GENERAL INTRODUCTION
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Surface active agent is the name given to the class of compounds which reduces the surface tension of water and the interfacial tension of the aqueous solution against a mineral oil. A large number of compounds belong to this category. They are naturally occurring substances, like proteins, saponins, clay bentonite, glue, egg white, gums, and other organic colouring matters and synthesised ones, like, soaps, alkyl sulphates, sulphonates, quarternary ammonium compounds, ethylene glycol poly ethers, poly glycerols, etc. Almost all of them have been put to a number of uses in industry and technology. The well known cases are the use of soaps as water proofing, wetting and emulsifying agents and so also their uses in dyeing, bactericides, ore dressing, solubilization, etc. Recently Kamada and Mutsumoto have described the use of these compounds in the preparation of pharmaceutical products, while Hirose and Mitani have used them in the refining of Au, Ag, Hg, Te, Se, etc. Besides the importance of surface active agent is being gradually realised in allied sciences, like, soil chemistry, medicine, biochemistry and biology.

Synthetic surface active agents are normally divided into two classes, namely ionic and non-ionic. Of the two, the
former have undergone further subdivision into anionic and cationic surface active agents, depending upon the charge which the large hydrophobic part attains when brought into solution. It is this long elongated hydrophobic part which is mostly responsible for donating surface active properties and all investigators in the field of colloid science agree to the presence of aggregated ions in their aqueous solutions.

A large number of brilliant physical chemists like Mc Bain, Lottermoser, Hartley, Wright and Ralston, had remained associated with fundamental work on solution of soaps and related compounds. Amongst them the most notable contribution is that of McBain, who for the first time, with the help of physical methods, showed the existence of micelles in solutions and also introduced the term critical micelle concentration on the basis of his research on the conductivity of alkali metal soaps. Mc Bain's concept of the existence of various kind of micelles, in solutions was, however, criticised by Hartley who considered the existence of only one kind of micelle. His work found support in the investigations of Harkins, with the only difference that Harkins' micelle was cylindrical in shape, while those of Hartley was spherical ones. The existence of micelles in the solutions of dyes like methylene blue, congo-red, benzopurpurin, etc. has been shown by many workers.

A number of physical methods, namely, conductivity, surface tension, viscosity, refractometry, turbidimetry
spectrophotometry\textsuperscript{27}, freezing point\textsuperscript{28}, Osmotic pressure\textsuperscript{29}, vapour pressure\textsuperscript{30}, solubility\textsuperscript{31}, partial molal volume\textsuperscript{32}, dipole moment\textsuperscript{33,34} etc. have been employed by different workers to study their physico-chemical behaviour. Recently Few and Ottewill\textsuperscript{35} used spectrophotometric method for the determination of cationic detergents, while Tamamushi and Shiara\textsuperscript{36} measured the electrophoretic mobility of micelles of long chain amine hydrochlorides. Baccareda, Baldacci and Danusso\textsuperscript{37} saw their effect on ultrasonic velocity. More recently colichman\textsuperscript{38} introduced the polarographic technique, while Boyd\textsuperscript{39} used tracer technique for the study of micelles in such compounds.

There are certain phenomena\textsuperscript{40} which provide indirect evidence of micelle formation in solutions of surface active compounds. Physico-chemical methods like, spectrophotometry\textsuperscript{41} X-ray diffraction\textsuperscript{42}, turbidimetry\textsuperscript{43}, surface tension\textsuperscript{44} have been used by many workers to study the phenomenon of solubilization. Different theories\textsuperscript{45-47} have been proposed from time to time to explain the mechanism of solubilization. Mc Bain\textsuperscript{48} introduced the term cosolvency to a process in which a substance becomes soluble in a mixture of two liquids when the same substance is not soluble in each of them separately.

The affinity of surface active agents towards big molecules like proteins\textsuperscript{49}, polymers\textsuperscript{50}, or small molecules like dyes\textsuperscript{51} and simple metal ions\textsuperscript{52} is also worth considering.
Recently Misch, Berstein and McDonald had studied the influence of surface active agents on the permeability of a Pd cathode. The interaction of copper with dodecyl sulphate have been studied by Schulman. Recently Ottewill had studied the effect of surface active substances on the stability of hydrophobic sols, while Bogoyavlenskii studied their effect on thixotrophic setting of ferric hydroxide hydrosols. A number of interesting problems like the nature of the micelle existing, formation of complexes, metachromacy seem to emerge out from studies on the interaction of dyes with surface active agents.

The thermodynamic functions of some of these compounds have also been a matter of concern to some workers. Stauff and Rasper determined the free energy of adsorption of dodecyl polyglycerols, while the activity coefficient of many surface active substances were determined by Scholberg. Hutchinson had studied the E.M.F. of the cell.

\[ \text{H}_2/\text{HCl(m}_1\text{), C}_{12}\text{H}_{25}\text{NH}_3\text{Cl (m}_2\text{)/AgCl/Ag} \]

at different temperatures, to see micelle formation and to calculate temperature dependence of the cell.

The effect of surface active agents on various electrochemical processes is another worth mentioning problem. Malulu's and Bodnevas described a rule for change in the cathode polarization in deposition of metal in presence of surface active substances while Kheifets and Kaasikov have
seen the effect of surface active substances on the overvoltage for the liberation of hydrogen on platinum. Levin and coworkers studied the effect of these compounds on the electrode potentials of Cu and Zn electrodes, they further found that a shift in the electrode potential occurs in such systems. Losev and Kabanov studied the adsorption of surface active substances on an iron electrode.

Surface active agents play an important role in polarographic analysis. Meits studied the suppressive action of a number of surface active agents like gelatine, dodecyl, hexadecyl trimethyl ammonium bromides, sodium laurate, Triton X-100, agar, etc., whereas Zuman studied the effect of barbituric acid and their derivatives in the suppression of oxygen maximum. Reilley and Smoler had studied the effect of surface active agents on polarographic currents. Badinand and Boucherle showed that the inhibiting power of polyethylene glycols decreased with the increase in the length of the carbon chain. Kolthoff had recommended the use of poly-acryl amide as maximum suppressor in the case of rotated dropping electrode. Capitanio and Pittoni studied the suppression coefficient of sulfoo-naphthyl stearic acid and lauric acid, while many others have studied the effect of surface active substance on the rate of mercury drop. Holleck and Exner had shown that these compounds exerted an appreciable influence on the mechanism of reduction of nitro compounds at the droppin mercury electrode. Stromberg had studied the effect of
camphor on the electrode process of cadmium-amalgam electrode, while Silvestroni had shown that the half wave potential of oxygen shifted to more negative value by the presence of these compounds. The effect of various surface active compounds on the reduction wave of copper has been the subject of extensive study by a number of workers like Kemula, Shwab (effect of monohydric alcohols on the maximum), and Kolthoff (more reversible nature of copper wave in perchloric acid medium in the presence of surface active substances).

More recent work includes the polarographic behaviour of fatty acids and quarternary pyridinium salts, the effect of surface active agents on the maxima of anions, inorganic ions, behaviour of some such compounds at the dropping mercury electrodes at different frequencies, and the research of Doss and coworkers on the effect of gelatine, acetone, thymol blue, etc., on the capacity of the double layer. The latter author also studied the behaviour of bromocresol purple blue, bromothymol blue and cetyl pyridinium bromide at the dropping mercury electrode in order to see their effect on the capacity of the double layer. More recently Chaki had studied the effect of these compounds in oscillography polarography while Nagi had studied the effect on the chronopotentiograms of Cu++, Pb++, Cd++ and Bi+++ in various supporting electrolytes.

Another class of soaps which are equally important
but have attracted lesser attention are called heavy metal soaps, which differ from the above discussed compounds in the sense that they are insoluble in water but show enhanced solubility in non-polar solvents. This property, namely, their solubility in non-polar solvents make these compounds technically quite important. Many a fundamental problems with such compounds remain uninvestigated. Amongst these the most important ones are (i) their structure, (ii) physico-chemical changes involved during their solubilization, (iii) their characterisation, and (iv) application of physico-chemical methods to determine the metal ion content.

The work described in this thesis deals with the short resume of the work on surface active compounds described in the preceding pages. It may be seen that enough scope exist for more comprehensive investigations in this particular branch. The class of compounds known as Twitchelts reagent have almost escaped the attention of workers engaged in researches on colloidal electrolytes and this is equally true for Isothioureas and related compounds. Heavy metal soaps like Cu^{++}, Ni^{++}, Co^{++} and Zn^{++} myristates and palmitates etc., also require a more systematic approach in order to understand the intricacies accompanying their dissolution in non-aqueous media. It was therefore thought worthwhile to study some salient features of these compounds. The work
described in the thesis deals with the following:

(i) Use of sulphonated phenyl, tolyl, and xylyl stearic acid, dodecyl pyridinium bromide and Isothiourea dodecyl ether hydrobromide as maximum suppressors in polarographic analysis.

(ii) Determination of critical micelle concentration of the above compounds using polarographic, conductometric, and turbidimetric methods.

(iii) Spectrophotometric studies on the interaction of the above compounds with some dyes.

(iv) Application of some instrumental methods like polarography and spectrophotometry to heavy metal soaps.
REFERENCES


