CHAPTER-1

Introduction

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1.1 GENERAL INTRODUCTION

Surface science is a vital component of knowledge because of its numerous use in industrial processes. However, its importance in bioscience and biomedical engineering cannot be over-stressed. Self aggregating system is an area of surface science which represents areas like micelles, bilayers, microemulsions, vesicles etc.[1-3]. The spontaneous self aggregation of surface active molecules has given rise to various uses including formation of nanoparticles, catalysing the reaction, formation of micelles, bilayers etc.

Due to the spontaneous formation, variety of structures are formed by surface active agents depending upon the conditions. There are many direct and indirect applications of microemulsion. When a surface active agent is added to the two immiscible liquids, one being water (polar) and other being an oil (non-polar), a significant phenomenon, that is the reduction of interfacial tension takes place as the surfactant gets adsorbed at the interface. The decrease in the interfacial tension helps oil to disperse in water with definite size and shape or vice versa. Most of the time the dispersed droplets are large in size with diameter (> 100 nm) in the presence of a surface active agent and the resultant liquid is opaque or turbid which is not kinetically stable and phase separation occurs after some time. This is called an emulsion. Under certain conditions a very large amount of organic substance (i.e. non-polar organic) can apparently get dissolved in an aqueous solution of surfactant or a large quantity of water can be dissolved in an apolar solvent. The resulting 'solutions' are optically clear and are indefinitely stable. The diameter of these dispersed droplets are in between 10 to 100 nm. These systems are called microemulsion.

1.2 MICROEMULSIONS

For the stability of microemulsion a low interfacial tension between water and oil is required. Some times the surfactants cannot decrease the interfacial tension to a very low value and so a fourth component (e.g. a short chain alcohol, amine or carboxylic acid) is added. This fourth component is called 'cosurfactant'. The spontaneous decrease of free energy of interface formation helps in the stability of microemulsion. Thus, the single phase, spontaneously forming, thermodynamically stable, transparent, isotropic, oil-water mixed system is called microemulsion[4-11]. The fourth component is not always required. There are also microemulsions without detergent known as microemulsion without detergent or detergentless microemulsion[12].

In the microemulsion the size of the dispersed phase is between 10 and 100 nm as a result of which the white light does not scatter[13] but passes through and hence the microemulsion is a transparent medium. Thus, in microemulsion (μE) either oil or water is the dispersed phase. If water is dispersed in an oil, then the microemulsion is called water in oil microemulsion (w/o). If oil is the dispersed phase then the microemulsion is called oil in water (o/w) (Fig. 1.1).

Microemulsions are of interest today because these are made up of dissimilar components like water and oil though they look like isotropic, translucent phase. Also during the past 10-20 years there has been complete revolution in utilizing microemulsion system in a variety of chemical and industrial processes.These are utilized in cleaning and washing[14-16], as fuels[17-19], in enhanced oil recovery[20-21](EOR), acidizing, in preparation of nanoparticles, preparation of silver[22] and gold colloids, preparation of metal sulphides, polymerization, in food industries[23-25], for flavours[26-28] and aromas, dye solubilization, solubilization of vitamins and preservatives[29-31], etc. They are used in protein extraction[32,33], hydrophobic solute extraction[34,35] as well as process development[36], etc.

1.3 HISTORICAL BACKGROUND

Schulman and Hoar introduced the scientific concept of microemulsion in 1943[37] though the term 'microemulsion' was first introduced by Schulman et al.[38] in 1959. The four essential components of microemulsions were oil, soap, water and a short

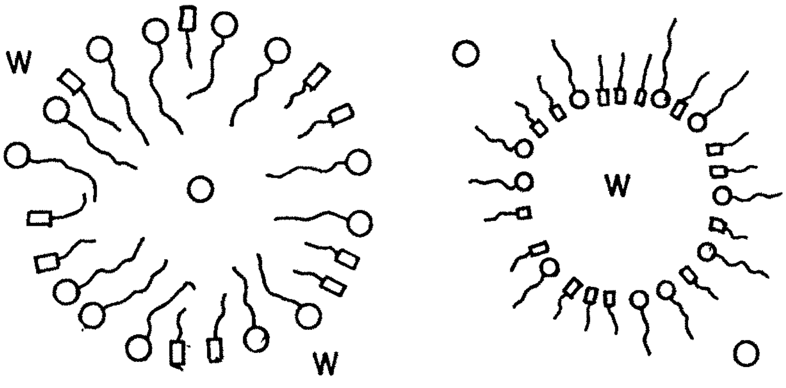


Fig. 1.1 : Representation of O/W and W/O microemulsion droplet (Surfactant ∼O; co-surfactant ∼□).

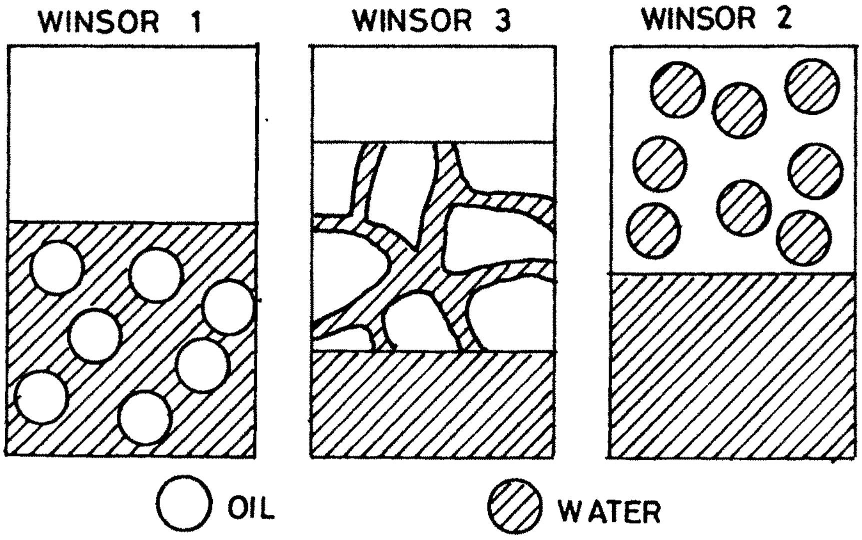


Fig. 1.2 : Representation of Winsor I, Winsor II and Winsor III microemulsion.

chain alcohol[39-43]. The solution was prepared with four components water, benzene, hexanol and potassium oleate[41-42]. The conditions of formation of microemulsion were -

1. Water to surfactant ratio should be high.
2. The ratio between surfactant to alcohol [37], amine or another non-ionic material should be equal.

J.H.Schulman[38] et al. postulated that the microemulsions are formed when the interfacial tension between water and oil reduced near to zero. But this idea was contradicted by their own experiment in which they used alkyl sulfates, benzene and water and could not form the microemulsion. They explained the observation using the spreading pressure concept of Gibbs. The surface pressure (Π) can be obtained spontaneously by the monolayer penetration of an alkyl alcohol or cholesterol monolayer with ionic surface active agents like alkyl sulfates and alkyl amines and substituted amines injected into the underlying solution.

They also described the radii (r) of the dispersed droplet of water in oil (w/o) -

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

in which the radius of dispersed phase droplet is the sum of radius of the water droplet and the thickness of the interfacial film of surfactant and alcohol.

The microemulsion was given different names by different groups. Shinoda[44-46] and coworkers termed the microemulsion as "solubilized micellar solutions" as they observed the transitions in microemulsion obtained by Schulman[37]. Also the microemulsion was called "soluble oils"[47], "inverted micelle"[48], "oleopathic hydromicelle"[49], "transparent emulsions"[50], "micellar emulsion" and "micellar solutions"[51], etc. Shinoda and Friberg suggested the word "colloidal"[52] but at the end the term microemulsion as was given by Schulman in 1959[38] persists. But much before 1959 there were several microemulsion based products[53] which were patented and were commercially available in the market. Bowden and Holmstein in 1936 patented the simple method to make the microemulsions from Carnauba wax - a natural wax with a significant proportion of polar molecules. They gave the procedure of formulation which contain 15% wax, about 3% of potassium soap and remainder being water. The product was made at high temperature. So, the molten wax forms an oil-in-water microemulsion. On cooling the small droplet size is retained and the wax solidifies to form a stable dispersion in water particles of around 100 nm. Thus, the product has an almost transparent appearance and easy to apply to large areas like floor and requires no buffing. This product was sold under the name of "Dribrite". Similar kind of products like cutting oil, pine oil emulsions[52], flavour emulsions[24], pesticide emulsions, etc. were being utilized in daily life.

1.4 STRUCTURE, THEORY AND THERMODYNAMIC ASPECTS OF MICROEMULSION

There are various techniques used for studies of phase behaviour, structure, dynamics and thermodynamics of microemulsion[53] systems. The methods like viscosity[54], conductance[55], NMR[56], fluorescence[57], small angle neutron scattering, positron annihilation, light scattering etc. have been used. The structure of microemulsion depends on the nature of surfactant. Oil as well as the cosurfactant plays a major role in the formation of microemulsions as it provides the kinetic stability to the microemulsion system. It was P.A.Winsor[58] who in 1968 distinguished between four different types of microemulsions (Fig. 1.2).

The Winsor I is oil in water microemulsion, where excess oil is in equilibrium with microemulsion. This system occurs at a low temperature for the non-ionic and at a low electrolyte concentration for the ionic, the surfactant is preferentially soluble in the water and oil-in-water microemulsions are formed where no surfactant aggregate exist in the oil phase and only a small concentration of surfactant monomer. This system is also referred to as L_1 phase (Fig. 1.2).

The second system which is known as Winsor two (WII) is a water in oil microemulsion in equilibrium with excess water also known as L_2[59] phase. Winsor II system results from the Winsor III system where the temperature in non-ionic surfactant system is increased or with ionic surfactant, the concentration of any electrolyte is increased so that it is converted to Winsor II (Fig. 1.2).

The third system is known as Winsor three (WIII). This system is called the 'middle phase microemulsion', where water and oil both are in equilibrium with microemulsion phase. This system is formed when temperature is raised (for the non-ionic) surfactant or electrolyte concentration is increased (for the ionic) of the Winsor I system. The middle phase contains oil, water and the majority of the surfactant. No surfactant aggregates now exist in either the aqueous or the oil phase. The fourth system which is known as Winsor four (WIV) is an isotropic, clear and transparent phase. The transition shown in above is from WI → WIII → WII, this transition also changes from WII → WIII → WI in certain systems (Fig. 1.2).

Bancroft's[60] rule governed all structures of microemulsion by the phase behaviour. In a qualitative way it is the Winsor R ratio, which compares the surfactant-oil interactions to those between surfactant and water.

It can be taken as -

$$R_1 = \frac{A_{SO}}{A_{SW}}$$

where A_{SO} is a measure of the surfactant-oil interactions for the surfactant molecules present in the bulk phase (Fig. 1.3), and A_{SW} is the measure of the surfactant - water interaction and where $R_1 < 1$, the layer of surfactant tends to expand towards oil which will form oil in water microemulsion. As surfactant is more soluble in water than in oil, this forms a convex layer towards water. If surfactant is more soluble in oil than in water, then the surfactant will tend to expand towards water and it will

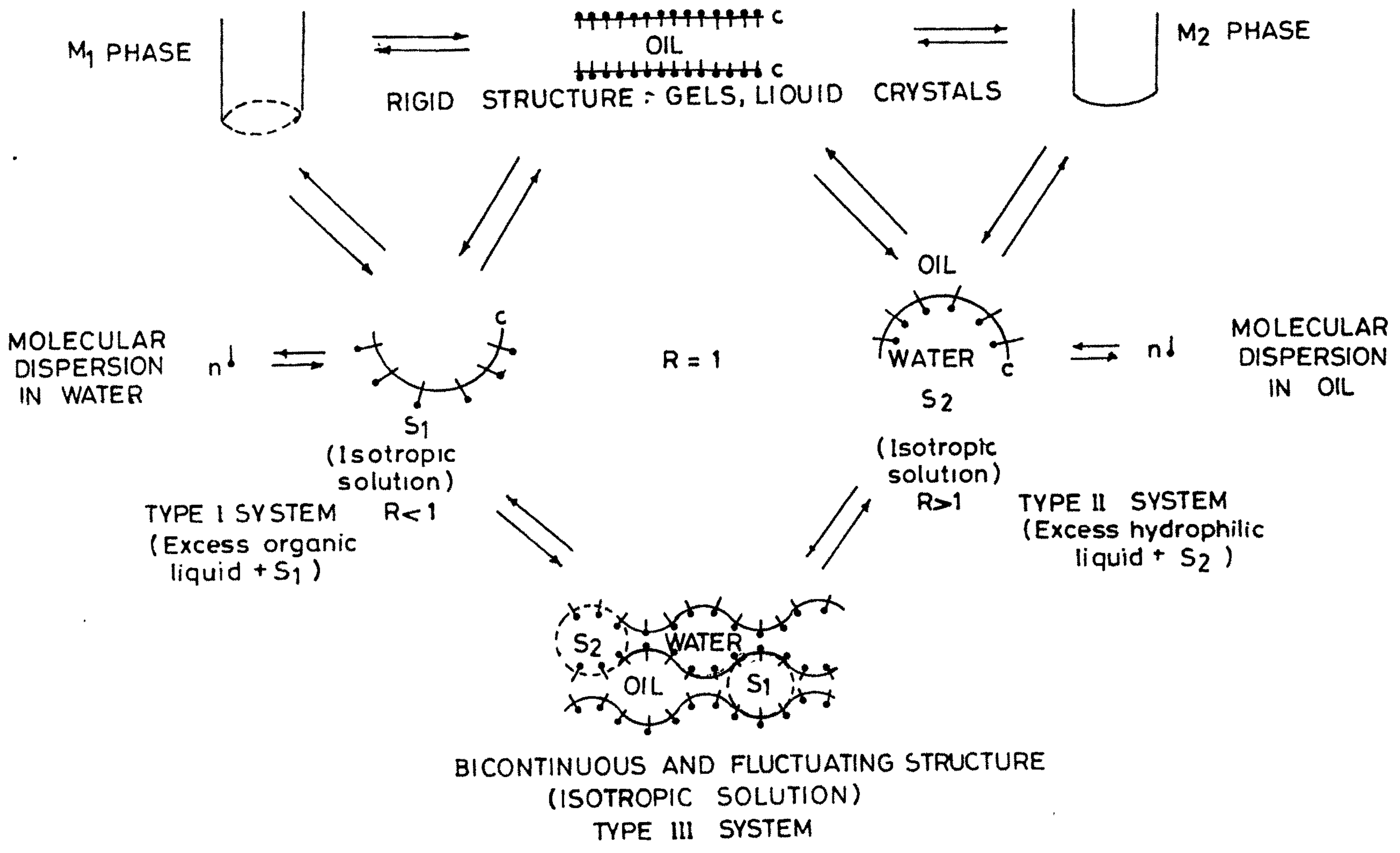


Fig. 1.3 : Presentation of changes of phases.

form convex interfaces towards oil in the case of water-in-oil microemulsion (μE) and of reverse micelles that is WII. If R=1 then surfactant layer is soluble equally in the water and oil phases and it corresponds to WIII (Fig. 1.3). The same discussion can be made in terms of the surfactant partition coefficient Kp between water and oil. The system can be optimum when partition coefficient Kp $\cong$ 1 and then the surfactant will have maximum solubility and it will show lowest interfacial tension. The above phase sequence can also be rationalized on the basis of the surfactant packing ratio (P).

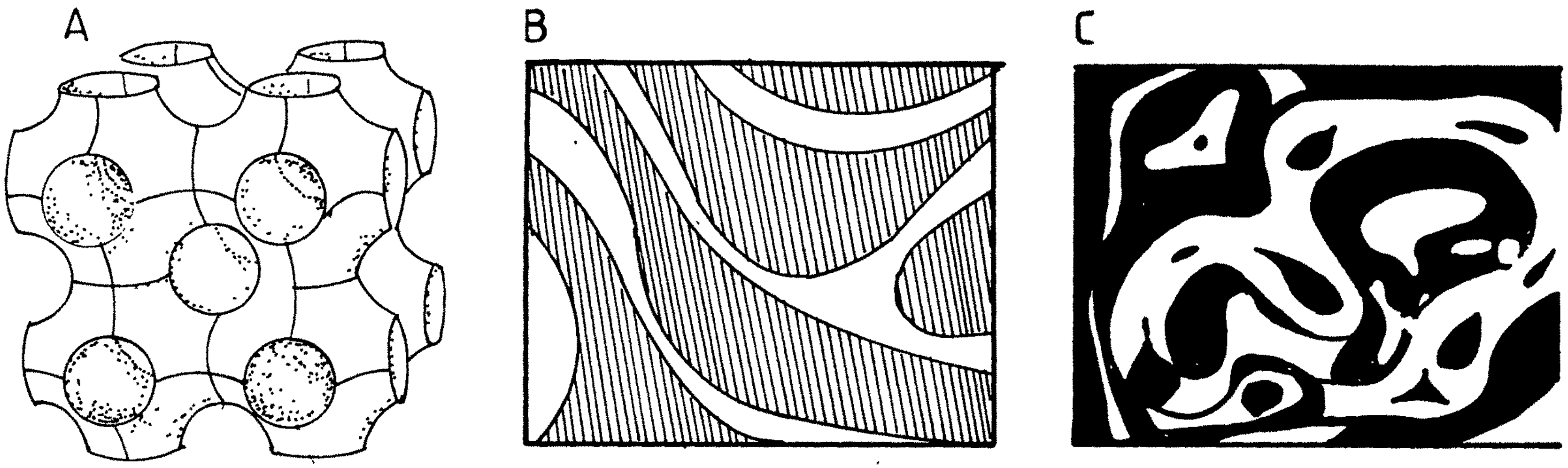
$$P = V / al$$

where V and l are the volume and length of the alkyl chain and a is the surface area available to one surfactant molecule at the interface. It has been argued that if $P > 1$ the interface is concave towards water and it is convex towards water if $P < 1$. If $P \cong 1$ i.e. there is no curvature at the interface then a WIII system is obtained.

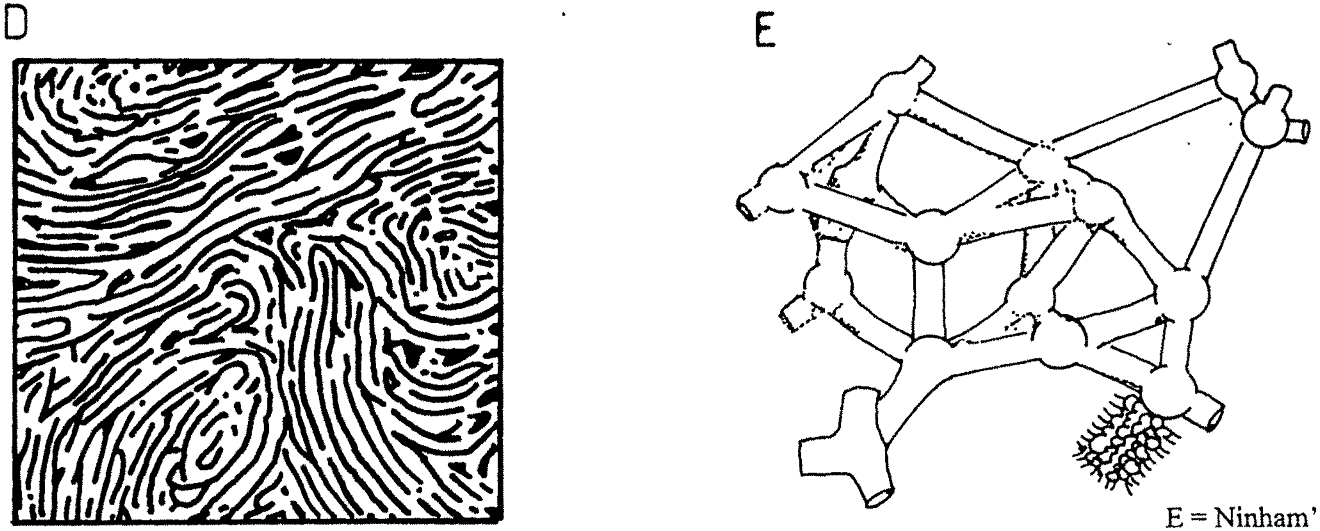
Structures and Models for Microemulsion :

The structures of microemulsion i.e. w/o or o/w or bicontinuous can be determined by various methods. However, the bicontinuous structure is still not clearly understood. The bicontinuous structure (Fig. 1.4) was first proposed by Scriven in 1976 (he observed that systems where comparable amount of oil and water were present were neither globular nor lamellar).

He observed that equal amounts of an oil or water did not show w/o or o/w microemulsion and it is without interval or zone. He presented the structure as the truncated octahedral with same cubic symmetry of spherical droplets. Talmon and Prager[62-63] gave a simple procedure to generate random two fluid geometries. They considered the entropy and curvature. In the model by the use of statistical mechanics the bicontinuous microemulsion was derived with interconnected Voronoi polyhedron randomly filled with oil and water. This model was modified later by de Gennes and



A = Scriven's model; B = Prager's model; C = Lindman's model,



D = Optimized bicontinuous model

E = Ninham's model.

Fig. 1.4 : Representation of models of bicontinuous microemulsion.

coworkers[65]. They introduced the term "persistence length" (ξ) to denote the size of the cube which represents the length of a cubic side which is randomly filled with oil and water and is equal to

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

where ϕ_o and ϕ_w are the volume fractions of oil and water respectively. Σ is the area per surfactant molecule, and C_S is the concentration of surfactant. But in the three phase equilibrium this model was not suitable and hence Widom[64a] modified the models. He further introduced important advancement in the theory by allowing the cell size to vary and then determined the self-consistency at each point of the phase diagram. Two and three phase equilibria were obtained by introducing a microscopic cut off area per surfactant molecule in the interfacial film.

It was also found that the degree of freedom depends on the oil-water interfacial tension and less on the bending properties of the surfactant film. Thus, in contradiction to the de Gennes[65] model; the characteristic length scale predicted for the middle phase microemulsion was not related to the persistence length ξ. Widom's theory does not explain all the aspects of the properties of the microemulsion. So, Andelman suggested a new model[64b]. This model depends on following assumptions :

1) 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) Space in this model is divided in to the cubes of size ξ .
3) Random mixing approximation accounts for the entropy of the interface at length scales larger than the cell size ξ.

So, the free energy per unit volume of the microemulsion phase is -

$$f = \frac{1}{\xi^3} [TS (\phi) + 8 \Pi P (\phi) K (\xi) (1 - \frac{2 \xi\cdot(1-2\phi)}{\rho_0})]$$

The first term in the above can represent the entropy of mixing of water and oil domains, where T is the temperature. Next term represents the bending energy of the surfactant film at the water-oil interface. Still there are certain approximation in the treatment of the entropy and the bending energy. Ninham[66] et al. described the bicontinuous structure for the spheres connected by cylinders as the cylinders are connected through random open channels. So, the model is called disordered open connected cylinder (DOC) model. With water alone the surfactant form the micellar phase i.e. the surfactant parameter, V/al is close to 1 and V is the volume of the hydrocarbon tail region, and a is the group area and l is the length of surfactant chain. The model for microstructure can be put together as where all the network sphere centres are first located at the centres of hard spheres whose positions are frozen in a random packing, which ensures that the interface lacks long range translational order. The density of the packing is determined 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. The model provides a characteristic distance for the structure and gives rise to the broad peak measured by SAXS. 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. Thus, Fig.14 shows the DOC structure formed by placing spheres centred at each vertex and surrounding each link in the Z-coordinated net by cylinders, which can explain many properties of bicontinuous microemulsion like conductance, self-diffusion, viscosity, etc.

Theories of Microemulsion :

There are various theories which have been put forward to explain the formation of the microemulsion. The theories are a) mixed film theory[67]; b) solubilization theory and c) thermodynamic theory.

The mixed film theory suggests that the two dimensional liquid film is in equilibrium with both oil and water. The film is a duplex film having different properties on the oil and the water side. Schulman and coworkers proposed that the surfactant, cosurfactant and oil reduces the interfacial tension at oil / water interface. The value of Π the spreading pressure either exceeds $\gamma_{o/w}$ or becomes equal to $\gamma_{o/w}$. So, the total interfacial tension (γ_T) at the interface becomes

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

The main disadvantage of the above theory is that Π cannot reach higher value i.e. $\Pi > \gamma_{o/w}$, and the condition $\gamma_T < O$. Many hydrocarbon oil gives the value of the interfacial tension of the order of 50 mN/m but later Prince[49] suggested that the presence of the cosurfactant in the oil phase reduces $\gamma_{o/w}$ considerably and therefore $\gamma_{o/w}$ should indeed reach the lesser value in presence of a cosurfactant and hence the above equation becomes -

$$\gamma_T = (\gamma_{o/w})_a - \Pi$$

which can reach the postulated values. The advantage of above theory is that the duplex film can be used to explain both the stability of microemulsion as well as the bending of the interface. In this theory they suggested γ_T value cannot be negative though it can go to a very small value.

In the solubilization theory, the microemulsion was treated as swollen micellar system in which oil or water are solubilized in normal or reverse micelles. This was supported by Shinoda and coworkers[44]. They used nonionic surfactant with particular stress on polyoxyethylene group. At low temperature the ethoxylated surfactant is soluble in water. They show the impact of temperature on solubilization as well as the cloud point curve of the surfactant. The excess oil separates. In the same system if temperature increases the oil starts solubilizing but at the same time water starts separating out of the system and hence it forms w/o system. Thus, water will remain as a separate phase. Thus the theory shows that the system is solubilized in normal or reverse micelle.

The thermodynamic theory was proposed by Ruckenstein[68-71] and Overbeek[72a]. According to them the driving force for the formation of microemulsion droplets is the entropy of dispersion of one liquid in the other. However, the free energy of formation of microemulsion ΔG_m is the contribution from three term, : ΔG_1 an interfacial free energy term, ΔG_2 an average of interaction between the droplets term and ΔG_3 is an entropy term, accounting for the dispersion of the droplets into the continuous medium. However, this dispersion greatly increases the surface of contact between the oil and water which results in an unfavourable interfacial free energy term rapidly increasing as the droplet radius decreases.

Thus, the total ΔG_m is negative with droplet radius R. However, the total free energy is related to the droplet.

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

So, from the equation the spontaneous microemulsion formation with the most stable droplet size (R*) will be given by i.e. rate of change of free energy with respect to droplet radius R

$$\left.\frac{dG_M}{dR}\right|_{R = R^*} = O$$

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

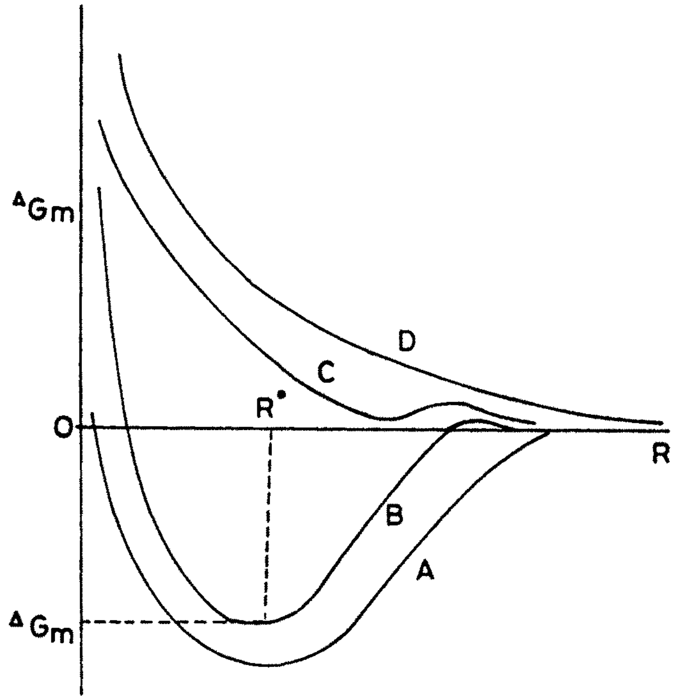


Fig. 1.5 : Variation of ΔGM with R.

Simple calculations indicate that the formation of stable droplet requires the interfacial tension (IFT) to be below about 0.01 mN/m.

Fig. 1.5 represents how ΔG_M is related with radius R of the droplet. Most of the surfactants are unable to bring about such a large lowering of interfacial tension (IFT) which is achieved through the addition of a cosurfactant.

1.5 ROLE OF OIL AND COSURFACTANT

Different authors[72b,72c] have discussed the role of non-polar phase i.e. an oil in the microemulsion formation. Ninham, Chen and Evans[73] in 1984 discussed the role of non-polar phase. They compared microemulsions containing alkane and alkenes. Microemulsions are formed at much lower initial water content with alkenes than with the alkanes. This difference can be understood in terms of work on alkane uptake in bilayers which indicate that the surfactant parameter V/al measures curvature. This is determined by alkane penetration into the surfactant regions, where V is the hydrocarbon volume of the surfactant including adsorbed oil, a is the head group area and l is the surfactant chain length. Alkanes with chain length less than that of the surfactant penetrates much more than those with greater chain length. The surfactant itself forms lamellar phase in water so that it has an intrinsic V/al < l with n-hexane as oil except high oil penetration (V/al >1) consistent with the reverse structure which forms at lower water content, and a systematic decrease to tetradecane

(where $\frac{V}{al} > 1$)

Differences in the densities between alkanes and alkenes are small and the major effect on oil penetration should be that due to the small dipole moment associated with the terminal double bond.

In various[73-74] papers, it was speculated that the alkenes are more hydrophilic and penetrate more than alkanes which form the opposite curvature than the alkenes.

On the basis of the conductance, viscosity and phase diagram data it has been further proposed that there are two structures for the curvature in the alkenes. The first involves a discontinuous oil phase contained in rhombo decahedral (RDH) structures covered by surfactant. The space between RDH structures is occupied by the water which provides continuous conducting pathways.

NMR and diffusion coefficient measurements show that both the oil and water phases are continuous[78-79]. The second structure involved is a bicontinuous system containing interconnected conduits filled with water which are dynamic and fluctuating in nature. The oil-water interfacial area is determined by the concentration of surfactant while the curvature of the conduits is dictated by the volume of the surfactant chain plus penetrating oil. For a fixed surfactant concentration, high oil penetration gives conduits of small diameter and thus less water is required to form the initial microemulsion.

In formation of microemulsion it is essential to reduce the interfacial tension to a very low value. Yet the individual structure of a microemulsion will depend on the nature of surfactant, temperature, salinity and amount of added cosurfactant[78-80]. Early on Schulman found that microemulsions required alcohols usually mid or short chain alcohol as cosurfactant. Structure of microemulsion will be determined by the interfacial curvature and for this the governing parameters are the interfacial tension and the bending elasticity at the interface. By use of different cosurfactants[81,82a], we can change the structure of microemulsion. So on addition of surfactant the total head charge will be changed. The most commonly used cosurfactants are the short chain fatty alcohols. The small size of -OH group makes them useful when mixed with ionic surfactants with large hydrated head groups such as the sulphates and sulphonates. When n-alkanols are used as a cosurfactant with an ionic surfactant the chain length has a significant effect over the microemulsion formed. For shorter chain alcohols less than C_6 the oil / water interface is found to be very fluid and the middle phase microemulsions form spontaneously with a bicontinuous structure. Longer chain alcohols with chain length higher than C_6 tend to form more rigid structures with a possibility of bicontinuous structure. The evidence of dependence on cosurfactant chain length comes from electrical conductivity measurements and from self-diffusion coefficient and NMR studies.

For the multicomponent system Gibbs extended his equation in following manner which can be written as follows

$$\partial\gamma = -\sum_i \Gamma_i \, d\mu_i = -\sum_i \Gamma_i \, RT \, d\ln c_i$$

where γ is the interfacial tension, μi is the chemical potential of component i, c_i, its concentration, Γ_i the amount of i adsorbed per unit area. But it is well known that temperature and required cosurfactant concentration have reciprocal relationship and that successful microemulsion production at low temperature is difficult. Burrel et al.[82b] studied the role of alcohols and their impact on solubilization by amphiphilic systems and concluded as follows "separating the surfactant molecules at the interface or at least introducing some disorder into the interfacial membrane is an obvious method to achieve reduction of the surfactant molecular interactions. Thus the alcohol fluidizes the phases and decreases the viscosity, destroys the lamellar liquid crystalline structure, provides an additional interfacial area, reduces the electrical repulsion between droplets by decreasing the surface charge density and induces the appropriate curvature changes.

1.6 EFFECT OF ADDITIVES ON MICROEMULSION

When salinity[83,84] or an equivalent variable is changed, the microemulsion generally undergoes orderly phase transitions from a lower phase transitions to a middle phase and then to an upper phase state. The knowledge of the microstructure of the different microemulsion phases is important in understanding the properties of microemulsions. Lower phase microemulsions (μE) are far from the middle phase state and are generally consist of droplets of oil dispersed in water, while upper phase microemulsions are far from the middle phase state and are formed of water drops dispersed in oil. The middle phase microemulsions are of special interest for surfactant based enhanced oil recovery process[85] and also to understand how the spherical drop structures of lower and upper phase microemulsions change when changes in salinity or some other variables move these into the middle phase region.

There is a large effect of the water soluble polymers[86] on the phase diagram when these[87,88,89a,89b] are added to the 1ϕ microemulsion with a high surfactant / co-surfactant ratio. It changes the boundaries of plait point in the phase diagram.

Different polymers with salts[89c,89d,89e,89f,89] gives different properties at different temperatures[89a]. Generally the polymers used are polyoxyethylene oxide, polyvinyl pyrrolidone, dextrin, xanthan, polyacrylamide or hydrolysed polyacrylamide[89b]. Most of these polymers[90,91] are used in the enhanced oil recovery. It is therefore necessary to understand this technologically important phenomenon[92]. The molecular weight of polymer is also important. For understanding this effect a model which successfully predicts many qualitative features of phase separation is coacervation model. This model is studied as follows[93]. The polymer microemulsion incompatibility can manifest itself by two sorts of phase separation that occur; when polymer is added to a single phase oil internal microemulsion. That is it results in a phase consisting of microemulsion similar in appearance to the original, together with another phase concentrated in polymer and the latter phase may be concentrated and viscous to form a "gel".

So, it is important to study the dilutable or "non dilutable" system. The coacervation model is postulated on the following process which shows that if a homopolymer is added to the dilutable microemulsion then various things can happen as for example

a) Some surfactants may adsorb on the polymers.
b) Polymers may adsorb on the surfactants.
c) Polymers may adsorb on the microemulsion droplets.

The above process can take place if there is attraction between polymer and surfactant but if there is repulsion then the process can be modified.

The model is examined on the following major assumptions.

I. The particle size and shape of the microemulsion do not change when coacervated then only their number densities in the two phases change.

II. The microemulsion particle should be treated as macromolecules. The particle is taken as "given" entity which can be dilutable with its external phase in the same way that polymer solution can be diluted with a solvent. No composition changes other than the addition of polymer are carried out in this treatment.

So, from the coacervation model the main conclusions drawn are :

a) The transition from a lower or upper phase changes in salinity or an equivalent variable may occur as the lower or upper phase becomes unstable and separates into a "drop rich middle phase" and a "drop poor excess phase". The instability in microemulsion formation arrives due to an increase in the vander Waal's attraction among the constituent drops in the microemulsions.
b) The ultralow interfacial tension between the separated phases, support the possibility of phase separation as a mechanism for the generation of a middle phase.
c) The "universal" scaling relation near the critical state, proposed earlier for microemulsion systems can be explained with the observation that phase separation is determined only by the vander Waal's parameter and any variable which effects phase separation does so as a result of its effect on this parameter.

d) In a ternary phase diagram when a middle phase zone is generated from a lower phase zone upon increase in salinity it is accompanied by a zone of oil-in-water “Upper phase” microemulsion. Correspondingly, when a middle phase zone appears from an upper phase zone it is accompanied by a zone of water-in-oil “lower phase” microemulsion.

e) The incompatibility between a lower phase microemulsion and an added polymer can be explained in terms of the phase separation of the microemulsion polymer mixture into a “drop-rich phase” and a “polymer rich phase”. Phase separation may be enhanced by the repulsion between the microemulsion drop and polymer molecule, which arises when a polymer[95] molecule approaching a microemulsion drop loses its configurational freedom.

The polymer microemulsion mixtures studies show a number of qualitative features[96]. Also if the surfactant chain in the outside of microemulsion were sufficiently longer then the expression for the chemical potential would be expected to be more nearly alike to that for polymer solvent interaction. The coacervation occurs near the polymer threshold overlap concentration so that the Cloud point exponent is the same as the Mark Houwnik exponent in the intrinsic viscosity-molecular weight relation ship.

1.7 NON-AQUEOUS MICROEMULSION

Microemulsions in which a non-aqueous polar solvent is dispersed in a hydrocarbon were introduced rather late[97-99] inspite of the fact that micellization in polar organic solvents was investigated for some time. Thus, when water is replaced by polar organic solvent in an oil / surfactant - cosurfactant / water system then such a system is called non-aqueous microemulsion. Rico and Lattes[98] attempted first to make such kind of microemulsion in which they replaced water by using polar solvent formamide as they prepared a system of formamide, butanol, cetyl trimethyl ammonium bromide (CTAB), cyclohexane and studied the effect of electrolytes and the other additives. There are several reports that non-aqueous microemulsions are stabilized by nonionic and ionic surfactants and also by a medium chain alcohol as a cosurfactant.

Also several reports[100-101] show that the non-aqueous microemulsion has less organized structure of an inverse micelle or a microemulsion droplet. The instability of the droplet interface appears reasonable and actually an expected consequence. Also non-aqueous microemulsion with polar organics have structure like oil in water or water in oil type as well as bicontinuous microemulsion.

And also there are reportes of non-aqueous microemulsion where water was replaced by dimethyl sulfoxide or γ-butyrolactone[102-107] e.g. dimethyl sulfoxide, Triton X-114 / n-pentanol / dodecane and γ-butyrolactone / Triton X-114 / n- pentanol / dodecane.

1.8 APPLICATIONS OF MICROEMULSIONS

Microemulsions are relevant to various technological applications[108] and hence extensive multidisciplinary studies were carried out on various microemulsions in last 50 to 60 years. It is difficult to include all the applications in this chapter. So, we summarise a few of them here.

Microemulsions are applied in washing[109] and cleaning[110], as fuels, in crude oil exploration and as enzyme free reaction media[17]. In preparation of small size particle[111-112] and in many organic reaction like hydrolysis of an esters[113-115], the microemulsions are used, to reduce or decrease the toxicity of the pollution. Also in the field of photochemical and electrochemical reactions, in the field of lubrication and cutting, ultrafine cleaning etc.

One of earliest technical application of microemulsion is their use as cleaning systems. The industrial cleaning process involves simultaneous removal of all hydrophobic contaminants like salt, pigment, protein etc. In a classical cleaning process the contaminant is removed by long range electrostatic repulsion which is induced between the contaminant and underlying solid surface. Because of these processes the contaminants can either be solubilised into the surfactant solution or dispersed or suspended and stabilised by surfactant in the aqueous solutions. The best advantage of applying microemulsion in washing is that it can both solubilise hydrophilic as well as hydrophobic components at the same time i.e. the two step process could be done in a single step. Also another advantage of this process is that the temperature of the system can be optimised with solubilisation which would save considerable amount of energy in the household.

Microemulsion as a fuel[116a] is used for internal combustion engines. Here water is vapourised during the combustion which will lower the heat released and also the combustion temperature. As a direct consequence the emission rate of CO_x and NO_x will drop. Further advantages with the presence of water include improved fuel atomization. Also it will reduce the particulate emission and soothing and improved fuel economy in terms of both price and miles per unit volume of fuel. Also microemulsion has capacity to increase the octane number of gasoline and corresponding cetane number for diesel.

A microemulsion allow water soluble and compatible substances such as drugs and enzymes to be solubilized in organic solvents. Microemulsion can be converted into organogels, which could allow direct application to the safe parts of the body such as skin, eye or ears and higher molar mass of water soluble polymers. The large quantities of polyacrylamide is used in bench processes for water clarification and sewage treatment where there can be flocculation of colloids prior to filtration. For these applications a high molar mass is desirable.

The polymerisation process can be carried out in an aqueous interior of w/o microemulsion. Polymerisation where very high molecular mass is obtained increases the viscosity and that can be controlled by the use of microemulsion. It is essential to control the size of the particle for the use in the specific field. The reduction of dihydrogen hexachloro platinate (H_2PtCl_6) gives the required product of platinum particle. Also the microemulsion method offers interesting possibility to prepare particles, since the salts used as starting materials can be dissolved together in the aqueous microemulsion droplets[116b]. In microemulsion it is possible to prepare homogeneous alloys under mild conditions[116c-] .

Traditionally microemulsions have been considered as of high potential value in different aspects of crude oil exploration[117]. The technological application as in enhanced oil recovery (EOR) is an important one. It is well known that only minor part of the crude oil present in an oil bearing formation can be captured in the primary production step. Chemical flooding might be a key to the problem in cases where the pressure gradient (ΔP) over an oil domain exhibited by a mobile phase will not overcome the capillary forces. In order to move the bulk oil in capillary it is required to reduce the IFT ~ 0.001 mNm^{-1}. This can be achieved for properly balanced microemulsions.[119-123]

Rico et al[118]. have studied the Wacker process for the catalytic oxidation of alkanes in formamide microemulsions. The microemulsion system consist of formamide, 1-hexane, 2-propanol and C_9H_{19}-C_6H_4-$(OCH_2)_8OH$. When the reaction was carried out in a dimethyl formamide (DMF)-water mixture. It started after an induction period of about 100 min. In the corresponding microemulsions the main feature was the absence of an induction period. There is good contact between reactants and catalyst and the reaction starts immediately. The overall reaction was faster than in the DMF-water mixture, particularly in the olefin rich microemulsion.

Lattes[116d] investigated various reactions in the formamide microemulsion. They used isooctanol / 1-butanol, CTAB / formamide microemulsions. It is known that the endo/exo selectivity of reaction increases with increasing polarity of the solvent. The use of formamide a homogeneous reaction medium significantly improved the yield.

1.9 PERSPECTIVE OF PRESENT WORK

Though the work in the field of microemulsion is growing rapidly, it is essential to study basic and fundamental aspects of certain systems in detail for characterisation of their structure, We used cetyl trimethyl ammonium bromide (CTAB) which is a cationic surfactant and is neutral in water and has various application in personal care products etc.

In this thesis, the first chapter is a general introduction to the subject with literature references, the second chapter deals with various procedures of experiments. It discusses the techniques which are utilized to characterise the structure of microemulsion e.g. viscosity, conductance, adiabatic compressibility, interfacial tension, volume measurements etc.

In the third and fourth chapters, we have investigated the phase behaviour of cyclohexane / CTAB + 1-propanol / water. PEG-400 is used in various applications in the cosmetics and pharmaceuticals. We studied the effect of different amounts of polyethylene glycol-400. After phase behaviour study, the different physico-chemical properties like viscosity, conductance, interfacial tension, salt effect, phase volume measurement etc. were studied to characterise the one phase microemulsion.

The last part of the thesis describes the various physico-chemical properties with water soluble polyacrylamide, a polymer used as antiflocculant for reduction of dragging etc. It is also used in the field of enhanced oil recovery.

Though, water is in general present in the microemulsion as a polar phase, it is useful to study the non-aqueous polar organic liquid with higher dielectric constant in place of water. So fifth chapter describes the microemulsions with DMF and DMF + water in place of water in our systems. The effect of polyethylene glycol 4000 was determined on various physico-chemical properties.

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