Ph.D. Thesis

On the use of Electrometric, Spectrophotometric and Radiotracer Techniques in the Study of Surfactants and Heavy Metal Soaps

Thesis submitted for the award of the
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C E R T I F I C A T E

Certified that the thesis entitled " ON THE USE OF ELECTROMETRIC, SPECTROPHOTOMETRIC AND RADIOTRACER TECHNIQUES IN THE STUDY OF SURFACTANTS AND HEAVY METAL SOAPS" which is being submitted by Mr. Ajay Kumar Jain for the award of the degree of Doctor of Philosophy in Chemistry of the University of Roorkee, Roorkee is a record of his own work under my supervision and guidance. The matter embodied in this thesis has not been submitted for the award of any other degree of any University.

This is further to certify that he has worked from November, 1964 to June, 1968 at this University to prepare this thesis.

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LIST OF PUBLICATIONS

1. "Electrometric determination of critical micelle concentration of soap solutions"; J.Electroanal. Chem.,14, 37 (1967).

2. "Electrometric studies of copper,copper soap electrode in determining the critical micelle concentrations of soap solutions"; Kolloid-Z., 218, 155 (1967).

3. "Solubility of cobalt laurate in water and non-aqueous solvents"; Experientia; 23, 346 (1967).

4. "On the use of Co^{58} in determining the critical micelle concentration of potassium laurate"; J.inorg. nucl. Chem., 29, 2825 (1967).

5. "On the solubility of cobalt laurate in methanol-benzene mixtures"; Indian J.Appl. Chem.,30, 184 (1967).

6. "Temperature coefficient of e.m.f. of the cell Cu ¦ Cu-soap(s), K-soap, Ag-soap(s) ¦ Ag and the entropy of reactions"; J.Electroanal. Chem.,16, 271 (1968).

7. "Determination of the critical micelle concentration of cationic surfactants from counterion activity measurements"; J.Electroanal. Chem.,16, 442 (1968).

8. "Electrometric studies of nickel, nickel soap electrode in determining the critical micelle concentration of soap solutions"; Indian Journal of Chemistry, ~~(In Press).~~ 6, 140 - 42(1968) ~~(Revised proof of the above paper was sent in March, 1968).~~

9. "Studies on the solubilization of p-dimethyl amino anil of phenyl glyoxal nitrile by cationic surfactants and effect of electrolytes on micelle formation", (communicated), Presented at the 5th Annual Convention of the Indian Chemical Society held at the University of Roorkee, Roorkee from 3rd to 5th November,1967.

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C O N T E N T S

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GENERAL INTRODUCTION

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Certain solutes, even when present in very low concentrations, have the unusual property of altering the surface energy of their solvents to an extreme degree. The effect is invariably a lowering rather than an increase of the surface energy. Solutes having such properties are known as surface-active agents or simply surfactants. The best known and often quoted surfactant is soap which is an alkali metal salt of higher fatty acids. Within the past two decades,however, the newer synthetic surfactants, with their obvious advantage over ordinary soaps with regard to their stability to hard or acidic water, have received an increasingly wider recognition. The earliest surfactants to be developed were probably the "sulphonated oils", used as dyeing and wetting assistants. The development of synthetic surfactants reached its most active phase in the period between the two World Wars.

The tendency of surfactants to be adsorbed at interfaces or surfaces is most frequently due to a property for which G.S.Hartley has coined the name "amphipathy", i.e., the occurrence in a single molecule or ion, with a suitable degree of separation, of one or more groups which have affinity (sympathy) for the phase in which the molecule or ion is dissolved, together with one or more groups which are antipathetic to the medium (i.e., which tend to be expelled by it). It is convenient, from analogy in

colloid chemistry, to refer to these two types of groups as " lyophilic" and "lyophobic", respectively.

Classification of the surfactants:-

Surfactants may be classified under two general heads: (i) Aqueous surfactants (ii) Non-aqueous surfactants.

Aqueous surfactants :

In contrast to non-aqueous surfactants, physical chemistry of surfactants soluble in water has been thoroughly investigated. These surfactants may be further divided under following heads :

(a) Anionic surfactants

If the elongated, low-affinity(hydrophobic) portion of the surfactant molecule is included in the anion, the surfactant is called anion active or simply anionic. This class of surfactants includes soaps, Twichell's reagents (alkyl-aryl sulphonates), alkane sulphonic acids, alkyl sulphates etc..

(b) Cationic surfactants

The cationic surfactants give a cation containing the elongated hydrophobic portion of the surfactant molecule on dissociation in water. This class consists of quaternary ammonium compounds, salts of long chain primary, secondary and tertiary amines etc..

(c) Non-ionic surfactants

They do not ionise in aqueous solution. This class contains non-ionisable hydrophilic groups, usually containing a number of oxygen, nitrogen or sulphur atoms in non-ionising configurations. This class mainly includes surfactants derived from ethylene oxide.

Behaviour of the surfactants in their aqueous solutions:

The physical chemistry of aqueous solutions of ionic surfactants is particularly fascinating since it involves two widely separated fields of strong electrolytes and simple solutes on the one hand and soluble macromolecular colloids on the other.

The existence of hydrophobic and hydrophilic portions in single molecule of the surfactants imparts them properties markedly different from ordinary solutes. When a surfactant is put in water, water molecules, due to very strong cohesive force between them, tend to push out hydrophobic portions out of the solution and simultaneously this tendency is opposed by the solubilising influence of hydrophilic portion. The result is that in dilute solutions, such molecules concentrate at surfaces/interfaces with hydrophilic portion oriented towards the aqueous phase. This orientation brings about decrease in surface/interfacial tension. However, in concentrated solutions all the

solute molecules cannot remain at the surface/interface. In that case, the surfactant molecules begin to aggregate is such a way that hydrophobic portions remain in the interior of the aggregate and hydrophilic portions on the exterior. All the pioneering workers namely, McBain, Hartley, Lottermoser, Wright, Tartar, Ralston, Hoerr, Harkins etc. agree on the presence of aggregates in aqueous solutions of surfactants. These aggregates of the surfactant ions were first termed by McBain(1) as "ionic micelles".

The micelles in aqueous solutions of surfactants are not formed at any arbitrary concentration but begin to form in large amounts only when a definite concentration range is reached. The concentration above which micelle formation starts is referred to as critical micelle concentration (c.m.c.). The c.m.c. is not a specific concentration value but a narrow concentration range within which the constitution of the surfactant in solution changes from molecularly dispersed state to an equilibrium between molecules and aggregates.

A number of methods, viz., electrical conductance (2-5), surface tension(6-8), freezing point (9,10), osmotic pressure(11), vapour pressure(12), solubility(13,14), viscosity(15,16), solubilization(17), partial molal volume(18), refractive index(19) etc. have been employed to determine the c.m.c. values of su

The size and Shape of Micelles:

Although there is general agreement on the presence of micelles in aqueous solutions of surfactants, there is disagreement as to their kinds, shapes and structure. Various types of micelles have been postulated to explain a large amount of physico-chemical data collected on aqueous solutions of surfactants. However, there have been two leading school of thought in this field, one represented by McBain and the other by Hartley. Other workers, while agreeing with general outlines of one or the other theory, differ on some minor points. According to Hartley(20-22), the ionic surfactants below c.m.c., are completely dissociated and unaggregated. At the c.m.c., aggregation begins abruptly with the formation, at first, of relatively small micelles which grow rapidly over a very limited concentration range to a size which for a given surfactant remains approximately constant. Hartley believes that the micelles are liquid and essentially spherical and that their interior approximates to the random distribution state of liquid paraffin, but with the hydrophilic end of the ion constrained to remain at the surface of the micelle. His spherical micelle contains, in addition to a large number of paraffin chain ions, a considerable number of counterions held on the surface of the micelle. Hartley thus postulates only one type of micelle of approximately constant size at all concentrations above c.m.c..

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On the other hand, McBain(23-25) visualises two types of micelles. The one is highly conducting, spherical ionic micelle of not more than 10 like ions retaining their charges, formed in dilute solutions even before c.m.c. is reached; the other is large, poorly conducting micelle with little or no ionic charge, referred to as "neutral-colloid", formed just beyond the c.m.c.. The "neutral-colloidal micelle" has been identified by McBain(25) with the lamellar micelle postulated on the basis of X-ray diffraction patterns(26-29). The lamellar micelle is described as being composed of alternate layers of water and double amphipathic molecules. Harkins and co-workers(30-32) agree with Hartley's concept of one type of micelle, but from their X-ray results consider it to have some regularity of structure and picture it as cylindrical or disc-shaped. Hartley(20) believes the disc shape to be improbable and has indicated(33) that the results of X-ray diffraction patterns are capable of being interpreted on the basis of the spherical micelle.

The size, shape and charge of the micelles have been studied mostly by light scattering techniques. The most powerful single method for estimating micellar size is the light scattering technique originally developed by Debye(34) and subsequently described by a number of workers(35-38). The presence of salts decreases the c.m.c. and increases the micellar size (39,40).

The charges of the micelle have been estimated by light scattering(35-39), electrophoretic mobility(41,42), colligative properties(43,44), osmosis(45) etc..

Effect of Environmental Factors on Micelle Formation:

The c.m.c. of any given surfactant and the properties of micelles are markedly influenced by such environmental factors as the presence of salts, the nature of the solvent, the presence of solubilized material, temperature, etc.. The effect of alcohols(46,47), hydrocarbons (48-50), dioxane and glycol(51), inorganic salts(52-55) on the micelle formation of surfactants has been thoroughly investigated.

Solubilization:

Solubilization for an aqueous system may be defined as the spontaneous dissolving of a normally water insoluble substance by a relatively dilute aqueous solution of a surfactant. The phenomenon of solubilization is of interest from practical as well as the theoretical viewpoint. The major factor which controls the amount of material solubilized in a given system is the chemical composition of the surfactant and solubilizate. Various methods,viz., turbidimetry(56,57), spectrophotometry(58,59), X-ray diffraction(51,60) etc. have been employed to study solubilization.

X-ray diffraction has very clearly distinguished between two different types of solubilization. In one type, the spacings representing the thickness of micelle

layers increase in proportion to the quantity of material solubilized. In this case the hydrocarbon is visualized as occupying the space between the hydrophobic ion tails. The second type of solubilization is represented by the fatty alcohols in dodecyl sulphate. Here the micelle thickness does not change significantly. This indicates that fatty alcohols penetrate into the micelle and become oriented in the same way as the ions or molecules which were originally present in the micelle(51,60). Apart from these two types of solubilization, the solubilization of dimethyl phthalate has been explained on the basis of its adsorption on the exterior of polar groups of the micelles(61).

E.M.F. measurements:

Metal, metal-surfactant electrodes have been rarely employed in studying the behaviour of surfactants in their aqueous solutions. Walton(62) employed a mercury, mercurous dodecanesulphonate electrode for determining the activity coefficient of the anion in n-dodecanesulphonic acid both with and without salt additions. The same electrode was employed by Tartar(63) and co-workers for studying the transference numbers of l-dodecanesulphonic acid and by Vader(64) for determining the c.m.c. and pre-association of the surfactant ions in sodium dodecyl sulphonate. Kolthoff and Johnson(65) employed silver, silver laurate electrode for measuring laurate ion activity variation in aqueous solutions of potassium laurate.

Interactions:

Interactions of surfactants with other materials offer an entirely new field of study of both fundamental and applied importance. The materials with which surfactants' interaction has been studied include proteins(66), polymers(67,68), clays(69), nucleic acid(70), dyes(71), colloids(72) etc..

Interaction with proteins:

The interactions between proteins and surfactants have been extensively studied both from biochemical and industrial viewpoints(73-78). Pankhurst(75-77)investigated the interaction between dodecyl sodium sulphate and gelatin and concluded that the surfactant became attached by its head group to the amide linkage of the backbone of protein molecules.

A number of techniques have been employed to study the interaction. The interaction of serum albumins with dodecyl sulphate has been studied by surface and interfacial tension measurements(79,80); between alkyl aryl sulphonates and fatty alkyl sulphates and various albumins by electrophoresis and equilibrium dialysis techniques(81-83). Sedimentation(84), absorption spectroscopy(85), surface viscosity and surface eleasticity(86) methods have also been employed.

Interaction with colloids:

The interaction of surfactants with hydrophobic colloids has been studied mainly from stability point of

view. In the last twenty years, studies on the action of cationic as well as anionic surfactants on the stability of hydrophobic (oleophilic) colloids have been made by a number of investigators (87-95). The colloids used in these studies included positive colloids, such as iron oxide and aluminium oxide, and negative colloids, such as gold, arsenic sulphide, silver halides and manganese oxide. The surfactants used included alkyl carboxylates, alkyl sulphate, quaternary compounds, etc.. Some of the characteristic results obtained from the observation of the interaction between these surfactants and colloids are as follows: (i) the interaction takes place more remarkably between colloids and paraffin chain ions of opposite sign. (ii) In certain ranges of concentration of an electrolyte (cationic or anionic surfactant), flocculation of colloids occurs, the flocculation value of the electrolyte being rapidly decreased as the number of carbon atoms contained in the electrolyte molecule increases. (iii) The flocculate thus formed is deflocculated at higher concentrations of electrolyte, provided that the electrolyte contains more than certain number - usually 10 - of carbon atoms in its molecule. (iv) The electric charge of the original sol is reversed at the deflocculation zone, the electrophoretic mobility of colloid particles being changed with the concentration of the surfactant electrolyte.

R.H. Ottewill (95-98) and co-workers have studied extensively the stability of positive silver

iodide sol in presence of anionic surfactants and of negative silver iodide sol in presence cationic surfactants.

Interaction with dyes:

The interaction of surfactants with dyes present some interesting features worth considering. For quite long time, dyes have been used for the qualitative and quantitative determination of surfactants. Methylene blue(99), for the determination of cetyltrimethyl ammonium bromide, bromocresol purple(100) and thymol blue(101) for anionic surfactants have been recommended. The colour change of dyes in presence of surfactants has been employed for the determination of c.m.c. by Harkins and co-workers (102-104). Mysels and Mukerjee(105) have shown that the colour change of dyes in presence of surfactants involved the formation of a surfactant-dye insoluble complex.

Radiotracer technique in the study of surfactants:

Radioisotopes giving soft beta radiations, viz., S^{35} and C^{14}, have been used by a number of workers for studying the adsorption of aqueous surfactants at a solution-air interface. Matsuura and co-workers(106-108) have thoroughly studied the adsorption of alkyl sulphates at a solution-air interface with and without the presence of electrolytes, using S^{35} as a tracer. Other workers, who have also employed S^{35} as a tracer for this purpose, are Dixon and co-workers(109-110). Rideal and Flengas(111) have made use of soft beta radiation of C^{14} for studying the adsorption of sodium stearate at the solution-air interface.

Another field, in which isotope as a tracer has been used, is the solubility determination of heavy metal soaps. Yoke(112) determined the solubility of calcium soaps in water using Ca^{45} as a tracer.

Uses and industrial applications:

Surfactants are of great importance(113) in detergency, in the textile industry, biological actions, emulsification, in cosmetic preparations, in metal and mineral technology, etc. due to their distinctive properties— (1) their moderate maximum concentration of molecularly dispersed species,(2) surface and interfacial tension depression in very dilute solutions, due to the adsorption and orientation of molecules at the interface,(3) micelle formation above a certain concentration and (4) solubilization of water insoluble substances by micelles.

A very large proportion of the total surfactant production is used in washing of fabrics and textile materials. The surfactants are also used in cleaning hard surfaces — metal surfaces, glass, ceramic, non-metallic inorganic surfaces, paint surfaces, plastics, linoleum, etc.(114). In textile and drycleaning industries, they are used for several textile processing operations such as dyeing, wetting, emulsification, dispersing and other similar gross effects(115). In the dyeing of textiles, surfactants are used as dispersing agents, levelling agents, fixing agents and stripping agents(116).

Apart from detersive applications, the use of surfactants in many fields of medical and pharmaceutical practice has increased appreciably within recent years. A large number of surfactants have found striking application as germicides and among the quaternary ammonium salts many of the most powerful modern bactericides have been found(117). Anionic surfactants such as lauryl sulphate and nonionic surfactants such as Tweens and Spans have been widely adopted for preparing skin lotions in which effective medicament is suspended or emulsified.

In metal and mineral technology surfactants are used in flotation, electroplating and surface finishing of metals(118).

In building and construction industries too, the importance of surfactants is being realised. Specific areas in which surfactants have brought about major changes include the preparation and use of asphalt bonding materials, concrete, soil stabilization, etc.(119).

Besides above listed applications, surfactants are used in agriculture, leather industry, preparation of synthetic rubbers, polymers, plastics, paints, in petroleum and chemical processing industry and in fire fighting.

Heavy Metal Soaps:

Heavy metal soaps differ from other surfactants in being very slightly soluble in water. They dissolve only in organic solvents. The physical properties of

heavy metal soaps in organic solvents are interpreted in terms of the micellar theory. A number of methods, viz., fluorescence depolarization(120), viscosity and osmotic pressure(121), ebullioscopic(122), solubility(123), have been employed to determine c.m.c. and micellar molecular weight.

The solubility of heavy metal soaps in non-polar solvents makes them technically quite useful(124). In general, heavy metal soaps have been used in preparing lubricants, greases, paints; as catalysts and as dewaxing and water proofing agents.

In this laboratory, Malik and co-workers are engaged for quite some time in carrying out physico-chemical studies on surfactants and heavy metal soaps. They have extensively studied the role of surfactants in the suppression of polarographic maxima(125-129); have developed polarographic (130-132) and spectrophotometric (133,134) methods for the estimation of metal content of heavy metal soaps and have carried out quantitative studies on surfactant-dye interactions(135). Later it was thought worthwhile to extend these studies as to incorporate other developing techniques for the systematic and comprehensive study of surfactants including heavy metal soaps. With this aim in view, potentiometric and radiotracer techniques were developed to determine the c.m.c., transport number, composition, thermodynamical constants, counterion activity, solubility in aqueous

and non-aqueous media, etc. of the ionic surfactants and heavy metal soaps. Besides another aspect of technological importance, viz., the reaction of surfactants with dyes was taken up for more detailed consideration, using absorbance measurements in the visible region. The above aspects of study form the main theme of the present thesis.

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CHAPTER - 1

" The use of metal, metal-soap electrodes in determining the c.m.c. of potassium soaps, transport number and composition of heavy metal soaps "

INTRODUCTION

Three kinds of reversible electrodes have been used in electrochemical work. The simplest, called "electrodes of the first kind" consist of a metal in contact with a solution of its own kind, e.g., silver in silver nitrate solution. Electrodes of the "second kind" involve a metal, a sparingly soluble salt of this metal, and a solution of a salt with a common anion. Electrodes of the "third kind" consist of a metal, one of its insoluble salts, another insoluble salt of the same anion, and a solution of a salt having the same cation as the latter salt, e.g.,

$$Pb/PbC_2O_4(s),\ CaC_2O_4(s),\ CaCl_2(Soln.)$$

Electrodes of the second kind have proved to be very useful in electrochemical measurements, especially in the form of standard electrodes. Amongst these the most frequently employed is the calomel electrode, which is reversible with respect to chloride ion and has its potential dependent upon the concentration of potassium chloride in contact with the calomel layer spread over mercury. This electrode has not only found use in potentiometric work but also in polarography.

Another important electrode of the second kind is silver, silver chloride electrode. Silver chloride electrodes have proved to be an important aid in many studies of solutions of electrolytes. Although many forms of these

electrodes have been described, they may be grouped into three main classes, those prepared (a) with precipitated silver chloride (1),(b) by the electrolytic chloridizing of reduced silver oxide paste(2),(c) by the electrolytic deposition of both silver and silver chloride (3-5). These electrodes have been used by a number of workers(6-10).

Recently Larson(11), and Covington and co-workers(12) have studied mercury, mercurous acetate electrode. Malik and Dass(13) have reported the use of cobalt, cobalt ferrocyanide electrode for the estimation of ferrocyanide ion. Besides, above listed "second kind" electrodes, numerous references are available in the literature on them.

Besides, the above common electrode systems, there are few less familiar type which have not attracted much attention so far. To this class belongs the metal, metal-surfactant electrode system. Walton(14) employed a mercury, mercurous dodecane sulphonate electrode for determining the activity coefficient of dodecane sulphonic acid. The same electrode was employed by Tartar and co-workers(15) for studying the transference numbers of 1-dodecane sulphonic acid and by Vader(16) for determining the critical micelle concentration(c.m.c.) and pre-association of the surfactant ions of sodium dodecyl sulphonate. Kolthoff and Johnson(17) employed silver, silver laurate electrode for measuring detergent anion activity variation

in aqueous solutions of potassium laurate.

From the above discussion it is clear that surfactant electrodes employed so far have made use of mercury and silver as their metallic part. Less noble metals like copper, nickel and cobalt have not been used for this purpose. Besides systematic investigations incorporating the studies on various electrochemical and thermodynamical constants have not been taken up as yet. With these aims in view, the suitability and performance of copper, copper soap; cobalt, cobalt soap; and nickel, nickel soap electrodes was tested. These electrodes were put to use in determining the c.m.c. of potassium salts of higher fatty acids, transport number of detergent ions and to carry out potentiometric titrations between potassium soaps and metal salts.

EXPERIMENTAL

Reagents:

Lauric, myristic, palmitic and stearic acids were reagent-grade (B.D.H.) products. Copper sulphate, nickel sulphate and cobalt sulphate were A.R. grade materials. Reagent-grade potassium and sodium hydroxides were employed.

Preparation of potassium laurate, myristate, palmitate and stearate:

Lauric, myristic, palmitic and stearic acids were purified by repeated crystallization from alcohol. Potassium soaps were obtained by refluxing equivalent amounts of fatty acids and potassium hydroxide in alcohol for 10-12 hrs. on a water bath. These soaps were further purified by extraction within a soxhlet using acetone. Finally, the soaps were recrystallized from alcohol.

Preparation of sodium laurate, myristate, palmitate and stearate:

Sodium soaps were prepared in the same way as potassium soaps. Instead of potassium hydroxide, sodium hydroxide was taken.

Preparation of heavy metal soaps:

Of the two general methods of preparing the metallic soaps, viz., fusion and precipitation, the latter was chosen for the preparation of various metallic soaps(18).

On dissolving in warm water, the potassium or sodium soaps yielded a clear solution. By running a warm solution of potassium soap into an excess of 1% solution of chlorides or sulphates of heavy metals with vigorous mechanical stirring, heavy metal soaps were precipitated. These soaps were washed with water till free from adsorbed ions and then with ethanol to remove free precipitant and acid. They were dried in vacuum desiccator and stored in stoppered bottles for use.

Preparation of cobalt soaps:

Cobalt laurate, myristate, palmitate and stearate were prepared by direct metathesis at 50-55° from corresponding sodium soaps (1.5%, 500 ml) and cobalt sulphate solution (1.0%, 500 ml) in water. The precipitated cobalt soaps were washed with water and then with ethanol to remove free precipitant and acid.

Estimation of cobalt:

A known amount of the cobalt soap was ashed in a crucible and the ash was dissolved in hydrochloric acid. The cobalt in solution was estimated gravimetrically (19) :

Found : Co,9.31%; $(C_{17}H_{35}COO)_2Co$ required Co, 9.42%
Co,10.32%; $(C_{15}H_{31}COO)_2Co$ required Co,10.35%
Co,11.6%; $(C_{13}H_{27}COO)_2Co$ required Co,11.47%
Co,12.9%; $(C_{11}H_{23}COO)_2Co$ required Co,12.88%

Preparation of nickel soaps:

Nickel laurate, myristate, palmitate and stearate were prepared by direct metathesis at 50-55° from corresponding sodium soaps (1.5%) and nickel sulphate (1%) solution in water. Precipitated nickel soaps were filtered through Buchner funnel and washed with distilled water and ethanol to remove free precipitant.

Estimation of nickel:

A known amount of the soap was ashed in a crucible. The ash was dissolved in nitric acid and nickel was estimated with dimethyl glyoxime.

Found : Ni,9.28%; $(C_{17}H_{35}COO)_2Ni$ required Ni, 9.39 %
Ni,10.5%; $(C_{15}H_{31}COO)_2Ni$ required Ni,10.31 %
Ni,11.4%; $(C_{13}H_{27}COO)_2Ni$ required Ni,11.43 %
Ni,12.9%; $(C_{11}H_{23}COO)_2Ni$ required Ni,12.84 %

Preparation of copper soaps:

Copper laurate, myristate, palmitate and stearate were prepared by direct metathesis at 50-55° from corresponding sodium soaps (1.5%) and copper sulphate solution (1.0%) in water. The precipitated copper soaps were washed with distilled water and then with ethanol to remove free precipitant and acid. These soaps were greenish blue in colour.

Estimation of copper:

The copper soaps were analysed for the metal content by ashing a known amount of the soap in

crucible. The ash was dissolved in concentrated nitric acid and copper was estimated iodometrically,

Found: Cu,10.10%; $(C_{17}H_{35}COO)_2Cu$ required Cu,10.09%
Cu,10.96%; $(C_{15}H_{31}COO)_2Cu$ required Cu,11.08%
Cu,12.20%; $(C_{13}H_{27}COO)_2Cu$ required Cu,12.26%
Cu,13.95%; $(C_{11}H_{23}COO)_2Cu$ required Cu,13.75%

Preparation of Metal Electrodes:-

Preparation of cobalt electrodes:

Cobalt electrodes were prepared by depositing cobalt on platinum wires by the electrolysis of a solution containing 8% cobalt sulphate and 2.5% ammonium sulphate. The solution was taken in beaker and two platinum wire electrodes were dipped into the solution. The electrodes were connected to a 4-volt battery and a current of 25 mA was passed for 3 hrs..

Preparation of copper electrodes:

Copper electrodes were prepared by depositing copper on platinum wires (diameter 0.25 mm) by the electrolysis of a solution containing 8% copper sulphate and 4.6% sulphuric acid. The electrodes were connected to a 2-volt battery and a current of 15 mA passed for 4 hrs. .

Preparation of nickel electrodes:

Nickel electrodes were prepared by depositing nickel on platinum wires (diameter 0.25 mm)

by the electrolysis of a solution containing 15% nickel sulphate, 1% boric acid and 0.6% sodium chloride. The electrodes were connected to a 4-volt battery and current of 20 mA was passed for about 2 hrs. .

Preparation of metal, metal-soap electrodes:

Attempts were made to deposit a thin layer of metal soap on metal electrodes electrolytically. However, the layer of metal soap deposited electrolytically on the metal electrode was not coherent and used to get detached on slight stirring of the solution. Therefore, the metal, metal-soap electrodes were set up by inserting a metal electrode in a half-cell containing potassium soap solution saturated with corresponding metal soap. Some solid metal soap was always added to the half-cells to make certain that the soap solution was saturated with respect to metal soap.

Procedure:

(A) c.m.c.determination of potassium soaps:

The following cells were set up:

Cu	$CuD_2(s)$, KD(C)	satd. KCl salt bridge	KCl satd., $Hg_2Cl_2(s)$	Hg
Co	$CoD_2(s)$, KD(C)	satd. KCl salt bridge	KCl satd., $Hg_2Cl_2(s)$	Hg
Ni	$NiD_2(s)$, KD(C)	satd. KCl salt bridge	KCl satd., $Hg_2Cl_2(s)$	Hg

('D' stands for laurate, myristate, palmitate and stearate).

The E.M.F. measurements of the cells were carried out with a Cambridge portable potentiometer in conjunction with a sensitive suspended coil galvanometer with lamp and scale arrangement. Standard solutions of potassium soaps were prepared in doubly-distilled water and were transferred to conical flasks. Excess of the metal soap was added to potassium soap solutions. The capped conical flasks were placed in a water thermostat at $35 \pm 0.1^{\circ}C$. When the solutions were saturated with the metal soap, they were transferred to half-cells provided with corresponding metal electrodes. A saturated calomel electrode was attached through a saturated potassium chloride salt bridge. Some solid metal soap was always added to the half-cells to make certain that the potassium soap solution was saturated with respect to the metal soap. Since the metal, metal-soap electrodes were rather slow in coming to equilibrium, each solution was allowed to stand for some time (usually 15-20 mts.) before noting down the potential.

The experimental observations are given in Figs.1-6.

(B) Transport number determination:

Triple-distilled mercury was taken for preparing sodium amalgam. Sodium amalgam (0.05%) was prepared by adding small pieces of sodium metal (0.05 gm.) into dried and triple-distilled mercury (99.95 gm.) in a mortar with constant stirring by means of a pastle.

This was kept in a air free amalgam reservoir for using in experiments.

Apparatus:

The electrode vessels and the amalgam reservoir ~~used~~ were of the type used by MacInnes and co-workers(9,20).

E.M.F. measurements of the cell with and without transference:

Cells of the type I (without transference) and II (with transference) were set up.

Amalgam cell without transference:

$$\text{Cu} \;/\; \underset{\text{Na-soap}(C_1)}{\text{Cu-soap(s)}},\; /\; \text{0.05\% sodium amalgam} \;/\; \underset{\text{Na-soap}(C_2)}{\text{Cu-soap}_{(s)}},\; /\; \text{Cu}$$

I

Corresponding cell with transference:

$$\text{Cu} \;\Big|\; \text{Cu-soap(s)}, \text{Na-soap}(C_1) \;\vdots\; \text{Na-soap}(C_2), \text{Cu-soap(s)} \;\Big|\; \text{Cu}$$

II

A small bed of glass wool was placed over the narrow mouth of the constriction provided in the short limb of the electrode vessel, and an amount of copper soap sufficient to cover the copper electrode was placed over it. The copper electrode then was inserted into the copper soap. The air from the vessel was removed by evacuation and subsequent replacement by hydrogen. As quickly as possible aqueous solutions of sodium soaps were introduced into the electrode vessel.

For the measurement of the E.M.F. of the cell without transference, the amalgam reservoir was put in place, its capillaries dipping into the sodium soap solutions contained in longer limbs of the two electrode vessels facing each other. The amalgam was allowed to fall drop by drop through capillaries. E.M.F. measurements of the cell were recorded on a portable Cambridge potentiometer.

Afterwards the amalgam reservoir was removed. The two half-cells were connected by a bridge containing sodium soap solution of concentration C_1. The two solutions of concentration C_1 and C_2 impinged into each other through jets. As soon as the E.M.F. of the cell was constant, it was recorded.

The E.M.F.values of the cells with and without transference are given in the following Tables 1,2 :

Table -1

Amalgam cell without transference:

Cu	Cu-laurate(s), Na-laurate(C_1)	0.05% Na amalgam	Na-laurate(C_2), Cu-laurate(s)	Cu

Corresponding cell with transference:

Cu	Cu-laurate(s), Na-laurate(C_1)	Cu-laurate(s), Na-laurate(C_2)	Cu

Sod.laurate concn., C_1 ($\times 10^{-3}$M)	Sod.laurate concn., C_2 ($\times 10^{-3}$M)	E.M.F.of the cell with transference, E_t (volts)	E.M.F.of the cell without transference, E (volts)
2	1	0.0240	0.0351
3	2	0.0152	0.0223
5	3	0.0192	0.0274
8	5	0.0172	0.0243
10	8	0.0081	0.0112
20	10	0.0260	0.0361

Table -2

Amalgam cell without transference:

Cu	Cu-myristate(s), Na-myristate(C_1)	0.05% sodium amalgam	Cu-myristate(s), Na-myristate(C_2)	Cu

Corresponding cell with transference:

Cu	Cu-myristate(s), Na-myristate(C_1)	Cu-myristate(s), Na-myristate(C_2)	Cu

Sod.myristate concn., C_1 ($\times 10^{-3}$M)	Sod.myristate concn., C_2 ($\times 10^{-3}$M)	E.M.F.of the cell with transference, E_t (volts)	E.M.F.of the cell without transference, E (volts)
2	1	0.0264	0.0356
3	2	0.0165	0.0214
4	3	0.0123	0.0162
5	4	0.0089	0.0115

(C) Potentiometric titrations between metal salts and potassium soaps:

Potentiometric titrations between metal salts and potassium soaps were carried out employing copper, copper soap electrodes as indicator electrodes. The following cell was set up:

Cu	Cu-soap(s), K-soap(C)	satd.KCl salt bridge	KCl satd., Hg_2Cl_2(s)	Hg

20 ml of aqueous solutions of potassium soaps were taken in the half-cell provided with a copper electrode. Excess of solid copper soap was added to

saturate the potassium soap solution with respect to copper soap. The half-cell was attached through a saturated potassium chloride salt bridge to a saturated calomel electrode. Known volumes of the aqueous solutions of metal salts were added from the burette to potassium soap solution. The E.M.F. of the cell was noted after the equilibrium was attained. All measurements were carried out at room temperature (28 $\pm$ 2°C).

Following titrations were carried out :

(1) Potentiometric titrations of 20 ml of M/100 potassium laurate against copper sulphate(M/20), cobalt sulphate (M/20), nickel sulphate (M/20) and cadmium sulphate (M/20) were carried out by using copper, copper laurate electrode.

The experimental observations are given in Fig.7.

(2) Potentiometric titrations of 20 ml of M/1000 potassium myristate against copper sulphate (M/200), cobalt sulphate (M/200), nickel sulphate (M/200) and cadmium sulphate (M/200) were carried out by using copper, copper myristate electrode.

The experimental observations are given in Fig.8.

(3) Potentiometric titrations of 20 ml of M/1000 pot. palmitate against copper sulphate (M/200), cobalt sulphate (M/200), nickel sulphate (M/200) and cadmium sulphate (M/200) were carried out by using copper, copper

palmitate electrode.

The experimental observations are given in Fig.9.

(4) Potentiometric titrations of 20 ml of M/2000 pot. stearate against copper sulphate (M/400), cobalt sulphate (M/400), nickel sulphate (M/400) and cadmium sulphate (M/400) were carried out by using copper, copper stearate electrode.

The experimental observations are given in Fig.10.

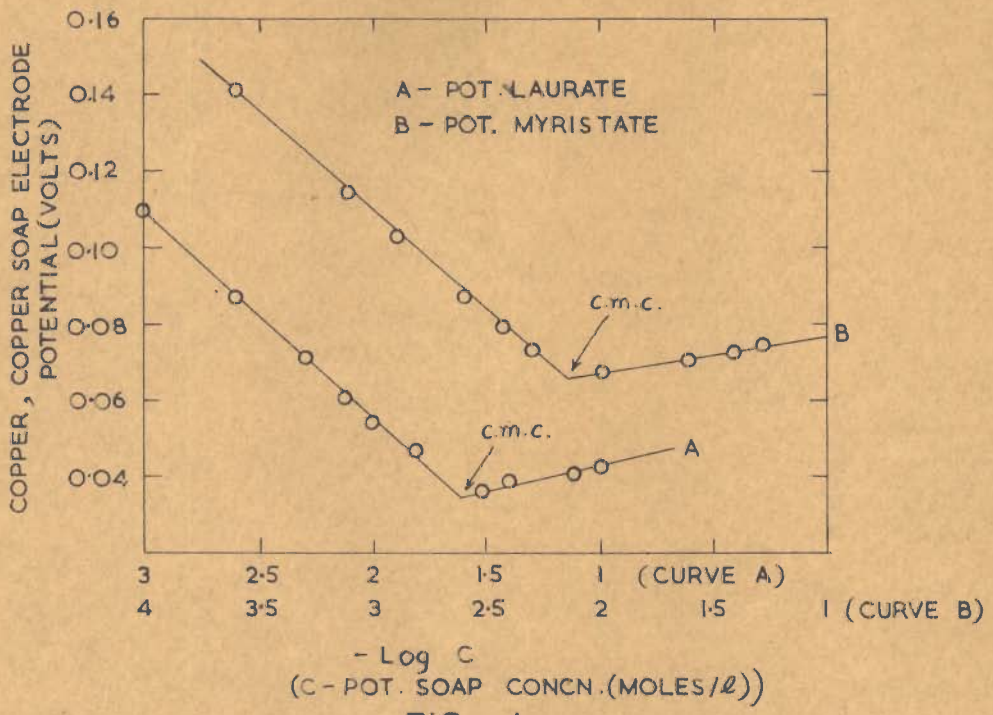
COPPER, COPPER SOAP ELECTRODE POTENTIAL (VOLTS)
0·16
0·14
0·12
0·10
0·08
0·06
0·04
A – POT. LAURATE
B – POT. MYRISTATE
c.m.c.
c.m.c.
B
A
3 2·5 2 1·5 1 (CURVE A)
4 3·5 3 2·5 2 1·5 1 (CURVE B)
– Log C
(C – POT. SOAP CONCN. (MOLES/ℓ))

FIG. 1

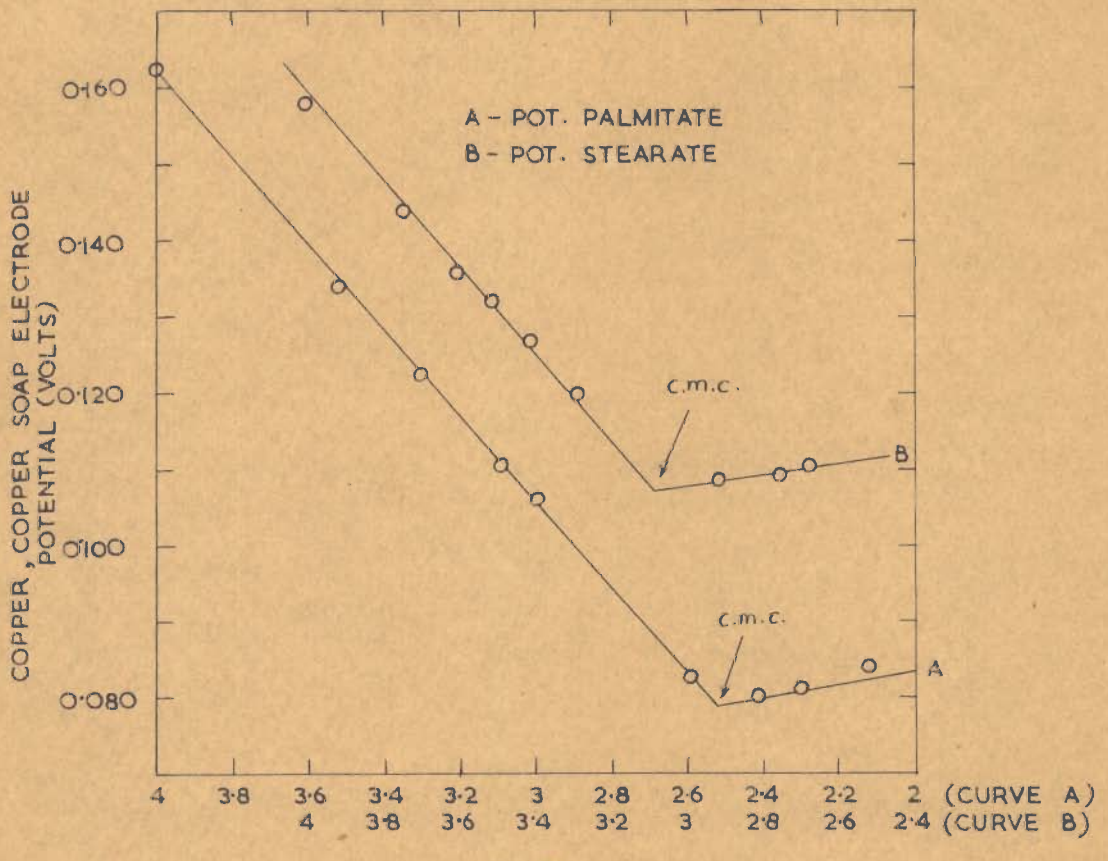
COPPER, COPPER SOAP ELECTRODE POTENTIAL (VOLTS)
0·160
0·140
0·120
0·100
0·080
A – POT. PALMITATE
B – POT. STEARATE
c.m.c.
c.m.c.
B
A
4 3·8 3·6 3·4 3·2 3 2·8 2·6 2·4 2·2 2 (CURVE A)
4 3·8 3·6 3·4 3·2 3 2·8 2·6 2·4 (CURVE B)
– Log C
(C – POT. SOAP CONCN. (MOLES/ℓ))

FIG. 2

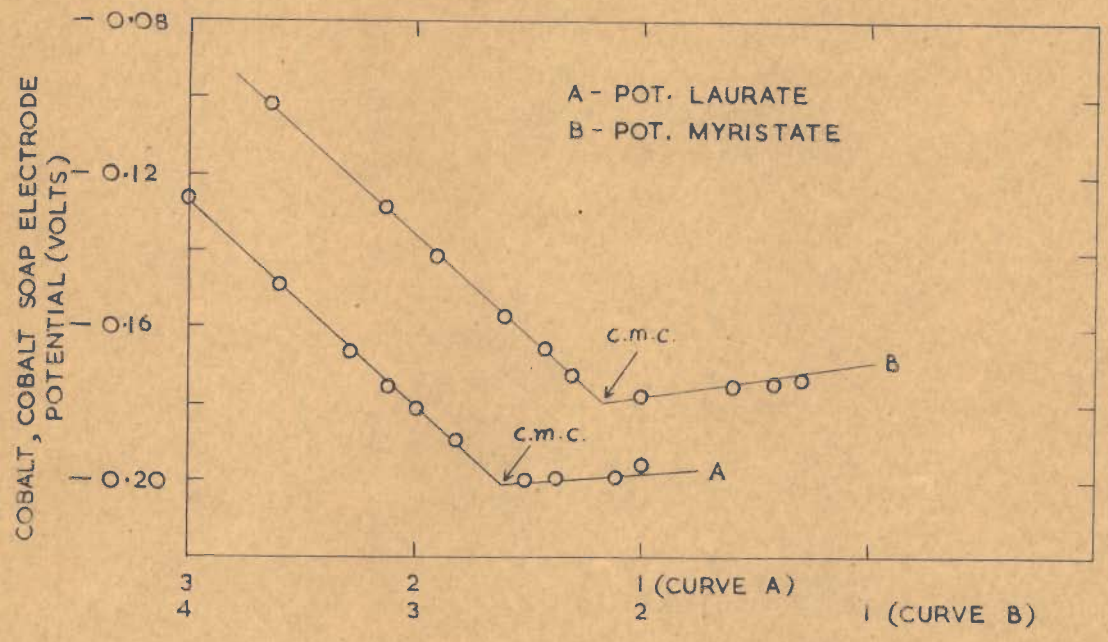
COBALT, COBALT SOAP ELECTRODE POTENTIAL (VOLTS)
- 0·08
- 0·12
- 0·16
- 0·20
A - POT. LAURATE
B - POT. MYRISTATE
c.m.c.
c.m.c.
B
A
3
4
2
3
1 (CURVE A)
2
1 (CURVE B)
- Log C
(C - POT. SOAP CONCN. (MOLES/ℓ))

FIG. 3

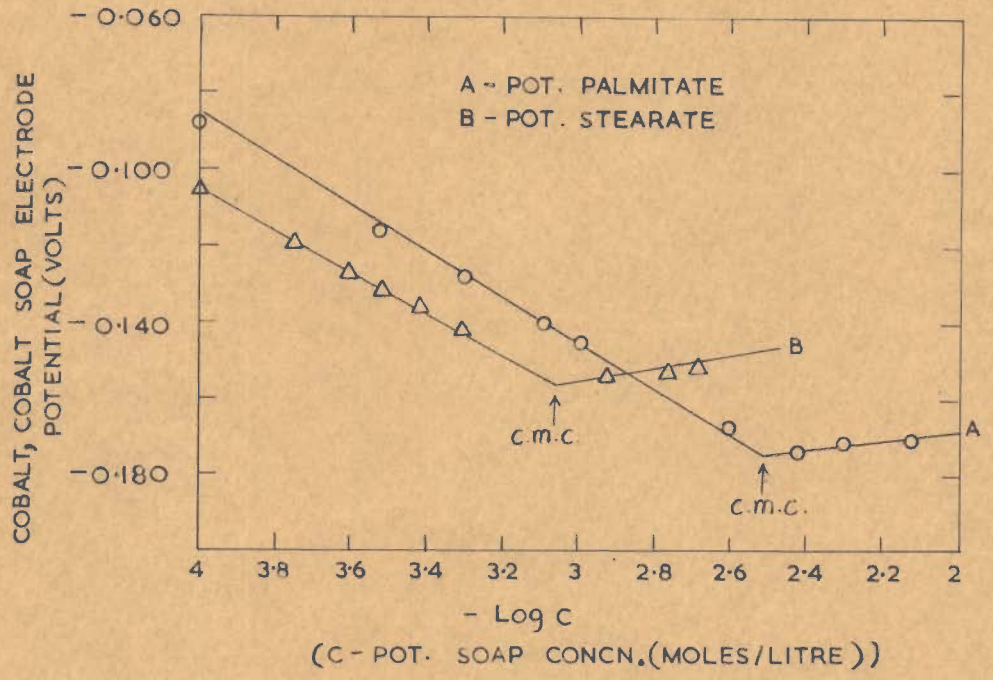
COBALT, COBALT SOAP ELECTRODE POTENTIAL (VOLTS)
- 0·060
- 0·100
- 0·140
- 0·180
A - POT. PALMITATE
B - POT. STEARATE
c.m.c.
c.m.c.
B
A
4
3·8
3·6
3·4
3·2
3
2·8
2·6
2·4
2·2
2
- Log C
(C - POT. SOAP CONCN. (MOLES/LITRE))

FIG. 4

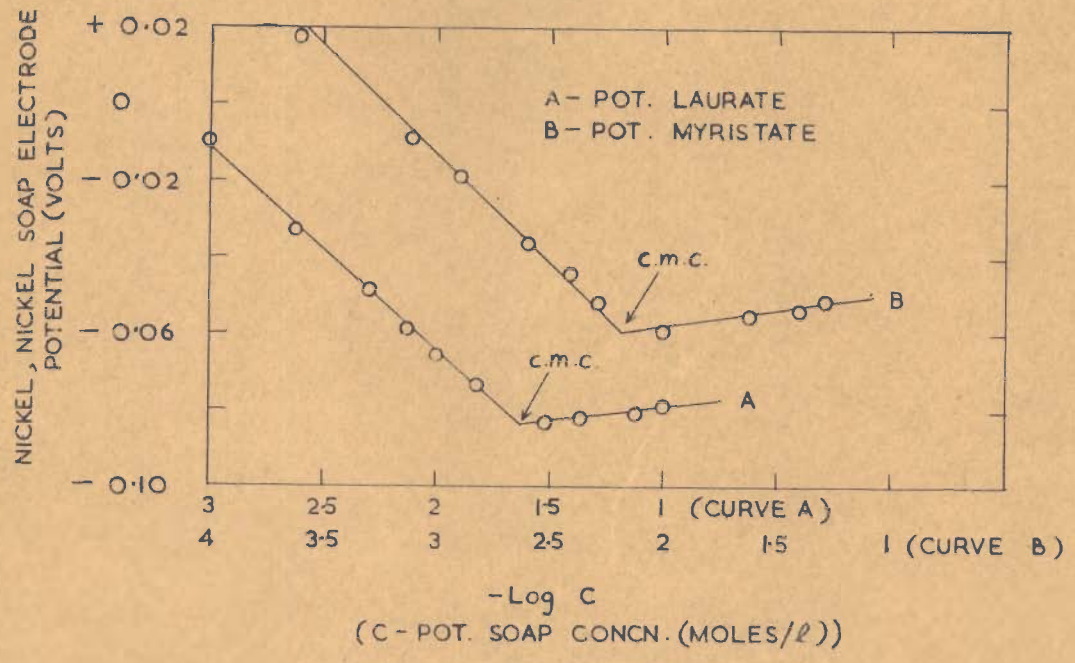
NICKEL, NICKEL SOAP ELECTRODE POTENTIAL (VOLTS)
+ 0·02
0
− 0·02
− 0·06
− 0·10
A − POT. LAURATE
B − POT. MYRISTATE
c.m.c.
c.m.c.
A
B
3
4
2·5
3·5
2
3
1·5
2·5
1 (CURVE A)
2
1·5
1 (CURVE B)
−Log C
(C − POT. SOAP CONCN. (MOLES/ℓ))

FIG. 5

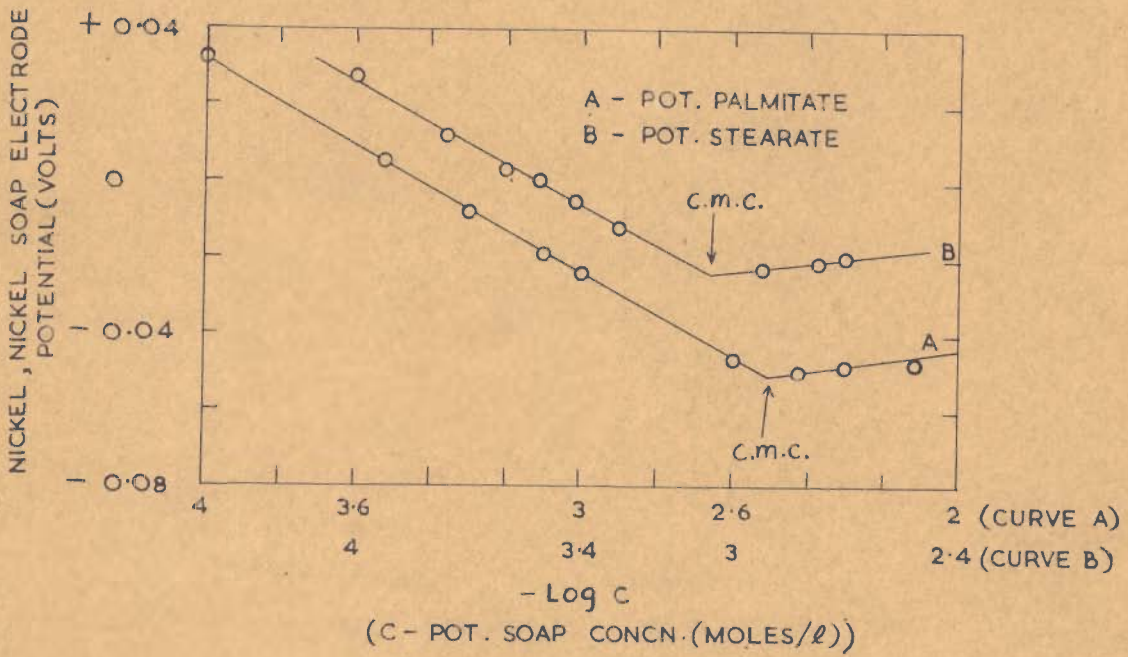
NICKEL, NICKEL SOAP ELECTRODE POTENTIAL (VOLTS)
+ 0·04
0
− 0·04
− 0·08
A − POT. PALMITATE
B − POT. STEARATE
c.m.c.
c.m.c.
A
B
4
3·6
4
3
3·4
2·6
3
2 (CURVE A)
2·4 (CURVE B)
−Log C
(C − POT. SOAP CONCN. (MOLES/ℓ))

FIG. 6

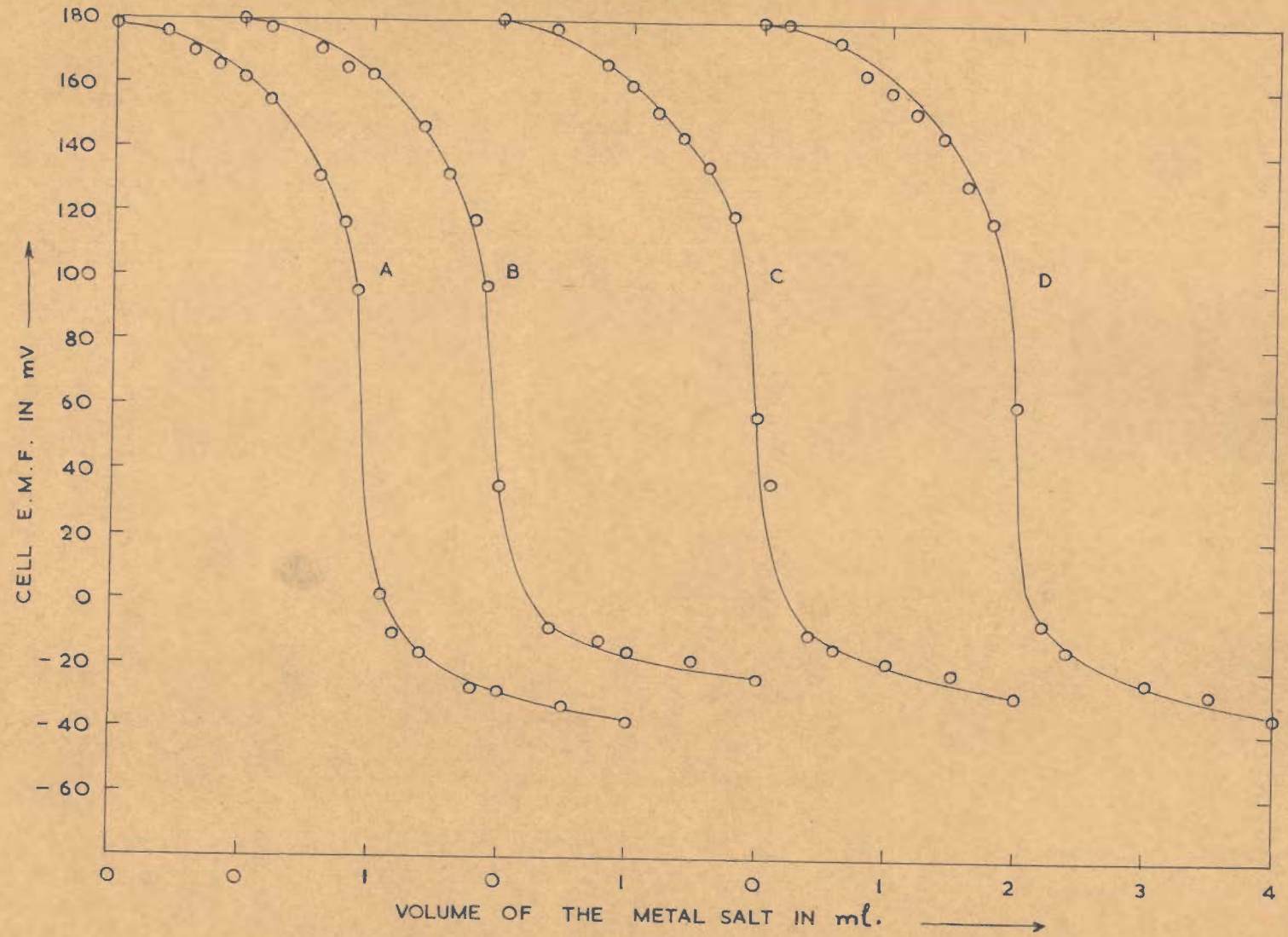

FIG. 7. POTENTIOMETRIC TITRATIONS OF POT. LAURATE (M/100) AGAINST METAL SALTS ; VOLUME TITRATED = 20 ml.

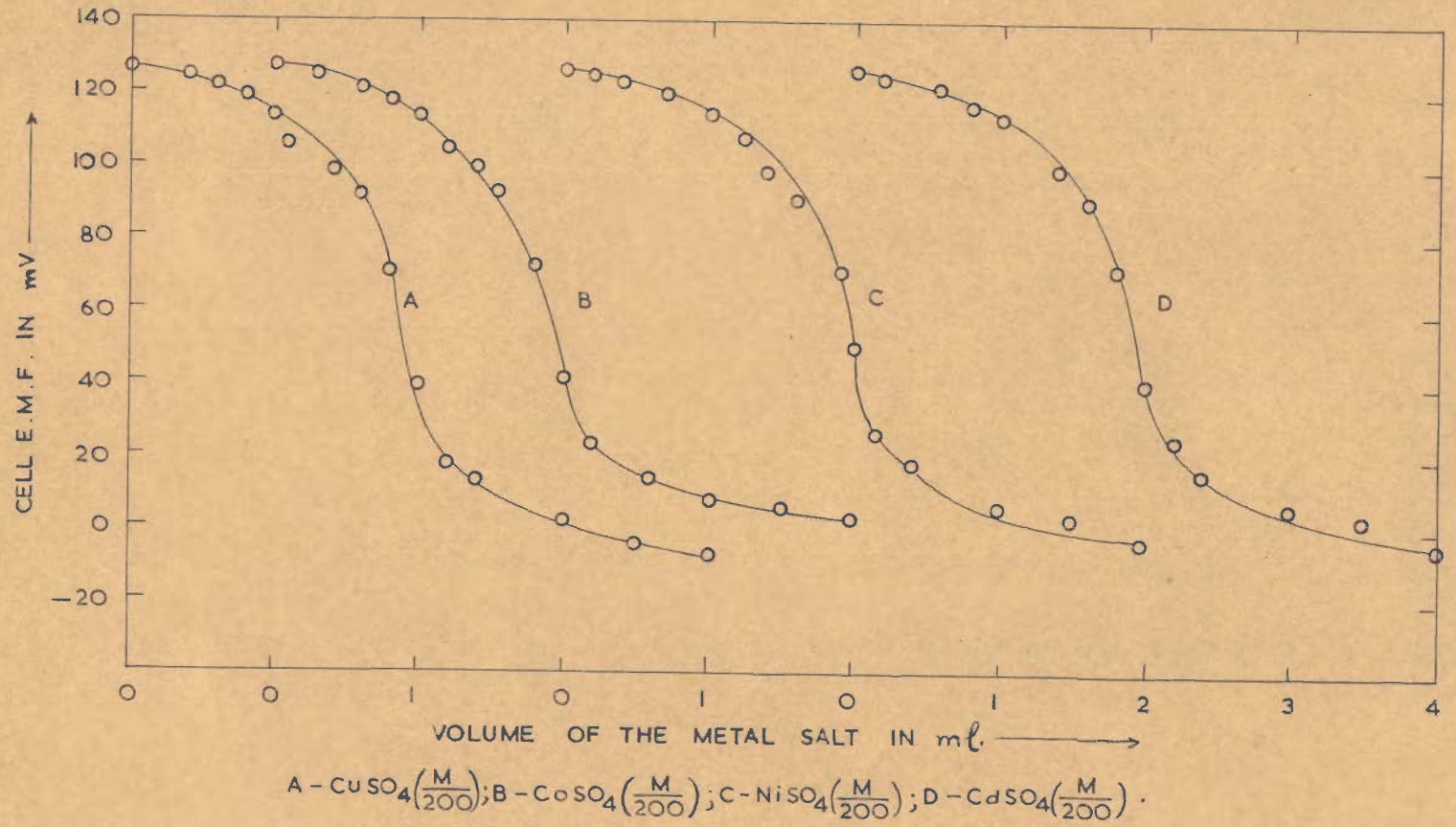

FIG. 8. POTENTIOMETRIC TITRATIONS OF POT. MYRISTATE (M/1000) AGAINST METAL SALTS ; VOLUME TITRATED = 20 mℓ.

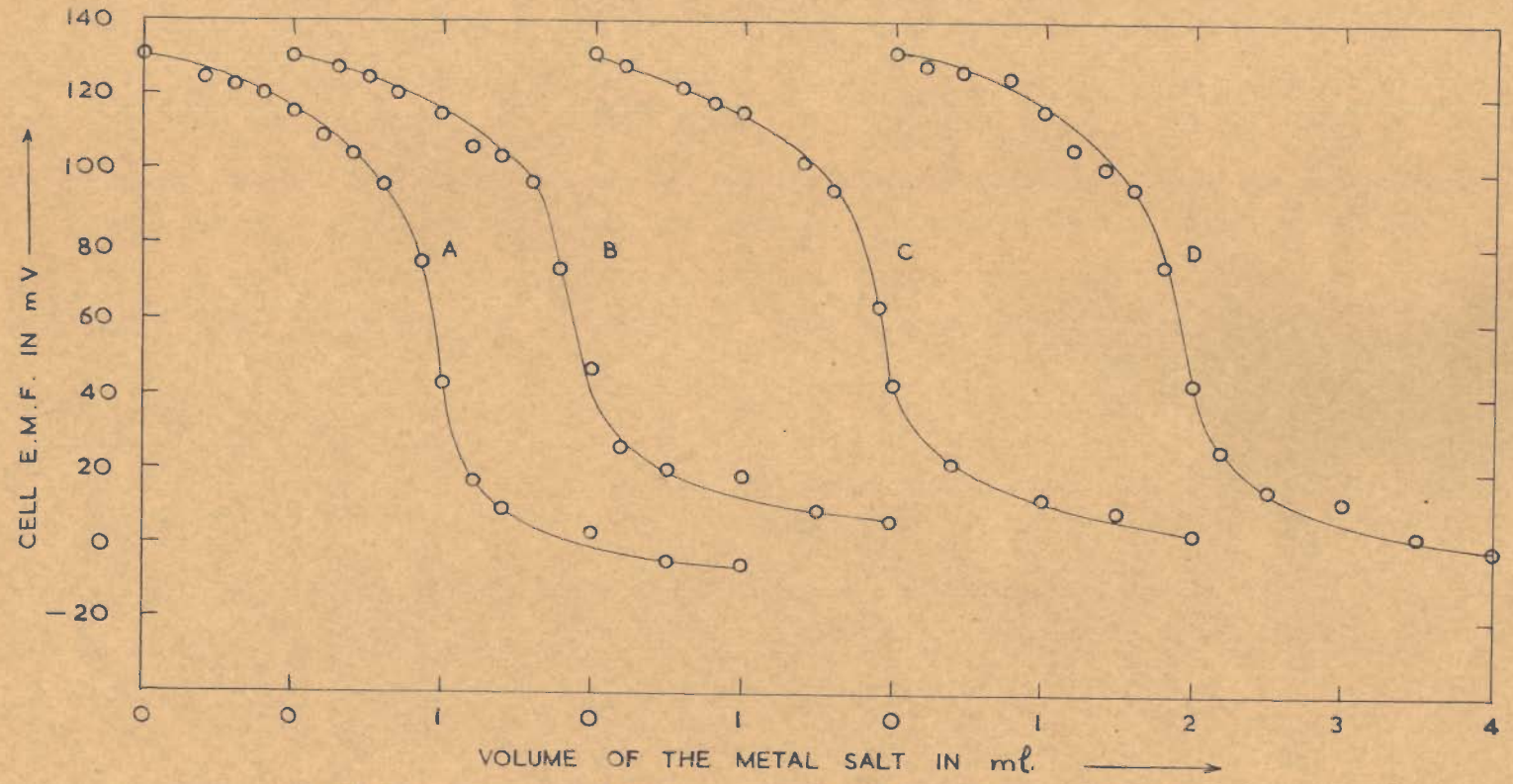

FIG. 9. POTENTIOMETRIC TITRATIONS OF POT. PALMITATE (M/1000) AGAINST METAL SALTS ; VOLUME TITRATED = 20 mℓ.

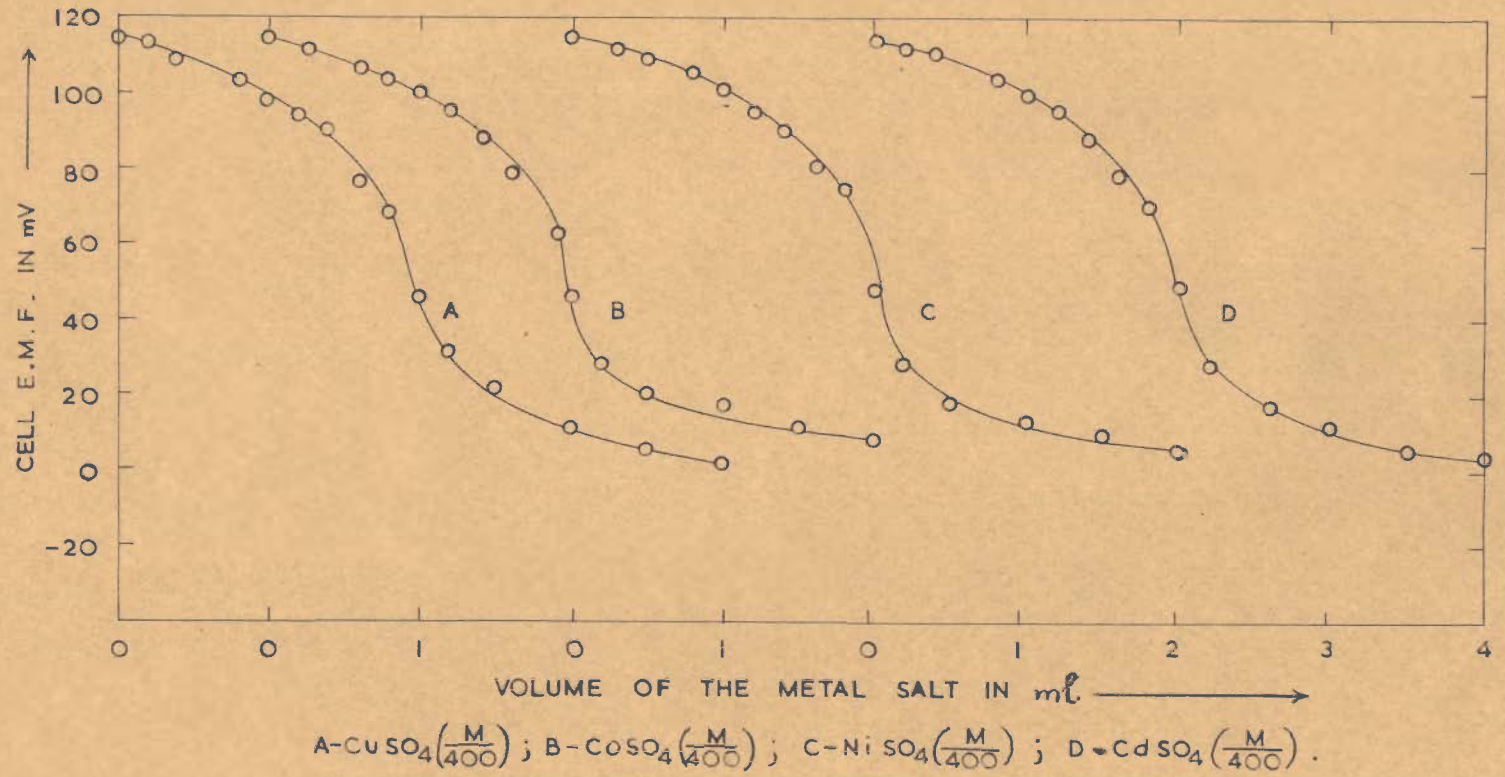

FIG. 10. POTENTIOMETRIC TITRATIONS OF POT. STEARATE (M/2000) AGAINST METAL SALTS ; VOLUME TITRATED = 20 mℓ.

RESULTS AND DISCUSSION

(A) Determination of c.m.c.of potassium soaps from detergent anion activity variation:

The electrode reactions taking place at various metal, metal-soap electrodes are as follows:-

Copper, copper soap electrodes:

$$Cu^{++} + 2e \rightleftharpoons Cu$$
$$CuD_2 \rightleftharpoons Cu^{++} + 2D^-$$
$$CuD_2 + 2e \rightleftharpoons Cu + 2D^-$$

The reduction potential of the copper, copper soap electrode is given by the following equation:

$$E_{CuD_2 \rightarrow Cu} = E^o_{CuD_2 \rightarrow Cu} - \frac{2.303\ RT}{F} \log a_{D^-} \quad \ldots\ldots\ldots (1)$$

where a_{D^-} is the activity of detergent anions.

Cobalt, cobalt soap electrodes:

$$Co^{++} + 2e \rightleftharpoons Co$$
$$CoD_2 \rightleftharpoons Co^{++} + 2D^-$$
$$CoD_2 + 2e \rightleftharpoons Co + 2D^-$$

The reduction potential of the electrode is given by the equation,

$$E_{CoD_2 \rightarrow Co} = E^o_{CoD_2 \rightarrow Co} - \frac{2.303\ RT}{F} \log a_{D^-} \quad \ldots\ldots\ldots (2)$$

Nickel, nickel soap electrodes:

$$Ni^{++} + 2e \rightleftharpoons Ni$$
$$NiD_2 \rightleftharpoons Ni^{++} + 2D^-$$
$$NiD_2 + 2e \rightleftharpoons Ni + 2D^-$$

The reduction potential of the electrode is given by the equation,

$$E_{NiD_2 \rightarrow Ni} = E^{o}_{NiD_2 \rightarrow Ni} - \frac{2.303\ RT}{F} \log a_{D^-} \quad \ldots\ldots\ldots(3)$$

Since the E.M.F. of the complete cell is equal to the algebraic difference of reduction potentials of metal, metal-soap electrode and calomel electrode, the metal, metal-soap electrode potential can be evaluated as the potential of calomel electrode is known(21) at 35°C.

E.M.F. of the cell = reduction potential of calomel electrode - reduction potential of metal, metal soap electrode

$$E_{Cell} = E_{Hg_2Cl_2 \rightarrow Hg} - E_{MD_2 \rightarrow M}$$

$$E_{MD_2 \rightarrow M} = E_{Hg_2Cl_2 \rightarrow Hg} - E_{Cell}$$

$$= 0.2339 - E_{Cell}$$

(M stands for copper, cobalt and nickel)

The concentration ranges of potassium laurate, myristate, palmitate and stearate used were 0.001-0.1M, 0.00025-0.05M, 0.0001-0.0075M and 0.0001-0.002M, respectively. Curves A,B (Fig.1),A,B (Fig.2) are the plots between reduction potentials of copper, copper laurate; copper, copper myristate; copper, copper palmitate; and copper, copper stearate electrodes and the logarithm of the concentrations of corresponding potassium soaps; curves A,B (Fig.3), A,B (Fig.4) are the plots between reduction potentials of cobalt, cobalt laurate; cobalt, cobalt

myristate; cobalt, cobalt palmitate;and cobalt, cobalt stearate electrodes and the logarithm of the concentrations of potassium soaps; curves A,B (Fig.5), A,B (Fig.6) are the plots between the reduction potentials of nickel, nickel laurate; nickel, nickel myristate; nickel, nickel palmitate;and nickel, nickel stearate electrodes and the logarithm of the concentrations of potassium laurate, myristate, palmitate and stearate, respectively.

The curves (Figs.1-6) give breaks which can provide useful information regarding the nature of the soap solutions. In dilute solutions, i.e., below the c.m.c, the soaps deviate only slightly from the ideal behaviour of an electrolyte. They behave as moderately strong electrolytes. Increase in the soap concentration results in increase in the activity (concentration) of the detergent anions. Following the electrode potential equations(1-3), the reduction potential of the metal, metal-soap electrode changes to more negative values with increase in soap concentration. Therefore, the first linear branch in the curves A,B (Figs.1-6) corresponds to the increase in activity of detergent anions. This observation is, therefore, in agreement with the accepted concept of a soap (surfactant) behaving as a moderately strong electrolyte below c.m.c.. However, at concentration ranges above the c.m.c., the behaviour of the soap is non-ideal due to the micellization of detergent anions and the increase in the soap concentration does not result in increase in the activity of the detergent anions. Therefore, the concentration of detergent

anions above c.m.c. remains almost constant and so does the electrode potential. Obviously the second linear branch of the curves A,B (Figs.1-6) corresponds to the behaviour of soaps above c.m.c. and these breaks in the curves must correspond to the c.m.c. of the soaps. The c.m.c. values determined by this method are given in Table -3 and compared with those obtained by other methods :

Table -3

Comparative c.m.c. values of potassium soaps

Soap	Tempr., (°C)	c.m.c.	Method of determination
Potassium laurate	35	2.512×10^{-2}M	Copper, copper laurate electrode
	35	2.512×10^{-2}M	Cobalt, cobalt laurate electrode
	35	2.427×10^{-2}M	Nickel, nickel laurate electrode
	35	2.70×10^{-2}M	Interferometric method (22)
	25.8	2.40×10^{-2}M	Spectral dye method (23)
	50	2.45×10^{-2}M	Solubilization method (24)
Potassium myristate	35	6.823×10^{-3}M	Copper, copper myristate electrode
	35	6.918×10^{-3}M	Cobalt, cobalt myristate electrode
	35	6.761×10^{-3}M	Nickel, nickel myristate electrode
	25.8	6.00×10^{-3}M	Spectral dye method (23)
	30	7.00×10^{-3}M	Solubilization method (24)
Potassium palmitate	35	3.02×10^{-3}M	Copper, copper palmitate electrode
	35	3.162×10^{-3}M	Cobalt, cobalt palmitate electrode
	35	3.02×10^{-3}M	Nickel, nickel palmitate electrode

Soap	Tempr., (°C)	c.m.c.	Method of determination
Potassium stearate	35	8.31×10^{-4}M	Copper, copper stearate electrode
	35	8.71×10^{-4}M	Cobalt, cobalt stearate electrode
	35	8.51×10^{-4}M	Nickel, nickel stearate electrode
	50	$< 10.00 \times 10^{-4}$M	Solubilization method(24)
	60	$< 8.00 \times 10^{-4}$M	Solubilization method(24)

From Table-3 it is seen that the c.m.c. values of the soaps, determined by studying the detergent anion activity variation using copper, copper soap; cobalt, cobalt soap; and nickel, nickel soap electrode systems agree well with those found by other methods. This agreement may be taken as an evidence that the activity of detergent anions in the soap solutions can be conveniently and accurately measured by a metal, metal soap electrode system.

A closer survey of the results (Figs.1-6) would reveal that the metal, metal-soap electrode potential does not exactly remain constant but changes gradually to more positive values with increase in concentration of the soap. This gradual change in electrode potential indicates the decrease in the activity of the detergent anions after c.m.c.. These results agree well qualitatively with the measurements of laurate ion activity as determined

by using positively charged collodion membrane(25). In the latter work it was found that the laurate ion activity went through an apparent maximum and declined thereafter. The results obtained by electrode systems also indicate that detergent anion activity reaches a maximum at c.m.c. and declines thereafter.

The decline in detergent anion activity after c.m.c. may be due to two reasons:(1) further micellization of unmicellized detergent anions after c.m.c. (ii) the decrease in activity coefficient of detergent anions after c.m.c.. Therefore, even if the concentration of detergent anions after c.m.c. remains constant, the decrease in activity coefficient will cause decrease in activity of detergent anions. (It is difficult to assume that activity coefficient of detergent anions will remain constant after c.m.c. throughout the entire concentration ranges, as the interionic interactions are changing).

(B) Transport number:

The E.M.F. of the cell (without transference)

Cu	Cu-soap(s), Na-soap(C_1)	0.05% sodium amalgam	Cu-soap(s), Na-soap(C_2)	Cu

is given by the following equation,

$$E = \frac{2RT}{F} \ln \frac{a_1}{a_2} \quad \ldots\ldots\ldots\ldots (4)$$

where 'a_1' and 'a_2' represent mean activities of sodium soap in the two solutions of concentrations 'C_1' and 'C_2', respectively.

The E.M.F. of the cell (with transference)

Cu | Cu-soap(s), Na-soap(C_1) ¦ Cu-soap(s), Na-soap(C_2) | Cu

is given by the following equation,

$$E_t = \frac{2t_{Na^+} RT}{F} \ln \frac{a_1}{a_2} \quad \ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Therefore,

$$\frac{E_t}{E} = t_{Na^+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

and

$$t_{D^-} = 1 - t_{Na^+} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where t_{Na^+} and t_{D^-} represent the transport numbers of sodium and detergent ions, respectively.

The transport numbers of sodium and detergent ions calculated from E.M.F. measurements are given in the following Tables 4,5 :

Table -4

Transport number of sodium and laurate ions in aqueous solution of sodium laurate determined from E.M.F. measurements employing copper, copper laurate electrode.

Concentration range of sodium laurate	t_{Na^+}	$t_{C_{11}H_{23}COO^-}$
1×10^{-3}M to 2×10^{-3}M	0.683	0.317
2×10^{-3}M to 3×10^{-3}M	0.681	0.319
3×10^{-3}M to 5×10^{-3}M	0.700	0.300
5×10^{-3}M to 8×10^{-3}M	0.707	0.293
8×10^{-3}M to 10×10^{-3}M	0.723	0.277
10×10^{-3}M to 20×10^{-3}M	0.720	0.280

Table -5

Transport number of sodium and myristate ions in aqueous solution of sodium myristate determined from E.M.F. measurements employing copper, copper myristate electrode.

Concentration range of sodium myristate	t_{Na^+}	$t_{C_{13}H_{27}COO^-}$
$1x10^{-3}$M to $2x10^{-3}$M	0.741	0.259
$2x10^{-3}$M to $3x10^{-3}$M	0.771	0.229
$3x10^{-3}$M to $4x10^{-3}$M	0.753	0.247
$4x10^{-3}$M to $5x10^{-3}$M	0.773	0.227

The transport numbers of sodium and detergent ions have been determined for concentration ranges $1x10^{-3}$M to $20x10^{-3}$M and $1x10^{-3}$M to $5x10^{-3}$M for sodium laurate and myristate, respectively. These concentration ranges investigated are below the c.m.c. values of respective sodium soaps. The transport numbers above c.m.c. values could not be determined as the equation(6) does not hold good. Moreover, the concentration of detergent anions remains almost same in both the half-cells resulting in practically nil E.M.F. for the cell without transference.

It is evident from Tables 4,5 that, in general, transport number of sodium ions increases with increase in sodium soap concentration. It is difficult to comment on the reliability of the data as the possible interaction between solution and sodium metal at such

dilutions may affect E.M.F. measurements. Moreover, the hydrolysis of sodium soaps will also affect the results.

(C) Potentiometric titrations:

The concentration of potassium laurate, myristate, palmitate and stearate used in potentiometric titrations has been chosen below the c.m.c. of the respective soaps.

Titration between potassium soaps and copper sulphate:

Potentiometric titration curve A (Figs.7-10) is obtained by plotting cell E.M.F. vs volume of the copper sulphate added. These curves are of S shaped. From these curves, it is evident that E.M.F. of the cell

$$Cu \;\vdots\; CuD_2(s),\ KD(C) \;\vdots\; \begin{matrix}\text{satd.KCl}\\ \text{salt bridge}\end{matrix} \;\vdots\; \begin{matrix}\text{KCl satd.,}\\ Hg_2Cl_2(s)\end{matrix} \;\vdots\; Hg$$

decreases slowly in the beginning followed by a sharp fall in the E.M.F. at the equivalence point. The change in the E.M.F. of the cell is due to the change in the potential of indicator electrode. The curve can be explained on the basis of the electrode reaction taking place at the indicator electrode.

$$CuD_2 + 2e \rightleftharpoons Cu + 2D^-$$

$$E = E^{o}_{CuD_2 \rightarrow Cu} - \frac{2.303\ RT}{F} \log a_{D^-}$$

Up to the equivalence point the indicator electrode behaves as reversible to detergent (laurate, myristate, palmitate and stearate) ions. The removal of

detergent ions from the solution in the form of the precipitate on the addition of copper sulphate changes the potential of copper, copper soap electrode (indicator electrode) and thereby causes the decrease in the E.M.F. of the cell.

Beyond equivalence point, further addition of copper sulphate simply increases the concentration of copper ions and the indicator electrode is simply reversible to copper ions. The electrode reaction taking place at the indicator electrode is

$$Cu^{++} + 2e \rightleftharpoons Cu$$

$$E = E^{o}_{Cu^{++} \rightarrow Cu} + \frac{2.303\ RT}{2F} \log a_{Cu^{++}}$$

Therefore, the indicator electrode will behave reversibly w.r.t. Cu^{++} ions beyond equivalence point and the E.M.F. of the cell will decrease with the further addition of $CuSO_4$ (even after the equivalence point) and S shaped curve is obtained.

From the inflexion point of the curve A (Figs.7-10) the combining ratio for copper sulphate and potassium soaps comes out to be 1:2

$$2KD + CuSO_4 = CuD_2 + K_2SO_4$$

Titration between potassium soaps and cobalt sulphate:

The curve B (Figs.7-10) is obtained by plotting cell E.M.F. vs volume of cobalt sulphate added. It is rather surprising that the titration curve B (Figs.7-10)

is also of the S type inspite of the fact that copper, copper soap electrode was used as the indicator electrode. The indicator electrode, up to the equivalence point, behaves reversibly with respect to detergent ions. The electrode potential is again governed by the same equation,

$$E = E^{o}_{CuD_2 \rightarrow Cu} - \frac{2.303\ RT}{F} \log a_{D^-}$$

up to the equivalence point.

However, it is noted from the curve B (Figs.7-10) that even beyond equivalence point, the E.M.F. of the cell is decreasing with the further addition of cobalt sulphate, indicating thereby that the indicator electrode is now behaving reversibly w.r.t. cobalt ions. It is likely that the indicator electrode may now behave as an electrode of the "third kind"(26). The electrode system may be written as

$$Cu \;\vdots\; CuD_2(s), CoD_2(s), \quad CoSO_4 \text{ soln.}$$

The following electrode reaction of the indicator electrode is assumed to take place.

The copper is deposited from the solution, thus

$$Cu^{++} + 2e \rightleftharpoons Cu(s)$$

Hence, copper soap will dissolve

$$CuD_2(s) \rightleftharpoons Cu^{++} + 2D^-$$

The addition of detergent ions, due to the shift in above equilibria towards right, in the solution causes the precipitation of cobalt soap so that its

solubility product may be maintained, thus

$$Co^{++} + 2D^{-} \rightleftharpoons CoD_2(s)$$

The net reaction is

$$CuD_2(s) + Co^{++} + 2e \rightleftharpoons CoD_2(s) + Cu(s)$$

The electrode system thus behaves as an electrode reversible with respect to cobalt ions. The electrode potential is given by the equation,

$$E = E^{o} + \frac{2.303\ RT}{2F} \log a_{Co^{++}}$$

Therefore, further addition of cobalt sulphate, beyond equivalence point, causes the E.M.F. of the cell to decrease (because electrode behaves reversible w.r.t. Co^{++} ions) and the titration curve of the S type is obtained.

It is evident from the inflexion point on the curve B (Figs.7-10) that cobalt sulphate and potassium soaps combine in the molar ratio of 1:2

$$CoSO_4 + 2KD = CoD_2 + K_2SO_4$$

Titration between potassium soaps and nickel sulphate:

The titration curve C (Figs.7-10) is obtained by plotting the cell E.M.F. vs volume of nickel sulphate added. This curve is also of S type. Here again the same reasoning as put forward for the titration between potassium soaps and cobalt sulphate may be applied. Up to the equivalence point, the indicator electrode behaves reversibly w.r.t. detergent ions. However, beyond

equivalence point, the indicator electrode behaves reversibly w.r.t. nickel ions. The net electrode reaction at the indicator electrode now is following :

$$CuD_2(s) + Ni^{++} + 2e \rightleftharpoons NiD_2(s) + Cu(s)$$

The electrode potential is given by the equation,

$$E = E^o + \frac{2.303\ RT}{2F} \log a_{Ni^{++}}$$

From the inflexion point, it is evident that nickel sulphate and potassium soaps combine in the molar ratio of 1:2

$$NiSO_4 + 2KD = NiD_2 + K_2SO_4$$

Titration between potassium soaps and cadmium sulphate:

The titration curve D (Figs.7-10) is obtained by plotting cell E.M.F. vs volume of cadmium sulphate added. This curve is also of S type. Up to the equivalence point, the indicator electrode behaves reversibly w.r.t. detergent ions as usual. However, beyond equivalence point, the indicator electrode behaves reversibly w.r.t. cadmium ions. The net electrode reaction taking place, beyond equivalence point, at the indicator electrode is following:

$$CuD_2(s) + Cd^{++} + 2e \rightleftharpoons CdD_2(s) + Cu(s)$$

The electrode potential is governed by the equation,

$$E = E^o + \frac{2.303\ RT}{2F} \log a_{Cd^{++}}$$

It is evident from the inflexion point on the curve D (Figs.7-10) that cadmium sulphate and potassium soaps combine in the molar ratio of 1:2.

$$2KD + CdSO_4 = CdD_2 + K_2SO_4$$

The behaviour of the three soaps, viz., cobalt, nickel and cadmium towards copper, copper soap electrode is in accordance with their positions in electrochemical series.

Analytical utility of potentiometric titrations:

It is obvious from the above discussion that these potentiometric titrations between soaps and metal salts can be conveniently used to determine the composition of heavy metal soaps. This method is, no doubt, more convenient to the chemical method which is usually employed to determine the composition of heavy metal soaps. Moreover, once the composition of heavy metal soaps is established, the potentiometric titrations can be usefully and conveniently employed to determine the concentration of sodium or potassium soaps in their aqueous solutions with or without the presence of impurities.

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CHAPTER - 2

" Determination of the thermodynamical constants of the reactions involving heavy metal soaps "

INTRODUCTION

Galvanic cells provide a convenient means of measuring directly the free energy change (ΔG) accompanying certain reactions. The electrical work done by a reversible galvanic cell is a measure of free energy change accompanying the cell reaction. Therefore, ΔG for a reaction can be determined from E.M.F. measurements provided an appropriate cell can be set up in which the reaction under consideration takes place reversibly. Furthermore, by making use of Gibbs-Helmholtz equation and the second law of thermodynamics, change in heat content (ΔH) and entropy change (ΔS) accompanying the cell reaction can also be obtained provided the temperature coefficient ($\frac{dE}{dT}$) of E.M.F.(E) of the cell is known. The articles dealing with the determination of these thermodynamical functions from E.M.F. measurements are numerous and so only few may be cited. Taylor and Perrott(1) studied following cell combinations :

Cd(Amg.) / $CdCl_2 2.5H_2O$ and satd. solution / AgCl / Ag

Cd(Amg.) / $CdCl_2 2.5H_2O$ and satd. solution / $PbCl_2$ / Pb

Cd(Amg.) / CdI_2 and satd. solution / AgI / Ag

Cd(Amg.) / CdI_2 and satd. solution / PbI_2 / Pb

and determined ΔH for cell reactions from their E.M.F. measurements.

Gerke(2) determined ΔG, ΔH and ΔS for the following reactions:

$$Pb + 2AgCl \rightleftharpoons PbCl_2 + 2Ag$$
$$Pb + 2AgI \rightleftharpoons PbI_2 + 2Ag$$
$$Ag + \tfrac{1}{2}Hg_2Cl_2 \rightleftharpoons AgCl + Hg$$
$$Ag + \tfrac{1}{2}Cl_2 \rightleftharpoons AgCl$$

from E.M.F. measurements.

Larson(3) determined the value of ΔS for the reaction occurring in the cell Ag/AgBr(s), KBr aq., $Hg_2Br_2(s)$/Hg from its E.M.F. measurements.

The above considerations can also be applied to reactions involving detergent ions provided suitable reversible cells (simple or amalgam type) can be set up. The thermodynamical constants of the following heavy metal soaps reaction were determined :

$$Cu + 2AgD \rightleftharpoons CuD_2 + 2Ag$$
$$Ni + CuD_2 \rightleftharpoons NiD_2 + Cu$$
$$Co + CuD_2 \rightleftharpoons CoD_2 + Cu$$
$$Co + NiD_2 \rightleftharpoons CoD_2 + Ni$$

with the help of the following cells :

$$Cu \,/\, CuD_2(s),\ KD,\ AgD(s) \,/\, Ag$$
$$Ni \,/\, NiD_2(s),\ KD,\ CuD_2(s) /\ Cu$$
$$Co \,/\, CoD_2(s),\ KD,\ CuD_2(s) /\ Cu$$
$$Co \,/\, CoD_2(s),\ KD,\ NiD_2(s) /\ Ni$$

(D = laurate, myristate, palmitate and stearate)

EXPERIMENTAL

Nickel, Copper and Cobalt soaps :

These soaps were prepared as described in Chapter 1.

Silver soaps :

Silver soaps were prepared by direct metathesis at 50-55°C from their corresponding potassium soaps and silver nitrate solution in water. The precipitated silver soaps were washed with water and then with ethanol to remove free precipitant. They were kept in dark.

Potassium laurate, myristate, palmitate and stearate :

These potassium soaps were prepared as described in Chapter 1.

Preparation of nickel, cobalt and copper electrodes :

These electrodes were prepared as described in Chapter 1.

Preparation of silver electrode :

Silver electrodes were prepared by depositing silver on platinum wires. To silver nitrate solution (containing 0.2 gm. of silver per 100 ml) KCN was added until the precipitate of silver cyanide got dissolved and then an excess of KCN was added. The platinum electrodes placed in this solution, were connected to a 4 volt battery and a current of 30 mA was passed for about 2 hrs. The silver electrodes were washed with doubly-distilled water

and then put to use.

E.M.F. measurements :

A Cambridge portable potentiometer was used for E.M.F. measurements of the following cells:

Cu / CuD_2(s), KD(C), AgD(s) / Ag.....(1)

Ni / NiD_2(s), KD(C), CuD_2(s)/ Cu.....(2)

Co / CoD_2(s), KD(C), CuD_2(s)/ Cu.....(3)

Co / CoD_2(s), KD(C), NiD_2(s)/ Ni.....(4)

at different temperatures in a water thermostat. The cell vessel employed was of H type. Standard solutions of potassium soaps were prepared in doubly-distilled water and transferred to H type cell, placed in thermostat.

For cell number(1) the two limbs of the cell were provided with silver and copper electrodes, respectively and it contained potassium soap solution saturated with silver and copper soaps; for cell number(2) the two limbs were provided with nickel and copper electrodes, respectively and potassium soap solution was saturated with nickel and copper soaps; for cell no.(3) the two limbs were provided with cobalt and copper electrodes, respectively and potassium soap solution was saturated with cobalt and copper soaps; for cell number(4) the two limbs were provided with cobalt and nickel electrodes, respectively and potassium soap solution was saturated with cobalt and nickel soaps. Some solid metal soaps were always added to the cell to make certain that potassium soap solution was always saturated with respect to metal soaps.

The experimental observations are given in the following Tables 1-16:

Table -1

Temperature coefficient of E.M.F. of the cell

$Cu/(C_{11}H_{23}COO)_2Cu(s)$, $C_{11}H_{23}COOK(C)$, $C_{11}H_{23}COOAg(s)/Ag$

Pot.laurate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	25	0.285		
8	25	0.285		
10	25	0.285		
10	30	0.290	0.0010	
10	35	0.295	0.0010	
10	40	0.3005	0.0011	0.001
10	45	0.305	0.0009	

Table -2

Temperature coefficient of E.M.F. of the cell

$Cu/(C_{13}H_{27}COO)_2Cu(s)$, $C_{13}H_{27}COOK(C)$, $C_{13}H_{27}COOAg(s)/Ag$

Pot.myristate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1	30	0.270		
2.5	30	0.270		
5	30	0.270		
5	40	0.2795	0.00095	
5	50	0.289	0.00095	0.00095

Table - 3

Temperature coefficient of E.M.F. of the cell
$Cu/(C_{15}H_{31}COO)_2Cu(s)$, $C_{15}H_{31}COOK(C)$, $C_{15}H_{31}COOAg(s)/Ag$

Pot.palmitate concn., C ($\times10^{-3}$M)	Temperature T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1.0	30	0.241		
1.5	30	0.241		
2.5	30	0.241		
2.5	40	0.250	0.0009	0.0009
2.5	50	0.259	0.0009	

Table - 4

Temperature coefficient of E.M.F. of the cell
$Cu/(C_{17}H_{35}COO)_2Cu(s)$, $C_{17}H_{35}COOK(C)$, $C_{17}H_{35}COOAg(s)/Ag$

Pot.stearate concn., C ($\times10^{-4}$M)	Temperature T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	30	0.210		
7	30	0.210		
8	30	0.210		
8	35	0.214	0.0008	
8	40	0.218	0.0008	0.000816
8	50	0.2265	0.00085	

Table -5

Temperature coefficient of E.M.F. of the cell
$Ni/(C_{11}H_{23}COO)_2Ni(s)$, $C_{11}H_{23}COOK(C)$, $(C_{11}H_{23}COO)_2Cu(s)/Cu$

Pot.laurate concn., C ($x10^{-3}M$)	Temperature T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	25	0.1285		
8	25	0.1285		
10	25	0.1285		
10	30	0.1242	-0.00086	
10	40	0.1162	-0.00080	-0.000826
10	45	0.1120	-0.00082	

Table -6

Temperature coefficient of E.M.F.of the cell
$Ni/(C_{13}H_{27}COO)_2Ni(s)$, $C_{13}H_{27}COOK(C)$, $(C_{13}H_{27}COO)_2Cu(s)/Cu$

Pot.myristate concn., C ($x10^{-3}M$)	Temperature T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (Volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1	30	0.1287		
2.5	30	0.1287		
5	25	0.1325		
5	30	0.1287	-0.00076	
5	35	0.1250	-0.00074	
5	40	0.1212	-0.00076	-0.00075
5	45	0.1175	-0.00074	

Table -7

Temperature coefficient of E.M.F. of the cell
$Ni/(C_{15}H_{31}COO)_2Ni(s)$, $C_{15}H_{31}COOK(C)$, $(C_{15}H_{31}COO)_2Cu(s)/Cu$

Pot.palmitate concn., C ($\times10^{-3}$M)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1.0	25	0.1350		
1.5	25	0.1350		
2.5	25	0.1350		
2.5	30	0.1315	-0.00070	
2.5	35	0.1280	-0.00070	
2.5	40	0.1246	-0.00068	-0.0007
2.5	45	0.1210	-0.00072	

Table -8

Temperature coefficient of E.M.F. of the cell
$Ni/(C_{17}H_{35}COO)_2Ni(s)$, $C_{17}H_{35}COOK(C)$, $(C_{17}H_{35}COO)_2Cu(s)/Cu$

Pot.stearate concn., C ($\times10^{-4}$M)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	30	0.1345		
7	30	0.1350		
8	25	0.1375		
8	30	0.1343	-0.00064	
8	35	0.1310	-0.00066	-0.00066
8	40	0.1276	-0.00068	
8	45	0.1243	-0.00066	

Table -9

Temperature coefficient of E.M.F. of the cell

$Co/(C_{11}H_{23}COO)_2Co(s)$, $C_{11}H_{23}COOK(C)$, $(C_{11}H_{23}COO)_2Cu(s)/Cu$

Pot.laurate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	30	0.240		
8	30	0.240		
10	22	0.250		
10	30	0.240	-0.00125	
10	40	0.230	-0.0010	-0.001133
10	50	0.2185	-0.00115	

Table -10

Temperature coefficient of E.M.F. of the cell

$Co/(C_{13}H_{27}COO)_2Co(s)$, $C_{13}H_{27}COOK(C)$, $(C_{13}H_{27}COO)_2Cu(s)/Cu$

Pot.myristate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1	21	0.259		
2.5	21	0.259		
5	21	0.259		
5	30	0.250	-0.001	
5	40	0.241	-0.0009	-0.00095
5	50	0.2315	-0.00095	

Table -11

Temperature coefficient of E.M.F. of the cell

$Co/(C_{15}H_{31}COO)_2Co(s)$, $C_{15}H_{31}COOK(C)$, $(C_{15}H_{31}COO)_2Cu(s)/Cu$

Pot.palmitate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1.0	25	0.258		
1.5	25	0.259		
2.5	19	0.2645		
2.5	25	0.2595	-0.000833	
2.5	30	0.255	-0.0009	
2.5	40	0.246	-0.0009	-0.0008832
2.5	50	0.237	-0.0009	

Table -12

Temperature coefficient of E.M.F. of the cell

$Co/(C_{17}H_{35}COO)_2Co(s)$, $C_{17}H_{35}COOK(C)$, $(C_{17}H_{35}COO)_2Cu(s)/Cu$

Pot.stearate concn., C ($x10^{-4}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	30	0.269		
7	30	0.269		
8	21	0.2755		
8	30	0.268	-0.000833	
8	40	0.260	- 0.0008	-0.000811
8	50	0.252	- 0.0008	

Table -13

Temperature coefficient of E.M.F. of the cell

$Co/(C_{11}H_{23}COO)_2Co(s)$, $C_{11}H_{23}COOK(C)$, $(C_{11}H_{23}COO)_2Ni(s)/Ni$

Pot.laurate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	25	0.121		
8	25	0.121		
10	20	0.127		
10	25	0.121	-0.00120	
10	30	0.115	-0.00120	
10	40	0.1025	-0.00125	-0.001225
10	50	0.090	-0.00125	

Table -14

Temperature coefficient of E.M.F. of the cell

$Co/(C_{13}H_{27}COO)_2Co(s)$, $C_{13}H_{27}COOK(C)$, $(C_{13}H_{27}COO)_2Ni(s)/Ni$

Pot.myristate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1	25	0.131		
2.5	25	0.131		
5	21	0.135		
5	25	0.131	-0.0010	
5	30	0.126	-0.0010	
5	40	0.1155	-0.00105	-0.001025
5	50	0.105	-0.00105	

Table -15

Temperature coefficient of E.M.F. of the cell

$Co/(C_{15}H_{31}COO)_2Co(s)$, $C_{15}H_{31}COOK(C)$, $(C_{15}H_{31}COO)_2Ni(s)/Ni$

Pot.palmitate concn., C ($x10^{-3}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
1.0	30	0.128		
1.5	30	0.1285		
2.5	20	0.138		
2.5	30	0.1285	-0.00095	
2.5	35	0.124	-0.00090	
2.5	44	0.1155	-0.000944	-0.0009275
2.5	50	0.110	-0.000916	

Table -16

Temperature coefficient of E.M.F. of the cell

$Co/(C_{17}H_{35}COO)_2Co(s)$, $C_{17}H_{35}COOK(C)$, $(C_{17}H_{35}COO)_2Ni(s)/Ni$

Pot.stearate concn., C ($x10^{-4}M$)	Temperature, T (^oC)	Cell E.M.F., E (volts)	$\frac{dE}{dT}$ (volts/deg.)	Mean $\frac{dE}{dT}$ (volts/deg.)
5	30	0.1370		
7	30	0.1373		
8	21	0.1435		
8	30	0.1360	-0.000833	
8	40	0.1275	-0.000850	-0.0008357
8	45	0.1233	-0.000840	
8	50	0.1192	-0.00082	

RESULTS AND DISCUSSION

Since both the electrodes involved in cells under considerations are reversible with respect to the detergent anion, the E.M.F. of the cells should be independent of the concentration of potassium soap and should be equal to algebraic difference of standard reduction or oxidation potential of the electrodes. The concentration ranges of pot. soaps investigated were from 1×10^{-2}M to 5×10^{-3}M, 5×10^{-3}M to 1×10^{-3}M, 2.5×10^{-3}M to 1×10^{-3}M and 8×10^{-4}M to 5×10^{-4}M for potassium laurate, myristate, palmitate and stearate, respectively. These concentrations of potassium soaps are just below the c.m.c. values. Higher concentrations were not studied because above c.m.c. values, the concentration of detergent anions will not increase with increase in potassium soap concentration. It is evident from Tables 1-16 that the E.M.F. of the cells, in general, is independent of the concentration of potassium soap solutions. However, in some cases a variation of $\pm$ 0.001 volt is observed. Due to high dilution of potassium soap solution, this much variation is quite plausible.

The following equations have been used for calculating ΔG, ΔH and ΔS at $303^{\circ}K$.

$$\Delta G = - nEF \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

$$\Delta G - \Delta H = T\left[\frac{d(\Delta G)}{dT}\right]$$

or

$$- nEF - \Delta H = - nFT\left(\frac{dE}{dT}\right)$$

or

$$\Delta H = - nEF + nFT\left(\frac{dE}{dT}\right) \ldots\ldots\ldots \quad (2)$$

$$\Delta S = nF\left(\frac{dE}{dT}\right) \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

where

n = number of the electrons involved in cell reaction.

F = Faraday = 96500 coulombs

E = Cell E.M.F.

$\frac{dE}{dT}$ = Temperature coefficient of the cell E.M.F.

The values of ΔG, ΔH and ΔS for the cell reactions at $303^{o}K$ are given in the following Tables 17-20.

Table -17

E.M.F. of the cell Cu/Cu-soap(s), K-soap, Ag-soap(s)/Ag, temperature coefficient of E.M.F. and ΔG, ΔH and ΔS for the cell reactions.

Cell reaction for the passage of 2 faraday of electricity.	Cell E.M.F. at 303°K, E (volts)	$\frac{dE}{dT}$ (volts/deg.)	$\Delta G_{303°K}$ (cal.)	$\Delta H_{303°K}$ (cal.)	$\Delta S_{303°K}$ (cal./deg.)
$2C_{11}H_{23}COOAg+2e \rightleftharpoons 2Ag+2C_{11}H_{23}COO^-$					
$Cu+2C_{11}H_{23}COO^- \rightleftharpoons (C_{11}H_{23}COO)_2Cu+2e$					
$Cu+2C_{11}H_{23}COOAg \rightleftharpoons (C_{11}H_{23}COO)_2Cu+2Ag$	0.290	0.001	-13380	590	46.13
$Cu+2C_{13}H_{27}COOAg \rightleftharpoons (C_{13}H_{27}COO)_2Cu+2Ag$	0.270	0.00095	-12460	810	43.81
$Cu+2C_{15}H_{31}COOAg \rightleftharpoons (C_{15}H_{31}COO)_2Cu+2Ag$	0.241	0.0009	-11110	1460	41.51
$Cu+2C_{17}H_{35}COOAg \rightleftharpoons (C_{17}H_{35}COO)_2Cu+2Ag$	0.210	0.000816	- 9685	1695	37.62

Table -18

E.M.F. of the cell Ni/Ni-soap(s), K-soap, Cu-soap(s)/Cu, temperature coefficient of E.M.F. and ΔG, ΔH and ΔS for the cell reactions.

Cell reaction for the passage of 2 faraday of electricity	Cell E.M.F. at 303°K, E (volts)	$\frac{dE}{dT}$ (volts/deg.)	$\Delta G_{303^\circ K}$ (cal.)	$\Delta H_{303^\circ K}$ (cal.)	$\Delta S_{303^\circ K}$ (cal./deg.)
$(C_{11}H_{23}COO)_2Cu+2e \rightleftharpoons Cu+2C_{11}H_{23}COO^-$ $Ni+2C_{11}H_{23}COO^- \rightleftharpoons (C_{11}H_{23}COO)_2Ni+2e$					
$Ni+(C_{11}H_{23}COO)_2Cu \rightleftharpoons (C_{11}H_{23}COO)_2Ni+Cu$	0.1242	-0.000826	- 5728	- 17268	- 38.11
$Ni+(C_{13}H_{27}COO)_2Cu \rightleftharpoons (C_{13}H_{27}COO)_2Ni+Cu$	0.1287	-0.00075	- 5936	- 16416	- 34.59
$Ni+(C_{15}H_{31}COO)_2Cu \rightleftharpoons (C_{15}H_{31}COO)_2Ni+Cu$	0.1315	-0.0007	- 6064	- 15845	- 32.28
$Ni+(C_{17}H_{35}COO)_2Cu \rightleftharpoons (C_{17}H_{35}COO)_2Ni+Cu$	0.1343	-0.00066	- 6194	- 15415	- 30.44

Table -19

E.M.F. of the cell Co/ Co-soap(s), K-soap, Cu-soap(s)/Cu, temperature coefficient of E.M.F. and ΔG, ΔH and ΔS for the cell reactions.

Cell reaction for the passage of 2 faraday of electricity.	Cell E.M.F. at 303°K, E (volts)	$\frac{dE}{dT}$ (volts/deg.)	$\Delta G_{303^\circ K}$ (cal.)	$\Delta H_{303^\circ K}$ (cal.)	$\Delta S_{303^\circ K}$ (cal./deg.)
$(C_{11}H_{23}COO)_2Cu+2e \rightleftharpoons Cu+2C_{11}H_{23}COO^-$ $Co+2C_{11}H_{23}COO^- \rightleftharpoons (C_{11}H_{23}COO)_2Co+2e$					
$Co+(C_{11}H_{23}COO)_2Cu \rightleftharpoons (C_{11}H_{23}COO)_2Co+Cu$	0.240	-0.001133	-11070	-26900	- 52.26
$Co+(C_{13}H_{27}COO)_2Cu \rightleftharpoons (C_{13}H_{27}COO)_2Co+Cu$	0.250	-0.00095	-11530	-24800	- 43.81
$Co+(C_{15}H_{31}COO)_2Cu \rightleftharpoons (C_{15}H_{31}COO)_2Co+Cu$	0.255	-0.0008832	-11760	-24100	- 40.74
$Co+(C_{17}H_{35}COO)_2Cu \rightleftharpoons (C_{17}H_{35}COO)_2Co+Cu$	0.268	-0.000811	-12360	-23690	- 37.41

Table -20

E.M.F. of the cell Co/Co-soap($_s$), K-soap, Ni-soap($_s$)/Ni, temperature coefficient of E.M.F. and ΔG, ΔH and ΔS for cell reactions.

Cell reaction for the passage of 2 faraday of electricity	Cell E.M.F. at 303°K, E (volts)	$\frac{dE}{dT}$ (volts/deg.)	$\Delta G_{303°K}$ (cal.)	$\Delta H_{303°K}$ (cal.)	$\Delta S_{303°K}$ (cal./deg.)
$(C_{11}H_{23}COO)_2Ni+2e \rightleftharpoons Ni+2C_{11}H_{23}COO^-$ $Co+2C_{11}H_{23}COO^- \rightleftharpoons (C_{11}H_{23}COO)_2Co+2e$					
$Co+(C_{11}H_{23}COO)_2Ni \rightleftharpoons (C_{11}H_{23}COO)_2Co+Ni$	0.115	-0.001225	-5304	-22424	- 56.50
$Co+(C_{13}H_{27}COO)_2Ni \rightleftharpoons (C_{13}H_{27}COO)_2Co+Ni$	0.126	-0.001025	-5812	-20132	- 47.28
$Co+(C_{15}H_{31}COO)_2Ni \rightleftharpoons (C_{15}H_{31}COO)_2Co+Ni$	0.1285	-0.0009275	-5927	-18887	- 42.78
$Co+(C_{17}H_{35}COO)_2Ni \rightleftharpoons (C_{17}H_{35}COO)_2Co+Ni$	0.136	-0.0008357	-6272	-17952	- 38.55

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CHAPTER - 3

" Determination of c.m.c. of ionic surfactants with and without the presence of additives by potentiometric and solubilization methods "

INTRODUCTION

Ionic surface-active agents are characterized by a departure in their ideal behaviour as moderately strong electrolytes above a narrow concentration range. This range is referred to as c.m.c., which is a characteristic for each material. Ever since McBain introduced the concept of ionic micelles (aggregates of the amphipathic ions in aqueous solution), the explanation of the behaviour of ionic surfactants in their aqueous solutions on the basis of micelle formation is generally accepted. Any physical property of the surfactants' solutions should, therefore, show an abrupt change above the c.m.c. values. The various physical properties, which have been mostly employed for this purpose, are colligative properties, solubility, refractivity, surface tension, partial molal volume, viscosity, electrical conductance, vapour pressure and colour change of dyes. Methods based on the variation in these properties have been put forward from time to time by colloid chemists for c.m.c. determination.

The oldest methods developed by J.W.McBain and co-workers for determining c.m.c. are based on electrical conductance(1) and osmotic coefficient(2-5) measurements. The former method(6-9) has been widely employed by a number of workers for determining the c.m.c. values of a variety of surfactants. The discontinuities in the vapour pressure vs concentration curves have also been employed to

determine c.m.c. values (10,11). Improved methods for measuring surface tension have lately been put to use to derive c.m.c. values(12-15). Interestingly enough Klevens(16) has argued that c.m.c. values can be determined more precisely from refractive index measurements. Surfactants' property of dissolving water insoluble materials in their solutions has also been quite conveniently used to determine the c.m.c. values(17,18).

Some other methods which are of fundamental importance but have been put to relatively lesser use are Wien effect(19), solubility(20-22), partial molal volume (23,24), viscosity(25,26), transport number(27,28) and suppression of polarographic maxima(29,30).

A rapid technique for c.m.c. determination based on spectral change of dyes was developed by Harkins and co-workers(31,32) and has become by far the most popular one. The articles describing its use are numerous to be all quoted and so only few may be cited(33-35). Recently Malik and Verma(36) have reported the use of alizarin red S for determining the c.m.c. of cationic surfactants.

Potentiometric methods:

These methods have attracted relatively less attention but offer great potentialities. Since the activity of detergent ions exhibits a marked abrupt change above c.m.c., any electrode system whose potential depends

on the activity of detergent ions can be employed for c.m.c. determination. Kolthoff(37) determined the c.m.c. of potassium laurate by measuring laurate ion activity in aqueous solutions of the soap, employing silver, silver laurate electrode. Van Voorst Vader(38) employed mercury, mercurous dodecane sulphonate electrode for determining the c.m.c. and pre-association of surfactant ions of sodium dodecyl sulphonate.

The applicability of potentiometric method in determining the c.m.c. can be viewed from an altogether different angle. So far the methods employed for this purpose were based on the determination of detergent ion activity and the possibility of putting to use electrode systems reversible with respect to counterions was not considered. An attempt in this direction was made by Malik and Verma(39) for determining the c.m.c. of alkyl-aryl sulphonates by pH metric methods. Extension of these studies involving the use of electrode systems of the second kind like metal, metal insoluble electrodes was considered worth undertaking. With this aim in view silver, silver bromide, and mercury, mercurous bromide electrodes were used to determine the counterion activity of cetylpyridinium bromide(CPB), cetyltrimethyl ammonium bromide (CTMAB) and dodecylpyridinium bromide (DPB), and, therefore, the c.m.c. of these cationic surfactants.

Solubilization method:

Solubilization for an aqueous system may be defined as the spontaneous dissolution of a normally water insoluble substance by a relatively dilute aqueous solution of a surfactant. Although the solubilization of a number of water insoluble substances, viz., orange OT(40), azobenzene(17), dimethyl phthalate(41), p-methyl cyclohexanol(42,43), dimethyl amino azobenzene(18), aliphatic alcohols(44) has been investigated, there remains a series of structurally important organic compounds which can be advantageously put to use for studying solubilization phenomenon. To such a class of uninvestigated compounds belong the anils. They are water insoluble compounds showing bathochromic effect in non-aqueous medium in presence of lewis acids. Their solubilization can,therefore, be of great interest if such structural changes accompanied by colour effects are to be studied in aqueous medium in the case of anils. For the present, however, one aspect, viz., the c.m.c. of cationic surfactants by the solubilization of anils, using light absorption method was taken up for study. The anil chosen for this purpose was p-dimethyl amino anil of phenyl glyoxal nitrile.

Effect of electrolytes on c.m.c:

The addition of foreign substances to surfactants' solutions markedly affects their c.m.c. values. This behaviour has been found in presence of electrolytes, organic solvents and other solubilized material.

The effect of solvent on the c.m.c. is very important, when mixed solvents are used. It has been found that c.m.c. of surfactants is a linear function of alcohol concentration in aqueous solutions (45,46).

The effect of solubilized material on the micellar size and shape, and on the c.m.c. depends largely on the chemical structure and particularly on the polarity of the solubilized material. Solubilized benzene reduces the c.m.c. of fatty soaps(47). Ralston and Eggenberger(48) studied the effects of several solubilized long chain hydrocarbons, alcohols, halides and amides on the c.m.c. of dodecyl amine hydrochloride. They found that all except two compounds, heptadecane and octadecane, lowered the c.m.c..

The effect of inorganic electrolytes on the c.m.c. has been examined from a different angle. Their presence affect the detergent action of surfactants. Micelle formation for most surfactants begins in the range of concentration used for practical detergent operations. Data presented by Preston(49) indicate that a great increase in detergent action occurs at about the concentration at which micelle formation becomes apparent. Any material which lowers the minimum concentration necessary for micelle formation in a surfactant solution may likewise decrease the concentration necessary for good detergency and so promote the detergent action of the surfactant. Numerous investigations(17,32,50-52) have shown that various inorganic

electrolytes decrease the c.m.c. of surfactants. The use of various silicates and other alkaline electrolytes as soap builders to improve their detergent action is based on this property of lowering the c.m.c..

According to Corrin and Harkins(32) the ions which have electrical charge of the same sign as that of the micelle have a negligible effect but the ions of the opposite sign have a marked influence on the c.m.c.. It has been subsequently shown by Lange(53) and independently by Vold(54) that this effect is fully in accord with the considerations of mass action law. The specific effect of counterions in lowering the c.m.c. was studied by Lange(55) and according to him negatively charged univalent counterion depresses the c.m.c. of dodecyl pyridinium chloride depending on their position in Hofmeister series, viz., in the order $Cl^- < NO_3^- < Br^- < I^- < SCN^-$.

Another searching question based on the above considerations but not so far answered, is to assess the effect of ion carrying the same charge as the micelle on c.m.c.. To meet this aim, the effect of LiCl, NaCl and KCl on the c.m.c. of CPB was studied so that information about the specific role of Li^+, Na^+ and K^+ ions may be obtained. The investigations have been carried out by solubilization method and the results interpreted in terms of water structure.

Effect of urea on the micelle formation of surfactants:

During the course of last twenty years it has been realised that water structure plays an important role in influencing the physical properties of solutes in their aqueous solutions. This concept has been mainly applied to proteins(56-58) where the hydrophobic bonds help in stabilising the protein structure. The addition of urea results in the disruption of water structure(59) and, therefore, the denaturation of protein in urea may be indirectly connected to such effects but no straight forward explanation is forthcoming.

Recently Mukerjee and Ray(60), and Brunning and Holtzer(61) have used urea as a probe for investigating the water structure contribution to micelle formation and hydrophobic bonds. Since aqueous solutions of surfactants are in nature similar to aqueous solutions of proteins to some extent, the study of effect of urea on the hydrophobic bonds in surfactants' solutions can be indirectly employed to explain the mechanism of denaturation.

Since surfactants have been sparsely studied from this viewpoint, it was thought worthwhile to experimentally determine the effect of urea on both cationic and anionic surfactants. Potentiometric method was found to be quite suitable and convenient for this purpose.

EXPERIMENTAL

Materials:

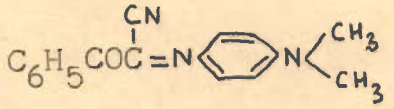
Cetylpyridinium bromide(CPB) and cetyltrimethyl ammonium bromide (CTMAB) were B.D.H. products and were recrystallized from acetone. Dodecylpyridinium bromide(DPB) was prepared in the laboratory.

Preparation of dodecylpyridinium bromide (DPB):

DPB was prepared by the method described by Adderson and Taylor(62) and Ames and Bowmann(63). Dodecyl bromide (12 gm.) was heated with pyridine (4 gm.) at 150°C for an hour in a round bottom flask fitted with a water condenser. The crude DPB was obtained on cooling. The crude product was recrystallized from ethyl methyl ketone. The crystallized product was kept in a desiccator over anhydrous silica gel.

Preparation of p-dimethyl amino anil of phenyl glyoxal nitrile:

The anil which has the following structural formula,



was prepared as described by Krohnke and Borner(64).

Preparation of silver electrodes:

These electrodes were prepared as described in Chapter 2.

Preparation of cobalt electrodes :

These electrodes were prepared as described in Chapter 1.

Preparation of silver bromide :

Silver bromide was prepared from $AgNO_3$ and KBr (A.R.).

Preparation of Hg_2Br_2 :

Mercurous bromide was prepared from $Hg_2(NO_3)_2$ and KBr (A.R.).

Procedure:

(A) Counterion (bromide ion) activity measurements in aqueous solutions of DPB, CPB and CTMAB by Hg, Hg_2Br_2 electrode:

E.M.F. measurements of the following cell

Hg	KCl(satd.), Hg_2Cl_2(s)	NH_4NO_3 salt bridge	Hg_2Br_2(s) CTMAB or CPB or DPB	Hg

were carried out by a Cambridge portable potentiometer at 30 ± 0.1°C. Standard solutions of CTMAB, CPB and DPB were prepared in doubly-distilled water. Triple-distilled mercury was used for the preparation of the mercury, mercurous bromide electrode. The standard solutions of the cationic surfactants were transferred to half-cells provided with Hg, Hg_2Br_2 electrodes. These half-cells were attached through an ammonium nitrate salt bridge to saturated calomel electrodes and were placed in a water

thermostat maintained at 30 ± 0.1°C.

The observations are given in Figs.1-3.

(B) Counterion (bromide ion) activity measurements in aqueous solutions of DPB, CPB and CTMAB by Ag, AgBr electrode:

The following cell was set up:

$$Hg \mid Hg_2Cl_2(s), KCl(Satd.) \mid NH_4NO_3 \text{ salt bridge} \mid AgBr(s), \text{CTMAB or CPB or DPB} \mid Ag$$

All experimental details were the same as described above except that instead of Hg, Hg_2Br_2 electrode, Ag, AgBr electrode was employed. Ag, AgBr electrode was set up by immersing the silver electrode in standard solutions of CPB, DPB and CTMAB saturated with silver bromide. Some solid AgBr was always added to make certain that cationic surfactant solutions always remained saturated with respect to AgBr.

The observations are given in Figs.4-6.

(C) c.m.c. determination of DPB in presence of urea:

For the determination of c.m.c. of DPB in presence of urea, E.M.F. measurements of the following cell

$$Ag \mid AgBr(s), DPB(C), \text{Urea (nM)} \mid NH_4NO_3 \text{ salt bridge} \mid KCl \text{ satd.}, Hg_2Cl_2(s) \mid Hg$$

were carried out at 30 ± 0.1°C. The experimental observations are given in Fig.7.

(D) c.m.c.determination of potassium laurate and myristate in presence of urea :

The c.m.c.values of potassium laurate and myristate in presence of urea have been determined from detergent anion activity variation by employing cobalt, cobalt soap electrodes. E.M.F. measurements of the following cells

Co	Co-laurate(s), K-laurate (C), Urea (nM)	KCl salt bridge	KCl satd., Hg_2Cl_2(s)	Hg
Co	Co-myristate(s) K-myristate (C), Urea (nM)	KCl salt bridge	KCl satd., Hg_2Cl_2(s)	Hg

were carried out at 35 ± 0.1°C.

The experimental observations are given in Figs.8,9.

(E) Solubilization of p-dimethyl amino anil of phenyl glyoxal nitrile by cationic surfactants,viz., CPB, CTMAB and DPB:

Series of solutions of varying surfactant concentrations were made by diluting a definite volume of stock solutions. These solutions were placed in capped conical flasks, with sufficient amount of anil added to form a small amount of excess solid. The solutions were agitated at room temperature (27 ± 2°C) till equilibrium was established. The excess anil was allowed to settle down and clear solution was used to estimate the amount of anil solubilized. The absorbance of clear solutions

were measured at 505 mμ (absorption maximum of the anil).

A calibration curve (Fig.10) between absorbance and the amount of anil solubilized was obtained by solubilizing known amounts of the anil in M/100 CPB. Since the absorption maximum of the solubilized anil in CPB, CTMAB and DPB is at 505 mμ and the same amount of anil solubilized in these three surfactants has the same absorbance, hence the above calibration curve (Fig.10) was employed to evaluate the amount of anil solubilized from absorbance measurements in all the three cases.

In case of CPB, the solubilization of the anil in presence of LiCl, NaCl and KCl was also similarly studied.

The observations are given in Figs.10-14.

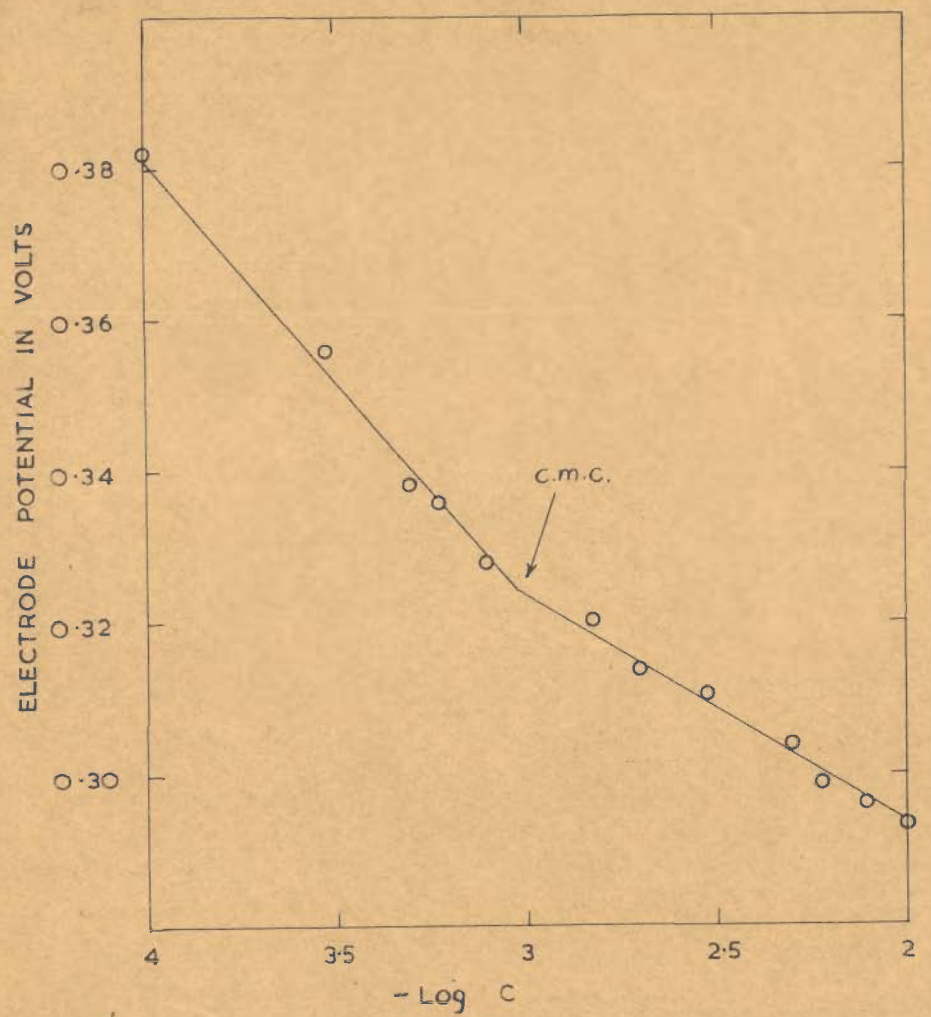


FIG. 1. PLOT BETWEEN Hg, Hg_2Br_2 ELECTRODE POTENTIAL AND LOGARITHM OF CTMAB CONCENTRATION (MOLES/ℓ).

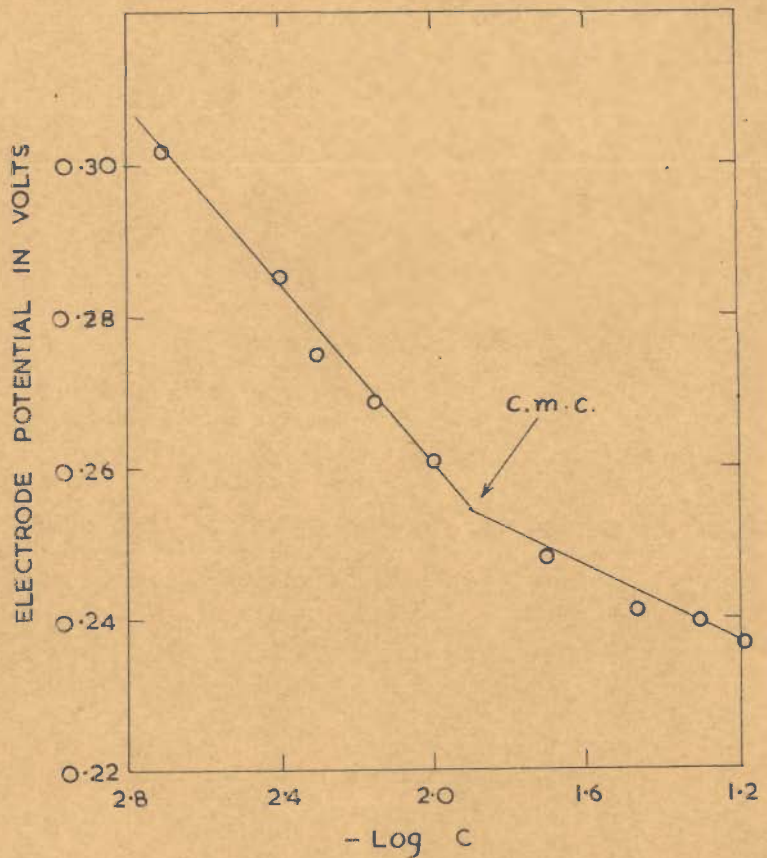


FIG. 2. PLOT BETWEEN Hg, Hg_2Br_2 ELECTRODE POTENTIAL AND LOGARITHM OF DPB CONCENTRATION (MOLES/ℓ)

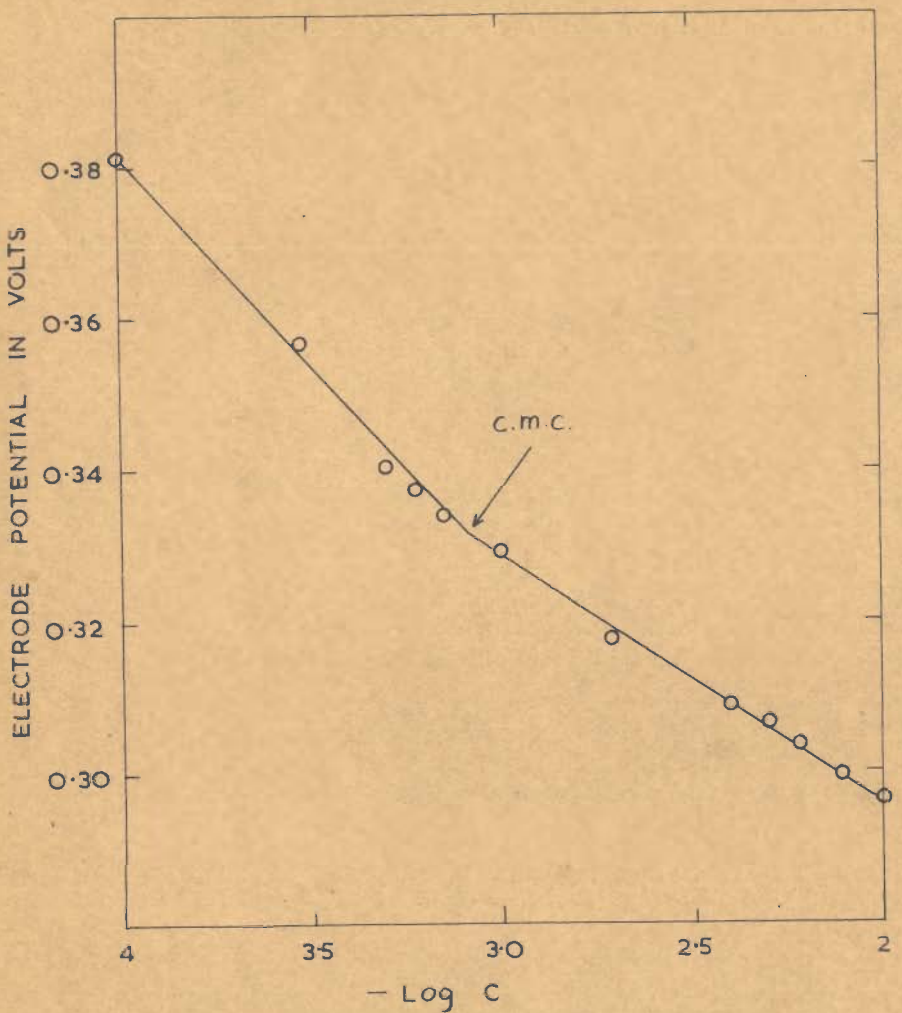


FIG. 3. PLOT BETWEEN Hg, Hg_2Br_2 ELECTRODE POTENTIAL AND LOGARITHM OF CPB CONCENTRATION (MOLES/ℓ).

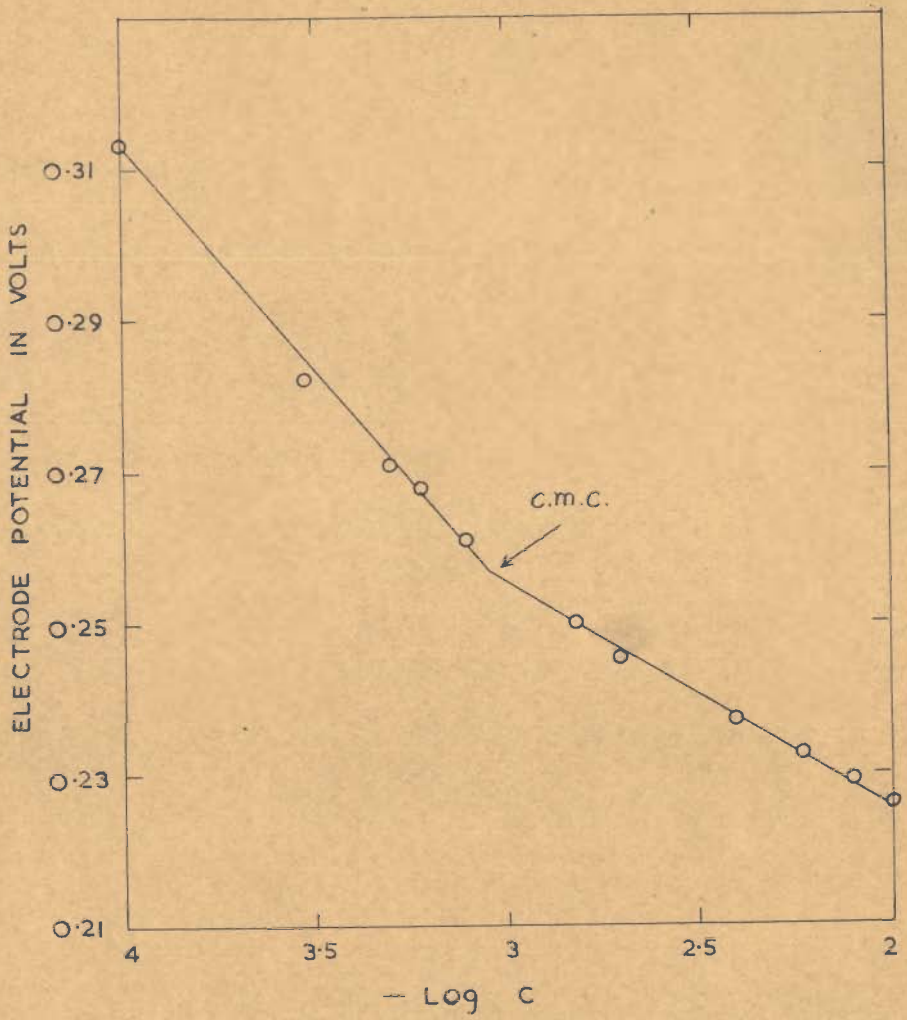


FIG. 4. PLOT BETWEEN Ag, AgBr ELECTRODE POTENTIAL AND LOGARITHM OF CTMAB CONCENTRATION (MOLES/ℓ).

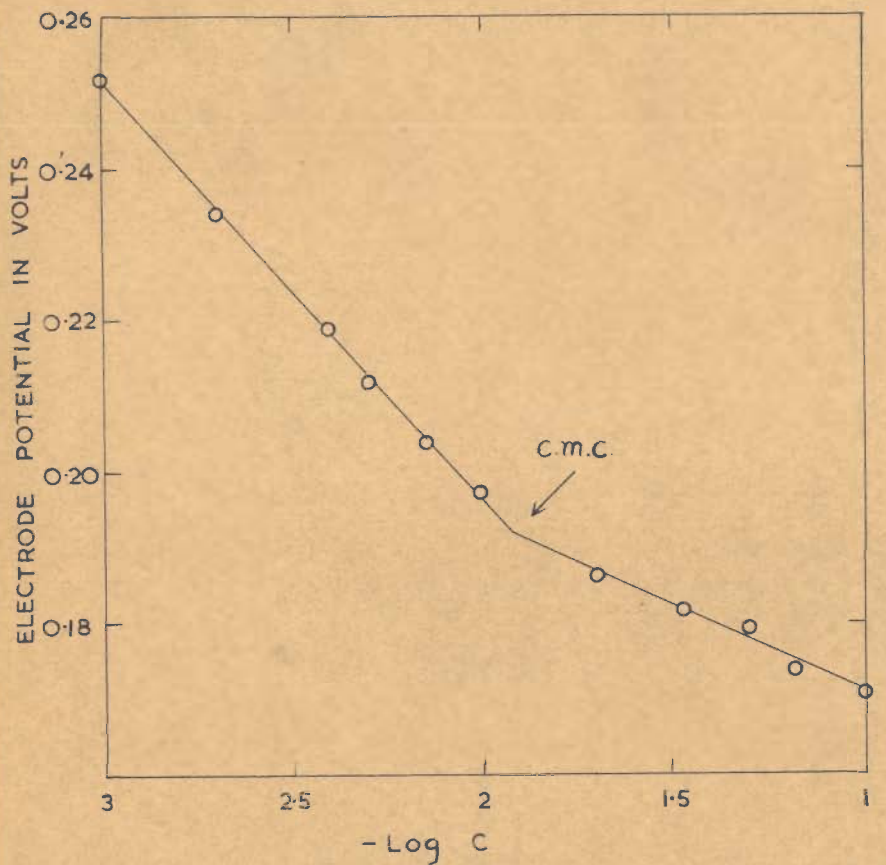


FIG. 5. PLOT BETWEEN Ag, Ag Br ELECTRODE POTENTIAL AND LOGARITHM OF DPB CONCENTRATION (MOLES/ℓ).

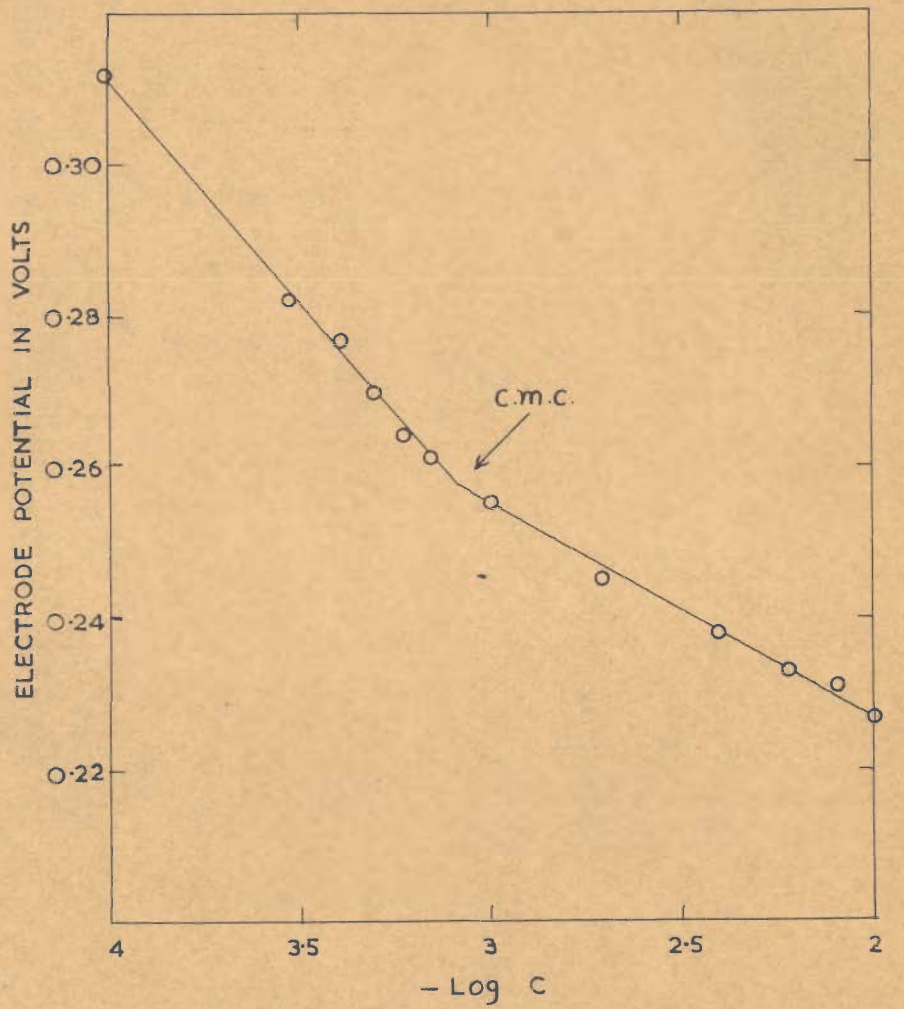


FIG. 6. PLOT BETWEEN Ag, Ag Br ELECTRODE POTENTIAL AND LOGARITHM OF CPB CONCENTRATION (MOLES/ℓ).

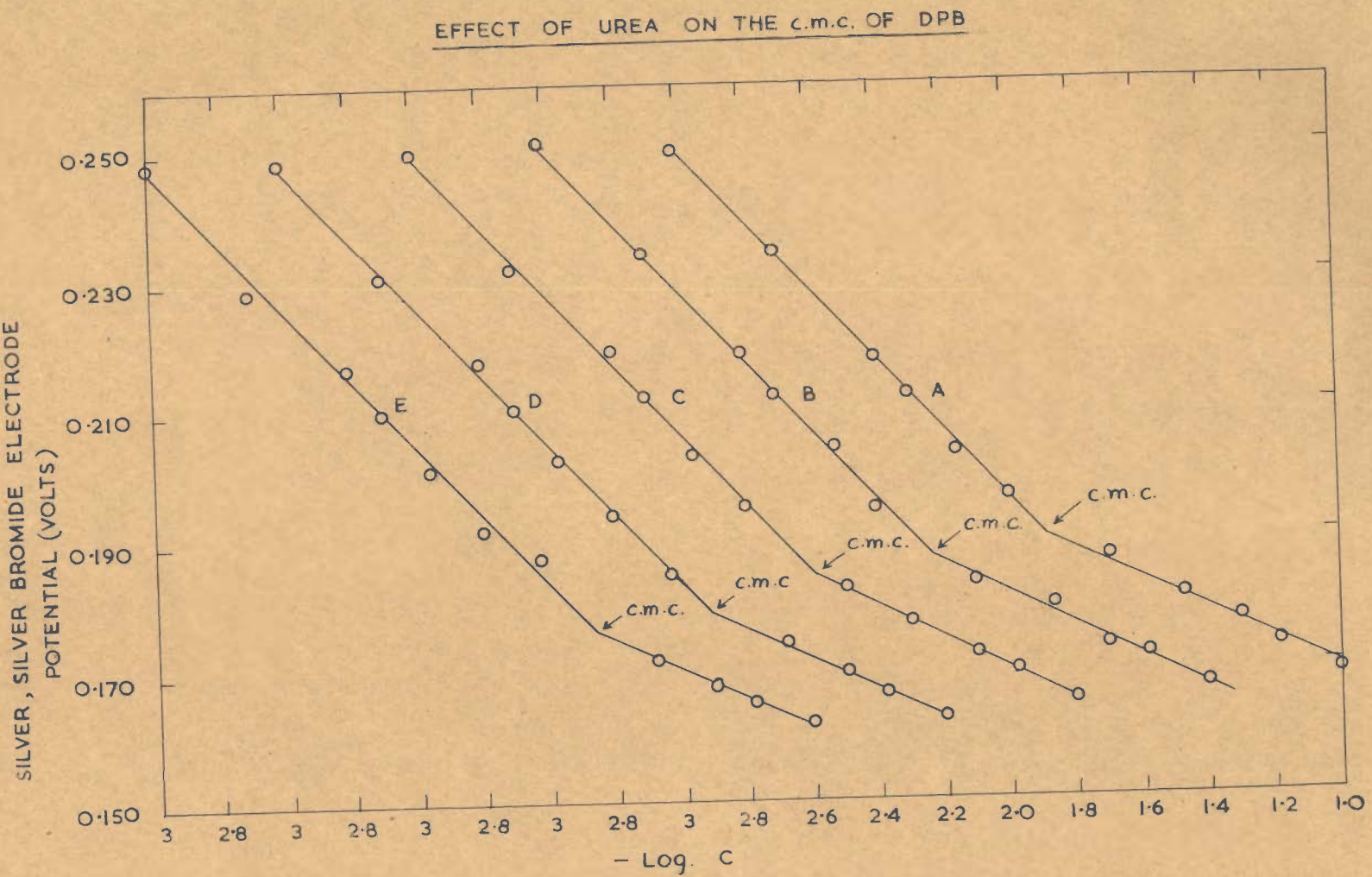


FIG. 7. PLOT BETWEEN SILVER, SILVER BROMIDE ELECTRODE POTENTIAL AND LOGARITHM OF DPB CONCENTRATION (M /ℓ) IN PRESENCE OF UREA; UREA CONCN.– A(0·5M), B(1M), C(2M), D(3M), E (4M).

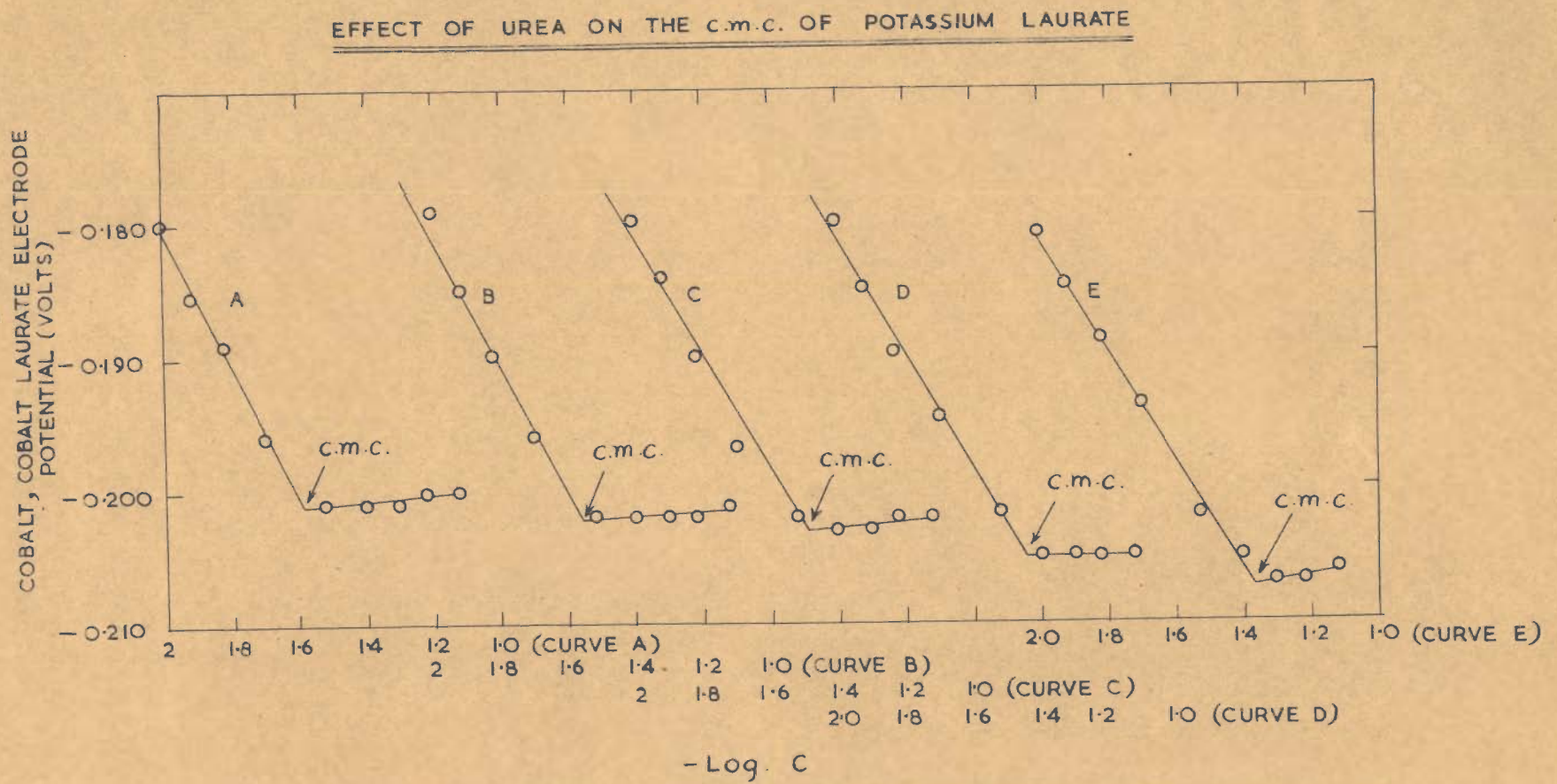


FIG. 8. PLOTS BETWEEN COBALT, COBALT LAURATE ELECTRODE POTENTIAL AND LOGARITHM OF POT. LAURATE CONCN. (M/ℓ) IN PRESENCE OF UREA ; UREA CONCN.→A(0·5 M), B(1M), C(2M), D(3M) E(4M).

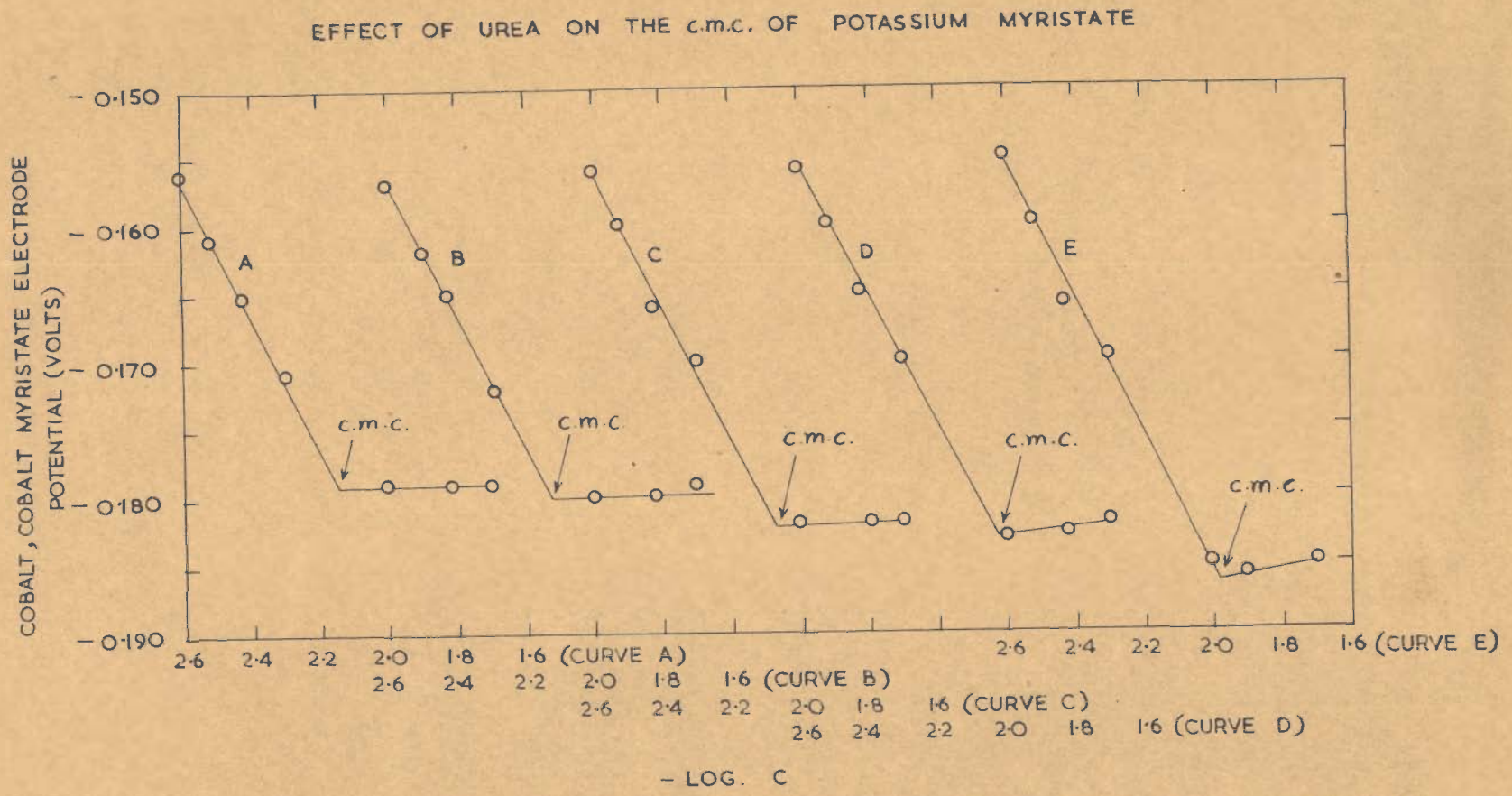


FIG. 9. PLOTS BETWEEN COBALT, COBALT MYRISTATE ELECTRODE POTENTIAL AND LOGARITHM OF POT. MYRISTATE CONCN. (M/ℓ) IN PRESENCE OF UREA; UREA CONCN.–, A (0·5 M), B (1M), C (2M), D (3M) E (4M).

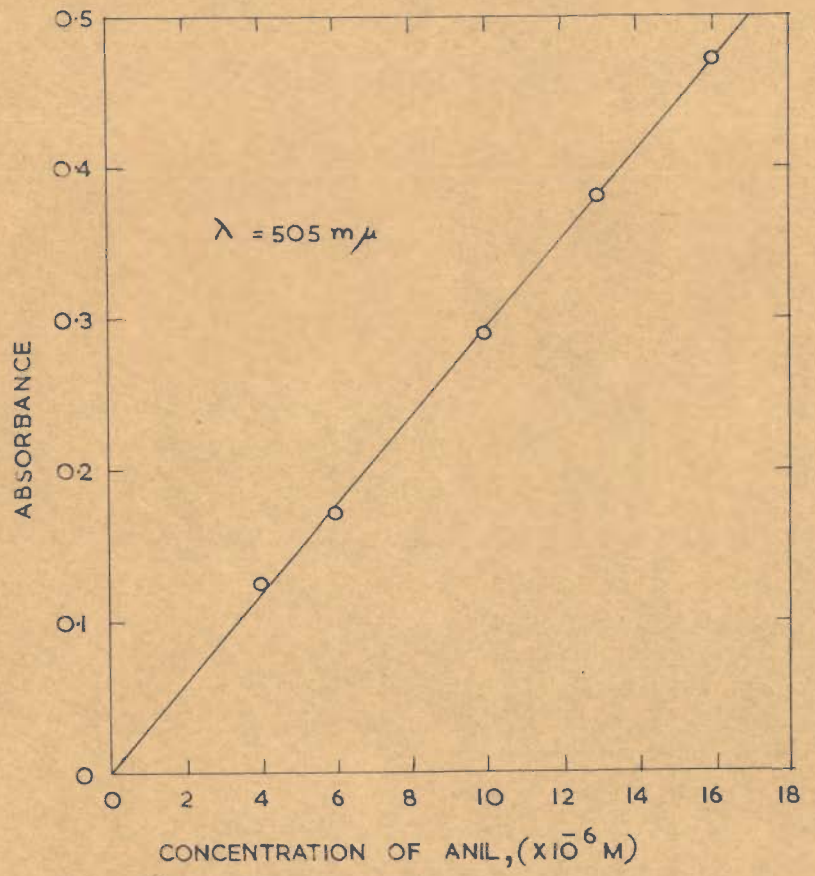


FIG. 10. CALIBRATION CURVE BETWEEN ABSORBANCE AND CONCENTRATION OF THE ANIL.

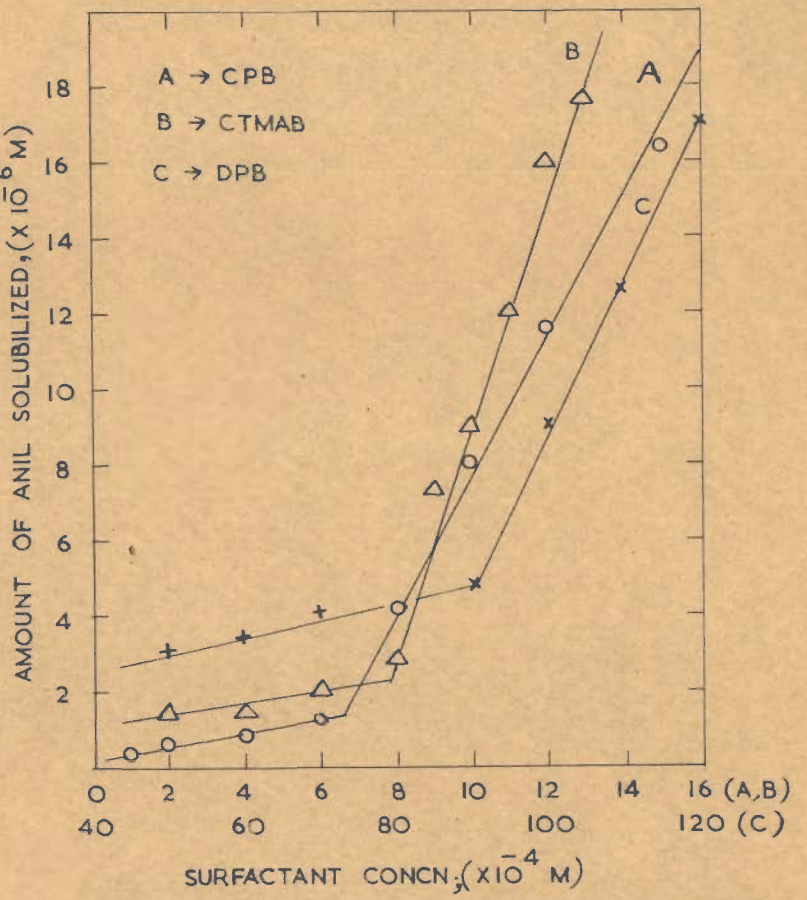


FIG. 11. PLOTS BETWEEN THE AMOUNT OF ANIL SOLUBILIZED AND SURFACTANT CONCENTRATION.

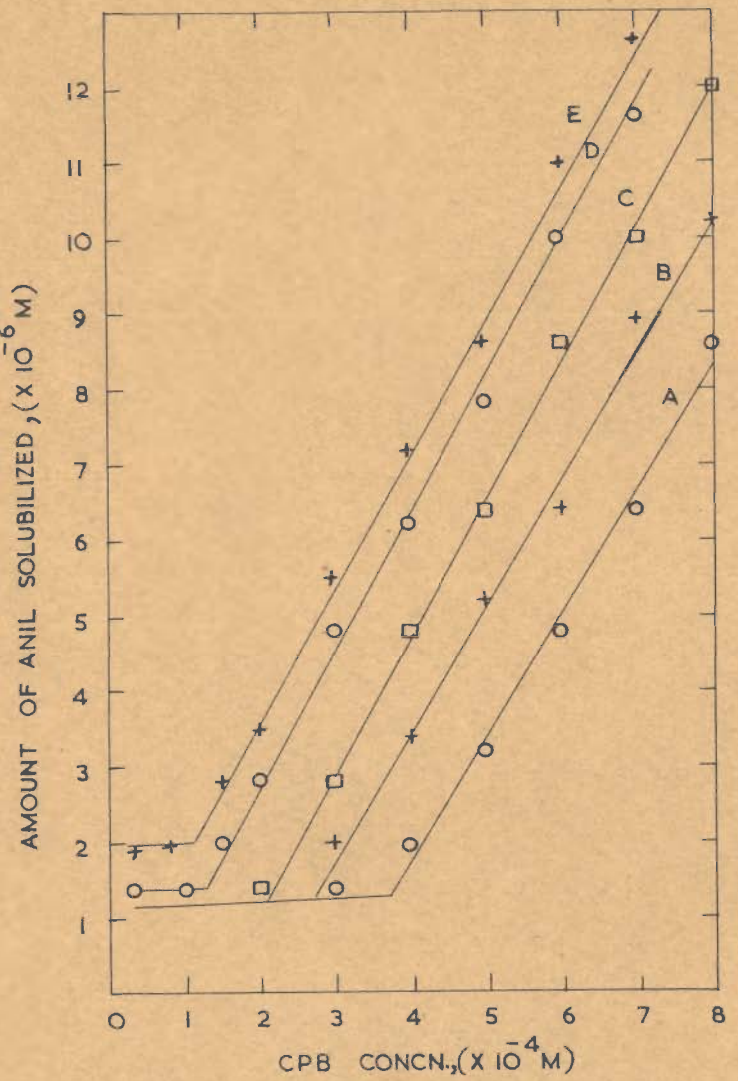


FIG. 12 PLOTS BETWEEN THE AMOUNT OF ANIL SOLUBILIZED AND CPB CONCN. IN PRESENCE OF LiCℓ; LiCℓ CONCN.–, A-$1X10^{-3}$M, B-$3X10^{-3}$M, C-$1X10^{-2}$M, D-$3X10^{-2}$M, E-$1X10^{-1}$M.

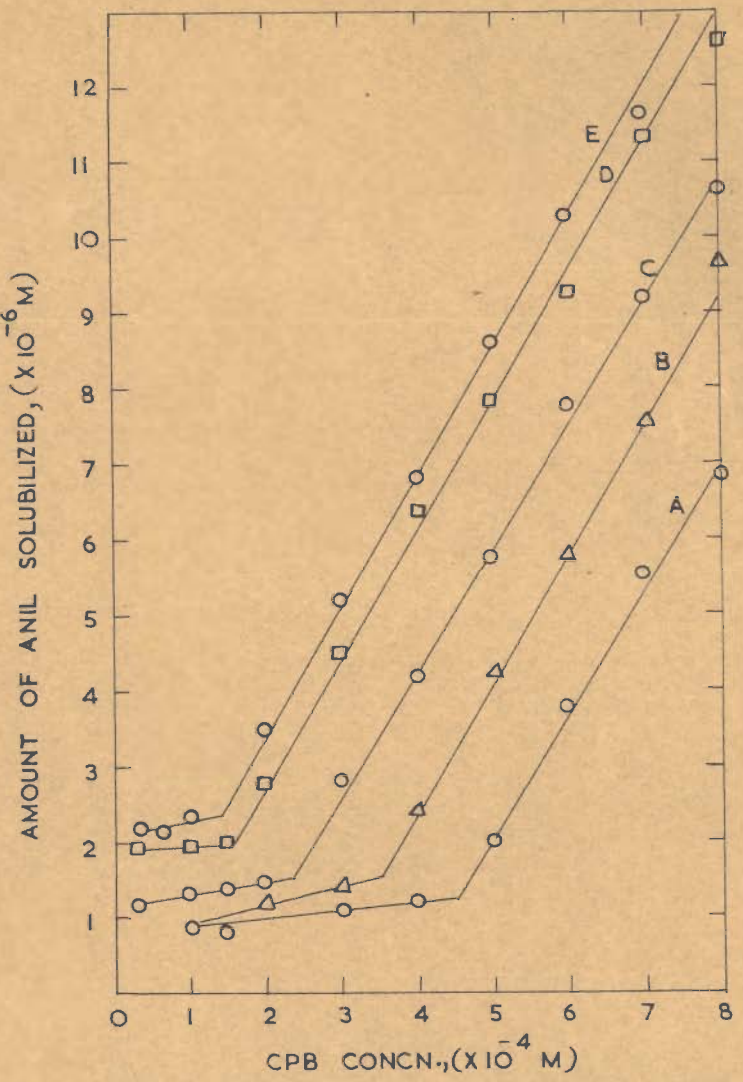


FIG. 13. PLOTS BETWEEN THE AMOUNT OF ANIL SOLUBILIZED AND CPB CONCN. IN PRESENCE OF NaCℓ; NaCℓ CONCN.–, A-$1X10^{-3}$M, B-$3X10^{-3}$M, C-$1X10^{-2}$M, D-$3X10^{-2}$M, E-$1X10^{-1}$M.

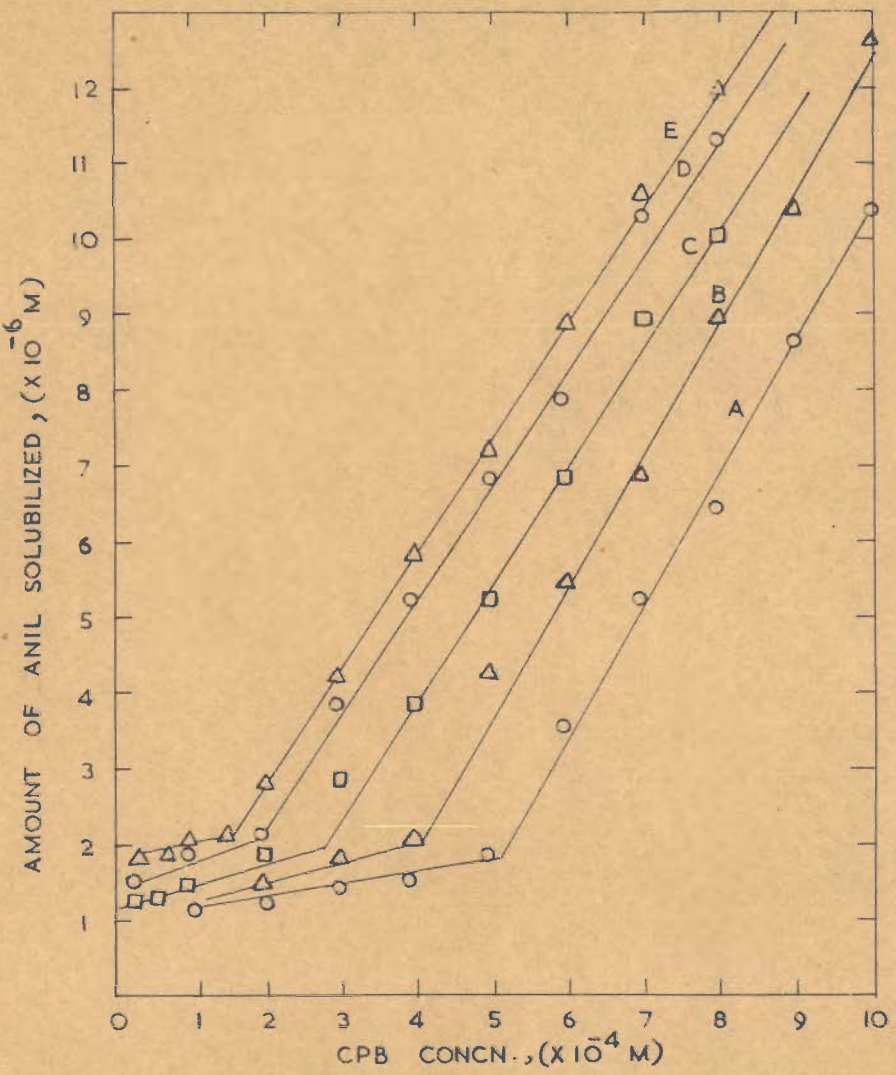


FIG. 14. PLOTS BETWEEN THE AMOUNT OF ANIL SOLUBILIZED AND CPB CONCN. IN PRESENCE OF KCℓ; KCℓ CONCN.–, A-1×10^{-3} M, B-3×10^{-3} M, C-1×10^{-2} M, D-3×10^{-2} M, E-1×10^{-1} M.

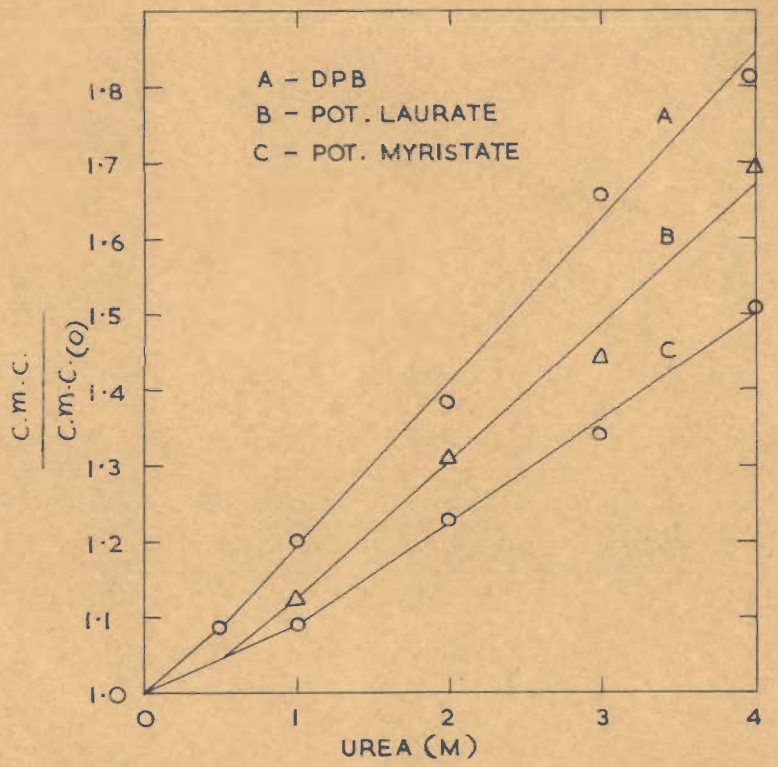


FIG. 15. EFFECT OF UREA ON THE c.m.c. OF DPB, POTASSIUM LAURATE AND MYRISTATE.

RESULTS AND DISCUSSION

Determination of the c.m.c. of cationic surfactants from counterion activity measurements:

The curves in Figs.1-3 and in Figs.4-6 are the plots between the electrode potentials of Hg, Hg_2Br_2 and Ag, AgBr electrodes and the logarithms of surfactant concentrations. The reduction potential of Hg, Hg_2Br_2 and Ag, AgBr electrodes is given by the following equations :

$$E_{Hg_2Br_2 \rightarrow Hg} = E^{o}_{Hg_2Br_2 \rightarrow Hg} - \frac{2.303\ RT}{F} \log a_{Br^-}$$

$$E_{AgBr \rightarrow Ag} = E^{o}_{AgBr \rightarrow Ag} - \frac{2.303\ RT}{F} \log a_{Br^-}$$

The curves in Figs.1-6 give breaks which provide useful information about the nature of the surfactants' solution. Since the electrode potential is a measure of bromide ion activity, the first linear branch of the curves corresponds to the increase in bromide ion activity as the surfactant concentration is increased. This observation is in agreement with the accepted concept of a surfactant behaving as moderately strong electrolyte below the c.m.c.. However, above the c.m.c., the behaviour of surfactants is non-ideal owing to micellization.

According to Hartley (65,66) the micelles contain, in addition to number of detergent ions, a considerable number of counterions which are bound to the micelle surface and number at least one-half of the number of deter-

-gent ions in the micelle. Therefore, above the c.m.c., the increase in concentration of surfactant will not cause the same increase in the concentration (activity) of free bromide ions (counterions) as it would have done had there been no counterion association with the micelles. Consequently, the Hg, Hg_2Br_2 and Ag, AgBr electrode potential will show an abrupt change as the concentration of the surfactant exceeds the c.m.c. value. Obviously the breaks in curves (Figs.1-6) must correspond to the c.m.c. values of cationic surfactants.

The c.m.c. values of DPB, CPB and CTMAB determined by this method together with those values obtained by other methods are given in the following Table-1:

Table -1

Comparative c.m.c.values of CTMAB, DPB and CPB

Surfactant	Electrode employed		c.m.c.values mentioned in the literature
	Hg, Hg_2Br_2	Ag, AgBr	
CTMAB	9.12×10^{-4}M	9.33×10^{-4}M	10×10^{-4}M (68)
DPB	1.23×10^{-2}M	1.202×10^{-2}M	1.18×10^{-2}M(62)
CPB	8.31×10^{-4}M	8.12×10^{-4}M	8×10^{-4}M (67)

Effect of urea on the micelle formation of DPB, potassium laurate and myristate:

The c.m.c. of DPB in presence of different amounts of urea has been determined from counterion activity measurements using Ag,AgBr electrode. The curves A,B,C,D and E (Fig.7) are the plots between Ag,AgBr electrode

potentials and logarithm of DPB concentrations in presence of 0.5M, 1M, 2M,3M and 4M of urea, respectively. The breaks in the curves correspond to the c.m.c. of DPB in presence of urea. The Table-2 gives the values of c.m.c. of DPB in presence of urea.

Table -2

Effect of urea on the c.m.c. of DPB at 30°C

Urea (M)	c.m.c. ($x10^{-2}$M)	$\frac{\text{c.m.c.}}{\text{c.m.c.}_{(o)}}$
0	1.202 (From Table-1)	1.00
0.5	1.318	1.09
1.0	1.445	1.20
2.0	1.660	1.38
3.0	1.995	1.66
4.0	2.188	1.81

Fig.15(A)

The c.m.c. values of potassium laurate and myristate in presence of urea have been determined from detergent anion activity variations studied by using cobalt, cobalt laurate, and cobalt, cobalt myristate electrodes, respectively. The breaks in the curves (Fig.8) correspond to the c.m.c. of potassium laurate in presence of urea and in the curves (Fig.9) correspond to the c.m.c. of potassium myristate in presence of urea. Table-3 gives the c.m.c. values of potassium laurate and myristate

in presence of urea.

Table -3

Effect of urea on the c.m.c. of potassium soaps at 35°C

Soap	Urea (M)	c.m.c., ($x10^{-3}$M)	$\frac{c.m.c.}{c.m.c._{(o)}}$
Potassium laurate	0	25.12 (From Chapter 1) Table-3	1
	0.5	26.3	1.04
	1.0	28.18	1.12
	2.0	33.11	1.31
	3.0	36.31	1.44
	4.0	42.66	1.69
Potassium myristate	0	6.918 (From Chapter 1) Table-3	1
	0.5	7.244	1.04
	1.0	7.586	1.09
	2.0	8.511	1.23
	3.0	9.333	1.34
	4.0	10.470	1.51

Fig.15(B,C)

The ratio of the c.m.c. in presence of urea to the c.m.c.in the absence of urea, $c.m.c./c.m.c._{(o)}$, has been adopted as a convenient way of representing the data(60). Small concentrations of urea have little influence on the micelle formation of surfactants (Tables 2,3) but higher concentrations bring about a marked increase in the c.m.c.

of the surfactants. From Fig.15, it is evident that there is almost a linear relationship between $\frac{c.m.c.}{c.m.c._{(o)}}$ and urea concentration in the range 1-4M of urea. These results are in agreement with those reported by earlier workers (60,61).

The role that urea plays in increasing the c.m.c. of the surfactants can be explained on the basis of changes in water structure that urea causes. Liquid water has long been known to possess distinctive structural features which can be roughly described by the statement that it retains a certain degree of similarity or analogy to ice.

Recent investigations(69-73) have shown that micelle formation in aqueous solution is primarily an entropy directed process in which enthalpy changes play minor role. The current hypothesis (70,71) for micelle formation is based on "iceberg" picture of water structure (74). According to Frank and Evans(74), water molecules become more ordered around the non-polar solute,with an increasing extent of hydrogen bonding in this region. This microscopic region of ordered water molecules is referred to as "iceberg". Thus, in case of aqueous solution of the surfactants, the hydrocarbon chains of the detergent ions are surrounded by a water structure (so called " iceberg structure "). These "iceberg structures" so induced by non-polar hydrocarbon chains represent a comparatively low entropy and energy state. Therefore, the transfer of the surfactant molecules into aggregated forms

will bring about the disappearance of "iceberg" structures around them and consequently gain in entropy will take place. Thus the presence of "iceberg structures" around non-polar detergent ions is the cause of primary driving force for aggregation and this is an entropy effect. Therefore, the more ordered the "iceberg structure" around detergent ions, the greater will be the driving force for aggregation. It is anticipated, therefore, that structure-promoting substances should enhance the tendency of micellization and consequently decrease the c.m.c. of the surfactants, whereas substances that break up the "iceberg" water structure around detergent ions should retard the tendency of micellization and consequently increase the c.m.c.. The effect of urea can be explained in the light of the "iceberg" picture of water structure around the non-polar detergent ions. Rupley(59) observed that aqueous solutions of urea exhibit anomalously low viscosities and he explained this behaviour by suggesting that urea disrupts the water structure. On this basis, urea, as a water structure-breaking substance, should increase the c.m.c..

The increase in the c.m.c. of the surfactants in presence of urea is an indication of the breaking of hydrophobic bonds between hydrocarbon chains in the micelles. The mechanism by which urea breaks the hydrophobic bonds is clear in the light of above discussion. The hydrophobic bonds which are induced and stabilized by the existence of structural regions ("icebergs"), break up on the addition of urea because the structural regions are partially destroyed by urea.

The above conclusion derived can be extended to understand the mechanism of denaturation of proteins by urea. Various types of bonds that are responsible for protein structure are hydrophobic bonds, hydrogen bonds, salt linkages,etc.(56). The existence of structural regions around non-polar groups of proteins imparts a tendency to these groups to adhere to one another (aggregate through hydrophobic bonding) in aqueous environments to form intramolecular "micelles" analogous to the micelles in aqueous solutions of surfactants. Thus the hydrophobic bond is probably one of the more important factors involved in stabilizing the folded configuration in many native proteins(56). Urea can, therefore, cause the denaturation of proteins by breaking structural regions of water and thereby weakening the hydrophobic bonds.

It must, however, be accepted that the breaking of hydrophobic bonds, though important, is not the only factor. There may be other factors, though equally important, but may not be as decisive.

Solubilization of p-dimethyl amino anil of phenyl glyoxal nitrile:

The anil is insoluble in water but gets solubilized in aqueous solutions of surfactants. It is evident from Fig.11 that the solubility of the anil, beyond certain concentration value given by breaks in the curves (Fig.11), increases rapidly with increase in concentration of surfactants. These breaks in the curves correspond to

the c.m.c. values, because above these concentrations micelles start forming which can incorporate the insoluble anil in their hydrophobic core. The c.m.c.values of DPB, CPB and CTMAB so determined are found to be 9×10^{-3}M, 6.6×10^{-4}M and 7.8×10^{-4}M, respectively. These values are slightly lower than those mentioned in the literature (62,67,68). It is well known that the c.m.c. values determined by solubilization method are usually lower than those determined by other methods (16,47,48).

It is noted from Fig.11 that even in sufficiently dilute solutions, below c.m.c., the anil is soluble to some extent. This much solubilization may be either due to the presence of micelles even below c.m.c. (so called pre-association region (38)) or due to the binding of individual anil molecule with an individual surfactant molecule by van der Waals forces(75). This behaviour appears to be specific and should be governed by the structure of the organic molecule undergoing solubilization.

Effect of LiCl, NaCl and KCl on the c.m.c. of CPB:

The c.m.c. values of CPB in presence of LiCl, NaCl and KCl calculated from the breaks in the curves A,B,C,D,E (Figs.12-14) are given in the Table -4.

Table -4

Effect of LiCl, NaCl and KCl on the c.m.c. of CPB

Electrolyte	Concn.of electrolyte (M)	c.m.c. of CPB, ($x10^{-4}$M)
LiCl	0	6.6
	$1x10^{-3}$	3.7
	$3x10^{-3}$	2.7
	$1x10^{-2}$	2.1
	$3x10^{-2}$	1.3
	$1x10^{-1}$	1.1
NaCl	$1x10^{-3}$	4.5
	$3x10^{-3}$	3.5
	$1x10^{-2}$	2.4
	$3x10^{-2}$	1.6
	$1x10^{-1}$	1.4
KCl	$1x10^{-3}$	5.2
	$3x10^{-3}$	4.0
	$1x10^{-2}$	2.8
	$3x10^{-2}$	2.0
	$1x10^{-1}$	1.6

It is evident from Table 4 that LiCl, NaCl and KCl lower the c.m.c. of CPB to different extent. The chloride ions being oppositely charged will cause the lowering of c.m.c.(17,32,34). Since the lowering caused by chloride ions should be same for the three electrolytes studied, it follows that Li^+, Na^+ and K^+ ions also affect the c.m.c. of the surfactant. This stand point is in contradiction to that of Corrin and Harkins(32).

The contribution of Li^+, Na^+ and K^+ ions in affecting the c.m.c. of the surfactant may be interpreted in terms of water structure. It is well known (74,76) that ions either promote or break the water structure. Li^+ ion has structure promoting influence and Na^+ and K^+ ions have water structure breaking influence in the order $K^+ > Na^+$ (74,76). It has already been discussed that structure promoting substances decrease the c.m.c. and water structure breaking substances increase the c.m.c. of the surfactants. Therefore, Li^+ ion as a structure promoter should cause the decrease in c.m.c. and Na^+ and K^+ ions as structure breaking substances should cause an increase in c.m.c. in the order $K^+ > Na^+$. Over and above the specific contributions of Li^+, Na^+ and K^+ ions in affecting the c.m.c., the large c.m.c. lowering effect of chloride ions is superimposed. Therefore, it follows that these electrolytes should lower the c.m.c. in the order LiCl > NaCl > KCl. This is what has been experimentally observed (Table -4).

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CHAPTER - 4

" Spectrophotometry of surfactant-dye mixtures "

INTRODUCTION

The interaction of surface active agents with many substances has been studied in order to elucidate the fundamental properties of surfactants and to extend the domain of their applications. In the existing literature data are available on the interaction of surfactants with proteins(1-4), polymers(5,6), nucleic acid(7), hydrophobic sols(8,9), metal ions(10) and dyes(11-16). Amongst these, the interaction of surfactants with dyes present some interesting features worth considering.

In 1934, Hartley(11) studied the effect of a number of anionic, cationic and nonionic surfactants on a large number of dyes. He reported that the colour of dyes in buffered solutions is altered by the addition of the surfactants possessing charge opposite to that on the indicator ion, and later on utilized this property in determining the concentration of surfactants(17,18). The work of Sheppard and Geddes(19) on the spectrum of pinacyanol chloride in presence of cationic surfactants was further extended by Corrin et al.(20), whose investigations led them to develop a method, known as spectral change method, for determining the c.m.c. of surfactants.

One of the most comprehensively investigated interaction is that between cationic surfactants (quaternary salt) and brom phenol blue dye by Colichman. With the help of conductance measurements(14), surface tension and interfacial tension titrations(21) and spectral studies(15), he

could establish the formation of "ion pair" compound between quaternary compounds and divalent dye anions followed by mixed micelles formation.

The formation of surfactant - dye complex in such systems is another aspect worth mentioning. The shift in the absorption spectrum of dyes in presence of surfactants is attributed to this property. Mysels and Mukerjee(13) have shown that the colour change involves the formation of a highly insoluble dye-surfactant simple salt which forms a stable suspension in excess of the surfactant. They also isolated some dye-surfactant complexes like methylene blue-lauryl sulphate, cetyltrimethyl ammonium-brom phenol blue and dicetyltrimethyl ammonium-brom phenol blue, and characterized them by chemical analysis.

Although it is fairly established that surfactants and dye interact to give some sort of complexes, the problem still offers fresh avenues for further investigations, especially when the formation of non-stoichiometric complexes is envisaged. Efforts in this direction were initiated by Malik and Verma(22) who calculated the extent of binding of the dye to the surfactants by colorimetric measurements. These studies have now been extended to the reactions of acid dyes with cationic surfactants of the quaternary type.

EXPERIMENTAL

Reagents and materials :

The dyes methyl orange, congo red, alizarin red S and benzopurpurine 4B were B.D.H. products. The cationic surfactant,viz., dodecyl pyridinium bromide (DPB) was prepared in the laboratory by the method described in Chapter 3.

Walpole(pH 2.32), McIlvaine (pH 7) and Borax buffers (pH 9.12) were prepared in the laboratory(23).

Apparatus and techniques:

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

$$\epsilon = \frac{1}{Cd} \log \frac{I_o}{I}$$

where I_o is the intensity of the light emerging from the solvent, I, the intensity of light emerging from the solution, d, the length of light path through the absorption cell and 'C' the concentration of the absorbing substance in moles/litre.

pH measurements were carried out by a Cambridge bench-type pH meter.

Procedure :

Stock solutions of dyes ($1x10^{-3}M$) and DPB($1x10^{-1}M$) were prepared in doubly-distilled water. To a number of pyrex boiling tubes a fixed amount of dye,

requisite amount of buffers and varying amounts of DPB were added and final volume was made up to 20 ml with water. This resulted in a number of solutions with same dye concentration and varying concentration of DPB at the desired pH value. In cases where precipitation took place, the boiling tubes were allowed to stand until all the precipitate had settled. Then samples were withdrawn for absorption measurements, taking care to keep sediment undisturbed. In some cases centrifugation was also done to expedite sedimentation.

Equation used for bound dye calculations :

Klotz(24) studied spectrophotometrically the interaction between proteins and dyes. He calculated the concentrations of bound and unbound dye using the following equation :

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

where ϵ_{app} is the apparent molar extinction coefficient, ϵ_B the molar extinction coefficient of the bound dye, ϵ_F the molar extinction coefficient of the unbound (free) dye and α is the fraction of the free dye.

The above Klotz's equation was applied to surfactant - dye mixtures for calculating the amount of dye bound with surfactants(22).

ϵ_F was calculated from absorption measurements of dye solutions at different pH values containing no DPB. Absorption measurements of dye solutions in presence of

different concentrations of DPB were employed to calculate ϵ_{app} in Klotz's equation. The method used by Malik and Verma(22) to determine ϵ_B was based on the tentative assumption that a small quantity of dye would be completely bound with the excess of the surfactant. How far this assumption is valid is difficult to say. Therefore, in order to exclude this assumption, the following modified procedure was employed for determining ϵ_B.

From our absorption data, it appeared that the absorbance of dye solutions decreases with increase in DPB concn..However, beyond a certain concentration of DPB the absorbance did not decrease further with increase in DPB concentration (Figs.1,4 & 7-10) for practically all the dye is bound to the surfactant in the form of complex. Therefore, the absorbance on the flat portion of the curves is completely due to bound dye. ϵ_B, therefore, could be determined by dividing the absorbance from the flat portion of the curve by the dye concentration.

All the three molar extinction coefficients, viz., ϵ_{app}, ϵ_F and ϵ_B were determined only at the absorption maximum of the dyes.

The experimental observations are given in the following Tables 1-24.

DPB - METHYL ORANGE interaction at pH 2.32:

Table -1

Absorption spectra of methyl orange ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	Absorbance at different wavelengths(mμ)									
	400	410	425	435	450	475	490	500	510	525
0	0.11	0.14	0.19	0.26	0.35	0.55	0.66	0.69	0.67	0.58
20	0.12	0.16	0.22	0.29	0.38	0.50	0.58	0.59	0.53	0.46
80	0.23	0.24	0.26	0.30	0.33	0.34	0.34	0.335	0.31	0.28
120	0.29	0.32	0.35	0.36	0.34	0.30	0.28	0.23	0.20	0.18
150	0.34	0.39	0.42	0.41	0.38	0.32	0.25	0.20	0.17	0.14
200	0.39	0.44	0.45	0·43	0.41	0.30	0.21	0.15	0.11	0.09

Table -2

Absorbance of methyl orange ($2x10^{-5}M$) at 500 mμ in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	0	10	20	40	60	80	100	120	150	200	250
Absorbance	0.69	0.65	0.59	0.49	0.39	0.335	0.28	0.23	0.20	0.15	0.15

Fig. 1

DPB - Methyl orange interaction at pH7

Table -3

Absorption spectra of methyl orange ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	Absorbance at different wavelengths(mμ)										
	400	410	420	425	430	440	450	460	470	480	500
0	0.32	0.35	0.39	0.41	0.42	0.44	0.46	0.48	0.45	0.38	0.28
1	0.17	0.19	0.21	0.22	0.23	0.25	0.29	0.30	0.28	0.23	0.16
50	0.11	0.13	0.17	0.18	0.17	0.15	0.12	0.10	0.08	0.06	0.04
100	0.32	0.37	0.41	0.42	0.41	0.39	0.36	0.32	0.26	0.18	0.10
150	0.40	0.41	0.46	0.48	0.46	0.43	0.39	0.36	0.30	0.25	0.15
200	0.40	0.42	0.47	0.49	0.46	0.44	0.40	0.37	0.30	0.26	0.16

Table -4

Absorbance of methyl orange ($2x10^{-5}M$) at 460 mμ in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	0	0.4	1.0	1.5	2.0	3	5	50	80	100	150	200
Absorbance	048	0.42	0.30	0.19	0.03	Nil	Nil	0.10	0.25	0.32	0.36	0.37

Fig. 2

DPB - Methyl orange interaction at pH 9.12

Table -5

Absorption spectra of methyl orange ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	Absorbance at different wavelengths(mμ)										
	400	410	420	425	430	440	450	460	470	480	500
0	0.33	0.35	0.39	0.42	0.43	0.44	0.46	0.47	0.45	0.38	0.29
1	0.16	0.20	0.21	0.24	0.26	0.28	0.30	0.32	0.29	0.24	0.17
50	0.08	0.10	0.13	0.14	0.13	0.11	0.10	0.08	0.07	0.06	0.04
100	0.32	0.34	0.37	0.38	0.34	0.30	0.27	0.25	0.21	0.17	0.10
200	0.41	0.44	0.48	0.50	0.47	0.45	0.41	0.39	0.31	0.27	0.17
250	0.41	0.43	0.48	0.50	0.48	0.45	0.41	0.39	0.31	0.27	0.18

Table -6

Absorbance of methyl orange ($2x10^{-5}M$) at 460 mμ in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	0	0.5	1.0	1.5	2.0	5	50	80	100	150	200	250
Absorbance	0.47	0.41	0.32	0.25	0.05	Nil	0.08	0.20	0.25	0.32	0.39	0.39

Fig.3

DPB - Congo Red interaction at pH 2.32 :

Table -7

Absorption spectra of congo red ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	Absorbance at different wavelengths (mμ)										
	430	450	460	470	490	500	530	550	560	570	590
0	0.17	0.18	0.19	0.21	0.23	0.24	0.28	0.29	0.30	0.29	0.22
1	0.17	0.19	0.20	0.21	0.22	0.22	0.24	0.25	0.25	0.23	0.19
5	0.18	0.21	0.24	0.24	0.22	0.21	0.19	0.14	0.13	0.11	0.09
8	0.20	0.26	0.27	0.25	0.20	0.19	0.14	0.07	0.06	0.05	0.04
10	0.20	0.27	0.28	0.26	0.21	0.18	0.13	0.07	0.05	0.04	0.03

Table -8

Absorbance of congo red ($2x10^{-5}M$) at 560 mμ in presence of different concentrations of DPB

DPB conc., ($x10^{-5}M$)	0	0.5	1	2	3	4	5	6	8	10	14
Absorbance	0.30	0.28	0.25	0.23	0.20	0.15	0.13	0.1	0.06	0.05	0.05

Fig. 4

DPB - Congo Red interaction at pH7

Table -9

Absorption spectra of congo red ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	Absorbance at different wavelengths(mμ)							
	440	450	460	470	480	490	500	520
0	0.46	0.51	0.55	0.58	0.59	0.60	0.59	0.42
1.0	0.40	0.44	0.49	0.50	0.52	0.54	0.53	0.37
10	0.23	0.25	0.26	0.25	0.22	0.20	0.18	0.12
15	0.32	0.37	0.39	0.35	0.32	0.30	0.24	0.16

Table -10

Absorbance of congo red ($2x10^{-5}M$) at 490 mμ in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	0	0.5	1.0	2.0	3.0	3.5	4.0	5.0	8.0	10	15	20
Absorbance	0.60	0.57	0.54	0.40	0.3	0.21	0.05	Nil	0.08	0.20	0.30	0.30

Fig. 5

DPB - Congo Red interaction at pH 9.12 :

Table -11

Absorption spectra of congo red ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	Absorbance at different wavelengths (mμ)							
	440	450	460	470	480	490	500	520
0	0.45	0.50	0.53	0.57	0.59	0.61	0.56	0.43
2	0.31	0.37	0.40	0.42	0.44	0.45	0.39	0.33
10	0.22	0.27	0.29	0.27	0.23	0.20	0.17	0.11
15	0.30	0.36	0.40	0.38	0.35	0.32	0.19	0.14

Table -12

Absorbance of congo red ($2x10^{-5}M$) at 490 mμ in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	0	1	2	3	4	5	7	8	10	12	15	18	20
Absorbance	0.61	0.55	0.45	0.27	0.07	Nil	0.05	0.09	0.20	0.27	0.32	0.32	0.32

Fig. 6

DPB - Alizarin Red S interaction at pH 2.32:

Table -13

Absorption spectra of alizarin red S (10×10^{-5}M) in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	Absorbance at different wavelengths (mμ)									
	350	380	400	405	410	415	420	425	435	440
0	0.15	0.22	0.27	0.28	0.29	0.30	0.29	0.27	0.24	0.22
20	0.145	0.21	0.25	0.26	0.27	0.28	0.27	0.26	0.25	0.22
60	0.14	0.18	0.22	0.23	0.24	0.245	0.245	0.245	0.23	0.21
100	0.13	0.16	0.19	0.21	0.215	0.225	0.225	0.23	0.22	0.20
150	0.13	0.16	0.20	0.21	0.21	0.22	0.22	0.23	0.22	0.20

Table -14

Absorbance of alizarin red S (10×10^{-5}M) at 415 mμ in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	0	10	20	30	40	60	70	80	100	130	150
Absorbance	0.30	0.29	0.28	0.27	0.26	0.245	0.235	0.23	0.225	0.22	0.22

Fig.7

DPB - Alizarin Red S interaction at pH 7:

Table -15

Absorption spectra of alizarin red S (10×10^{-5}M) in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	Absorbance at different wavelengths(mμ)								
	450	480	500	510	520	525	530	540	550
0	0.25	0.37	0.42	0.44	0.43	0.42	0.40	0.37	0.29
20	0.24	0.35	0.39	0.40	0.41	0.41	0.39	0.38	0.30
50	0.20	0.27	0.33	0.36	0.37	0.38	0.385	0.37	0.32

Table -16

Absorbance of alizarin red S (10×10^{-5}M) at 510 mμ in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	0	5	10	15	20	25	30	35	40	50	70
Absorbance	0.44	0.43	0.425	0.41	0.40	0.39	0.38	0.37	0.365	0.36	0.36

Fig. 8

DPB - Alizarin Red S interaction at pH 9.12 :

Table -17

Absorption spectra of alizarin red S (10×10^{-5}M) in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	Absorbance at different wavelengths (mμ)										
	450	460	470	480	490	500	510	520	530	540	550
0	0.31	0.32	0.33	0.32	0.31	0.30	0.29	0.29	0.28	0.27	0.26
7	0.25	0.26	0.275	0.28	0.29	0.29	0.30	0.30	0.29	0.28	0.27
10	0.24	0.245	0.255	0.26	0.27	0.30	0.30	0.31	0.30	0.29	0.28

Table -18

Absorbance of alizarin red S (10×10^{-5}M) at 470 mμ in presence of different concentrations of DPB

DPB concn., ($\times 10^{-5}$M)	0	2	3	5	6	7	9	10	15	20
Absorbanace	0.33	0.32	0.305	0.29	0.285	0.275	0.26	0.255	0.255	0.26

Fig. 9

DPB - Benzopurpurine 4B interaction at pH 2.32:

Table -19

Absorption spectra of benzopurpurine 4B ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	Absorbance at different wavelengths (mμ)										
	400	425	450	460	470	490	500	505	510	520	530
0	0.16	0.20	0.22	0.28	0.31	0.36	0.39	0.40	0.39	0.37	0.31
1	0.17	0.21	0.24	0.29	0.35	0.37	0.38	0.38	0.37	0.35	0.30
5	0.23	0.30	0.34	0.355	0.35	0.30	0.27	0.27	0.25	0.18	0.16
8	0.24	0.30	0.36	0.37	0.36	0.31	0.27	0.26	0.24	0.17	0.15
10	0.24	0.30	0.36	0.37	0.365	0.31	0.28	0.26	0.23	0.18	0.15
15	0.24	0.31	0.36	0.37	0.36	0.32	0.28	0.26	0.24	0.18	0.15

Table -20

Absorbance of benzopurpurine 4B ($2x10^{-5}M$) at 505 mμ in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	0	0.5	1.0	2.0	3.0	3.5	4	5	6	8	10	15
Absorbance	0.40	0.39	0.38	0.35	0.32	0.31	0.30	0.27	0.26	0.26	0.26	0.26

Fig. 10

DPB - Benzopurpurine 4B interaction at pH 7:

Table -21

Absorption spectra of benzopurpurine 4B ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	Absorbance at different wavelengths (mμ)								
	430	440	450	460	470	480	490	500	525
0	0.23	0.30	0.37	0.44	0.475	0.48	0.47	0.43	0.26
1	0.21	0.28	0.34	0.42	0.46	0.46	0.45	0.42	0.23
2	0.16	0.22	0.31	0.37	0.39	0.40	0.39	0.36	0.19
8	0.10	0.16	0.22	0.23	0.22	0.20	0.19	0.17	0.11
12	0.18	0.27	0.36	0.38	0.36	0.33	0.31	0.29	0.16
15	0.19	0.26	0.36	0.38	0.37	0.33	0.31	0.28	0.17

Table -22

Absorbance of benzopurpurine 4B ($2x10^{-5}M$) at 480 mμ in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	0	0.5	1	1.5	2	2.5	3	4	6	7	8	12	15
Absorbance	0.48	0.47	0.46	0.42	0.40	0.36	0.31	0.06	0.08	0.15	0.20	0.33	0.33

Fig.11

DPB - Benzopurpurine 4B interaction at pH 9.12:

Table -23

Absorption spectra of benzopurpurine 4B ($2x10^{-5}M$) in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	Absorbance at different wavelengths (mμ)								
	430	440	450	460	470	480	490	500	525
0	0.24	0.31	0.37	0.45	0.47	0.48	0.47	0.44	0.27
1	0.20	0.29	0.34	0.42	0.44	0.45	0.44	0.41	0.23
10	0.14	0.21	0.29	0.30	0.28	0.26	0.23	0.20	0.13
12	0.19	0.27	0.37	0.39	0.38	0.34	0.30	0.27	0.17
15	0.19	0.27	0.38	0.39	0.38	0.34	0.30	0.27	0.18

Table -24

Absorbance of benzopurpurine 4B ($2x10^{-5}M$) at 480 mμ in presence of different concentrations of DPB

DPB concn., ($x10^{-5}M$)	0	1	1.5	2	3	4	6	8	10	12	15
Absorbance	0.48	0.45	0.42	0.39	0.31	0.04	0.03	0.13	0.26	0.34	0.34

Fig.12

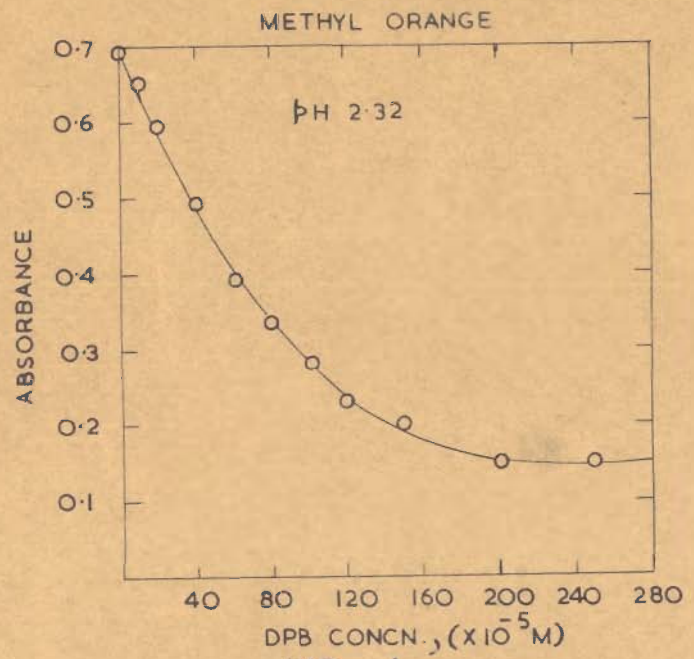


FIG. 1

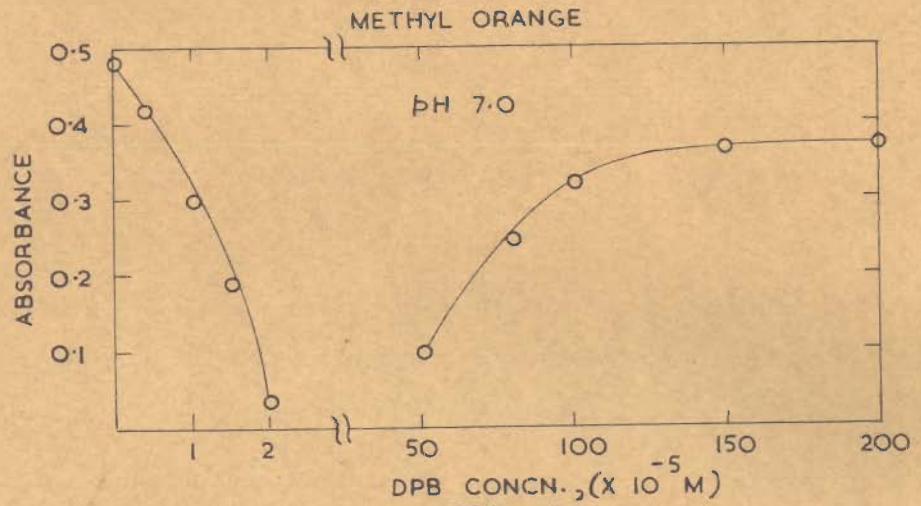


FIG. 2

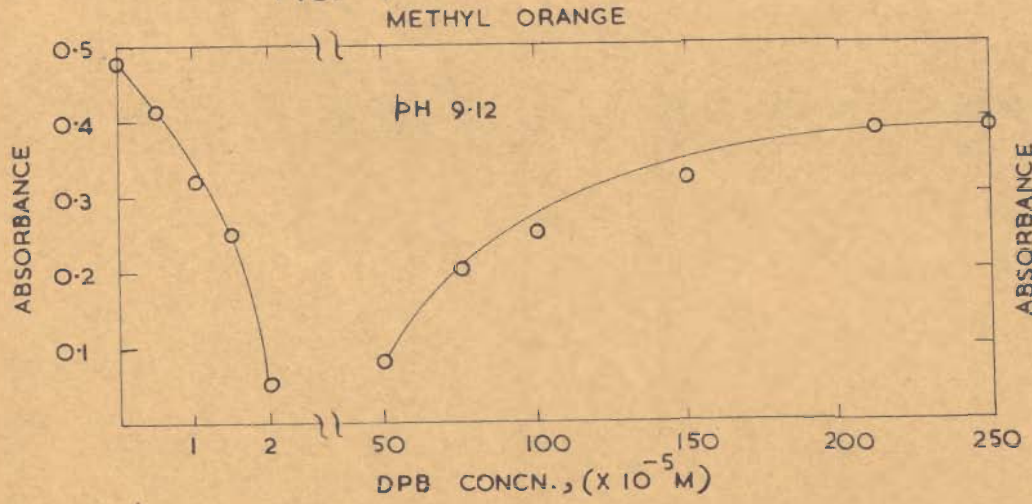


FIG. 3

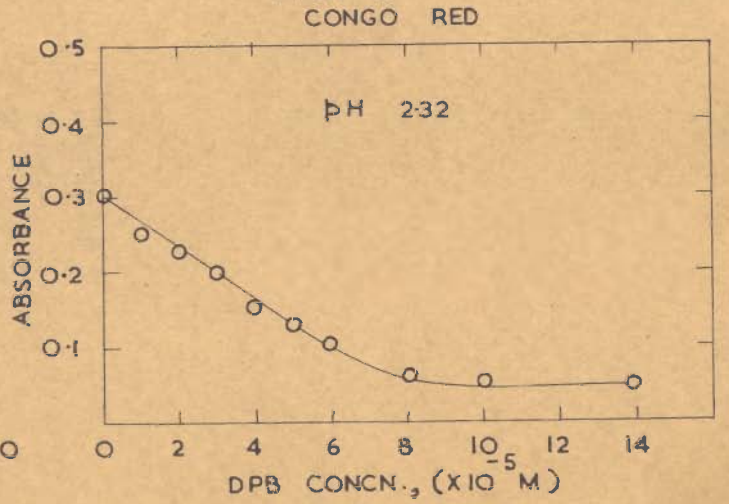


FIG. 4

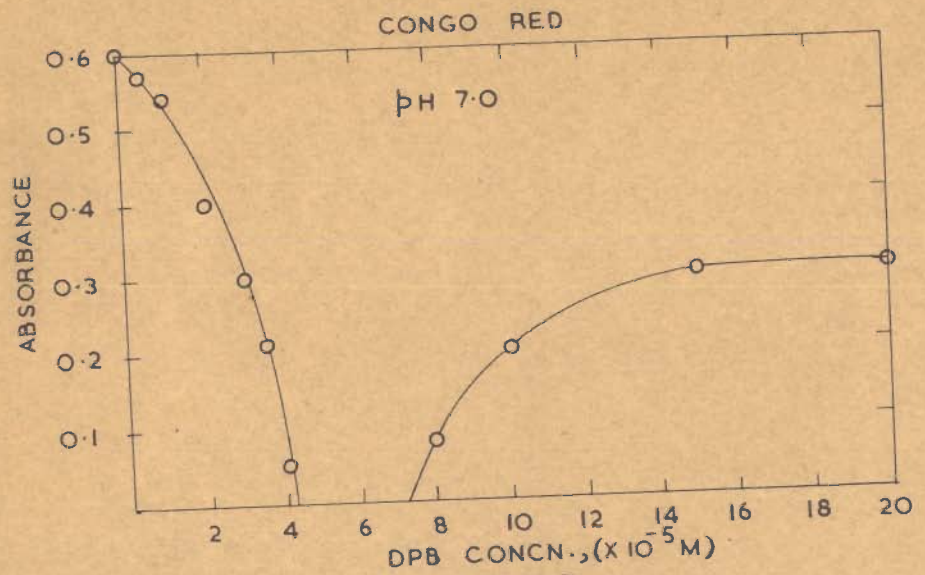


FIG. 5

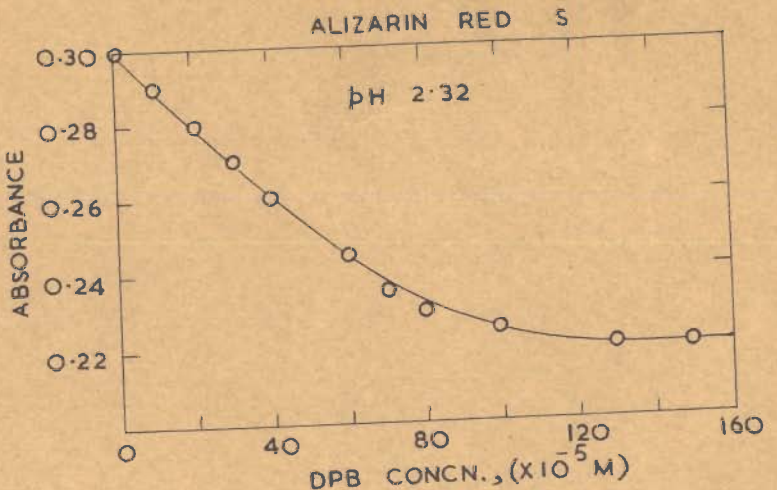


FIG. 7

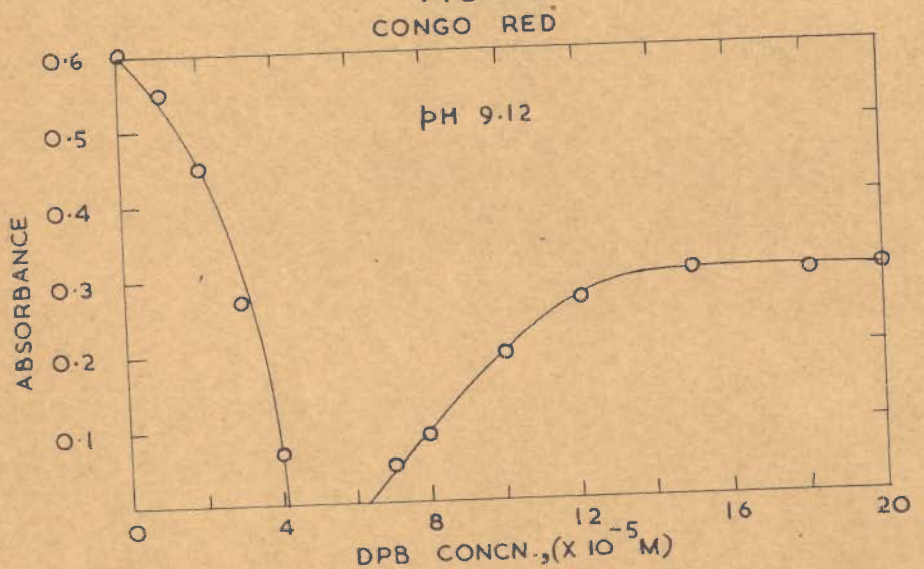


FIG. 6

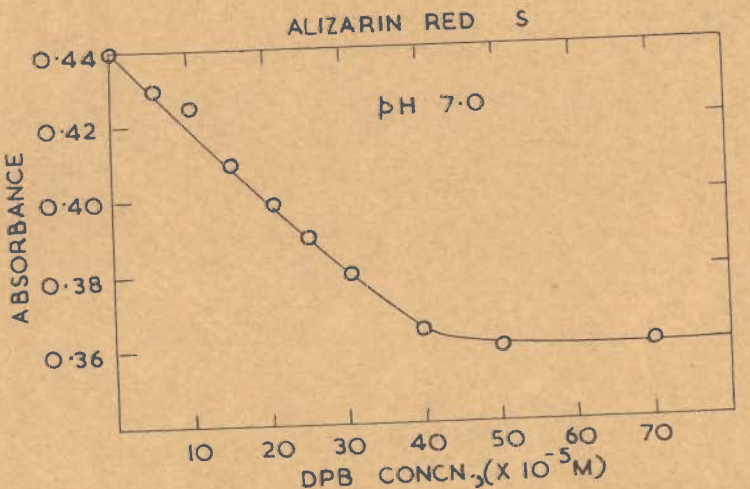


FIG. 8

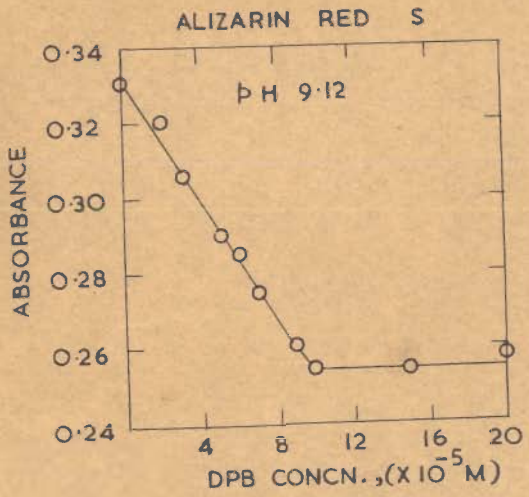


FIG. 9

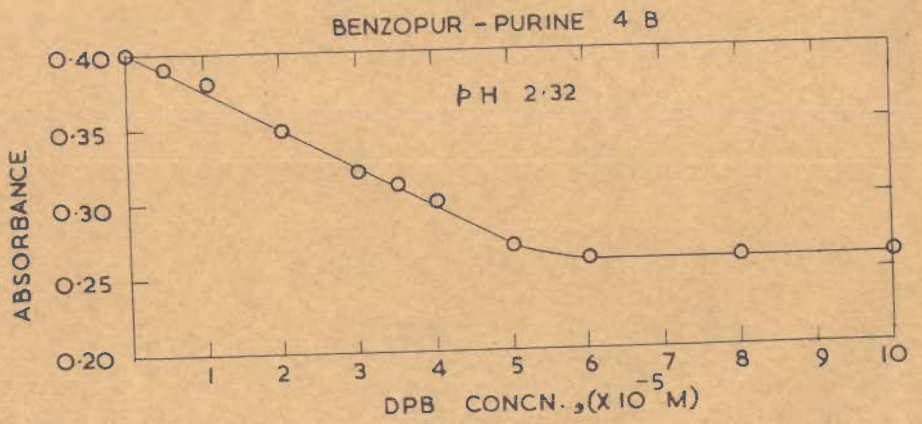


FIG. 10

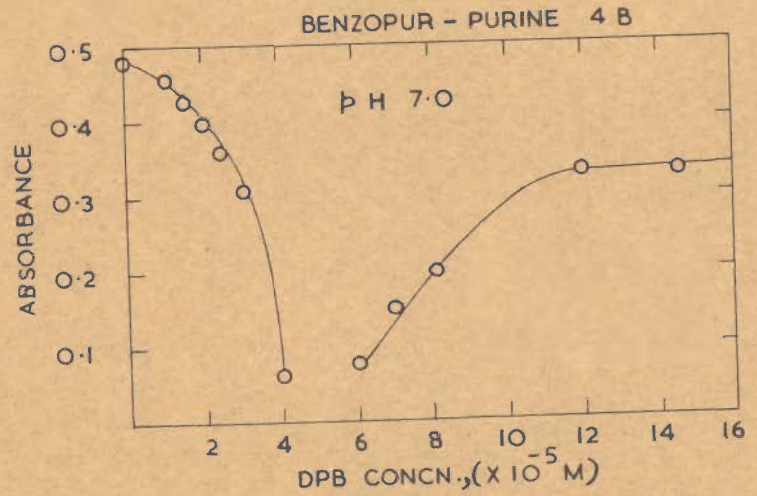


FIG. 11

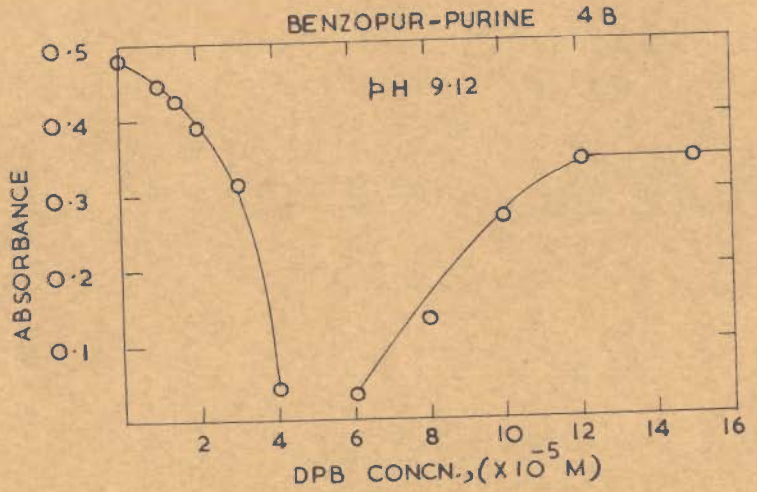


FIG. 12

RESULTS AND DISCUSSION

The absorption maximum of methyl orange, congo red, alizarin red S and benzopurpurine 4B is shifted in presence of DPB. The following factors may be operative:-

(i) The change in pH of the dye solution.

(ii) The disturbance in the monomer-polymer equilibria of the dye.

(iii) The reaction between the dye and the surfactant.

That the spectral shift may be due to change in the pH of the solution is ruled out for the experiments were carried out in buffered solutions and the addition of DPB brings about inappreciable change in the pH of the solution.

The second possibility, viz., the spectral shift due to the disturbance in monomer-polymer equilibria is also ruled out since all the experiments were carried out in the concentration range in which the dye remains in monomeric form. To confirm that the dye is only in monomeric form, absorbance of dyes at different concentrations were measured. It was found that for concentration ranges employed in our investigations, the Beer's law was obeyed proving thereby that the dye is present only in monomeric form.

It, therefore, becomes apparent that the reaction between the surfactant and dye can only be the cause of spectral shift and absorbance change (Tables 1-24).

DPB - Methyl orange interaction :

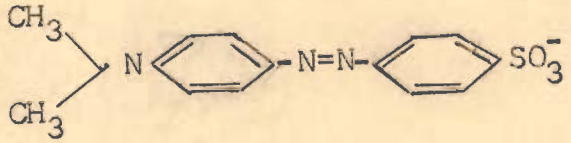
Table -25

The effect of DPB on the absorption maximum of methyl orange.

DPB concn., ($x10^{-5}$M)	Absorption maximum(in mμ) at different pH values		
	pH 2.32	pH 7	pH 9.12
0	500	460	460
1	-	460	460
20	500	-	-
50	-	425	425
80	475 - 490 (ill defined)	-	-
100	-	425	425
120	435	-	-
150	425	425	425
200	425	425	425
250	-	-	425

Interaction at pH 7 and 9.12:

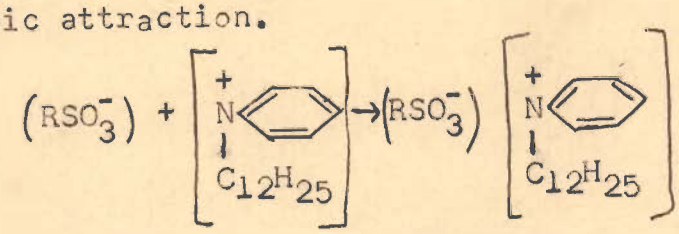
In neutral and alkaline medium methyl orange is orange-yellow in colour and exists in the following anionic form :



The above anionic form which is called basic form of the dye will be referred to as RSO_3^- and has an absorption maximum at 460 mμ. As DPB is added to basic form, interaction takes place and the interaction product precipitates out.

It is evident from Figs.2,3 that when methyl orange and DPB are present in molar ratio of 1:1, the complete precipitation of the interaction product takes place and absorbance of the supernatant liquid becomes nil.

Dodecyl pyridinium ion being positively charged and basic form of the dye being negatively charged, the following reaction may be assumed to take place due to coulombic attraction.

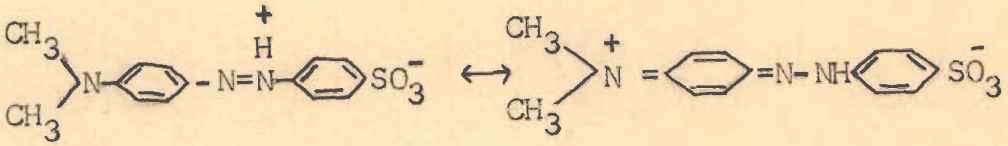


However, when the DPB concentration is increased and becomes 50×10^{-5}M, the dissolution of the surfactant-dye interaction product starts as seen by absorbance (Figs.2,3). The levelling off points in the curves (Figs.2,3) correspond to the complete dissolution of the surfactant-dye interaction product. The interaction product on dissolution in the excess of DPB gives an absorption peak at 425 mμ. Since the interaction product starts dissolving at a concentration of 50×10^{-5}M of DPB, the dissolution cannot be simple solubilization of the product inside the hydrophobic core of the surfactant micelles because the c.m.c. value of DPB is of the order of 10^{-2}M in water. No doubt the c.m.c. will be lower than this value due to the presence of electrolytes (buffer constituents) but in no case it would reach a value as low as 50×10^{-5}M. Therefore, the dissolution of the surfactant-dye product at such low concentrations may be due to mixed

micelle formation which takes place at much lower concentrations than the c.m.c. value of the surfactant. This viewpoint finds support in the work of Mysels and Mukerjee(13) on the interaction of sodium lauryl sulphate with pinacyanol chloride.

Interaction at pH 2.32:

At pH 2.32, red form of methyl orange exists and has an absorption maximum at 500 mμ. The azo nitrogen takes on a proton and the dipolar ion is then formed as a resonant hybrid of the following two structures(25) :



The above form of the dye is called acid form and will be referred to as $(RH)^{+}SO_3^{-}$.

It is evident from Table-25 that when DPB is added in excess to methyl orange in acid form, the absorption maximum shifts from 500 mμ to 425 mμ accompanied by the decrease in absorbance (with increase in DPB concentration) and finally absorbance becomes constant (Table 2, Fig.1). This behaviour is undoubtedly due to interaction.

The fact that the interaction product between DPB and dye at pH 2.32 has an absorption maximum at 425 mμ which is also the absorption maximum of the DPB-dye interaction product at pH 7 and 9.12 strongly suggests that the interaction product should be the same at all the three pH values. This points out that the

addition of DPB to methyl orange at pH 2.32 causes the transition of the dye from acid form to basic form provided it exists in the bound state with the surfactant.

The following equilibria exists,

$$\left[(RH^+)SO_3^-\right] + \left[\text{N}^+(C_{12}H_{25})\text{C}_5\text{H}_5\right] \rightleftharpoons \left[RSO_3^-\left(\text{N}^+(C_{12}H_{25})\text{C}_5\text{H}_5\right)\right] + \left[H^+\right] \quad \ldots\ldots(I)$$

where $\left[(RH^+)SO_3^-\right]$, $\left[\text{N}^+(C_{12}H_{25})\text{C}_5\text{H}_5\right]$, $\left[RSO_3^-\left(\text{N}^+(C_{12}H_{25})\text{C}_5\text{H}_5\right)\right]$ and $\left[H^+\right]$ refer to the concentration of acid form of dye, dodecyl pyridinium ion, the interaction product and hydrogen ions.

This transition is evidently due to preferential affinity of anionic form of the dye to get bound with dodecyl pyridinium ion over the dipolar ionic form. Since interaction brings about continuous decrease in absorbance of the dye solution with gradual increase in DPB concentration (Fig.1, Table 2), hence the DPB concentration corresponding to the levelling off point in the curve (Fig.1) is the amount required to cause the complete transition of acid form to basic form bound to dodecyl pyridinium ion. This concentration of DPB comes out to be 200×10^{-5}M. Out of this much amount of DPB, only 2×10^{-5}M goes to bind 2×10^{-5}M of methyl orange in basic form. The remaining amount is, therefore, used up in deprotonating the nitrogen of azo group, i.e., in shifting the equilibria(I) from left to right.

The following Table-26 gives the amount of dye bound to DPB at its different concentrations calculated

by employing Klotz's equation.

Table -26

Methyl orange Concn. = 2×10^{-5}M, ϵ_F = 34500, ϵ_B = 7500

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn. free dye, ($\times 10^{-5}$M)	Concn. bound dye, ($\times 10^{-5}$M)
0	34500	1.0	2.0	0
10	32500	0.925	1.850	0.150
20	29500	0.814	1.628	0.372
40	24500	0.629	1.258	0.742
60	19500	0.444	0.888	1.112
80	16750	0.342	0.684	1.316
100	14000	0.240	0.480	1.520
120	11500	0.148	0.296	1.704
150	10000	0.092	0.184	1.816
200	7500	0	0	2.00
250	7500	0	0	2.00

DPB - Congo red interaction :

It is seen from Tables 7,9,11 that the absorption maximum of congo red is shifted towards shorter wavelengths on the addition of DPB.

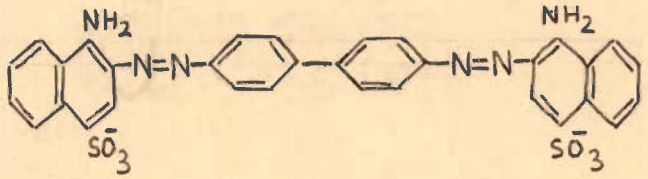
Table-27

Effect of DPB on the absorption maximum of congo red

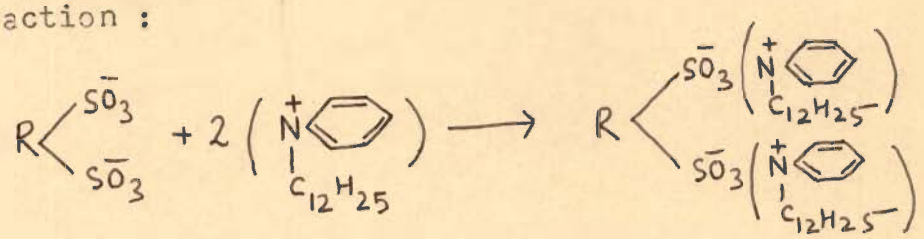
DPB concn., ($\times 10^{-5}$M)	Absorption maximum (in mμ) at different pH values		
	pH 2.32	pH 7	pH 9.12
0	560	490	490
1.0	550-560 (ill defined)	490	-
2.0	-	-	490
5.0	460-470 (ill defined)	-	-
8	460	-	-
10	460	460	460
15	-	460	460

Interaction at pH 7 and 9.12 :

In neutral and alkaline medium congo red is red in colour and exists in the following anionic form :



The above anionic form of the dye which is called the basic form will be referred to as $R\langle^{SO_3^-}_{SO_3^-}$ and has an absorption maximum at 490 mμ. When DPB is added to the basic form, interaction takes place and the product starts precipitating out. It is seen from Figs.5,6 that when the molar ratio of congo red to DPB is 1/2, the complete precipitation of the interaction product takes place and the absorbance of the supernatant liquid becomes nil. The following reaction may be assumed to be taking place due to coulombic attraction :

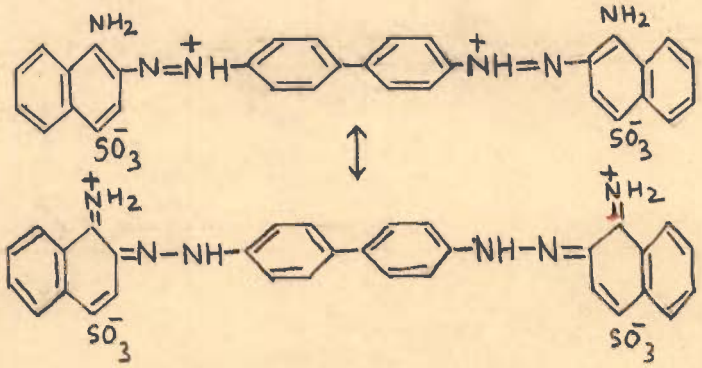


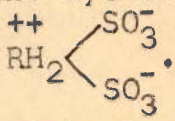
However, when the concentration of DPB is increased beyond 4×10^{-5}M, the dissolution (or dispersion) of the product starts taking place as indicated by the absorbance of the solution (Figs.5,6). The levelling off points in the curves (Figs.5,6) correspond to the complete dissolution of the surfactant-dye interaction product. This concentration of DPB required for complete dissolution of interaction product is found to be 15×10^{-5}M for pH 7 and 14×10^{-5}M for

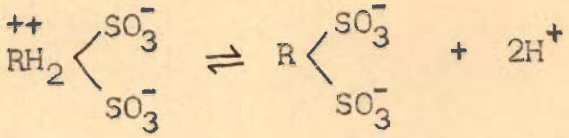
pH 9.12. The dissolution of the product at such low concentrations of DPB cannot be taken as solubilization. The dissolution may be due to the attachment or adsorption of hydrophilic dodecylpyridinium ions on interaction product. It is interesting to note that if the interaction product is separated and made to dissolve in 15×10^{-5}M DPB, it is found to be insoluble. It is only when congo red (2×10^{-5}M) is added to 15×10^{-5}M DPB, the interaction product does not precipitate out and remains in solution. The only probable explanation is that in the excess of DPB, before the interaction product molecules can agglomerate with each other and precipitate out, the adsorption of dodecyl pyridinium ions on them takes place. This adsorption of dodecyl pyridinium ions on the interaction product renders them positively charged and the electrostatic repulsion between interaction product molecules prevent the agglomeration and consequently the precipitation. The dye in excess of DPB has an absorption peak at 460 mμ (Table 27).

Interaction at pH 2.32:

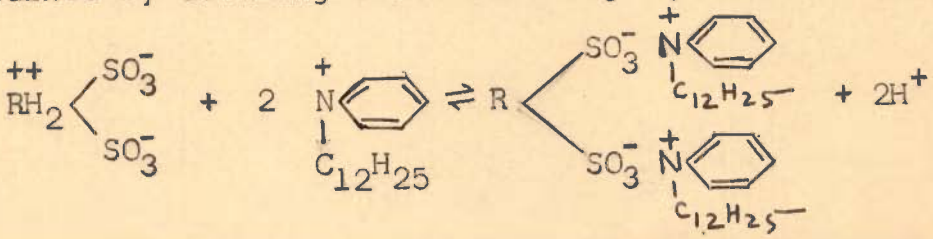
At pH 2.32 congo red is blue in colour and has an absorption maximum at 560 mμ. The azo nitrogen takes on a proton and the dipolar ion is then formed as a resonant hybrid of the following two structures(26):



The above dipolar ionic form of the dye is called acid form and will be referred to as  . The dye at pH 2.32 is present both in acid and basic form and the equilibrium between them exists:



The colour of congo red in presence of DPB changes from blue to orange and the absorption maximum is shifted from 560 mμ to 460 mμ. Such a large shift in the absorption maximum suggests that the addition of DPB to congo red brings about the transition of the dye from acid form to basic form. This is further confirmed by the fact that the interaction product at all the three pH values, viz., 2.32, 7 and 9.12 has an absorption maximum at 460 mμ, indicating that the product is same. The spectral data can only be explained by assuming that following equilibrium exists:



The transition is evidently due to preferential affinity of anionic form of the dye to get bound to cationic surfactant over dipolar ionic form. The levelling off point in the curve (Fig.4) corresponds to the concentration of DPB when whole of the dye is present in basic form bound to dodecyl pyridinium ion. This concentration is found to be 9×10^{-5}M. Out of this much amount of DPB,

only 4×10^{-5}M goes to bind 2×10^{-5}M of congo red in basic form and remaining 5×10^{-5}M DPB is used up in the deprotonation of nitrogen of azo group.

The following Table-28 gives the amount of dye bound to DPB at its different concentrations calculated by employing Klotz's equation :

Table -28

Congo red concn. = 2×10^{-5}M, ϵ_F = 15000, ϵ_B = 2500

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn.free dye, ($\times 10^{-5}$M)	Concn.bound dye, ($\times 10^{-5}$M)
0	15000	1.0	2.0	0
0.5	14000	0.960	1.920	0.080
1.0	12500	0.800	1.600	0.400
2.0	11500	0.720	1.440	0.560
3.0	10000	0.600	1.200	0.800
4.0	7500	0.400	0.800	1.200
5.0	6500	0.320	0.640	1.360
6.0	5000	0.200	0.400	1.6000
8.0	3000	0.040	0.080	1.920
10.0	2500	0	0	2.000
14.0	2500	0	0	2.000

DPB - Alizarin red S interaction :

The spectrum of alizarin red S (Tables 13,15, 17) changes very markedly with increasing concentration of DPB.

Table -29

Effect of DPB on the absorption maximum of alizarin red S.

DPB concn., ($\times 10^{-5}$ M)	Absorption maximum (in mμ) at different pH values		
	pH 2.32	pH 7	pH 9.12
0	415	510	470
7	-	-	510-520 (ill defined)
10	-	-	520
20	415	520-525 (ill defined)	-
50	-	530	-
60	415-425 (ill defined)	-	-
100	425	-	-
150	425	-	-

The shift in the absorption maximum (Table-29) suggests the possibility of alizarin red S and DPB interaction. The interaction is electrostatic involving attraction between the quaternary cation and the dye anion. Unlike congo red and methyl orange, the absorption maximum in excess of DPB is different at all the three pH values showing thereby that interaction product is not the same.

The amount of dye bound with DPB calculated by Klotz's equation is given in following Tables 30-32 :

Table -30

Binding of alizarin red S with DPB at pH 2.32

Alizarin red S concn.=10×10^{-5}M, ϵ_F = 3000, ϵ_B = 2200

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn.free dye, ($\times 10^{-5}$M)	Concn.bound dye, ($\times 10^{-5}$M)
0	3000	0	10.00	0
10	2900	0.875	8.75	1.25
20	2800	0.750	7.50	2.50
30	2700	0.625	6.25	3.75
40	2600	0.500	5.00	5.00
60	2450	0.312	3.12	6.88
70	2350	0.187	1.87	8.13
80	2300	0.125	1.25	8.75
100	2250	0.062	0.62	9.38
130	2200	0	0	10.00
150	2200	0	0	10.00

Table -31

Binding of alizarin red S with DPB at pH 7

Alizarin red S concn.=10×10^{-5}M, ϵ_F = 4400, ϵ_B = 3600

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn.free dye, ($\times 10^{-5}$M)	Concn.bound dye, ($\times 10^{-5}$M)
0	4400	0	10.00	0
5	4300	0.875	8.75	1.25
10	4250	0.812	8.12	1.88
15	4100	0.625	6.25	3.75
20	4000	0.500	5.00	5.00
25	3900	0.375	3.75	6.25
30	3800	0.250	2.50	7.50
35	3700	0.125	1.25	8.75
40	3650	0.062	0.62	9.38
50	3600	0	0	10.00
70	3600	0	0	10.00

Table -32

Binding of alizarin red S with DPB at pH 9.12

Alizarin red S concn.= 10×10^{-5}M, ϵ_F = 3300, ϵ_B = 2550

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn. free dye, ($\times 10^{-5}$M)	Concn. bound dye ($\times 10^{-5}$M)
0	3300	0	10.00	0
2	3200	0.866	8.66	1.34
3	3050	0.666	6.66	3.34
5	2900	0.466	4.66	5.34
6	2850	0.400	4.00	6.00
7	2750	0.266	2.66	7.34
9	2600	0.066	0.66	9.34
10	2550	0	0	10.00
15	2550	0	0	10.00

It is noted from the Tables 30-32 and Figs.7-9, that the amount of DPB required for complete dye binding is 120×10^{-5}M, 45×10^{-5}M and 10×10^{-5}M at pH 2.32, 7 and 9.12, respectively. Therefore, at lower pH values, amount of DPB required for complete binding of dye is larger as compared to that required at higher pH values.

DPB - Benzopurpurine 4B interaction:

It is evident from Tables 19,21,23 that the absorption spectrum of benzopurpurine 4B changes markedly with increasing concentration of DPB.

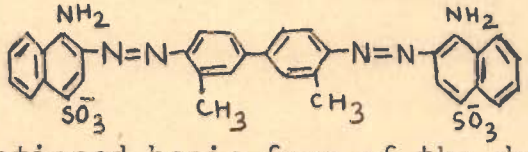
Table -33

Effect of DPB on the absorption maximum of benzopurpurine 4B

DPB concn., ($x10^{-5}$M)	Absorption maximum(in mμ) at different pH values		
	pH 2.32	pH 7	pH 9.12
0	505	480	480
1	500-505	480	480
2	-	480	-
5	460	-	-
8	460	460	-
10	460	-	460
12	-	460	460
15	460	460	460

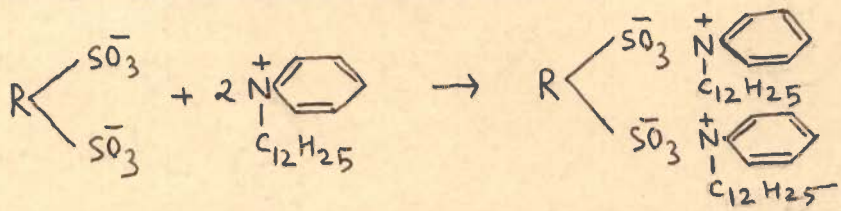
Interaction at pH 7 and 9.12:

In neutral and alkaline medium benzopurpurine 4B is red and exists in the following anionic form:



The above mentioned basic form of the dye will be referred to as $R\begin{smallmatrix}SO_3^-\\SO_3^-\end{smallmatrix}$ and has an absorption maximum at 480 mμ. On the addition of DPB to the dye in basic form, interaction takes place and the interaction product starts separating out. It is seen from Figs.11,12 that when the molar ratio of benzopurpurine 4B to DPB is 1/2, the complete precipitation of the interaction product takes place and the absorbance of the supernatant liquid becomes practically nil. The behaviour is quite similar to the behaviour of congo

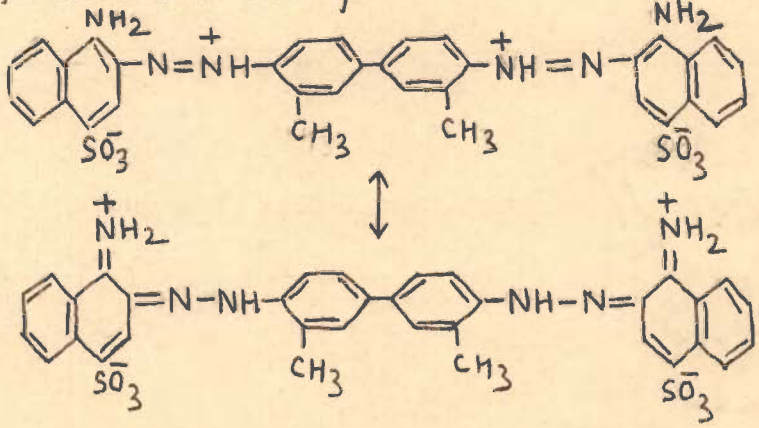
red. The following reaction may be assumed to be taking place due to coulombic attraction :



However, when DPB concentration goes beyond 4×10^{-5}M, the dissolution of the product takes place as indicated by definite absorbance of the solution (Figs.11,12). Consequently, the levelling off points in the curves (Figs.11,12) correspond to complete dissolution of the surfactant-dye interaction product. The concentration of DPB required for complete dissolution of the interaction product is found to be 11×10^{-5}M for pH 7 and 12×10^{-5}M for pH 9.12. The dissolution of the product at such low concentrations of DPB can be explained on the basis of the same arguments as those advanced for the dissolution of DPB-congo red interaction product earlier. The dye in excess of DPB has an absorption maximum at 460 mμ (Table 33).

Interaction at pH 2.32:

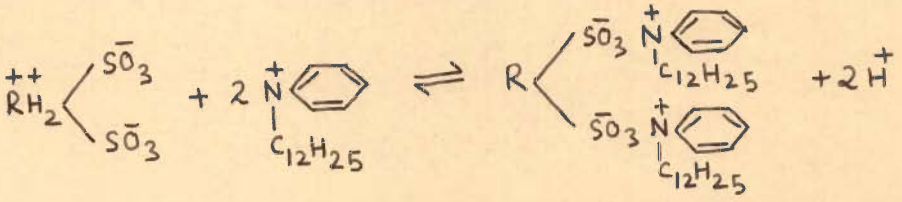
At pH 2.32, because some of the dye is present in the form of dipolar ion, the absorption maximum of the dye occurs at 505 mμ.



The above dipolar ionic form of the dye is called acid form and will be referred to as $^{++}RH_2\begin{matrix}SO_3^-\\SO_3^-\end{matrix}$. Both the acid and basic forms of the dye are in equilibrium.

$$^{++}RH_2\begin{matrix}SO_3^-\\SO_3^-\end{matrix} \rightleftharpoons R\begin{matrix}SO_3^-\\SO_3^-\end{matrix} + 2H^+$$

The absorption maximum of the dye shifts from 505 mμ to 460 mμ in presence of excess of DPB (Table 33). Since the absorption maximum of the dye in presence of excess of DPB is at 460 mμ at all the three pH values, viz., 2.32, 7 and 9.12, hence the interaction product is same in all the three cases. Therefore, the shift in absorption maximum can be explained by assuming that following equilibrium exists :



The levelling off point in the curve (Fig.10) corresponds to the concentration of DPB when whole of the dye is present in basic form bound to dodecyl pyridinium ion. This concentration is found to be 6×10^{-5}M. Out of this much amount of DPB, only 4×10^{-5}M goes to bind 2×10^{-5}M of benzopurpurine 4B and remaining 2×10^{-5}M DPB is used up in the deprotonation of nitrogen of azo group. Since the structure of benzopurpurine 4B is basically similar to congo red with the only difference that benzopurpurine 4B contains two methyl groups extra on diphenyl ring, the behaviour of both the dyes in presence of DPB is expected

to be the same. The results also prove this view point. However, in contrast to congo red where $5x10^{-5}$M of DPB is used up in the deprotonation of nitrogen of azo group, only $2x10^{-5}$M of DPB is required for deprotonating the nitrogen of azo group in case of benzopurpurine 4B at pH 2.32. The lesser amount of DPB required for the deprotonation process of benzopurpurine 4B as compared to congo red may be due to the fact that relatively small amount of benzopurpurine 4B is present in acid form. In case of congo red the shift in absorption maximum with pH change was from 490 mμ (in neutral and alkaline medium) to 560 mμ at pH 2.32, while in case of benzopurpurine 4B the shift is from 480 mμ (at pH 7 and 9.12) to 505 mμ at pH 2.32.The relatively smaller shift (480 mμ to 505 mμ) suggests that benzopurpurine 4B is protonated to smaller extent as compared to congo red. The lesser extent of protonation is due to the presence of methyl groups on diphenyl ring of the benzopurpurine 4B.

The amount of the dye bound to DPB at its different concentrations calculated by Klotz's equation is given in the following Table -34.

Table -34

Benzopurpurine 4B concn.=2×10^{-5}M, ϵ_F = 20000 , ϵ_B = 13000

DPB concn., ($\times 10^{-5}$M)	ϵ_{app}	α	Concn.free dye, ($\times 10^{-5}$M)	Concn.bound dye, ($\times 10^{-5}$M)
0	20000	1	2.000	0
0.5	19500	0.928	1.856	0.144
1.0	19000	0.857	1.714	0.286
2.0	17500	0.642	1.284	0.716
3.0	16000	0.428	0.856	1.144
4.0	15000	0.282	0.564	1.436
5.0	13500	0.071	0.142	1.858
6.0	13000	0	0	2.000
8.0	13000	0	0	2.000
10.0	13000	0	0	2.000
14.0	13000	0	0	2.000

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CHAPTER - 5

" Solubility of cobalt laurate "

INTRODUCTION

The solubility of a number of heavy metal soaps, viz., silver(1), barium(1), copper(2,3), calcium(4-10) in water, and of nickel, manganese, calcium, silver dodecanoates(11), zinc(12) and chromium carboxylates(13) in non-aqueous media is reported in the literature. However, no corresponding data on the solubility of cobalt soaps are available.

The cobalt soaps differ from other heavy metal soaps in a number of ways. Firstly, they are less soluble than others. Secondly, their solubility in non-aqueous media is greatly influenced by methanol. During the course of preliminary experiments, it was found that small amounts of methanol in benzene, toluene, xylene etc. enhance the solubility of cobalt soaps in these solvents tremendously. This is a behaviour peculiar to cobalt soaps and, therefore, needs comprehensive study.

Experimentally the solubility of heavy metal soaps has been determined by evaporation method, chemical and instrumental analysis of saturated solutions and potentiometric method. Except evaporation method, other methods mentioned above could not be employed to determine the solubility of cobalt laurate both in water and non-aqueous solvents. Evaporation method gave less reliable and less reproducible results because of extremely low solubility of cobalt laurate. Moreover, this method could

not be used to determine the effect of varying amounts of the detergent ion on the solubility of the heavy metal soap. To overcome these limitations a new technique which can be successfully employed to cobalt soaps was sought for. The radiotracer technique well known for its high sensitivity was expected to give satisfactory results. Therefore, the solubility of cobalt laurate in water, non-aqueous solvents and in aqueous solutions of potassium laurate was determined with the help of Co^{58} as a tracer. However, in methanol-benzene mixtures, where the solubility was found to go high, the evaporation method could be employed for this purpose.

Another interesting aspect of these studies can be to develop a method to determine the c.m.c. of alkali metal soaps from the data on the solubility of corresponding heavy metal soaps. Due attention to this aspect has not been given so far. The solubility data on cobalt laurate in presence of varying amounts of potassium laurate can be used to determine the c.m.c. of the latter soap. As already stated in the preceding paragraph, the radiotracer technique can be of immense use in such determinations.

EXPERIMENTAL

Solubility determination by radiotracer technique :-

Preparation of the labelled cobalt laurate :

Cobalt-58 in the form of $CoCl_2$ in HCl solution was obtained from the Isotope Division, Atomic Energy Establishment, Bombay. Cobalt laurate was precipitated by the addition of a mixture of ordinary reagent $CoCl_2$ with Co^{58} enriched $CoCl_2$ sample (pH adjusted to approximately 6) to stoichiometric amount of sodium laurate (prepared from reagent grade NaOH and lauric acid) in water. The precipitated cobalt soap was filtered, washed with distilled water and then with alcohol to remove free precipitant and acid. It was dried in vacuum desiccator and stored in stoppered bottle. The activity labelled was about 1.2 ± 0.12 millicurie per gram of cobalt laurate.

Preparation of standard solution of active cobalt laurate:

Standard solution of cobalt laurate was prepared by dissolving a weighed amount of the soap in a known volume of 1:1 benzene-methanol mixture.

Saturated solutions of cobalt laurate in various solvents:

Saturated solutions of cobalt laurate were prepared by the agitation of an excess of cobalt laurate in large Pyrex stoppered bottles about 1/2 full of the solvent. Agitation was continued till equilibrium was established. Attainment of this equilibrium was indicated

by constancy of the counting rate(activity) on successive leaching cycles, independent of time of additional agitation and the amount of excess solid phase present. Each saturated solution in contact with solid cobalt soap was placed after agitation in a thermostat maintained at $30^{\circ} \pm 0.5^{\circ}C$ for a period of about 3 to 4 hrs.. Solubility measurements were run in duplicate.

Analysis of saturated solutions:

Samples withdrawn at different time intervals were filtered through a fine paper. 10 ml of the saturated solutions were taken for counting purposes. Specific activity of cobalt laurate was determined in terms of count rate by measuring the activity of 10 ml of standard solution of cobalt laurate in 1:1 benzene-methanol mixture.

Gamma ray scintillation spectrometer (Atomic Energy Establishment, Bombay) employing NaI(Tl) crystal was used for activity measurement. The spectrometer was calibrated by using Ba^{133}, Cs^{137} and Co^{60} standard gamma sources. A calibration curve was drawn between the base line voltage of the single channel analyser of the gamma ray spectrometer and gamma ray energy (Fig.2). Gamma ray spectra of Co^{58} was taken using single channel analyser with window width of 1 volt. The photopeak of the Co^{58} gamma ray of energy 0.81 Mev was located at base line voltage of 57 volts (Fig.1). Both the differential and integral countings were carried out for activity measurements of the saturated solutions of cobalt laurate.

Differential counting measurements were carried at the photopeak of gamma ray of 0.81 Mev; the channel was of 6 volts (equivalent to 0.09 Mev gamma ray energy absorption from Fig.2) width with base voltage of 54 volts (equivalent to 0.77 Mev gamma ray energy absorption from Fig.2). For integral counting the base voltage was kept at 3 volts (equivalent to 0.04 Mev energy absorption) and so all the pulses for which gamma ray energy absorption was above 0.04 Mev were recorded. All precautions were taken to ensure that activity measurements with saturated solutions of cobalt laurate in various solvents and its standard solution were made under the same geometrical conditions. Counting of each solution was done for a period of 10 minutes.

Coincidence loss correction:

After a counting assembly has registered a pulse, there is usually a period when no pulse can be recorded even if an ionizing event takes place in the detector. The time, after a pulse has been registered, during which no pulse can be recorded is called resolving time of the counting assembly. In scintillation counters the resolving time is usually due to the characteristic resolving time of the electronic equipment used in scaling circuit. As a consequence of resolving time some counts are missed. The loss of counts due to resolving time is called "coincidence loss". Obviously at low counting rates the coincidence loss is negligible. However,

at high counting rates this loss is appreciable and coincidence correction must be applied to the observed counting rate. If a radioactive source gives the observed counting rate X and the resolving time of the counting assembly is T minutes, then true count rate X_o is given by the following equation :

$$X_o = X + X^2T \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

Since counting measurements were carried out for a period of 10 minutes, the coincidence error can be calculated for 10 minutes. Multiplying the equation (1) by 10,

$$10\,X_o = 10\,X + 10X^2T$$

$$10\,X_o = 10\,X + \frac{(10X)^2T}{10}$$

or

$$X_o' = X' + \frac{(X')^2T}{10} \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where X_o' = True counts per ten minutes

X' = observed counts for ten minutes

T = resolving time of the counting assembly in minutes.

The Resolving time of the counting assembly used was 10 μ sec., i.e., $\frac{10\times10^{-6}}{60}$ minutes. Substituting the value of resolving time in equation(2)

$$X_o' = X' + \frac{(X')^2 \times 10^{-6}}{60}$$

$$X_o' = X' + \frac{(X')^2 \times 10^{-7}}{6}$$

Therefore, the coincidence loss for any observed counts X' per ten minutes is $\frac{(X')^2 \times 10^{-7}}{6}$

Decay correction :

The solubility determination of sparingly soluble substance by radiotracer technique is based on the fact that specific activity of active solute remains same in various solvents. However, if the half-life of radioactive nuclei is short, it will decay appreciably during the course of measurements and specific activity will change from day to day. In order to account for the decay either the activity measurements of both the standard solution and unknown solution should be made together at the same moment daily or decay correction should be applied to the observed activity taking the time interval between the countings of standard solution and unknown solution as decay time.

Since Co^{58} has a half-life of 71 days, and activity measurements were spread over a period of about 30 days, the decay of Co^{58} was quite appreciable and, therefore, decay correction was applied to the observed activity.

The decay of a radioactive substance follows the exponential law: $N=Noe^{-\lambda t}$, where N is the number of unchanged radioactive atoms at time t, N_o is the number present when t=0, and λ is the decay constant. Since activity is proportional to the total number of radioactive atoms, hence decay law may be written as $A = Aoe^{-\lambda t}$,

where A = activity at time t

Ao = activity at time t = 0

The time interval between activity measurements of standard solution and unknown solution is taken as decay time 't', because t=0 for activity measurements of standard solution.

Half-life of Co^{58} = 71 days = 71x24 hrs. = 1704 hrs.

$$\therefore \quad \lambda = \frac{0.6931}{\text{Half-life}} = \frac{0.6931}{1704} = 4.068 \times 10^{-4} \text{ (hrs.)}^{-1}$$

Therefore,

$$A = Ao\, e^{-4.068 \times 10^{-4} \times t}$$, t = decay time in hrs.

Hence, with the help of above relationship, the true counts per ten minutes at any time 't' for any saturated solution have been changed to counts that would have been recorded if the activity measurements had been made at the time of activity measurements of standard solution.

Statistical error:

Since radioactive disintegration is a statistical process, counts registered due to a radioactive source are subject to statistical fluctuations. Fluctuations associated with radioactive decay are properly described by the Poisson-distribution law. For values following poisson distribution, the standard deviation is given by the following expressions :

Standard deviation σ of average counts N is given by

$$\sigma = \sqrt{N}$$

Standard deviation σ_s of sum of two count values N_1 and N_2 is given by

$$\sigma_s = \sqrt{\sigma_1^2 + \sigma_2^2}$$

where σ_1 and σ_2 are standard deviations of N_1 and N_2, respectively.

Standard deviation σ_d of difference of two count values N_1 and N_2 is given by

$$\sigma_d = \sqrt{\sigma_1^2 + \sigma_2^2}$$

Standard deviation of the ratio of two count values N_1 and N_2 is given by

$$\sigma_r = \frac{N_1}{N_2}\sqrt{\left(\frac{\sigma_1}{N_1}\right)^2 + \left(\frac{\sigma_2}{N_2}\right)^2}$$

The standard deviations of activity measurements were calculated using above expressions.

Determination of solubility of cobalt laurate in methanol-benzene mixtures by evaporation method:

Each saturated solution of cobalt laurate in methanol-benzene mixtures was prepared by the agitation of an excess of inactive cobalt laurate with methanol - benzene mixtures. The saturated solutions in contact with solid cobalt laurate were placed in a thermostat maintained at 30±0.5°C for sufficiently long time. After solubility equilibrium was established, 10 ml of clear supernatant solutions were withdrawn and evaporated to dryness in weighed glass beakers. The amount of residue left was determined by weighing. Knowing the amount of cobalt laurate present in 10 ml of saturated solution, the solubility

of cobalt laurate could be calculated. The methanol - benzene mixtures were made by volume.

x

Activity measurements of standard solution and saturated solutions of cobalt laurate are given in the following Tables 1-14.

Following notations have been used:

CPTM = counts per ten minutes

A = True (net) activity in terms of CPTM at the moment of counting = average observed CPTM + coincidence loss - background.

Ao = Activity in terms of CPTM after decay correction has been applied on true observed activity (A).

Table -1

Gamma ray spectra of cobalt -58 :

Width of the channel = 1 volt

CPM = counts per minute

Net CPM = observed CPM - background

Base voltage (volts)	Net CPM	Base voltage (volts)	Net CPM
3	901	46	198
4	846	47	129
5	903	48	117
6	959	49	97
7	1028	50	69
9	1143	51	104
10	1187	52	158
12	1294	53	277
14	1528	54	567
16	1467	55	1033
18	1144	56	1358
20	922	57	1570
22	906	58	1230
24	786	59	730
26	620	60	349
28	631	61	135
30	602	62	32
32	595	64	19
34	718	66	15
36	1435	68	9
37	1520		
38	1343		
40	764		
42	574		
44	352		

Fig.1

Table -2

Calibration of the gamma ray spectrometer :

Position of photopeaks of various gamma ray energies on single channel analyser.

Gamma standard sources	Energy of gamma ray (Mev)	Position of photopeak on single channel analyser, base line voltage
Ba^{133}	0.36	25 volts
Cs^{137}	0.662	48 volts
Co^{58}	0.81	57 volts
Co^{60}	1.17	79 volts
	1.33	85 volts

Fig. 2

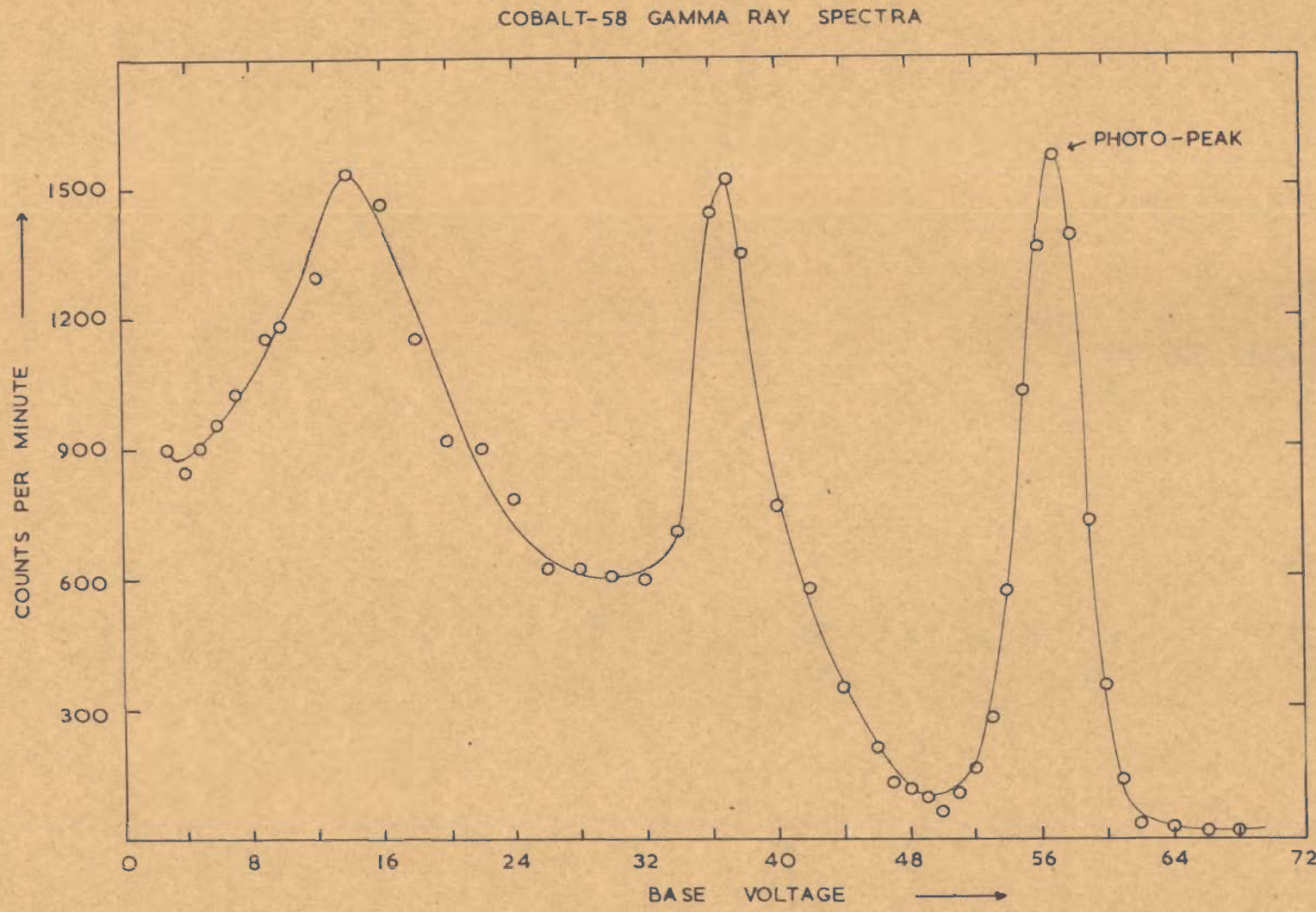

FIG. 1. PLOT BETWEEN COUNTS PER MINUTE & BASE VOLTAGE.

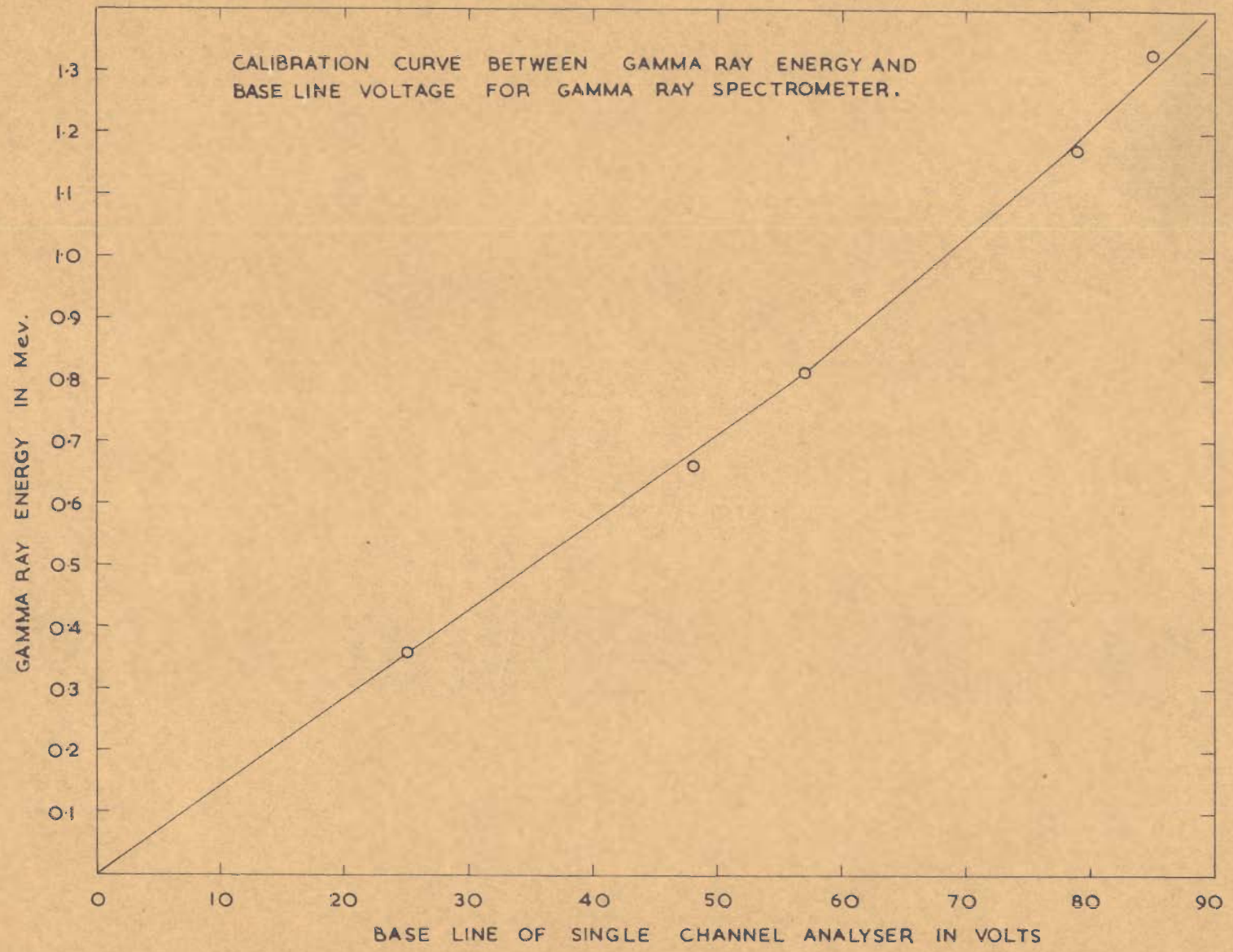

FIG. 2. PLOT BETWEEN GAMMA RAY ENERGY AND BASE LINE VOLTAGE.

Table -3

Activity measurements of cobalt laurate standard solution in 1:1 benzene - methanol mixture :

Amount of cobalt laurate dissolved = 0.005 gm./50 ml of 1:1 benzene-methanol mixture.

Volume taken for counting = 10 ml

Integral counting :

CPTM = counts per ten minutes

Observed CPTM	Average CPTM	Coincidence loss	Background CPTM	True CPTM A_o
98720 99987 98224	98977	166	981	98162

Differential counting at photopeak :

Observed CPTM	Average CPTM	Coincidence loss	Background CPTM	True CPTM, A_o
10970 11170 11070	11070	negligible	50	11020

Table -4

Activity measurements of saturated solution of cobalt laurate in acetone:

Volume taken for counting = 10 ml

Integral counting :

Decay time = t = 56 hrs.

Background = 981 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	11408 11504 11610	11507	negligible	10526	10761
II	11435 11502 11621	11519	negligible	10538	10770

Differential counting at photopeak:

Decay time = t = 58 hrs.

Background = 54 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	1240 1260 1269	1256	negligible	1202	1230
II	1214 1247 1274	1245	negligible	1191	1219

Table -5

Activity measurements of the saturated solution of cobalt laurate in methyl ethyl ketone

Volume of the saturated solution taken for counting = 10 ml

Integral counting:

t = Decay Time = 169 hrs.

Background = 960 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	9844 9748 9937	9843	negligible	8883	9523
II	9764 9880 9971	9871	negligible	8911	9543

Differential counting at photopeak:

Background = 52 CPTM

Decay time = t = 170 hrs.

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM (A)	A_o (CPTM)
I	1055 1073 1092	1073	negligible	1021	1094
II	1077 1074 1052	1067	negligible	1015	1087

Table -6

Activity measurements of the saturated solution of cobalt laurate in dimethyl formamide :

Volume taken for counting = 10 ml

Integral counting :

Background = 971 CPTM

t = Decay time= 173 hrs.

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	9326 9416 9212	9318	negligible	8347	8957
II	9321 9428 9192	9313	negligible	8342	8950

Differential counting at photopeak:

Background = 56 CPTM

t = Decay time = 174 hrs.

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	1008 1031 989	1009	negligible	953	1023
II	1010 985 972	989	negligible	933	1001

Table -7

Activity measurements of the saturated solution of cobalt laurate in methanol:

Volume of solution taken for counting = 10 ml

Integral counting :

t = Decay time = 457 hrs.
Background = 980 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	2170084 2169346 2172502	2170644	78570	2248234	2709400
II	2178002 2179221 2181341	2179522	79196	2257738	2719130

Differential counting at photopeak:

t = Decay time = 459 hrs.
Background = 60 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	255242 252202 253346	253596	1072	254608	306850
II	255149 257183 256180	256157	1093	257190	309910

Table -8

Activity measurements of the saturated solution of cobalt laurate in ethanol:

Volume taken for counting = 10 ml

Integral counting:

t = decay time = 460 hrs.

Background = 980 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	15791 15881 15692	15788	negligible	14808	17852
II	15462 15558 15660	15560	negligible	14580	17580

Differential counting at photopeak:

t = decay time = 461 hrs.

Background = 60 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	1750 1722 1701	1724	negligible	1664	2006
II	1680 1722 1707	1703	negligible	1643	1982

Table -9

Activity measurements of the saturated solution of cobalt laurate in benzene :

Volume taken for counting = 10 ml

Integral counting :

t = decay time = 463 hrs.
Background = 996 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	30609 30715 30425	30583	negligible	29587	35710
II	30907 30940 30747	30864	negligible	29868	36041

Differential counting at photopeak:

t = decay time = 465 hrs.
Background = 57 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	3410 3375 3368	3384	negligible	3327	4019
II	3428 3418 3390	3412	negligible	3355	4052

Table -10

Activity measurements of the saturated solution of cobalt laurate in carbon tetra chloride:

Volume taken for counting = 10 ml

Integral counting :

t = decay time = 467 hrs.

Background = 971 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	5253 5245 5192	5230	negligible	4259	5148
II	5260 5315 5390	5321	negligible	4350	5268

Differential counting at photopeak:

t = decay time = 469 hrs.

Background = 44 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	532 541 506	526	negligible	482	583
II	520 538 554	537	negligible	493	596

Table -11

Activity measurements of the saturated solution of cobalt laurate in cyclohexane :

Volume of the saturated soln.taken for counting = 10 ml

Integral counting:

t = decay time = 480 hrs.
Background = 966 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	17212 17349 17153	17238	negligible	16272	19803
II	17445 17433 17517	17465	negligible	16499	20050

Differential counting at photopeak:

t = decay time = 482 hrs.
Background = 54 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM, A	A_o (CPTM)
I	1896 1868 1922	1895	negligible	1841	2240
II	1905 1895 1943	1914	negligible	1860	2262

Table -12

Activity measurements of the saturated solution of cobalt laurate in toluene:

Volume of the saturated solution taken for counting = 10 ml

Integral counting:

t = decay time = 483 hrs.
Background = 966 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	15425 15587 15341	15451	negligible	14485	17632
II	15607 15697 15767	15690	negligible	14724	17930

Differential counting at photopeak:

t = decay time = 485 hrs.
Background = 50 CPTM

Set No.	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	A_o (CPTM)
I	1682 1660 1710	1684	negligible	1634	1990
II	1701 1748 1694	1714	negligible	1664	2026

Table -13

Activity measurements of the saturated solution of cobalt laurate in water:

Volume of the saturated soln.taken for counting = 10 ml

Integral counting:

Coincidence loss = negligible

Background = 981 CPTM

Set No.	Decay time (hrs.)	Observed CPTM	Average CPTM	True CPTM, (A)	A_o (CPTM)
I	599	9124 9068 9201	9131	8150	10400
II	599	8821 8902 8736	8819	7838	10000
III	600	9262 9201 9312	9258	8277	10630

Table -14

Activity measurements of the saturated solution of cobalt laurate in aqueous solution of potassium laurate:

Volume of the saturated soln. taken for counting purposes = 10 ml

Integral counting:

Background = 981 CPTM

Coincidence loss = negligible

Potassium laurate concn., C	Decay time (hrs.)	Observed CPTM	Average CPTM	True CPTM, (A)	A_o (CPTM)
0.001M	625	7292 7282 7238	7270	6289	8110
0.003M	626	5236 5210 5172	5206	4225	5448
0.005M	627	4632 4612 4583	4609	3628	4678
0.01M	628	3520 3535 3498	3517	2536	3271
0.02M	628	2520 2526 2497	2514	1533	1978
0.03M	629	2342 2320 2285	2315	1334	1721
0.05M	630	2372 2360 2338	2356	1375	1774
0.1M	631	2448 2422 2411	2427	1446	1866
0.2M	632	2636 2672 2641	2649	1668	2153

CALCULATIONS, RESULTS AND DISCUSSION

Calculations:

If a radioactive isotope is mixed with an inactive isotope of the same element, then because of their virtual identity in physical and chemical properties, the two isotopes will always remain in the same proportion in any of its compound. The proportion of active isotope in a compound will remain same in whatever solvent it is dissolved, i.e., the specific activity (activity/unit wt.) for a given active compound will remain same in all the solvents. Specific activity of the active compound can be determined by preparing its standard solution in a solvent in which it is sufficiently soluble. By knowing the activity of the compound present in its saturated solution in some other solvent, the amount of the compound present in the other solvent can be computed by comparing ~~the~~ its activity in saturated solution with that obtained in standard solution.

Specific activity of cobalt laurate:

Weight of the cobalt laurate dissolved in 50 ml of 1:1 methanol-benzene mixture = 0.005 gm.

Volume taken for counting = 10 ml

Amount of cobalt laurate present in 10 ml of the solution = 0.001 gm.

Activity of 10 ml of the standard solution:-

(A) Integral counting:

Activity of 0.001 gm. of cobalt laurate present in 10 ml of standard solution in terms of counts = 98162 CPTM

Specific activity of cobalt laurate = $\frac{\text{Activity}}{\text{Amount of cobalt laurate}}$

$= \frac{98162}{0.001} = 98162 \times 10^3$ CPTM/gm.of cobalt laurate

(B) Differential counting at photopeak:

Activity of 0.001 gm.of cobalt laurate present in 10 ml of standard solution in terms of counts = 11020 CPTM

Specific activity $= \frac{11020}{0.001} = 11020 \times 10^3$ CPTM/gm.of cobalt laurate.

Solubility determination in any solvent:

Let the amount of cobalt laurate present in any of its saturated solution in a solvent be W gm./10 ml of the satd. soln..

Volume taken for counting = 10 ml

Let the activity of W gm.of cobalt laurate present in 10 ml of the satd. soln. be A_o CPTM (When counting is integral).

Then the specific activity of cobalt laurate $= \frac{A_o}{W}$ CPTM/gm.of cobalt laurate

Since the specific activity of cobalt laurate is same in all solvents, hence

$$\frac{A_o}{W} = 98162 \times 10^3$$

$$W = \frac{A_o}{98162 \times 10^3} = \text{wt.of cobalt laurate in 10 ml of the solution}$$

Therefore, the solubility of cobalt laurate $= \frac{A_o \times 100}{98162 \times 10^3}$ gm./litre

Molecular weight of cobalt laurate = 457.6

$\therefore$ Solubility $= \frac{A_o}{98162 \times 10 \times 457.6}$ Moles/litre

Knowing A_o, the solubility can be calculated.

Differential counting:

If differential counting is done and activity observed is A_o, then

$$\frac{A_o}{W} = 11020 \times 10^3$$

$$W = \frac{A_o}{11020 \times 10^3}$$

$\therefore$ Solubility $= \frac{A_o \times 10^2}{11020 \times 10^3}$ gm./litre

Solubility of cobalt laurate $= \frac{A_o}{11020 \times 10 \times 457.6}$ Moles/litre

Results:

The solubility values of cobalt laurate together with standard deviations are given in the following Tables 15-18 :

Table -15

Solubility of cobalt laurate in ketones at 30±0.5°C

Solvent	Counting technique	Set No.	Solubility, ($\times 10^{-5}$ M/ℓ)	Mean solubility, ($\times 10^{-5}$ M/ℓ)
Acetone	Differential counting	I	2.438±0.074	2.427±0.085
		II	2.416±0.074	
	Integral counting	I	2.395±0.0243	2.396±0.0253
		II	2.397±0.0243	
Methyl ethyl ketone	Differential counting	I	2.167±0.070	2.1615±0.0755
		II	2.155±0.069	
	Integral counting	I	2.119±0.0226	2.1215±0.0252
		II	2.124±0.0227	

Table -16

Solubility of cobalt laurate in alcohols at 30±0.5°C

Solvent	Counting technique	Set No.	Solubility, ($\times 10^{-5}$ M/ℓ)	Mean solubility, ($\times 10^{-5}$ M/ℓ)
Methanol	Differential counting	I	608.3±6.00	610.475±8.175
		II	612.7±5.95	
	Integral counting	I	603.2±1.96	604.25±3.01
		II	605.3±1.96	
Ethanol	Differential counting	I	3.977±0.097	3.953±0.121
		II	3.929±0.097	
	Integral counting	I	3.972±0.0323	3.9431±0.0612
		II	3.912±0.032	

Table -17

Solubility of cobalt laurate in aromatic hydrocarbons at 30 ± 0.5°C

Solvent	Counting technique	Set No.	Solubility, ($\times 10^{-5}$ M/ℓ)	Mean solubility, ($\times 10^{-5}$ M/ℓ)
Benzene	Differential counting	I	7.967±0.147	8.0005±0.1805
		II	8.033±0.148	
	Integral counting	I	7.947±0.0490	7.985±0.0876
		II	8.023±0.0492	
Toluene	Differential counting	I	3.944±0.097	3.9805±0.1335
		II	4.016±0.098	
	Integral counting	I	3.925±0.032	3.9672±0.0743
		II	4.009±0.0325	
Cyclo-hexane	Differential counting	I	4.440±0.103	4.4625±0.1255
		II	4.484±0.104	
	Integral counting	I	4.407±0.0293	4.4358±0.0582
		II	4.461±0.033	

Table -18

Solubility of cobalt laurate in dimethyl formamide, carbon tetra chloride and water at 30 ± 0.5°C

Solvent	Counting technique	Set No.	Solubility, ($\times 10^{-5}$ M/ℓ)	Mean solubility, ($\times 10^{-5}$ M/ℓ)
Dimethyl formamide	Differential counting	I	2.025±0.067	2.005±0.087
		II	1.985±0.067	
	Integral counting	I	1.993±0.0219	1.9925±0.0224
		II	1.992±0.0219	
Carbon tetra-chloride	Differential counting	I	1.156±0.050	1.1705±0.0645
		II	1.184±0.051	
	Integral counting	I	1.146±0.0162	1.1591±0.0294
		II	1.172±0.0165	
Water	Integral counting	I	2.314±0.0243	2.2954±0.0947
		II	2.224±0.0233	
		III	2.366±0.0241	

Discussion :

It is evident from Tables 15-18 that cobalt laurate is very sparingly soluble both in aqueous and non-aqueous solvents. However, its solubility in methanol is abnormally high. This high solubility can be attributed to some sort of solute-solvent interaction. The equilibrium $CoL_2 \rightleftharpoons Co^{2+} + 2L^-$ exists in the methanol solution of the cobalt laurate; 'L' stands for laurate. The above equilibrium is shifted towards the right due to the removal of cobalt ions by methanol resulting in high solubility of cobalt laurate. Luz(14-16) recently reported the existence of a hexamethanol complex $\left[Co(MeOH)_6\right]^{2+}$, in methanol solution of Co^{2+} ions containing different amounts of chloride ions, at very low temperatures and the existence of the equilibrium $\left[Co(MeOH)_6\right]^{2+} \rightleftharpoons \left[Co(MeOH)_5Cl\right]^{+}$ at higher temperatures. The relatively higher solubility of cobalt laurate in methanol may be explained in terms of the existence of such cobalt complexes as $\left[Co(MeOH)_6\right]^{2+}$ and $\left[Co(MeOH)_5L\right]^{+}$.

Solubility of cobalt laurate in aqueous solutions of potassium laurate and critical micelle concentration of potassium laurate:

The solubility values of cobalt laurate in aqueous solutions of potassium laurate of different concentrations determined by radiotracer technique are given in the Table-19 :

Table -19

Solubility of cobalt laurate in aqueous solutions of potassium laurate:

Potassium laurate concn., (C) (M/l)	- log C	Solubility of cobalt laurate, S, ($x10^{-5}$ M/l)
0.001	3.0000	1.805
0.003	2.5229	1.212
0.005	2.301	1.040
0.01	2.000	0.7276
0.02	1.699	0.4392
0.03	1.5229	0.3823
0.05	1.301	0.3933
0.1	1.000	0.4152
0.2	0.699	0.4785

Fig.3

It is evident from the Table-19 that the solubility of cobalt laurate in aqueous solutions of potassium laurate decreases with increase in potassium soap concentration. Cobalt laurate when dissolved in water will exhibit the following equilibrium:

$$CoL_2 \rightleftharpoons Co^{2+} + 2L^- \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

The activity solubility product, K_s, will be given by the following equation:

$$\begin{aligned} K_s &= (a_{Co^{2+}})(a_{L^-})^2 \\ &= (C_{Co^{2+}} f_+)(C_{L^-} f_-)^2 \\ &= (C_{Co^{2+}})(C_{L^-})^2 f_+ f_-^2 \\ &= (C_{Co^{2+}})(C_{L^-})^2 (f_\pm)^3 \quad \ldots\ldots\ldots\ldots\ldots\ldots (2) \end{aligned}$$

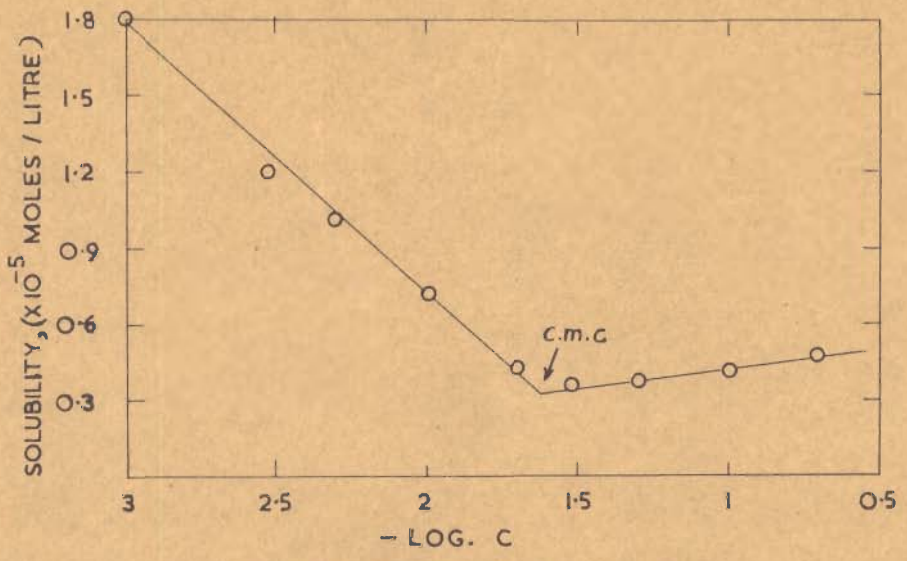

FIG. 3. PLOT BETWEEN THE SOLUBILITY OF COBALT LAURATE AND LOGARITHM OF POT. LAURATE CONCENTRATION.

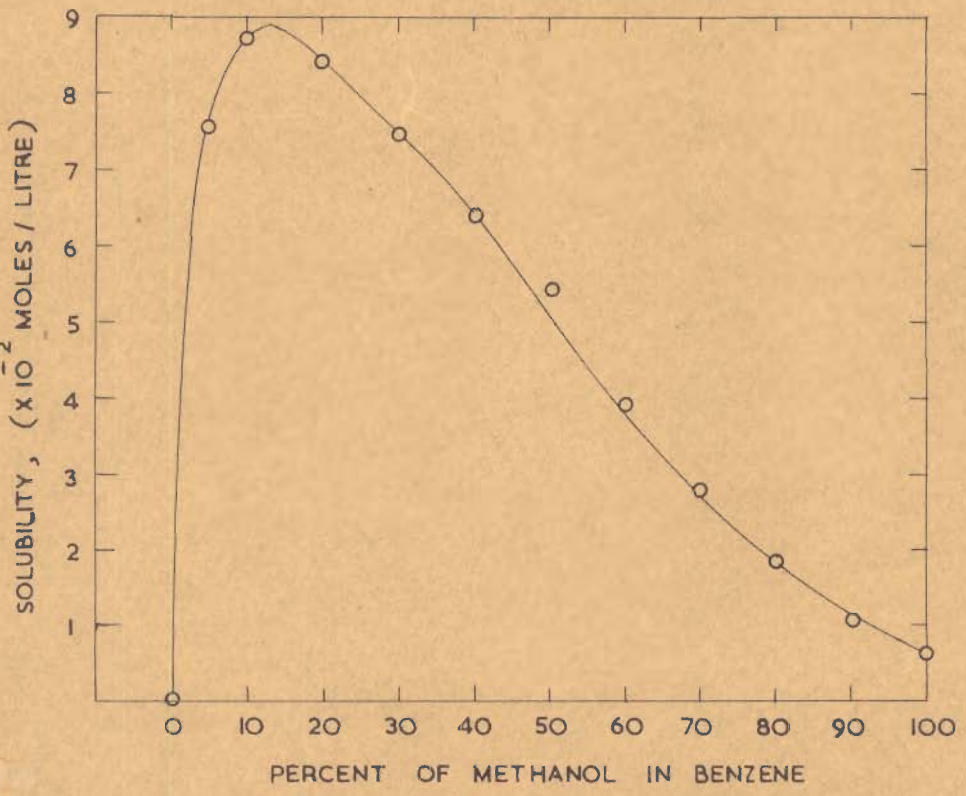

FIG. 4. PLOT BETWEEN COBALT LAURATE SOLUBILITY AND COMPOSITION OF METHANOL–BENZENE MIXTURES.

(a,f,C stand for activity, activity coefficient and concentration, respectively; $f_{\pm}$ stands for mean activity coefficient).

Since the cobalt laurate is highly sparingly soluble, its saturated solution is sufficiently dilute for dissociation to be complete. If S_o is the solubility of cobalt laurate in moles per litre in pure water, then $C_{Co^{2+}}$ and C_{L^-} are equal to S_o and $2S_o$, respectively. Consequently equation(2) takes the following form :

$$K_s = (S_o)\ (2S_o)^2 f_{\pm}^3 = 4S_o^3\ f_{\pm}^3 \quad \ldots\ldots\ldots\ldots\ (3)$$

Since the solutions are sufficiently dilute, the activity coefficient may be taken to be approximately unity. The equation(3) may now be written as

$$K_s = 4S_o^3 \quad \ldots\ldots\ldots\ldots\ (4)$$

The addition of x moles per litre of potassium laurate which contains a common ion (laurate) must decrease the solubility of cobalt laurate in water from S_o to S because according to solubility product principle the value of K_s remains constant. The concentration of Co^{2+} ions, resulting from complete dissociation of cobalt laurate, is S, while that of laurate ions is 2S+x; it follows, therefore, by the solubility product principle that

$$K_s = 4S_o^3 = (S)\ (2S+x)^2$$

$$4S^3 + 4S^2x + Sx^2 - 4S_o^3 = 0 \quad \ldots\ldots\ldots\ldots\ (5)$$

Theoretically the solubility of cobalt laurate in presence of laurate ion concentration should be governed by the equation(5). However, experimentally it is found as evident from Fig.3 (plot between cobalt laurate solubility in aqueous solutions of potassium laurate and the logarithm of potassium laurate concentration) that there exists an almost linear relationship between the solubility and logarithm of potassium laurate concentrations. The deviation from the expected theoretical behaviour may be due to the following factors:

(i) The neglect of the activity coefficient in the application of the simple solubility product principle.

(ii) Since surfactants(17) are well known for their use in preparing dispersions of insoluble solids in liquid media, it is just probable that potassium laurate disperses a sufficient quantity of insoluble cobalt laurate as a colloidal suspension. The dispersion of cobalt laurate will enhance the cobalt laurate solubility and it will no more be strictly governed by the equation(5).

It is evident from Fig.3 and Table-19 that solubility decreases with increase in potassium laurate concentration only up to a certain concentration region beyond which an abrupt change occurs. This abrupt change is caused due to the micellization of laurate ions. Below c.m.c., the potassium laurate behaves as moderately strong electrolyte (18,19). The increase in the concentra-

tion of potassium laurate results in the increase of laurate ion concentration and consequently, cobalt laurate solubility decreases due to the common ion (laurate) effect. However, since above c.m.c. the concentration of laurate ions remains constant due to micellization, the solubility should also remain constant. But it is interesting to note (Fig.3) that the solubility value above c.m.c. is not exactly constant but increases gradually with increase in potassium laurate concentration. This may be accounted for as follows: The micelle of potassium laurate contains, in addition to aggregated laurate ions, a considerable number of potassium and cobalt ions held on its surface. Since cobalt ions, due to their higher valence, are adhered more strongly on the micelle surface, the concentration of free cobalt ions in solution will be reduced. Consequently, the equilibrium (1) is shifted towards right, resulting in enhanced solubility of cobalt laurate.

Obviously the break in the plot (Fig.3) would correspond to the c.m.c. of potassium laurate. The c.m.c. value obtained by this method is found to be 2.34×10^{-2}M which compares favourably with those reported in the literature (20-22) as evident from Table -3 in Chapter-1.

Solubility of cobalt laurate in methanol-benzene mixtures:

The solubility values of cobalt laurate in methanol-benzene mixtures of different compositions

as determined by evaporation method are given in Table -20 :

Table -20

Solubility of cobalt laurate in methanol-benzene mixtures at 30 ± 0.5°C

Composition of mixture, % of methanol by volume	Solubility, gm./litre	Solubility, ($x10^{-2}$ Moles/litre)
0	-	0.007985 (From Table-17)
5	34.52	7.54
10	39.86	8.71
20	38.5	8.41
30	34.2	7.47
40	29.5	6.44
50	24.9	5.44
60	17.84	3.89
70	12.81	2.79
80	8.44	1.84
90	4.82	1.05
100	-	0.604 (From Table 16)

Fig.4

It is evident from the Table-20 that small amounts of methanol in benzene enhance the solubility of cobalt laurate by a factor as high as 1000. From Fig.4, it is observed that the methanol-benzene mixture with 13% of methanol dissolves cobalt laurate in highest amount.

Ordinarily the solubility of heavy metal soaps is dependent on the temperature and the solvent employed, but the role played by the metallic portion of

the soap is not clear.

The above data on the solubility of cobalt laurate in benzene in presence of small amounts of methanol lend support to the view point that metallic cobalt portion of the molecule plays a definite role in determining the solubility of cobalt laurate in organic solvents. It appears that cobalt laurate inspite of its big hydrophobic residue resists dissolution due to metallic cobalt. No sooner the metallic cobalt portion comes in contact with a solvent (methanol) with which it has great affinity (formation of solvation complexes(14-16)), the solubility of the cobalt soap molecule as a whole is tremendously enhanced.

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CHAPTER - 6

" Solubility of cadmium laurate "

INTRODUCTION

Cadmium soaps are very sparingly soluble in water and inert non-aqueous solvents. Due to difficulties involved in estimating trace amounts of the metal in the soaps, their solubilities in different solvents have not been investigated. As already emphasized in the preceding Chapter, radiotracer technique can prove to be quite useful in such cases. This method was, therefore, utilised for determining the solubility of cadmium laurate in water and non-aqueous solvents.

Since micelle forming substances show an abrupt change in their solubility vs temperature curve, another interesting aspect of these studies can, therefore, be to investigate this behaviour for cadmium laurate in organic solvents. Therefore, the solubility of cadmium laurate in benzene, toluene and m-xylene was also considered worth studying.

In the preceding Chapter, it was described that heavy metals' soap solubility data in aqueous solutions of corresponding potassium soaps can be put to use for the c.m.c. determination of the latter soaps. This technique was extended as to include surfactants other than alkali metal soaps. For this purpose the solubility of cadmium laurate in aqueous solutions of Manoxol OT was determined employing Cd^{115m} as a tracer. The data were computed to know the c.m.c.. value of Manoxol OT.

Finally the effect of methanol in influencing the solubility of cadmium laurate in methanol-benzene mixtures was studied. The solubility was found to be reasonably high to permit evaporation method for its determination.

EXPERIMENTAL

Materials :

Manoxol OT was B.D.H. product and was used without further purification. Solvents employed were purified by standard methods. Doubly-distilled water was used throughout.

Solubility determination by radiotracer technique:-

Preparation of the labelled cadmium laurate:

Cd-115m in the form of $Cd(NO_3)_2$ in dilute HNO_3 solution was obtained from the Isotope Division, Atomic Energy Establishment, Bombay. Aqueous solutions of cadmium sulphate and Cd^{115m} enriched cadmium nitrate were boiled together for 1 hr. to bring about complete isotopic exchange. The pH of this solution was adjusted to approximately 6 with the help of pH paper. To this solution, stoichiometric amount of warm sodium laurate solution was added gradually with constant stirring. The precipitated cadmium laurate was filtered, washed with doubly-distilled water and then with alcohol to remove free precipitant and acid. The soap was dried under suction and finally in vacuum desiccator. The activity labelled was about 1 ± 0.1 mc/gm. of cadmium laurate.

Specific activity of cadmium:

The specific activity of cadmium solution was determined by precipitating cadmium (from a portion of cadmium salt solution used for preparing cadmium laurate) as

cadmium oxalate, dissolving a definite mass of the oxalate in a known volume of dil.hydrochloric acid and counting aliquots.

Preparation of standard solution of active cadmium laurate:

Standard solution of cadmium laurate was prepared by dissolving a definite mass of the soap in a known volume of pyridine.

Saturated solutions of cadmium laurate in various solvents:

Excess of solid cadmium soap and the solvents were equilibrated at different temperatures by thorough stirring. The thermostat bath was controlled to within $\pm$ 0.5°C.

Analysis of saturated solutions :

(A) Apparatus and technique:

A G.M.counter (Atomic Energy Establishment, Bombay) was employed for beta counting measurements. In order to determine the operating characteristics of the G.M.tube, its plateau was drawn (Fig.1, Table -1).

The slope of the plateau is given by the following expression:

$$\text{Slope} = \frac{\frac{C_2 - C_1}{C_2 + C_1}}{2} \times \frac{100}{V_2 - V_1}$$

where C_2 and C_1 are counting rates at voltages V_2 and V_1.

From Table -1 and Fig.1,

V_2 = 1500 volts, C_2 = 7345 counts/min.

V_1 = 1350 volts, C_1 = 6659 counts/min.

$$\therefore \text{Slope} = \frac{7345-6659}{\frac{7345+6659}{2}} \times \frac{100}{1500-1350} = 0.065$$

Therefore, the slope of the G.M. tube employed for activity measurements is 0.065/100 V. The length of plateau is 150 volts. The operating potential of G.M.counter starts at 1350 volts and ends at 1500 volts. For all activity measurements, G.M.counter was operated at 1400 volts.

A standard beta source, Ra D-E, was employed to check the response of G.M.counter for day to day work.

(B) Procedure :

Suspension free saturated solutions of cadmium laurate in various solvents were taken through Whatman No.42 filter paper. 0.5 ml of saturated solutions were withdrawn, transferred to steel planchets and evaporated to dryness under infra red heat lamp. These planchets carrying labelled cadmium laurate were placed under G.M.tube and beta activity was measured for a period of 10 minutes. For each activity, three counting measurements were done.

Specific activity of cadmium laurate was determined in terms of count rate by measuring the activity of 0.5 ml of standard solution of cadmium laurate in pyridime after drying it on a planchet. Similarly specific activity per gram of cadmium was determined in terms of count rate by measuring the activity of 0.5 ml of cadmium oxalate solution in dil.hydrochloric acid after drying it on a planchet.

All precautions were taken to ensure that activity measurements of saturated solutions of cadmium laurate and its standard solution were made under same geometrical conditions.

Coincidence loss corrections:

Details about coincidence loss corrections have already been given in Chapter 5.

The resolving time of G.M. counter used was 250 μ sec..

Resolving time = 250 μ sec. = $\frac{250 \times 10^{-6}}{60}$ minutes

Therefore, the coincidence loss for any observed counts, X', per ten minutes is $\frac{(X'^2) \times 250 \times 10^{-6}}{10 \times 60}$.

Decay correction:

Details about decay correction have already been given in Chapter 5.

Half-life of Cd^{115m} = 43 days = 43x24 = 1032 hrs.

Therefore, $\lambda = \frac{0.6931}{\text{Half-life}} = \frac{0.6931}{1032} = 6.71 \times 10^{-4}$ $(\text{hrs})^{-1}$

Therefore, $A = Ao\ e^{-\lambda t} = Ao\ e^{-6.71 \times 10^{-4} \times t}$

where 't' is the decay time in hrs., and A and Ao have the same significance as given in Chapter 5.

(Note- While calculating decay time, only integral values of hours were taken).

Statistical error :

Details about standard deviation calculations have been described in Chapter 5.

Determination of solubility of cadmium laurate in methanol-benzene mixtures by evaporation method:

Inactive cadmium laurate was prepared in the same way as active cadmium laurate. Each saturated solution of cadmium laurate in methanol-benzene mixtures was prepared by thorough stirring of excess of cadmium laurate with methanol-benzene mixtures. 10 ml of clear supernatant solutions were withdrawn and evaporated to dryness in weighed glass beakers. The amount of residue left was determined by weighing. Knowing the amounts of cadmium laurate present in 10 ml of solution, its solubility could be calculated.

Table -1

Plateau of G.M.counter

Standard beta source used = Ra D-E

Voltage applied (volts)	Observed counts/min.	Average counts/min.
1300	470 535 337	447
1325	6429 6326 6358	6371
1350	6670 6602 6705	6659
1375	6823 6754 6749	6775
1400	6888 6826 6907	6873
1450	7236 7245 7121	7200
1500	7317 7416 7304	7345
1550	7782 7809 7912	7834

Fig - 1

Table -2

Activity measurements of cadmium laurate standard solution in pyridine.

Amount of cadmium laurate dissolved = 0.0135 gm./50 ml of pyridine

Volume of solution taken for counting = 0.5 ml

(CPTM = counts per ten minutes)

Observed CPTM	Average CPTM	Coincidence loss	Background CPTM	True CPTM Ao
22516 22240 22103	22286	207	205	22288

Table -3

Activity measurements of cadmium oxalate standard solution in dil. HCl

Amount of cadmium oxalate dissolved = 0.01 gm./100 ml of dil.HCl

Volume of solution taken for counting = 0.5 ml

Decay time = t = 2 hrs.

Background = 205 CPTM

Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
21682 21605 21642	21643	195	21633	21664

Table -4

Activity measurements of saturated solution of cadmium laurate in various non-aqueous solvents.

Background = 211 CPTM Tempr. = 30°C

Volume of solution taken for counting = 0.5 ml

Solvent	Decay time t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
Acetone	24	2104 2073 1996	2057	negligible	1846	1875
Methyl ethyl Ketone	25	5444 5551 5492	5495	negligible	5284	5373
Carbon-tetra chloride	27	3420 3292 3365	3359	negligible	3148	3203
Dimethyl formamide	28	11025 11001 11172	11066	50	10905	11110

Table -5

Activity measurements of saturated solution of cadmium laurate in benzene.

Volume taken for counting = 0,5 ml

Background = 205 CPTM

Tempr., °C	Decay time, t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
30	45	1402 1348 1367	1372	negligible	1167	1203
35	47	1539 1570 1552	1553	negligible	1348	1391
40	49	1725 1780 1736	1747	negligible	1542	1593
45	51	2137 2183 2098	2139	negligible	1934	2001
50	53	3628 3615 3683	3642	negligible	3437	3593
55	55	6520 6571 6530	6540	negligible	6335	6569
60	57	16432 16495 16302	16409	111	16315	16914

Table -6

Activity measurements of saturated solution of cadmium laurate in toluene

Volume of solution taken for counting = 0.5 ml

Background = 215 CPTM

Tempr., ^{o}C	Decay time, t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
30	70	1608 1583 1572	1587	negligible	1372	1437
35	72	1810 1830 1784	1808	negligible	1593	1671
40	74	2714 2752 2701	2722	negligible	2507	2634
45	76	3292 3320 3338	3316	negligible	3101	3263
50	78	3802 3760 3754	3772	negligible	3557	3748
55	80	26252 26368 26201	26273	287	26345	27830
60	82	60420 60145 60394	60319	1516	61620	65102

Table -7

Activity measurements of saturated solution of cadmium laurate in m-xylene

Background = 210 CPTM

Volume of solution taken for counting = 0.5 ml

Tempr., ^{o}C	Decay time, t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
30	95	1748 1756 1692	1732	negligible	1522	1622
35	97	2010 1905 1984	1966	negligible	1756	1874
40	100	2505 2532 2412	2483	negligible	2273	2431
45	102	3312 3325 3302	3313	negligible	3103	3322
50	104	4012 4073 3969	4018	negligible	3808	4168
55	106	20452 20693 20366	20503	175	20468	21973
60	109	46810 46795 46252	46619	903	47312	50902

Table -8

Activity measurements of saturated solution of cadmium laurate in methyl, ethyl, n-propyl and n-butyl alcohol.

Background = 222 CPTM, Tempr. = 30°C

Volume of solution taken for counting = 0.5 ml

Solvent	Decay time t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
Methyl alcohol	121	92124 93105 94342	93190	3616	96584	104710
Ethyl alcohol	123	65342 65905 64872	65373	1782	66933	72688
n-propyl alcohol	126	181346 182005 181652	181667	13743	195188	212343
n-butyl alcohol	130	195653 195998 196504	196051	16010	211839	231124

Table -9

Activity measurements of saturated solution of cadmium laurate in isopropyl alcohol, isobutyl alcohol and water

Background = 228 CPTM, Tempr. = 30°C

Volume of solution taken for counting = 0.5 ml

Solvent	Decay time, t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
Isopropyl alcohol	165	48544 48725 48604	48624	984	49380	55138
Isobutyl alcohol	168	52405 52102 52495	52334	1140	53246	59591
Water	172	2102 2195 2086	2127	negligible	1899	2121

Table -10

Activity measurements of saturated solution of cadmium laurate in aqueous solutions of dioctyl sodium sulfosuccinate (Manoxol OT)

Background = 220 CPTM , Tempr. = 30°C

Volume taken for counting = 0.5 ml

Concn.of Manoxol OT, ($x10^{-4}$M)	Decay time, t (hrs.)	Observed CPTM	Average CPTM	Coincidence loss	True CPTM A	Ao CPTM
1	210	2008 2065 2032	2035	negligible	1815	2088
2	213	2212 2160 2155	2175	negligible	1955	2255
3	216	2226 2202 2250	2226	negligible	2006	2318
5	220	2308 2356 2340	2334	negligible	2114	2438
7	232	4042 4092 3963	4032	negligible	3812	4452
10	234	6002 6055 6123	6060	negligible	5840	6829
20	236	17120 17195 17264	17193	123	17096	20024
30	239	24112 24242 24163	24172	243	24195	28393
50	242	39413 39607 39620	39546	650	39976	47027

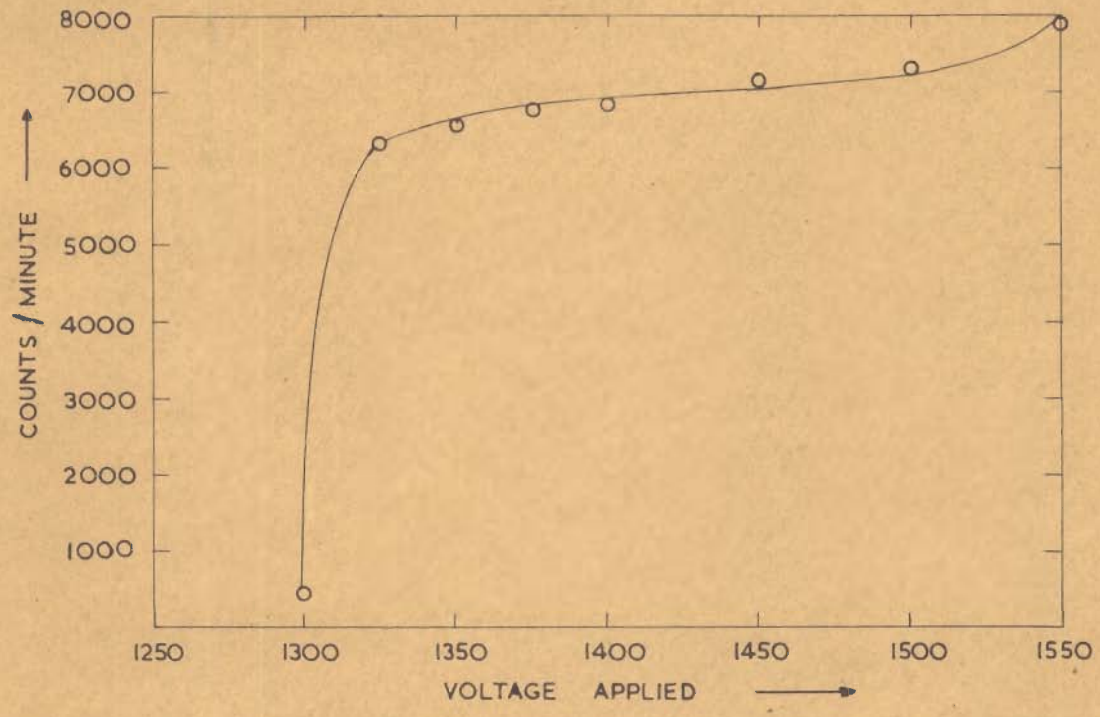

FIG. 1 PLATEAU OF G.M. COUNTER

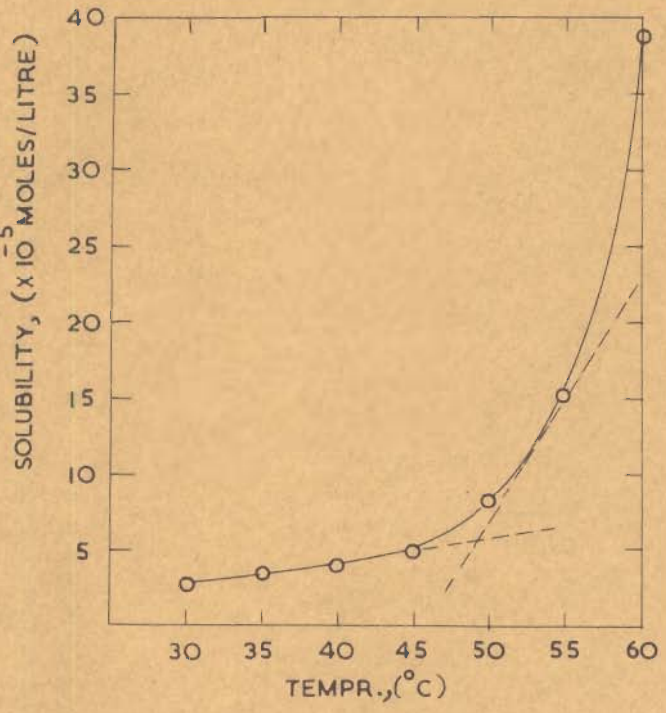

FIG. 2 . SOLUBILITY OF CADMIUM LAURATE IN BENZENE

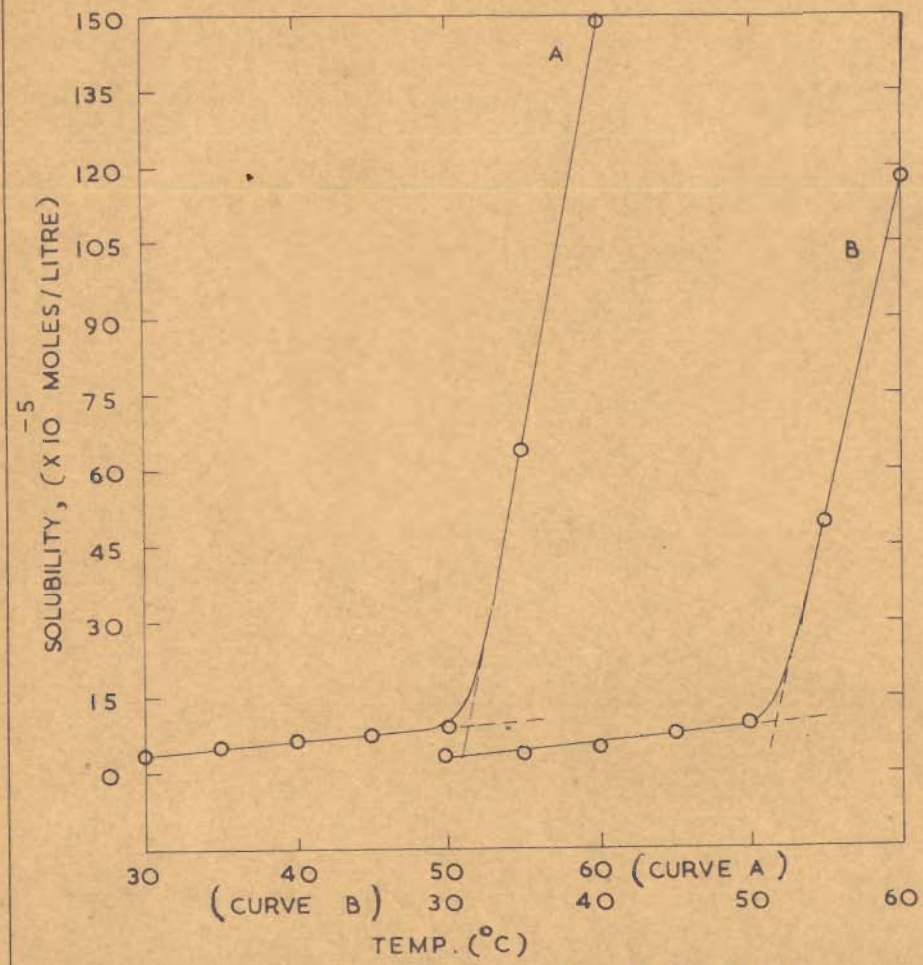

FIG. 3 · SOLUBILITY OF CADMIUM LAURATE IN TOLUENE (A) AND m-XYLENE (B)

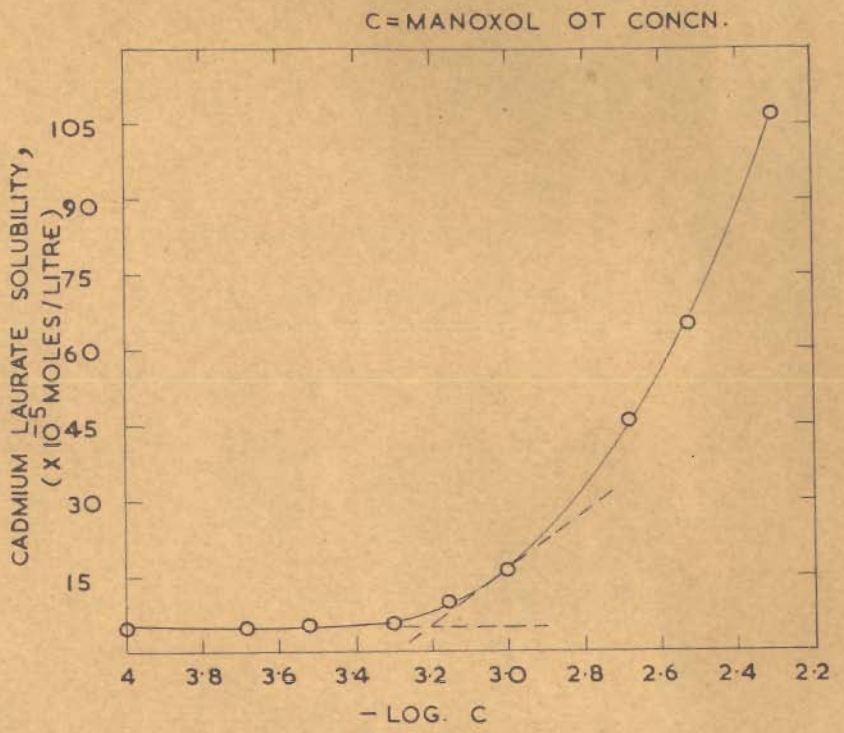

FIG. 4

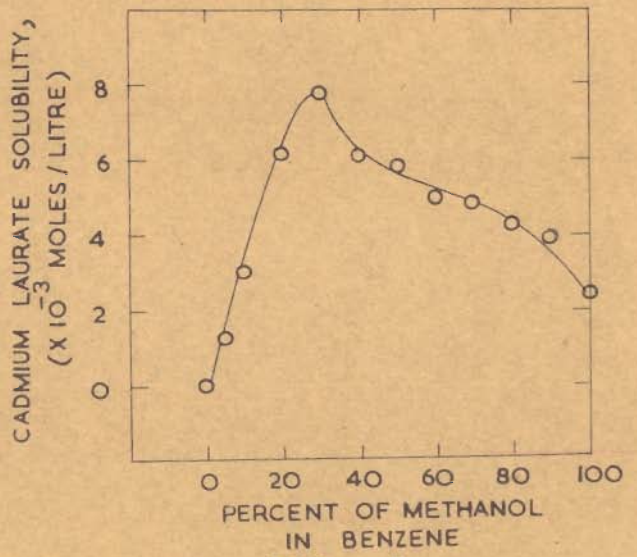

FIG. 5

CALCULATIONS, RESULTS AND DISCUSSION

Calculations :-

Specific activity of cadmium :

Since the composition of cadmium laurate was yet to be established, the specific activity per gram of cadmium could not be determined from the activity measurements of standard solution of cadmium laurate.

From a portion of cadmium solution which was used for the preparation of labelled cadmium laurate, cadmium was precipitated as cadmium oxalate. A definite mass of cadmium oxalate was dissolved in known volume of dil. hydrochloric acid.

Amount of cadmium oxalate dissolved = 0.01 gm./100 ml dil.HCl

Volume of this solution taken for counting = 0.5 ml

Amount of cadmium oxalate present in 0.5 ml solution $= \frac{0.01 \times 0.5}{100}$

$= 5 \times 10^{-5}$ gm.

Molecular weight of cadmium oxalate = 200.43

Therefore, amount of cadmium present in 0.5 ml solution $= \frac{5 \times 10^{-5} \times 112.4}{200.43}$

$= 2.805 \times 10^{-5}$ gm.

From Table -3, activity of 0.5 ml solution, i.e., of 2.805×10^{-5} gm.of cadmium = 21664 CPTM

Therefore, specific activity of cadmium $= \frac{21664}{2.805 \times 10^{-5}}$ CPTM/gm. of Cd

$\therefore$ Specific activity = 7.721×10^{8} CPTM/gm.of Cd .....(I)

Composition of cadmium laurate :

Amount of cadmium laurate dissolved = 0.0135 gm./50 ml of pyridine

Volume of cadmium laurate soln. taken for counting=0.5 ml

Amount of cadmium laurate present in 0.5 ml solution $= \frac{0.0135 \times 0.5}{50}$

$= 1.35 \times 10^{-4}$ gm.

Let the amount of cadmium present in 1.35×10^{-4} gm.of cadmium laurate be W gm.

From Table-2, the activity of 1.35×10^{-4} gm.of cadmium laurate,i.e., of W gm. of Cd = 22288 CPTM

Therefore, the specific activity of cadmium

$= \frac{22288}{W}$ CPTM/gm. of Cd ..... (II)

Since the same cadmium salt solution containing Cd^{115m} was employed for preparing cadmium oxalate and cadmium laurate, the specific activity of cadmium present both in cadmium laurate and cadmium oxalate should be same. Therefore, equating (I) and (II),

$$7.721 \times 10^{8} = \frac{22288}{W}$$

$$W = \frac{22288}{7.721 \times 10^{8}} \text{ gm.}$$

$$W = 2.886 \times 10^{-5} \text{ gm.}$$

Therefore, 1.35×10^{-4} gm.of cadmium laurate contains 2.886×10^{-5} gm. of cadmium.

$\therefore$ Amount of cadmium in cadmium laurate = $\frac{2.886 \times 10^{-5} \times 100}{1.35 \times 10^{-4}}$

= 21.38 % .....(III)

Nelson and Pink(1) reported on chemical analysis, the formation of monohydrate of cadmium laurate.

If the composition $Cd(C_{11}H_{23}COO)_2.H_2O$ is given to cadmium laurate, the calculated amount of cadmium in cadmium laurate comes out to be 21.24%. The amount of cadmium in labelled cadmium laurate is found to be 21.38%. The calculated and experimental values are very close to each other. Hence cadmium laurate has the composition $Cd(C_{11}H_{23}COO)_2.H_2O$.

Specific activity of cadmium laurate :

Amount of cadmium laurate present in 0.5 ml of pyridine solution = $\frac{0.0135 \times 0.5}{50}$

= 1.35×10^{-4} gm.

From Table-2, activity of 0.5 ml solution of cadmium laurate in pyridine = 22288 CPTM.

Therefore, the specific activity of cadmium laurate = $\frac{\text{Activity}}{\text{Amount of cadmium laurate}}$

Specific activity = $\frac{22288}{1.35 \times 10^{-4}}$ CPTM/gm.of cadmium laurate.....(IV)

Solubility determination in any solvent :

Volume of saturated solution of cadmium laurate in any solvent taken for counting = 0.5 ml

Let the amount of cadmium laurate present in 0.5 ml of its saturated solution be W gm.

Let the activity of W gm. of cadmium laurate be Ao CPTM.

Then, the specific activity = $\frac{Ao}{W}$ CPTM/gm.of cadmium laurate .....(V)

As described in Chapter 5, the specific activity of cadmium laurate should be same in all solvents.

Therefore, from expressions(IV) and (V)

$$\frac{Ao}{W} = \frac{22288}{1.35\times10^{-4}}$$

$$W = \frac{135 \times Ao}{22288\times10^{6}} \text{ gm.}$$

Therefore, the solubility of cadmium laurate = $\frac{135\times Ao\times10^{3}}{22288\times10^{6}\times0.5}$ gm./litre.

Molecular wt. of cadmium laurate = 529

Solubility = $\frac{Ao \times 135}{22288\times10^{2}\times5\times529}$ moles/litre..... (VI)

Knowing the value of Ao in any solvent, cadmium laurate solubility can be calculated.

Results :

The solubility values of cadmium laurate together with standard deviations are given in the Table -11.

Table -11

Solubility of cadmium laurate in water and non-aqueous solvents at 30°C

Solvent	Solubility, ($\times 10^{-5}$ Moles/litre)
Acetone	4.29 ± 0.11
Methyl ethyl ketone	12.30 ± 0.19
Carbon tetrachloride	7.33 ± 0.14
Dimethyl formamide	25.44 ± 0.29
Benzene	2.75 ± 0.09
Toluene	3.29 ± 0.10
m-xylene	3.71 ± 0.10
Methyl alcohol	239.7 ± 1.76
Ethyl alcohol	166.4 ± 1.27
n-propyl alcohol	486.1 ± 3.42
n-butyl alcohol	529.1 ± 3.67
Isopropyl alcohol	126.3 ± 1.00
Isobutyl alcohol	136.5 ± 1.07
Water	4.85 ± 0.12

It is evident from the Table-11 that the cadmium laurate is very sparingly soluble both in water and inert non-aqueous solvents. However, its solubility in alcohols is relatively much higher. This high solubility suggests the possibility of some sort of solute-solvent interaction. The following equilibrium exists in alcohols.

$$CdL_2 \rightleftharpoons Cd^{2+} + 2L^-$$

(where 'L' stands for laurate)

Cadmium ion probably forms solvation complexes with alcohols resulting in the shifting of the above equilibria towards right and thereby increasing the solubility. The solubility order in alcohols is n-butyl alcohol > n-propyl alcohol > methyl alcohol > ethyl alcohol > iso-butyl alcohol > iso-propyl alcohol. As expected the solubility of cadmium soap is greater in methanol than ethanol.

Another factor which may control the solubility appears to be the carbon chain length in various alcohols. With increase in chain length the possibility of interaction between hydrophobic ends of the solute and the solvent would increase resulting in greater solubility. The solubility order given above supports this view point. However, when solvation is predominately high as in the case of methanol (being smallest molecule), the effect of chain length will be relatively negligible. Moreover, in contrast to the solubility in n-butyl and n-propyl alcohol, the solubility in iso-butyl and iso-propyl alcohol is much less. This is due to stearic effects which hinder the solvation of the metal with alcohols and the interaction between hydrophobic groups of solute and solvent.

Effect of temperature on the solubility of cadmium laurate in benzene, toluene and m-xylene:

The solubility of cadmium laurate at

different temperatures in benzene, toluene and m-xylene are given in Tables 12-14.

Table -12

Effect of temperature on cadmium laurate solubility in benzene:

Tempr., (°C)	Solubility, ($x10^{-5}$ Moles/litre)
30	2.75 ± 0.09
35	3.18 ± 0.10
40	3.64 ± 0.10
45	4.58 ± 0.11
50	8.22 ± 0.15
55	15.04 ± 0.21
60	38.73 ± 0.39

Fig. - 2

Table -13

Effect of temperature on cadmium laurate solubility in toluene

Tempr., (°C)	Solubility, ($x10^{-5}$ Moles/litre)
30	3.29 ± 0.10
35	3.81 ± 0.10
40	6.03 ± 0.13
45	7.47 ± 0.14
50	8.58 ± 0.15
55	63.72 ± 0.51
60	149.0 ± 1.15

Fig. -3(A)

Table -14

Effect of temperature on cadmium laurate solubility in m-xylene

Tempr., (^{o}C)	Solubility, ($x10^{-5}$ Moles/litre)
30	3.71 ± 0.10
35	4.29 ± 0.11
40	5.56 ± 0.12
45	7.60 ± 0.14
50	9.54 ± 0.16
55	50.30 ± 0.45
60	116.50 ± 0.94

Fig.3(B)

It is seen from Tables 12-14, Figs.2,3 that at low temperature ranges, the solubility of cadmium laurate in benzene, toluene and m-xylene is quite small but increases slowly and regularly as the temperature increases. Then within a rather narrow critical temperature range, the solubility begins to increase enormously. The temperature at which the abrupt change occurs is known as the Krafft point(2) or critical solution temperature, and the concentration at which it occurs is the c.m.c. at that temperature. This type of solubility behaviour is the characteristic of micelle forming substances. The explanation of this very remarkable increase in solubility is obviously that single surfactant molecule is relatively insoluble whereas the micelle is highly soluble.

This critical solution temperature for aqueous surfactants has been observed by Murray and Hartley(3), and Adam and Pankhurst(4). Recently, Malik and Ahmad(5) have extended this solubility method for the determination of c.m.c.of chromium soaps in benzene. The values of c.m.c. and critical solution temperature calculated from Figs.2,3 are given in Table -15:

Table -15

Critical solution temperature and c.m.c.for cadmium laurate

Solvent	c.m.c., ($x10^{-5}$ Moles/litre)	Critical solution temperature, (^oC)
Benzene	5.5	49.0
Toluene	9.0	51.0
m-xylene	9.9	51.5

Solubility of cadmium laurate in aqueous solutions of Manoxol OT and c.m.c. of Manoxol OT:

Table -16

Solubility of cadmium laurate in aqueous solutions of Manoxol OT at 30^oC

Manoxol OT concn., (C) ($x10^{-4}$M)	- log C	Solubility, ($x10^{-5}$ Moles/litre)
1	4.0000	4.78 ± 0.11
2	3.6990	5.16 ± 0.12
3	3.5229	5.30 ± 0.12
5	3.3010	5.58 ± 0.12
7	3.1549	10.20 ± 0.17
10	3.0000	15.64 ± 0.22
20	2.6990	45.83 ± 0.44
30	2.5229	65.01 ± 0.52
50	2.3010	107.60 ± 0.87

Fig.4

It is evident from Table-16 and Fig.4 (plot between cadmium laurate solubility in aqueous solutions of Manoxol OT and logarithm of Manoxol OT concentration) that in low concentrations, below c.m.c., the solubility of cadmium laurate remains almost constant. However, beyond the c.m.c. of Manoxol OT, the solubility increases abruptly. This increase in solubility may be due to two factors. Firstly, cadmium laurate dissolved in water will exhibit the following equilibrium :

$$CdL_2 \rightleftharpoons Cd^{++} + 2L^-$$

The micelle of Manoxol OT contains, in addition to ~~aggregate~~ a number of of detergent ions, a considerable number of sodium and cadmium ions held on its surface. Since cadmium ions, due to their higher valence, are adhered preferentially and more strongly on the micelle surface, the concentration of free cadmium ions in the solution will be reduced, resulting in the shifting of above equilibria towards the right and, therefore, resulting in greater solubility of cadmium laurate above c.m.c.value of Manoxol OT.

The second factor responsible for enhanced solubility above c.m.c. of Manoxol OT appears to be the solubilization of insoluble cadmium laurate, especially through mixed micelle formation mechanism.

The c.m.c. value of Manoxol OT obtained by this method comes out to be 6.31×10^{-4}M (From Fig.4) which compares favourably with the literature value, 6.8×10^{-4}M, determined by surface tension method(6).

Solubility of cadmium laurate in methanol-benzene mixtures:

The solubility values of cadmium laurate in methanol-benzene mixtures of different compositions as determined by evaporation method are given in Table-17 :

Table -17

Solubility of cadmium laurate in methanol-benzene mixtures at $30^{o}C$

Composition of mixture, % of methanol by volume	Solubility, gm./litre	Solubility, ($x10^{-3}$ Moles/litre)
0	-	0.0275 (From Table-11)
5	0.7	1.32
10	1.6	3.02
20	3.3	6.28
30	4.1	7.74
40	3.2	6.04
50	3.1	5.86
60	2.7	5.05
70	2.6	4.91
80	2.3	4.34
90	2.1	3.96
100	-	2.397 (From Table-11)

Fig. -5

It is evident from Table-17 that small amounts of methanol in benzene enhance the solubility of cadmium laurate tremendously. From Fig.5 (plot between cadmium laurate solubility and composition of methanol-benzene mixtures) it is observed that cadmium laurate

solubility is highest in methanol-benzene mixture containing 30% of methanol by volume. In this mixture the solubility is increased by a factor as high as 280.

The cadmium laurate inspite of its big hydrophobic residue resists dissolution in non-aqueous media due to metallic cadmium portion. No sooner the metallic cadmium portion comes in contact with a solvent (methanol) with which it has great affinity (formation of solvated molecules), the solubility of cadmium laurate molecule as a whole is tremendously increased.

A comparison of solubility data of cadmium laurate and cobalt laurate (Table-20, Chapter-5) in methanol-benzene mixture reveals that methanol is more effective in enhancing the solubility of cobalt laurate in comparison to cadmium laurate. This behaviour is not unexpected since cobalt is well known for forming definite complexes with methanol as against cadmium which undergoes either simple solvation or very weak coordination with methanol.

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