CHAPTER 1

INTRODUCTION

1.a. General Introduction

The latter half of the twentieth century probably will be remembered for its continuing technological revolution that changed the life style of the human kind. Rapid development of scientific insights, fabrication of new materials and invention of myriads of sophisticated devices all occured at very high pace. Miniaturisation was one of the most important goals in this revolution. During this same period, the study of amphiphiles and their self assembly or aggregation phenomenon gathered significant momentum. The surface active molecules can self assemble into a variety of microstructures like micelles, vesicles, liposomes, microtubules, bilayers, microemulsions etc [1-4]. Among all these, microemulsions have recently emerged as a centre of both fundamental and applied research interest due to its evergrowing applicability in various fields. This stimulated a rush for finding the fundamental and structural aspects of these microstructures.

Mixtures of oil and water are unstable and do not homogenize because of very high interfacial tension prevailing at the interface between these two phases. But these mixtures can in general be stabilized by addition of suitable "surfactants". These molecules, by adsorbing at the oil-water interface, decrease the interfacial tension considerably. With finite but small interfacial tension one can prepare emulsions of oil in water (o/w) or of water in oil (w/o). Here the globules are rather large (10 μm) and the interfacial energy at the droplet interface is large enough to destroy this interface which ultimately leads to the slow coalescence of the globules. Hence these systems are of only kinetical stability. However with some surfactants or some surfactant mixtures it is possible to reach a state of very very low interfacial tension, nearly zero, though positive. Such systems will tend to increase the total area of interface between oil and water leading to highly divided systems. They are thermodynamically stable and are termed "Microemulsions".

1.b. What are Microemulsions?

Microemulsions are transparent or translucent homogeneous, thermodynamically stable, isotropic mixtures of water and oil in presence of a surfactant or a surfactant - cosurfactant mixture [5-10]. They are extraordinary kind of mixtures, form spontaneously and are generally low viscous. Like macroemulsions or coarse emulsions they can also assume oil in water (o/w) or water in oil (w/o) internal structures. In o/w or w/o type, the microdroplets of oil or water are dispersed in the continuous medium of water or oil respectively and are stabilized by a monolayer of amphiphiles. Since these structures resemble the micelle structure very much, they are often referred to as swollen micelles or swollen reversed micelles and represent an intermediate state between micellar solutions and true emulsions [11]. In addition to this, microemulsions can also assume a third type of structure called bicontinuous in which both the oil and water can be considered to form the dispersion medium simultaneously. In this bicontinuous model, the water is assumed to be forming an interconnected randomly oriented tube (conduits) like structure in an oil continuum. A diagramatic representation of these three structures is depicted in Fig. 1.1. The microemulsions can exist in equilibrium with excess water, excess oil or both. The dispersed phase particle size in these versatile systems fall in the range 10-100 nm. Since for particles of such small sizes, the scattering of light is proportional to the square of the volume of the scattering particles [12] these systems are unable to scatter white light and hence remain visibly transparent. That is why the microemulsions are generally transparent or translucent.

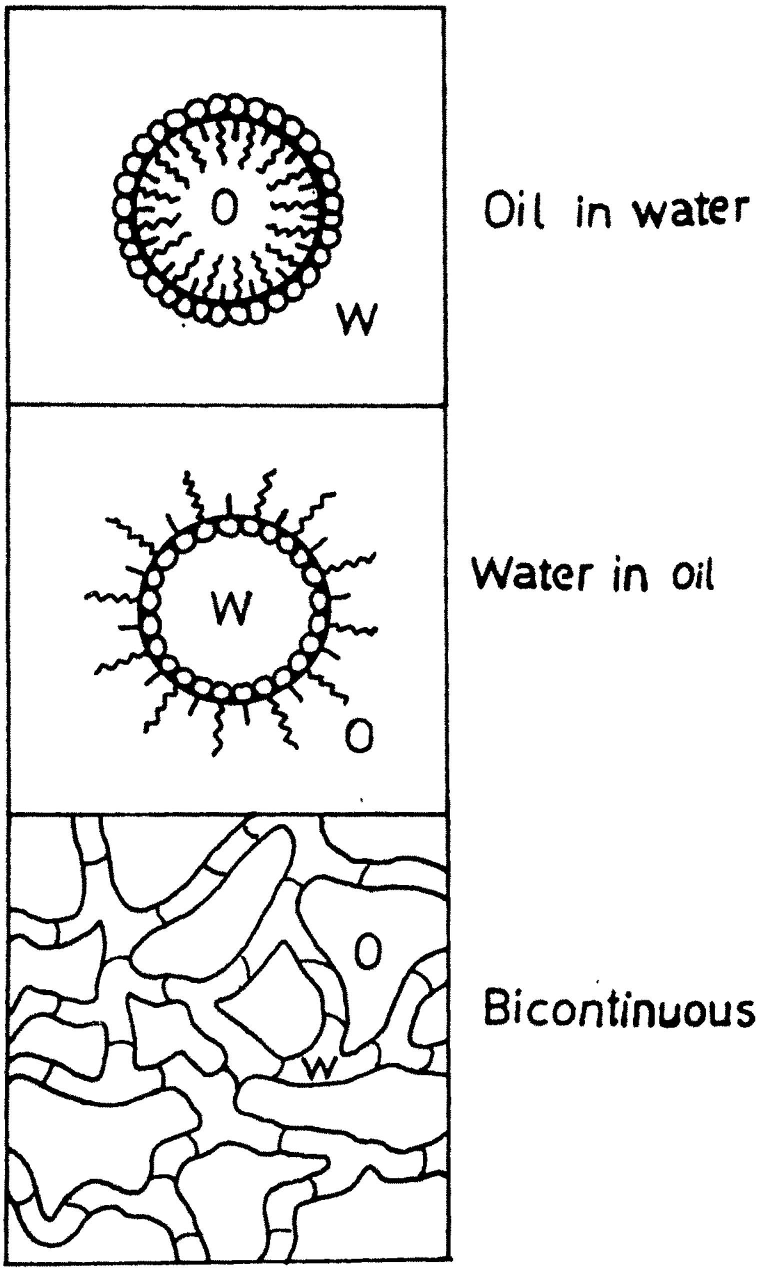

Fig.1.1 Diagramatic representation of oil in water (o/w) water in oil (w/o) and bicontinuous microemulsion structures.

1.c. History of Microemulsions

In 1940 J.H.Schulman of Cambridge University, U.K. and his co-workers published three papers [13-15] on the molecular interactions at oil/water interfaces. In these papers they presented the various aspects of oil in water or water in oil emulsions such as their stability, phase inversion and interfacial tensions at the oil/water interfaces. From these studies they inferred that the reactions occurring at the oil/water interface were in many ways analogous to the corresponding reactions at an air/water interface. These articles may be considered as the precursors to the attempts to correlate the properties of the interfacial film with emulsion characteristics. The knowledge gained from these studies and the contributions made by many other outstanding colloid chemists in coarse classical emulsions [16,17] helped T.P.Hoar and J.H.Schulman to develop a novel class of transparent isotropic emulsions, the microemulsions of today, latter in 1943 [18]. This was obtained by the titration of a milky emulsion of water/potassium oleate/benzene with a medium chain alcohol pentanol latter named as cosurfactant. In their article [18] appeared in "Nature" they used the term "oleopathic hydromicelle" for the transparent oil-water dispersions. During this era such oil-external dispersions were widely known as "soluble oil" and the essential conditions for their formation were a high surfactant/ water ratio and the presence of a nonionized amphipathic substance such as short chain alcohol, fatty acid, amine etc.in a mole fraction comparable with that of the soap. They suggested an equation

$$r = \frac{3\ (\text{volume of water})}{\text{area of oil/water interface}}$$

to calculate the radius 'r' of water droplets in such oil continuous systems. These authors viewed the microdroplets as composite globules consisting of an inner aqueous (w/o) or organic (o/w) core surrounded by a monomolecular film of mixed surfactant and cosurfactant molecules. The polar heads of these amphiphile molecules are oriented towards the aqueous medium. The radius of the dispersed globules is the sum of the radius of the central water core and the thickness of the interfacial film of amphiphiles. Latter the above model for the structure was proved by Schulman and coworkers from the results of several other complementary techniques [19-24].

Though Schulman's attempt was the first of its kind towards the scientific aspects of microemulsions, stable dispersions of this kind had been in the market place for about fifteen years prior to 1943 [25]. Many of the products of commercial or industrial use during this time were microemulsion preparations. Carnauba wax emulsions, cutting oils, pine oil emulsions, flavour emulsions, pesticide emulsions etc. were prominent among these. Carnauba wax emulsion was the first born of this family and was sold by the brand name "Dri Brite" [25]. Cutting oils were stable emulsions of lubricating oils in water and served both as a lubricant as well as coolant. Pine oil emulsions were obviously oil in water microemulsions and was in use as bactericide, fungicide, essential oil fixative and as selective floatation agent. There were many other forms of microemulsion, but they were purely of commercial origin and lacked proper scientific backing to consider them as foundation stones in the microemulsion research.

A 'controversial' matter regarding the microemulsions was its terminology [26,27]. Various names eg."solubilized" [28], "soluble oils" [28], "oleopathic hydromicelle" [18], "swollen micellar solutions" [21], "transparent emulsions" [21], "micellar emulsions" or "micellar solutions" had appeared in the literature [28]. Adamson opted for the term "micellar emulsions" [29] whereas Shinoda and Friberg [30] suggested that microemulsions could be considered as colloidal solutions. But this suggestion was not acceptable to many, because the word "colloidal" had been used to identify systems with dispersed phase of 100 A° to more than 1 micron in dimension. Friberg et al [31] also stated that when interfacial tension becomes nearly zero, the so called microemulsions are solutions with solubilized water or oil. This viewpoint agrees closely with that of Winsor [32] who considered his clear solutions to be true solutions. Amidst all these controversy, it was the term "Microemulsions" suggested by Schulman himself [24], after identifying such transparent dispersions of oil and water as a different class of emulsions from the known coarse classical ones, which gained wide acceptance and is being used today.

1.d. Role of Surfactant and cosurfactant

The surfactants are essential components of microemulsions. These molecules get adsorbed at the oil-water interface and orient themselves in such a way that their hydrophilic parts are directed towards the aqueous phase and hydrophobic parts embedded in the oil phase. This causes marked degree of reduction in the free energy of the interface [33,34], stabilizing the interface. According to thermodynamics, for the spontaneous formation of microemulsion, the free energy of formation ΔG_m must be a negative quantity. One contribution to this free energy term is $\gamma \Delta A$ where γ is the tension at the droplet surface and ΔA is the change in the interfacial area [35]. Since γ and ΔA both are positive, this contribution is always a positive quantity. Then according to the equation

$$\Delta G_m = \gamma \Delta A - T \Delta S$$

the negative quantity arises from the dispersion of the droplets in the medium, which provides a positive entropy change ΔS. Calculations show that for ΔG_m to become negative, the tension must be low and of the order of $10^{-2} - 10^{-3}$ mNm^{-1} [35]. Although surfactants lower the interfacial tension (IFT) substantially, in many cases the critical micelle concentration (cmc) or the limit of solubility is reached much before the interfacial tension is close to this low value. In such cases, the addition of a second tensioactive agent of a completely different nature can lower the interfacial tension further [36]. These second type of tensioactive agents are called "cosurfactants". Cosurfactants are mostly medium chain alcohols or amines etc. with three to seven carbon atoms. After confirming that alcohols in microemulsions distribute themselves between the aqueous and the oil rich bulk phases and the interfacial layer, Kahlweit et al. [37] preferred to call these as "Cosolvents" rather than cosurfactants. Short chain alkyl amines, carboxylic acids, thiols etc. have also been used as cosurfactants [38-40]. In some cases surfactants can alone lower the interfacial tension far enough to the desired level for the microemulsion formation. Surfactants having double hydrocarbon chains like Aerosol OT (AOT), Didodecyl dimethyl ammonium bromide (DDAB) etc and many nonionic surfactants are the examples for this type [41-44]. But generally the ionic surfactants are comparatively more hydrophilic in nature. Hence they require the assistance of more hydrophobic cosurfactants for attaining the required balance between its hydrophilicity and lipophilicity and there by the microemulsion formation. The surfactant molecules are generally present at the interface in a regular array. Because of the relatively large difference in size between surfactant and cosurfactant molecules, the cosurfactant molecules can efficiently accommodate themselves between the larger surfactant molecules at the interface. The electrostatic interaction between the surfactant head groups can thus be screened by the smaller head groups (eg. hydroxyl group of alcohol) of low hydrophilicity [40]. The ultimate result is a densely packed interfacial layer of surfactant and cosurfactant with higher mobility and flexibility. The microemulsion systems owe their stability, structural complexity, phase continuity etc. completely to this interfacial film. Detailed discussion of molecular interactions within this interfacial layer and how this film determine the microstructure of microemulsion systems can be found in several articles of old and recent origin [7,21,45-47]. The theory related to this interfacial film is given in section 1.h.

Generally ionic or nonionic surfactants have been used in the formulation of microemulsions. Zwitterionic surfactants have also been used [48]. Shinoda et al described [49] various important factors in the surfactant formulation for microemulsion formation. Complete miscibility of oil and water occurs only when the hydrophilic-lipophilic property (HLB) of the surfactant balances each other [50]. The HLB of a surfactant varies with temperature, counter ion valency, salt concentration etc. Since surfactant hydrophobe structure has significant effects on cosurfactant requirements of microemulsions, Sunwoo and Wade tried [51] to optimize surfactant structures with an objective to minimize and possibly eliminate the cosurfactants from microemulsion formulations. Their study concluded that twin tail surfactants have minimal cosurfactant requirements while single tail surfactants have high cosurfactant requirements.

The detergentless microemulsions [52] involving no surfactants, but only alcohols are also known. Though these are different, they have some similar properties to the surfactant containing ones.

The effects of varying the alcohol chain length in microemulsions and their interfacial properties have been investigated by Schulman et al. [53], Shah et al. [54], Clausse et al. [55], Lang et al. [56] and many others [57,58]. Schulman and McRoberts measured electrical conductivity of microemulsion systems of various alcohols of increasing chainlength [53] and found that alcohols from ethanol to pentanol yielded conducting systems while the higher alcohol containing ones were non conducting. They suggested an inversion of continuous phase between n-pentanol and n-hexanol. This is because of the preferential wetting of the interface by oil or water [54]. For longer alcohols i.e. the greater hydrophobicity of the mixed film prefers water in oil. However the short chain alcohols make the interface more hydrophilic and prefer oil in water. Leung and Shah stated that smaller alcohol chain length means shorter hard sphere radius and hence higher fluidity of the interface [59]. These effects result in increase in attractive interdroplet interaction. Clausse et al. [55] showed that with alcohol chain length going from C_2 to C_4, the one phase microemulsion area increases before it begins to decrease with higher alcohol. They suggested that C_4 (butanol) is in the threshold. The alcohols from pentanol onwards decrease the one phase microemulsion zone. Long Chain alcohols cannot act as cosurfactants [60]. Mineral acids e.g. HCl and H_2SO_4 also behave as cosurfactants[61].

1.e. Nature of Oil Phase

The nature of the oil phase is also equally important in deciding the structure and formation of microemulsions [62,63]. The interfacial layer around the microemulsion droplet is considered to have two distinct interfaces, one between the film and the aqueous phase and the other between the layer and the oil phase. It is the net effect of these two tensions which determines the curvature of the film [54]. The association between the molecules of the interface and the hydrocarbon in the dispersed or continuous phase is important in microemulsions. A degree of disorder in the interfacial layer produced by the penetration of hydrocarbon molecules of oil into the hydrophobic tail region of the interfacial film is essential for the formation of microemulsion [24]. Shah and coauthors tried to elucidate the chain length compatibility of various components of microemulsions on solubilization and phase equilibria [59,64]. Oil molecules influence the interfacial film property through a solvation effect. With decreasing chain length and aromaticity of the oil, its penetration into the interface increases and thus lead to a more rigid hardened interface. On the other hand, the long chain oil molecules penetrate less into the interfacial film and hence a more flexible interface ensures. More flexibility of the interface means the droplets become 'sticky' and therefore attractive interactions between the droplets increase during their collisions. Bansal et al. have shown that the maximum water solubilization into w/o microemulsion occurs when la + lo = ls where la, lo and ls are the chain lengths of alcohol, oil and surfactant respectively [64]. Ninham's group also studied and stressed for the necessity of oil penetration into the interfacial layer particularly for bicontinuous type of structure [65,66]. Different types of hydrocarbons can also bring about significant changes in the monophasic region in the ternary phase diagrams of oil-wate surfactant systems. A previous work reported from our laboratory [67] shows that when heptane was replaced by nonane, the monophasic microemulsion area decreased. Further, the mixing of two alkanes was found to be nonideal with respect to the microemulsion area as well as some of their properties [68].

Above cmc, for micelle forming surfactants like AOT, in presence of alkanes and aqueous NaCl, aggregation can take place [69] either in the oil phase or in the aqueous phase giving w/o or o/w microemulsion respectively depending on the conditions. In such systems the shorter alkanes penetrate into surfactant layer more effectively than do longer chain homologues and are likely to induce inverted surfactant aggregates (w/o microemulsion) [63]. Aveyard et al.[70] further used various alkanes of increasing number of carbon atoms, N, in such system and observed that for $N < 9$,the aggregation takes place in the oil phase to give water in oil microemulsion where as for $N > 10$,the surfactant aggregates in aqueous phase to form oil in water microemulsion. In the region of $N=9$,much of the surfactant was found to be present in the surfactant rich bicontinuous phase at the middle.

1.f. Nature of Polar Phase: Additive effects

Water has generally been accepted as one of the components of microemulsion. Water-surfactant head group interaction is responsible for various structures of microemulsion. Waterless microemulsion was first reported in 1984 [71-73]. Additives which affect water structure have influence on phase behaviour and physico-chemical properties of microemulsions. Two groups of additives have been used. These are electrolytes and nonelectrolytes. The electrolytes include NaCl, NaBr, $MgCl_2$, $CaCl_2$, $AlCl_3$ etc.[74-77] and these induce intensive phase behavioural changes in microemulsions. Commencing with a system of oil in water microemulsion in equilibrium with excess oil at the top, if one increases the salinity gradually, then at an intermediate range of electrolyte concentration a three phase system evolves in which the middle microemulsion phase is in equilibrium with excess aqueous layer at the bottom and excess oil layer at the top. Further increase in the salinity reverts the system back to a two phase one with water in oil microemulsion at the top and excess water at the bottom. These different formations of microemulsions have been named as Winsor I, Winsor III and Winsor II systems respectively [78]. They are also referred to as lower, middle and upper phase microemulsions [79]. The trivalent electrolyte $AlCl_3$ behaved somewhat differently and opposite to those for monovalent or divalent salts [77]. Here the phase transition occured from an upper Winsor II → Winsor III →Winsor I with increasing $AlCl_3$ concentration.

The pH sensitivity of microemulsion systems has also undergone investigation [80,81]. Under appropriate conditions the effect of salinity on the phase behaviour can be counterbalanced by adjustment of pH [81]. The added electrolyte interacts with water and thereby decreases the interaction of polar head group of the surfactants with water and hence makes the hydrophobic character of the surfactant relatively more predominant over its hydrophilicity. Correspondingly an increase in pH increases the hydrophilic nature for the similar reason.

The list of nonelectrolyte additives studied in microemulsions include water soluble polymers as well as dextran, gelatin, bovine serum albumin, urea etc.[82,83]. Moulik et al.[82] determined the effect of urea, polyethylene glycol, NaCl, polyacrylamide and gelatin on the microemulsion stabilized with Triton X-100 and butanol. The urea has shown a significant effect by increasing the monophasic microemulsion zone. The study of solubilization of aqueous phase into surfactant containing oil phase in presence of these additives show that the solubilization decreases with increasing additive concentration. Zana and coworkers have also demonstrated, by means of flourescence probing method [84], a decrease in the aggregation number of oil in water microemulsion, when the water soluble polymer poly (ethylene oxide) was present in the system.

The microemulsions studied by replacing water with other polar organic compounds like formamide, glycerol, ethylene glycol etc. have answered to some extent, the question as to how these molecules interact with surfactant polar heads and influence the microemulsion formation [71-73,85-87]. In a recent publication, Kahlweit et al. presented a study with formamide [88] as replacement for water. Since the hydrocarbons are slightly more soluble in formamide, the repulsive hydrophobic interaction between the amphiphile hydrocarbon tail and formamide molecules is weaker than in water. Consequently, an increase in the cmc and mutual solubility of phases will result. This effect can be compensated either by increasing the carbon number of the surfactant tails or by proceeding from a single tailed to a double tailed amphiphile.

1.g. Proposed Theories of Microemulsions

Right from the days of introduction of "Microemulsions", many theories have been proposed to satisfactorily explain their extraordinary stability and unique properties. These attempts may be summarized into three most important theories namely (i) mixed film theory, (ii) solubilization theory and (iii) thermodynamic theory. In the first attempt to explain the formation and stability of microemulsion, Bowcott and Schulman [21] attributed the formation to the molecular interactions taking place at the interface. Here the interfacial surfactant layer was treated as a third phase which is in equilibrium with other two phases (water and oil). The two dimensional spreading pressure of this duplex film compensates for the high interfacial tension between water and oil to give zero or negative value for the interfacial tension. The total interfacial tension (γ_T) during microemulsion formation is

$$\gamma_T = \gamma_{o/w} - \pi$$

where π is the spreading pressure and $\gamma_{o/w}$ is the original oil-water interfacial tension. Latter Prince replaced the $\gamma_{o/w}$ term with $(\gamma_{o/w})_a$, the interfacial tension between oil and water in presence of alcohol alone, to make the concept more realistic [89]. Though this theory could explain the spontaneous formation and structural variation of microemulsions, the basic concept of negative interfacial tension was questioned because of its experimental unreality.

In most of Shinoda's earlier work with nonionic surfactants,he treated microemulsion systems as swollen micelles [90-93]. From these studies he concluded that micellar solutions in water or oil dissolves a certain amount of oil or water respectively and swells up to o/w and w/o microemulsions [93]. This solubilization theory is consistant with most of the phase diagram studies, but failed to explain the microstructural changes observed by modern techniques.

More recently, Ruckenstein and collaborators [94-97] and Overbeek [98] published quantitative thermodynamic treatments to deal with microemulsion formation and stability. In these approaches,it was considered that the free energy of microemulsion formation ΔG_m consists of three main contributions, ΔG_1, an interfacial free energy term, ΔG_2, an energy of interaction between the droplets term and ΔG_3, an entropy term arising from the dispersion of the droplets into the continuous medium.

$$\text{i.e. } \Delta G_m = \Delta G_1 + \Delta G_2 + \Delta G_3$$

All these three contributing terms together assumes a negative value for the free energy change and hence the thermodynamic stability. ΔG_1 consists of two contributions. One is due to the creation of an uncharged surface and the other due to the formation of an electrical double layer. ΔG_2 is calculated by adding the pair interaction potential of the droplets either by a continuous integration method or a discontinuous addition method where the interaction potentials of nearest neighbours are summed up. For the computation of entropy term ΔG_3, a lattice model was used to calculate the number of configurations possible (Ω) for a liquid mixture with N_1 molecules of continuous phase and N_2 molecules of dispersed phase. Then by using the Boltzmann relationship, the entropy term can be expressed as $\Delta S_m = k \ln \Omega$ where k is the Boltzmann constant. The variation of ΔG_m with droplet radius R and constant volume fraction of the dispersed phase can be expressed as

$$\Delta G_m(R) = \Delta G_1 + \Delta G_2 - T\Delta S_m \cdot$$

From this equation, the condition for the spontaneous formation of microemulsion with the most stable droplet size R* for a known volume of dispersed phase is given by

$$\frac{d\Delta G_m}{dR}\Big/_{R=R^*} = 0$$

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

The variation of ΔG_m with R can follow four paths which illustrates the transition from instability (D) to kinetic stability (C) and then to thermodynamic stability (A and B) (see Fig.1.2). ΔG_m reaches a minimum value when $R=R^*$ and this value is negative and contributes to thermodynamic stability. R^* which is the radius corresponding to the minimum in the ΔG_m-R curve represents the most stable radius. From a comparison of the values of $\Delta G_m'{}^*$ for o/w and w/o, it is possible to predict the most stable type of microemulsion (lowest value of ΔG_m gives the maximum stability). The phase inversion occurs when ΔG_m for both o/w and w/o type become equal.

Ruckenstein further extended this theory to account for the reduction of specific surface energy (Fs) to sufficiently small values (and hence ΔG_1) in terms of so called dilution effect [95]. Accumulation of surfactant and cosurfactant at the interface does decrease the

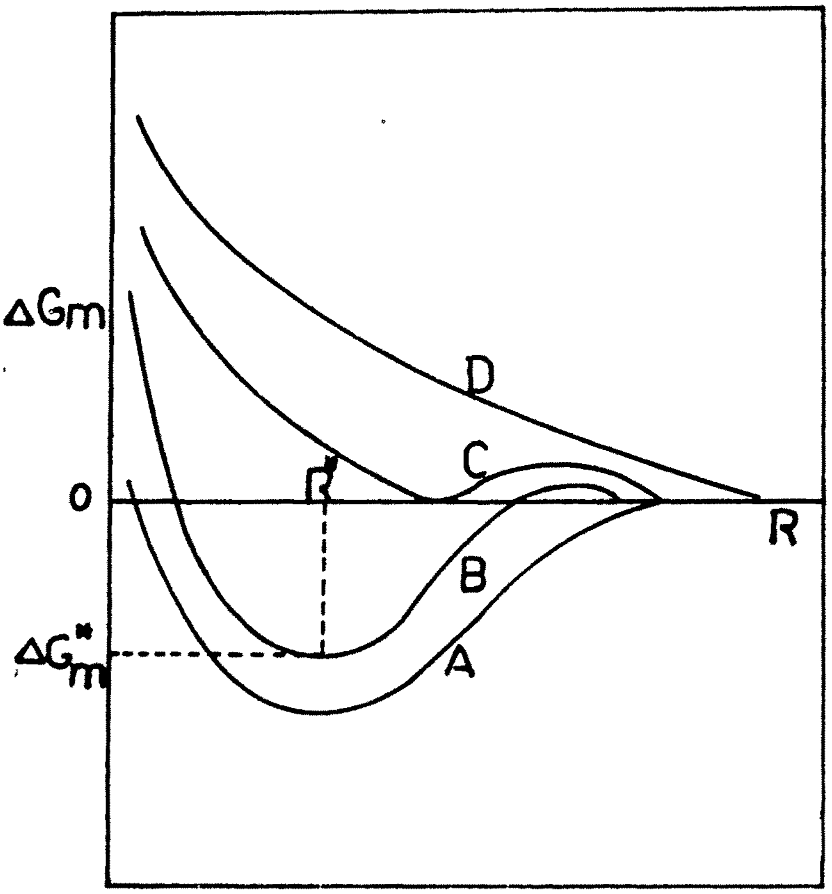

Fig.1.2 The variation of free energy change, ΔG_m, of microemulsion droplet formation, against the radius of the droplet, R. (Ref.122)

interfacial tension and thus Fs. Moreover it results in the reduction of chemical potential of surfactant and cosurfactant in the bulk solution. The latter reduction overcompensates the slight positive free energy caused by the interfacial tension and hence overall ΔG of the system becomes negative.

Overbeek's thermodynamic treatment is also similar to Ruckenstein's in approach but differs in detail [98]. In this approach also ΔG_m is subdivided into three terms ΔG_1, ΔG_2 and ΔG_3. ΔG_1 is due to the Gibbs energy of mixing of surfactant with water and of cosurfactant with oil. ΔG_2 is due to the interfacial area and ΔG_3 is due to the distribution of droplets into the continuous medium.

The thermodynamic theory explains most of the microemulsion properties quantitatively and has been amply recognized.

1.h. Theory Related to Interfacial Film

The properties of interfacial film, composed of surfactant and cosurfactant molecules, are critical for microemulsion formation.

The energy needed for the interfacial film to overcome the restoring forces, like bending energy and interfacial energy, is termed curvature energy [99]. Curvature energy per unit area (E_c) can be written as [100,101,102]

$$E_c = \frac{K}{2} [\frac{1}{R} - C_o]^2$$

where constant K has the dimension of energy and is called rigidity of the film. C_o ($=1/2R_o$) is termed as the spontaneous curvature and it represents, by convention , the tendency of the film to curve towards either water ($R_o > 0$) or oil ($R_o < 0$) [103].

This energy determines the nature of phase that results in the mixture of oil, water and surfactant [46,100,101]. It may be noted from the equation that it is the K and C_o which control E_c and hence the structure and stability of microemulsion. It has been elucidated that persistence length of the interfacial film, which determines the size and structure inversion in microemulsion, is related to K by the relation

$$\xi_K = a \exp (\frac{2\pi K}{kT})$$

where 'a' is the molecular length [104]. The role of K is clear from this equation.

Taupin et al.[102] studied K value for anionic surfactant film and reported that presence of cosurfactant decreases the K value. Langevin et al.[46] also discussed the effect of alcohol on K and C_o. They conclude that the role of alcohol in the system is to decrease film rigidity and thus achieve necessary flexibility to the interfacial film for curving towards the preferred phase. Kellay [103] determined C_o of the surfactant film for various NaCl concentration and found that it varies linearly with the square root of salt concentration. It was found to reach a value close to zero at Winsor III – Winsor II transition point. The zero value for C_o is associated with the bicontinuous structure and hence it was established that the surfactant rich middle phase in the three phase equilibrium is bicontinuous. Many other studies can also be sited in the literature about the determination of rigidity of interfacial film [105].

1.i. Applications

Microemulsions are quite ubiquitous and forms the base for a number of products of commerce and Industry today. The potential applicability of these fluids in various fields, ranging from food industry to oil industry are being explored every day. Since listing of all the applications of microemulsions is rather tedious, a few important and recent ones are mentioned here below.

The most important and spectacular application of microemulsions is found in the tertiary oil recovery

[79,106,107]. In the oil exploration process, after the first two phases of recovery, more than 50% of the oil remains occluded in the porous interiors of the reservoirs and this cannot be recovered by normal methods of water flooding, steam flooding or by applying pressure. At this stage, flooding with surfactant containing microemulsions is a promising technique to extract the remaining oil. Microemulsions can produce ultralow interfacial tensions with excess water and excess oil at optimum conditions (Winsor III systems). Under these conditions the oil trapped in the pores can be driven out without applying much pressure.

Microemulsions are excellent media for performing chemical reactions between a water soluble reactant and an oil soluble reactant [108,109,110]. Since water and oil can form homogeneous mixture, these reactants can come into direct contact with each other at the large interface between these media. Thus the reactions can take place very fast compared to phase transfer catalysed reactions [109]. Moreover microemulsion droplets can act as microreactors for certain normal reactions taking place in a single phase by providing very small domains within the droplets [111]. Thus by a suitable control of the size of the droplets, the growth process of particle and polymer formations in particular, can be regulated.

Microemulsification is an important technique adopted in many pharmaceutical and cosmetic industry to impart stability to their products. In many drug applications, the microemulsion medium is employed as carriers [112,113]. The role of the carriers is to keep the drug activated and to carry it to the specific places in the body and to release it in a controlled manner. The thermodynamic stability associated with their ability to solubilize increased amount of drug materials make microemulsions efficient drug carriers.

Microemulsions of fluorocarbons evoke extraordinary interest because of the exceptionally high solubility of oxygen in them [114]. Such formulations may act as O_2 carriers in cases of circulatory disfunction [115].

Microemulsion methods are advantageous for the preparation of homogeneous alloys of metals compared to impregnation method [112,116]. This alloying can be achieved by reduction of metallic salts dissolved in microemulsion water pools under mild conditions while the impregnation method requires high temperature.

Microemulsion can be used as a cleaning agent for many purposes including dry cleaning of clothes and fabrics as they can solubilize both oil soluble as well as water soluble dirt or stain. In a lab study Erra et al. proved the efficient role played by microemulsions in the scouring of raw wool [117].

In the analytical application a new method for the purification of surfactants has also been suggested recently [118]. A three phase microemulsion is prepared with impure surfactants when hydrophobic and hydrophilic impurities migrate towards the relevant phases leaving most of the pure surfactant in the middle layer.

There are reports of microemulsions being used as diesel fuels in combustion engines also [119]. Its advantage is that with a certain amount of water content in it they show simultaneous large decrease in emitted nitric oxide and smoke.

1.j. Perspective of the present work

The literature in microemulsion has been growing at a fast rate with many workers formulating and studying microemulsions of varying component combinations with a variety of techniques. Despite all these studies, a clear picture of the microstructure and behaviour of these systems is unknown. In this thesis we present a study of the phase behaviour and physicochemical properties of an anionic microemulsion system involving SDS (surfactant), n-propanol (cosurfactant), cyclohexane (oil) and water (polar phase). Cazabat et al.have studied such systems with SDS and cyclohexane but with pentanol as cosurfactant [120,121]. In the literature we failed to notice a systematic study carried out with propanol and hence decided to choose the above system for the present work. The physicochemical properties studied are conductance, viscosity and adiabatic compressibility. The newly introduced scattering and spectroscopic techniques in microemulsions have succeeded in providing quantitative and direct informations about their microstructure. But these techniques have their own limitations that they are best applicable to dilute systems [122]and theinstruments are not easily accessible. Hence the classical methods of viscosity, conductance etc. studies are important and in this thesis these methods have been used.

In the third chapter of this thesis, study of the effect of water soluble polymer, polyacrylamide (PAA) on the microemulsion phase behaviour and properties is presented. Polyacrylamide is one of the widely used polymer in the oil field [123] and hence its effect on microemulsion was a desirable aspect to be studied.

The reservoir water is usually rich in salinity content. The presence of salinity does influence the ionic microemulsion considerably. The fourth chapter deals with the study of the effect of NaCl on microemulsion behaviour together with temperature variation.

The mixtures of two surfactants have been reported to show more efficiency than pure surfactants in many areas where they are employed [124]. Microemulsions stabilized with mixture of two surfactants have been studied [125]. But we failed to locate any reference in literature to the study of microemulsion where mixed cosurfactants were used. Hence the mixing of cosurfactants of varying chain lengths in microemulsions need be investigated. Therefore in the fifth chapter the phase behaviour and properties of the systems where various mixtures of n-hexanol and n-propanol were used as cosurfactants are discussed.

In the last chapter the thermodynamic quantities for the solubility of oil in water at low oil concentration are computed and discussed.