

INTRODUCTION

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1. Amphiphiles and surfactants

The word “amphiphile” was coined by Paul Winsor more than fifty years ago. It comes from two Greek roots. The prefix ‘amphi’ means double and the word ‘philos’ expresses friendship or affinity, as in. An amphiphilic substance exhibits a double affinity, which can be defined from the physico-chemical point of view as a polar-apolar duality. A typical amphiphilic molecule consists of two parts: on the one hand a polar group which contains hetero atoms such as oxygen, sulphur or nitrogen included in functional groups such as alcohol, thiol, ether, ester, acid, sulfate, sulfonate, phosphate, amine, amide, etc. On the other hand the apolar group is in general comprised of hydrocarbon chain/s of the alkyl or alkylbenzene type; sometimes halogen atoms and even a few nonionizable oxygen atoms. The polar portion is often called ‘hydrophilic part’ or ‘hydrophile’ as it exhibits strong affinity to polar solvents, particularly water. The apolar part is called ‘hydrophobe’ or ‘lipophile’¹.

Some of the amphiphiles can undergo self-organization in solution through the formation of “association colloids” or “micelles.”^{2,3} Micelles, formed by amphiphiles, can have several potential applications. Such amphiphiles are also termed as SURFACTANT. In English the term surfactant (acronym for surface-active-agent) designates a substance which exhibits some superficial or interfacial activities. It is worth remarking that all amphiphiles do not display such activity; in effect, only the amphiphiles with more or less equilibrated hydrophilic and lipophilic tendencies are likely to migrate to the surface or interface. It does not happen if the amphiphilic molecule is too hydrophilic or too hydrophobic, in which case it stays in one of the phases. Surfactants, through the process of interfacial adsorption, could substantially reduce the surface free energy (Gibbs adsorption)^{4,5}. A schematic diagram of a typical surfactant molecule can be described as follows:

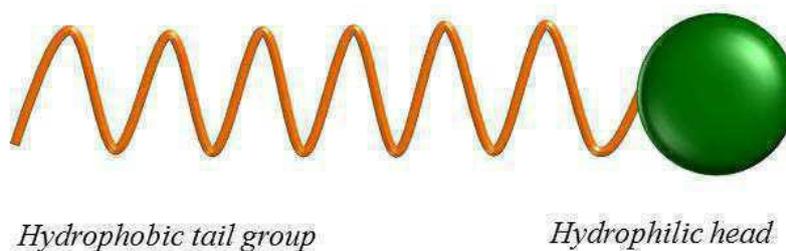


Figure 1. General structure of a surfactant molecule.

1.2. Classification of surfactants

1.2.1. Classification based on origin:

Based on the origin, surfactants are classified as soaps and detergents.

Soaps: Strictly speaking the term soap refers to the sodium or potassium salt of fatty acids. By extension the acid may be any carboxylic acid, and the alkaline metal ion may be replaced by any metallic or organic cation. Soaps are made from fats and oils, or their fatty acids, by treating them chemically with a strong alkali⁶⁻⁸. Examples include sodium palmitate, sodium oleate, sodium cholate, etc.

Detergents: In the late 1940 and early 1950 synthetic detergents displaced soaps in domestic washing particularly in washing machine use, because they displayed several advantages, such as better tolerance to hard water, better detergency, and cheaper price. Detergents refer to the synthetically prepared surfactants. Alkylbenzenesulfonates, a family of compounds that are similar to soap but are more soluble in hard water, because the polar sulfonate (of detergents) is less likely than the polar carboxylate (of soap) to bind to calcium and other ions found in hard water. Examples of detergents include sodium dodecyl benzene sulphonate (SDBS), sodium dodecyl sulfate (SDS), hexadecyltrimethylammonium (cetyltrimethylammonium) bromide ($C_{16}TABr$), cetylpyridinium chloride (CPC), polyoxyethylene sorbitan monolaurate (Tween 20 or Polysorbate 20), etc.

1.2.2. Classification based on the charge on the polar head groups:

Based on the charge carried by the hydrophilic head groups surfactants can be classified into non-ionic, ionic (cationic and anionic) and zwitterionic.

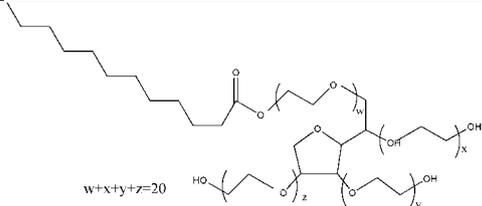
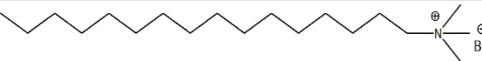
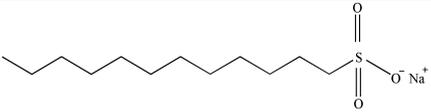
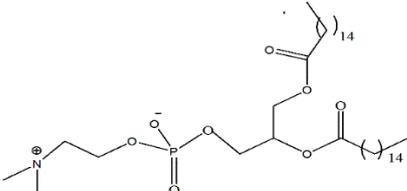
Nonionic Surfactants: These surfactants, because of their non-dissociable hydrophilic groups, they do not ionize in aqueous solution. A large portion of these nonionic surfactants are made hydrophilic by the presence of a

polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics. Examples include polyoxyethylene sorbitanmonolaurate (Tween 20), t-octylphenoxypolyethoxyethanol (Triton X100), polyethylene glycol lauryl ether (Brij35), sorbitanmonolaurate (Span 20), etc.

Cationic Surfactant: Cationic surfactants are dissociated in water into amphiphilic cation and counter anion, most often of the halogen type. Long chain alkyltrimethylammonium bromide (C_nTABr , $n=10 - 18$), cetylpyridinium chloride, benzylhexadecyltrimethylammonium chloride, etc., are some of the examples of cationic surfactants.

Anionic Surfactant: These are dissociated in water as an amphiphilic anion, and a cation, which is in general an alkaline metal (Na^+ , K^+) or a quaternary ammonium. They include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc. comes under this category.

Table 1: Classification of surfactants on the basis of charge on the polar head groups.

Type	Structure
Nonionic	 <p>Polyoxyethylene sorbitan monolaurate (Tween 20)</p>
Cationic	 <p>Cetyltrimethylammonium bromide ($C_{16}TAB$)</p>
Anionic	 <p>Sodium Dodecylsulfate (SDS)</p>
Zwitterionic	 <p>Dipalmitoylphosphatidylcholine</p>

Zwitterionic Surfactants: When a single surfactant molecule exhibit both anionic and cationic dissociations it is called **amphoteric** or **zwitterionic**. 1,2-diacyl-sn-glycero-3-phosphatidylcholine (lecithin), 3-(ethyltrimethylammonio) propane-1-sulfonate (NDSB-195) are some of the examples of this type of surfactant.

1.2.3. Other Classification: The other classes of surfactants which were developed with the advancement of surface chemistry are gemini surfactant, bolaamphiphile and catanionic surfactant.

Gemini Surfactants: These are surfactants which have special molecular structure where two amphiphilic moieties are linked through “spacer”⁹⁻¹¹. The two terminal hydrocarbon tails can be short or long; the two polar head groups can be cationic, anionic or nonionic; the spacer can be short or long, flexible or rigid. The spacer can be attached directly to the identical ionic groups (Figure 2), each of which is in turn bonded to an identical hydrocarbon tail. Alternately, the two identical amphiphiles are joined midway¹²⁻¹⁴.

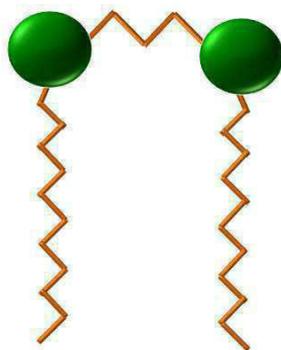


Figure 2. General structure of gemini surfactants.

Bolaamphiphile: Bolaamphiphiles (also known as bolaform surfactants, bolaphiles, or alpha-omega-type surfactants) are amphiphilic molecules that have hydrophilic groups at both ends of a sufficiently long hydrophobic hydrocarbon chain^{15,16}.

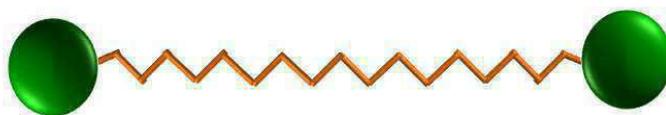


Figure 3. General Structure of bolaamphiphiles.

Catanionic Surfactant: In this class of surfactants, the heads of two oppositely charged surfactants (cationic and anionic) are linked with ionic bond^{17-20 21-23}.

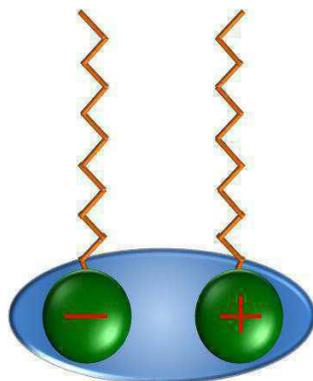


Figure 4. General Structure of catanionic surfactant.

2. Hydrophilic-Lipophilic Balance

The hydrophile-lipophile-balance (HLB) System simplifies the choice of surfactants to meet emulsion formulation requirements. It is based on the balance between the hydrophilic and the lipophilic proportions that give each surfactant its functionality. The most hydrophilic surfactants usually have the highest HLB values and vice versa²⁴⁻²⁶.

HLB enables one to measure the emulsifying potential of a surfactant in terms of emulsion quality and stability. HLB value of a surfactant could be computed from its chemical structure and could be matched with the corresponding HLB of the oil phase to be dispersed. There are different empirical formulae to calculate the HLB value. The HLB values lie within a range of 0 - 20 on some arbitrary scale. Surfactants having highest HLB are usually highly soluble in water, could form stable o/w microemulsion. On the other hand, surfactants lying on the low end of the HLB scale are good for w/o microemulsion (μ E) formulation²⁴⁻²⁶.

The effectiveness of a given surfactant in stabilizing a particular emulsion system could be controlled by the balance between the HLBs of the surfactant and oil phase. HLB value for the nonionic surfactants possessing polyoxyethylene sorbitan group could be expressed as ²⁶:

$$HLB = \frac{\text{mole\% of the hydrophilic group}}{5} \quad (1)$$

Surfactants based on polyhydric alcohol-fatty acid esters such as glycerol monostearate can be handled by the following relationship: ²⁶

$$HLB = 20 \left(1 - \frac{S}{A}\right) \quad (2)$$

Where, S is the saponification number of the ester and A is the acid number of the acid.

There are several other methods available in determining the HLB values of different surfactants. However, herein only the relevant equations have been presented. Tween 20 has an S value of 45.5 while it's A value is 276. Therefore it's HLB value is found to be 16.7. HLB values of the used surfactants are listed in Table 2.

Table 2. HLB values of some surfactants

Surfactant	Commercial Name	HLB value
POE(20) sorbitan monolaurate	Tween 20	16.7
POE(20) sorbitan monopalmitate	Tween 40	15.6
POE(20) sorbitan monostearate	Tween 60	14.9
POE(20) sorbitan monooleate	Tween 80	15.0
Hexadecyltrimethylammonium bromide	C ₁₆ TAB	21.4
Sodium dodecyl sulphate	SDS	40.0

3. Packing Parameter:

Israelachvili²⁷ suggested a parameter, called the packing parameter P, which gives a kind of measuring scale to recommend the shape of the amphiphilic aggregates. According to him, the nature of amphiphile-packing in micelles and their structural geometry can be predicted using a packing parameter (P) defined by the relation,

$$P = v/Al_c \quad (3)$$

$$R^M = 3v/A \quad (4)$$

Where, P is the packing parameter, v is the volume of hydrophobic chain (nm^3) (considered as incompressible fluid), l_c is the maximum effective length of the hydrophobic chain of surfactant monomer (nm), R^M is the radius of the micelle (nm) and the surface area of the head group ($\text{nm}^2\text{molecule}^{-1}$) at the micellar interface is denoted by A .

For the pure surfactants, the effective length for a saturated hydrocarbon chain (l_c) with n numbers of carbon atoms and their corresponding volumes (v) can be calculated using Tanford's formula²⁸. Thus,

$$l_c \leq l_{\max} \approx (0.154 + 0.1265n) \quad (5)$$

and

$$v = (0.0274 + 0.0269n) \quad (6)$$

where, l_{\max} is the maximum length of the hydrophobic chain.

From the magnitude of packing parameter, the shapes of the aggregates formed can be predicted. For spherical micelle, $P < 0.333$; for non-spherical aggregates, $0.333 < P < 0.50$; for vesicles and bilayers, $0.50 < P < 1$ and for inverted structures, $P > 1$. For spherical micelles, the radius (R^M) should not exceed the critical chain length of the monomer²⁹.

4. Interfacial and Bulk Properties of surfactant solution:

Due to their amphiphilic nature, surfactants can lower the surface tension at the air-liquid interface and oil-water interface³⁰. By virtue of this property they can assist solubilization, cleaning, emulsification and dispersion, etc. Under specific conditions (temperature, pressure, solvent nature, etc.) in solution the surfactant molecules, at a threshold or critical concentration, can undergo self-aggregation or self-organization, termed as critical micelle concentration, CMC.^{1,31-35} The main driving force, also the causative factor of surfactant aggregation, is dependent on the contact area between the alkyl chain and water of a dissolved surfactant. The retarding factor for surfactant aggregation is the repulsive force between surfactant head-groups, especially in case of ionic surfactants. Usually micelles are of two types, viz., (i) normal micelles (formed in aqueous or polar solvents) and (ii) reverse micelles (in non-polar medium the formation topology is reversed and aggregates formed

therein). Both the types of micelles are guided by the equilibrium thermodynamic principle.^{2,36,37}

In case of ionic surfactants, the high charge density around the micellar surface is counter balanced partially through the process of counter-ion binding. However, as nonionic surfactants do not have such counter ions in stabilizing their micellar aggregates, usually nonionic surfactants have lower CMC values in water than the corresponding ionic surfactants.³⁸

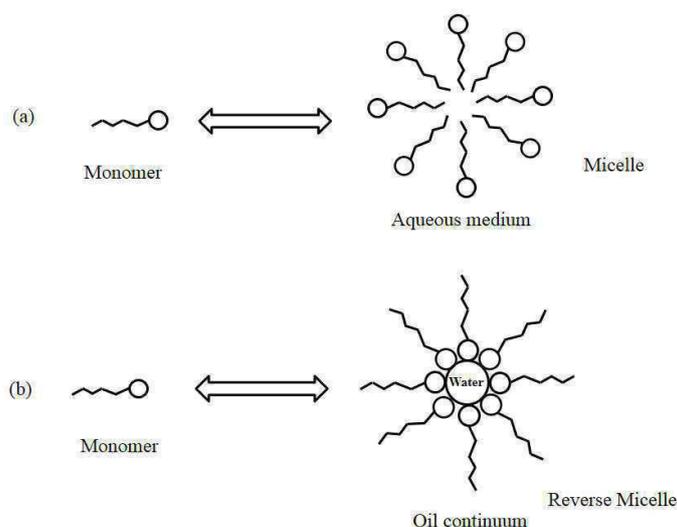


Figure 5. Schematic representation of (a) normal micelle and (b) reverse micelle.

Surfactants can get dissolved into water like common water soluble solutes. After the completion of surface adsorption, surfactants are compelled to congregate to form micelle. When some water-insoluble oil is used as solvent, reverse micelles are formed. The core of micelle is oil like which would accommodate additional oil molecules through the formation of swollen micelles. Further addition of oil results in the formation of oil-in-water emulsion.^{28,30,39-55} The core of a reverse micelle on the other hand, is more hydrophilic. Thus it can solubilize some water molecules through forming swollen reverse micelle and subsequently water-in-oil emulsion.

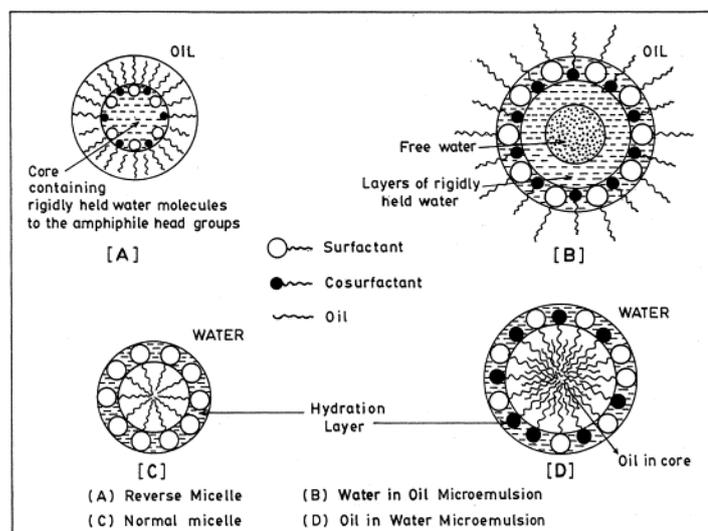


Figure 6. Pictorial representations of reverse micelles and microemulsions (adapted from ref. ^{39 28}).

5. Definition of Microemulsion (μE):

In 1943, the transparent dispersion of water-in-oil was termed as “oleopathichydromicelle” by Schulman and Hoar^{28,56,57}. Later on Schulman, Stockenium and Prince coined the term “microemulsion”(μE).^{58,59}. One of the best definitions of microemulsion is from Danielsson and Lindman ⁶⁰ “a microemulsion is a system of water, oil and an amphiphile which is a single optically isotropic and thermodynamically stable liquid solution”. Now-a-days, all the transparent combinations of oil, water and amphiphilic compounds forming thermodynamically stable, microheterogeneous and optically isotropic solutions, are defined as μE s as distinct from kinetically stable emulsion (macroemulsion)^{37 61 28 62}. In some respects, microemulsions can be considered as small-scale versions of emulsions, i.e., droplet type dispersions either of oil-in-water (o/w) or of water-in-oil (w/o), with a size range in the order of 1–100 nm in drop radius. Such a description, however, lacks precision since there are significant differences between microemulsion and ordinary emulsion (or macroemulsion). In emulsions, the average droplet size grows continuously with time so that phase separation ultimately occurs under gravitational force, i.e., they are thermodynamically unstable and their formation requires input of work. The drops of the dispersed phase are generally large ($> 0.1 \mu m$) so that they often take on a milky, rather than a translucent appearance. For microemulsions, once the conditions are right,

spontaneous formation occurs. As for simple aqueous systems, microemulsion formation is dependent on surfactant type and structure.

Though μ Es usually comprise both the surfactant and co-surfactant (e.g., short chain alcohols, amines, alkyl amines and alkyl halides, etc.), in some cases (e.g., sodium dioctyl sulphosuccinate, AOT), μ E can be formed without any co-surfactant^{63,64}. Besides, the surfactant less μ E (e.g., water, 2-propanol and toluene or hexane) can also be formed^{65 66}.

Actual structure of μ E is still controversial. For emulsion (size 100-2000 nm) interfacial tension ($\gamma_{w/o}$) values is typically in the range of 0.1 – 1mJm⁻². For a μ E, this value is as low as 0.001 mJ m⁻², i.e., it is 1000 fold lower. Surfactant molecules provide a protecting monomolecular film at the oil-water interface^{59 67}. μ Es, therefore, could be defined as thermodynamically stable, clear, isotropic dispersion of oil-in-water or vice versa, stabilized by monomolecular surfactant film^{30 61 28 62}. The type of surfactants used determines the type of an emulsion (oil-in-water, O/W or water-in-oil, W/O). Nature of surfactant could also be categorized on the basis of their hydrophobicity or hydrophilicity. This is also alternately termed as hydrophilic-lipophilic balance (HLB). Judicial choice of surfactants, according to their HLB values, could help in the formulation of proper and desired μ E.

5.1. Reason behind stability of microemulsions:

Microemulsion formation and stability can be explained on the basis of a simplified thermodynamic rationalization. The free energy of microemulsion formation can be considered to depend on the extent to which surfactant lowers the oil/water interfacial surface tension and the change in entropy of the system such that,

$$\Delta G = \Delta H - T\Delta S + \gamma\Delta A \quad (7)$$

where, ΔG , ΔH and ΔS is the change in free energy, enthalpy and entropy (dispersion) associated with the microemulsification, γ is the surface tension of the oil/water interface, ΔA is the change in interfacial area and T is the temperature. When a microemulsion is formed, there is a large change in interfacial area (ΔA) due to the formation of large number of very small droplets. Though γ is positive at all times, on the onset of microemulsion

formation it is very small ($\gamma < 0.02 \text{ mN/m}$). The dominant favourable entropic contribution is arising from the mixing of one phase into the other (in the form of large numbers of small droplets) and from other dynamic processes such as surfactant diffusion in the interfacial layer, monomer-micelle surfactant exchange etc. The first term (ΔH , a very small positive quantity) and the third term of equation (7) are offset by the entropic component. Thus, a negative free energy of formation is achieved when large reductions in surface tension are accompanied by significant favorable entropic change.

5.2. Water-in-oil (w/o) microemulsion:

The w/o microemulsion is topologically similar to the reverse micelles where the polar head groups of surfactants are oriented inwards and the hydrocarbon tails remain solubilized in the bulk oil phase³¹. In case of swollen reverse micelle the water molecules do not have the freedom to behave like bulk water. However, in case of w/o microemulsion the topology is little bit different. The very first layer of water remains immobilized as they are used up in hydrating the surfactant head groups and the counter ions (if present). After satisfying the hydration of the surfactant head group, the excess water would behave as bulk water.³⁴

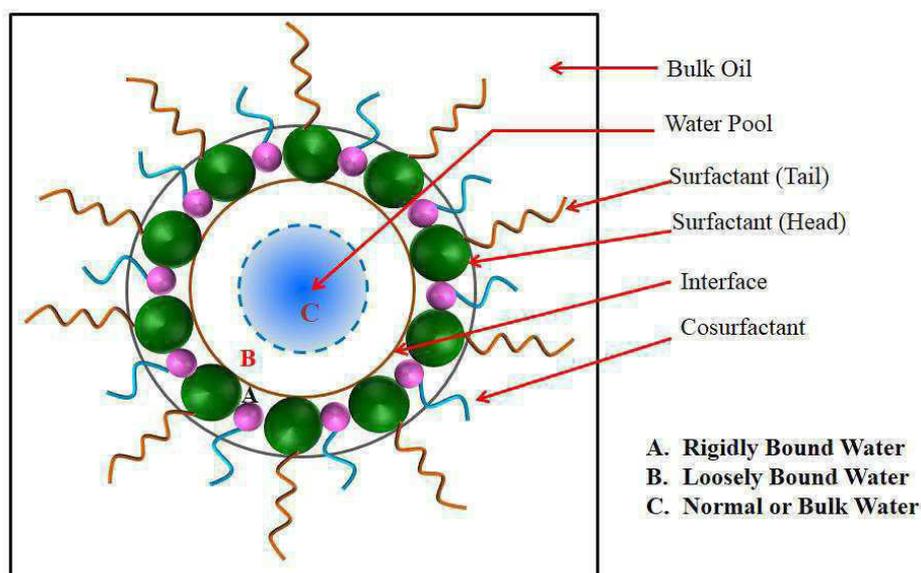


Figure 7. Schematic representation of W/O microemulsion.

6. Phase behavior of mixed water-oil-amphiphile (surfactant + cosurfactant) systems:

Winsor⁶⁸ described elaborately the different characteristics of phase manifestation of the ternary mixtures of water-surfactant-oil or the quaternary mixtures of water-surfactant-cosurfactant-oil. The concerned mixed systems fall into four categories:

Winsor I: The surfactant is preferentially soluble in water and oil-in-water (o/w) microemulsions form. The surfactant-rich water phase coexists with the oil phase where surfactant is only present as monomers at small concentration.

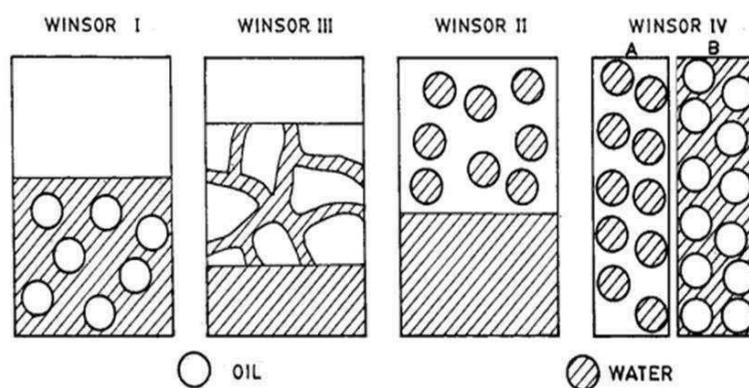


Figure 8. Different phase-forming situations for water-amphiphile-oil mixtures (adapted from ref. ³⁰).

Winsor II: The surfactant is mainly in the oil phase and water-in-oil (w/o) microemulsions form. The surfactant-rich oil phase coexists with the surfactant-poor aqueous phase.

Winsor III: A microemulsion phase which is in equilibrium with an excess oil phase and an excess water phase. Here both o/w and w/o dispersions are simultaneously present in the same domain in mixed state in separate contacts with both oil and water.

Winsor IV: A single-phase of dispersion either o/w or w/o not in contact with any other phase.

In spite of the above mentioned four categories there are also some reports ⁶⁹⁻⁷¹ of simultaneous presence of two microemulsion phases in contact

with each other and one in separate contact with water and the other with oil. This may be considered as fifth category of Winsor's classification.

Size of w/o microemulsion could be controlled by varying the amount of water in it. The molar ratio, [water]/[surfactant] (ω) gives one a rough idea about the dimension of the water pool.^{72 28 62 30}

7. Role of cosurfactant in microemulsions:

The nature of the surfactant and the cosurfactant influence the phase diagram. In all four types of microemulsions, the interface is stabilized by an appropriate combination of surfactants or surfactant-cosurfactant combinations. The distribution of the cosurfactant between the oil and the interface imparts stability to the dispersion. Alcohols with short alkyl chain length are commonly added as 'cosurfactants', have the effect of further reducing the interfacial tension, while increasing the fluidity of the interface thereby increasing the entropy of the system. It also increases the mobility of the hydrocarbon tail and also allow greater penetration of the oil into this region. The alkyl chain length of cosurfactant have significant on the formation and physico-chemical properties of microemulsion.^{73 74}. The electrical conductance, dielectric constant, interfacial polarization are greatly influences by the chain length of alkanols⁷⁴. Also the phase behavior and microstructure of a microemulsion is reported to be affected by the chain length of the cosurfactant^{75; 76}. The effect of alkyl chain length of oil on microemulsion formation is also studied by different research groups^{77 78}. The solubilization capacity of w/o microemulsion was interrupted by the partitioning of alcohol between oil, water and the interface depending on the chain length of oil and alcohol⁷⁸. The shorter the carbon chain length of the oil and longer the carbon chain length of the alcohols, the higher is the solubilization capacity of the microemulsion.

8. Role of additives in microemulsions:

The microstructural state of a microemulsion may be affected by the presence of additives. Additives especially salts can significantly change the structural properties and hence the phase behavior of microemulsions.^{79 80 81,82}. The droplet size of a microemulsion varies with increasing salinity and smaller droplets are formed for w/o microemulsion systems whereas it

increases in case of o/w microemulsion system ⁸³. Amaral et.al. investigated the structural effect of urea in water-AOT-n-hexane reverse micelles and found that the attractive intermicellar interaction increases as the urea concentration increases ⁸⁴. The study of Kahlweit et al. ⁷⁹ revealed that the influence of both lyotropic (decreases aqueous solubility of surfactants, e.g., NaCl) and hydrotropic salts (increases aqueous solubility of surfactants, e.g., NaClO₄) on the physico-chemical behavior of non-ionic microemulsion system is more or less similar. Dynamic light scattering studies of a polymer-reverse micelle indicated that the spherical droplet structure is preserved in presence of the polymer ⁸⁵. Garcia-Rio et. al. ⁸⁶ studied the effect of various alkyl amines on the percolation phenomenon of water/AOT/isooctane microemulsion and suggested the association of amine with AOT as the reason for the percolation. Eicke et.al. have investigated water-AOT-isooctane microemulsion system in presence of gelatin and block copolymers and found the formation of soft condensed microemulsion mediated polymer networks that can evident fluidity displaying viscous flow ⁸⁷.

9. R- ratio

The R-ratio was first proposed by Winsor ⁶⁸ to account for the influence of amphiphiles and solvents on interfacial curvature. The primary concept is to relate the energies of interaction between the amphiphile layer and the oil and water regions. Therefore, R-ratio is defined in terms of the cohesive interaction energy between those molecules residing within the surfactant layer. He also proposed that the cohesive energies act on amphiphilic compound positioned at the interfacial region and the cohesive energy ratio (CER), 'R' would explain the type of microemulsion formed. It is defined as:

$$R = \frac{C_{LO}}{C_{HW}} \quad (8)$$

where, C_{LO} and C_{HW} are the interaction parameters between the lipophilic group and oil, and the hydrophilic group and water, respectively.

When R > 1, a w/o microemulsion is formed and for an o/w microemulsion R is less than 1. The cohesive energy ratio concept has been

used in the formulation of polymerization microemulsion⁸⁸. When $R=1$, the mutual solubility of amphiphile, oil and water is maximum and there is no tendency for the amphiphile layer to be preferentially convex towards either oil or water, its optimum form will be planer (optical systems) where the micellar phase contains equal volumes of oil and water^{89 90}.

Taking in account of all the interaction terms (cohesive energies between oil molecules (C_{OO}), between lipophile molecules (C_{LL}), between water molecules (C_{WW}), between hydrophile molecules (C_{HH}), an extended definition of R is proposed by Bourrel et al.⁹¹

$$R = \frac{C_{LO} - C_{OO} - C_{LL}}{C_{HW} - C_{WW} - C_{HH}} \quad (9)$$

All the cohesive energy terms are found to be dependent on the chemical nature of the components of the microemulsion, their relative concentrations and the temperature.

10. Characterization of microemulsion:

10.2. Physico-chemical studies on microemulsion through phase manifestation:

Microemulsions comprising water, oil and surfactant-cosurfactant can exhibit ranges of phases, viz., viscous solution, lamellar liquid crystals, thin or thick gels, single phase (clear and transparent mixtures), two phase (turbidity appears followed by a phase separation) and three phase regions etc. depending upon the composition and nature of the ingredients, environmental condition (temperature, presence of additives)^{28,92}. The knowledge on the areas of the formed phases is a useful characteristic of a multicomponent microemulsion forming system. The amount of surfactant and cosurfactant to be added and the percent of oil phase that can be incorporated shall be determined with the help of pseudo-ternary phase diagram. Usually, pseudo-ternary phase diagrams comprising of oil, water, and surfactant-cosurfactant (amphiphiles) are constructed at definite cosurfactant/surfactant weight ratios considering the mixture as a single component. Formation of monophasic/biphasic system is confirmed by visual inspection. The area covered by the monophasic points is considered as the

microemulsion region of existence. Experimentally, the weight percent compositions at the end points of all the above mentioned titrations (which are either appearance or disappearance of turbidity) are then plotted on a triangular coordinate to create a pseudo-ternary phase diagram, which illustrates different regions in it e.g. microemulsions and other types of entities as shown in Figure 9.

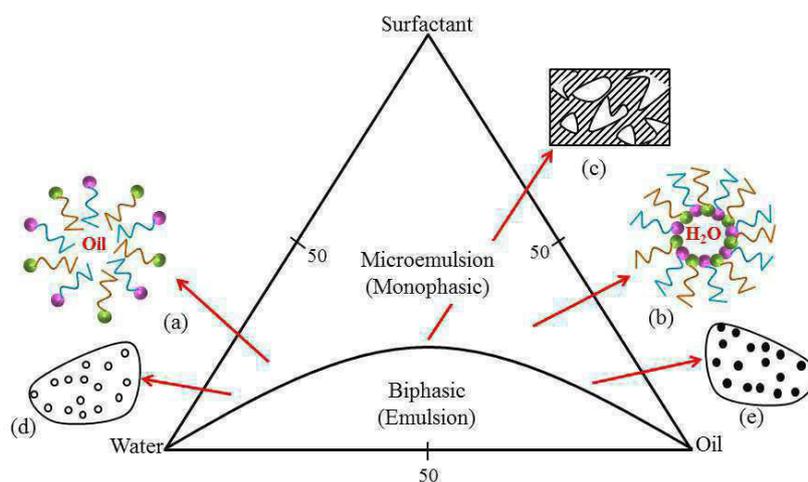


Figure 9. A comprehensive ternary phase diagram showing probable internal structures: (a), o/w microemulsion; (b), w/o microemulsion; (c), bicontinuous dispersion; (d), isolated and aggregated o/w dispersion; and (e), isolated and aggregated w/o dispersion.

10.3. Thermodynamics of w/o microemulsion formation by the method of dilution:

The energetics of formation of microemulsion systems can be obtained from a simple but a potential method, named dilution technique^{93 94 28 95 74 96 97,98 99}. The w/o microemulsion consisted of dispersion of water droplets in oil continuum wherein the whole surfactant molecules were considered to populate the oil/water interface in partial association with the cosurfactant which remained distributed between the interface and the bulk oil besides its scanty residence in the water pool due to low solubility. The distribution constants at different temperatures lead to the evaluation of energetics of the process, and additionally the droplet density, size, interfacial population of surfactant and cosurfactant, etc. Such vital information on the dispersed w/o microemulsion system from the model experiments on dilution is a remarkable physico-chemical data generating procedure. In the dilution experiment, the stability of the aforesaid distribution was disturbed by the addition of oil and

was regained by subsequent addition of cosurfactant in the system. It was considered that the following relation holds by mass balance,^{97,99 97}.

$$n_a^t = n_a^w + n_a^i + n_a^o \quad (10)$$

where, n_a^t , n_a^w , n_a^i and n_a^o are total number of moles of cosurfactant present, moles of cosurfactant in water, its number at the interface and that in oil, respectively. At a constant temperature and ω , the n_a^o and n_o (number of moles of oil in the system) bear a constant ratio. Consequently, the mole fraction ratio of alkanol at the interface (X_a^i) and in oil (X_a^o) should also be constant. Thus,

$$n_a^o/n_o = k \quad (11)$$

and,
$$k_d = \frac{X_a^i}{X_a^o} \quad (12)$$

where, k and k_d are constant and the distribution constant respectively. By replacing equation (12) in equation (11) one sets the following relation:

$$\frac{n_a^t}{n_s} = \frac{n_a^w + n_a^i}{n_s} + k \frac{n_o}{n_s} \quad (13)$$

n_s represents the number of moles of surfactant. The distribution constant k_d is related to the slope and intercept of equation (13) as:

$$k_d = \frac{X_a^i}{X_a^o} = \frac{n_a^i/(n_a^i + n_s)}{n_a^o/(n_a^o + n_o)} = \frac{n_a^i \left(1 + \frac{n_o}{n_a^o}\right)}{n_a^o \left(1 + \frac{n_a^i}{n_s}\right)} = \frac{\alpha(1+S)}{S(1+\alpha)} \quad (14)$$

where,
$$\alpha = \left(I - \frac{n_a^w}{n_s}\right) = \frac{n_a^i}{n_s} \quad (15)$$

and $S=K$, I and S are the intercept and slope of equation (13). The number of moles of cosurfactant in water (n_a^w) was obtained from its solubility in water (for long chain alkanols, $n_a^w \approx 0$ because of their negligible solubility to make $\alpha = I$).

The energetic parameters for the transfer of cosurfactant from oil to interface can then follow from the following relations,

$$\Delta G_t^0 = -RT \ln k_d \quad (16)$$

$$\Delta H_t^0 = \left[\frac{\partial(\Delta G_t^0/T)}{\partial(1/T)} \right]_p \quad (17)$$

and,
$$\Delta S_t^0 = \frac{\Delta H_t^0 - \Delta G_t^0}{T} \quad (18)$$

where, ΔG_t^0 and ΔH_t^0 represent standard Gibbs free energy, enthalpy and entropy of transfer respectively.

The results derived from the dilution experiments were used to evaluate structural parameters of the dispersed water droplets in microemulsion. The microemulsion droplets are approximated to have spherical shape in general, mono dispersed with a surface mono layer comprising surfactant and cosurfactant to be present at the interface. The total volume of the dispersed droplets (V_d) per unit volume (here in mL) can be expressed as follows:

$$V_d = \frac{4}{3} \pi R_e^3 N_d \quad (19)$$

R_e and N_d represents the effective diameter and total number of the droplets respectively. The droplet surface area (A_d) of droplets per unit volume is therefore:

$$A_d = 4\pi R_e^2 N_d = (n_s A_s + n_a^i A_a) N_A \quad (20)$$

where, A_s and A_a are the cross sectional area of the surfactant and cosurfactant molecules respectively, N_A Avogadro's constant.

The equation for R_e from equation (19) and (20) can be written as:

$$R_e = \sqrt[3]{3V_d/A_d} \quad (21)$$

Total volume of the dispersed phase, herein the water droplet embedded by the surfactant and n-alkanols at the oil-water interface, is the sum of the volume contribution of water (V_{H_2O}), surfactant (V_S) and the interfacial n-alkanol molecules (V_a^i) at the interface respectively. Thus one could write:

$$V_d = V_{H_2O} + V_S + V_a^i \quad (22)$$

One can determine the respective volumes using the values of number of moles (n_a^i), molar mass (M_a) and density of the components (ρ_a) according to the relation:

$$V_a^i = n_a^i M_a / \rho_a \quad (23)$$

The total droplet surface area (A_d) can be obtained from the equation:

$$A_d = (n_s A_s + n_a^i A_a) N_A \quad (24)$$

where, A_s and A_a are the polar head group area of surfactant and alkanol, respectively, and N_A is the Avogadro constant.

Putting the value of R_e in equation (19) we get the values of N_d

$$N_d = \frac{3V_d}{4\pi R_e^3} \quad (25)$$

The average aggregation number of surfactant (N_s) and cosurfactant (N_a) in a microemulsion droplet can be expressed as:

$$N_s = \frac{n_s N_A}{N_d} \quad (26)$$

$$N_a = \frac{n_a^i N_A}{N_d} \quad (27)$$

Volume of a microemulsion droplet is contributed by dispersed water, surfactant and cosurfactant molecules. Thus the radius of water pool in a

microemulsion droplet is related to the effective radius (i.e., the sum of pool radius and surfactant tail) according to the relation:

$$R_w = \left(\frac{V_{H_2O} + V_s^h + V_a^h}{V_d} \right)^{1/3} R_e \quad (28)$$

where, V_{H_2O} , V_s^h and V_a^h are volume of water droplet, surfactant head group, and alkanol head group, respectively. Volume contribution due to surfactant head group and cosurfactant head group could be evaluated from the following two equations:

$$V_s^h = \frac{4}{3\pi^{1/2}} A_s^{3/2} N_s \quad (29)$$

$$V_a^h = \frac{4}{3\pi^{1/2}} A_a^{3/2} N_a \quad (30)$$

Various structural parameters, as described in the earlier section can be computed by employing the dilution data into the aforementioned equations.

10.4. Transport properties of microemulsion (Percolation of electrical conductance):

Microemulsions are good physical examples for dynamic percolation studies. They are thermally stable mixtures that respond reversibly to changes in relevant physical parameters. It can show striking conductance behavior. Normally, o/w systems with ionic amphiphiles have conductance levels comparable to electrolyte solutions: whereas w/o systems show poor conductance at low water content and at lower temperatures. The water droplets in a w/o microemulsion are in constant motion in the oil continuum. The droplets collide, fuse and subsequently break apart and during the process, exchange of mass between two fusing droplets may take place^{34,100,101}. Although the continuous oil medium in w/o microemulsion is an insulator, w/o microemulsion (containing charged species in the water pool) are capable of electrical conduction. Depending upon this phenomenon the ion conduction of o/w, w/o and bicontinuous microemulsions are drastically different from one another. A water continuous o/w microemulsion behaves almost like normal aqueous medium and thus is good conducting, whereas oil continuous w/o

microemulsion is resistant to ion migration making it low conducting. Conductivity of a bicontinuous microemulsion is, however, significantly higher than w/o microemulsion, although not as high as o/w microemulsion¹⁰². The transfer of ions from one droplet to another progressing in certain direction under an applied electric field by way of fusion and fission can register increase in conductance which at a particular water content (ω) or temperature may show drastic change (normally increase). This phenomenon is called percolation and the threshold temperature or the threshold water concentration associated with the process are called percolation threshold^{48 103 52,55,100,104-107}.

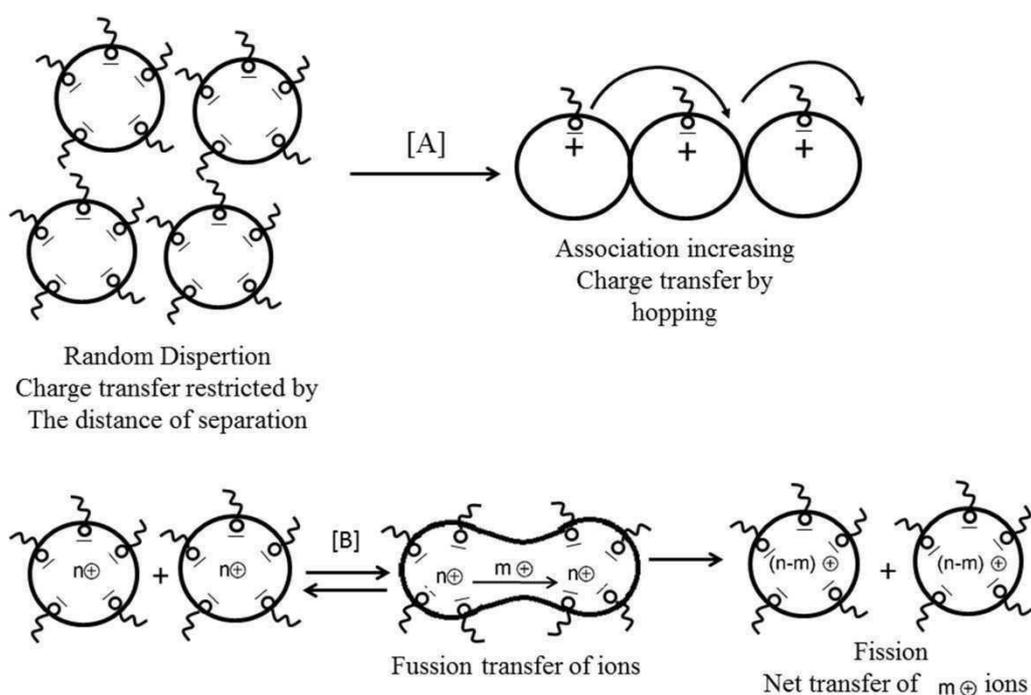


Figure 10. A Hopping mechanism. Ions hop in the direction indicated by the curl heads; B. Ion transport by fusion and fission. $n\oplus$ cations in the droplets. $m\oplus$ cations are involved in the transfer process.

For microemulsion system, two types of percolation can arise (i) volume percolation^{108 109 110 111,112 113 114} and (ii) temperature percolation^{113 114 115 97 116 54}. In the first, at a fixed amount of amphiphile (surfactant + cosurfactant), increase in water content increases droplet size for their easier merging thus to provide increased mass transfer and conductance i.e. favoring percolation. At a constant ω , increased temperature may increase droplet collision, i.e., fusion among the microdroplets leading to infinite cluster formation; thus, easier transfer of mass or increased conductance increasing temperature percolation. In these situations, the systems change from

insulators to conductors. The droplets having surfactant ions on the surface and counter ions in the interior core come closer and the increased conductance has been considered to be due to (i) the hopping of the surfactant ions from one to another droplet^{54 117} and (ii) the transfer of counter ions from one to another through water channels¹¹⁸ formed by the clustering effect of the droplets; a channel opens during their ‘sticky collusion’ which result exchange of materials among the droplets¹¹⁹. The ion transfer in this process (fusion followed by fission) leads to increase in conductance. The difference between the percolation of a ‘conductor-nonconductor’ composite system and ‘droplet-fusion-fission’ associated microemulsion system is that the former produce ‘static percolation’ whereas the other results ‘dynamic percolation’. The presence of additives can have striking effect on percolation, and various different additives including polymers have demonstrated different characteristics^{116 85}.

In w/o microemulsion, the droplets containing surfactant ions come to a threshold distance where transfer of charge between them occurs efficiently; they are physico-chemically dynamic and by diffusion they approach their neighbors to transfer charge¹²⁰. This is how ‘dynamic percolation’ occurs after a threshold volume fraction (φ_t) at a constant temperature.

10.4.1. Mathematical rationale of percolation:

The phenomenon of percolation is guided by scaling law^{94,115,121,122}. At a constant temperature and in the percolation range, the conductance of water droplets dispersed in oil in w/o microemulsions follows the relation,

$$\sigma = k(\varphi - \varphi_t)^m \quad (31)$$

or, $\ln \sigma = \ln k + m \ln(\varphi - \varphi_t)$ (32)

where, σ is the specific conductance of the microemulsion system, k and m are constants and φ is the volume fraction of water, φ_t is the threshold value. Theoretically, the exponent ‘ m ’ should be 1.9 for both static and dynamic percolation¹²³.

At a fixed ω , the scaling law for the temperature percolation^{124 125 126} in w/o microemulsion is,

$$\sigma = P(\theta - \theta_t)^n \quad (33)$$

or, $\ln \sigma = \ln P + n \ln(\theta - \theta_t)$ (34)

where, θ is the temperature corresponding to the specific conductance σ , θ_t is the threshold temperature for transition and n is an exponent. Both ϕ_t and θ_t in equation (18) and (20), obtained from the plots between σ and ϕ , and σ and θ respectively, as showed in Figure 11.

Like m , the expected value of n is also 1.9^{123,124}. In most of the cases the values of m and n found from experiments are at odds with the expected value of 1.9.

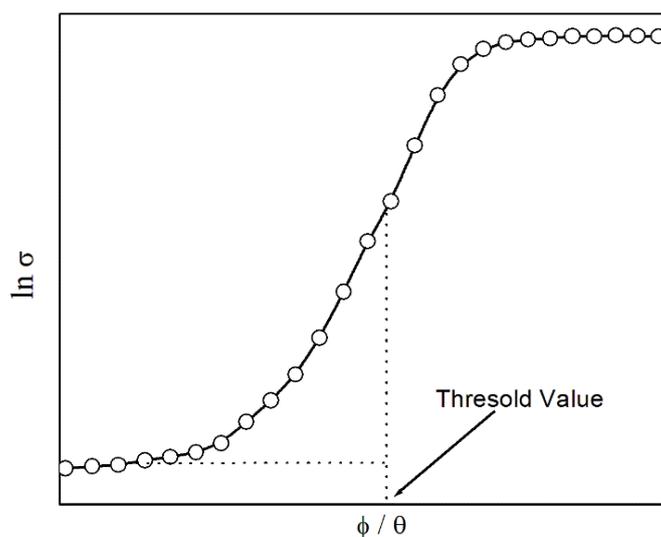


Figure 11. Schematic representation of volume and temperature percolation diagram of a w/o microemulsion system

11. Viscosity of microemulsions:

Viscosity measurement of microemulsion provides firsthand information on both the internal consistency of the colloidal dispersions and knowledge on the overall geometry of the particles of the dispersed phase. microemulsion systems have varied Newtonian and non-Newtonian flow behaviors. Newtonian flow behavior can be seen from low viscous

microemulsions. Non-Newtonian flow behavior is present in the bicontinuous type (Winsor III) of microemulsions and they can show plasticity. The viscosity data obtained for a microemulsion can be further computed to get the knowledge about the activation enthalpy (ΔH^*), which is equivalent to the activation energy, free energy (ΔG^*), entropy change (ΔS^*) and the change in specific heat capacity (ΔC_p)^{38,114,127,128}. The activation enthalpy for the viscous flow and the associated entropy change can be expressed by the following equation,

$$\eta = \left(\frac{hN}{V}\right) e^{\Delta H^*/RT} e^{-\Delta S^*/RT} \quad (35)$$

Where, ΔS^* , h , N , and V are the activation entropy, Planck's constant, Avogadro number, and molar volume, respectively. The terms R and T have their usual significance. The logarithmic form of equation (21) gives:

$$\ln \eta = \left\{ \ln \left(\frac{hN}{V}\right) - \frac{\Delta S^*}{R} \right\} + \frac{\Delta H^*}{RT} \quad (36)$$

The first term on the right hand side of Eq. (36) was considered to be constant so that a plot between $\ln \eta$ and T^{-1} should have yielded ΔH^* from the slope. $\ln \eta$ was found to vary with T^{-1} in a binomial way; hence one can derive ΔH^* from its differential with respect to temperature in the following way;

$$\ln \eta = a + bT + cT^2 \quad (37)$$

Thus,
$$\frac{d \ln \eta}{dT} = -\frac{\Delta H^*}{RT^2} = b + 2cT \quad (38)$$

The fitting parameters a , b , and c have been found by computation, and the ΔH^* are then calculated at different temperatures using equation (38). $\ln \eta$ has a nonlinear dependence on T^{-1} . Therefore, ΔH^* is not independent of temperature.

The change in heat capacity, ΔC_p , then follows from the relation,

$$\Delta C_p = \frac{d\Delta H^*}{dT} = -2RT(b + 3cT) \quad (39)$$

The ΔG^* values are obtained from the relation,

$$\Delta G^* = RT \ln \frac{\eta V}{hN} \quad (40)$$

and ΔS^* values are calculated using the Gibbs-Helmholtz equation,

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T} \quad (41)$$

12. Techniques for determination of microemulsion structure:

The characteristics of microemulsions have been established by different physical methods. Knowledge of the various methods available to thoroughly characterize a microemulsion system is essential. Both traditional methods (dilution method, conductance, viscosity, etc.) and emerging techniques such as dynamic light scattering (DLS), small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), time resolved fluorescence quenching (TRFQ), NMR etc. are required for their characterization and property illumination. Among them DLS, SEM, TEM, cyclic voltammetry are most frequently used for the determination of internal structure of a microemulsion system.

12.2. Size of μE droplet as studied by dynamic light scattering technique:

DLS (also known as photon correlation spectroscopy or quasi-elastic light scattering) has gained potential importance in analyzing particle size and related physical characteristics of microemulsions^{129 130 131}. When a coherent beam of light (as in lasers) interacts with colloidal particles in motion, the intensity correlation function provides information on the translational diffusion coefficient of the scattering particles and hence the hydrodynamic radius according to Stokes-Einstein equation.

$$D = \frac{kT}{3\pi\eta d} \quad (42)$$

where, k , T and η indicate the Boltzmann constant, temperature and viscosity respectively^{132-134 135 136,137}.

Dynamic light scattering provides insight into the dynamic properties of microemulsion by measuring single scattering events, meaning that each detected photon has been scattered by the sample exactly once. Usually, the measurements are taken at 90° in a dynamic light scattering spectrophotometer which uses a neon laser beam. The data processing is done in the built-in

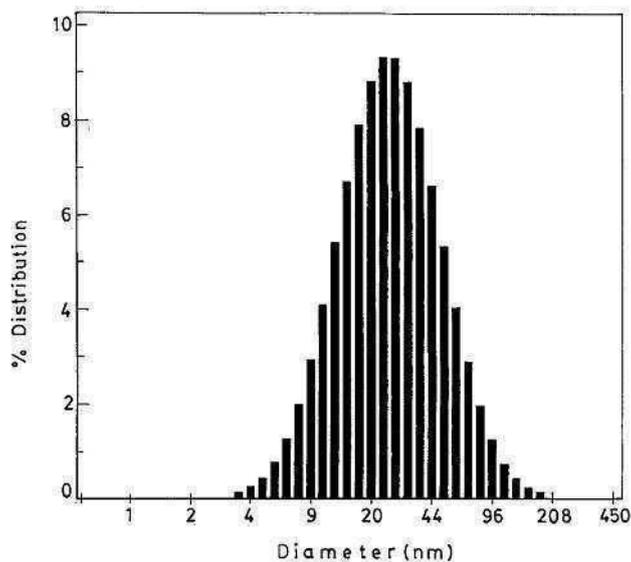


Figure 12. Droplet size distribution of H₂O/AOT/n-heptane system studied by dynamic light scattering technique (adapted from Ref. ¹⁰¹)

computer with the instrument. Acharya et. al. ³⁸ have determined the diffusion coefficients and the polydispersity through DLS measurement of eucalyptol / polyoxyethylene(4)lauryl ether (Brij-30) / ethanol / water microemulsion system. Majhi et.al. ¹³⁸ determined the particle size of the microwater droplets of microemulsion systems comprising AOT, water and different oils like heptane, octane, isooctane, decane, and eucalyptol. The structural study of water / sodium bis(2-ethylhexyl) phosphate / benzene microemulsion system by Feng et.al. ¹³⁹ by DLS technique has revealed that at $\omega < 3$ rod shaped aggregates are formed whereas in water content dipolar crystallites dissolve successively and at $\omega > 3$, nonpolar reverse micelle overcome.

12.3. Spectroscopic investigation on microemulsion:

The local environment within a microemulsion droplet can be characterized with UV-Vis solvatochromic probes. As is well known, solubilization of a solute and chemical reactivity are dependent on the micro polarity of dispersed droplets in reverse microemulsions¹⁴⁰. The

solvatochromic probes selected should be anchored to the polar core of the aggregates, to satisfy the procedural requirement of being soluble in the local environment media. Furthermore, this probe must be sensitive to the polarity of its environment and reflect the polarity through a shift of absorption maximum. Han and co-workers employed UV-Vis spectroscopy to monitor the extraction of trypsin solubilized in AOT/decane/water reverse micelles into compressed CO₂¹⁴¹. Clarke et. al. investigated the the formation of water in supercritical carbon dioxide microemulsions stabilized by an ammonium carboxylate perfluoro polyether (PFPE) surfactant and found that the aqueous acidified K₂Cr₂O₇ is completely soluble in water-in-CO₂ microemulsion by UV-Vis spectroscopy¹⁴².

The method of fluorimetry is based on the fluorescence spectra of a dye which varies substantially with its environment. The state of water in the waterpool of the w/o microemulsion has been elaborately investigated by a fluorescence probe technique by Hasegawa et.al.¹⁴³ for water/AOT/n-alkanes (C₆-C₁₂), using a viscosity sensitive fluorescence probe, auramine O and a xanthene dye. They found that upto ω 10, the microviscosity of the AOT anionic heads falls gradually till the upper limit of water tolerance. Sarkar et.al.¹⁴⁴ investigated the interaction of ionic liquid with water in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆])/Triton X-100 (TX-100)/H₂O ternary microemulsions by the dynamics of solvent and rotational relaxation of coumarin 153 and coumarin 151 and found that for coumarin 153, the probe is located at the interfacial region of the microemulsions. Whereas, for, with an increase in the [bmim][PF₆] content the number of coumarin 151 molecules in the core of the microemulsions gradually increases.

12.4. Other Techniques:

12.4.1. Scanning electron microscope (SEM):

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons (from 0.5 keV to 40 keV) in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals which contain information about the sample's surface topography, composition, and

other properties. In SEM, direct images of the microstructures of a microemulsion under varied conditions of dispersant composition and concentration can be taken. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance and very useful for understanding the surface structure of a sample. In modern instruments, the image (magnified by 10 to 500,000 times) is digitally captured and displayed on a computer monitor.

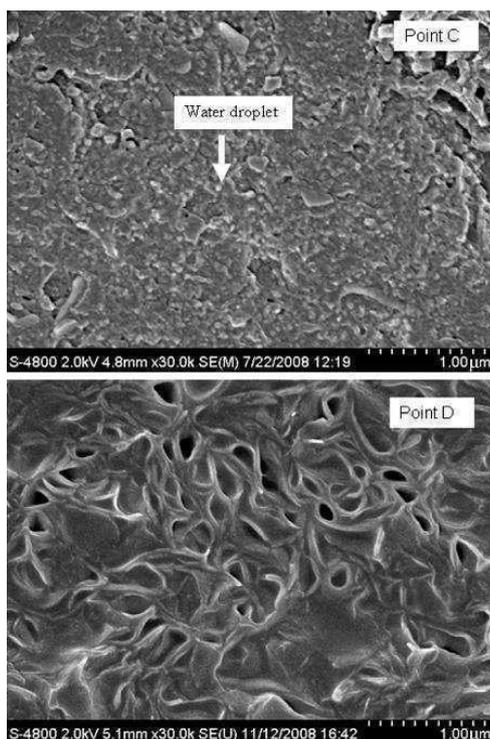


Figure 13. Cryo-SEM micrographs of microemulsion system CTAB/toluene–pentanol (1:1)/IL–water(1:1), two different points (C and D)²¹³

12.4.2. Transmission electron microscopy(TEM):

Transmission electron microscopy (TEM) is a major analysis technique in both physical and biological sciences whereby a beam of electrons is transmitted through an ultrathin specimen, interacting with the specimen as it passes through it and the image formed by the interaction of the transmitted electrons of the specimen is magnified and detected by a sensor such as a CCD camera. TEMs are capable of imaging at a significantly higher resolution than light microscopes owing to the small de Broglie wavelength of electrons. TEM technique has been limitedly but potentially used in the understanding of the microstructure under varied conditions of dispersant composition and concentration^{41 145-148}.

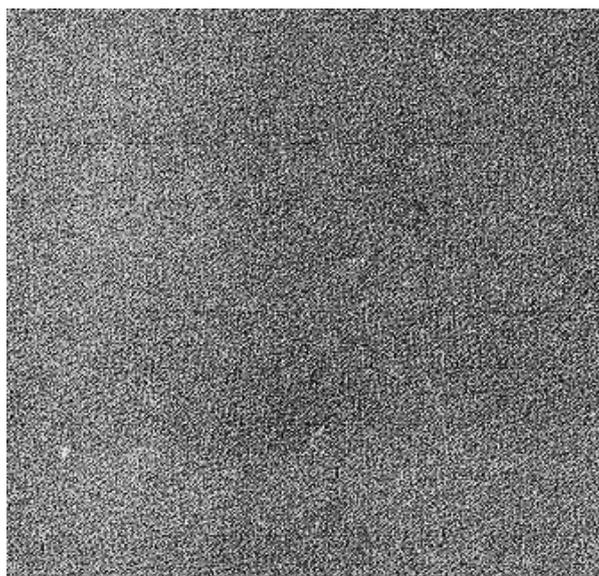


Figure 14. TEM of vitreous 20:1 diluted microemulsion on Triton-treated (at 139000X) grid showing higher droplet density and ordered structure¹⁴⁹.

12.4.3. NMR method:

The reverse micelles and microemulsions can be understood by the possibilities of determination of the self-diffusion coefficients of the constituting species; water, oil and amphiphile. The advantage of NMR method is that two- or three-phase characteristics can be monitored with single-phase domains on the micrometer scale. It also helps in finding out the degree of anisotropy and the presence of long-range discontinuities or continuities. Using high resolution ¹H, ²H and ¹³C NMR techniques, intermolecular interaction and structural rearrangement of non-ionic and anionic amphiphile-aided microemulsions have been investigated^{150,151,152}. The technique can directly reveal the nature of mono- and polydispersity, as well as particle anisotropy¹⁵³. According to Das et al.^{154,155} NMR probing revealed glycerol-SDS-hexanol system to be structureless. A number of other NMR probed microemulsion structure elucidation have been carried out by other research groups¹⁵⁶⁻¹⁶³.

12.4.4. Cyclic Voltammetry:

Mackay and co-workers have been first to suggest that electrochemical methods can be used to obtain information about the microstructure of microemulsions¹⁶⁴. Electrochemical cyclic voltammetry has been successfully used to obtain information about the microstructure of micelles or

microemulsions¹⁶⁵⁻¹⁷⁴. Changes in the microstructure were identified by using electrochemical probes such as ferrocene or its derivatives, ferricyanide, or methyl viologen. This detection was actually accomplished by determining diffusion coefficients of the probes which made it possible to investigate different microenvironments, in that the electrochemical reversibility of the probes was affected by the structure of the microemulsions and appeared to reflect the ease of mobility across interphases¹⁶⁶. Chokshi et. al.¹⁷⁵ and Shah et. al.¹⁷⁴ showed that the diffusion coefficients probed by electrochemical probes and cyclic voltammetric measurements could also be considered self-diffusion coefficients in microemulsion systems. Gao et.al.¹⁷⁶ investigated microemulsions consisting of the IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]), Tween 20 and water at various scan rates in order to verify the diffusion-controlled nature of the process.

13. Ionic liquid:

“The Structure and Properties of Ionic Melts” was the title of a Faraday Society Discussion held in Liverpool in 1961; it dispensed solely with molten inorganic salts¹⁷⁷. An IL is a liquid that contains essentially only ions. Today, however, the term “ionic liquid” is commonly used for salts whose melting point is relatively low (below 100⁰C). In particular, the salts that are liquid at room temperature are called room temperature ILs, or RTILs. There also exist mixtures of substances which have low melting points, called deep eutectic solvent, or DES, that have many similarities with ILs.

The earliest discovery of an IL can be dated to the middle of the nineteenth century, when some “red oil” was observed in a Friedel-Crafts reaction^{178 179}. Ethanolammonium nitrate (m.p. 52–55 °C) was reported in 1888 by Gabriel and Weiner¹⁸⁰. However one of the earlier known truly room temperature ILs was ethylammonium nitrate [EtNH₃]⁺ [NO₃]⁻ (m.p. 12 °C), synthesized in 1914 by Paul Walden. In the 1970s and 1980s ILs based on alkyl-substituted imidazolium and pyridinium cations, with halide or trihalogenoaluminate anions, were initially developed for use as electrolytes in battery applications. An important property of the imidazolium halogenoaluminate salts is that their physical properties such as viscosity,

melting point, and acidity could be adjusted by changing the alkyl substituents and the imidazolium/pyridinium and halide/halogenoaluminate ratios.

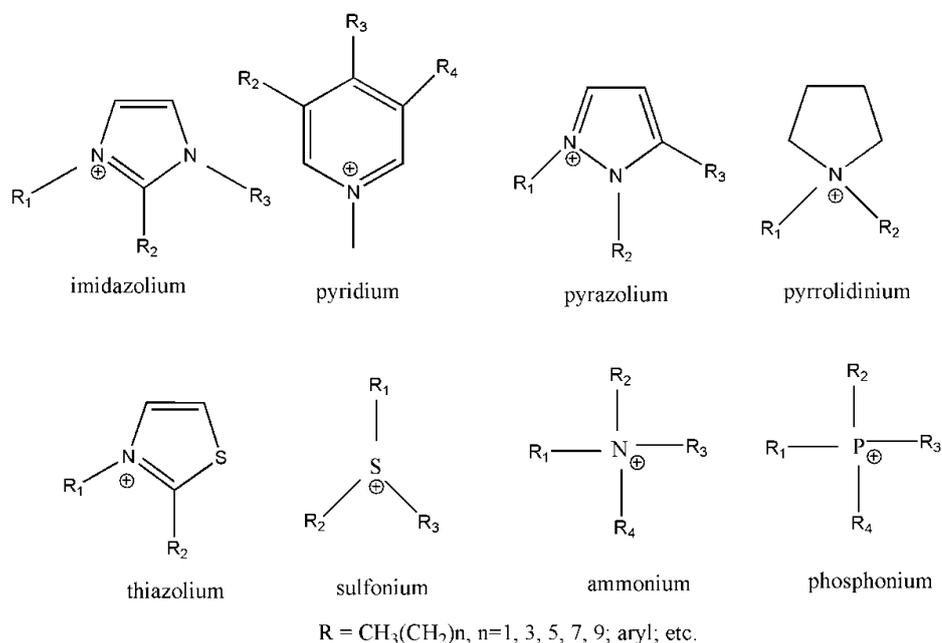


Figure 15A. Structures of some common types of ILs cations.

ILs are one of the most promising classes of new materials investigated in the last decade. They do not easily fit the conventional description of molecular fluids therefore promoting a necessary exploration of their physical properties at a microscopic level. Their negligible vapor pressure, high thermal stability, and properties tunability upon slight changes in the chemical architecture (including polarity, hydrophobicity, density, solvating activity etc.) have made these materials tailored for a constantly increasing range of applications¹⁸¹⁻¹⁸³. Among these applications we find: catalysis^{184,185}, synthesis¹⁸⁶, pharmaceuticals^{187,188}, electrochemistry^{189,190} and green chemistry¹⁹¹ in general.

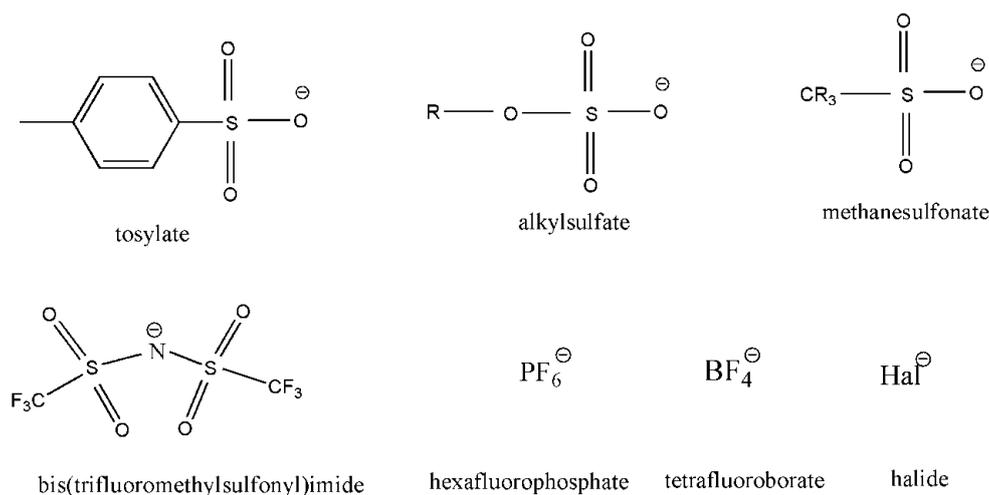


Figure 12B. Structures of some common types of ILs anions.

Two major drawbacks for some applications of ILs were moisture sensitivity and acidity / basicity. In 1992, Wilkes and Zawarotko¹⁹² reported the preparation of ILs with alternative 'neutral', weakly coordinating anions such as hexafluorophosphate [PF₆]⁻ and tetrafluoroborate [BF₄]⁻, allowing a much wider range of applications for ILs.

Most recently, people have been moving away from [PF₆]⁻ and [BF₄]⁻ since they are highly toxic¹⁹³, and towards new anions such as bistriflimide [(CF₃SO₂)₂N]⁻ or even away from halogenated compounds completely like methanesulfonate [MS]⁻. Moving towards less toxic cations have also been growing, with compounds like ammonium salts (such as choline) showing to be as flexible a support as imidazole.

14. Advantages of binary mixture comprising ionic liquid (ionic liquid + water):

The study of thermo physical properties is important in order to obtain sufficient information to predict properties and characteristics of ILs. The lack of physical property data and fundamental understanding of ILs prevent their further application to industry¹⁹⁴. Water is the most abundant fluid on earth and is important in many biological and chemical systems. Water has unique physico-chemical properties based on strong hydrogen bonding¹⁹⁵. Therefore, needless to mention that detailed investigation on IL-water binary mixtures have importance in terms of application and fundamental understanding. The presence of water may have a dramatic effect on properties of IL. Knowledge

of the physico-chemical and thermodynamic properties of binary mixtures formed by one or two components associated through hydrogen bonds is important and can give some information of the structural and energetic consequences of the interactions between ILs and water¹⁹⁶. Even a small amount of water can dramatically influence the liquid properties of ILs without any reaction taking place. For example, the diffusion coefficient¹⁹⁷, viscosity,¹⁹⁸ polarity¹⁹⁹ and surface tension²⁰⁰ of ILs varied considerably upon adding water. To facilitate the use of ILs in industrial processes, it is essential to assemble a frame of knowledge about these changes taking place in the physico-chemical properties of IL/water mixtures.

15. Ionic liquid microemulsion:

It is needless to mention that μ E comprising ILs in the polar domain can have some unknown but some novel properties owing to the unique and combined features of the ILs and μ Es. Research works involving IL microemulsion are ever increasing^{202,210,214-216,348,356}. Different review works on IL μ Es are available in the literature^{191,213,347,349,357,358}. Ionic liquid microemulsions find application in various fields, viz., preparation and characterization of polymeric nanoparticles²³⁶, synthesis of inorganic nanoparticles²³⁷, renewable lubricants²³⁸, and catalysis²³⁹, etc. Han and co-workers²⁰³ first reported the formation of μ E comprising IL. Very recently Sarkar and co-workers²¹² have reported a new strategy to prepare IL-in-oil μ Es. IL based μ Es in drug formulation has been explored by the research group of Moniruzzaman et al.¹⁸⁷ and Althanyan et al.³⁵⁹ Estoe et al.³⁴⁸, for the first time, have reported the characterization of IL μ E using small angle neutron scattering (SANS) technique. Koetz and co-workers²¹³ have studied the structure of IL modified μ E. Gao et al.^{176,204,205} undertaken extensive works on μ Es comprising of [bmim][PF₆] and water by different techniques. While Friberg et al.³⁴⁹ have reported about the works on [bmim][BF₄] based μ E, the structural studies of [bmim][BF₄]-in-oil μ E have been reported by Gao et al.¹⁷⁶. IL-in-oil μ Es have also been extensively studied by Zheng and co-workers³⁶⁰ using Triton X-100 and Tween 20. In the work of Gao et al.⁹¹ comparative studies between the properties of microemulsions comprising TX-100 and Tween 20 have been reported. In another work of Zheng et al.³⁶¹

extensive investigation were carried out on IL μ E comprising Tween 80 as surfactant.

16. Microemulsion comprising IL+water:

A major drawback to use ILs is their inability to dissolve a number of chemicals including some hydrophilic substances, although the properties of ILs can be tuned^{199,201}. To overcome this problem, the use of surfactants to create microemulsions containing water is an alternative method, as it is obvious that hydrophilic substances can be solubilized in the dispersed water phase. Furthermore, the microemulsion may possess some unexpected advantages in applications due to unique properties of ILs. Microemulsions with (IL+water) as polar cores or the microemulsions with nano-sized (IL+water) droplets dispersed in oil continuous phase by suitable surfactants may have some unknown properties and find various potential applications due to the unique features of ILs and microemulsions. Even so, these IL microemulsions have not been intensively investigated so far, especially their potential applications have rarely been reported. Cheng et.al.²⁰² demonstrated that 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) could form polar nanosized droplets dispersed in oil continuous phase. Gao et.al.²⁰³ have prepared and characterized [bmim][BF₄]/TX-100/cyclohexane microemulsion with the ionic liquid as the polar core. Microemulsions consisting of water and a hydrophobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆], stabilized using Triton X-100 and Tween 20 have also been reported^{204,205}. Atkin et. al.²⁰⁶ studied the microstructure of the microemulsion comprising nonionic alkyl oligoethyleneoxide surfactants, alkanes, and a IL ethylammonium nitrate (EAN) through phase behavior and small angle X-ray scattering (SAXS). Gracia-Rio et.al.²⁰⁷ investigated the IL based microemulsions of [bmim][BF₄]/Triton X-100/cyclohexane by absorption solvatochromic shifts, ¹H NMR in order to investigate the properties of the IL within the restricted geometry provided by microemulsions and the interactions of the ionic liquid with the interface. Zech et.al.²⁰⁸ characterized high thermal stability of the microemulsions composed of 1-hexadecyl-3-methyl imidazolium chloride ([C₁₆mim][Cl]), an IL that exhibits surfactant properties, decanol as cosurfactant, dodecane as continuous

phase and the RTIL ethylammonium nitrate (EAN) as polar phase at ambient temperature. Very recently Klee et.al.²⁰⁹ prepared magnetic microemulsion by the aid of a magnetic RTIL, [bmim][FeCl₄]. Such a magnetic microemulsion is a novel type of self-assembled system which due to its magnetic properties may open interesting paths for formulating functional and responsive systems. The increasing number of publications reflects the still growing interest in microemulsions containing room-temperature ILs^{113,133-135,144,193,203,210-216}.