SPECTROSCOPIC AND THERMODYNAMIC STUDIES OF MICELLAR INTERACTION WITH ORGANIC SOLUTES AND STUDIES ON THE EFFECT OF CONCENTRATION AND TEMPERATURE ON CATIONIC TRANSFERENCE NUMBER OF $CuSO_4$ AT CONSTANT pH.

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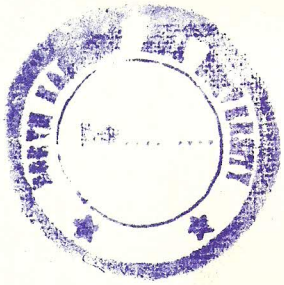
SCHOOL OF PHYSICAL SCIENCES

A THESIS
SUBMITTED IN FULFILMENT OF THE REQUIREMENT OF
THE DEGREE OF

DOCTOR OF PHILOSOPHY



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APRIL, 1991

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Date: 10th April, 1991

This is to certify that Mr. Aseem Sinha has satisfactorily completed the following Pre-Ph.D courses, as prescribed by this University:

1.	Organometallic Chemistry	Chem 620
2.	Solid State Chemistry	Chem 660
3.	Experimental Technique	SPS 630
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Aseem Sinha

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C O N T E N T S

C H A P T E R I

INTRODUCTION

In this chapter, the general aspects of Surfactants and their properties pertaining to solubilization and cationic transport number of electrolytes in aqueous solution, which are of relevance to the studies reported in this thesis and of general interest, have been briefly reviewed.

I.1 SURFACTANTS

Soaps and detergents have very similar properties. Soaps are salts of straight-chain fatty acids produced by a reaction between fats and a strong base such as potassium hydroxide, while detergents are generally made from chemical compounds other than fats and lye.Soaps and detergents are the surface-active agents, usually referred to as surfactants. A surfactant molecule possesses both hydrophobic and hydrophilic characteristics. This is called the amphipathic structure of the surfactant molecule[1]. The hydrophobic group is usually a long-chain hydrocarbon residue (sometimes with a halogenated or oxygenated hydrocarbon or siloxane chain), whereas the hydrophilic group is an ionic or highly polar group. Surfactants are broadly divided into two groups (i) naturally occurring surfactants and (ii) synthetic surfactants[2]. A few common examples of the surfactants belonging

to first group are bile salts, lipids, etc. whereas the second group, depending on the nature of hydrophilic group, is further divided into four different types of surfactants. They are :

(a) *Anionic surfactant* :

These are alkali or alkaline-earth metal salts of mono or polybasic carboxylic acids and of sulphonic or phosphonic acids containing saturated or unsaturated hydrocarbon substituent. The surface-active portion of the molecule bears a negative charge, for example, $RCOO^-Na^+$ (soap), $RC_6H_4SO_3^-Na^+$ (alkylbenzene sulphonate) or $RSO_4^-Na^+$ (sodiumalkyl sulphate).

(b) *Cationic Surfactant* :

The surface - active portion of the molecule bears a positive charge. Surfactants of this group possess a general formula of $R_nX^+ Y^-$, where R represents one or more hydrophobic chains, X is an element capable of forming an `onium' structure and Y is the counterion; X may be N, P, S, As, Te and Sb, whereas Y may be the halogens, e.g., $RNH_3^+Cl^-$ (salt of a long-chain amine), $RN(CH_3)_3^+Cl^-$ (quaternary ammonium chloride).

(c) *Zwitterionic Surfactant* :

The surface -active portion of the surfactants posseses both, positive and negative charges. These show the characteristics of either cationic or anionic surfactants depending on the pH of the solution, and may even behave as zwitterionic when they are pH-independent. The examples of the surfactants of this class, are $RN^+H_2CH_2COO^-$ (long-chain amino acid), $RN^+(CH_3)_2CH_2CH_2SO_3^-$ (sulphobetaine), etc.

(d) *Non-ionic Surfactant* :

The surface-active portion of the surfactant molecule posseses no

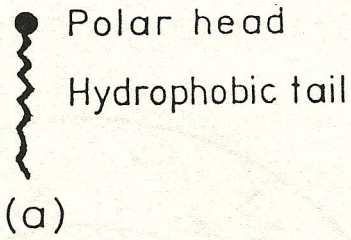
charge. This class consists of a large number of surfactants, most common to them are polyoxyethylenated alkylphenols ($RC_6H_4(OC_2H_4)_xOH$), monoglyceride of long-chain fatty acid ($RCOOCH_2CHOHCH_2OH$), tertiary acetylenic glycols ($R_1R_2C(OH)C{\equiv}CC(OH)R_1R_2$), etc.

The surfactants are used for a variety of applications, such as in household detergency[3], as vehicles for pharmaceuticals drug delivery[4], in motor oils as lubricating agents[1], in enhanced-oil recovery from the drilling muds[5], as the floatation agents used in benefication of ores[6], in micelle-enhanced ultrafiltration techniques for removing hazardous materials from industrial waste-water streams,[7] and in the alteration of reaction pathways, rates and equilibria[8-10]. In the field of analytical chemistry, the surfactants are used in the development of new methods of metal-ion determination[11-18].

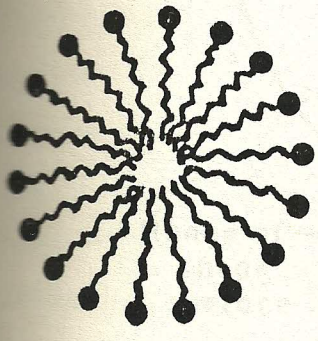
In very dilute solutions the surfactants exist as monomers, but when their concentration exceeds certain minimum, the critical micelle concentration (c.m.c), they associate spontaneously to form aggregates. The aggregated or clustered form of the surfactant molecules at or above the c.m.c is commonly known as "micelle" which was first proposed by McBain[19], and the number of surfactant molecules or monomers utilised in forming a micelle is termed as the "aggregation number" of surfactant. The micelle is a well-defined aggregation of surfactant molecules in such a way that in aqueous solution, the hydrophilic part of surfactant molecules is directed towards the water-surface while the hydrophobic part away from the water-surface and consists of

interior of the micelle. In an aqueous solution the surfactants may generate micelle (or normal micelle) whereas in organic (or nonaqueous) solvent they give "reverse micelles", where the orientations of hydrophilic and hydrophobic parts of the molecules are reversed (Fig.I.1). The c.m.c and aggregation number of surfactants depend on temperature[20-21], nature of solvent[22], presence of an electrolyte[23,24] or an organic additive[25-27] in the solution.

The formation of surfactant micelles is the result of the hydrophobic effect[28]. The process of micelle formation occurs with a positive change in entropy, when based on the ideal dilute solution standard state, by removing the hydrophobic groups from contact with the surrounding water molecules. However, it is interesting to note that although it is usually assumed that there is a fairly well-defined layer around the micellar surface, there is no agreement on the composition of the micellar core, i.e., whether it consists of pure hydrocarbon or of hydrocarbon chains mixed with water. At not so high concentrations (above c.m.c.), micelles may acquire a nearly spherical shape but the ellipsoidal shape of micelles is considered to be more stable from geometric consideration[2]. However, the shape depends on total concentration of surfactant in solution, which has been discussed, in detail, by Tanford[29]. An increase in concentration of surfactant will promote the formation of larger micelles with a reduced surface area per molecule, i.e., at higher surfactant concentrations, micelles tend to become more rod-shaped or lamellar. The cross section of a spherical ionic micelle is shown in Fig.I.2.



(a)



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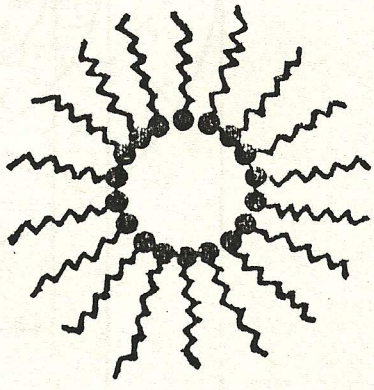

(c)

Fig.I.1 : Assembly of surfactant molecules in aqueous and nonaqueous media : (a) surfactant molecule, (b) micelle and (c) reverse micelle.

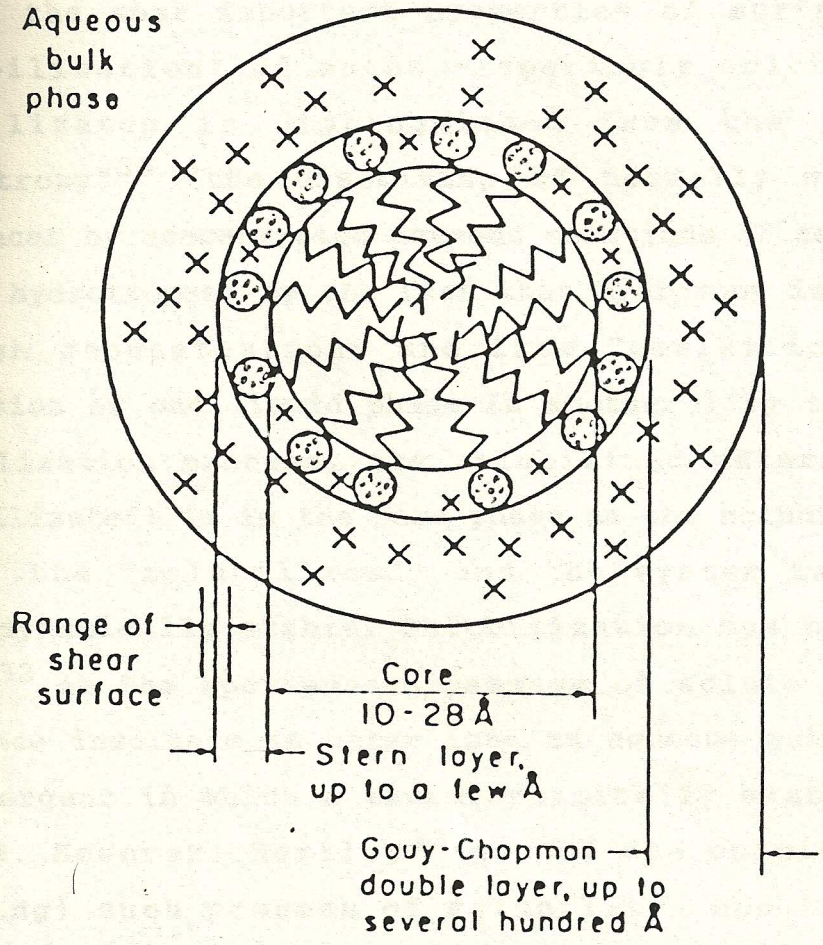

Fig.I.2 : A two-dimensional schematic representation of the regions of a spherical ionic micelle.[2]

I.2 SOLUBILIZATION IN AQUEOUS SURFACTANT SOLUTIONS

One of the most important properties of surfactants is the "solubilization" of water - sparingly soluble materials. Solubilizaton is distinguished from the phenomenon of "hydrotropy"[30] (the dissolving of normally water-insoluble substances by concentrated aqueous solutions of certain materials called hydrotropes) by the fact that hydrotopy is effective only at high concentrations and from "emulsification"[31] (the dispersion of one liquid phase in another) by the fact that in solubilization process, the solubilized material (i.e., the "solubilizate") is in the same phase as the solubilizing solution (i.e., the "solubilizer") and the system is consequently thermodynamically stable. Solubilization has been defined by McBain[32] as the spontaneous passage of solute molecules of a substance insoluble in water into an aqueous solution of a soap or detergent in which a thermodynamically stable solution is formed. However, Hartley[33] was of the opinion that (while defining) such process of solubility, one implies that an essentially new process is under investigation and that it is often held that the resulting solutions are not in equilibrium. On the other hand, Winsor[34] extended the point of view put forward by Lindau[35] and by von Hahn[36] that hydrotropy and solubilization are essentially similar processes.

The exact location in micelle at which solubilization occurs is known as the locus or site of solubilization and it varies with the material solubilized, i.e., the solubilizate (Knowledge of locus of solubilization is important as it reflects the type of

interaction between surfactant (solubilizer) and the solubilzate). X-ray diffraction,[37,38] electronic[39] and NMR[40,41] spectral studies have been used to investigate the locus of solubilization in different systems (diffraction studies measure the changes in micellar dimensions on solubilization, whereas electronic and NMR spectra indicate the changes in the environment of the solubilizate on solubilization). It was inferred from these studies that (i) small polar molecules like short-chain phenols generally solubilize close to the surface of the micelle in the palisade layer (between the hydrophilic groups and first few carbon atoms of the hydrophobic groups) or by adsorption at the water -micelle interface, (ii) large polar molecules such as long-chain alcohols or polar dye-stuffs are solubilized, in aqueous medium, between the individual molecules of surfactant between the palisade layer in such a way that polar groups of the solubilizate are oriented towards the polar groups of the surfactants and the non-polar groups are oriented towards the interior of the micelle, (iii) the solubilization of polarizable hydrocarbons such as short-chain arenes may be initially located at micelle-water interface which may be shifted deep in the palisade layer towards the inner core of the micelle following the addition of more solubilizate, and (iv) the non-polar solubilizates such as saturated aliphatic or alicyclic hydrocarbons may be incorporated in the inner core of the micelle, i.e., residing in a completely non-polar environment. The different loci of solubilization are shown in Fig.I.3.

The solubilization of organic compounds has been reported to affect the shape and size of surfactant micelle; with the

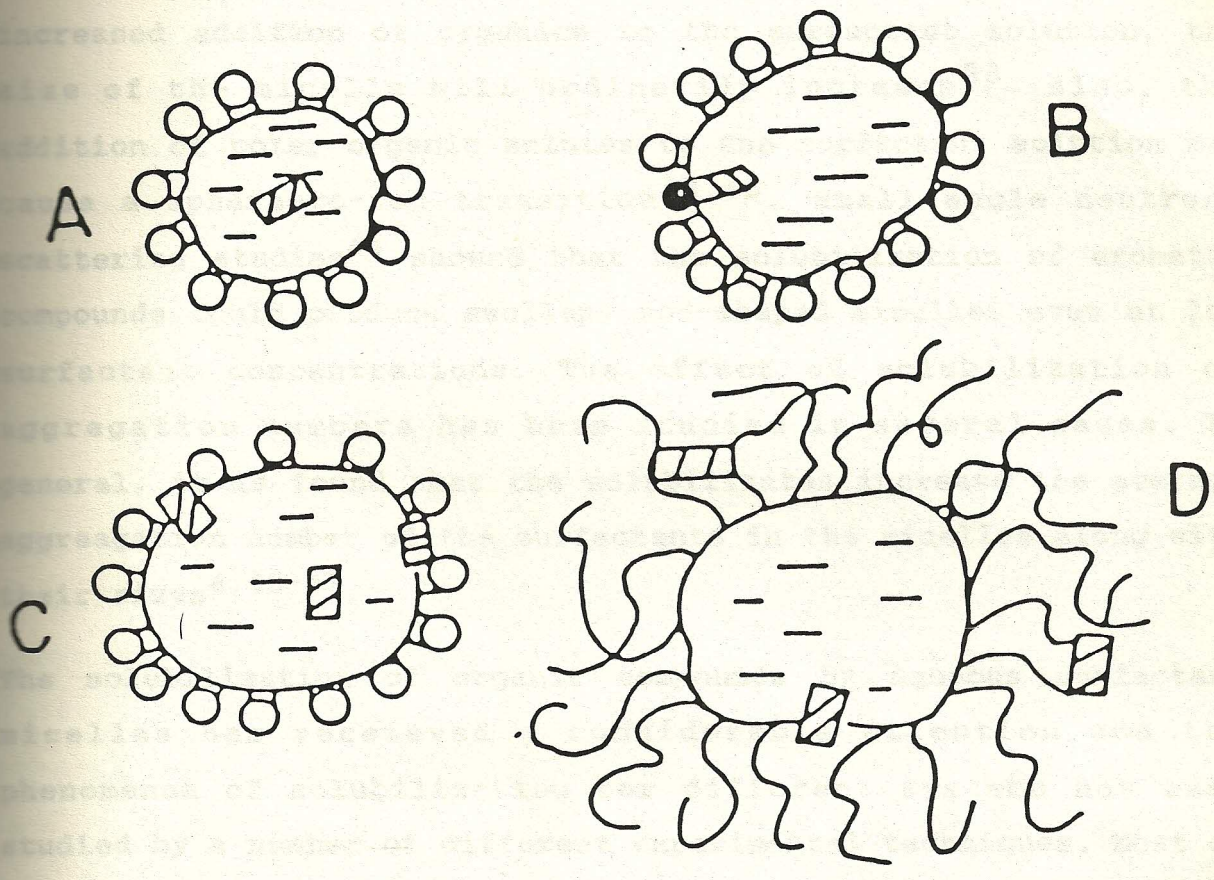

Fig.I.3 : Representation of solubilization process showing probable loci of solubilization for different types of organic compounds ; (A) nonpolar, (B) amphipathic, (C) slightly polar, and (D) polar solubilizates in nonionic micelle.

increased addition of organics to the surfactant solution, the size of the micelle will ordinarily increase[23]. Also, the addition of polar organic solutes to the surfactant solution may cause a sphere-to-rod transition[42,43]. Small angle neutron-scattering studies[44] showed that the solubilization of aromatic compounds could produce swollen, rod-shaped micelles even at low surfactant concentrations. The effect of solubilization on aggregation numbers has been studied in several cases. In general, it is found that the solubilizates increase the average aggreagation number of the surfactants in the micelles along with their sizes[4,45-47].

The solubilization of organic compounds by aqueous surfactant micelles has receieved a considerable attention and the phenomenon of solubilization for different systems has been studied by a number of different experimental techniques. Most of the earlier investigations on (surfactant) solubilization was based on the solubility measurements[48-50], in which a surfactant solution of known concentration was saturated with the solubilizate whose concentration was determined by some analytical method. The gas-chromatographic technique was used by Nagarajan et al[51] to measure the amount of hydrocarbon (benzene) solubilized in different types of surfactants. Apart from gas-chromatographic technique, the solubilization studies in aqueous surfactant solutions were carried out by high-performance liquid chromatographic[52] and thin layer chromatographic techniques[53]. The solubilization of benzene in different surfactant micelles were studied by various researchers from different experimental

methods. Eriksson and Gillberg[41] carried out ^{1}H NMR chemical shift measurements in cationic surfactant micellar solutions containing benzene as solubilizate and observed that small amount of benzene had caused a shift in the signal of the proton near the polar group of surfactant. This was interpreted to imply that benzene was located close to the micelle-water interface. Stilbs[54] used an NMR spin-echo technique to infer solubilization equilibrium constants for a number of different organic compounds (of lower concentrations) within the micelle. The solubilization data of organic solutes like benzoic acid, preservative, salicylamide, etc. of low concentrations were obtained by ultrafiltration and molecular-sieve techniques[55-57]. Micellar - phase separation and acid-dissociation methods were employed to determine the distribution coefficients of some substituted phenols between micellar and aqueous -bulk phases[58]. An extensive use of very reliable vapour-pressure technique for compounds (of low concentration) having enough vapour pressure is reported in the literature[59-65].

Abu-Hamidiyyah and Mysels[66,67] had first made use of equilibrium-dialysis technique to study the solubilization of organic solutes in aqueous surfactant micellar solutions. In dialysis method the solubilizate (under study) in an aqueous surfactant solution was taken in a dialysis (semi-permeable) bag which was kept immersed in a water-bath at constant temperature for several days till the equilibrium was achieved by both the components of the solution across the semi-permeable bag. However, the method was found to be very tedious in addition to the limitations like leakage through the bag and the possibility of its contamination with the

surroundings thereby affecting the results of solubilization. Moreover it was very difficult to estimate small amount of the solute in large amount of water very precisely. Recently, Christian and co-workers[68] had modified the previously reported equilibrium-dialysis technique, and the technique is, generally, known as "Semi-Equilibrium Dialysis (SED)" technique (the technique is described, in detail, in Chapter II). From SED technique the solubilization data of non-volatile organic solutes could be determined in aqueous surfactant solutions, over a wide range of organic solute concentration. As the name indicates, in this method the equilibrium is attained with respect to only one component of the system, i.e., the organic solute solubilized in suractant micelle. It is reported, however, that in case of SED - experiments the surfactant continues to diffuse through the dialysis membrane till the difference in its concentration persists between both sides of the membrane[68].

There have been numerous studies on different aspects of solubilization of organic solutes (polar or non-polar) by aqueous surfactant solutions. The thermodynamic properties of association of benzene-phenol dimers in dilute aqueous solutions (at diferent temperatures) were studied from precise vapour-pressure solubility measurements[69]. The results were consistent with a mass-action model that attributes to formation of benzene dimers and heterodimers between benzene and phenol. This was interpreted in terms of hydrophobic interctions. The solubilization studies of hexane, cyclohexane and benzene, in different surfactant micelles, viz., sodiumoctyl sulphate,

sodiumdodecyl sulphate and sodiumdeoxycholate, were carried out using vapour-pressure measurement technique[59,64,65,70]. The results were interpreted in terms of variation in solubilization of hydrocarbon with change in surfactant concentration at fixed temperature. A mass-action model was used to infer the formation constants of surfactant micelle with organic solute. The thermodynamic parameters for the transfer of the hydrocarbon from aqueous bulk to surfactant micelles and the solubilization constants as function of the intramicellar mole fraction of hydrocarbons were reported by Smith et al[71] as well as by Mahmoud and coworkers[72]. The results were interpreted in terms of interaction between hydrocarbon molecule and surfactant micelles.

The other group of organics which were used for solubilization studies consisted of alcohols. The solubilization study of α-naphthol by cationic surfactant micelles was based on the investigation of effect of nature of micelle on the type nature of interaction between the organic molecule and the micelle[73,74]. The interaction of α-naphthol with surfactant micelle was explained on the basis of hydrogen bonding between naphthol and the counterion of the surfactant. The solubilization equilibria for some analytical reagents like 8-quinolinol, 2-(2-thiazolylazo)-4-methyl phenol, *p*-nitrophenol, etc. in aqueous non-ionic surfactant solutions were studied and the data were analysed using the two-phase partition model[58], whereas the partition-coefficient of *p*-nitrophenol between 0.5N HCl and $CHCl_3$ was measured with and without methyl-β-cyclodextrin at varying temperatures[75]. The partition coefficients were found to increase with increase in surfactant concentration, which was

accounted for on the basis of 1:1 complex formation between the organic solute and the surfactant. Abu-Hamidiyyah et al[76] determined the effect of surfactant chain-length on the solubilization of a number of aliphatic alcohols by various cationic surfactant micelles in aqueous solutions. The solubilization tendency was found to decrease with increasing surfactant-chain length. The variation in solubility of cholesterol (a high molecular weight hydroxy-compound) and cholesteryl benzoate in mixed micellar solutions of a few bile salts are reported in the literature[77]. The solubility in lipid-ionic surfactant mixtures normally increased with the increase in lipid concentration (like that in mixed-surfactant systems), whereas in the case of non-ionic surfactant, the behaviour of solubility change was opposite. The changes in solubilization phenomena were attributed to the effects of electrostatic and hydrophobic interactions of the organic molecules incorporated into the micelles.

Christian et al[78] have made exhaustive studies on the solubilization of volatile and non-volatile organic solutes in aqueous cationic surfactant solutions and the results were analysed in terms of dependence of activity-coefficients of surfactant and organic solute on the mole fraction of organic in the micelle. The difference in activity coefficients of different organic solutes was accounted for difference in nature of interactions of the organics with the surfactant micelle. The solubilization studies of phenols, anilines and aldehydes in cationic micellar surfactant, by using semi-equilibrium dialysis

technique, were reported[68,79-81], and the solubilization constants were reported to decrease with the increase in mole fraction of organic in surfactant micelles. Mahmoud et al[82], from semi-equilibrium dialysis technique had investigated the solubilization of benzoate anions by cationic micelles of cetylpyridinium chloride. The equilibrium constants were correlated with an ion-binding model as well as partial incorporation of the anion into the surfactant micelle. Higazy, Christian and coworkers[83] had studied the effect of carboxylic side-chain length in three aromatic acids on their solubilization by aqueous cationic surfactant micelles. The solubilization constants of all three acids were found to be nearly the same indicating that there was no significant effect of the presence of one or more methylene groups between the carboxylate and phenyl groups of benzoic acids. Seno et al[84] examined the transport of various fatty-acids by micelles of cationic surfactant through a liquid membrane system of heptane solution, and reported that the transport rates increased with increasing surfactant concentration and decreased after a certain maximum value.

There have been a few investigations on the solubilization of preservatives[55,85], steroidal harmones[86] and drugs[87-90] by cationic, anionic and non-ionic surfactant micelles in aqueous media.

The effect of temperature on the process of solubilization has been studied by many researchers. Saito and Shinoda[50] reported in their solubilization studies (of hydrocarbons by some non-ionic

surfactants) that due to the change in solubilization (limits) with change in temperature, the solubilization measurements as a function of temperature are indispensible in solutions of non-ionic surfactants in order to compare the solubilizing power of surfactants. Patel and Foss[91] studied the solubilization of some organic compounds of pharmaceutical importance, like parabens and phenols by certain macromolecules such as polysorbate 80 and polyethylene glycol 4000. It was reported that in the case of polysorbate 80, the extent of solubilization of the organics decreased with the increase in temperature, whereas polyethylene glycol 4000 exhibited the opposite trend; and phenol-polysorbate 80 binding was found to be temperature independent. Alauddin et al[92] investigated the effect of temperature and concentrations of surfactant and solubilizate on the interaction or solubilization of organics of biological importance with/in an anionic surfactant. An increase in the magnitude of Gibbs energies of transfer of organic (from aqueous bulk to surfactant micelle) with increase in temperature was noticed. This was attributed to the enhancement of hydrophobic effect with the increase in temperature, i.e., the ease of penetration of the solubilizate into the micelles at higher temperatures.

I.3 SPECTROSCOPIC STUDY OF DYE-SURFACTANT INTERACTION

Hartley[93] was the first researcher who had noticed that the colour of sulphonaphthalein indicators changed on the addition of surfactants and this effect occurred (only) when the charge on the surfactant aggregate (i.e., the micelles) was opposite to that on the (dissociated) indicator molecule. This behaviour was

noticed with the other dyes - as azo[94], triphenylmethane[95-97] and merocyanine dyes[98] too. In such systems, the addition of surfactants (above c.m.c'.s) not only shifted the absorption band maxima but also changed the molar absorptivities of the dyes. Kapoor[99] feels that the shifts in the dye-spectra in dye-surfactant systems, (towards the longer or shorter wavelength) are due to dye-surfactant interaction in the vicinity of c.m.c. of surfactant; a red shift indicates the presence of attractive forces while a blue shift in the absorption maximum is indicative of repulsive forces. Such variation in the spectral properties observed in dye-surfactant systems carrying opposite charges are attributed to the micellar effect on the aqueous dye systems. Malik et al[100-102] reported that the spectral changes of several dyes are due to the electrostatic interaction between the anionic (or cationic) surfactant and the basic (or acidic) dye. They, however, feel that chemical interaction giving a stoichiometric dye-surfactant complex was very imporbable. It was pointed out by Guha et al[103] that a small red-shift in the absorption band of the dye (and increased molar absorptivity) is due to the incorporation of the dye into the micelles. Hayashi[104] studied the interaction of congo red with cationic and non-ionic surfactants and interpreted the data in terms of preferential affinities of the surfactant micelles with the dye-species. The effect of anionic surfactant on xanthane dyes was studied by Matibinkov et al[105] and they observed the shifts in the λ max of dyes at low surfactant concentrations. Rohatgi-Mukherjee et al[106] had investigated the interaction between phenosafranin dye and the surfactants, CTAB, SDS and Triton - X 100 by

spectroscopic and photogalvanic techniques. Lee et al[107] examined the interaction of three azo dyes with synthetic cationic surfactants and they had noticed remarkable changes in the spectra of the dyes (in the presence of surfactants) which they feel are due to the aggregation of the dye molecule in the hydrophobic regions of the surfactants.

A remarkable colour change (and appearance of a new absorption band) was observed by Muto et al[108-113] when tetracyanoquinodimethane (TCNQ) and iodine were solubilized in three different surfactants (above their c.m.c's), both in aqueous and organic solvent solutions. Such spectral changes were attributed to charge-transfer or electron donor-acceptor interaction of surfactants (the electron donors) with TCNQ and iodine (the electron acceptors). The (CT) complex formation between hydrophobic electron donors and hydrophilic electron acceptors were studied[114,115]. Rohatgi-Mukherjee et al[116] and Bhowmik et al[117-120] studied the (CT) interaction of Triton X-100 micelles with different electron acceptors, like iodine and various dyes, and they are of the opinion that the nature of interaction depends on the surfactant micelles. The effect of micellar sodiumdodecyl sulphate solution on the electron donor-acceptor interaction between methyl viologen and naphthylamines were studied spectroscopically by Bertolotti et al[121]. The interaction was reported to be affected in the presene of SDS and was dependent on surfactant concentration. The enhancement in the interaction between electron donor and acceptor was attributed to an increase in their local concentrations in the micellar pseudophase. Moulik et al[122] had carried out detailed

investigations on the effect of cationic, anionic and non-ionic surfactants as well as a low-molecular weight polymer, viz., polyethylene glycol on the proton-transfer complexation equilibrium between *p*-nitrosalicylic acid and ethylenediamine. It is reported that the equilibrium was favoured in ionic surfactants whereas it was reversed in non-ionic surfactants and the polymers (the polymer resembled closely the non-ionic surfactant in structure). The alteration in the proton-transfer process was believed to be due to both electrostatic (i.e., the charge) and hydrophobic effects exhibited by ionic surfactants on the system, whereas in case of non-ionic surfactant and polyethylene glycol, the entropy effect was held responsible for the reverse trend in the process. The same reaction-process was studied by Bandyopadhyay and Moulik[123], where the effects of bile-salts and their mixtures with several surfactants were investigated on the proton-transfer equilibrium between *p*-nitrosalicylic acid and ethylenediamine. Weissman et al[124] had studied the metachromasy of toluidine blue in presence of nucleic acids, and two types of linkage, polar and non-polar (between the dye and nucleic acids) were said to be involved in the interactions, and these were affected by various factors like ionic strength, type of solvent, temperature, etc. Following the Hartley's[93] investigations of the interactions of several surfactants with a number of dye-indicators, it were Sheppard and Geddes[125] who had investigated the spectral changes of pinacyanol chloride in aqueous micellar solutions of cetylpyridinium chloride. Their study, which was preliminary in nature, was greatly extended by Harkins and his colleagues[126] whose

investigations led them to develop a method[127] for determining the c.m.c. of surfactants (from the spectral shifts of the dye solutions in surfactant solutions).

The interaction of acridine orange with polyions and polymers has been reported[128-132], whereas very few studies on the interaction of this dye with surfactants are known[133-135]. A similar study of the interaction of acridine organge monohydrochloride with (three) different surfactants (cationic, anionic and non-ionic; all above their c.m.c.'s) was carried out by Moulik et al[136]. Platonova et al[137] studied spectroscopically the mechanism of the interaction between a number of cationic dyes and surfactants, and the results were rationalized in terms of formation of 2:1 surfactant - dye complexes. The mechanism and thermodynamics of interaction of ether-type non-ionic surfactants with anionic dyes was reported by Nemoto and Funahashi[138]. The spectra of methylene blue and acridine organge were affected when they were in micellar media (of SDS)[139]. Chiang and Lukton[140], from the studies of 2-*p*-toluidinylnaphthalene-6-sulphonate and SDS, suggested that the binding force in this interaction is hydrophobic in nature, and this was supported by Birdi et al[141] from the interaction studies of SDS and 1-anilinonaphthalene-8-sulphonate. Stevenson and coworkers[142] from their experiments concluded that interaction between some monoazodyes and (a series of) non-ionic surfactants is hydrophobic in nature. They feel that the factors responsible for the spectral changes are (i) deaggregation of the dye molecules by association with surfactant micelles[143], (ii) the joint effect of deaggregation and the

change in molecular environment[144,145], and/or (iii) the localization of the chromophore within the hydrophobic micellar interior[146].

Sato and his coworkers[147] investigated the effect of concentration of sodiumdodecyl sulphate on the energy transfer between two cationic dyes, rhodamine 6G (donor) and pinacyanol (acceptor). The energy-transfer is interpreted in terms of the change in absorption spectra of pinacyanol which varied with change in concentration of the surfactant (i.e., SDS) as well as with the association behaviour of the dye in the microenvironment of the micelles. A similar study was carried out by Pelizzetti and Pramauro[148], where the kinetics and equilibria of electron-transfer reactions between benzenediols and hexachloroiridate (IV) or octacyanomolybdate (V) in the presence of cationic and anionic surfactants were investigated, and it was shown how the surfactant micelles influence the reactions.

Fluorescence spectroscopy was used in the study of effect of micelles on the fluorescence spectra of dyes[149-151]. Kapoor and coworkers[143,152-155] studied the effect of various surfactants on the fluorescence spectra of a number of dyes, viz., rhodamine B, eosin, erythrosin and rose bengal. The absorption and fluorescence spectra of mazindol show that the spectral position was affected in the presence of SDS (anionic surfactant), whereas no change was noticed in CTAB (cationic surfactant) micellar media[156]. The change in fluorescence of fluorescein dye by its dimer and rose bengal was studied in presence of cationic micelles[157].

Some studies have been reported on the interaction of a few oil dyes with different surfactants[158,159], and of a few azo-oil dyes with a few anionic surfactants[160-166]. The kinetic and thermodynamic investigations of the interaction of a membrane - dye, MC 540 with biological macromolecules (DNA - acting drug from ellipticine series) were carried out by temperature-jump spectroscopic method[167]. The effects of polyethylene glycol (PEG) on the solubilization of oil soluble monoazo dyes in sodiumdodecylbenzene sulphonate were studied by Ueda and coworkers[168]. The amount of solublized dye and the solubilizing power of sodiumdodecylbenzene sulphonate were found to increase with the increase in concentration and weight - average molecular weight of PEG, and the results were interpreted in terms of complex formed between PEG and the surfactant. The antiredeposition/cleaning capacity of the surfactant towards cotton and nylon fabrics was also attributed to increase with increase in PEG concentration in the system. The photoreduction and electron back-transfer reactions between acridine organge dye and aromatic amines were studied in the presence of cationic micelles[169]. The reaction is affected in presence of micelles due to incorporation of the semireduced dye species into the micelle. Wormuth et al[170] examined the solubility of (six) dyes (of increasing amphiphilicity) in microemulsions in presence of surfactants with different charge. The solubility of the dyes was much enhanced in microemulsion over that in pure solvents; this was attributed to the dye - solubilization at the surfactant - rich interfacial region separating oil - rich and water -rich domains. Hayakawa et al[171] examined the solubilization of water

- insoluble dye, oil yellow OB (OY) by a cooperative binding system of surfactant, alkyltrimethyl ammonium salt and the polyelectrolyte, poly (vinyl sulphate). The sorption of 51 organic dyes, indicators and stains by polyester and polyether type polyurethane foams was investigated using aqueous solutions and powder foam material[172]. A comparative study was done with the sorption of several dyes from various organic solvents, and a relation between the structure of the test substances and their sorption was suggested.

I.4 MICELLAR EFFECT ON INDICATOR EQUILIBRIA

It is well known that the colour of an indicator in solution depends, within certain limits, on the concentration of hydrogen ion (or hydroxyl ion) in the solution[173]. All the indicators are very weak organic acids or bases. According to Kolthoff[174], "indicators are (apparent) weak acids or bases of which the ionogenic (aci- or baso- respectively) form possesses a colour and constitution different from the colour and structure of the pseudo- or normal compound". They acquire an acid -base equilibrium in solution and are accompanied with the change in colour of the indicators corresponding to the hydrogen - ion concentration (i.e., the pH) of the medium in which they are dissolved, and therefore, each indicator is said to possess a "pH range". According to Ostwald, the ions of an indicator possess a different colour from that of the undissociated molecule[173]. For example, the undissociated molecule of methyl orange is red, while its anion (designated as MO^-) is light yellow. It has been shown in many cases that the colour change of acid-base

indicators is generally understood as a consequence of the change in the molecular structures accompanying the distributions of electrons on the transformation between the indicator acids and their conjugate bases.

The lowest hydrogen-ion concentration (in terms of pH) at which the indicator exhibits its acid colour, which the eye can detect, will be $pK_{In}-1$ and the highest hydrogen-ion concentration for an alkaline colour of the indicator will be $pK_{In}+1$. Thus, the colour change for an indicator lies approximately in the range of 2 pH units, and so, it is essential to know the pK_a of an indicator before its selection. From the pK_a values of the weak acids and bases reported in the literature, one can notice that depending on the medium, and the ionic strength of the medium the pK_a values of the indicators vary to a considerable extent[175,176]. A change in the composition of the solvent (medium) often influences chemical equilibria much more profoundly than do changes normally encountered in the total concentration of ionic solutes. Acid-base equilibria are, in general, rather sensitive to changes in the dielectric constant and in the basicity of the medium[177]. As the dielectric constant is lowered, the formation of ion-pairs and aggregates of even high order assumes more importane. Kortüm et al[178] found, however, that the relatively labile ion-pairs present in methanolic solutions cannot be distinguished spectroscopically from free ions. In the study of acid-base equilibria in an aprotic solvent like benzene, it was proposed that the free ions probably play a negligible role in the interaction of acids and bases, yet indicator exhibits colour transformations[179]. Brooker

and his coworkers[180] investigated the effect of solvents (aqueous and non-aqueous) on the spectral behaviour and colour change of phenol blue and the variation was interpreted in terms of varying dielectric constants of the medium. Kolthoff et al[181] studied the effect of different media for six aromatic acids and observed an increase of about 4 to 6 units in the pK_a for an uncharged weak acid when the solvent composition (H_2O: alcohol) was varied from pure water to alcohol. In another investigation by Larsen and Tomsicek[182], the variation in pK_a values of methyl red indicator in varying alcohol-water mixtures was studied, and the pK_a was found to increase with the decrease in dielectric constant of the medium. A similar study was performed by many other researchers on a number of indicators in water - methanol mixtures as the media[183-187].

It has been known for quite some time that indicator dyes have different colours in solutions of soaps and detergents[188,189]. This has been explained on the basis of the preferential adsorption of one form of the indicator molecule on the detergent micelles with consequent displacement of the acid-base equilibrium in favour of this form. Deutsch[190] noticed a colour change of the indicator when it was adsorbed at oil-water interfaces. When water and benzene were shaken together after the addition of nearly colourless rhodamine, the temporary emulsion gave a bright pink colour, and the colour disappeared as soon as the liquids were separated. Hartley[93,191], in the early thirties had studied the effects of anionic, cationic and non-ionic surfactants on a large number of dye-indicators and had

come to the conclusion that the greatest colour change occurs when the charge on the detergent (or surfactant) was opposite to that on the indicator ion, and one should not expect any influence on the indicator equilibria when the charges on the detergent micelles and the indicator ions were similar. This was later designated as Hartley's `sign-rule'. Sorensen[192], in investigations involving acid-base equilibria in the presence of proteins noted the "protein-error", and these errors were attributed to the effects of micelles on the indicator equilibria.

The influence of cetyltrimethylammonium bromide (CTAB) and sodiumdodecyl sulphate (SDS) on the equilibrium constant of several triphenylmethane and sulphonphthalein indicators has been investigated by Duynstee and Grunwald[193,194]. In triphenylmethane indicators, the equilibrium of the type,

$$(In)_{acid} + OH^- \underset{}{\overset{K}{\rightleftharpoons}} (In)_{base}$$

was shifted in the forward diretion by CTAB, whereas in the presence of SDS the equilibrium was shifted to the backward direction. On the other hand, SDS hardly affected the equilibrium constant, K, of sulphonphthalein indicators, while CTAB had increased it. These micellar effects on the equilibria of the indicators were reported to be consistent with Hartley's sign-rule. Reeves et al[195] studied the effects of dodecyl and hexadecyltrimethylammonium bromide on the hydrazo-azo tautomeric equilibrium of 4-phenylazo-1-naphthol-2,4 -disulphonate by spectral, solubility and stopped - flow kinetic methods, and the

data were interpreted in terms of kinetically controlled formation of small dye-surfactant aggregates which subsequently grew in size to a micelle. Tong and Glesmann[196] had investigated the effect of a non-ionic surfactant, Triton X-100, on the dissociation constants of a number of phenols and naphthols. It was found that the surfactant micelles increased the pK_a of these phenols and naphthols, which was attributed to the solubilization of un-ionized species of phenols/naphthols in the micelle interior where the environment was similar to that of n-octanol. Further, it was suggested from these observations (on comparing the results with those of ionic surfactants) that the electrostatic factors were relatively less important in the distribution of the indicator species between the two phases for non-ionic surfactants and that the change in the dissociation constants might arise primarily from the differences in the environment of the solubilized species as well as from the distribution between the micellar and the bulk phases.

The effect of certain ionic surfactant micelles, e.g., dodecyl trimethylammonium bromide, tetradecyltrimethylammonium bromide, CTAB and SDS on the pK_a values of bromophenol blue and bromocresol blue (the sulphonphthalein indicators) were investigated by Mukerjee and Banerjee[197]. The differences between the bulk and the micellar pK_a's of the indicators were interpreted in terms of the electrical potential difference and changes in the pK_a. Similarly, the effect of different surfactants, like, dodecyltrimethylammonium bromide (DTAB), Triton X-100 and SDS on pK_a values of various other indicators like, 7-hydroxycoumarin, bromothymol blue and methyl red, were

investigated, and the shifts in pK_a's were rationalised in terms of surface potential changes[198]. Albrizzio et al[199] investigated the effect of surfactant concentration and structure as well as the role of added electrolytes on the colour change of crystal violet, and it was reported that an increase in alkyl-chain length of n-alkyltrimethylammonium bromides enhanced the catalytic efficiency markedly.

The effect of the cationic surfactant micelle of 1-carbethoxypentadecyltrimethylammonium bromide on the absorption spectra and pK_a values of phenol red, bromophenol blue and bromocresol green were studied by Rosendorfova and his coworkers[97], and the influence of a strong electrolyte (NaCl) on these micellar effects was investigated as well. Kohara and coworkers[200,201] have studied the effect of tetradecyldimethyl-benzylammonium chloride (zephiramine) on the shift in pK_a's of bromophenol blue and bromocresol green. From the rates of association of three azo-indicators, viz., methyl orange, methyl red and pyridine-2-azo-*p*-dimethylaniline (PADA), with the micelles of SDS and CTAB, it was suggested that the interactions between the neutral indicator species and the surfactant micelles were much weaker as compared to those between the charged indicator species and the micelles of opposite charges[202]. Rychlovsky and Nemcova[203] investigated the effect of ionic and non-ionic surfactants on the acid - base equilibria of phenothiazine derivatives, diethazine hydrochloride and chlorpromazine hydrochloride, and they are of the opinion that the presence of cationic and non-ionic surfactants strongly

enhance the dissociation of the derivatives, while the anionic surfactant had a reverse effect. They had made an attempt to explain these effects on the basis of the theory based on a pseudophase, ion-exchange model of micelles. Fernandez and Fromherz[204] had investigated the effect of micelle on the pK_a of hydroxycoumarin and aminocoumarin dyes and the shift in pK_a was attributed to the change in polarity of the indicator species, whereas polarity change and difference in electric potentials (at micelle surface and the aqueous bulk) were said to be responsible in case of ionic surfactants. The change in absorption spectra of methyl orange and analogous *p*-aminophenylazobenzenes in organic and aqueous - organic solvents as well as in micellar surfactant media was interpreted in terms of different interactions existing between the indicator and the media[205]. Baumgartner et al [206] studied the change in apparent pK and visible spectra of neutral red and bromothymol blue produced by certain polyelectrolytes. They observed appreciable changes in the pK_a when the indicators had opposite charge to that of polyions, and this was attributed to the "polyelectrolyte effect" due to the large charge density on the polymeric chain. Ferguson and Mau[207] studied the spectral character of acridine organge, 3,6-diaminoacridine and rhodamine B, dissolved in ethanol, and demonstrated that the spectral changes, thought to involve monomer-dimer system are actually due to the acid-base equilibria of the indicator dyes. In another study, Hiskey and Downey[208] investigated the interaction between octadecyltrimethylammonium bromide and methyl organge over a wide range of pH at different concentrations of the surfactant, and the changes in spectral

character of the indicator was interpreted in terms of the association between the cationic micelle and basic form of the indicator, which eventually led to an increase in acid ionization constant of the indicator.

The reasons for the spectral changes in the micro-environment of (cationic) micelles have been given by several researchers[209-211] One of the possibilities was the different possible sites of solubilization of azo-indicators having different chromophores, like-COO^-, - SO_3^- groups, etc.,(and hence the feasibility of interactions between the chromophores and the surfactant micelle[212]). The micellar effect on the change in dissociation constants of triphenylmethane dye indicators was studied by Chernova and his colleagues[94,213,214], and the change was attributed to the interactions occurring between the sulphonic acid groups of the indicators and the surfactant micelles. Garcia and Medel[212] had proposed that the proton - release occurred during the interaction between an anionic dye and a cationic surfactant and this produced a spectral change similar to that observed on increasing the pH of the indicator solution. The changes in pK_a values and absorption spectra of various indicator dyes, in micellar media, have been attributed to a number of factors, namely due to the influence of surface potential of the micelles[198,204,215] or due to the reduction of the difference in free-energy between the acidic form of the indicator and its anionic in the micelle[141,208,210,216]. Oldfield et al[217] studied the acid - base behaviour of 4-nitrophenol and 4-nitrophenyl-2-sulphonate in w/o - microemulsions, stabilised by the surfactant sodiumbis-2-

ethylhexylsulphosuccinate (AOT). The pK_a values of 4-nitrophenol in microemulsions were found to be higher than those in aqueous solutions, whereas it was not so for the other compound. The shift in pK_a of nitrophenol was attributed to it partitioning out of the aqueous domain. Recently, Drummond and his coworkers[218-221] carried out extensive studies on acid - base equilibria of a number of phenols, amines, carboxylic acids and a variety of indicators, viz., a few sulphonphthalein and azo-indicators and azine - derivatives in aqueous and micellar media, in order to understand the effect of aqueous surfactant micelles and different organic solvent mixtures. For the majority of the compounds studied, the shift in their pK_a values in aqueous micellar phase was attributed to the differene in solvent (or medium) properties at the surface of the micelle and in the bulk with an additional contribution from the electrostatic micellar surface potential in the case of ionic aqueous micellar solutions. In case of equilibrium study of sulphonphthalein indicators in aqueous micellar solutions of cationic and non-ionic surfactants, the factors reported to be primarily responsible for the change in pK_a's in two different environments/media, were the electrostatic micellar surface potential, the low effective dielectric constant at the interface and either an interfacial `salt effect' or the formation of ion-pair between the oppositely charged indicator species and the surfactant micelle[219]. Similar interpretations were given for the azo-indicators, whose acid-base equilibria were investigated in aqueous micellar solutions of cationic, anionic and non-ionic surfactants, as well as in organic solvent-water mixtures[221].

For neutral red and acridine, in anionic surfactant micellar media, an additional factor, the specific molecular interaction, was proposed for the shift in pK_a values of the indicators[220].

The change in pK_a values of an azo-indicator, methyl red (discovered by Rupp and Loose[222]), in different solvents and solvent - mixtures have been studied by a number of researchers[175,182,221], and the effect was primarily interpreted in terms of the change in dielectric constant of the media. The indicator was reported to exist in three forms in an aqueous solution, cationic, zwitterionic and anionic; which made it highly complex in nature[223], due to which, probably, not many researchers had made attempts to study the effect of various micellar media on its pK_a.

I.5 TRANSPORT NUMBER STUDIES

The transport number measurements in electrolytic solutions have been the subject matter of investigation for more than a century. The transport number is generally defined as `the fraction of current/electricity carried by an ion-constituent of the electrolyte'. Noyes and Falk[224] had reviewed the earlier work (including the reliability of the data) on the transport number. From the literature data one can see that most of the studies on transport number determination were carried out on `uni-univalent' electrolytes of very low concentrations. Longsworth[225,226], in the thirties, determined the cationic transport number of some symmetrical (1:1) electrolytes, like a few alkali-halide salts, hydrochloric acid etc. at room

temperature by moving boundary method. A decrease in the transport number, [in all the cases (except HCl)] with an increase in electrolyte concentration was noticed. Stokes[227] had made an attempt to test the applicability of interionic attraction theory on the concentration dependence of transport numbers of uni-univalent electrolytes. Milios and coworkers[228] had derived a new equation applicable to moving boundary method for determining transference numbers at high as well as low concentrations of uni-univalent electrolytes. Perie et al [229] had examined the applicability of molar conductance equations for a number of electrolytes in order to obtain suitable equations for the concentration dependence of single ion conductances, which were reported to be useful in testing the concentration dependence of the transport numbers determined experimentally. Jones and Bradshaw[230] had determined the transport number of LiCl at room temperature by Hittorf method over a large concentration range 0.023 to 2.95N and were found to agree with the equation $t = [1.3337/(1+0.03605\sqrt{c})]-1$. These results were not found to agree with those obtained by MacInnes and Beattie[231]. Roessler and Roessler and Schneider[232] determined the cationic transport numbers of $AgNO_3$ over a large concentration range, and the data were used to calculate the transport coefficients. When one critically eamines the available data, it is evident that hardly any systematic work was carried out to investigate the effect of (higher) concentration on the transport number of ions[233-238].

The studies on the effect of concentration on the transport number of unsymmetrical electrolytes (2:1) reveal that the

transport numbers of such electrolytes at low concentrations exhibit the similar trend of variation with change in concentration (i.e., the decrease in transport number with an increase in concentration of the electrolyte) as that of symmetrical electrolytes (1:1)[239,240]. Lucasse[241] determined the transport numbers of alkaline - earth chloride salts from the e.m.f. measurements, and suggested that the equivalent conductance of chloride ions is independent of the cation-constituent at any given concentration of the electrolyte. Jones and Dole[242] from their experimental data on 2:1 electrolytes suggested that the e.m.f. method of transport number determination was as accurate as any other analytical method, and a correlation between transport number and electrolyte concentration was suggested.

There have been hardly a few reports on the effect of temperature on transport number of ions in aqueous solution [243-246]. From the existing limited data, one is not able to say whether the transport number of cation increases with the increase in temperature or decreases.

Even though measurements of transport numbers of ions in aqueous (1:1 electrolytic) solutions have been the subject matter of numerous investigations, data on 2:2 electrolytes in aqueous solutions and their dependence on electrolytic concentration and temperature have been very few[247,248]. Fritz and Fuget[249] determined the transport number of copper sulphate solutions of varying concentrations by moving boundary method. However, the experiments were carried out at very low concentration of

electrolyte. Dye et al[250,251] had made an attempt to apply the Fuoss-Onsager conductance theory[252-254] to the conductane data of the electrolyte, and the transport number of aqueous $ZnSO_4$ solution was measured as a function of concentration (the concentrations of the electrolyte were very very low). The transport number of Zn^{++} ions were reported to decrease with increase in concentration of $ZnSO_4$, and were consistent with the Onsager conductance law. Pikal and Miller[255] determined the cationic transport number of Cu^{++} ions in aqueous $CuSO_4$ solution at room temperatures by Hittorf method, and the cationic transport number was found to decrease with the increase in concentration of electrolyte; the trend was reported to be in agreement with that observed by Fritz and Fuget[249]. It was proposed by the researchers that transport number results could be used in determining the Onsager transport coefficients, l_{ig}[255]. The other system studied was $MgSO_4$, in which the cationic as well as anionic transport numbers were determined at constant temperature[256]. The concentration dependence of the transport number of the electrolyte was investigated for its fit to Fuoss-Onsager[257,258] and Pitts[259] theories of conductance, and the variation in transport numbers was well accounted for by the former. On the other hand, Sidebottom and Spiro[260] had pointed out that these two conductance theories were not valid at higher concentrations of the electrolyte.

From the literature it is evident that most of the researchers, on the basis of their data on 1:1 electrolytes (at low concentrations) were of the opinion that cation transport numbers decrease with an increase in electrolytic concentration and tend

to approach a value of 0.5 with increase in temperature[261], while in cases like, HCl[225], KNO_3 and CH_3COONa[226], K_2SO_4[239], $ZnBr_2$ and $AgNO_3$[243], it was not so. In addition, it is to be noted that when the concentration of electrolytes like $CuSO_4$ is changed, the pH of the aqueous medium (due to the hydrolysis of the salt) also changed[262] and this alters the amount of electricity carried by the ionic species. So, in such cases if one wants to determine the cationic transport number of electrolyte, the pH of the solution should be kept constant. The transport number measurements for aqueous $CuSO_4$ made by Emel'yanenko and cowokers[263] showed that the cationic transport number increased with increase in electrolytic concentration, at constant temperature, which was anamolous to the results reported earlier for other bi-bivalent electrolytes.

Care has been taken to give proper credit for the work of other authors in the literature. The author would like to apologize for any omission which may have occurred by oversight or error in judgement.

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