CHAPTER 1

INTRODUCTION

1.1 GENERAL INTRODUCTION

Efforts for achieving mutual solubility of two immiscible liquids were on from the prehistoric days. The solubility of one substance into the other depends upon various factors, particularly the structure of the molecules. A general rule of thumb is "Like dissolves like".

As substances can be roughly divided into polar and nonpolar, it was observed that the polar substances dissolve in polar liquids and nonpolar substances in nonpolar liquids. However, there are numerous natural products where nature gracefully combines two dissimilar properties together, leading to a new type of property called amphiphilic property and the corresponding substances are called amphiphiles. Surfactants are this type of substance. These are larger molecules having a long hydrocarbon chain, representing its hydrophobic group and a hydrophilic group which can be either ionic or nonionic.

These surfactant molecules, thanks to their characteristic structure, may reside at the interface of insoluble water and oil when they are in contact with each other. Adsorption of these molecules at the interface causes reduction of interfacial tension between the two liquids. (When two liquids are insoluble the interfacial tension between the liquids is said to be high). As a result one liquid may disperse into another as small droplets to give rise to kinetically stable systems called emulsions. But these kinetically stable systems did not always satisfy the ever increasing technological requirements. Thermodynamically stable systems were developed which were transparent and containing considerable amount of oil and water together for commercial applications. They used combination of surfactants and medium chain alcohols in such formulation. The medium chain alcohol was termed as cosurfactant. In 1959, Prof.Schulman termed these transparent and thermodynamically stable systems as 'microemulsions'[1] though first scientific paper was published by Hoar & Schulman about microemulsion in 1943 [2].

1.2 WHAT IS MICROEMULSION !

Initially the term microemulsion was given to the transparent system which was obtained by titrating the coarse emulsion with a short chain alcohol [3,4]. The presence of an alcohol causes drastic reduction of interfacial tension (IFT) between oil and water and hence decreases the free energy of interface formation. This helps one phase to disperse effectively into the other. These dispersed droplets are small. Their radii are much lower than the average wavelength of white light. Hence the solution appears transparent to visible radiation [5].

The structural investigations in the last two decades seem to provide a proper definition. Some researchers have strongly argued in favour of distinguishing the microstructural microemulsion systems from other weakly structured surfactant systems containing water and oil [6]. The suggested definition can be written as 'Microemulsions are optically transparent or translucent microstructured fluid systems of oil, water and amphiphiles which are optically isotropic, spontaneously forming, thermodynamically stable systems'. More recent definition by Lindman et al. simply states that microemulsion is a system of oil,water and amphiphile which forms a single optically isotropic, thermodynamically stable liquid solution [7].

1.3 HISTORICAL DEVELOPMENTS

Eventhough it was Prof.Schulman and his group who first did scientific study of microemulsion, such stable dispersions were already familiar to the commercial world [8]. Many of the commercial emulsion products available in early decades of this century, such as carnauba wax emulsion, cutting oils, pine oil, flavour emulsions, pesticide emulsions etc. were microemulsion preparations. Carnauba wax emulsion was the first among this group. It was formulated by George Rodawald in 1928, while trying to minimise the droplet size of his emulsion product. He applied this emulsion on leather surfaces and on floors. It dried to a glossy finish without much buffing to make it shine. He marketed this product under the brand name 'Dribrite' [8]. It was later replaced by higher quality Beeswax emulsion which was also a microemulsion formulation. Cutting oil used in that era also was oil in water (o/w) microemulsion in which lubricating oil was dispersed in water. It served both as lubricating oil and as coolant. Pine oil emulsion, an o/w microemulsion, was in use for many years as a bactericide, fungicide, essential oil fixative and as a floatation agent. Even soft drinks made from microemulsion flavour oil were in the market in 1940s [8]. However these formulations were purely commercial and no proper scientific study was ever made.

Three consecutive papers published in 1940 by Schulman and coworkers laid the foundation for microemulsion study [9-11]. In these papers, they discussed various aspects of oil in water and water in oil emulsions such as their stability, phase inversion and interfacial tension at oil/water interface. These were prelude to the more famous 1943 paper wherein for the first time microemulsion systems were discussed in the scientific literature [2].

The term 'microemulsion', which was first suggested by Schulman in 1959 [1], for this tranaprent stable, oil-water system was not palatable to some researchers [12,13]. Various authors used different terminology like solubilized oil [14], transparent emulsion [15], etc. Shinoda preferred to call it 'swollen micelle' considering the continuity of the formation of microemulsion from micellar solutions [16]. The term like micellar emulsion [17] was also used. But these terminologies seem to have faded away with time and only 'microemulsion' persists.

Conventionally some nonionic amphipathic substances such as medium chain alcohols, amines, fatty acids etc., called cosurfactants,were used in combination with ionic surfactants for the microemulsion formation [15-19]. But with the larger number of components involved, the analysis of data usually became very difficult. Later it was observed that the fourth component, cosurfactant, can be avoided if some nonionic surfactants were used [20,21]. Alternatively it was observed that double chain ionic surfactant like sodium di-2-ethyl hexyl Sulphosuccinate (AOT) serves the same purpose [22] of decreasing the IFT between oil and water. These three component microemulsions were found easier to understand [22-25].

1.4 THEORETICAL ASPECTS OF MICROEMULSION

Though the formulation of microemulsion systems was more or less well understood from the very beginning, the theoretical aspects remained an enigma. From time to time various theories have been suggested to explain the unique properties of these thermodynamically stable, transparent oil-water systems.

Earlier theories proposed by Schulman and others explained the spontaneous formation and thermodynamic stability of microemulsion in terms of negative interfacial tension (IFT) between oil and water [15, 26-29]. They treated the interfacial surfactant film as a third phase. According to these theories, molecular interactions taking place at the interface and the distribution of the alcohol molecules among the phases act together to bring down the IFT towards a negative value [15,28,29] and thereby dissolves water in oil or vice versa and forms microemulsion. However, presently people are not in favour of the concept of negative interfacial tension and hence earlier theories are not acceptable. Shinoda's theory of swollen micelle [16,20,30], is also not very consistant with modern structural studies [31].

Thermodynamic treatment

The thermodynamic treatments suggested by Ruckenstein et al. [32,33] and by Overbeek [34] succeeded to a fair measure to explain the thermodynamic stability of microemulsion.

According to Ruckenstein the free energy of microemulsion formation ΔG_m consists of three parts - an interfacial free energy term, ΔG_1; an energy of interaction between the droplets term, ΔG_2 and an entropic term arising out of the dispersion of the droplets in the continuous medium, ΔG_3.i.e.

$$\Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3$$

However ΔG_1 has contribution from two phenomena. One was due to the creation of an uncharged surface (γdA) where γ is IFT and dA is the change in area (A) and other was due to the formation of an electrical double layer which arises whenever an interface is formed. ΔG_2 was calculated by adding the pair interaction potential of the droplets either by a continuous integration method or a discontinuous addition method whereby the interaction potentials of nearest neighbours were summed up. The entropic contribution, ΔG_3 was calculated using a lattice model. The number of configurations possible (Ω) for a liquid mixture with N_1 molecules of dispersed phase and N_2 molecules of continuous medium was determined using this model. Then Boltzman relation was used to calculate entropy of distribution $\Delta S_m = K \ln \Omega$ and ΔG_3 was taken to be equal to $T \Delta S_m$.

Now condition for the spontaneous formation of microemulsion with most stable droplet size R^* for a given volume of dispersed phase is given by

$$\frac{d\,\Delta G_m}{dR} / R = R^* = 0 \quad \text{and}$$

$$\frac{d^2\,\Delta G_m}{dR^2} / R = R^* > 0$$

The variation of ΔG_m with 'R' can be four types (Fig.1.1). These illustrate the (i) instability (D) (ii) kinetic stability (C) and (iii) thermodynamic stability (A & B).

ΔG_m reaches a minimum value (i.e. very negative) when $R=R^*$ satisfying the condition of thermodynamic stability.

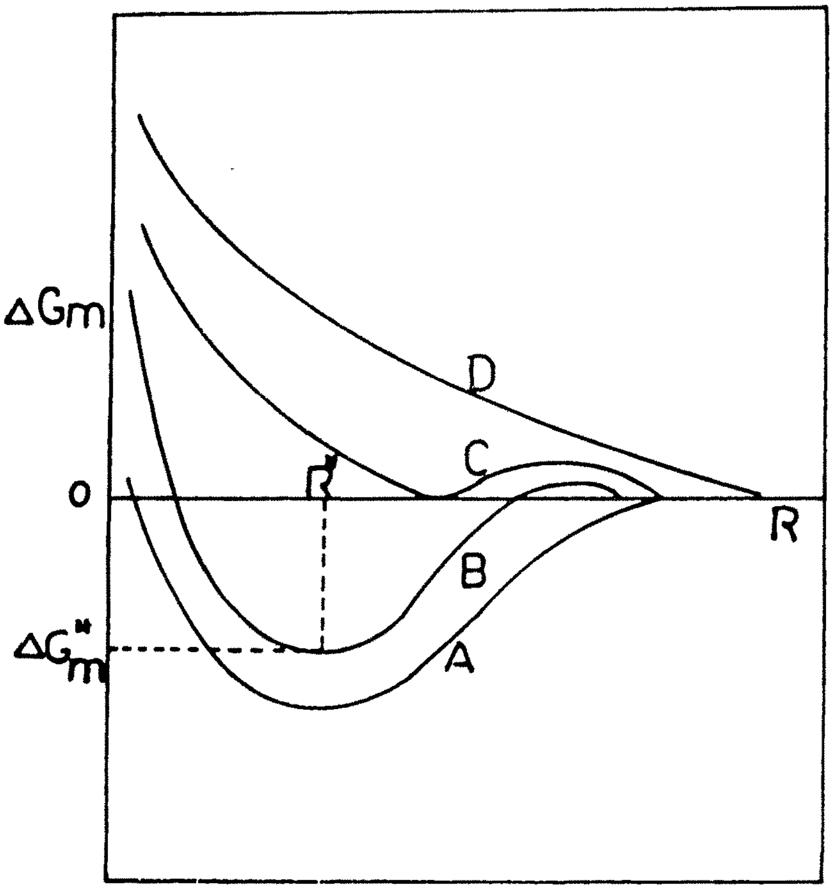

Fig.1.1 The variation of free energy change, ΔG_m, of microemulsion droplet formation, against the radius of the droplet, R. (Ref.26)

By comparing values of ΔG_m at R^* for o/w and w/o, one can easily predict the most stable type of microemulsion in a given composition (whichever gives the lowest value for ΔG_m, has the highest stability). The phase inversion becomes possible when ΔG_m for both oil in water (o/w) and water in oil (w/o) types become equal.

Ruckenstein further extended this theory to account for the drastic reduction of specific surface energy (f) (and hence ΔG_m) in presence of surfactant and cosurfactant. He explained it in terms of so called 'dilution effect' [35,36].

Accumulation of surfactant molecules at the interface in presence of cosurfactant does decreas the interfacial tension. Moreover it results in the reduction of the chemical potential of the surfactant in the bulk solution. This reduction overcomes the positive free energy caused by IFT and hence overall ΔG of the system becomes negative.

Overbeek's thermodynamic treatment is also similar to Ruckenstein's in approach but differ in details [34]. He also subdivided ΔG_m into three parts, ΔG_1, ΔG_2 and ΔG_3. ΔG_1 is due to Gibbs energy of mixing of surfactant with water and cosurfactant with oil. ΔG_2 is due to the interfacial area and ΔG_3 is because of the distribution of droplets into the continuous medium. By assuming negligible solubilization between oil and water, cosurfactant and water and surfactant and oil, ΔG, simply becomes the sum of the product of the number of moles of each component and the corresponding chemical potential. ΔG_2 is determined by the product of the final interfacial tension and area of interface plus a chemical potential term due to the adsorption of surfactant and cosurfactant. ΔG_3 is obtained by using the hard sphere model of Percuse - Yevick [37] and Carnahan and Starling [38]

The merit of these thermodynamic treatments is the quantitative approach it followed successfully to explain the stability and formation of microemulsion.

1.5 STRUCTURAL ASPECTS OF MICROEMULSIONS

Microstructure of the microemulsion which distinguishes it from other isotropic surfactant mixtures have been the subject of much discussion [39-42]. But many of unanswered questions remain which keep the researchers interest still alive [43,44] in the study of these complicated systems.

From the experimental results obtained from different studies using various techniques like viscosity, conductance, self diffusion, small angle neutron scattering (SANS), light scattering etc. [39-49], it has been concluded that microemulsion exists in three different forms viz oil in water, water in oil and bicontinuous microemulsion (Fig.1.2) The first two types generally exist when oil/water volume ratios (OWR) are either very low or very high. The bicontinuous system is formed, when oil and water are of comparable proportion, i.e. OWR is neither very low nor very high.

A simple hardsphere model is generally accepted for w/o and o/w microemulsion where the liquid with lower volume is dispersed as spherical droplets in to the liquid with higher volume, i.e the continuous medium. These droplets are covered with a layer of surfactant molecules. The radius of these spheres are in the range of 10-100 nm.

The structure of bicontinuous microemulsion is still an enigma. Scientists around the world are working to decipher the structure of such microemulsion [50-53]. Bicontinuous structure for microemulsion having comparable amounts of oil and water was first proposed by Scriven in 1976 [54]. It was observed that the discrete structure at comparable amount of oil and water was neither globular, tubular nor lamellar and the continuous zone was

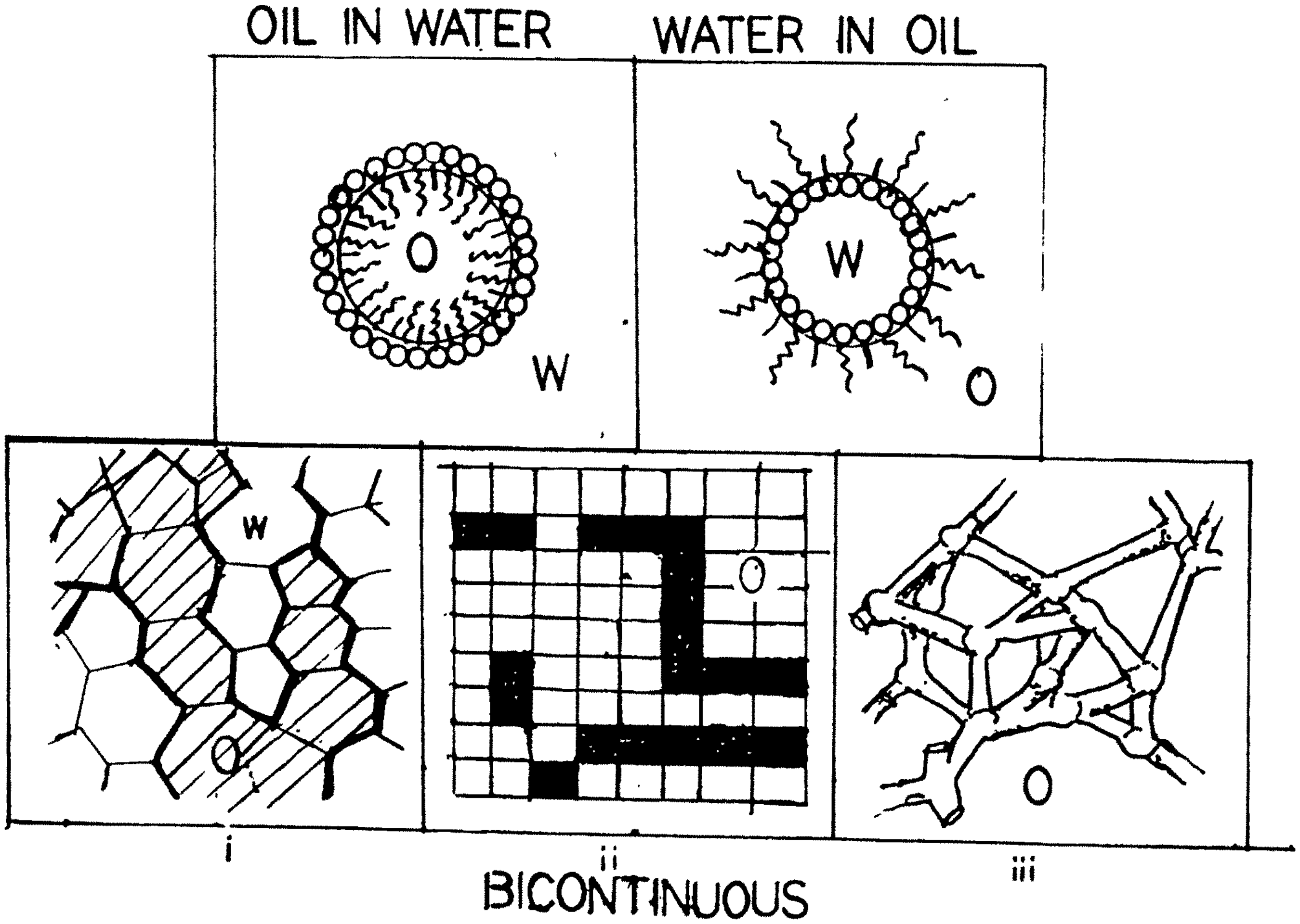

Fig.1.2 Types of microstructures possible in microemulsion
(i) Talmon - Prager model
(ii) de Gennes model
(iii) Ninham et al model

dominated by neither water nor oil. He pictured the bicontinuous structure as fused truncated octahedra with same cubic symmetry of spherical droplets [55]. He argued that this transformation is quite needed,at a particular volume fraction so as to minimise the surface energy to make the system stable [54,55].

But the experimental results seem to favour a random model than Scriven's ordered model. Talmon and Prager [56,57] proposed a random model using statistical mechanics. They modelled bicontinuous microemulsion as an interconnected voronoi polyhedron randomly filled with oil and water (Fig.1.2). de Gennes et al [58] further modified this model into simple cubic lattice where the cubic size is fixed. They introduced the term 'persistence length' to denote the size of the cube. It represents the length of a cubic side which is randomly filled with oil and water and is equal to

$$\xi = \frac{6\,\phi_o\,\phi_w}{C_s\Sigma}$$

where ϕ_o and ϕ_w are the volume fractions of oil and water respectively. C_s is the concentration of surfactant molecules and Σ is the area per surfactant molecule. But this model failed to predict the 3 phase equilibria. It was then modified by Widom [59] and also by Andelman [60] to overcome this inherent drawback.

Recently Ninham et al. described the bicontinuous structure in a much simpler way [61,62]. They modelled it as a chaotic, interconnected water filled conduits in oil medium which are dynamic in nature. This model could explain many physical properties of bicontinuous microemulsion like viscosity, self diffusion etc.

The volume fraction of the dispersed phase where the transition from oil in water to bicontinuous or water in oil to bicontinuous structure takes place is known as percolation threshold [63-65]. This structural transitions could be very well followed by many techniques like conductance measurements, self diffusion study etc. [64-67]. An abrupt increase of the electrical conductance is observed as the oil percolation threshold is crossed which usually comes in the range of $\Phi_w = 0.16-0.2$ [64]. It indicates the formation of water channel for ionic movement in microemulsion and is often taken as an indication of bicontinuous structure formation [63,64]. The percolation and percolation threshold are both affected by temperature, concentration and nature of additives, surfactants and cosurfactants [63,68-70]. The nature of the oil phase itself has tremendous effect on these properties [62, 70,71]. The external pressure also seems to affect these values [72, 73].

1.6 ROLE OF INTERFACIAL FILM ON MICROEMULSION FORMATION, STABILITY AND STRUCTURAL TRANSITION

The properties of interfacial surfactant film is critically important for microemulsion formation and stability [74]. When the droplets are formed and get dispersed in the continuous medium, their stability depends upon the nature of the droplet interface, where an interfacial film is present. The energy needed for the interfacial film to overcome the restoring forces like bending energy and interfacial energy is termed as curvature energy [75]. The curvature energy per unit area can be written as [58, 76, 77]

$$E_c = K/2 \; (1/R - C_o)^2$$

Here the constant 'K' has the dimension of energy and is called rigidity of the film. C_o which is equal to $1/2R_o$ is known as spontaneous curvature and R_o is the spontaneous radius of curvature. By convention [75] C_o value indicates the tendency of the film to curve towards water ($C_o > 0$) or oil ($C_o < 0$).

This energy determines the nature of the system that is formed as a result of the mixing of oil, water and surfactant [76-78]. It is obvious from the earlier equation that it is K and C_o that control E_c and hence the structure of microemulsion.

It has been deduced that persistence length of the interfacial film, with which the size and type of microdomains in microemulsion is related, was given by the relation

$$\varepsilon_k = a \exp (2\pi K/kT)$$

where 'a' is the molecular length of the surfactant [58]. The influence of 'K' on the microstructure of the microemulsion is clear from this equation.

Taupin et al. [74,79] determined K for anionic surfactant film using light scattering and spin labelling techniques. It was reported that presence of cosurfactant decreases the 'K' value. Langevin discussed the effect of alcohol on K and C_o and said that alcohol molecule acts strongly on the values of K and C_o [80]. They presume from the results that role of alcohol in the system is to decrease film rigidity and thus provide the necessary flexibility to the interfacial film for curving towards the preferred surface.

Kellay et al. [81] determined 'C_o' of the surfactant film at various NaCl concentration and found that it varies linearly with the square root of salt concentration. Aveyard et al. calculated the rigidity constant of nonionic surfactant monolayer from interfacial tension data and found that it is of the order of kT [82,83].

There are many other studies that can be cited which deal with the determination of rigidity of different types of interfacial film [84-86].

1.7 APPLICATIONS

Uniqueness of microemulsion lies in the fact that it is a stable system with a large amount of polar and apolar liquids together. It is thermodynamically stable and generally transparent in appearance. Some microemulsions are little bluish. Microemulsion phase can achieve very low IFT with water or oil phases. These qualities of microemulsion systems are well exploited for technological and commercial applications.

The explosive increment of research activities in the last decade is mainly due to its potential use in tertiary oil recovery. The occurrence of low IFT with petroleum oil helps in ovrcoming the capillary forces which prevent the recovery of crude oil trapped in the pores and cavities of underground rocks [87]. It is believed that microemulsion technology can be used to recover the so called 'tertiary oil' [88-90]. Though results are not very promising yet, a large number of patents have been taken on microemulsion flooding technology.

These microstructured systems are used in pharmaceutical industries due to their capacity to solubilize large amounts of drug materials [71]. Researchers recognised their potential as drug carriers also [91-93]. A carrier should be able to dissolve the drug, keeping the activity in tact. It should be able to deliver the drug in controlled manner at the required place.

Microemulsions have been found to mimic the natural biological membranes [94] and hence has importance in biological studies also. The stability, transparency and very small droplet size of the dispersed particles have been exploited in cosmetic industry [95].

Reactions in microemulsion media have attracted attention of many researchers [96, 97]. Many biphasic reactions have been carried out in microemulsion media. With its typical microstructure, microemulsion provides a medium having large area of contact for the reactive species with negligible contact barrier. Some reactions in microemulsions are much faster than one using phase transfer catalysts [98]. The microdomains of the dispersed phase in microemulsion can act as the microreactors for polymerization reactions and the microemulsion polymerization presently is a fast growing field [99-101].

Recently Tourode et al. have described a method to prepare alloys of higher qualtiies in microemulsion media [102]. Fluorocarbon microemulsions have attracted some interest due to exceptional high solubility of O_2 in these and consequent potential as O_2 carriers in case of circulatory dysfunction [103].

Microemulsion have also been used for metal extraction and to purify the surfactants [104,105]. To purify surfactants,Winsor III (a three phase equilibria) systems were prepared in which surfactant rich middle phase is in equilibrium with excess water and oil. Then the water soluble and oil soluble impurities will migrate towards respective phases and the middle phase contain purified surfactant. It can then be seperated and regenerated.

Fuels in the form of microemulsions have been used in combustion engine. Though as fuel it was not more efficient than conventional fuels, it decreases the amount of polluting gases like nitric oxide in the exhaust [106].

1.8 SCOPE OF THE PRESENT WORK

A survey of recent literature indicates tremendous interest on nonoinic surfactant microemulsions [82,107-113]. A microemulsion of this type is definitely intriguing as the system is expected to be uncharged and good for organic reaction medium. In this thesis we are presenting properties of microemulsions formed with nonionic Brij 35 [$CH_3(CH_2)_{11}$ O (CH_2 $CH_2O)_{23}$ H]as surfactant and with alkanes as the oil phase.

The nonionic surfactant, Brij 35, has been rarely used to prepare microemulsions [114]. n-Propanol has been used but rarely as cosurfactant [115-116]. Hence we decided to study a microemulsion system which has a combination of both Brij 35 and n-propanol. The properties of the microemulsions, we thought, would be interesting because of the high hydrophilicity of Brij 35. This system has very high cloud point (>100°C). We, hence, expected to get a wide temperature range to study the physical properties of one phase microemulsion.

Influence of oil on microemulsion properties is well studied [117-120]. Researchers have used various types of oil from crude oil [121] to edible oil [122] for this purpose. Some authors have discussed the effect of alkane chain length of oil, surfactant and cosurfactant towards the maximum solubilization [123]. A large number of publications have discussed the mutual relation between oil molecules and interfacial layer and the effect of that on microemulsion properties [123-126]. It was observed that the most important parameters of the interfacial film, rigidity and spontaneous curvature were functions of oil penetration on the surfactant tail region [81]. Hence the studies of nature of oil phase on microemulsion formation and properties are very important. Recently Aveyard et al. [127, 128] used mixed alkanes. These have some indirect implications on microemulsion formation. The results indicate ideal mixing nature of alkanes. Some other work have also been reported using alkane mixtures [129,130]. But in spite of the fact that mixed hydrocarbons are often involved in microemulsion applications, systematic studies of the effect of alkane mixing on microemulsion formation and properties are absent. Hence in the third chapter of the thesis we are presenting the results of our studies of microemulsion systems with mixed alkanes as oil. Phase diagram, conductance, viscosity and ultrasonic velocity measurements, were the methods used in this study. Recently Kahlweit discussed the potential of phase diagram in giving a closer feeling of these systems [120, 131-134]. We present a detailed study of some ternary phase diagrams in this thesis.

Microstructural investigations of microemulsion system are often done by modern techniques like SANS, Light scattering, Flourescence spectroscopy, NMR self diffusion study etc. [68, 117, 135-138]. But most of these techniques have the limitation of being applied only in dilute regions of microemulsions [26]. Hence importance of classical techniques like viscosity and conductance still persists [139-142].

Presence of electrolyte has marked influence on the properties of ionic microemulsion [143-146]. Variation of electrolyte concentration induces various Winsor transitions in multiphase microemulsions [147-149] and has been well exploited [150,151]. It provides a simple method to deduce the optimal salinity of the system [152-153]. Moreover the sensitivity of nonionic surfactant microemulsion towards the electrolyte concentration was noted [147-155]. In Fourth chapter of the thesis, the results of an intensive investigation of the effect of NaCl and temperature on the phase behaviour and other physical properties of these four component systems are being presented. Other than phase diagram, the properties studied were phase volume measurements, cloud point, interfacial tension, conductance, viscosity, adiabatic compressibility etc.

Most of the modern studies attribute the structural changes in microemulsion to the properties of the interfacial surfacant film [156-158]. Obviously, the properties of interfacial film depend on the nature of surfactant molecules. These aspects of microemulsion have been well studied by using all the three types of surfactant viz cationic, anionic and nonionic [156-160]. Zwitterionic [161] and biosurfactants [102,162] were also used. In many applications, mixtures of surfactants are generally exploited [163] because of the expected synergistic effect. But antagonistic effect can~~n~~not be wished away. The effect of mixed surfactants in the formation and properties of microemulsion is not clear due to insufficient available data [164,165]. In fifth chapter we present the results of the studies of the microemulsion systems where mixed surfactants have been used.

In the last chapter we discuss the thermodynamic data for a few chosen systems. These data were calculated from the solubility of oil in water under various conditions and temperature. All these give us much needed information about nonionic surfactants.