CHAPTER 1
INTRODUCTION

1.1 General Introduction

Mixing of oil with water was once a challenging problem to chemists and pharmacists. Through experience, knowledge and advent of new chemicals, the problem has been solved which has opened up a field of much potential application. Theromodynamic understanding of the interfacial barrier of mixing of two phases especially two immiscible liquids one polar, another non polar has provided a clue for the addition of a third component that can significantly lower the interfacial tension aiding mutual dispersion of oil and water.

The amphiphiles, commonly called surfactants can reduce the oil-water interfacial tension due to its high spreading pressure at the interface where it resides with the non polar head in the oil phase and the polar head anchored in the water phase and hence the formation of dispersion of either oil-in-water or water-in-oil. These dispersions, known as emulsion, are turbid and are kinetically relatively stable though thermodynamically unstable, which in course of time separates into two layers of liquid, through coalescence of the dispersed particles.

With proper choice of the ingredients and their concentration the particle size in macroemulsion may be brought down below ~100 nm. The dispersions thereafter appear to be transparent or bluish and optically isotropic i.e. no turbidity appears. The particle size in some composition may go down to ~10 nm. They are unique in their physical and chemical properties. They are thermodynamically stable systems. Such dispersions of oil in water or vice versa are called microemulsions. The thermodynamic stability means that the separation of oil and water over the time would not occur in these systems.

In the last decade, there are large number of attempts to tune the microemulsion for various applications. Scientists from various fields have tried to exploit microemulsions for different technological purposes.[1-7] It has found many applications ranging from that in household detergency to in superconductors. Colloid chemists and synthetic organic chemists have used microemulsions as medium for studying the chemical reactions because of the thermodynamic stability and macroscopic homogeneity. More importantly the microscopic inhomogeneity has been very useful to study chemical reactions because of the behaviour of the droplets as microreactors.[8]

1.2 What are microemulsions

Surfactants due to their characteristic structure can solubilize both oil in water or water in oil. They can organize themselves as vesicles, microemulsions etc.[9-10] That is the systems do self organize themselves. Microemulsions are stable dispersions of two immiscible liquids. Generally, one is a polar liquid and the other is a nonpolar liquid.[11,12] It is defined as a homogeneous, thermodynamically stable, isotropic and low viscous mixture of oil and water stabilized by surfactant and sometimes a mixture of surfactant and cosurfactant.[13-18] Generally, lower alcohols, amines, acids, etc. are used as cosurfactants. Microemulsions are dispersions of oil-in-water (O/W) or water-in-oil (W/O) where drops of oil or water are dispersed in the second liquid, the continuum, and the amphiphiles being located at the interfacial region (Fig1a) of the drop with the continuum. Generally, cosurfactant is present between the surfactant molecules.

However, both surfactant and cosurfactant can be molecularly dispersed in both the liquids at least to some extent. They can not scatter white light because of their very small size (~10-100 nm) and hence they are transparent to visible light. The interfacial tension between oil and water need to be very very low to achieve the mutual solubility and hence to make the system thermodynamically stable.

1.3 History

The concept of microemulsion was scientifically described by the English Chemist J.H. Schulman[17] about half a century ago although the term microemulsion was coined much later with emulsion as the frame of reference. In

1940. Schulman and coworkers[18-20] published a few papers on the molecular interactions at oil-water interfaces. In these papers, they studiesd the various aspects of oil-in-water or water-in-oil emulsion such as their stability, phase inversion and interfacial tension at the oil-water interfaces. From these studies, they concluded that the reactions occuring at the oil-water interface were in many ways analogous to the corresponding reactions at the air/water interface. The knowledge gained from these studies and the contributions made by other colloid chemists in classical emulsion helped T.P. Hoar and J.H. Schulman to develop a novel class of transparent isotropic solutions called microemulsion.[17,18]

The microemulsion was obtained by the titration of a milky emulsion of water/potassium oleate/benzene with a medium chain alcohol, pentanol, latter called cosurfactant. In their article[17] appeared in 'Nature', Hoar & Schulman used the term oleopathic hydromicelle for the transparent oil-water dispersions. During this time, 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 have described an equation[17] to calculate the radius 'r' of the water droplets in such oil continuous systems.

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

They considered 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. 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. Later, the above model for the structure was proved by Schulman and coworkers.[23,24]

Though, the first scientific study was reported by Schulman, a large number of commercial products like carnauba wax emulsion, cutting oils, cleaning fluids, antiseptic formulations, cosmetics and toiletries available in the market in the early decades of this century were microemulsion formulations.[25,26] Carnauba wax emulsion, first among these preparations, was formulated by a business man, Rodawald in 1928 to minimise the droplet size of his emulsion product. It was mainly used in floor-polish industry. He applied this emulsion on leather surfaces and on floors and dried to a glossy finish. This was the first oil-in-water microemulsion. This was known as 'Dri-Brite'[25] in the market place.

In 1930, cutting oil used was oil-in-water microemulsion in which lubricating oil was dispersed in water. It functions both as a lubricating oil and as a coolant.[25] Pine oil based microemulsions were used as bactericide, fungicide, essential oil fixative and as a floatation agent.[26]

Flavour oil based edible microemulsion such as cola, cream soda were in market in 1940 itself.[25,27,28] Many drugs are insoluble in water and hence the technique of microemulsification is employed for oral ingestion.

From 1930 to 1943 when Hoar and Schulman realized the insoluble oil (neat oils) as transparent oil-in-water emulsion, a large number of commercial products appeared in the market utilizing the principles of the carnauba wax microemulsion. They studied the oil-in-water and water-in-oil microemulsion, their stability, phase inversion, and interfacial tension at the oil-water interface.

There were controversies regarding the nomenclature.[29,30] Various authors used different terminology like solubilized oil,[31] transparent emulsion,[32] oleopathic hydromicelle,[17] etc. Shinoda named it swollen micelle considering the continuity of the formation of microemulsion from micellar solutions.[33-36] Micellar solutions and micellar emulsions also appeared in the literature.[25,37] But these terminologies have become obsolete and only microemulsion persists. The term microemulsion was first suggested by Schulman in 1959 for this transparent, stable, oil-water system.[37] This terminology is a bit unfortunate as `emulsion' conjures up, a kinetically stable system. These are however thermodynamically stable.

Conventionally, some nonionic amphipathic substances such as lower chain alcohols,[38,40] amines,[41,42] acids[43] etc. called cosurfactants or cosolvents were used in combination with ionic surfactants for the better formation of microemulsion. But with the larger number of components involved, the analysis of the data usually become very difficult due to more number of parameters. Later it was noted that the cosurfactants may not always be an essential requirement if nonionic surfactants are used.[44-46] It is also to be noted that all nonionic surfactants do not form microemulsion without cosurfactants. It was observed in this laboratory that a cosurfactant is required to form microemulsion when Brij 35 ($C_{12}E_{23}$) is used as surfactant.[47,49] It was also observed that double chain anionic surfactant like sodium bis-2-ethyl hexyl sulpho succinate (AOT) without a cosurfactant serves the same purpose of decreasing the interfacial tension between oil and water[50-53] and these three component system which are microemulsions were found easier to study.

Later, microemulsions were also reported with other polar liquids like dimethyl formamide, formamide, glycerol, ammonia etc.[54-61] Such systems are denoted by the term nonaqueous microemulsions. The first nonaqueous microemulsion was prepared with formamide and was reported by Rico and coworkers.[62] They have studied the amidation of olefin $C_8H_{17}CH = CH_2$ by γ-radiolysis in this nonaqueous system.[62] Both ionic and nonionic surfactants like SDS, AOT, CTAB, TX100 can form nonaqueous microemulsion. These microemulsions differ considerably from their aqueous analogues. A detailed investigation of glycerol/SDS/hexanol system, with the help of FTNMR and small angle neutron scattering reveals that there is no disconnected domains of different components and the system is rather structureless.[63] Similar results have been

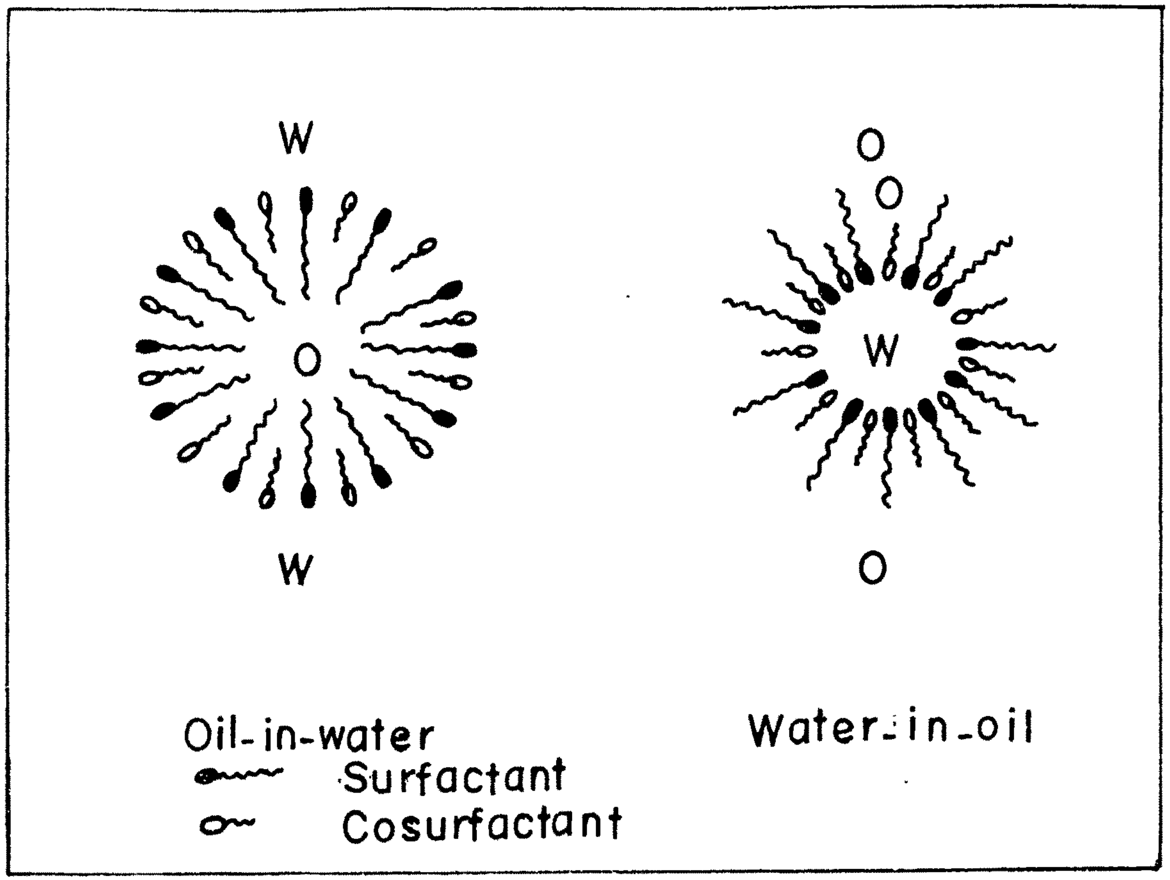

Fig 1.1a Types of microstructures in microemulsion.
Oil in water & water in oil

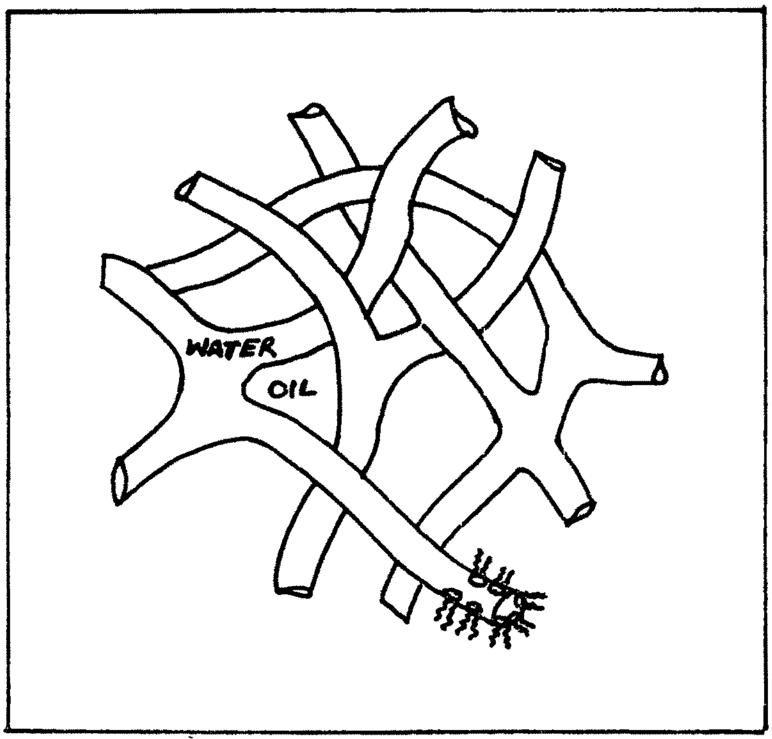

Fig 1.1b Bicontinuous structure

obtained for formamide system also.[64] But contrary to these, the glycerol/AOT/heptane system shows definite structure formation.[65]

Now, the literature on microemulsion - structure, dynamics and interaction is numerous. During last two decades, many chemical reactions were studied in microemulsion due to its thermodynamic stability and monodispersed droplets of oil-in-water and water-in-oil with large internal interface. Friberg and Ahmed for the first time used microemulsion formed by water/hexadecyl trimethyl ammonium bromide/hexanol to study the rate of hydrolysis of p-nitrophenyl laurate.[66] Since then many reactions have been studied in microemulsion.[67-73]

1.4 Structure

The structure of microemulsion is deduced from that of classical emulsions. From the experimental results obtained from different studies using various techniques like specific conductance, viscosity, self diffusion, small angle neutron scattering (SANS), light scattering etc. it has been concluded that microemulsion may exist in three different forms like oil-in-water, water-in-oil and bicontinuous structure. The first two types generally exist when oil to water volume ratios (OWR) are either very low or very high. They have droplet like structure. The oil droplets are dispersed in a continuous medium of water or the water droplets are dispersed in a continuous medium of oil.[75,76] The bicontinuous system is formed, when oil and water are of comparable proportion ie. OWR is neither very low nor very high. In this bicontinuuous model, the water or oil is assumed to be forming an interconnected randomly oriented tube (conduits) like structure in an oil/or water continuum.[77] A diagramatic representation of bicontinuous structure is presented (Fig1.1b).[78] Microemulsion can exist in equilibrium with excess water or with excess oil or with both.

Depending on the nature of surfactant, electrolyte, temperature, the mixture can exhibit the following distinct features which were proposed and experimentally demonstrated by Winsor.[79] (Fig1.2)

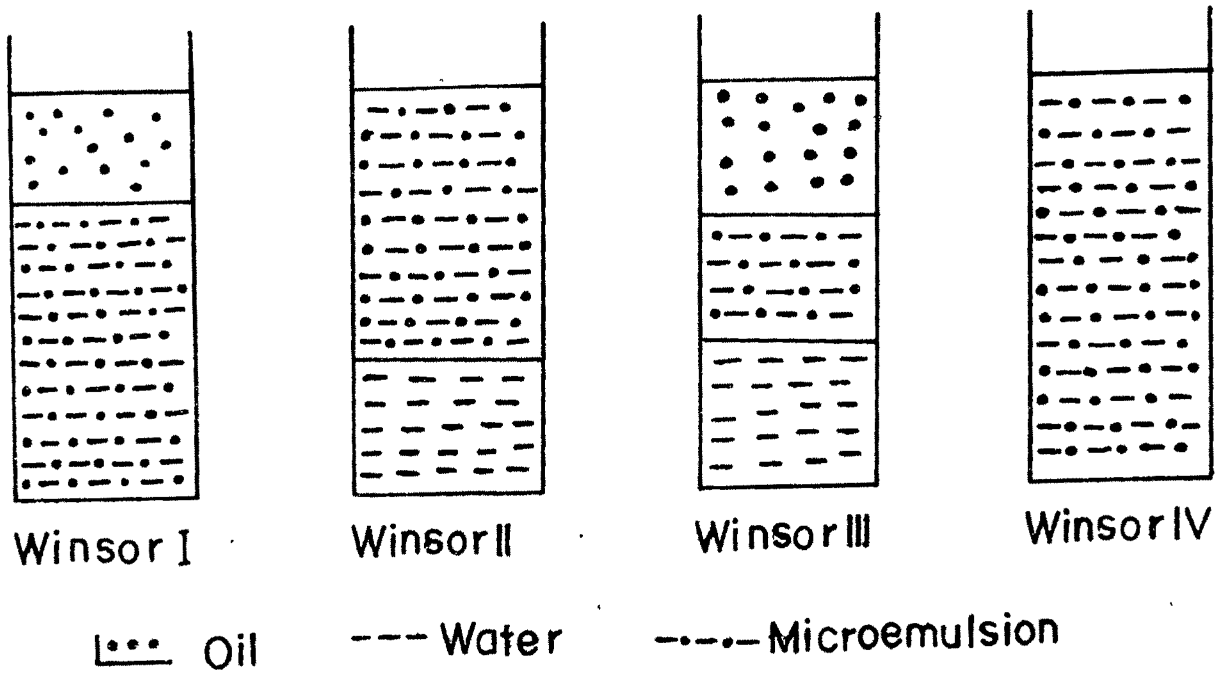

Fig 1.2 Pictorial representation of various Winsor systems.

1) A lower microemulsion phase and a top oil rich solution (lower phase microemulsion, $\underline{2}\ \phi$ or Winsor I).
2) An upper microemulsion phase with a lower water rich solution (upper phase microemulsion, $\overline{2}\ \phi$ or Winsor II).
3) A middle microemulsion with a top oil-rich and a bottom water rich solution (middle phase microemulsion (m), 3 ϕ or Winsor III).
4) A complete single phase homogeneous solution (Winsor IV).

Various Winsor transitions are possible as a function of salinity, temperature, nature of the components.[80-82] In ionic microemulsion system, this transformation is usually driven by increasing the salinity.[81,82] At low salinity, oil in water microemulsion is formed in equilibrium with excess oil at the top (Winsor I) and at high salinity water in oil microemulsion with excess aqueous phase at the bottom (Winsor II). At an intermediate range of salinity, the system separates into three phases in which microemulsion phase is in between the lower water layer and upper oil layer. In this intermediate range, the internal microstructure is in some kind of a bicontinuous state. The middle phase microemulsion consists of both oil and water.

In the case of nonionic surfactants, as it is sensitive to temperature,[80a,b] these Winsor transitions occur by increasing the temperature. At lower temperature, it forms a oil in water (Winsor I) and at higher temperature, it exists as water in oil (Winsor II) due to the dehydration of the polyoxyethylene group at higher temperature. At intermediate temperature it exists in equilibrium with both water and oil (Winsor III).

Structure of bicontinuous microemulsion is still an enigma. The bicontinuous structure was first proposed by Scriven[83] in 1976. It was observed that the discrete structure at comparable amount of oil and water was neither globular, tubular nor lamaellar and it was a continuous zone. He pictured the bicontinuous structure as fused truncated octahedra with same cubic symmetry of spherical droplets.[84] Talmon and Prager[85,86] proposed a random model using statistical mechanics. They pictured bicontinuous microemulsion as an interconnected voronoi polyhedron randomly filled with oil and water. Later de Gennes and coworkers[87] modified this model into simple cubic lattice where the cube size is fixed. They introduced the term 'persistence length', (ξ) 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

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

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 and it was later modified by Widom[88] and also by Andelman.[88]

Widom's model

Widom made an important advance in the theory by allowing the cell size to vary and then determining it self-consistently at each point of the phase diagram. He obtained two and three phase equilibria by introducing a microscopic cut off, and by allowing the area per surfactant in the interfacial film to vary. This degree of freedom was crucial to the phase equilibria he found, which depended strongly on the bare oil-water interfacial tension and only weakly on the bending properties of the surfactant film. Thus in contradiction to the previous models, by P.G. de Gennes, the characteristic length scale predicted for the middle phase microemulsion was unrelated to the persistence length ξ.

Moreover, Widom's theory does not explain the sensitivity of the experimental phase diagrams to the properties of the surfactant film.

Andelman's model is based on the following assumptions:

1) All the surfactants in the microemulsion phase is at the water-oil interface and the surfactant film is modelled as an incompressible liquid. This

assumption is consistent with experiments on globular and bicontinuous microemulsions.

2) Like de Gennes model, they divide space into cubes of size ξ.

3) A random-mixing approximation accounts for the entropy of the interface at length scales larger than the cell size ξ.

According to these assumptions, the free energy per unit volume of the microemulsion phase is -

$$f = \frac{1}{\xi^3}\left[TS(\phi) + 8\pi P(\phi)\ K(\xi)\left(1 - \frac{2\xi(1-2\phi)}{\rho_o}\right)\right]$$

the first term in the above eqn. represents the entropy of mixing of the water and oil domains, where T is the temperature. The second term represents the bending energy of the surfactant film at the water-oil interface. There were some unresolved issues remained. The first of these concerns deviations from the random mixing approximation in the treatment of the entropy and the bending energy. The renormalization of the bending energy has been computed perturbatively only to first order. The fact that this renormalization appears to be responsible for the middle phase and for the small value of ϕ_s in that phase should motivate more detailed calculations of the effective bending constant.

Recently, Ninham et al[89-96] described the bicontinuous structure as a network of spheres connected by cylinders. They called this model as the disordered open connected (DOC) cylinder model. This leads to analytic expressions for the surface area and volume of internal phase enclosed by the interface. The model for microstructure can be put together as follows. The network sphere centres are first located at the centres of hard spheres whose positions are frozen in a random packing. This ensures that the interface lacks long range translational order. The density of the random packing is determined

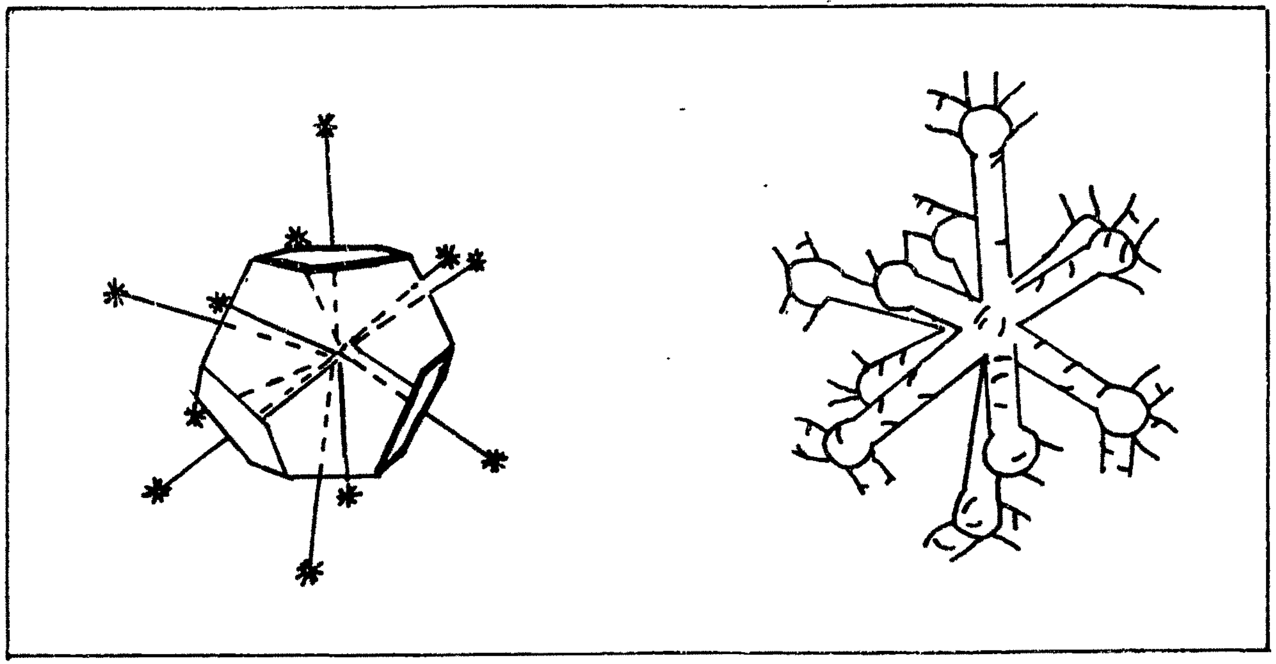

Fig 1.3 Construction of DOC model. A random three dimensional net is formed by placing vertices at the centres of spheres forming a random hardsphere packing. The vertices bisected by faces of Voronoi cells constructed about each vertex are linked by edges (left). This net is then decorated by spheres at the net vertices, and cylinders about the net edges (right).

by the composition of the ternary mixture. The hard sphere radius is related to the chain length of the surfactant molecules and the volume fraction of water, so that neighbouring interfacial regions are sufficiently spaced to accommodate the surfactant chains. This steric requirement is critical to the model, provides a characteristic distance for the structure, and gives rise to the broad peak measured in SAXS studies of these systems.

Closed polyhedral cells are now formed about each sphere centre, where the cell phases are planes that bisect the lines joining centres normally. These cells are of various shapes, and they define a Voronoi polyhedron about each centre (Fig1.3). The composition of the mixture, together with the preferred local curvature of the surfactant molecules, determines the average co-ordination number of the structure traced out by the surfactant interface. The internal tunnel labyrinth of the interface is described by a three-dimensional random net, of average connectivity Z. The net is formed by linking an average of Z neighbouring sphere centres. Linked centres must be separated by a face of the Voronoi space partition. Under this construction, a maximum Z of 134 can be achieved corresponding to the average number of faces in a random voronoi tesselation. The DOC structure is formed from the net by placing spheres (radius rs) centered at each vertex and surrounding each link in the Z-coordinated net by cylinders (radius rc). This model could explain many physical properties of bicontinuous microemulsion like conductance, self diffusion, viscosity, etc.

1.5 Theories of Microemulsion formation

There are mainly three theories which have been developed to explain the formation and stability of microemulsions namely mixed film theory, solubilization theory and thermodynamic theories.[97]

Mixed Film Theory

The essential features of the mixed film theories are to consider the film as a liquid, two dimensional third phase in equilibrium with both oil and water, implying that such a monolayer could be a duplex film i.e. one having different properties on the water side than in the oil side.[90] Schulman and coworkers[17] considered that the interactions in the interface among surfactant, cosurfactant and oil produce a reduction of the original oil/water, interfacial tension, $\gamma_{o/w}$ to zero or negative. In other words, the two dimensional spreading pressure of the mixed film, π, reaches a value that either becomes equal to $\gamma_{o/w}$ or even exceeds it. Thus the total interfacial tension can be represented by $\gamma_T = \gamma_{o/w} - \pi$ where π is the two dimensional spreading pressure of the mixed film. According to this equation, if $\pi > \gamma_{o/w}$; γ_T , the total interfacial tension becomes negative leading to expansion of the interface until γ_T reaches zero.

The main drawback of the above concept is the high values of π that need to be postulated to reach the condition $\gamma_T > 0$, since many hydrocarbon oils give an interfacial tension between oil and water $\gamma_{o/w}$ of the order of $50 mNm^{-1}$ and such high π values would tend to eject the hydrocarbon molecules from the mixed surfactant film. Presence of cosurfactant in the oil phase reduces $\gamma_{o/w}$ considerably to about $15 mNm^{-1}$ and therefore $\gamma_{o/w}$ should be replaced by the value reached in the presence of the cosurfactant. Thus the above equation can be written as $\gamma_T = (\gamma_{o/w})_a - \pi$ which implies that reasonable values of π (of the order of $15\ mNm^{-1}$) need to be postulated to reach the condition $\gamma_T < 0$.

The above concept of duplex film can be used to explain both the stability of microemulsion and the bending of the interface.

Solubilization theory

The idea of treating microemulsions as swollen micellar systems i.e. with oil or water solubilized in normal or reverse micelles stemmed from the studies of the three and four component phase diagrams on the one hand and the solubilization studies of water and hydrocarbon by nonionic surfactants on the other.[97-101] For example the phase diagram of a three component system of water, ionic surfactant and alcohol usually displays one isotropic aqueous liquid region L_1 and one isotropic liquid region from the alcohol corner containing reversed micelles L_2 and several liquid crystalline structures. The alcohol solution L_2

contains a large amount of water and surfactant in the form of reversed micelles. This solution can dissolve a large amount of a hydrocarbon oil.

Alternatively such inverse micelles may be produced if the alcohol is dissolved in the hydrocarbon followed by addition of water and surfactant. Since the final solution is isotropic and no phase separation takes place when going from the pure hydrocarbon state to the microemulsion state, there does not seem to be any justification of describing these systems as two phase microemulsions as has been done by some authors.[31,36]

Further support for consideration of microemulsions as solubilized systems came from Shinoda's[97] work using nonionic surfactant. Of particular significance in this respect is the solubilization observed with nonionic surfactants with polyoxyethylene oxide head groups. At low temperature, the ethoxylated surfactant is soluble in water. At a given surfactant concentration such a solution solubilizes a given amount of oil which rapidly increases with increase of temperature. As the amount of oil added exceeds a particular level, the excess oil separates as a separate phase. Moreover as the temperature is increased over the cloud point temperature, then the separation into oil, water and surfactant takes place. However, an isotropic region exists between the solubilization and cloud point and it is the O/W solubilized system.

If on the other hand, water is added to an oil solution of the surfactant, solubilization of the water takes place, which decreases with increase of temperature. Any increase in the water weight fraction beyond the solubilization limit, induces water separation. As the temperature is reduced below certain point, separation into oil, water and surfactant takes place. This solubilization theory is consistent with many of the phase diagram studied but failed to explain the microstructural changes observed by modern techniques.

Thermodynamic theories

E.Ruckenstein and coworkers[102-106] and Overbeek in their modern approach consider the free energy of formation of microemulsion $\Delta G_{M.}$ It consists of three main contributions. ΔG_1 an interfacial free energy term, ΔG_2 an energy of interaction between the droplets and ΔG_3 an entropy term accounting for the dispersion of the droplets into the continuous medium. The interfacial free energy term ΔG_1 was considered to consist of two contributions due to the creation of an unchanged surface and contribution due to the formation of electrical double layers. For calculation of ΔG_2 a pairwise additivity of interaction potentials was assumed using two approaches; a continuous approach which replaces the sum of interaction potentials by an integral and a noncontinuous approach whereby the sum was divided into a discrete part representing the interaction with nearest neighbours and an integral part accounting for the interaction with the rest of the droplets. For the calculation of the entropy term ΔG_3 , a lattice model was used to calculate the number of configurations Ω of a liquid mixture formed from N_1 molecules of continuous phase and N_2 molecules of the dispersed phase, the latter is in the form of m equal sized droplets. The entropy term can be calculated from the Boltzmann relationship, $\Delta S_M = k\ln\Omega$, where k is the Boltzmann constant.

The variation of ΔG_M with droplet radius R, and constant volume fraction ϕ_2 of the droplets was then determined using the relationship.

$$\Delta G_M(R) = \Delta G_1 + \Delta G_2 - T\,\Delta S$$

From the above equation, the condition for spontaneous microemulsion formation, with the most stable droplet size (R^*) for a given volume fraction may be obtained,

$$\left.\frac{d\,G_M}{dR}\right|_{R = R^*} = 0$$

$$\left.\frac{d^2\,G_M}{dR^2}\right|_{R = R^*} > 0$$

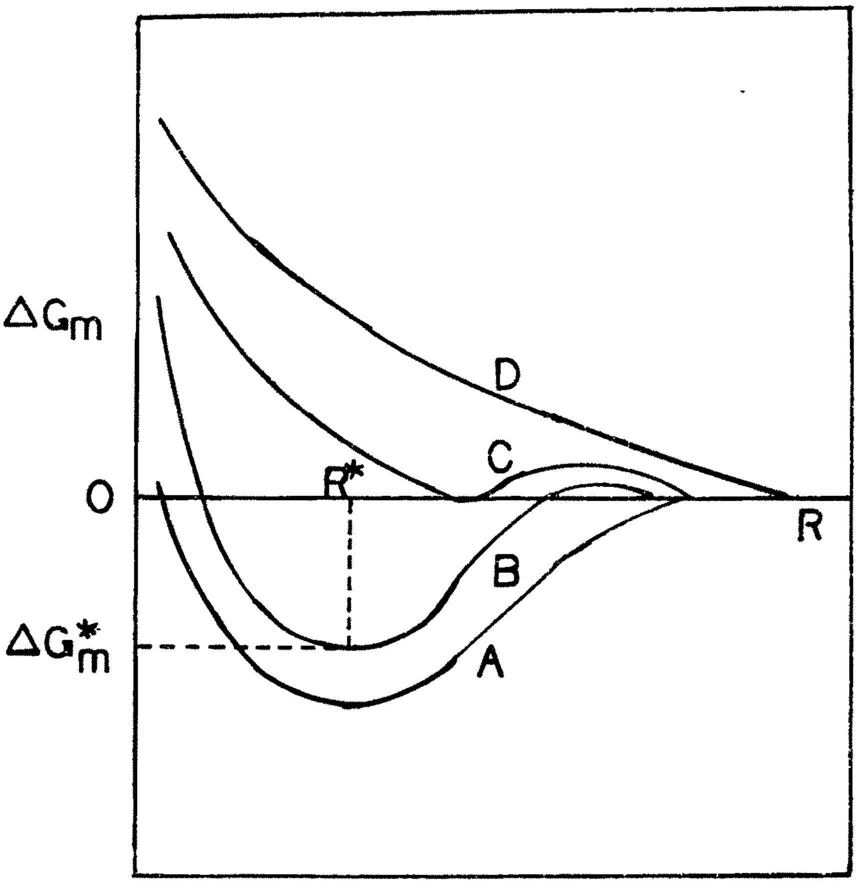

Fig 1.4 The variation of free energy change, ΔG_m, of microemulsion droplet formation, against the radius of the droplet, R.

The variation of ΔG_M with droplet radius R (Fig14) illustrates the transition from instability -----> kinetic stability -------> thermodynamic stability. Thus, curve D represents the case of instability since ΔG_M is positive for all values of R. With curve C, kinetic stability is possible providing the height of the energy maximum is significant. The curves A and B show the case where negative ΔG_M within certain range of R exists. This means that dispersions with droplet radii within that range are thermodynamically stable should show no phase separation and R^* represent the most stable radius. The transition from D --> C--> B-->A is obtained by reducing the value of ΔG_1 ; a reducing the specific surface energy f_s and that is possible by producing an ultralow interfacial tension.

The reduction of f_s to sufficiently small values was later accounted for by Ruckenstein in terms of the dilution effect. Accumulation of surfactant and cosurfactant at the interface not only causes significant reduction in the interfacial tension, but also results in the reduction of chemical potential of surfactant and cosurfactant in bulk solution. The latter reduction may exceed the positive free energy caused by the total interfacial tension and hence the overall ΔG of the system may become negative. Further analysis by Ruckenstein and Krishnan have shown that micelle formation encountered with water soluble surfactants reduce the dilution effect as a result of the association of the surfactant molecules. If a cosurfactant is added, it can reduce the interfacial tension by further adsorption and introduce a dilution effect. The treatments by Ruckenstein and Krishnan[104,105] highlighted the role of interfacial tension in the formation of microemulsion.

1.6 Reason for Combining Cosurfactant

The use of cosurfactants in making microemulsion has a long tradition. Starting with Schulman and Winsor, the cosurfactant was considered an indispensable ingredient of microemulsion.[107,108] The surfactants available commercially are not balanced with respect to their affinity towards aqueous and oleic phases[108], but can be made so by the addition of suitable short chain alcohol, amines etc. called cosurfactants. By getting partitioned between aqueous and oleic phases, they can modify the solvent properties of these phases ie., they change the aqueous and the oil phases to make them relatively more hydrophilic or hydrophobic.

Generally, alcohols, amines and carboxylic acids are used as cosurfactants. Furthermore, if one uses ionic surfactants, electrostatic interactions have to be screened by the addition of salt as a fifth component. The unwanted effects of salt can be compensated by adjusting the alcohol concentration.

The well known Gibbs adsorption equation for a two component system can be extended to multicomponent system.[25]

$$\left(\frac{\partial \gamma}{\partial \mu_{solute}}\right)_{P,T} = -\left(\frac{\partial n_{solute}}{\partial A}\right)_{P,T,\,n_1} = -\,\Gamma^1 \text{ solute}$$

$$\partial \gamma = -\sum_i \Gamma_i \, d\mu i \simeq -\sum_i \Gamma_i \, RT d\ln c_i$$

In these equations γ is the surface tension or interfacial tension, μ_i is the chemical potential of component i, ci its concentration, n_i is its amount, Γ_i is the amount of i adsorbed per unit area (= the surface excess), and A the surface or interfacial area. Component 1 is the solvent. Above equation shows that the addition to the system of a new surfactant which is positively adsorbed will always cause a further lowering of γ.

In some cases, single surfactant will lower the γ far enough for the microemulsion formation to become possible. Double tailed anionic surfactant Azobis-2-ethyl hexyl sulfosuccinate and nonionic surfactants form microemulsion without adding a cosurfactant,[38-40,50] that is they reduce the surface tension to a reasonably low value. Schechter et al[109] described the influence of alcohols on the formation of microemulsion and mentioned the following factors.

1. Depending on the molecular structure of the alcohol, the phase behaviour is changed.
2. Longer chain-length alcohols tend to promote a W I→III→II transition.

3. Alcohols also reduced the tendency for liquid crystals to form. In other words, alcohols tend to reduce the chain interaction energy of the primary amphiphiles stabilizing the microemulsions.

1.7 Non-aqueous microemulsion

A microemulsion (μE) is generally obtained by mixing water, oil and an amphiphile, either ionic or nonionic. In aqueous system, water surfactant head group interaction is responsible for various structures of microemulsion. Aqueous microemulsion is influenced by electrolyte, nonelectrolyte and additives, which affect the water structure. Microemulsion can also be formed with other polar organic solvents with high dielectric constant as a water substitute. Microemulsion is formed as a result of adsorption of amphiphiles between the polar and nonpolar liquids and hence reducing the interfacial tension. This is not a particular property of water as a polar solvent but can also be found in other polar protic solvents. The difference between the two solvents does not lie so much in the difference between their interaction with the head groups but rather in that with the hydrocarbon tails of the amphiphiles.[10,108] This holds for both nonionic and ionic amphiphiles. Nonaqueous microemulsion replacing water by other polar solvents like glycerol,[59,63,65] formamide,[62,64,110] propylene glycol [59,110], ethylene glycol, dimethyl acetamide[110], Dimethyl formamide[110] etc. were studied. Since hydrocarbons are slightly soluble in these solvents, repulsive interaction between the amphiphilic hydrocarbon tail and these organic solvents is weaker than in water, the interfacial tension is reduced and the mutual solubility of different phases will result.

Physical properties like conductivity, viscosity etc. as shown by nonaqueous systems are similar to the aqueous systems. Generally, aqueous microemulsion is greatly affected by electrolytes showing phase[81,82,111,201,202] changes, but for nonaqueous microemulsions there are little or no effect of electrolytes[112]. Regarding the structure, aqueous microemulsion system either exists as droplets of oil-in-water or water-in-oil or bicontinuous. NMR and SANS results reported by Friberg et al[63] indicates that glycerol sodium dodecyl sulfate / hexanol system is rather structureless whereas AOT stabilized[65] glycerol disperses in a heptane continuous phase consists of discrete droplets which are close to spherical in shape. The SAXS measurements of glycerol, propylene glycol/alkyl polyglycol ether (C_iE_j)/hydrocarbon suggest that aqueous and nonaqueous microemulsions[59] are structurally similar. This has also been confirmed by SANS studies reported by Kahlweit et al.[112] The phase behaviour i.e.transition of phases WI → WIII → WII shown by aqueous nonionic surfactant microemulsion with temperature is also shown by the nonaqueous system.[56]

1.8 Reaction in microemulsion

Friberg and Ahmed[66] for the first time used W/O CTAB microemulsion for studying the catalytic effect of these systems on reactions. Since then many reactions have been studied in the microemulsion. Contributions in this field made by R.A. Mackay,[113,114] C.A. Bunton [115-120] and R.Schomackor [121-123] have boosted many workers in the last two decades. Formation of macrocyclic lactones[124] and nucleophilic displacement reactions[125,126] have been reported by Jaeger et al[126] and Schomacker[123]. Photochemical reaction[127] and Wacker Process[128] for the oxidation of alkenes to ketones. e.g. the transformation of $RCH=CH_2$ to RCOMe in formamide microemulsion have also been reported. Tautomerization[129] and dissociation equilibria of β-diketones in microemulsion have also been studied. Acid-base equilibrium[130] and the inversion of cane Sugar were reported by Moulik et al.[131,132-134]

Many workers have studied the application of microemulsion as a reaction medium. The deactivation of mustard[135a] gas was carried out in oil in water microemulsion made by AOT, SDS, CTAB & Brij 96 surfactants. The destruction of organohalides[135b] have also been studied. Selective nitration of phenol to orthonitro phenol[136] was carried out in AOT based microemulsion.

Many reactions have also been studied kinetically in microemulsion.[137-139] The hydrolysis of phosphate ester[140], p-nitrophenyl phosphate ester,[141a] diethyl adipate[123], diethyl butyl malonate[123] have been reported. Kinetics of Alkaline fading of crystal violet was studied in SDS, AOT and Tween 20 microemulsion[141b,145]

Hydrolysis of benzoyl acetate[142] was also studied kinetically in CTAB based microemulsion. Oxidation of iodide[8,143,144] by persulfate was studied kinetically in AOT based microemulsion. Later, this particular reaction was also studied in hexanol/SDS/water[145] system. Recently, the effect of different aromatic hydrocarbons like benzene, toluene, xylene with SDS and cosurfactants propanol and isopropanol were used to study this particular[146] reaction. As this reaction was not well studied in SDS based microemulsion and as we could not obtain any reference of this reaction in CTAB and TX100 based microemulsion we decided to study this reaction in these solvent systems. As the structure of the microemulsion mainly depends on the oil-water ratio and hence may affect the rate of the reaction, we have studied the reaction with changing oil-water ratio. The hydrolysis of aliphatic esters like methyl, ethyl and butyl acetate was also studied kinetically in SDS and CTAB micellar systems by Moulik et al[147]. However we failed to locate in literature this particular reaction in any microemulsion system. So we have studied the hydrolysis of methyl acetate in microemulsions formed by SDS, CTAB & TX100 kinetically. A kinetic study of iodination of acetone[148] was also reported in micellar system and we have studied this particular reaction also in microemulsion.

1.9 Applications

Microemulsions and reverse micellar systems are applied in certain industrial fields, but there are potential applications[149-152] not yet established. Importance of microemulsion is due to their characteristic properties like thermodynamic stability, low interfacial tension and nanosized oil in water and water in oil droplets.

The potential application of microemulsion is found in the tertiary oil[153] recovery. 30% of the total content of an oil reservoir can be extracted by primary recovery and flooding with water. Approximately, another 20% can be obtained by enhanced oil recovery. A potential technique already applied today in pilot experiments which will undoubtedly be increasingly employed in the future, is flooding with surfactants, microemulsion and microemulsion-polymer systems. Principle is based on the very low interfacial tensions and good wetting properties of these systems. It considerably enhances the mobilization of oil droplets or oil ganglions entrapped in the rock pores. The interfacial tension between crude oil and water is typically 50mNm^{-1}, whereas values of 10^{-4} to 10^{-5} mNm^{-1} can be obtained in a suitable microemulsion system. But the process is not so simple because of high reservoir temperature and high salt content in the underground water, loss of expensive surfactant by adsorption in the reservoir.

Microemulsion is useful in metallurgy, for the extraction of metals from ores with low metal contents.[154-159] The mineral substances are dissolved in a strongly acidic or strongly alkaline aqueous medium from which they are then recovered by two-phase extraction using a specific extractant. These extractants are generally large organic molecules which can be dissolved in the oil-rich domains of the microemulsions. The metal ions on the other hand, are found in the water-rich domains. Since the interfacial area in microemulsion is much larger than in a conventionally stirred two phase system, higher rates of extraction can be achieved exceeding those in conventional two-phase systems by a factor of 10 to 102.[158,159] This technique is only suitable for extraction of rare earth metals.

At present, approximately 60% of all soil remediation in Germany is performed by chemicophysical soil washing. In conventional soil washings, organic pollutants are detached from larger soil particles by mechanical energy input. This causes increased adsorption of contaminants at the fine-grain fraction which must then be deposited or burnt. In soil washing with microemulsion,[49,160,161] the detached pollutants are solubilized in the oil fraction of microemulsion as extractive step in addition to washing. At the same time, the wettability improved due to the very low interfacial tensions occuring in microemulsions, so that the fine-grain fraction also becomes accessible to washing.

Microemulsion is used as lubricating and cutting oils. It inhibits corrosion due to surfactants which can solubilize corrosive and oxidizing agents. Because of their thermodynamic stability, microemulsion systems have succeeded over unstable emulsion systems in this field. The composition of such a system was patented in 1930[26] itself. Since that time the systems were improved steadily and are described in numerous patents.

Advantages of microemulsion in pharmaceutical and cosmetic industry are many.[162-164] The preparation of microemulsion is simple due to thermodynamic stability and spontaneous formation and therefore cheaper than that of emulsions. Inhomogeneties and precipitates can be easily detected due to optical transparency and thus avoided. Storage stability is improved due to the thermodynamic stability of the mixture and the stabilizing effects of the surfactants on pharmaceuticals and cosmetics. Formulations using microemulsions with suitable protein compatible surfactants can be used as injection solutions. These formulations can be chosen to be miscible with blood at any ratio. Microemulsion as solvents do not cause any immunoreactions or fat embolisms, in contrast to emulsions[4a]. Higher diffusion and skin penetration rates were observed for microemulsions in pharmaceuticals, compared to conventional formulations. Solubilization of strongly hydrophobic fluoroalkanes used as short-time blood plasma substitutes to maintain a patients oxygen supply.[5,165] These formulation have a low allergic potential, exhibit good physiological compatibility and high biocompatibility.[10] Immobilization[166] of enzymes are carried out in microemulsion.

In addition to conventional detergents, microemulsion can also be used in washing processes. The removal of contaminants from solid surfaces or tissue capillaries is significantly improved by the extremely low interfacial tension in microemulsion systems. Micromulsion is successfully used in dry cleaning.[167]

Another application is the use of microemulsion in textile finishing.[168-171] Many auxiliary agents in this field are of an amphiphilic nature. Affinity of the dye for the textile fibre can be altered by the use of a microemulsion. Greater homogenity in dyeing was observed in comparison to conventional dyeing agents. Higher emulsion stability, excellent product distribution on and in the substrate softness effect etc. can be achieved through microemulsion.

M. Joseph and coworkers[172] have patented edible microemulsion containing polyglycerol esters which can be used to disperse water soluble nutrients, vitamins, flavor and flavors precursors in oils.[173] Edible microemulsion prepared from food grade acetylated lard monoglycerides (Cetodan 90-40) is also reported by otherworkers.[173,174]

Microemulsions appear to be excellent media for facilitating chemical reactions,[117-127, 175] solubilizing a large number of very different compounds, possessing a large internal interface. As a consequence a variety of chemical reactions have been studied in these media.

It can be used to produce ultrafine particles with sharp particle size distribution by precipitation.[176-178] The particle size is found to be a function of the size of the water droplets. One of the important technical application of such submicron fine particles is in high density recording devices which are widely used in audio and video applications, instrumentation, computer data storage, optical detectors, photo catalysts and nonlinear optical devices.[179-184] The magnetic material extensively used for these purposes are γFe_2O_3, Fe_3O_4, Cobalt doped Fe_2O_3, CrO_2, CdS, PbS[185,186] etc. Technology demands that the material for high recording medium should be ultrafine, chemically homogeneous, stable with narrow size distribution and having a predetermined shape. Recently, immobilization of enzymes are carried out by entraping in nanosized ceramic particle like $Al(OH)_3$ prepared in microemulsion solvent.[162] For therapeutic application, particle size must be accurately controlled and hence should be of nanometer size.

In biochemical reactions,[187-189] enzyme can be solubilized in the water droplets of microemulsions without the activity being lost. Enzyme catalyzed synthesis with water insoluble substrates in microemulsions can be carried out by selecting the components for preparing the microemulsion so that no inhibition or denaturation of the enzyme occurs. Reaction control, product isolation and enzyme recovery from the microemulsion are possible.[4a]

Electrochemistry often faces the problem of finding a solvent which simultaneously dissolves an organic substrate and a sufficient amount of conducting electrolyte. The use of O/W microemulsion as the reaction medium offers very interesting new possibilities of electrochemical analysis and catalysis.[190]

Polymerization of water insoluble monomers in microemulsion yields monodisperse lattices.[191-195] Particle size of these polymers are regulated by this technique.

A number of organic reactions[103] have been carried out in microemulsion for the past 20 years. In microemulsions, both, water soluble and water insoluble compounds dissolve simultaneously and cause them to react together to give the products.

1.10 Scope of the present work

Microemulsions have both applications and potential applications in research and industry. Even though the research on microemulsion has been growing at a fast rate during last two decades, microemulsion being used as a reaction medium and its catalytic action have not been too well investigated in the literature.[196-198] The systematic and detailed study of kinetics of reactions in microemulsion mediated systems are still, in that sense, lacking.

Although nonionic surfactants are amply used in microemulsion studies TX100 a useful surfactant has been seldom[199-201] studied. So, in the third chapter of the thesis, we have studied a nonionic microemulsion with Triton X 100. The use of DMF as a polar liquid was also not reported before. Hence we have studied nonaqueous microemulsion with DMF as polar liquid. Generally, lower alcohols, amines etc are used as cosurfactants. We have also studied the effect of an ester, ethylpropionate as cosurfactant. In the literature, ester has been used as a nonpolar component [202,203] in forming microemulsions. A study of phase diagram, specific conductance, viscosity, adiabatic compressibility and effect of electrolyte etc. are discussed.

In the latter part of the thesis, various microemulsions have been used as a reaction medium to study the kinetics of some selected reactions.[204,205] Aqueous microemulsions formed by SDS, CTAB and TX100 have been used for this study. SDS and CTAB microemulsions were well characterized earlier[81,82,206,207] in our laboratory. Microemulsion is generally prepared with trace amounts of reactants which do not cause a change in the phase behaviour. The effect of temperature and changing oil-water ratios are studied.

The particular reactions studied are :

1. Oxidation of potassium iodide by potassium persulphate. This reaction in CTAB and TX100 containing microemulsion systems was not investigated so far.
2. In the literature, methyl acetate hydrolysis was studied in a micellar medium. Therefore, we have studied the methyl acetate hydrolysis in various microemulsions using aqueous HCl. This chapter also includes the study of iodination of acetone in TX100 and SDS based microemulsion systems.