CHAPTER - I

GENERAL INTRODUCTION
Surface Active Agents and Their Behaviour in Solution:

The modification of surface characteristics of fluids in the presence of substances introduced from outside is of tremendous utility. Such type of foreign substances derived mostly from fatty acids, fatty alcohols, alkyl phenols, alkylamines, mercaptans and from other variety of sources are known as surface active agents or surfactants. Surfactants, surface active agents, also called detergents, are amphiphilic, organic or organometallic molecules where a polar head group attached to a long non-polar tail provides distinct hydrophobic and hydrophilic functionalities. Owing to the polarity of the distinct regions these substances have also been referred to as amphipathic, heteropolar or polar-nonpolar substances. The polar-nonpolar character is responsible for the unique properties of surfactant molecules in solution which render possible applications in detergency, cleaning, wetting, flotation, emulsification, dispersion, foaming etc. The factor responsible for desired surface activity is the balance between lyophobic and lyophilic characteristics of these molecules.

Aqueous solutions of surfactants or amphipathic molecules, at a minimum concentration, referred to as critical micelle concentration (CMC), associate dynamically to form normal micelles. Depending upon the nature of the hydrophilic head group, micelles can have either cationic, anionic, zwitter-
rionic or nonionic surfaces. The number of monomers that aggregate to form a micelle is called the aggregation number \( N \). Typically the CMC's are in the range of 0.01-10.0 mM, with each micelle consisting of 40-180 monomers\(^{12}\). Micelles do not exist at all concentrations and temperatures. For a given surfactant at a given temperature, there is a narrow concentration range below which aggregation to micelles is absent and above which association leads to micelle formation. In other words certain amount of monomers can be accommodated in the cavities and any further addition of surfactant monomers provides a driving force to minimize contact of the monomer-hydrocarbon chains with water and resulting in the aggregation (micelle formation). This narrow concentration range during which micelle formation occurs is called the CMC.

It is interesting to note that although it is usually assumed that there is a fairly well-defined water 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 hydrocarbon chains mixed with water. Water penetration into the micellar core is still a matter of controversy. Many spectroscopic studies indicate that there is significant penetration of water into micelles\(^{13,14}\). Recent fluorescence studies on the hydrogen bonding in micellar aggregates\(^{15,16}\) indicate that the distinction between polar and non-polar sites in the micelle is inaccurate; in fact, it has been proposed
that micelles are loose and porous structures in which water and hydrophobic regions are constantly in contact\(^ {17,18}\).

Current thought on this controversial "water exposure of micelles" is founded mainly on low-angle neutron scattering experiments which allow the study of unperturbed micelles\(^ {19}\). This modern concept discusses the main characteristics of the molecular conformation in micelles in terms of the predictions of the "interphase model"\(^ {20}\). Interphase theory predictions are in agreement with experimental data and are particularly consistent with some principal features of micellar structure\(^ {19}\).

1. The micellar core is virtually devoid of water, according to Langmuir's original principles of differential solubility\(^ {21}\).
2. Micellar chains are randomly distributed and steric forces determine the final structure;
3. Contact of the hydrophobic sections of the micelles with water results from a disorderly structure in which terminal groups or chain ends are near the micellar surface and thus exposed to bulk water\(^ {19}\).

Although the "water penetration" concept of the hydrophobic sections of micelles is now less acceptable than the "water exposure" concept, this controversial topic is still a matter of debate\(^ {22,23}\). The exact structure of
Fig. 1 Various structural models for micelle
an aqueous micelle is not known with certainty, although several intelligent guesses have been put forth. Figure 1 depicts some of these models. A conventional representation of micelle is that by Hartley (Fig. 2) and is more acceptable and useful for visualization.

Though micelles provide a microscopically heterogeneous environment, they are generally small enough for the macroscopic properties to approximate to those of truly homogeneous solutions. Moreover, the surfactant molecules are in dynamic equilibrium either between two micelles or between a micelle and bulk water. The hydrophobic interior of a micelle provides a restricted volume of hydrophobic space in an aqueous environment.

Surfactant molecules can be considered as building blocks of micelles. It is possible to obtain various types of structures of surfactant molecules by simply increasing the concentration of surfactant in water with a concomitant change in the size of the aggregates. The spherical micelles formed near the CMC become cylindrical ones which may be converted into a hexagonal packing of surfactant molecules to lamellar structures by increasing the concentration of surfactant in aqueous medium. Further concentration increase leads to the conversion of lamellar structures to hexagonal packing of water cylinders (Figure 3).
Fig. 2   Hartlay model of a spherical micelle
Fig. 3

It is possible to induce a transition from one structure to another by changing the physico-chemical conditions such as temperature, pH or by addition of mono or divalent cations and other additives in the surfactant solution.

Upon sonication above their phase transition temperature, many long chain surfactants assemble to form single or multicomponent bilayer vesicles. Compared to micelles the kinetic stability of vesicles is much greater as is their size. Typically their size range 2000–10,000 monomers per vesicle. Also, they are more "rigid" and can entrap and retain solubilizates.

Surfactants in polar solvents, in the presence of traces of water, associate to form the so-called reversed/inverted micelles. The structure of these aggregates is inverted compared to that of normal micelles and can be thought of as a surfactant entrapped water pool in the bulk hydrocarbon solvent. The size and properties of reversed micelles vary with the amount of water present.

The reversed micellar system can be characterized by a variety of physical techniques such as viscosity, centrifugation, light scattering, NMR, IR, vapour pressure osmometry and small angle X-ray scattering. The reverse micellar size depends on the kind of polar groups.
of surfactant and the magnitude of their size decrease in the order: sulfonate > carboxylate > sulfate. It was reported that micellar size depends least on solvent character for anionic surfactant and independent for cationic surfactant. In recent years there has been an increasing interest in studying structure of aggregates of surfactants in apolar solvents because of their potential application as catalysts for chemical reactions, as a simple model for enzymatic reactions, and in the preparation of fine colloidal particles. A typical reverse micellar representation is shown in Figure 4.

When more than one surfactant are present in aqueous solution, they form a mixed micellar system. The surface activity of a mixed surfactant system is reported to be superior to that of the single one. The properties of surfactant solutions depend on the structure of mixed micelle i.e. the size and arrangement of components in the micelle. In the case of mixed micelles whose components have the same ionic nature i.e. ionic-ionic or nonionic-nonionic the structure of mixed micelle is expected to be similar to that of each single micelle. It means that mixed micelles are formed in the same manner as the single micelle, in which specific interactions between different surfactant molecules have been excluded. Therefore CMC of mixture of ionic-ionic or nonionic-nonionic surfactants in aqueous
FIGURE 4

Monomer solution
(Ideal solution)

Micelle
(Hydrocarbon part)
(Nonideal solution)

REVERSE MICELLE
solution and also the Kraft point have been predicted theoretically$^{42,43}$. However, it is difficult to predict theoretically the CMC of the mixture of nonionic and ionic surfactants in aqueous solution because of specific interactions between components and also because of the difference in status of hydrophobic and hydrophilic parts of components in the mixed micelles$^{44}$.

However, theoretical equations have been formulated to explain the changes in CMC of mixed surfactants$^{45,46}$. Pseudophase separation models have been developed to treat mixed micellization in binary surfactant mixtures$^{47}$. Recently a "mass action" model of mixed micellization was given, which may be preferred over the simpler pseudophase separation model$^{48-50}$.

Micelles provide several unique properties which make their extensive use in many disciplines and have many practical applications in analytical chemistry$^{51-54}$, enhanced oil recovery$^{55}$ and in many other areas$^{56,57}$. The solubilization capacity of micelles make them more useful in a variety of chemical and photophysical processes. An oversimplified artistic conception of a cross section of an aqueous normal micelle with different solubilization sites$^{58}$ is shown in Figure 5. Several other unique abilities and properties possessed by micelles are their capability to
Fig. 5 A cross section of an aqueous normal micelle with different solubilization sites. A and B represent same and opposite charge solute to the micelle while C and D represent the nonpolar and amphiphilic solutes (taken from "W.L. Hinze, H.N. Singh, Y. Baba and N.G. Harvey, trends in analytical chemistry, 3(8), 193 (1984),"
concentrate, compartmentalize, organize and localize reactants/solutes; alter effective microenvironments (such as polarity, dielectric constant, viscosity) about solubilized solutes; alter chemical pathways and rates; alter spectral parameters of solubilizates; alter photo-physical pathways and rates; stabilize reactants, intermediates and products, alter quantum efficiencies; alter the position of equilibrium (such as dissociation constants); alter redox properties (potentials); maintain product and/or reactant gradients; separate products (charges); alter drastically surface properties; be chemically stable, optically transparent, photophysically inactive, and on the whole, relatively "nontoxic".

Microemulsion Systems:

There are difficulties experienced by the researchers in reaching a common ground on the definition of the term "microemulsions". A number of definitions have been proposed, but no clearcut definition emerged. The only common definition described these clear (or sometimes lactescent) systems as containing one polar liquid (generally water or saline), a hydrophobic liquid (the "oil phase"), and a selected (one or several) surface active agent. These systems are thermodynamically stable, isotropic dispersions consisting of microdomains of oil and/or water stabilized by interfacial film of surfactants.
The word "microemulsion" was originally proposed by Jack H. Schulman and co-workers in 1959, although the first paper on the topic dates from 1943. They prepared a quaternary solution of water, benzene, hexanol, and potassiumoleate, which was stable, homogeneous, and slightly opalescent. These systems became clear by the addition of a medium chain alcohol. In the year between 1943 and 1965, Schulman and co-workers described how to prepare these transparent systems. The summary of the basic observation is that: when a cosurfactant is titrated into a coarse emulsion (composed of a mixture of water/surfactant in sufficient quantity to obtain microdroplets/oil), the result may be a system which is low in viscosity, transparent, isotropic, and very stable. The transition from opaque emulsion to transparent solution is spontaneous and well defined. It was found that these systems are made of spherical microdroplets with a diameter between 60-800 angstroms. It was only in 1959 that Schulman proposed to call these systems microemulsions; previously, he used the terms such as transparent water and oil dispersions, oleopathic hydromicelles, or hydrophatic oleomicelles.

Later on it was established that microemulsions or solubilized systems can exist in equilibrium with excess of oil, water or both. Winsor referred to these respective
equilibria as type I, II and III\textsuperscript{69-71}. He showed qualitatively that the transitions \( I \Rightarrow III \Rightarrow II \) are dependent on the hydrophilic versus lipophilic character of the surfactants (HLB)\textsuperscript{72}, salinity, oil composition and temperature. Shinoda and co-workers experimentally defined these transitions as functions of temperature and ethylene oxide content for cosolubilized oil and water systems prepared with nonionic surfactants\textsuperscript{73-76}. The single/2-phase boundaries for type I and type II systems were described on temperature composition diagrams\textsuperscript{77,78}. These boundaries were found to be shifted with variation in HLB (ethylene oxide content, hydrocarbon chainlength and added anionic surfactant), oil type and added salts\textsuperscript{77-79}. Similar effects were observed by Kon-no and Kitahara for the solubilization of water and aqueous salt solutions in non-aqueous media (Type II systems) by cationic\textsuperscript{80}, non-ionic\textsuperscript{81} and anionic\textsuperscript{82,83} surfactants.

In order to explain the "spontaneous" formation of these microdroplets and their stability, the following explanation was advanced by Schulman: recall that \( \gamma \)-surface pressures can be obtained spontaneously by the monolayer penetration of an alkyl alcohol or cholesterol monolayer with ionic surface active agents such as salts of alkylsulfate and alkylamines and substituted amines injected into the solution (at constant area of the insoluble monolayer).
The value of $\kappa$-surface pressures at the air/water interface can reach values of more than 60 dynes/cm (although the collapse $\kappa$-pressure for single component monolayers on their own are below 35 dynes/cm). If the surface pressure is held constant, or below the 60 dynes/cm but above the 35 dynes/cm, immediate expansion of the interfacial area takes place as the molecules of ionic surfactant penetrate the monolayer at the air/water interface. The analogous penetration of the mixed film by oil molecules at the oil/water interface increasing the surface area is the basis for the formation of microemulsions. However, the penetrating pressure in this case must be greater than the oil/water surface tension $\gamma_{o/w}$, which is always less than $\gamma_{a/w}$ tension of 72 dynes/cm, which is approximately 50 dynes/cm for aliphatic hydrocarbon and 35 dynes/cm for aromatic hydrocarbon compounds.

Therefore, it is progressively easier to obtain negative interfacial tension for these systems, provided that the oil molecules can penetrate the interfacial film. Rosano et al measured the change in the water-oil interfacial tension while alcohol was injected into one of the phases. It was found that the interfacial tension may be temporarily lowered to zero while the alcohol diffuses through the interface and redistributes itself between the water and oil phases making it possible for a dispersion to occur.
spontaneously. A sufficiently low positive value of $\gamma_i$ is always better for emulsion (macro-or microemulsion) formation; nevertheless, below a certain positive small equilibrium value of $\gamma_i$ phase separation, sol or gel formation will be produced but not emulsification.

Schulman referred to a microemulsion with special properties. This idea has been reiterated by, Gerbacia, Carey and Becher. Other workers consider microemulsions as solubilized systems or micellar solutions; a growing number in fact refer to the "so called microemulsion". Osipow in his discussion on transparent emulsions claims that there is no valid method to distinguish between microemulsions and solubilized systems. McBain and O'Connor distinguished between solubilization and emulsification. They showed that in the case of hydrocarbon solubilized in a soap solution, the vapour pressure of the solubilized material is lower than that in the bulk phase; such solutions are thermodynamically stable and their properties are solely dependent upon temperature, composition and pressure. In an emulsion, however, the vapour pressure of the droplet is actually higher than the vapour pressure of the bulk.

The phase behaviour of water, oil and surfactant mixtures is now a subject of considerable importance, primarily because of its importance to oil recovery but also
because transparent or translucent phases containing oil and water together with surfactant (microemulsion) are of scientific interest\textsuperscript{92-103}. In Winsor's terminology the simplest phase behaviour of microemulsion can be divided into three distinct categories\textsuperscript{70}. The phase study is convenient for determining the optimum mixing ratio of the surfactant and cosurfactant and also for determining the extent of solubilization of oil in water or water in oil in the presence of a definite amount of total surfactant together with cosurfactant\textsuperscript{104}. It also provides contour maps for studying the physical properties such as interfacial properties and stability of various useful phases.

Palit studied solubilization by a series of quaternary ammonium soaps, and found regions in phase diagram designated $S_1$ and $S_2$ which are thermodynamically stable micellar solutions with water or oil as the continuous phase respectively\textsuperscript{105}. He found that when solubilization is high, there may be a channel between the two regions $S_1$ and $S_2$, this channel region shows some properties of the neighbouring gel or liquid crystalline phase. However, the border line between the channel and gel phase is not clearly defined. It is possible therefore that systems in this region were mixture of the two phases that at equilibrium may separate, although such a separation process may take a long time\textsuperscript{106}. 
Winsor showed that regions $S_1$ and $S_2$ may be separated upon increase in temperature and could form a channel between $S_1$ and $S_2$.

Another group that studied microemulsion phase behaviour is that of Ekwall, Friberg and others. They refer to the $L_2$-region in the phase diagram which is a solution of reversed micelles similar to Palit's $S_2$ region, as the 'so-called microemulsion'. Friberg states that "when the interphase tension is zero, so-called microemulsions are formed which cannot be considered true emulsions. There are solutions with solubilized water or solubilized hydrocarbons." In phase diagrams presented by Ekwall et al., there is a sharp borderline between the emulsion region and $L_2$ or $L_1$ regions. NMR study of water peaks in $L_2$ region showed that this region is stabilized partially due to maximum amount of bound water. The correlation of phase diagrams and emulsion stability was dealt with by Friberg and coworkers. Friberg found that the emulsion stability of a system will depend on the position of that particular system in the phase diagram. Temperature changes and an addition of fourth component were found to affect the position, and shape and size of various phases due to structural changes in the system.

One aspect of phase diagram study that has been somewhat overlooked is the state of the systems. Some systems
which have been defined as "very stable" have been shown to be unstable after sometime, whereas some so-called microemulsions show excellent stability, others do separate into two phases. The question of whether the systems are in equilibrium or a state of reaching equilibrium at a very slow pace need attention. It is possible that micellar solutions, L systems, or microemulsions in certain areas of the phase diagram are in a metastable state particularly close to phase border. An optimum system is defined to be one for which the surfactant rich middle phase contains equal volumes of both oil and water and it has been shown that such systems are optimal or nearly optimal with respect to oil recovery\textsuperscript{115-117}. The conditions under which the surfactant has equal affinity for oil and water were found to correspond to those which are type III\textsuperscript{118,119}. Thus, factors which influence surfactant partitioning between oil and water also determine the surfactant phase behaviour.

Microemulsion phase behaviour is often described in terms of pseudo components which are assumed to behave as single component. Pseudocomponent pairs are for example, surfactant plus alcohol, salt(s) plus water. The effect of salt(s) on phase behaviour is very pronounced, although brine is frequently regarded as a single pseudocomponent\textsuperscript{120,121}. Recently it was shown that each component influences phase behaviour, which means that phase behaviour cannot be fully described by assuming single phase pseudocomponents\textsuperscript{122}. 
In Winsor type II systems, a non uniform partitioning of the system has been observed; namely, the concentration and composition of the inorganic electrolytes may be different in the excess brine phase and the brine contained in the micellar phase. Such partitioning yields difficulties in representing and interpreting the phase behaviour of surfactant-alcohol-brine and oil mixtures by considering brine as a pseudocomponent. In several cases, pseudophase model has been proved successful to choose appropriately the pseudocomponents able to draw simplified and tractable two-dimensional phase diagrams from three-dimensional experimental phase diagrams exhibiting quite complex tropologies. Such simplified phase diagrams, which turned out to exhibit the overall features of ideal Winsor's diagram, have recently proven convinient to incorporate the phase behaviour information into numerical simultors for enhanced oil recovery applications.

The effect of inorganic salts on the phase behaviour of mixtures of water, oil, and ionic surfactant is well known since the pioneering work of Winsor. In particular, special attention has been devoted to the transition between Winsor I, III and II systems which can be achieved through a number of ways, but changing the salt concentration has been specially investigated because of its application in the
salinity gradient technique\textsuperscript{132,133}. In these systems the interfaces between the microemulsions and the phases in excess were found flat by visual observation and appeared sharp or diffuse for systems far or close to critical points, respectively, the thickness being always smaller than $1000 \, \text{Å}$.\textsuperscript{134} The microemulsion domains were found to be considerably reduced in presence of inorganic salts\textsuperscript{122,135} because salt decreases the solubility of water and shrink the microemulsion region of the ternary phase diagram\textsuperscript{83}. Further, using viscometry and dynamic light scattering, Bedwell and Gulari reported that NaCl moderates the attractive interactions between the microemulsion droplets by making the droplets smaller\textsuperscript{136}. The droplets were assumed to behave more like hard spheres at low water content for a constant surfactant to salt molar ratio. It has been concluded that since sodium chloride being dispersed uniformly in the droplet core so that it does not have a preferential interaction with the interior surface occupied by the surfactant.

An understanding of phase behaviour under various conditions is indispensable in utilizing microemulsions as reaction media as well as a versatile solvent.

**Role of Cosurfactant in Microemulsion Systems:**

It is intrinsically important to change the HLB of a surfactant mixture continuously by various devices in order
to attain a large solubilization or ultimately complete mixing of hydrocarbon and water with less surfactant.\textsuperscript{104} The devices of cosurfactants, surfactants and their combination yielded very large solubilization.\textsuperscript{137} In most microemulsion systems, a cosurfactant (or cosolvent) is generally used in combination with the primary surfactant. The issue concerning the role of this added component and the understanding of necessity for adding them has paralleled the research and development of microemulsion technology since they were originated.\textsuperscript{70,71}

More recent studies for enhanced oil recovery processes have revealed several different phenomena associated with the presence of alcohol in microemulsion systems.\textsuperscript{102,103,134}

The most fundamental role of alcohol is probably its ability to destroy liquid crystalline and/or gel structures which obviate the formation of microemulsion.\textsuperscript{138} Under certain circumstances, alcohols may be employed not so much as a required ingredient for microemulsion formation but instead, to change surfactant partitioning characteristics or to modify microemulsion properties to meet a specific application such as a desire for clarity of solution. In a detailed phase behaviour study, Salager\textsuperscript{128,139} found that alcohol is only one common controlled variable capable of bringing the surfactant formulation to its optimum state. Salter showed that additions of alcohol depress solubilization in microemulsion,\textsuperscript{140} while others showed that it decreases the sensitivity to
composition fluctuations\textsuperscript{141}. Presumably, the effects of alcohol on solvent properties of oil and water, and the ability of cosurfactant molecules to penetrate the surfactant interfacial monolayer were among those responsible for the cosurfactant functions\textsuperscript{142}. The importance of molecular kinetic conditions of various components, including alcohol, during microemulsification have been emphasized by Gerbacia and Rosano\textsuperscript{87}. An example was given where the occurrence of a favourable kinetic regime was necessary for microemulsion formation. The same line of thought with regard to the dynamic role of cosurfactant was suggested in the work on micellar solution containing alcohols\textsuperscript{143}. The requirement of alcohols in microemulsion formation has been justified on the basis of the fact that alcohol molecules are sufficiently short in length to provide a fast molecular diffusion for spontaneous emulsification and sufficiently large in size to provide enough interfacial molecular interaction for good solubilization of water (or may be oil)\textsuperscript{144}.

Several authors have stressed the striking influence of alkanols conformation upon different physico-chemical properties of water-in-oil (w/o) microemulsion systems\textsuperscript{145,146}. A thorough comparative study of the electrical conductivity behaviour was performed by Clausse et al\textsuperscript{147}, who pointed out that the distinction between microemulsions and cosolubilized system have been analyzed using the percolation and effective
medium theories. At very high concentrations of hydrocarbon the solubilization of water in microemulsion droplet is strongly reduced owing to the transport of alcohol from the micelles into the hydrocarbon part of the solution.

Recently it has been reported that the use of hexylamine as cosurfactant in place of more commonly used medium chain-length alcohols holds promise of greatly reducing problems associated with solubilization of water at high hydrocarbon levels. It was observed that hexylamine gives excellent water solubilizing capacity at high hydrocarbon levels with extremely low surfactant and cosurfactant content. One of the possible factors which could be responsible for the behaviour is the good solubility of water in cosurfactant coupled with sparing solubility of the cosurfactant in water. The effectiveness of hexylamine as a cosurfactant would appear to hold great promise for industrial formulations where amines can be tolerated. Hexylamine does have a pungent odour and all amines tend to be aggressive. These do pose limitations on the uses of hexylamine. However, if the factor or factors responsible for the effectiveness of hexylamine can be uncovered, then other compounds may possibly be found which could be equally effective but have lower undesirable properties. We see that water is sparingly soluble in pentanol (11%) or hexanol (8%) while being quite soluble (62%) in hexylamine, but completely miscible with pentyamine. Thus hexylamine
is seen to be in an intermediate position between the two extremes as far as ability to dissolve water is concerned. Neither of the alcohols nor hexylamine is appreciably soluble in water. Hexanol is soluble to the extent of 0.6-0.7% by weight, hexylamine about 1% and pentanol about 1.5%\textsuperscript{152}. Therefore sparing solubility in water maybe a necessary condition for a compound to be a good cosurfactant for W/o microemulsion formation at high hydrocarbon levels, but does not seem to be a sufficient condition. These predictions are quite in agreement with the previous concept\textsuperscript{137}.

**Effect of Water in Microemulsion System:**

Depending upon its concentration, water may form water pool or work as a dispersion medium in microemulsion systems. It was demonstrated that as the water content of the inverted micelles was increased, the increase in droplet size was accompanied by an increase in the ratio of alcohol to surfactant in the interface\textsuperscript{153}. The importance of such an observation can be judged from the fact that zero interfacial tension, considered necessary for microemulsion systems, only occurs at intermediate values of this ratio. In benzene system this ratio was quickly exceeded resulting in a macroemulsion at low water content\textsuperscript{154}. In the hexadecane system, because of better association between oil molecules and tails of the surfactant species, the aggregates retained their aggregation status.
despite a high ratio, by changing into cylindrical or lamellar micelles. As more water was added to the lamellar micelles, o/w microemulsions were formed. By NMR studies Menger et al. have shown an increase in water pool size by increasing water contents in a typical microemulsion.

The microemulsions were shown to undergo a series of structural changes as the amount of water was increased. The same type of behaviour was reported by Singh et al. for a typical microemulsion system. Kojikano et al. have shown the morphological change in microemulsion systems upon dilution with water using fluorescence technique. Lindman et al. have shown how self-diffusion measurements on water can be used to study the structure of such systems. They suggest that the interaction of surfactant head group and water greatly influence the transport of water in these solutions.

**Effect of Oil in Microemulsions System:**

In an earlier work on Aerosol OT systems, it was found that the solubilization limit of water in the droplet increases with the increase in the alkyl chain length of hydrocarbons. In contrast, it was also reported that the maximum water solubilization capacity of microemulsions is independent of hydrocarbon nature. Microemulsion formation and their various physicochemical and structural properties are also reported.
to be influenced by the alkyl chain length of oil\textsuperscript{159,165}. The alkenes form water-continuous microemulsion at a considerably lower water content than the corresponding alkanes\textsuperscript{165}. Small angle neutron scattering studies showed the dependence of structure of water droplet on the hydrocarbon chain length of the oil medium\textsuperscript{167}. For a long chain length oil it was found that surfactant aggregation number (N) decreased, went through a minimum and then increased as the oil volume fraction was increased. The initial decrease was attributed to a change of shape of the aggregates from a possible disc like to a spherical shape\textsuperscript{168}. Shah reported that the partitioning of alcohol and surfactant subtly varied by changing the oil chainlength\textsuperscript{165}. Recently Clausse et al. demonstrated that the nature of the hydrocarbon has little influence on the configuration of microemulsion pseudoternary domain of a system whose cosurfactant is either a "long" alkanol (e.g. 1-hexanol) or a typically "short" alkanol (e.g. 1-butanol) but greatly for a medium chain alkanol i.e. n-pentanol\textsuperscript{169}.

**Role of Surfactant in Microemulsion System:**

Surfactant plays a central role in microemulsion system. Depending on the chemical nature of surface active agents and the relative constituent proportions, w/o or o/w systems can be obtained. Ionic surfactant is usually strongly hydrophilic hence ionic surfactant needs lipophilic
cosurfactant for larger solubilization. However, nonionic surfactants change their phase inversion temperatures (PIT) gradually with their oxyethylene chain length, so that a single optimum nonionic surfactant whose PIT is close to a given temperature exhibits large solubilizing power. The PIT is the temperature at which the emulsifier shifts its preferential solubility from water to oil when the temperature is increased. But it is well established that nonionic surfactant may be a good solubilizer at optimum temperature (PIT), but only for a limited temperature range. On the other hand, an ionic surfactant is stable with temperature change but needs higher concentration. If the size of the hydrophilic and lipophilic groups of the emulsifier increases, the CMC will decrease, the aggregation will increase and the solubilizing power will be enhanced. So in order to increase the solubilization as well as the size of micelle, ionic or nonionic surfactants with long hydrocarbon chain lengths should be used. This conclusion agrees with the findings by Rosano et al., i.e. the longer-chain sodium alkyl sulfates require a far small amount of alcohol to be added and Schulman's recipes with long chain (C16−C18) ionic surfactants were always employed.

Depending upon the relative effect of all the components of the system, ternary systems may be separate into two or three phases when equilibrium reached. The partitioning of
surfactant determines whether the microemulsion forms in the upper phase, lower phase, or the middle phase, if it is formed. From a surfactant partitioning in various oil/water systems, Shah et al. have shown that as the oil chain length was increased from n-hexane to n-hexadecane, the surfactant partitioning in oil decreased. This surfactant partitioning is important for water solubilization in w/o microemulsion system. In more recent studies it was again confirmed that longer chain quaternary salts are more effective at solubilizing water than are the shorter chain compounds. With quaternary salts of equal chain length, pyridinium salts are more effective at solubilizing water at high oil concentrations then are corresponding trimethyl salts. This was possibly due to the fact that with the aromatic pyridinium salts there would be delocalization of charge as well as less charge shielding than with the trimethyl salts. This affect the interaction of surfactant with water and therefore water solubilizing capacity.

**Thermodynamics of Microemulsion Systems:**

The concept of thermodynamically stable microemulsions evolved via the perceived need for a transient negative interfacial tension to spontaneously form these systems. Ruckenstein and Chi undertook a rigorous thermodynamic treatment of microemulsions to obtain information on stability. Their work indicated that when the free energy change of mixing, $\Delta G_m$, is

\[ \Delta G_m = \text{constant} \]
negative, spontaneous formation of microemulsions occurs, whereas $\Delta G_m$ is positive, macroemulsion can be produced, which although thermodynamically unstable, may be kinetically stable. They found that for a specified composition, it is possible to form thermodynamically stable emulsions of both type (o/w and w/o), of one type, or none at all, depending on the value of specific surface free energy. Moreover, they were able to account for the size of droplets in thermodynamically stable systems and to predict the occurrence of phase inversion. Conditions for thermodynamical stability of emulsions were considered by Wagner.\(^\text{175}\) A number of situations were described in which the interfacial tension was zero. Under these circumstances the Gibb's energy term is small and may be positive or negative. This was observed earlier by Hartley\(^\text{176}\) on the basis of qualitative considerations. In addition, Wagner postulated that a thermodynamically stable emulsion can be obtained only if the concentration of surfactant required for zero interfacial tension is lower than its CMC. He also noted that interfacial tension equal to zero can occur only at an intermediate ratio of surfactant and cosurfactant. Detailed thermodynamics of microemulsions with special reference to their structure and phase behaviour has been recently reviewed by Ruckenstein\(^\text{177}\).