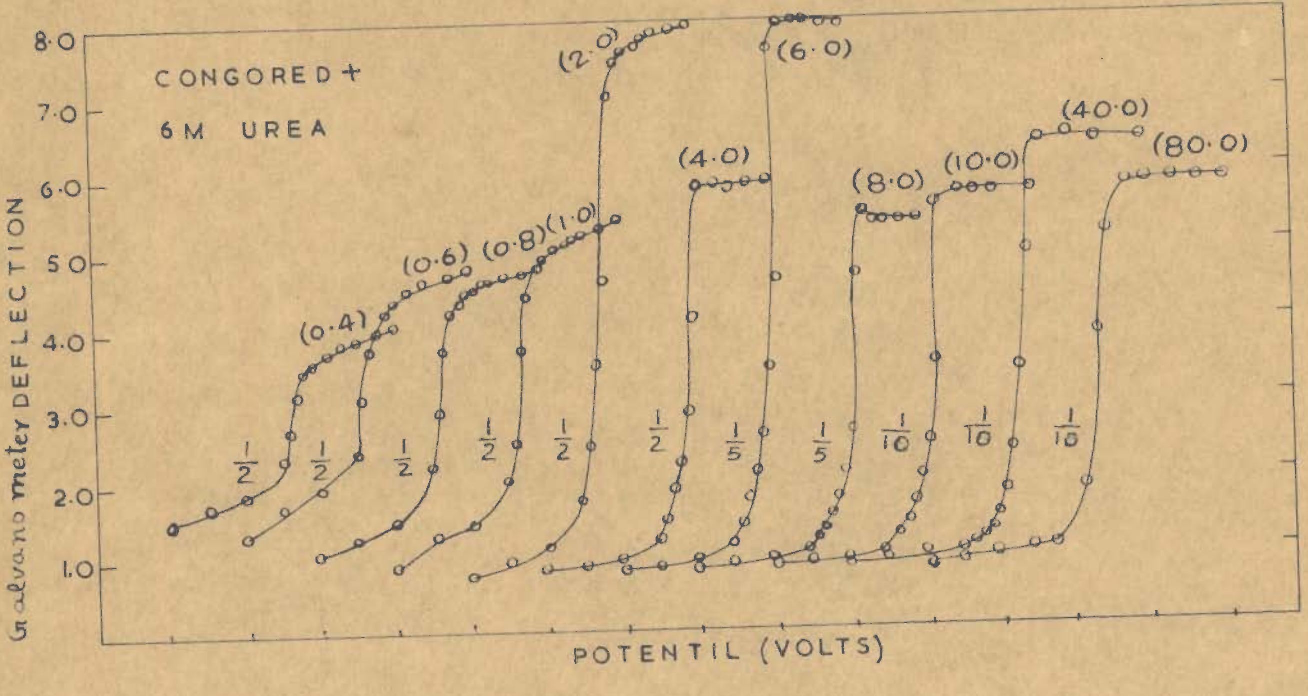


FIG. 6

1 DIV = 0.2 VOLT

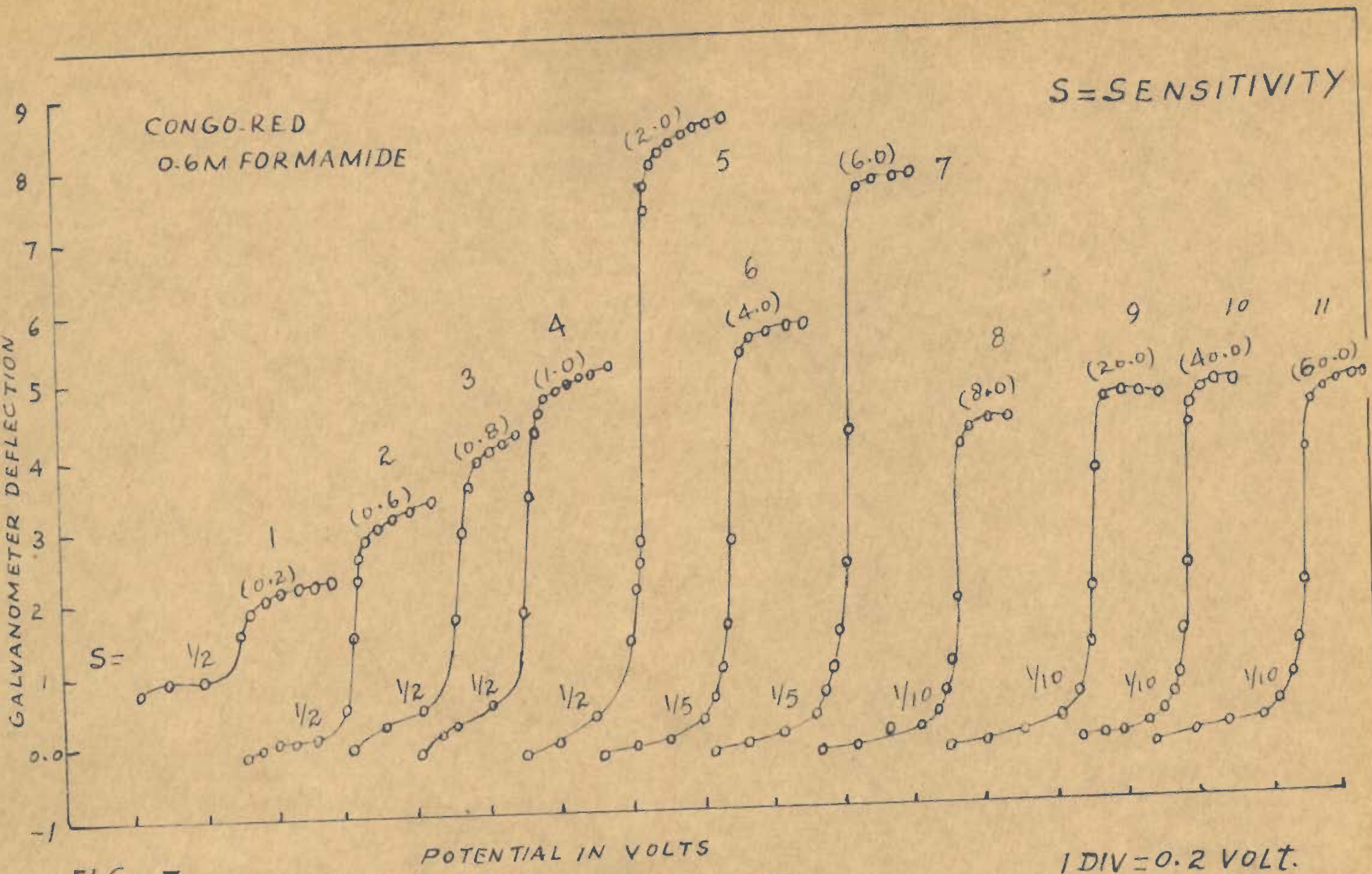


FIG- 7

EACH CURVE STARTS AT – 0.2 VOLTS

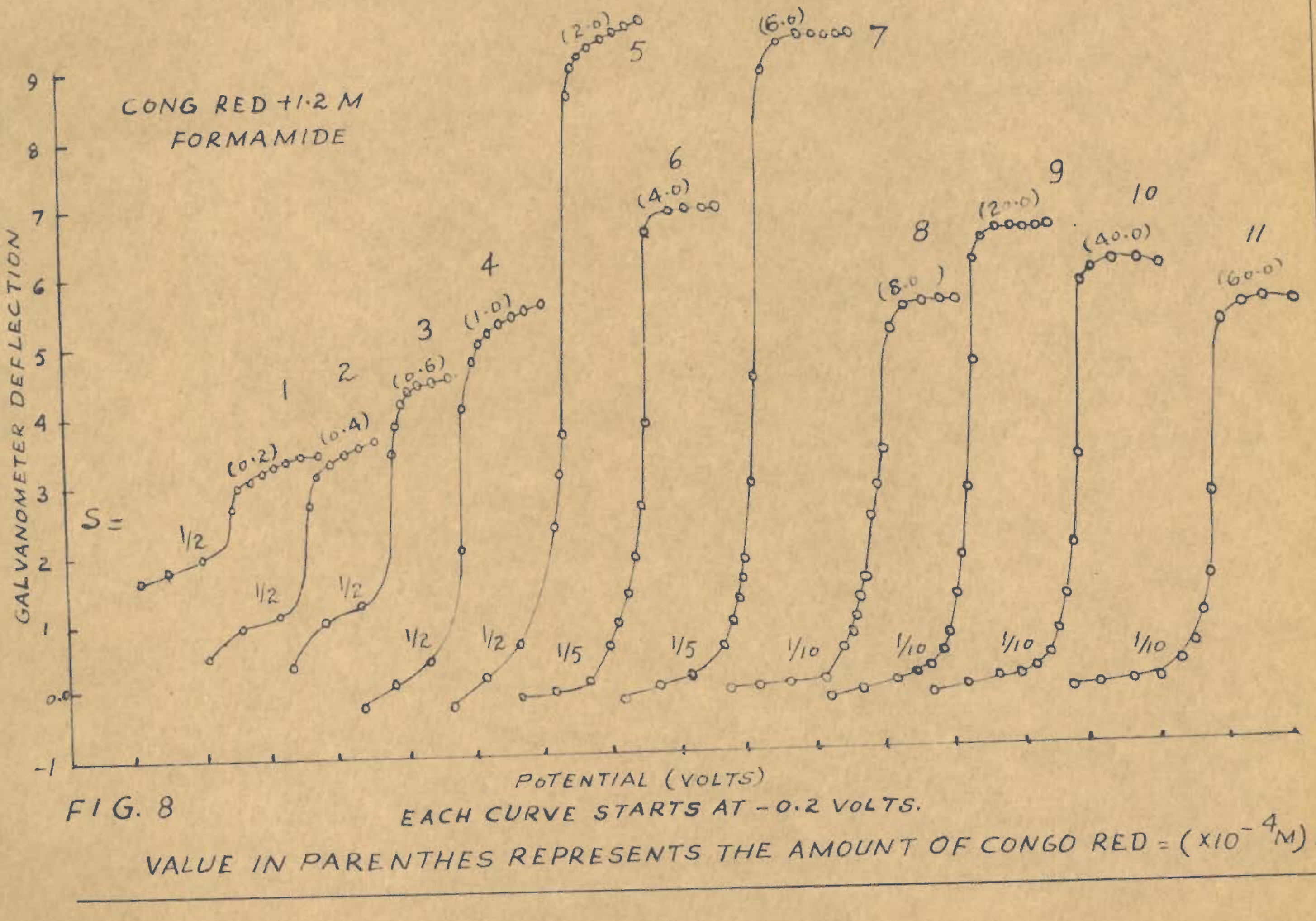


FIG. 8

EACH CURVE STARTS AT – 0.2 VOLTS.

VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CONGO RED = ($\times 10^{-4}$M).

POLAROGRAMS CONGORED+ FORMAMIDE

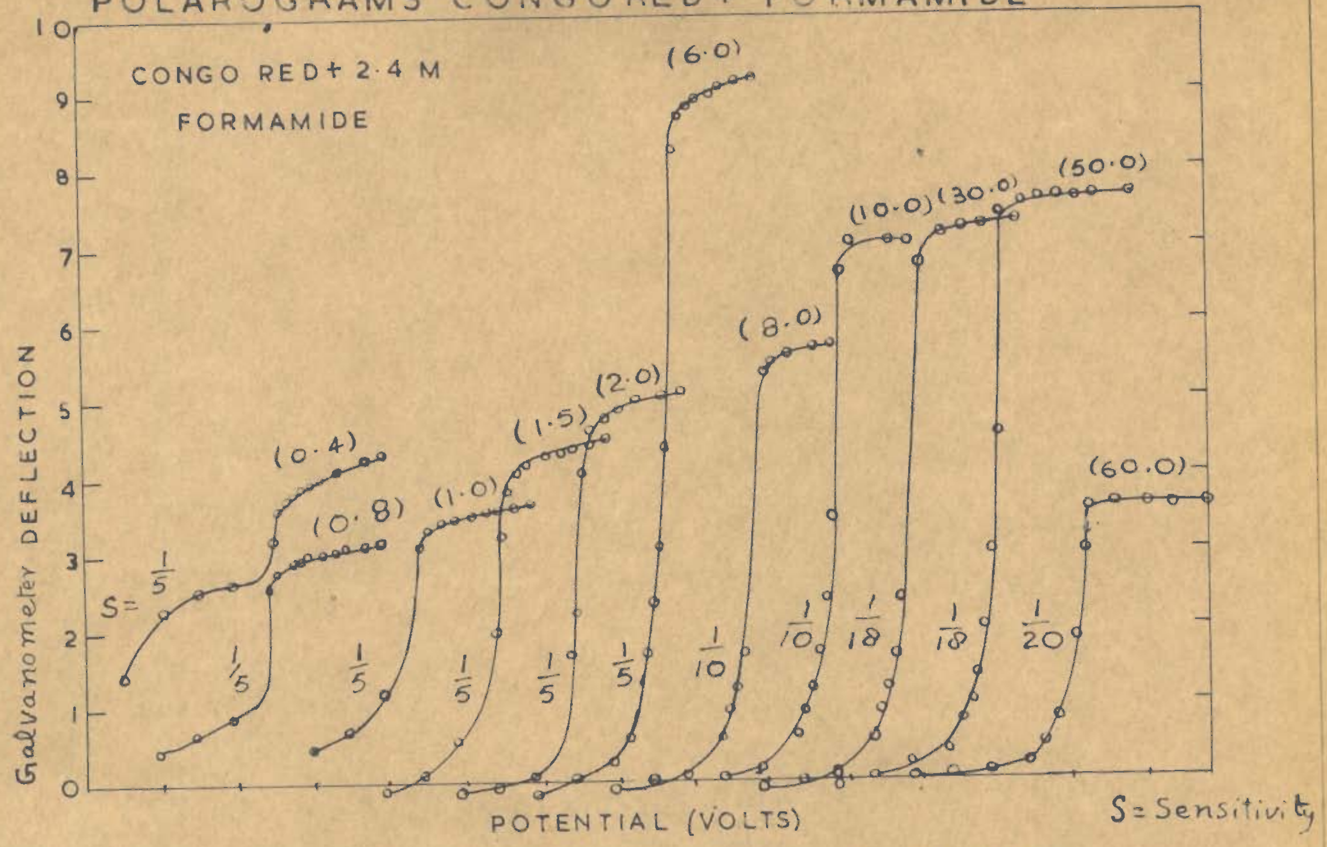


FIG. 9 VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CONGORED ($\times 10^{-4}$ M)

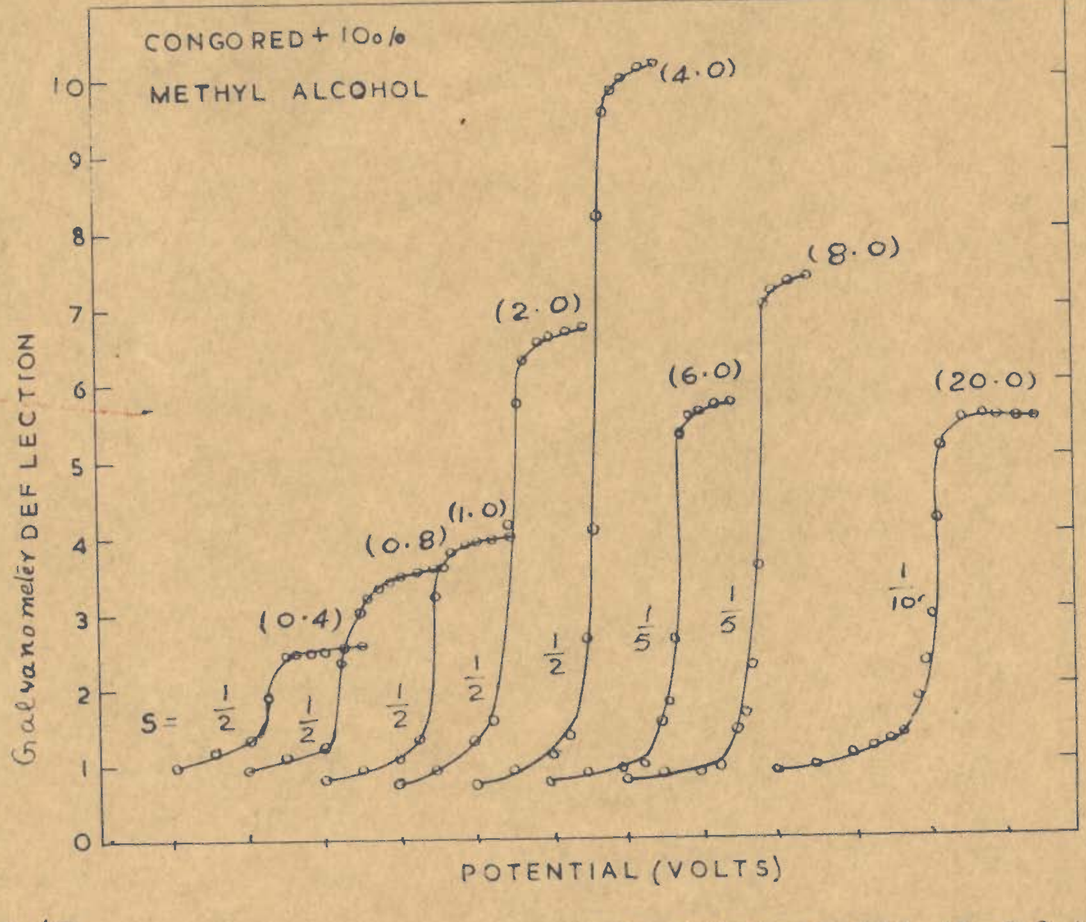
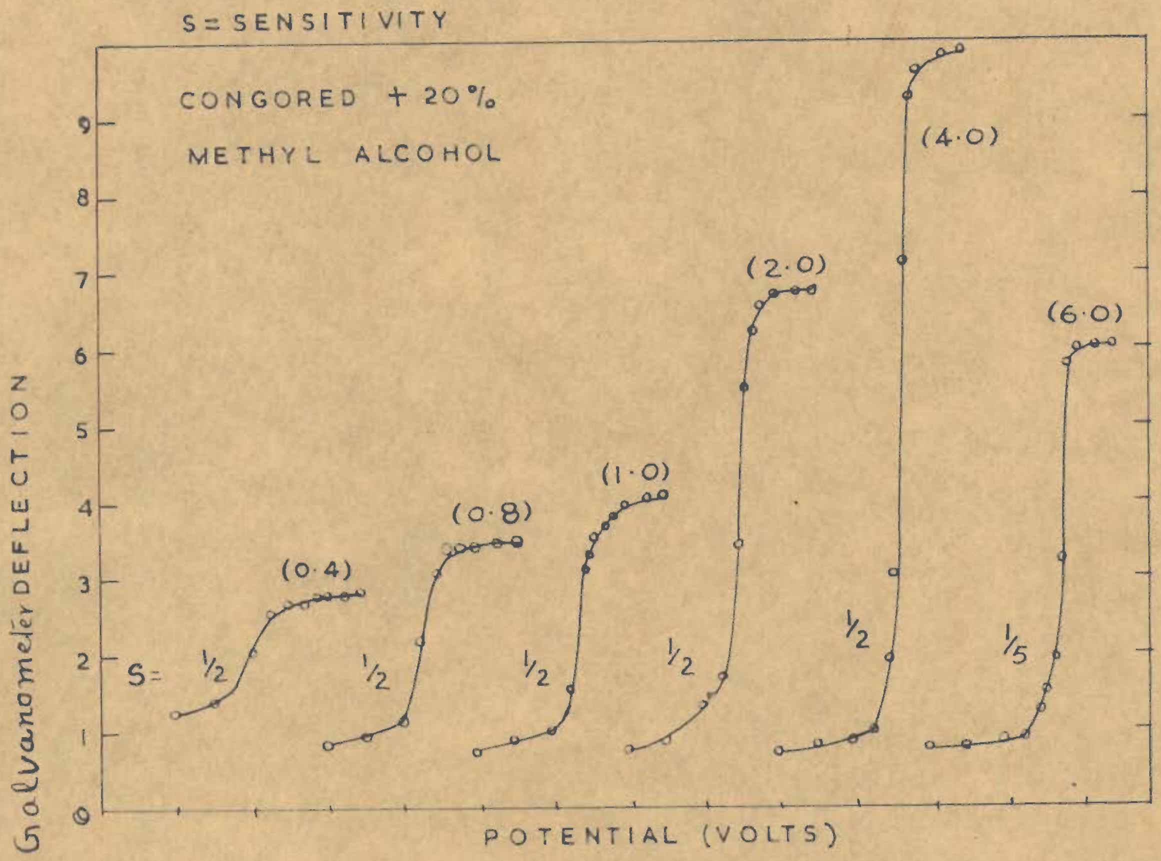


FIG. 10 1 DIV. = 0·2 VOLT EACH CURVE STARTS AT 0·2 VOLT

POLAROGRAMS OF CONGORED + METHYL ALCOHOL



EACH CURVE STARTS AT = 0·2 VOLT

FIG. 11 VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CONGORED = ($\times 10^{-4}$ M)

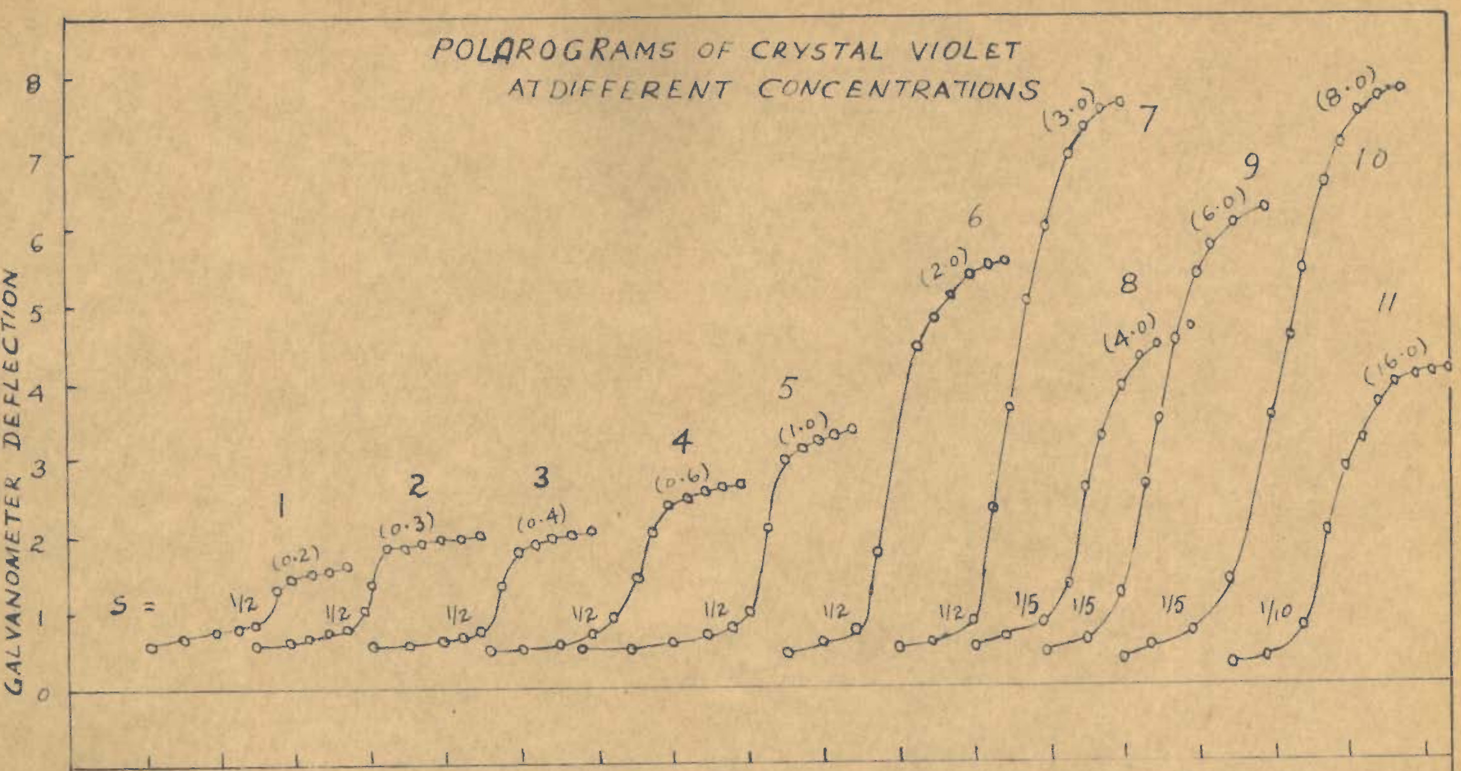


FIG- 12

EACH CURVE STARTS AT -0.4 VOLTS

S = SENSITIVITY

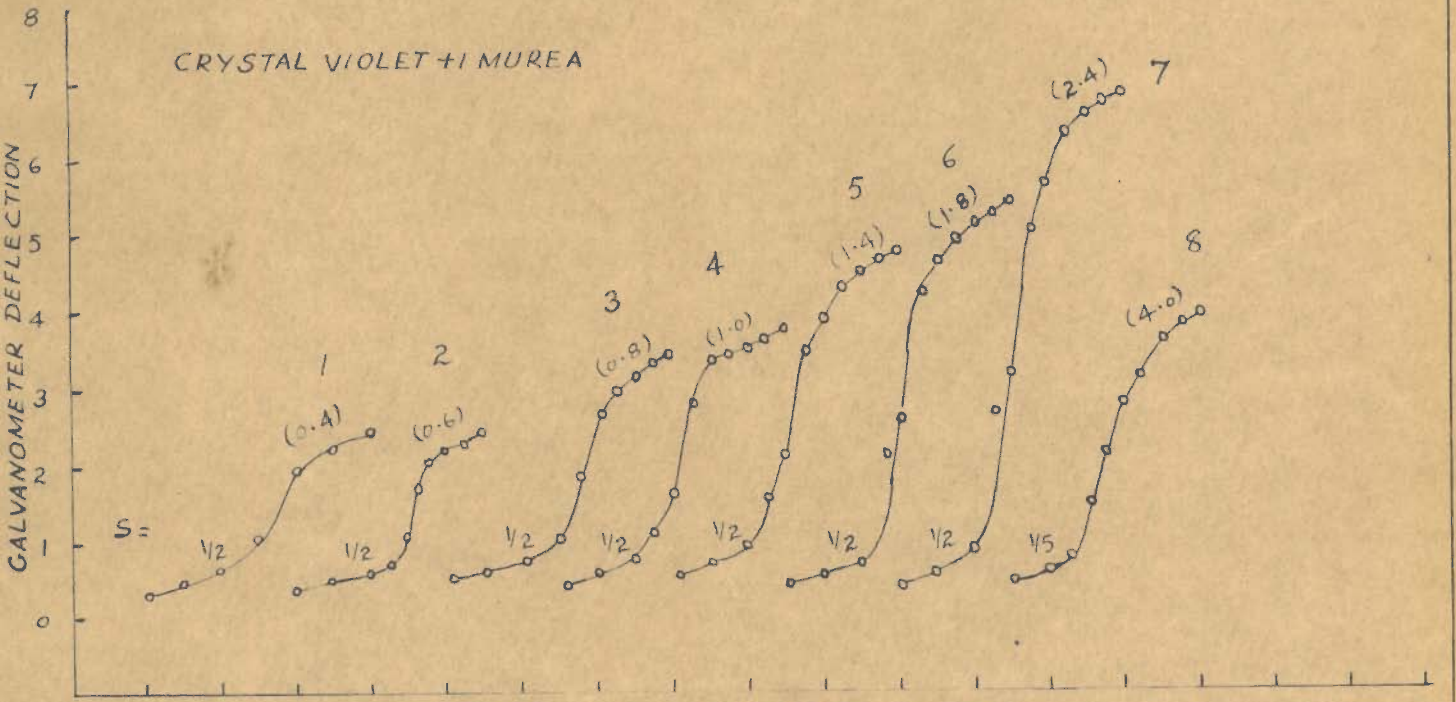


FIG- 13

EACH CURVE STARTS AT -0.4 VOLTS

VALUE IN PARENTHS REPRESENTS THE AMOUNT OF
CRYSTAL VIOLET ($\times 10^{-4}$ M)

1 DIV = 0.2 VOLT.

POLAROGRAMS CRYSTEL VOILT + UREA

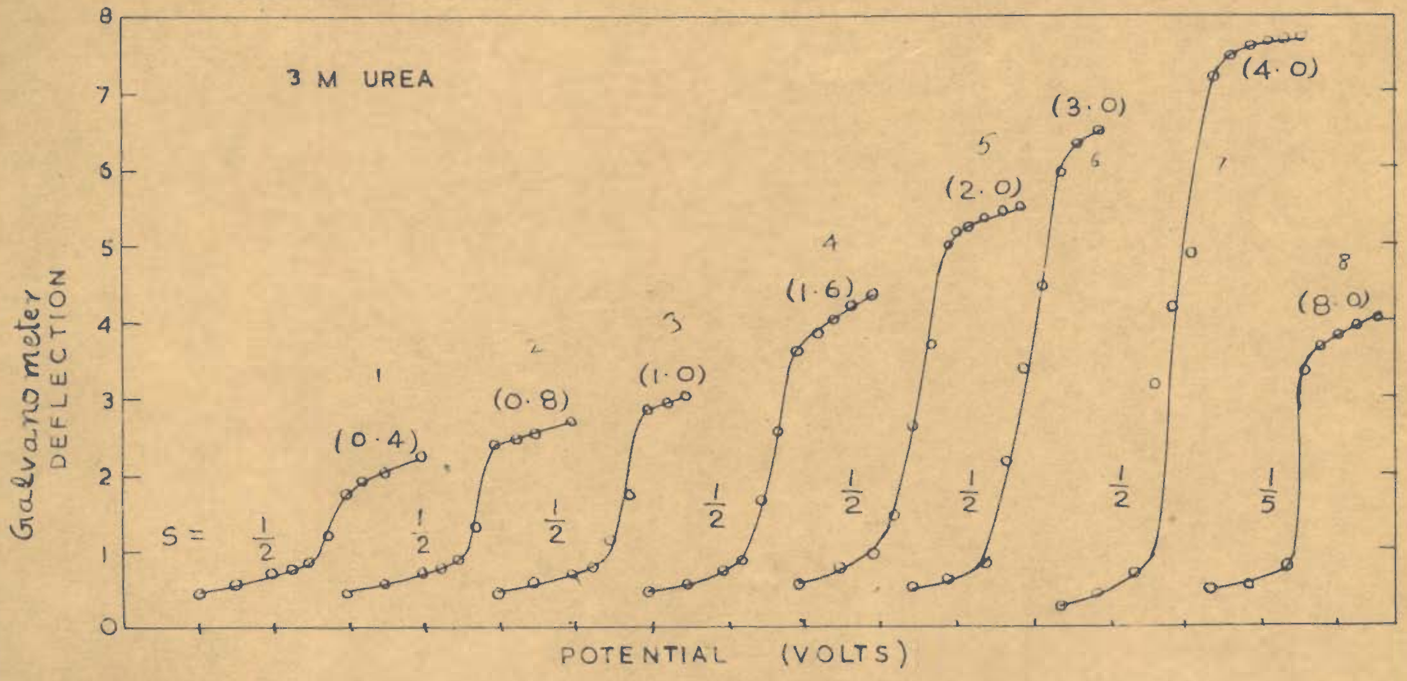
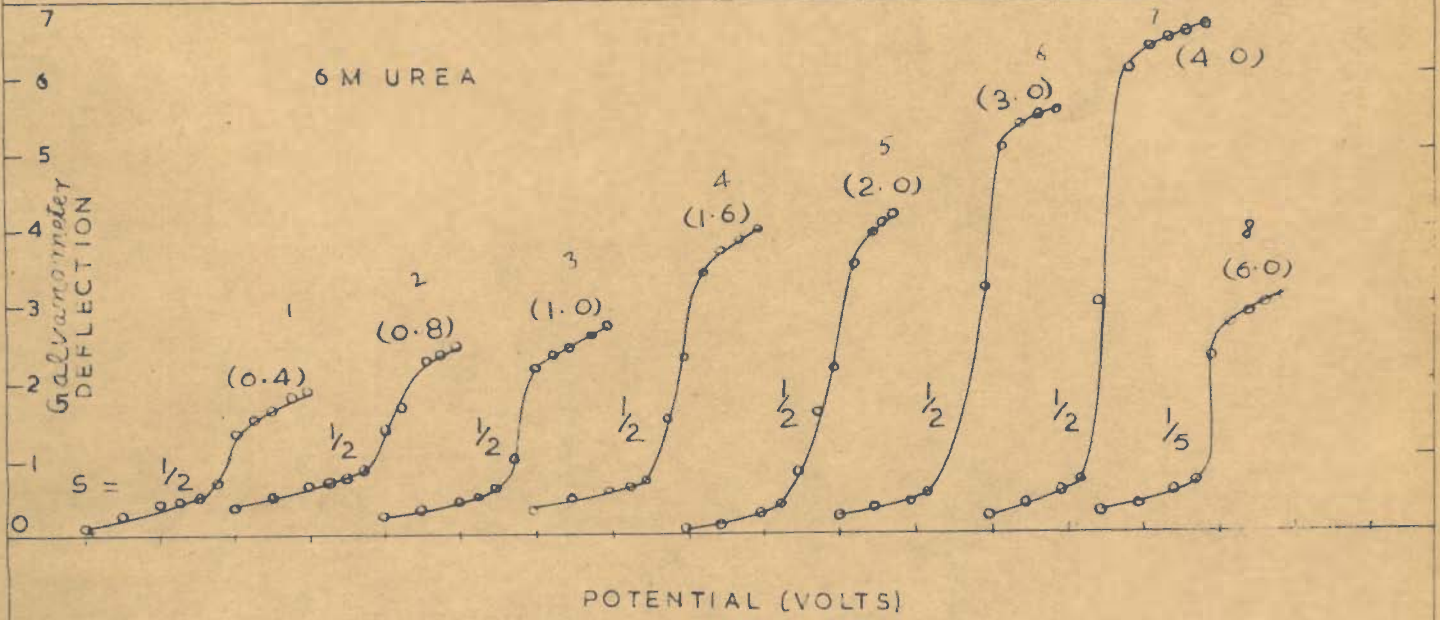


FIG. 14

VALUE IN THE PARENTHES REPRESENTS THE AMOUNT OF CRYSTAL VIOLET=(x 10^{-4}M)

S = SENSITIVITY



1 DIV. 0·2 VOLT

FIG. 15

EACH CURVE STARTS AT –0·4 VOLT

POLAROGRAMS OF CRYSTAL VIOLET+FORMAMIDE

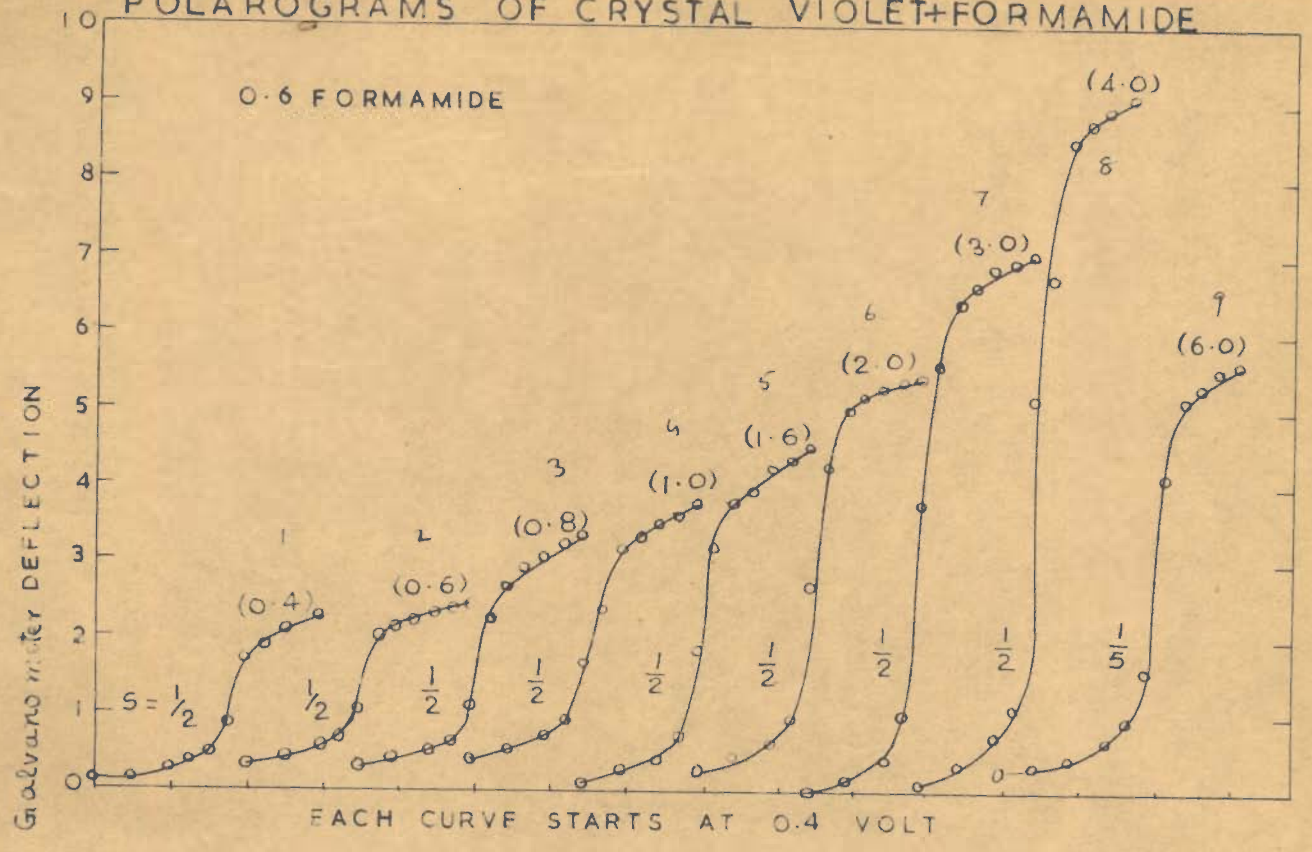


FIG. 16

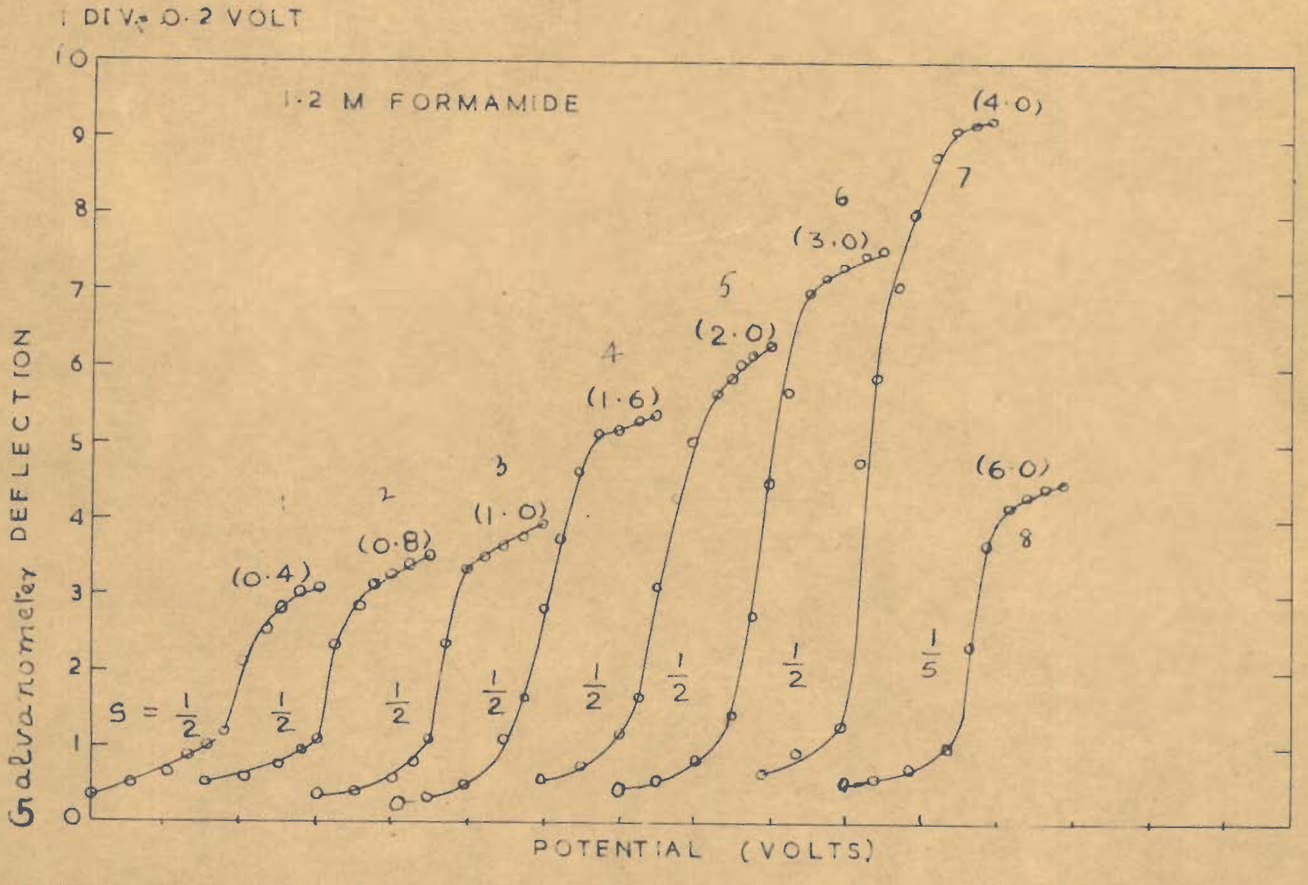


FIG. 17 VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CRYSTAL VIOLET=($\times 10^{-4}$ M)

POLAROGRAMS OF CRYSTAL VOILET + METHYL ALCOHAL

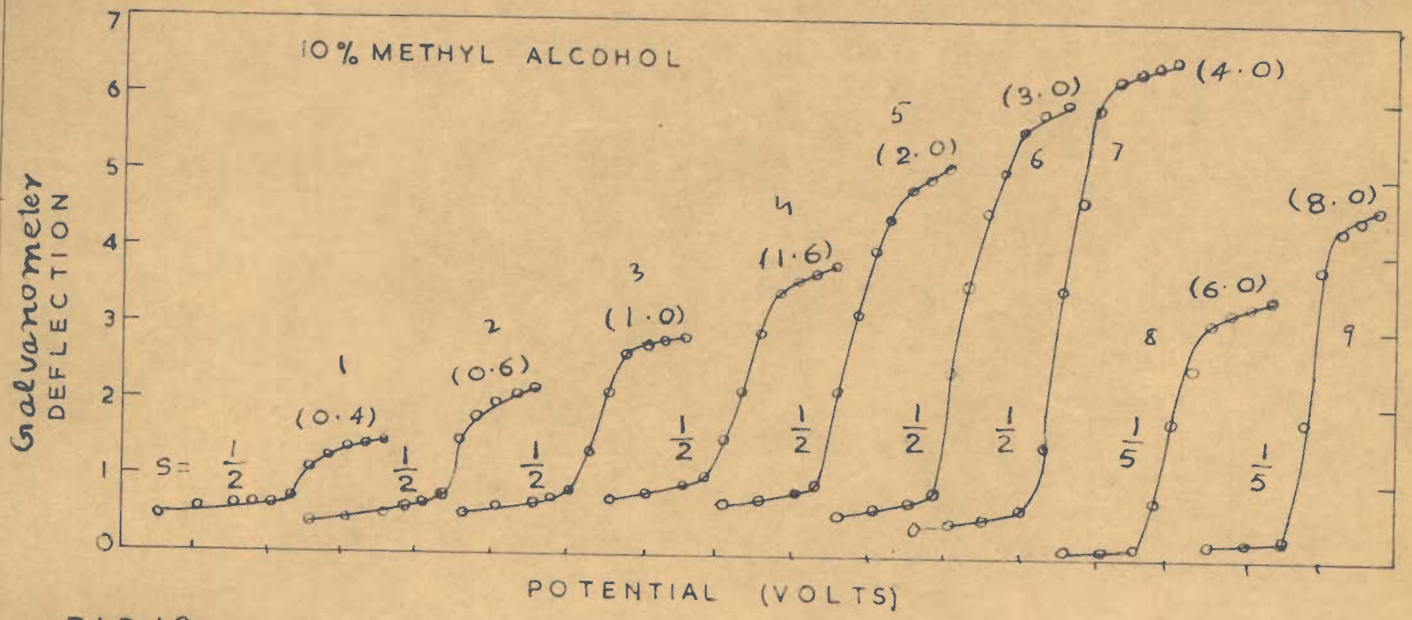


FIG. 18

VALUE IN PARENTHES REPRESENTS THE AMOUNT OF CRYSTAL VIOLAT ($\times 10^{-4}$ M)

S = SENSITIVITY

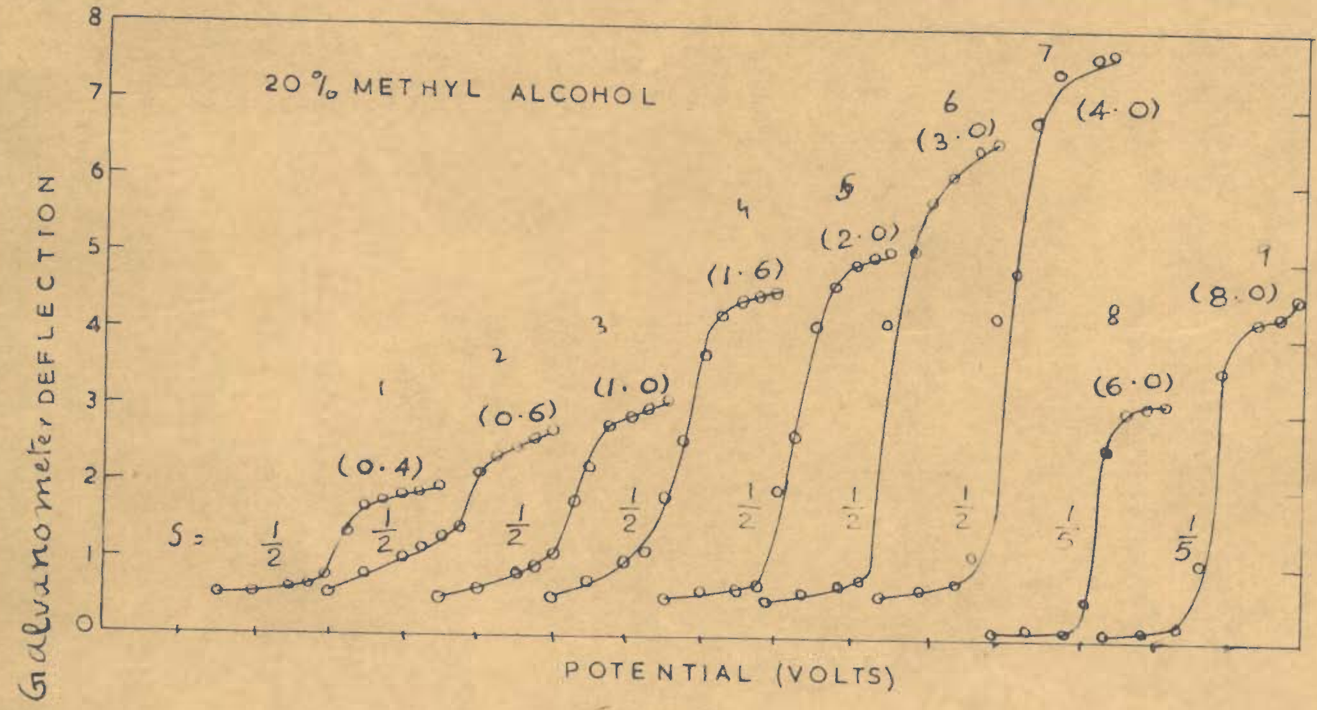


FIG. 19

1 DIV. 0·2 VOLT

EACH CURVE STARTS AT − 0·4 VOLT

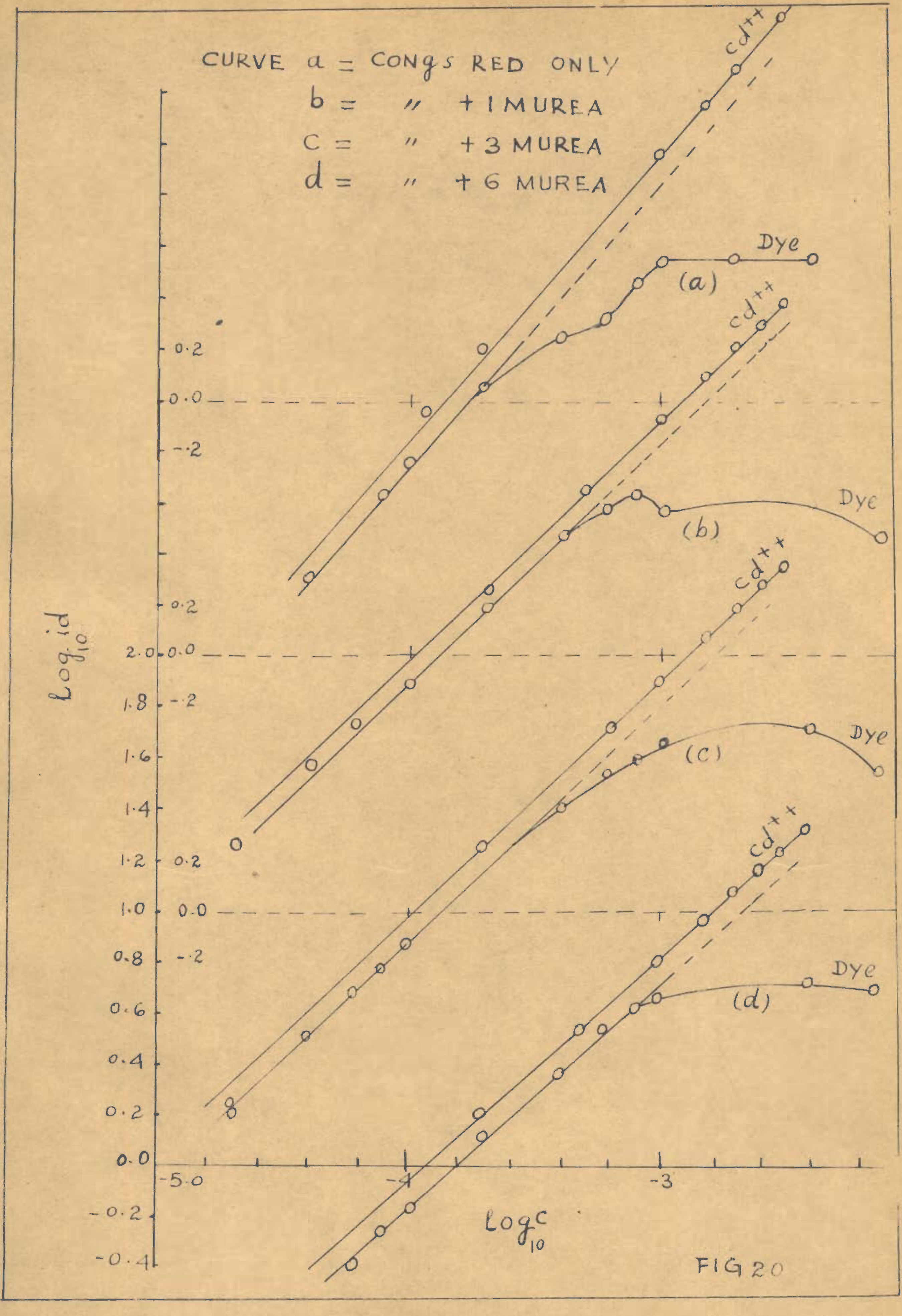

CURVE a = CONGO RED ONLY
b = " + 1 M UREA
C = " + 3 M UREA
d = " + 6 M UREA
cd++
Dye
(a)
cd++
Dye
(b)
cd++
Dye
(C)
cd++
Dye
(d)
0.2
0.0
-.2
0.2
2.0
0.0
1.8
-.2
1.6
1.4
1.2
0.2
1.0
0.0
0.8
-.2
0.6
0.4
0.2
0.0
-0.2
-0.4
-5.0
-4
-3
Log$_{10}$ id
Log$_{10}$ c

FIG 20

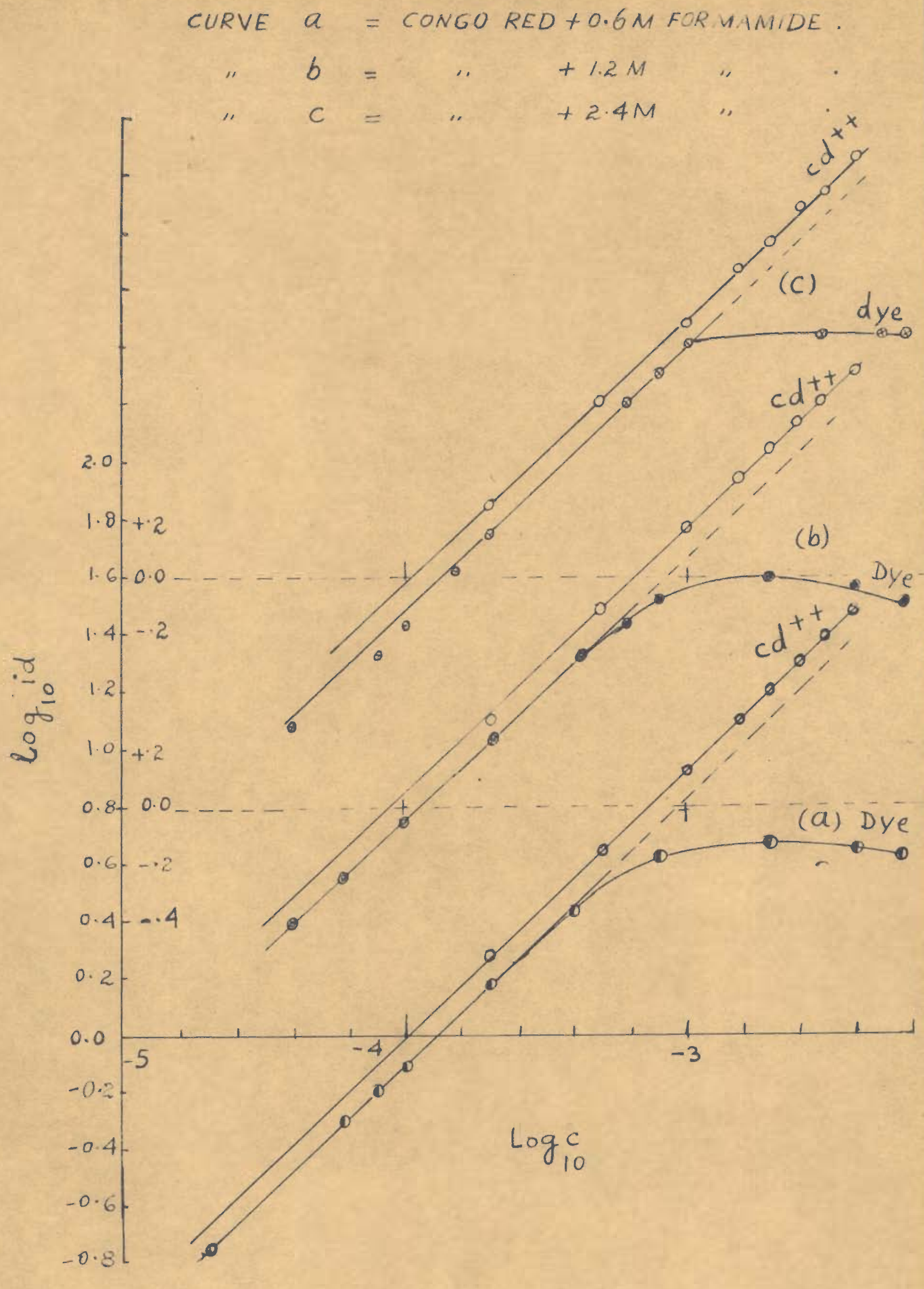


FIG. 21 PLOT BETWEEN $\log_{10} c$ AND $\log_{10} id$.

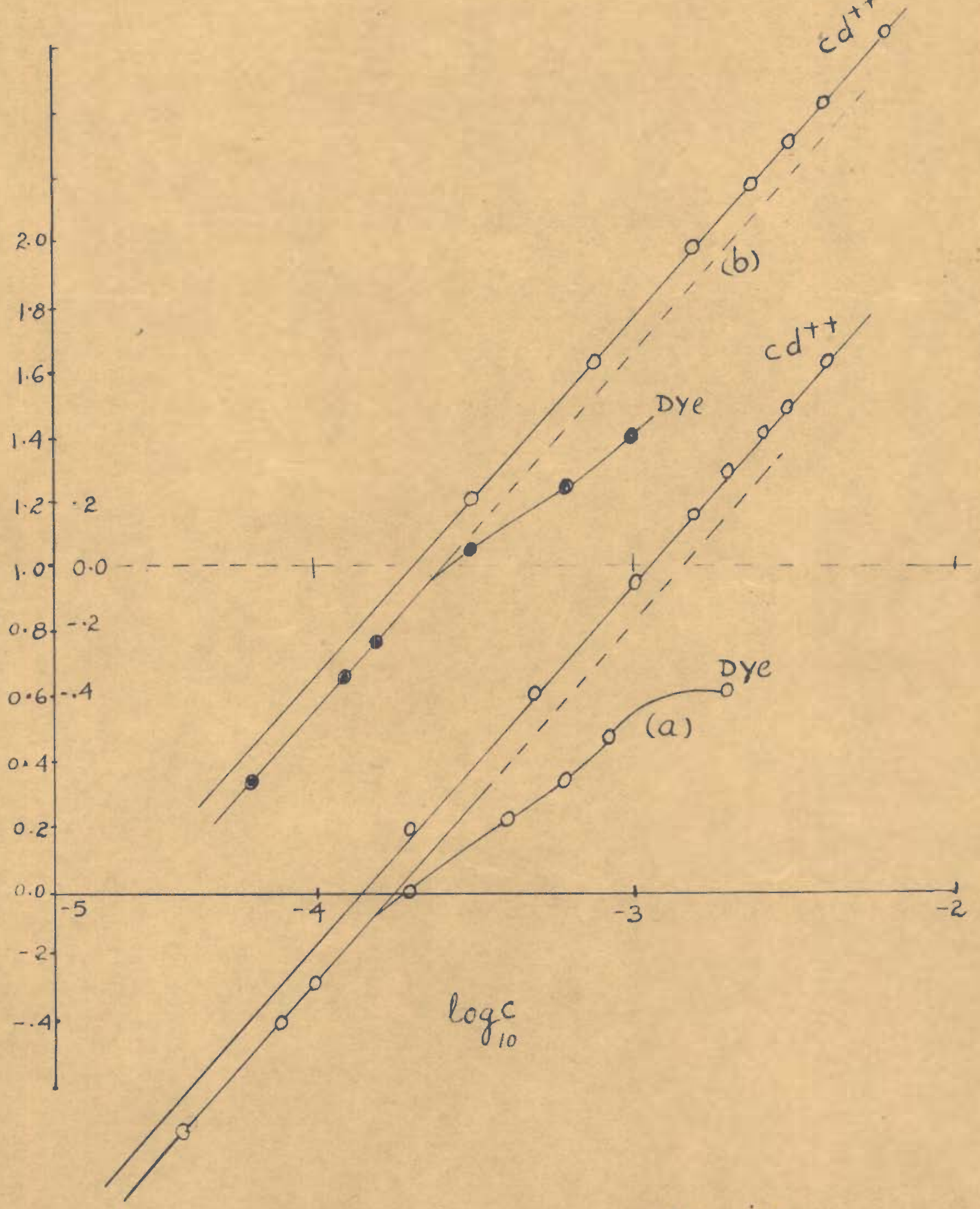


FIG. 22 PLOT BETWEEN $\log_{10}$ C AND $\log_{10}$ id

CURVE (a) = congo RED + 10% METHYAL ALCOHOL
" (b) = " " + 20% METHYAL ALCOHOL

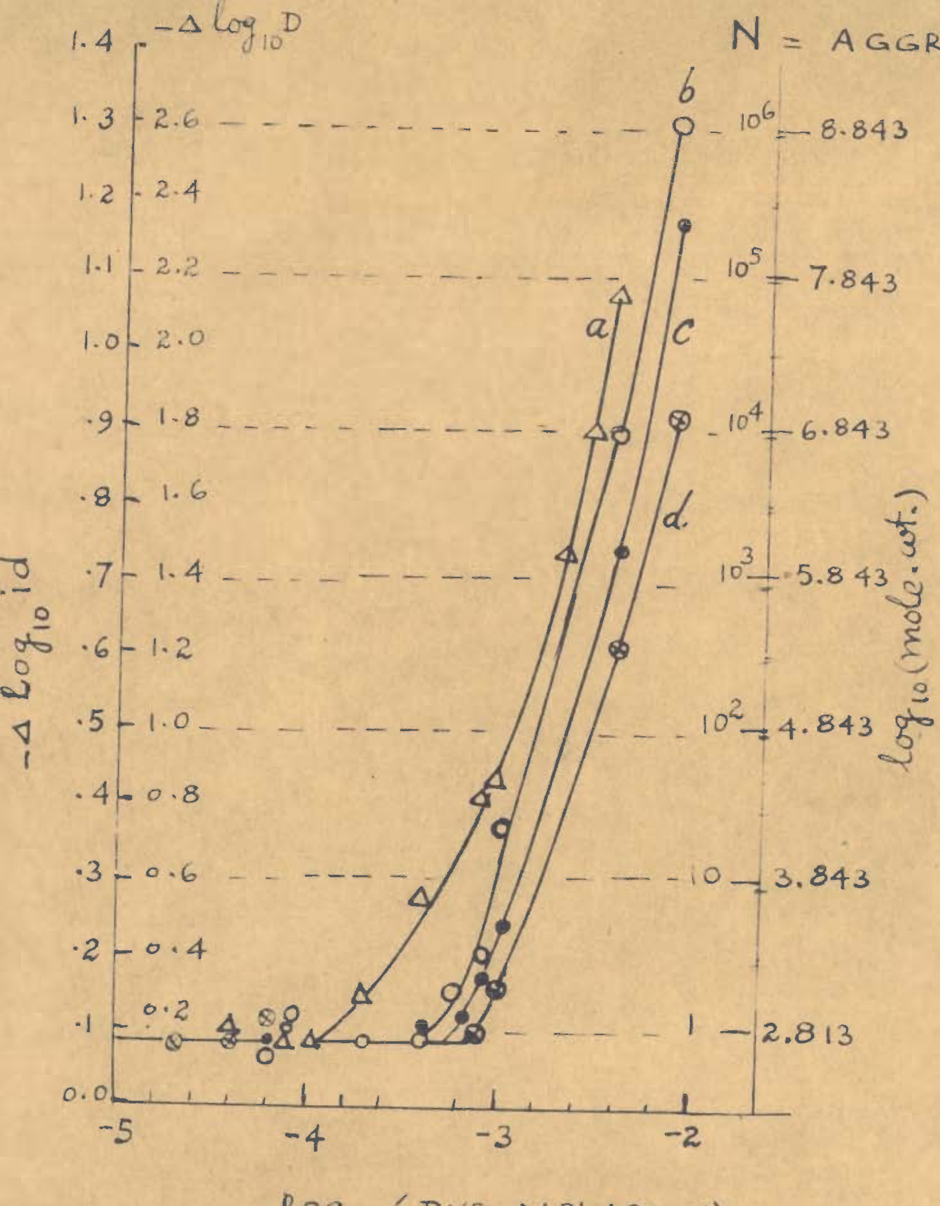


FIG. 23. EEEECT OF UREA ON AGGREGATION NUMBER OF CONGO RED.

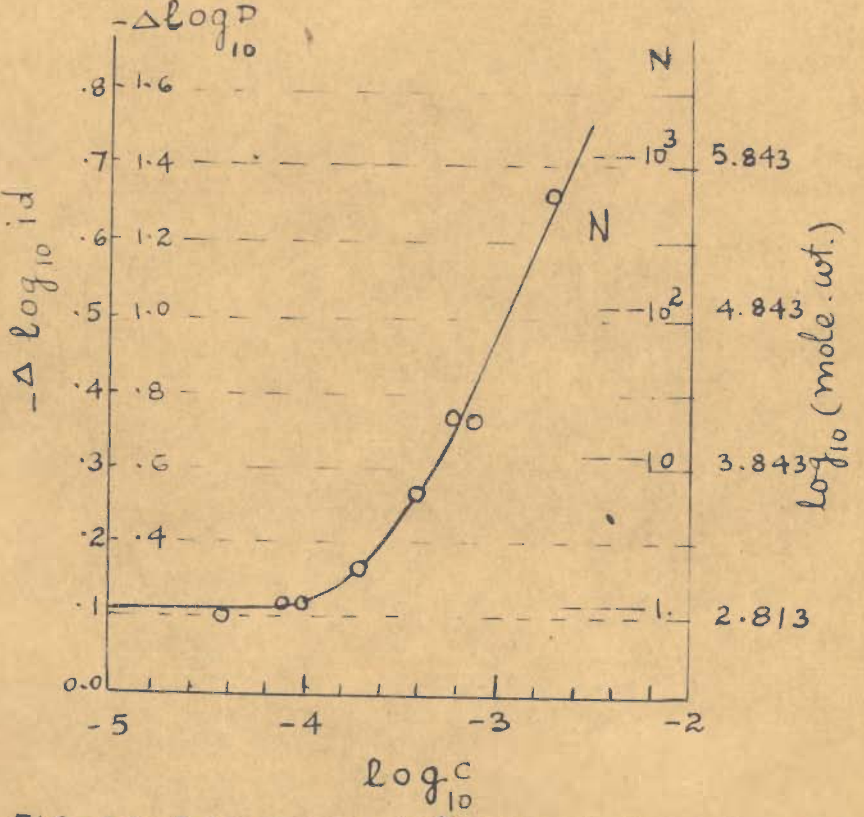


FIG. 25. EFFECT OF 10% METHYL ALCOHOL ON AGGREGATION NUMBER OF CONGO RED

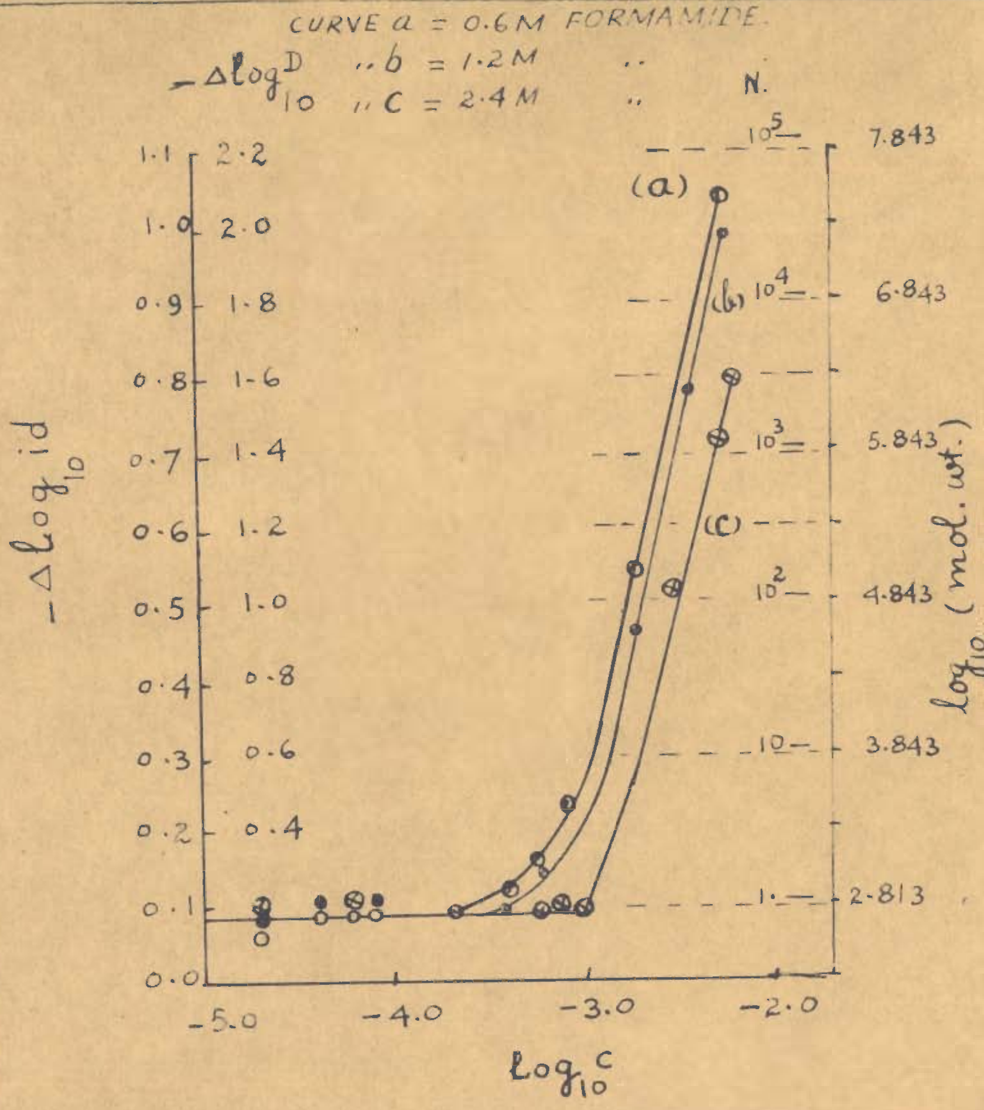


FIG.24 EFFECT OF FORMAMIDE ON AGGRIGATION NUMBER OF CONGO RED.

N = AGGREGATION NUMBER

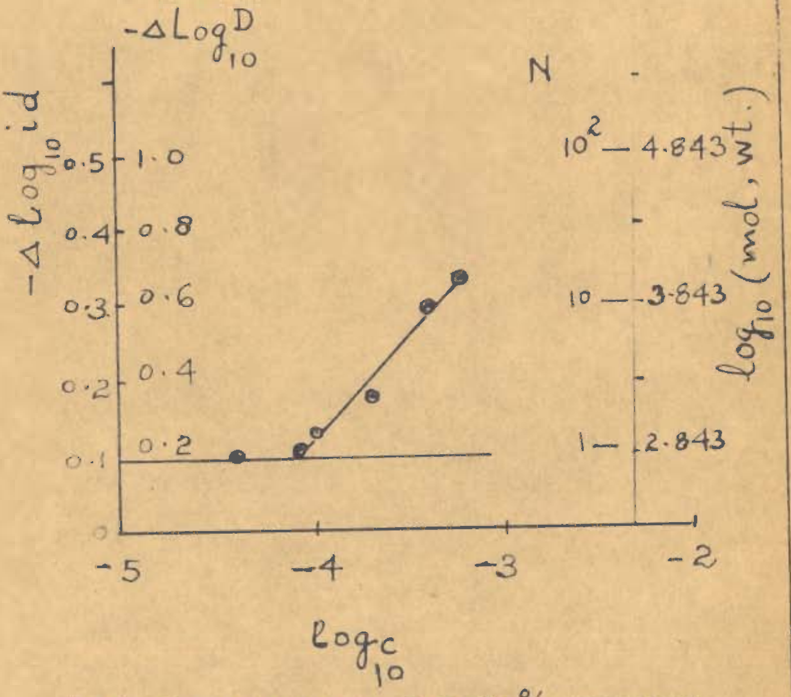


FIG. 26 EFFECT OF 20% METHYL ALCOHAL ON AGGREGATION NUMBER OF CONGO RED.

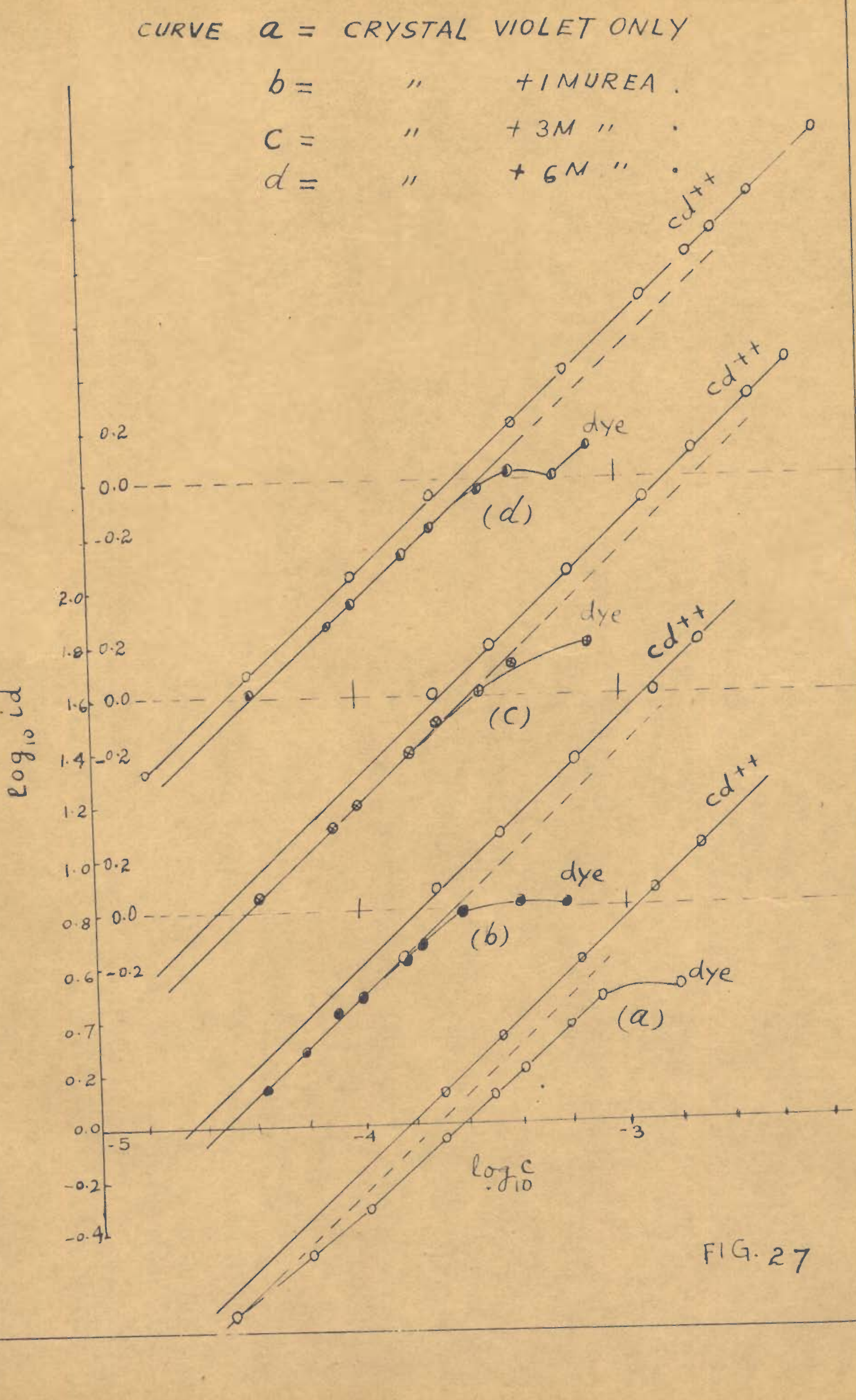

CURVE a = CRYSTAL VIOLET ONLY
b = " +1 M UREA.
C = " +3M ".
d = " +6M ".
cd++
cd++
cd++
cd++
dye
dye
dye
dye
(a)
(b)
(C)
(d)
0.2
0.0
-0.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.7
0.2
0.0
-0.2
-0.4
log10 id
-5
-4
-3
log10 c

FIG. 27

CURVE a = CRYSTAL VIOLET + 0.6 M FORMAMIDE
b = " + 1.2 M "

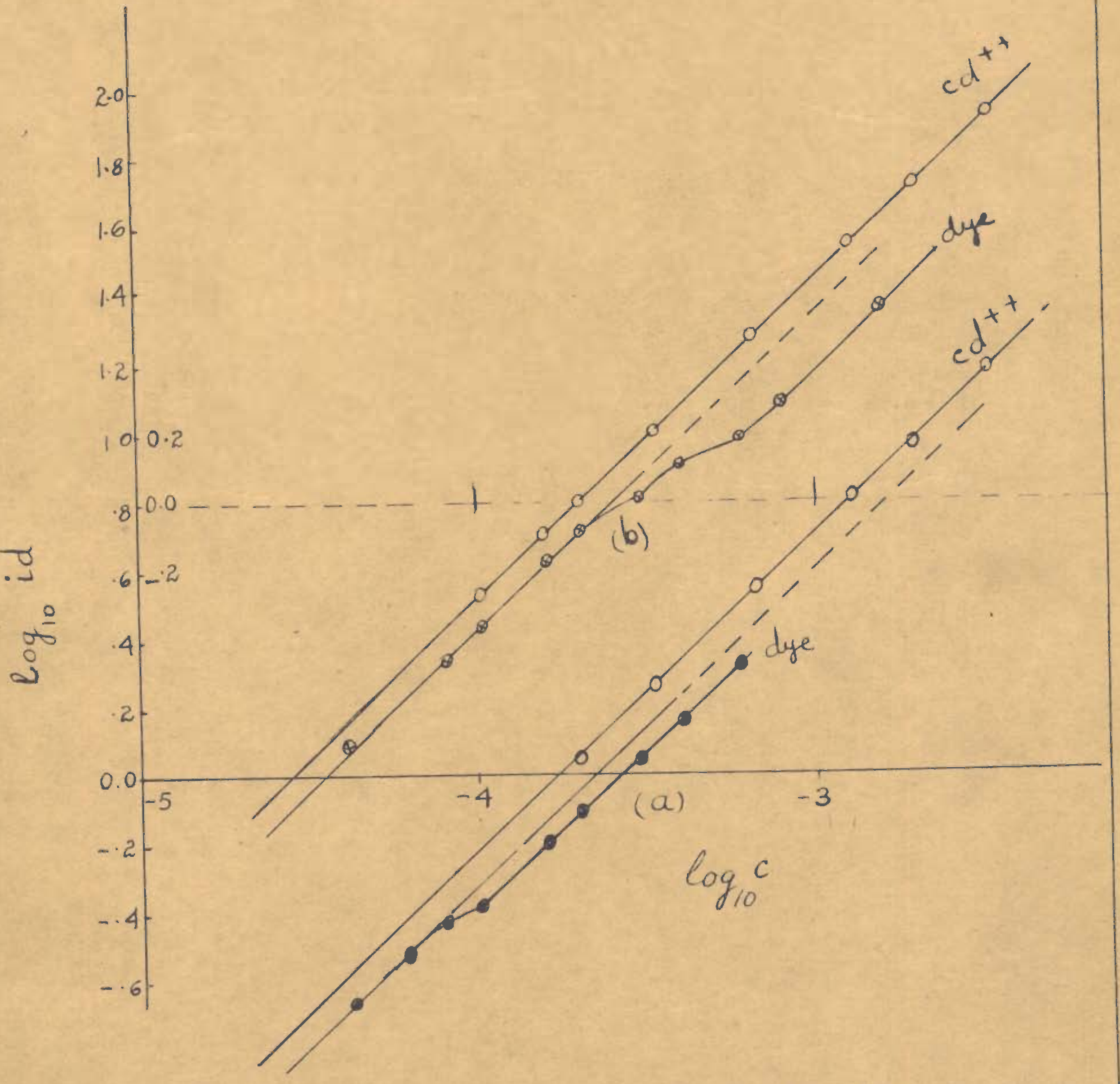


FIG. 28. PLOT BETWEEN $\log_{10} c$ AND $\log_{10} id$

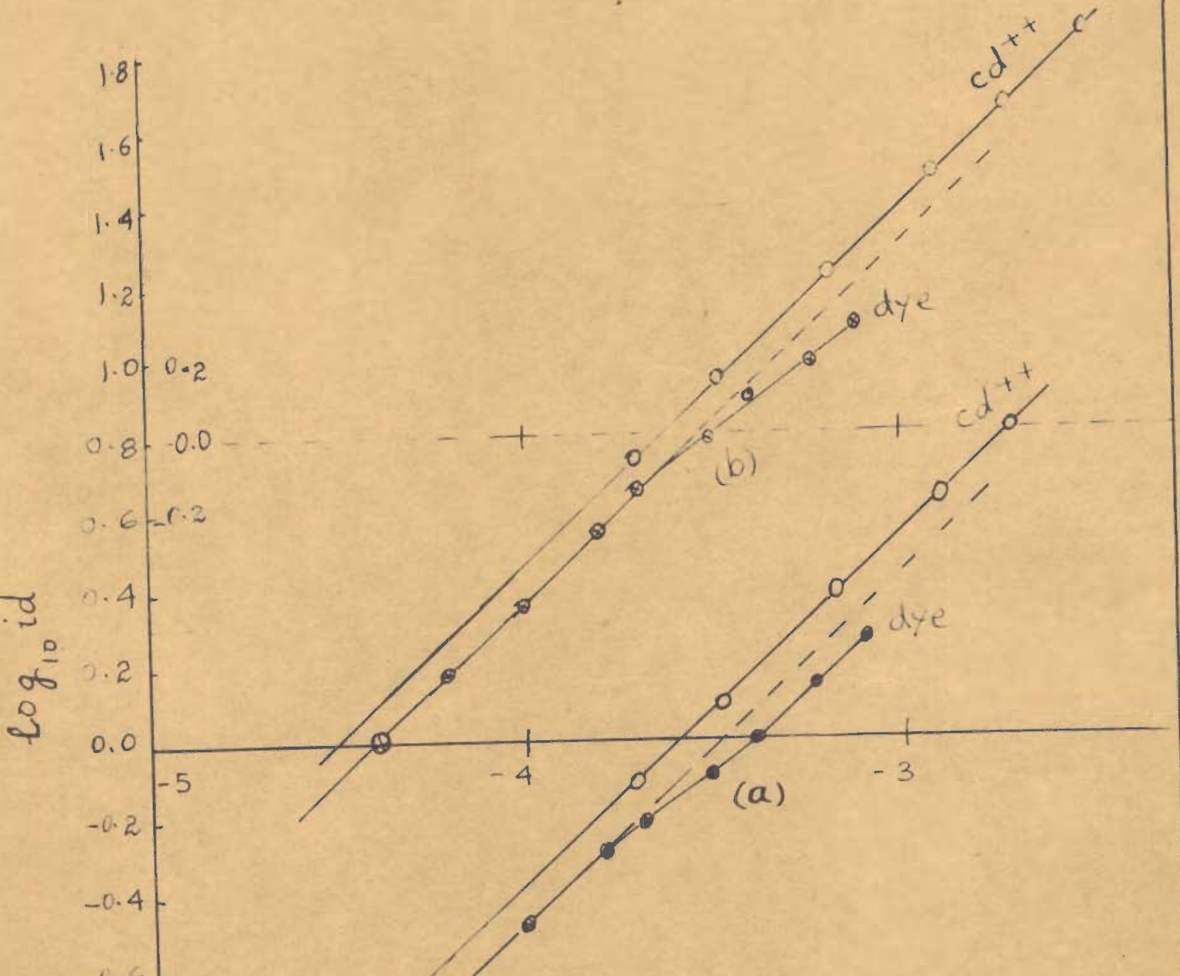


FIG. 29 PLOT BETWEEN $\log_{10} c$ AND $\log_{10} id$

(a) CRYSTAL VIOLET + 10% METHYL ALCOHOL

(b) ,, + 20% METHYL ALCOHOL

N = AGGREGATION NUMBER

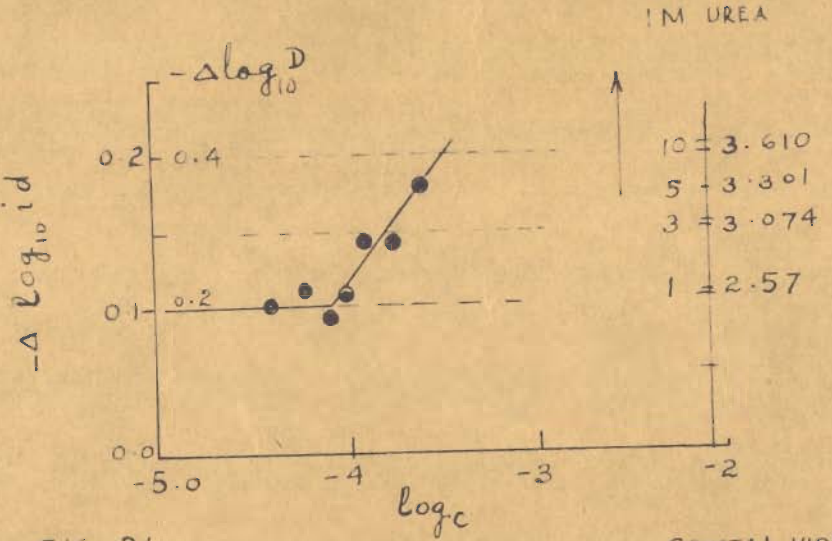


FIG. 31

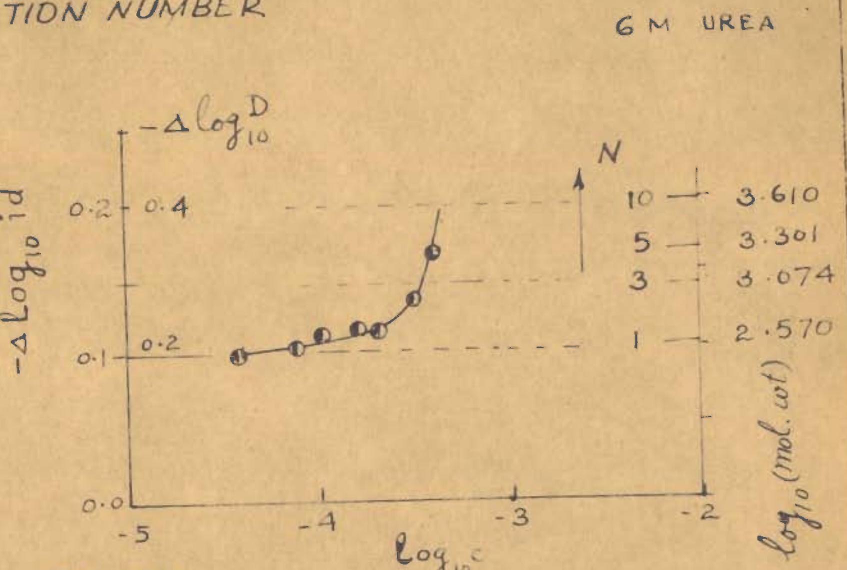


FIG. 33

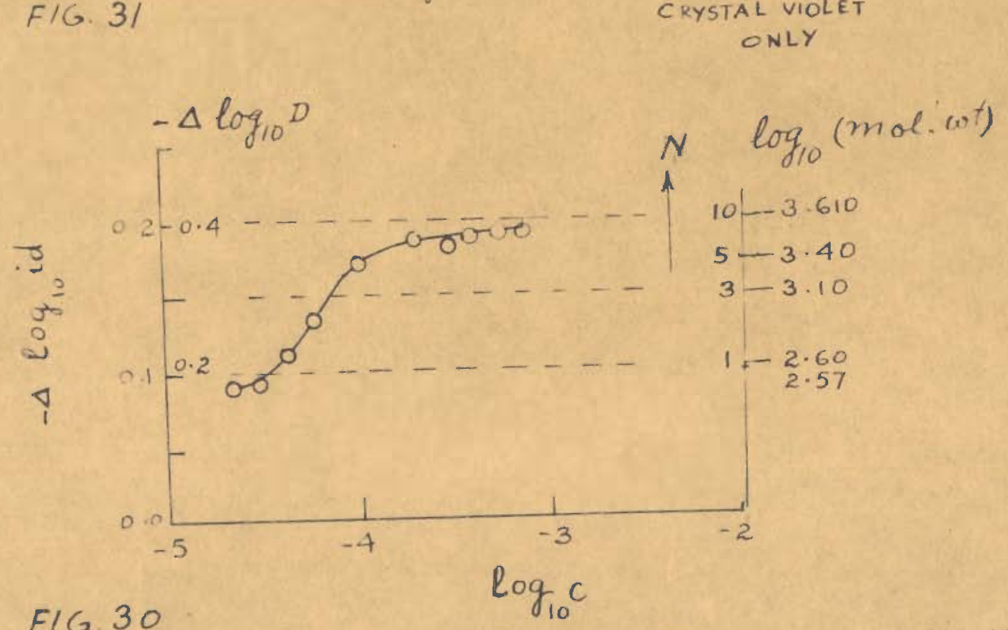


FIG 30

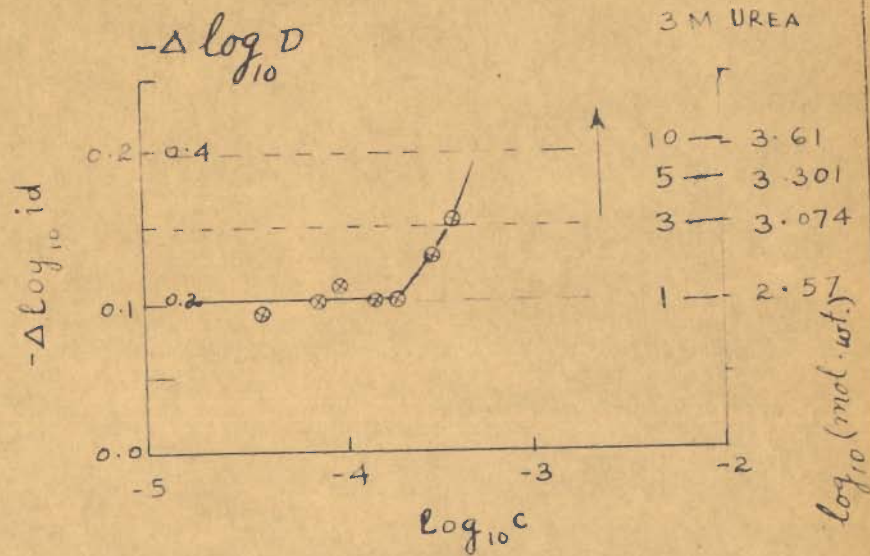


FIG. 32

EFFECT OF UREA ON AGGREGATION NUMBER OF CRYSTAL VIOLET

CRYSTAL VIOLET

0.6 M FORMAMIDE

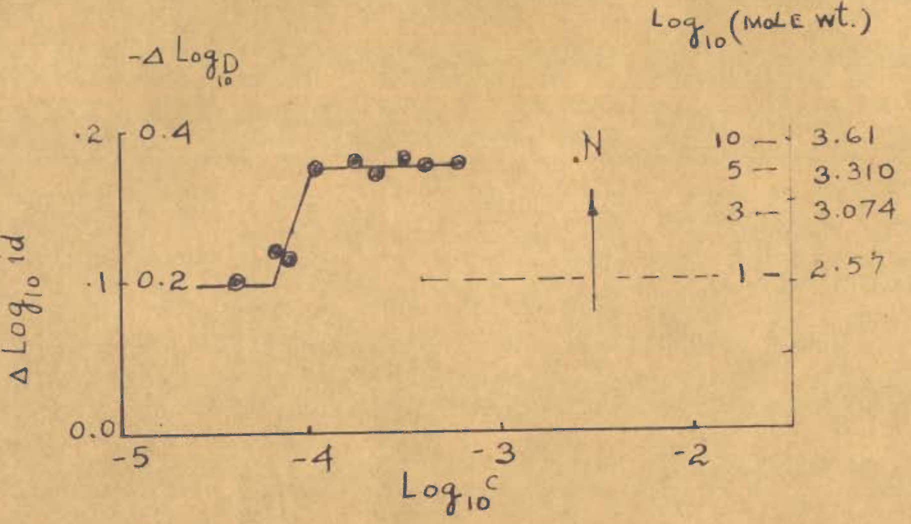


FIG. 34

10% METHYL ALCOHOL

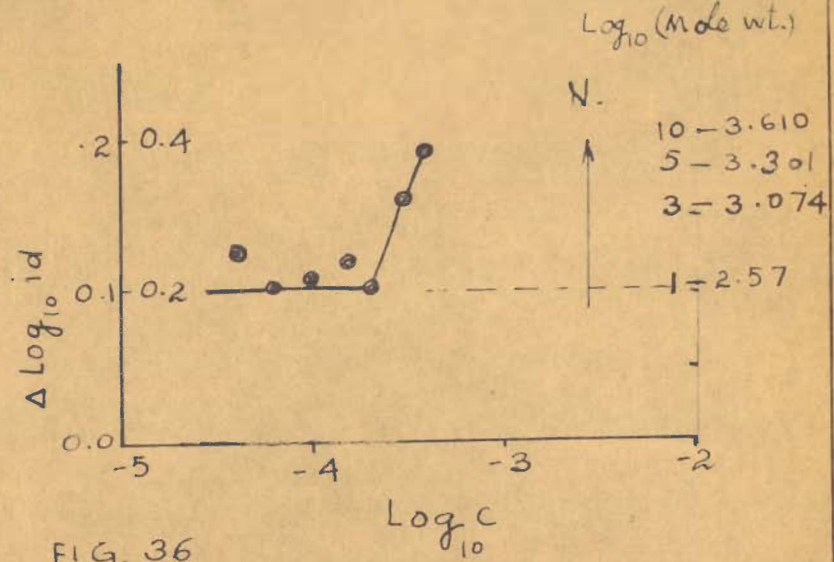


FIG. 36

1.2 M FORMOMIDE

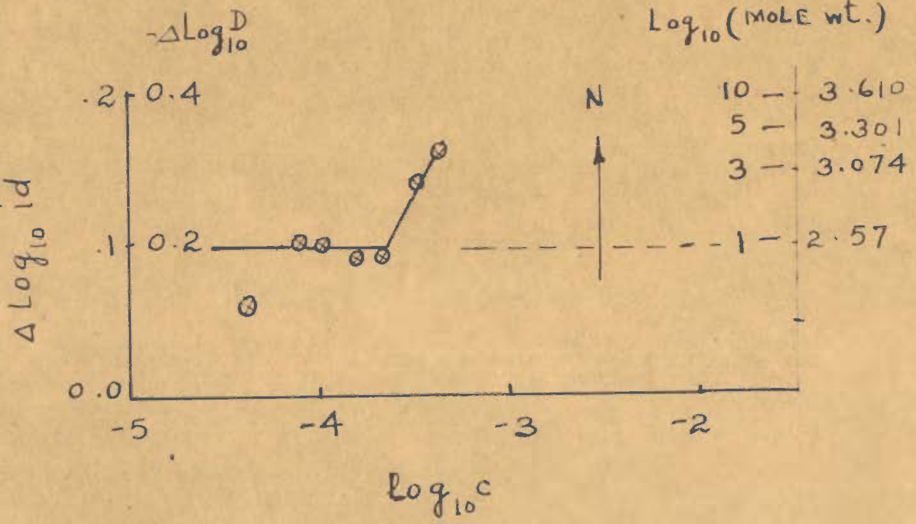


FIG. 35 EFFECT OF FORMANIDE ON AGGREGATEON

20% METHYL ALCOHOL

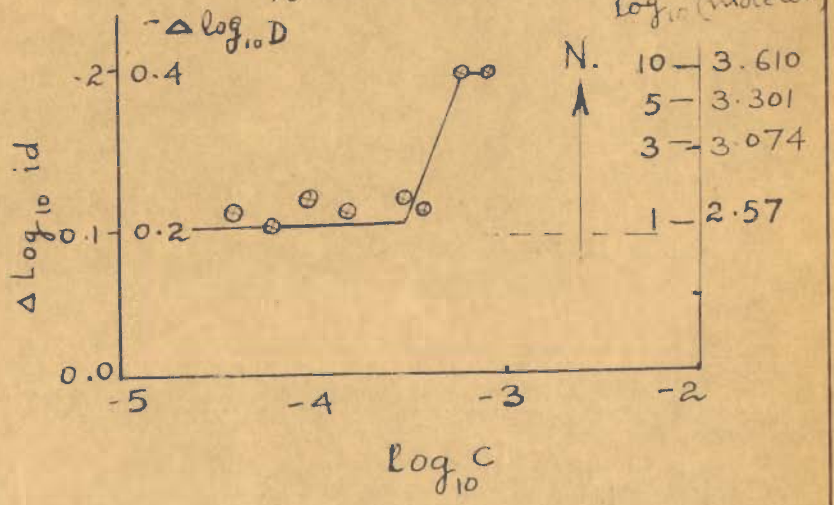


FIG 37 EFFECT OF METHYL ALCOLOL

RESULTS AND DISCUSSION

Assuming that the horizontal line in the plot of $-\Delta \log_{10} i_d$ vs. $\log_{10} c$ corresponds to the aggregation number equal to one and any deviation from it points towards the aggregation of the dye molecule (loc.cit.), the following information regarding the molecular state of the dye at different concentrations and in presence of various additives can be obtained:

CONGO RED:

It is seen from the fig.23, curve a, that congo red remains in an unaggregated form below 1.0×10^{-4}M. Beyond this concentration, there is an steep rise in the $-\Delta \log_{10} i_d$ vs. $\log_{10} c$ curve, thereby showing that the aggregation number varies widely within a narrow concentration range. The results given in table 1 reveal that a five fold increase in concentration brings about a tremendous increase in the aggregation number (7 to 1437).

Effect of urea and formamide on the aggregation number of congo red.

Table 1.

Dye conc. ($\times 10^{-4}$M)	Urea				Formamide		
	0.0	1.0M	3.0M	6.0M	0.6M	1.2M	2.4M
2.0	2	1	1	1	1	1	1
4.0	7	1	1	1	1	1	1
6.0	13	2	1	1	2	1	1
8.0	32	3	2	1	3	2	1
10.0	40.	20	5	2	4	3	1
20.0	1437	361	51	14	144	114	10
40.0	(With tendency to precipitate)	8080	1437	322	3216	2277	287

From the above table it is also evident that the aggregation numbers are very much effected in presence of the additives, the effect being most marked with urea and formamide. For example, the aggregation number is reduced from 40 to 20 in presence of 1M urea and the dye appears to exist as a dimer in 6M urea. Similarly the aggregation number of 1437 is reduced to 10 in 2.4M formamide.

Methyl alcohol also influences the aggregation number but its effect could only be realised at higher dye concentration (20.0×10^{-4}M) where a marked change from 1437 to 443 was observed with 10% alcohol.

CRYSTAL VIOLET.

From the plots of $-\Delta \log_{10} i_d$ vs. $\log_{10} c$ (Fig.30),it is seen that the dye remains in an unaggregated form at very low concentrations,4.0 $\times 10^{-5}$M (as against 1.0 $\times 10^{-4}$M for congo red). Moreover the deviation from the horizontal line is very little and the aggregation number (vide Table 2) does not go beyond 6 even with three fold increase in dye concentration. Unlike congo red the aggregation number does not go on increasing with concentration but assumes a constant value after an optimum dye concentration.

All the additives bring about a decrease in the aggregation number so much so that in presence of 3M urea 1.2M formamide,the dye exists as a dimer.

Table 2.

Effect of urea,formamide and methyl alcohol on the aggregation number of crystal violet.

Dye conc. ($\times 10^{-4}$M)	Urea				Formamide		Methyl alcohol	
	0.0	1.0M	3.0M	6.0M	0.6M	1.2M	10%	20%
0.4	1	1	1	1	1	1	1	1
0.6	2	1	1	1	1	1	1	1
0.8	3	1	1	1	1	1	1	1
1.0	5	1	1	1	5	1	1	1
2.0	6	4	1	1	5	1	1	1
3.0	6	6	2	2	5	2	3	1

The addition of methyl alcohol to the dye also brings about a reduction in the aggregation number. But here again this effect is realised at higher concentration

The effect of additives on the dye aggregation is more clearly observed by computing the data on aggregation point and dye concentration for an aggregate of a fixed number (1000 molecules in the case of congo red and 5 molecules in the case of crystal violet) of dye molecules.

Table 3.

Effect of urea and formamide on the aggregation point and concentration of an aggregate of 1000 molecules of congo red.

Additive	Additive conc.	Aggregation point (x 10^{-4}M)	Conc. of an aggregate (x 10^{-4} M)
Urea	0.0	1.0	20.0
	1.0 M	4.0	22.7
	3.0 M	6.0	36.4
	6.0 M	8.0	50.0
Formamide	0.6 M	2.0	31.7
	1.2 M	4.0	36.4
	2.4 M	10.0	50.0

From the above table it will be observed that both the aggregation point and dye concentration for aggregate is increased with the addition of increasing amount of the additive. Similar behaviour is observed with crystal violet as can be seen from the data in the following table.

Table 4.

Effect of urea,formamide and methyl alcohol on the aggregation point and concentration of an aggregate of 5 molecules of crystal violet.

Additive	Additive conc.	Aggregation point ($\times 10^{-4}$M)	Conc.of aggregate ($\times 10^{-4}$M)
Urea	0.0	0.4	1.0
	1.0 M	1.0	2.4
	3.0 M	2.0	5.0
	6.0 M	2.5	5.0
Formamide	0.6 M	0.6	1.0
	1.2 M	2.0	4.0
Methyl alcohol	10%	2.0	4.0
	20%	4.0	6.0

The increase in the aggregation point (and so also the concentration of the dye required to aggregate fixed number of molecules) can be explained on the basis of the breaking of the water structure by the addition of urea,formamide and methyl alcohol. Their addition not only brings about the weakening of hydrophobic bonding between the molecules of the dye aggregate but results in enhanced peptization. At higher concentrations where the dye would normally get precipitated, its dispersion in non-aggregated form takes place by the addition of substances which are well known for shifting the $nH_2O \rightleftharpoons (H_2O)_n$ equilibrium towards the left hand side.

The different additives influence the aggregation point to different extent. This may be attributed to factors like polymerization, dielectric constant, viscosity, interfacial tension etc. of the solutions of the additives. For example, amides which got polymerized at a lower concentration than urea can not be used in larger quantities to suppress aggregation.

Similarly in water-methanol system, few methanol molecules may penetrate into the aggregate due to the partition equilibrium bringing about disaggregation. Addition of large amounts, however, effects the solvent property and precipitation of the dye takes place with the result that aggregation point can not be shifted to high dye concentration.

The effect of urea seems to be quite general in preventing the aggregation of dye molecules of very different chemical constitutions. Mukerjee et.al. (12) observed that the solubility of orange OT, highly insoluble non-ionic azo dye is increased by a factor of roughly 10 in 10M urea. Alexander and Stacey (18) investigated several highly aggregating acidic and basic dyes and found that urea causes generally extensive disaggregation. Further Mukerjee et.al. pointed out that in the presence of urea,the transfer of methylene blue into a solid form or into a non-aqueous enviornment,or the association of methylene blue to form aggregates,are all less favourable because of less gain in entropy. They observed a marked lowering in the aggregation of pinacyanol chloride in presence of urea.

__oo__

REFERENCES

1. Vickerstaff,'The Physical Chemistry of dyeing (Oliver and Boyd,London),2nd edn.,Chapter 3 (1954).

2. Donnan and Haris,J.Chem.Soc. 99 ,1554 (1911).

3. Craven and Datyner,J.Soc.Dyers Col.,79 ,515 (1963).

4. Sheppard,S.E. and Geddes,A.L., J.Chem.Phys.13,63 (1945).

5. Rabinowitch,E. and Epstein,L.F.,J.Am.Chem.Soc. 63, 69 (1941).

6. Sheppard,S.E. and Geddes,A.L.,ibid. 66,2003 (1944).

7. Levschin,V.L. and Krotova,L.V.,opt.Spectry, (U.S.S.R.),13 ,457 (1962).

8. Sheppard,S.E.,Proc.Roy.Soc. (London) A 82 ,256 (1909)

9. Goddard,E.D.,Hoeve,C.A.J. and Benson,G.C., J.Phys. Chem.Soc. 61 ,593 (1957).

10. Goddard,E.D.,Benson,G.C.,Can.J.Chem. 35 ,936 (1957).

11. Schick,M.J., J.Phys.Chem.Soc. 67 ,1796 (1963), 68 ,3585 (1964).

12. Ghosh,A.K., Mukerjee,P., ibid. 67,193 (1963).

13. Frank,H.S. and Evans,M.W., J.Chem.Phys. 13 ,507 (1945).

14. Mukerjee,P. and Ray,A.,ibid. 67 ,190 (1963).

15. Holtzer,A. and Bruning,W., J.Am.Chem.Soc. 83 ,4865 (1961).

16. Whitney,P.L. and Tanford,C., J.Biol.Chem.237 , PC 1735 (1962).

17. Hilson,P.J. and McKay,R.B., Trans.Faraday Soc. 61, 375 (1965).

18. Alexander,P. and Stacey,K.A.,Proc.Ray,Soc. (London), A 212 ,274 (1952).

RESUME

RESUME

The utility of surface active agents in industry, technology,biology,medicine,agriculture etc. is being increasingly recognised. This recognition came through the painstaking researches on certain fundamental properties of surface active agents like,moderate maximum concentration of molecularly dispersed species,micelle formation,surface and interfacial depression,solubilization etc.. Most of the work on the above mentioned properties has been done with ionic surfactants and enough scope exists to carry out fundamental studies on non-ionic surfactants. Another aspect of the chemistry of surfactants which has not been satisfactorily investigated is the interaction between themselves or with other substances like dyes,proteins,clays,heavy metals,silicates,high polymers etc.. Investigations on these lines may form the basis of useful study both from the fundamental and applied viewpoint. The work described in the thesis incorporates the following of the above mentioned aspects: (i) the behaviour of non-ionic surfactants as polarographic maxima suppressors and their relative superiority to ionic surfactants, (ii) c.m.c.determination of non-ionic surfactants by polarography and spectrophotometry (iodine solubilization and spectral dye methods) and with the help of electrocapillary curves-a method which has not so far been used for c.m.c.determination and offer a new approach for extensive studies,(iii) quantitative studies on the binding of dyes with ionic surfactants carried out spectrophotometrically, (iv) polarographic estimation of ionic surfactants by determining the decrease in wave-height of dyes, (v) polarographic determination of aggregation number of dyes and the effect of additives,known for breaking the water structure, on the aggregation of dyes.

POLAROGRAPHIC MAXIMUM SUPPRESSION.

A comparative study on the efficacy of non-ionic and cationic surfactants in suppressing the polarographic maxima which are difficult to suppress in such cases as Pb^{++},Ni^{++},Co^{++}- Ni^{++} mixture in pyridine, Co^{++},CdI_2-KI complex,Cu-biuret,Cu-glycine complexes and U^{6+} in $KClO_3$ and phosphoric acid was studied. The following conclusions were arrived at:

(i) The non-ionic and cationic surfactants suppress both the positive and negative maxima with equal case.

(ii) The behaviour of non-ionic surfactants as maximum suppressors is not different from that of cationic surfactants, although in a few cases (e.g., maxima of Ni^{++}, Co^{++} and Pb^{++}) lesser quantity of non-ionics is required. Both type of surfactants are definitely superior to the anionic surfactants like alkyl aryl sulphonates, in the sense that much lesser quantities of these surfactants are required in suppressing the maxima which are not easily suppressed (pp.38-40).

(iii) Non-ionic surfactants have an extra advantage over the cationic ones in not undergoing chemical interaction with the depolarizer. Thus the cationic surfactants, cetyl trimethyl ammonium bromide (CTMAB) and cetyl pyridinium bromide (CPB) cannot be used for suppressing the maxima of CdI_2-KI complex due to precipitation. The maximum suppression point (M.S.P.) values of Nonidet P40, Nonex 501 are much lower (order 10^{-3} gms/l.) than lauric acid diethanolamine condensate (LDC) and Nonidet P42 (order 10^{-2} gms/l.) and follow the following order:

Nonex 501 $\geqslant$ Nonidet P40 $\gg$ Nonidet P42 $>$ LDC

(iv) The amount of the non-ionic and cationic surfactant required to suppress the maximum is dependent on the $E_{1/2}$ of the depolarizer. Those with $E_{1/2}$ in the vicinity of electrocapillary zero (e.c.z.) need very small amount of the surfactants. These surfactants have another advantage over the anionic surfactants in not being effected by the pH of the solution (pp.41,42).

(v) The pronounced maximum of U^{6+} in 0.05M $KClO_3$ and 3M phosphoric acid is suppressed with a very small amount of non-ionic and cationic surfactants without bringing about either any distortion or irreversibility in the polarographic wave or any shift in $E_{1/2}$ and i_d(p.42).

EFFECT OF NON-IONIC AND CATIONIC SURFACTANTS ON THE ELECTROCAPILLARY CURVES IN KCl.

It is observed that the gradual addition of these surfactants bring about a shift in the e.c.z.resulting in the distortion of the symmetry of the electrocapillary curves. The shape of these curves also provide evidence of desorption in the region where the curves merge with the normal one (pp.43,44).

With cationic surfactants like CTMAB,the shift in e.c.z.towards the positive potential is smaller than that observed in the case of non-ionic surfactants. From this it may be concluded that the non-ionic surfactants get more strongly adsorbed at the mercury surface than the cationic surfactants.

An altogether different behaviour,however,is observed in the case of LDC where the top of electrocapillary curve starts gradually flattening without bringing about a shift in e.c.z. (p.45).

The experimental evidence regarding the need of smaller amount of non-ionic surfactant in comparision to cationic ones can be explained in terms of greater adsorbability of non-ionic surfactants and their effect in bringing about large positive shift in e.c.s..

C.M.C.DETERMINATION OF NON-IONIC SURFACTANTS:

The polarographic and electrocapillary curves data described above were used to determine the c.m.c.values of non-ionic surfactants. The plots between $i_{maximum}$ / $i_{diffusion}$ and logarithms of surfactant concentration give two polarographic characterstics of the surfactants, viz.,polarographic micelle point (P.M.P.),and maximum suppression point (M.S.P.). The former is obtained from the point where the first discontinuity appears in the curve while the latter is determined by extrapolating the curve to $i_{maximum}/i_{diffusion} = 1$ (pp.75-77).

It is found that the P.M.P. values differ very littl from each other irrespective of the cations used or the supporting electrolyte added. These values range within narrow limits. For example,the range of the P.M.P.values lies between 0.8 and 3.0×10^{-3} gms/l.; 1.60 and 3.80×10^{-3} gms/l., and 7.84 and 15.40×10^{-3} gms/l. for Nonex 501,Nonidet P40 and Nonidet P42 respectively. Similar behaviour is observed with LDC,inspite of the fact that LDC is not so effective a maximum suppressor. The pH of the solution also does not markedly influence the P.M.P.values.

The P.M.P.and M.S.P. values can both be correlated to the c.m.c. of the surfactants,although it is usual to correlate it with the former. Any how the P.M.P.values are much lower than the c.m.c. values obtained by other methods like,iodine solubilization, spectral dye, and surface tension methods,which,incidently compare favourably with each other (p.80).

The c.m.c.of the surfactants can be found by the electrocapillary curves method. The plots of drop time vs.log concentration,show an initial slow change followed by a sharp decrease in drop time until a concentration of 10^{-3} gms/l. is reached,when the curves show the signs of flattening out. Since flattening sets in at the same concentration range irrespective of the potential applied, this concentration can be taken as the point of incipient micelle formation (p.80).

Unlike the polarographic method,the c.m.c.values determined by this method compare favourably with those obtained by iodine solubilization,spectral dye and surface tension methods. The small discrepency may be attributed to the presence of electrolyte,KCl. The importance of electrocapillary curves method can be all the more emphasised when dealing with non-ionic surfactants which have low c.m.c. values.

SPECTROPHOTOMETRIC STUDIES ON SURFACTANT-DYE INTERACTION

The quantitative studies on the interaction of anionic surfactants with basic dyes (malachite green, rhodamine 6G and rosaniline hydrochloride) and that of cationic surfactants with acid dye (congo red) were studied spectrophotometrically at different pHs. The spectral shift in the dye (both acedic and basic) maximum as well as an increase in absorbence on the addition of either anionic or cationic surfactants can be explained on the basis of the formation of the surfactant-dye complex after giving due allowance to intermolecular and interamolecular changes accompanying pH variations of the medium. The extent of binding was calculated by Klotz's method (vide J. Amer. Chem. Soc. 68 ,2299 (1946)).

From the results on the binding of malachite green and rhodamine 6G with anionic surfactants,it may be seen that small amount of dioctyl sodium sulpho succinate (Manoxl OT) is needed for the complete binding of the dye (p.126) whereas relatively larger amount of DS is required under the similar conditions (p.126). With rosaniline hydrochloride the behaviour is altogether different. Small amount of either of the surfactant is sufficient for the complete incorporation of the dye into the surfactant micelle.

The surfactant-dye interaction can be used to determine the amount of surfactant bound per molecule of dye from the plots between absorbence and surfactant concentration assuming that all the dye got bound with the surfactant at the inflexion point (p.127). Since these levelling off points are at concentrations higher than the c.m.c. (pp.140,141),it can be concluded that the surfactant interact with the dye only in the form of micelle. Assuming that 1:1 interaction between surfactant and rhodamine 6G and malachite green takes place,it may be inferred that the surfactant micelle interacting with the dye is made up of 100 surfactant anions. In the case of rosaniline hydrochloride, 1:3 dye-surfactant complex is formed resulting a possession of three surfactant micelles per dye ion, having about 66 surfactant molecules in each micelle (pp.128,129).

In the case of cationic surfactants and acid dye, a large shift in dye maximum was observed at pH 2.0 (from 560 to 460 mμ) by the addition of small amount of CTMAB or CPB. At pH 7.0 and 9.12, an insoluble dye-surfactant complex was found to be formed which got solubilized in excess of the surfactant (pp.131,132).

At pH 2.0, the extent of binding was calculated using Kltoz's formula. Absorption studies on cationic surfactants at this pH go to show that three molecules of CTMAB and four molecules of CPB are required to solublize the in soluble dye-surfactant complex formed at pH 7.0 and 9.12 (p.138).

POLAROGRAPHIC ESTIMATION OF IONIC SURFACTANTS

Polarographic reduction of dyes, viz., congo red and alizarin Red S with CTMAB and CPB and that of methylene blue in presence of DS and Manoxl OT provided the following information:

(i) Congo red is reduced by four electron transfer reaction while alizarin Red S and methylene blue by two electron transfer reaction.

(ii) A gradual decrease in the limiting current is observed by the addition of increasing concentration of the surfactants in the form of the precipitate of an insoluble dye-surfactant complex.

(iii) A linear behaviour is observed from the plots between decrease in wave height and surfactant concentration.

(iv) When stoichiometric amounts or excess of the dye is present, a fine precipitate settles out slowly. Excess of the surfactant reduced the flocculation resulting in the formation of a stable suspension non-reducible at the d.m.e..

(v) The binding ratio of congo red and alizarin Red S with CTMAB and CPB and that of methylene blue with Manoxl OT can also be computed from the polarographic data. In all the cases, the surfactant-bound dye ratio is found to be independent of the surfactant (pp.153-160). The binding ratios are 1:2 for congo red CTMAB or CPB; 1:10 for alizarin Red S-CPB; 2:1 for alizarin Red S-CTMAB mixtures. From these ratios it can be concluded that alizarin Red S has a greater affinity for CTMAB than CPB.

Some interesting results were obtained by the interaction of methylene blue with DS. In this case a second wave of constant height appears after the normal reduction wave in the mixtures containing excess of DS. The existence of the second wave of constant can be explained on the assumption that the dye-surfactant complex formed, gets adsorbed on the d.m.e. in excess of the surfactant. Moreover a shift in half wave potential towards the more positive side is observed. In cases where much higher concentration of the surfactant is used and anodic step is also realised (pp.161,162).

The computation of polarographic data in this case reveal that 0.2 mole of Manoxl OT is bound with one mole of the dye (p.161).

POLAROGRAPHIC DETERMINATION OF AGGREGATION NUMBER OF DYES AND THE EFFECT OF ADDITIVES ON THE AGGREGATION.

The aggregation number of two dyes, viz., congo red and crystal violet with and without presence of additives known for breaking the water structure was studied by polarographic method.

From the plot of the difference of logarithms of diffusion currents of Cd^{++} ions and dye ($-\Delta \log_{10} i_d$) vs. logarithms of dye concentration ($\log_{10} c$), the aggregation point and the aggregation number were calculated. It is observed that congo red remains in an unaggregated form below 1.0×10^{-4}M beyond this concentration, there is an steeprise in the $-\Delta \log_{10} i_d$ vs. $\log_{10} c$ curve, thereby showing that the aggregation sets in very rapidly. Five fold increase in concentration brings about a tremendous increase in the aggregation number (7 to 1437), although in the latter tendency for precipitation exists (p.182).

The addition of increasing amounts of urea and formamide lowers the aggregation number greatly. For example, the lowering in aggregation number from 40 to 20 takes place with 1M urea while the dye exists as a dimer in 6M urea at concentration 10.0×10^{-4}M. Similarly the aggregation number of 1437 is reduced to 144 in 0.6M formamide and 10 in 2.4M formamide at dye concentration 20.0×10^{-4}M (p.182).

It is seen from the $-\Delta \log_{10} i_d$ vs. $\log_{10} c$ curve, that crystal violet remains in the unaggregated form below 4.0×10^{-5}M. At higher concentration, upward deviation is observed but unlike congo red is limited to a small concentration range. Thus with tenfold increase in dye concentration,aggregation number attains the maximum value of six. As before the additives lower the aggregation number of the dye (p.183).

The effect of methyl alcohol also influences the aggregation number of congo red and crystal violet but this effect is realised only at the higher dye concentration. Likewise the aggregation point and the concentration of the dye required to form an aggregate of a fixed aggregation number (1000 dye molecules in case of congo red and 5 molecules in the case of crystal violet) is shifted towards the higher concentration range by the presence of urea, formamide and methyl alcohol (pp.154, 185).

The results has been explained on the basis of the breaking of the water structure by the addition of urea, formamide and methyl alcohol resulting in the loosening of the hydrophobic bonds in the dye aggregates.

--oo--

LIST OF PUBLICATIONS

1. Lauric acid-diethanolamine condensate as a polarographic maximum suppressor. Anal. Chem. 37 ,1592 (1965) Presented in Annual Session of National Academy of Sciences held at Mazzafar Pur in 1965.

2. Critical micelle concentration of lauric acid-diethanolamine condensate by polarographic and spectrophotometric methods: A comparative study. J. Amer. Oil Chemists Soc. 43 ,446-448 (1966). Presented in 21st Annual Session of Oil Technologists Association of India held at Kanpur, 1966.

3. Critical micelle concentration determination of non-ionic surfactants by electrocapillary curves. Talenta (In Press). Presented in the Symposium on 'Electrode Processes' held at Jodhpur in 1966, (communicated)

4. Effect of urea, formamide and methyl alcohol on the aggregation of congo red and crystal violet by polarographic method, (communicated). Presented in the VIth Seminar of Electro-chemistry held at Karaikudi in 1965.

5. Quantitative studies on surfactant-dye interaction (communicated). Presented in Annual Session of National Academy of Sciences held at Agra, 1966.

6. Polarographic estimation of ionic surfactants. Presented in 54th Annual Session of Indian Science Congress held at Hyderabad in 1967.

--

Reprinted from **ANALYTICAL CHEMISTRY**, Vol. 37, Page 1592, November 1965

Lauric Acid–Diethanolamine Condensate as a Polarographic Maximum Suppressor

SIR: A number of communications (*4–7*) have discussed the importance and utility of soaps (sulfonated phenyl, xylyl, and tolyl stearic acids, dodecyl and dodecyl benzene sulfonates, dodecyl pyridinium bromide, and isothiourea dodecyl ether hydrobromide) in suppressing the polarographic maxima of simple and complex metal ions which are not ordinarily suppressed by the usual maximum suppressors. In addition to the anionic and cationic soaps, nonionic soaps may also be used for this purpose. However, very few references describe this approach and those available refer to commercial products. Therefore, investigations on the use of these compounds in polarographic work was considered worth undertaking. This communication describes the results from the use of a simple nonionic soap, lauric acid–diethanolamine condensate (LDC), in suppressing the polarographic maxima of Pb^{+2}, Ni^{+2}, Co^{+2}, Ni^{+2}–Co^{+2} mixture, iodide cadmium complex, copper biuret, copper succinimide, and copper glycine complexes. Data on the influence of LDC on the electrocapillary curves of the dropping mercury electrode (d.m.e.) in suitable supporting electrolytes have been included to demonstrate the superiority of nonionic soaps in polargraphy.

EXPERIMENTAL

Reagents. LDC (*8*) was prepared by condensing pure lauric acid (BDH) with diethanolamine. Biuret (*2*) and succinimide (*9*) were prepared in the laboratory. Analytical reagents and chemically pure reagents were used in all the experiments. Double distilled water (all glass) was used in making the solutions. Triple distilled mercury was used for the dropping mercury electrode.

Table I. Relative Effectiveness of Ionic and Nonionic Soaps as Maximum Suppressors

Ions or complexes	LDC $10^{-5}M$	SPSA $10^{-5}M$	STSA $10^{-5}M$	SXSA $10^{-5}M$	DPB $10^{-5}M$	IDEH $10^{-5}M$
Pb^{+2} in KNO_3	2.0	23.5	23.8	12.1	6.17	7.38
Ni^{+2} in KCl	7.0	43.9	56.01	56.01	7.38	7.38
Co^{+2} in KCl	9.0	24.0	107.8	56.01	23.8	7.38
Co^{+2}–Ni^{+2} in pyridine	200.0	555.0	23.8	32.71	4.95	. . .
CdI_2–KI complex	10.0	238.0	23.8	23.8	14.55	8.599
Cu–biuret	6.0	83.3	60.5	4.9	4.95	34.88
Cu–glycine	9.0	16.9	60.05	6.05	6.172	7.38
Cu–succinimide	12.5	. . .	. . .	. . .	. . .	. . .

LDC = Lauric acid–diethanolamine condensate
SPSA = Sulfonated phenyl stearic acid
STSA = Sulfonated tolyl stearic acid
SXSA = Sulfonated xylyl stearic acid
DPB = Dodecyl pyridinium bromide
IDEH = Isothiourea dodecyl ether hydrobromide

Apparatus. The polarographic measurements were made using a Heyrovsky polarograph (No. Lp 55A) in conjunction with a Pye scalamp galvanometer (No. 7903/5). All measurements were carried out at 25° ± 0.1° C. in the water thermostat.

Procedure. Polarographic measurements were made after adding a known volume of the metal salt or complex metal ion solution to the polarographic cell, adding the supporting electrolyte, and making up the total volume to 20 ml. The solutions were deaerated by bubbling purified nitrogen gas through them for about 20 to 30 minutes. The polarogram was taken, and the process was then repeated in the presence of the nonionic soap. An increasing amount of soap was added until the maxima were completely eliminated. For studying the effect of soap on the electrocapillary curves, a known volume of the ion to be reduced was added to the polarographic cell and mixed with suitable supporting electrolyte. The drop time with and without the soap was measured between the potential range −0.0 volt to − 1.0 volt.

RESULTS AND DISCUSSION

Lauric acid–diethanolamine condensate is a useful maximum suppressor for a number of metal and complex ions

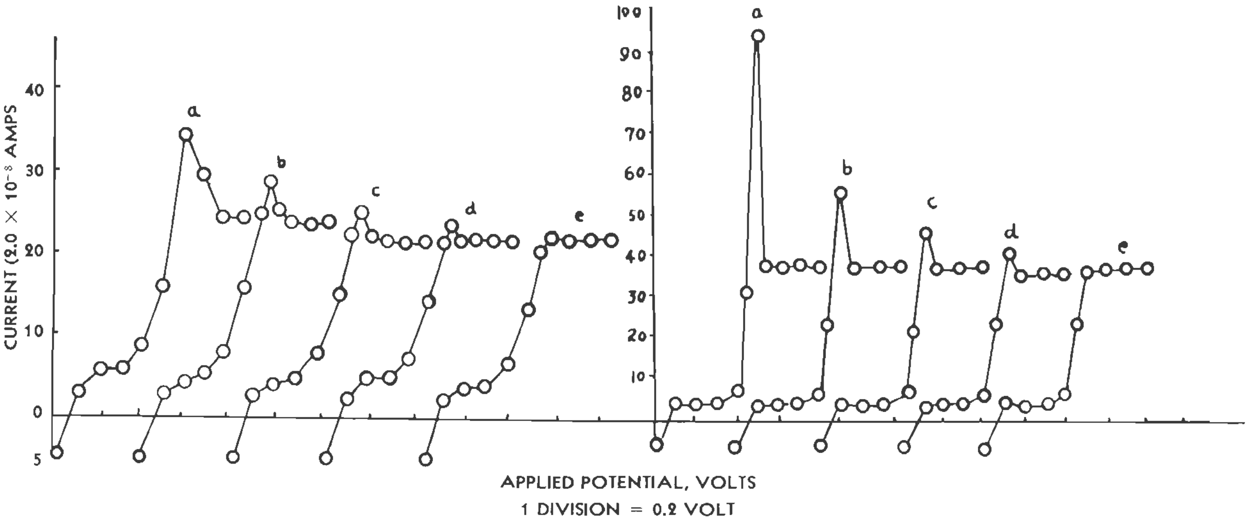


Figure 1. Effect of LDC concentration on suppression of maxima

A: 2.5 × $10^{-3}M$ $CuSO_4$ in 2.5 × $10^{-2}M$ biuret at
Concn. of LDC in *a*. None
b. 2.0 × $10^{-5}M$
c. 3.0 × $10^{-5}M$
d. 5.0 × $10^{-6}M$
e. 6.0 × $10^{-5}M$
Each curve starts at −0.0 volt

B: 2.5 × $10^{-3}M$ CdI_2 in 0.1M KI at
Concn. of LDC in *a*. None
b. 2.5 × $10^{-5}M$
c. 5.0 × $10^{-5}M$
d. 8.75 × $10^{-5}M$
e. 10.0 × $10^{-6}M$
Each curve starts at −0.3 volt

whose maxima could not be suppressed by the surfactants usually employed. For example, Kolthoff and Lingane (*3*) found that the iodide–cadmium complex gave a pronounced maximum which was difficult to suppress. Addition of LDC of concentration as low as 10.0 × $10^{-5}M$ could suppress the wave ($E_{1/2}$ = − 0.7 volt) without changing its reversible nature (Figure 1).

In our early investigations (*4–7*), it was found that the cationic soaps generally suppress the negative maxima and the anionic soaps eliminate the positive ones. LDC has an extra advantage over these suppressors because it can suppress both the positive (Pb^{+2}, copper biuret, and copper glycine complexes) and the negative (Ni^{+2}, Co^{+2}, Ni^{+2}–Co^{+2} mixture, iodide cadmium complex, and copper succinimide complex) maxima although it appears to be more sensitive toward the positive maxima. For example, the amount of LDC (2.0 × $10^{-5}M$) required to suppress the positive maxima (Pb^{+2}) is quite small in comparision to the amount of LDC (9.0 × $10^{-5}M$) required to suppress the negative maxima (Co^{+2}). Similar behavior has been observed in the case of copper glycine and copper biuret complexes (Figure 1). Moreover, a much smaller amount of the reagent is required for suppression as compared to the anionic and cationic soaps (Table I).

From Table I it is seen that a sufficiently large amount of anionic soap is required to eliminate the maxima, in comparison to LDC. It appears that in the higher pH range, the sulfonate ion of alkyl-aryl, dodecyl, and dodecyl benzene sulfonates causes increased repulsion at the d.m.e., with the result that a large quantity of the soap is required. No such effect is observed with LDC which is nonionic and is easily adsorbed at the mercury drop–solution interface as is evident from the electrocapillary curves studied in different supporting electrolytes. Figure 2 illustrates a typical case of the electrocapillary curve in 0.1*M* KNO_3, with and without the addition of LDC. The soap decreases the drop time to a great extent and a maximum decrease is observed as the potential reaches the electrocapillary maximum potential (−0.55 volt). Moreover, one observes a fairly large flat portion of the curve, which is characteristic of nonelectrolytes (*1*). Both observations—i.e., decrease in drop time and the appearance of a flat portion in the electrocapillary curve—indicate large adsorption of the soap. Ionic soaps do not behave in this manner.

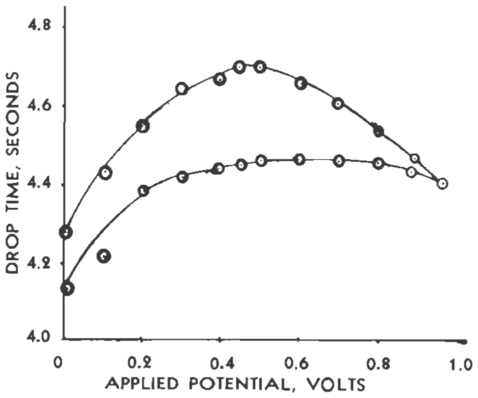


Figure 2. Electrocapillary curve

A. Without soap
B. With soap

Table II. Drop Time at Different Potential in Copper Glycinate + LDC Mixture in Supporting Electrolyte (KNO_3)

Potential volt	Copper glycinate +0.1*M* KNO_3 *t*, sec.	Copper glycinate + 0.1*M* KNO_3 + soap (9.0 × $10^{-6}M$)
−0.0	4.28	4.14
−0.1	4.43	4.22
−0.2	4.55	4.38
−0.3	4.65	4.42
−0.4	4.67	4.46
−0.5	4.7	4.46
−0.6	4.65	4.46
−0.7	4.60	4.45
−0.8	4.58	4.46
−0.9	4.52	4.44
−1.0	4.40	4.40

The effect of the soap concentration on the diffusion current also supports the above views. Just a slight excess of the soap considerably decreases the diffusion current without affecting $E_{1/2}$, and beyond a concentration of 5.0 × $10^{-4}M$ the polarographic wave vanishes althogether. It may, therefore, be concluded that LDC is strongly adsorbed at the mercury drop–solution interface.

LITERATURE CITED

(1) Frumkin, A., "Polarography," Kolthoff, I. M., ed., **Vol. I,** p. 143, Interscience, New York, 1952.
(2) Howorth, R. C., Mann, F. G., *J. Chem. Soc. (London)* **1943,** 603.
(3) Kolthoff, I. M., Lingane, J. J., "Polarography," 2nd ed. p. 509, Interscience, New York, 1952.
(4) Malik, W. U., Haque, R., ANAL. CHEM. **32,** 1528 (1960).
(5) Malik, W. U., Haque, R., *Z. Anal. Chem.* **180,** 425 (1961).
(6) Malik, W. U., Haque, R., *Naturwiss.* **49,** 346 (1963).
(7) Malik, W. U., Kafoor Khan, H. A., *Ind. J. Chem.* **2** (11) 455 (1964).
(8) Schwartz, A. M., Perry, J. M., "Surface Active Agents and Detergents," p. 212, Interscience, New York, 1949.
(9) Vogal, A. I., "Practical Organic Chemistry," p. 790, Longmans, Green, London, 1947.

WAHID U. MALIK
PURAN CHAND

Department of Chemistry
Roorkee University
Roorkee, India

The authors are grateful to C.S.I.R. (India) for the award of a fellowship to one of us (P. C.) to carry out this work.

PRINTED IN U. S. A.

Reprinted from the JOURNAL OF THE AMERICAN OIL CHEMISTS' SOCIETY, Vol. 43, No. 7, pp. 446–448

Critical Micelle Concentration of Lauric Acid-Diethanolamine Condensate by Polarographic and Spectrophotometric Methods: A Comparative Study

WAHID U. MALIK and PURAN CHAND, Chemical Laboratories, University of Roorkee, Roorkee, India

Abstract

The critical micelle concentration (cmc) values of surfactants obtained by different physical methods do not show any concordance especially in cases when determinations are made in presence of electrolytes. With lauric acid-diethanolamine condensate, the behavior is altogether different.

A comparison of the spectrophotometric and polarographic determinations, with and without the presence of extraneous electrolytes reveals that the cmc values in both cases are almost similar. The results indicate that the cmc values of nonionic surfactants are not affected by acids, bases and salts when added in low concentrations.

Introduction

NONIONIC SURFACTANTS of the fatty acid-diethanolamine condensate type, particularly lauric acid-diethanolamine condensate, have found wide application in detergent formulations and cosmetics as foam builders (1) for alkylaryl sulfonates, lime soap dispersing agents (2), softening agents (3), and principal ingredients in shampoos for controlling the viscosity, elasticity and stability of the fluid (4). These compounds also find use in industry and technology for the preparation of agricultural emulsions and textile treating compounds (5) and flotation materials (6). The mixtures of lauric acid-diethanol amine condensate with alkylaryl benzene sulfonates also find use in the preparation of liquid household washing compositions (7). In contrast to ionic surfactants, these compounds are indifferent to hard water and to salts, acids and bases (8).

From the purely physicochemical viewpoint, we have shown that the lauric acid-diethanolamine condensate (LDC) can be usefully employed as a suppressor of polarographic maxima (12) of difficult suppressable metal and complex ions with much smaller amounts of LDC than anionic or cationic surfactants.

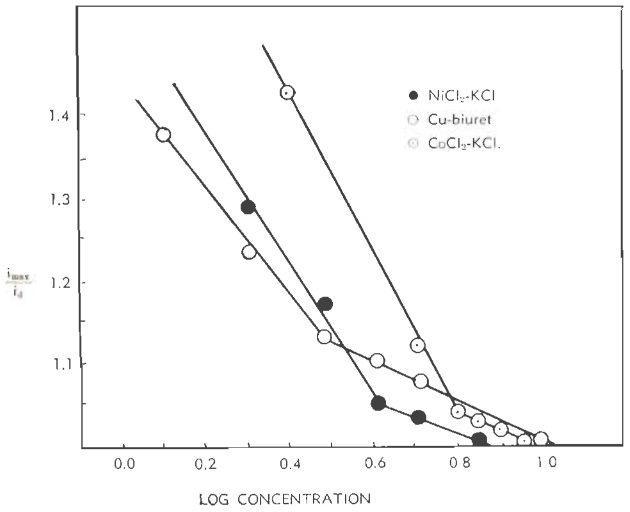


FIG. 1. Plots between log conc. and 'maximum/'diffusion current.

Another interesting aspect of the study on nonionic surfactants can be the determination of critical micelle concentration (cmc) of the surfactants as such and in the presence of extraneous electrolytes. Since nonionic surfactants should be less susceptible to the effect of the foreign ions, there should not be much difference in the cmc values obtained with and without the electrolytes. That is, the cmc values of LDC obtained by the polarographic method in different supportnig electrolytes (used in polarographic reduction) should be comparable among themselves and with the values obtaind by the spectrophotometric method. The work described in this paper was done with this object in view.

Experimental

Materials

LDC (9) was prepared by condensing pure lauric acid (BDH) with diethanolamine. AR and "chemically pure" reagents were used in all the preparations. Biuret (10) and succinamide (11) were also prepared in the laboratory. Double distilled water (all glass) was used in preparing the solutions.

Apparatus and Procedure

The polarographic apparatus and procedure used in this investigation are described in detail elsewhere (12). All the measurements were carried out at 25C ± 0.1C in a thermostated water bath. A Beckman pH meter model H was used for all pH measurements.

The polarographic micelle concentration (pmp) (13) obtained by plotting $i_{maximum}/i_{diffusion}$ vs. log concentration of LDC and taking the point where first sharp discontinuity appears and the maximum suppression point (MSP) (14) obtained by plotting $i_{maximum}/i_{diffusion}$ vs. log concentration of LDC and extrapolating to unity are shown in Figure 1.

For determining cmc by the iodine solubilization method of Ross and Olivier (15), absorption measurements were made by a Bausch and Lomb Spectronic-20.

The stock solution of iodine (A) was prepared of concentration 10^{-3} M. The stock solution of the nonionic surfactant (B) whose cmc was to be determined, contained a known concentration 10^{-3} M) of the surfactant well above its cmc. By diluting the solution (B) with solution (A), a wide range of concentrations of surfactant could be obtained containing a fixed concentration of iodine. The mixture thus comprised solutions of concentration above and below the cmc to be determined. The spectrophotometer readings are best made with solution A as the standard for 100% transmittance, although the pure solvent (distilled water) could be used.

The spectrophotometric measurements were made at a wavelength of 360 $m\mu$ (iodine-micelle complex

TABLE I

Comparative Values (Order 10^{-5}M) of MSP and PMP for LDC, SPSA, STSA and SXSA

Ions or complexes	pH	LDC		SPSA		STSA		SXSA	
		MSP	PMP	MSP	PMP	MSP	PMP	MSP	PMP
Pb^{+2} in KNO_3	5.15	1.99	1.00	17.38	9.80	5.62	2.18	3.80	1.29
Co^{+2} in KCl	2.95	8.99	5.99	17.38	4.90	120.20	34.67	83.18	10.47
Ni^{+2} in KCl	4.92	6.99	3.98	43.65	8.20	50.12	48.98	50.12	36.31
$Co^{+2}Ni^{+2}$ in pyridine	....	175.00	100.00	363.10	121.00	20.89	4.89	20.89	4.78
CdI_2 —KI complex	6.03	9.26	2.50	169.80	12.10	15.85	7.94	15.85	5.37
Cu-Glycinate	10.50	9.12	2.00	16.80	4.90	5.11	4.26	5.11	3.98
Cu-biuret	12.04	9.80	3.00	83.30	13.20	12.02	2.39	2.81	1.95
Cu-succinimide	11.50	12.50	4.99	....	....	....	....	....	....

LDC = Lauric acid —diethanol amine condensate.
SPSA = Sulfonated phenyl stearic acid.
STSA = Sulfonated tolyl stearic acid.
SXSA =Sulfonated xylyl stearic acid.

maximum). It was always found important to take the reading within an hour of the preparation of solutions, because of a slow fading of the color of iodine-micelle complex.

Results and Discussion

The results of the polarographic micelle concentration (pmp) and the maximum suppression point (MSP) values of LDC are given in Table I (Fig. 1).

The MSP values are almost of the same order (10^{-5}M) except for the Ni^{+2} $-Co^{+2}$ mixture in pyridine where a very high concentration of the LDC (10^{-4}M) is required to suppress the polarographic maxima. A similar discrepancy is observed in the case of PMP values for the Ni^{+2} $-Co^{+2}$ mixture in pyridine, otherwise the PMP values for other ions lie in the same concentration range, viz., 10^{-5}M. Although the order of the MSP and PMP values in the presence of different supporting electrolytes is $Cl^- > I^- > NO_3^-$, the values do not differ much from each other as observed in the case of ionic surfactants (Table I). Our results are in agreement with those of Hsiao and co-workers (16) and also of Schick (17) on polyoxyethylated nonionic compounds who showed that the cmc values of ionic surface active agents are lowered to a greater extent in presence of electrolytes than that of nonionic compounds.

The PMP values obtained in the higher pH range (pH 12.00) in the case of the polarograms for copper biuret and copper succinamide complexes also do not exhibit any appreciable deviation from the values obtained in the lower pH range (the pH in presence of the salts used as supporting electrolytes are in the range of pH 2.92 – 6.03). It may thus be concluded that like the salts, the pH also does not affect the cmc values of LDC. On the other hand, there is a large effect of pH on the PMP values in the case of ionic surface active agents (Table I).

Malik and co-workers (18,19) explained the results on the MSP and PMP values of alkylaryl sulfonates in the higher pH range on the basis of enhanced dissociation of the soap resulting in increased repulsion at dropping mercury electrode (dme). Such factors, however, cannot be operative in nonionic surfactants.

TABLE II

Comparative cmc Values of LDC, SPSA, STSA and SXSA by Different Methods

Method	cmc values (order 10^{-5}M)			
	Without electrolyte	KCl	KNO_3	KI
Polarographic				
LDC	. ...	3.98	1.00	2.50
SPSA	......	8.20	9.80	12.10
STSA	.....	48.98	2.19	7.94
SXSA	......	36.31	1.29	5.37
Spectrophotometric				
LDC	4.0	4.0	4.0	4.0
SPSA[a]	8.0	......	... ..	......
STSA[a]	10.0	... ..	. . .	. .
SXSA[a]	12.0	. ....	. .	.....

[a] The cmc values have been taken from the PhD thesis of S. P. Verma.

TABLE III

Relative Effectiveness of Anionic and Nonionic Surfactants

Surfactant	Molecular Weight	Concentration to suppress the polarographic maximax 10^{-5}M		
		Pb^{+2} in KNO_3	CdI_2 — KI complex	Cu-biuret
LDC	290	2.0	10.0	6.0
SPSA	441	23.5	238.0	83.3
STSA	454	23.8	23.8	60.5
SXSA	469	12.1	23.8	4.9

There are several factors which may be responsible for the lower cmc values of LDC as compared to the alkylaryl sulfonates: (i) the amido ($-CON <$) group is less hydrophilic than the sulfonate group ($x - SO_3^-$); (ii) it has a greater tendency to associate more strongly than the ionic ones because of lack of electrical charge; (iii) the latter factor is supported by the statement of Fowkes (20) that the tendency to form micelles is proportional to the square of the concentration of ionic detergents but only to the first power of the concentration of nonionic material. Another interesting fact emerges from these studies. Unlike ionic surfactants, the nonionic ones, even of low molecular weight suppress the polarographic maxima at much lower concentration. This is evident from the comparison of their molecular weights (Table III).

It has been found that the cmc value (4.0×10^{-5}M) of LDC obtained by the iodine solubilization method is of the same order as obtained by the polarographic method (Table II). It is also observed that the cmc value is not at all affected by the presence of different electrolytes viz., KCl, KNO_3 and KI by the solubilization method. The results on the cmc values of LDC described here go to show that unlike the ionic surfactants, the concentration for micelle formation is not affected by the changes in pH or by the presence of extraneous electrolytes. The concordance between

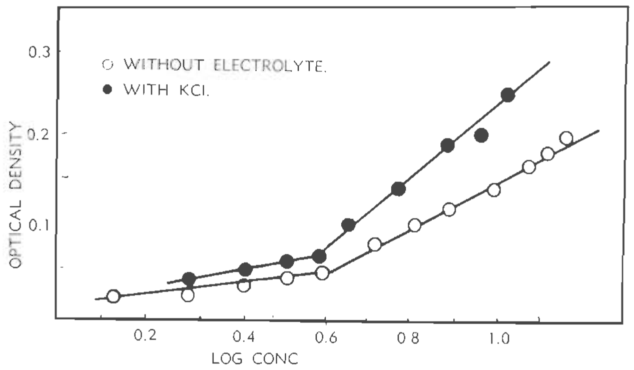


FIG. 2. Plots between log conc. and optical density.

the polarographic and spectrophotometric methods in this case is also very significant.

ACKNOWLEDGMENT

C.S.I.R. (India) provided the award of a fellowship to one of us (P.C.) and carry out this work.

REFERENCES

1. Sanders, H. L., and E. A. Knaggs, Soap Sanit. Chem. *29,* 45 (1953).
2. Young, H. H., and K. A. Spitzmueller (Swift and Co.), U.S. Pat. 2,586,496.
3. Swiss Pat. (CIBA Ltd.) 236,995.
4. Sanders, H. L., Knaggs and O. E. Libman, J. Soc. Cosmetic Chemists *5,* 29 (1954).
5. Ackelsberg, O. J. (E. F. Drew & Co. Inc.), U.S. Pat. 2,491,478.
6. Ackelsberg, O. J., op. cit.
7. Vitale, P. T., and R. S. Leonard (Colgate-Palmolive Peet Co.) U.S. Pat. 2,607,740.
8. McBain, J. W., "Colloid Science," D. C. Heath and Co., Boston, 1950, 241.
9. Schwartz, A. M., and J. M. Perry, "Surface Active Agents and Detergents," Interscience, New York 1949, p. 212.
10. Howorth, R. C., and F. G. Mann, J. Chem. Soc. (London) 603 (1943).
11. Vogel, A. I., "Practical Organic Chemistry," Longmans Green and Co. Ltd., London, 1947, p. 79.
12. Malik, W. U., and Puran Chand, Anal. Chem. *37,* 1592 (1965).
13. Colichman, E. L., J. Amer. Chem. Soc. *72,* 4036 (1950).
14. Hubbard, H. M., and C. A. Reynolds, J. Amer. Chem. Soc. *76,* 4300 (1954).
15. Ross, S., and J. P. Olivier, J. Phys. Chem. *63,* 1671 (1959).
16. Hsiao, L., H. N. Dunning and P. B. Lorenz, J. Phys. Chem. *60,* 657 (1956).
17. Schick, M. J., Paper presented at 138th Meeting of the American Chemical Society, New York, September, 1960.
18. Malik, W. U., and H. A. Kafoor Khan, Ind. J. Chem. *2,* 455 (1964).
19. Malik, W. U., and R. Haque, Ind. J. Chem. *2,* 35 (1964).
20. Fowkes, F. M., J. Phys. Chem. *63,* 1674 (1959).

[Received October 11, 1965]

Printed in the United States of America