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Microemulsions: Thermodynamic and Dynamic Properties

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1. Introduction

Mixing two immiscible liquids (such as oil and water) using emulsifier and energy inputs has been the matter of study for decades. In early 1890's extensive work have been carried out on macroemulsions (i.e. oil dispersed in water in the form of fine droplets or vice versa) (Becher, 1977) and several theories and methods of their formation have been vastly explored (Lissant 1976 and 1984). However going along the line, microemulsion systems were well opted because of their stability and isotropic nature. Microemulsions are basically thermodynamically stable, isotropically clear dispersions of two immiscible liquids such as oil and water stabilized by the interfacial film of any surfactant and/or cosurfactant. Although a microemulsion is macroscopically homogeneous, or quasi-homogeneous but structured microscopically. Microemulsions in comparison to micellar systems are superior in terms of solubilization potential and thermodynamic stability and offers advantages over unstable dispersions, such as emulsions and suspensions, since they are manufactured with little energy input (heat, mixing) and have a long shelf life (Constantinides, 1995). The term "microemulsion" was first coined by Schulman group (Schulman et al., 1959). However, ambiguity in the microemulsion terminology persists till today as some authors differentiate them from swollen micelles (which either contain low volume fraction of water and oil) and transparent emulsions (Prince, 1977, Malcolmson et al., 1998).

One of the unique factors associated with microemulsions is the presence of different textures such as oil droplets in water, water droplets in oil, bicontinuous, lamellar mixtures etc., which are formed by altering the curvature of interface with the help of different factors such as salinity, temperature, etc. Such a variety in structure of microemulsion is a function of composition of the system. Phase study greatly helps to elucidate different phases that exist in the region depending upon the composition ratios. One peculiarity of microemulsions lies in the fact that these structures are interchangeable.

Construction of phase diagram enables determination of aqueous dilutability and range of compositions that form a monophasic region (Fig. 1). One of the unique factor associated with microemulsions is the presence of different structures as classified by Winsor (Winsor, 1948). Winsor I (o/w), Winsor II (w/o), Winsor III (bicontinuous or middle phase microemulsion) and Winsor IV systems are formed by altering the curvature of interface with the help of different factors such as salinity, temperature, etc. Where Type I indicates

surfactant-rich water phase (lower phase) that coexists with surfactant-poor oil phase (Winsor I), Type II is surfactant-rich oil phase (the upper phase) that coexists with surfactant-poor water phase (Winsor II), Type III represents the surfactant rich middle-phase which coexists with both water (lower) and oil (upper) surfactant-poor phases (Winsor III) and Type IV is a single phase homogeneous mixture. Based upon the composition, these can be of various types *viz.*, water-in-oil (W/O) or oil-in-water (O/W) type or Lamellar or bicontinuous, hexagonal and reverse hexagonal, etc. (Fig. 2).

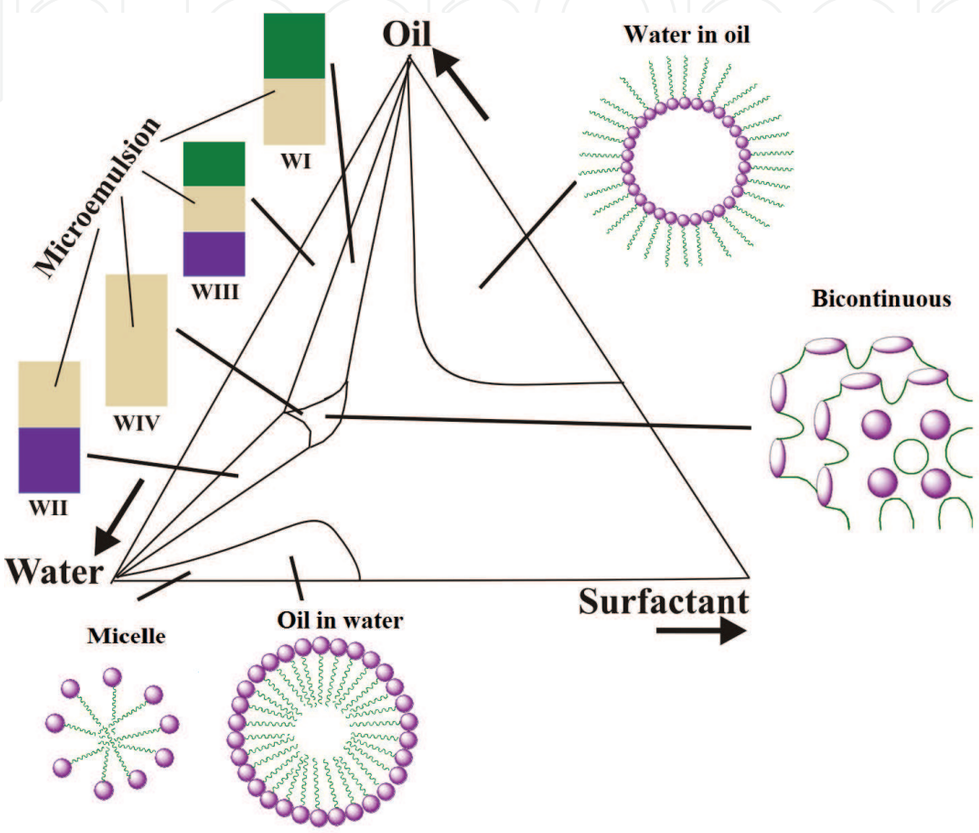


Fig. 1. A hypothetical ternary phase diagram representing three components of the system

Numerous attempts were made for predicting microemulsion types, the first was by Bancroft (later known as Bancroft's rule). It states that water-soluble emulsifiers tend to form o/w emulsions and oil-soluble emulsifiers tend to form w/o emulsions (Bancroft, 1913). Obviously, this is very qualitative, and therefore, it is of interest to put the area on a more quantitative footing. This section describes some of these concepts.

The preferred curvature of the interface is governed by the relative values of the head group area (a_o) and tail effective area (v/l_c) as described by Israelachvili et al., where v is the volume and l_c is the effective hydrocarbon chain (Fig. 3) (Israelachvili et al. 1976). By a simple geometrical consideration, the Critical Packing Parameter (CPP) is expressed as

$$CPP = v/l_c a_o \tag{1}$$

Theoretically, a CPP value less than $\frac{1}{3}$ corresponds to spherical micelles, between $\frac{1}{3}$ and $\frac{1}{2}$ corresponds to rod-like micelles and between $\frac{1}{2}$ and 1 to a planar structure (Fig. 4).

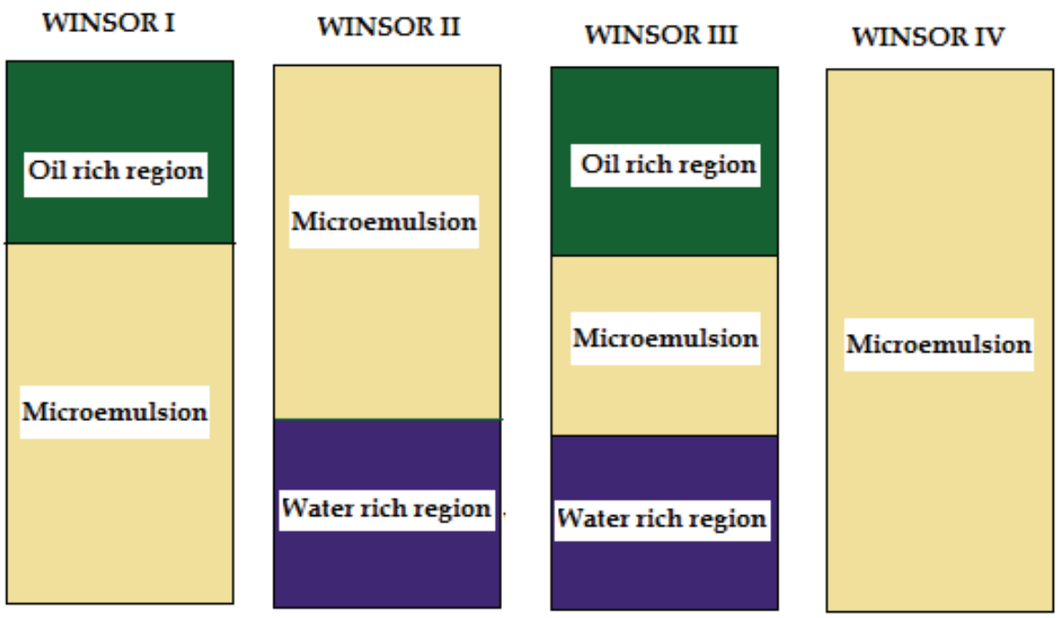


Fig. 2. Schematic presentation of most occurred surfactant associates

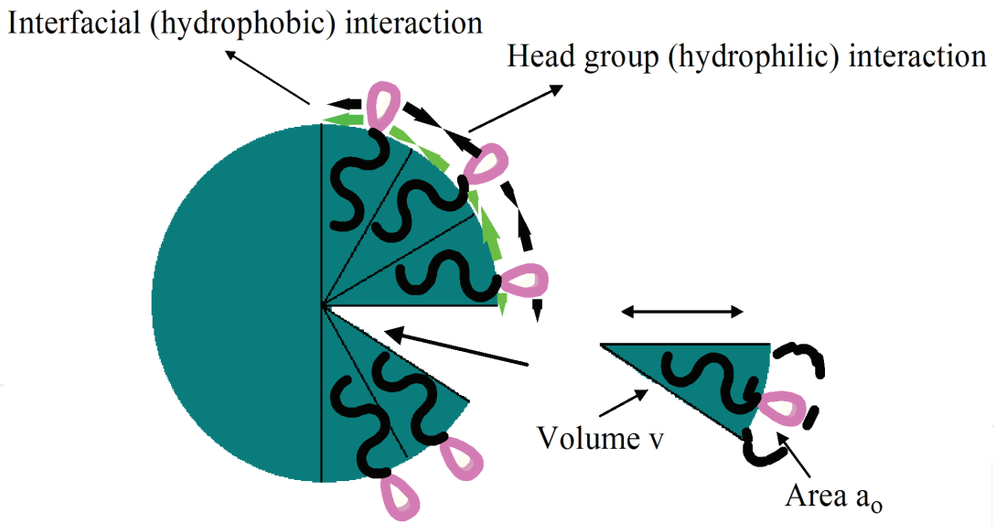


Fig. 3. The critical packing parameter relates the head group area, the length and the volume of the carbon chain into dimensionless number (eqn. 1)

The concept of HLB (Hydrophilic-Lipophilic Balance) was introduced by Griffin in 1949. As the name suggests, HLB is an empirical balance based on the relative percentage of the hydrophilic to the lipophilic moieties in the surfactant. Later, he (Griffin, 1954) defined an empirical equation that can be used to determine the HLB based on chemical composition. Davies et al. has offered a more general empirical equation (Davies et al., 1959) by assigning a number to the different hydrophilic and lipophilic chemical groups in a surfactant. The HLB number was calculated by the expression,

$$HLB = [(n_H xH) - (n_L xL)] + 7 \quad (2)$$

where H and L is the numbers assigned for the hydrophilic and lipophilic groups respectively, and n_H and n_L are the respective numbers of these groups per surfactant molecule. Both HLB and packing parameter numbers are closely correlated. However, it has been shown that, for a bicontinuous structure, which corresponds to a zero curvature, HLB ≈ 10. For HLB <10, negative curvature is favourable (i.e. w/o microemulsion), while for HLB >10, positive curvature results.

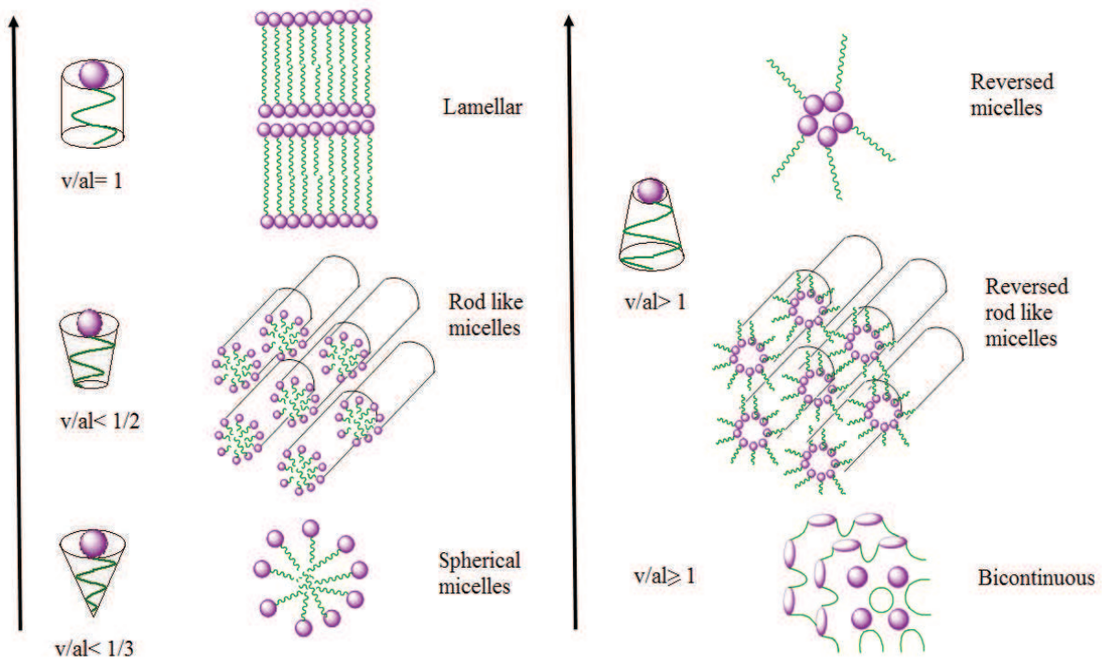


Fig. 4. The surfactant aggregate structure for critical packing parameters from < 1/3 (lower left) to >1 (upper right)

2. Basics of microemulsion formation

There are different theories relating to the formation of microemulsions i.e. interfacial, solubilization and thermodynamic theories, etc. The first theory known as mixed film theory considered the interfacial film as a duplux film. In 1955 (Bowcott & Schulman, 1955) it was postulated that the interface is a third phase, implying that such a monolayer is a duplex film, having diverse properties on the water side than oil side. Such a specialized liquid having two-dimensional region bounded by water on one side and oil on the other, has been based on the assumption that the spontaneous formation of a microemulsion is due to the interactions in the interphase and reducing the original oil/water interfacial tension to zero. However, zero interfacial tension does not ensure that a microemulsion is formed, as cylindrical and lamellar micelles are also believed to be formed. What differentiated an emulsion from other liquid crystalline phases is the kind of molecular interactions in the liquid interphase that produce an initial, transient tension or pressure gradient across the flat interphase, i.e., a duplux film, causing it to enclose one bulk phase in the other in the form of spheres. A liquid condensed film was considered essential to give the kind of

flexibility to the interphase that would allow a tension gradient across it to produce curvature. Following the concept of mixed film theory, Robbins developed the theory of phase behavior of microemulsions using the concept that interactions in a mixed film are responsible for the direction and extent of curvature and thus can estimate the type and size of the droplets of microemulsions (Robbins, 1976). It is believed that kind and degree of curvature is imposed by the differential tendency of water to swell the heads and oil to swell the tails.

The stability of microemulsions has been the matter of interest for various research groups working in this area. The workers however feel that along with the depression in the interfacial tension due to surface pressure, a complex relationship between zero interfacial tension and thermodynamic stability holds the key for the formation of microemulsion systems. The thermodynamic factors include stress gradients, solubility parameters, interfacial compressibility, chemical potentials, enthalpy, entropy, bending and tensional components of interfacial free energy, osmotic pressure and concentrations of species present in the bulk and interphase, etc.

Based upon these facts, another theory i.e., the solubilization theory, was proposed which considers microemulsions as swollen micellar system. A model has been presented by Adamson (Adamson, 1969) in which the w/o emulsion is said to be formed because of the balance achieved in the Laplace and osmotic pressure. However, it has been emphasised that micellar emulsion phase can exist in equilibrium with non-colloidal aqueous phase. The model also concluded that the electrical double layer system of aqueous interior of the micelle is partially responsible for the interfacial energy. It was assumed that the interface has a positive free energy. However, this gave a contradiction to the concept of negative interfacial tension.

Considering the thermodynamic theory, the free energy of formation of microemulsion, ΔG_m, consists of different terms such as interfacial energy and energy of clustering droplets. Irrespective of the mechanism, the reduction of the interfacial free energy is critical in facilitating microemulsion formulation. Schulman and his co-workers have postulated that the negative interfacial tension is a transient phenomenon for the spontaneous uptake of water or oil in microemulsion (Schulman et al., 1959). It has been proved from thermodynamic consideration that a spontaneous formation of microemulsions take place where the interfacial tension is of order 10^{-4} to 10^{-5} dynes/cm (Garbacia & Rosano, 1973). However, the stability and the size of droplets in microemulsion can also be adjudged using the thermodynamic approach. This approach accounts for the free energy of the electric double layer along with the van der Waals and the electrical double layer interaction potentials among the droplets. It also takes into consideration the entropy of formation of microemulsion. Schulmen et al. also reported that the interfacial charge is responsible in controlling the phase continuity (Schulman et al., 1959).

Conversely from the thermodynamical point of view, it can also be said that microemulsions are rather complicated systems, mainly because of the existence of at least four components, and also because of the electric double layer surrounding the droplets, or the rods, or the layers which contribute noticeably to the free energy of the system. The role of the electrical double layer and molecular interactions in the formation and stability of microemulsions were well studied by Scriven (Scriven, 1977). Ruckenstein and Chi quantitatively explained the stability of microemulsions in terms of different free energy components and evaluated enthalpic and entropic components (Ruckenstein & Chi, 1975). For a dispersion to form spontaneously, the Gibbs free energy of mixing, ΔG_m must be negative. For the dispersion to be thermodynamically stable, ΔG_m must, furthermore, show a minimum.

When applying these conditions to microemulsions with an amphiphilic monolayer separating the polar and the nonpolar solvent, it has been customary to attribute a natural curvature as well as a bending energy to the saturated monolayer, thereby making the interfacial tension depend on the degree of dispersion. Kahlweit and Reissi have extensively worked on the stability of the microemulsions and paid attention to the reduction of amphiphile surface concentration below the saturation level, an effect that also makes the interfacial tension depend on the degree of dispersion (Kahlweit and Reissi, 1991).

Thermodynamic treatment of microemulsions provided by Ruckenstein and Chin not only provided the information about its stability but also estimated the size of the droplets (Ruckenstein & Chin, 1975). Treatment of their theory indicated that spontaneous formation of microemulsions occurs when the free energy change of mixing ΔG_m is negative. However, when ΔG_m is positive, a thermodynamically unstable and kinetically stable macroemulsions are produced. According to them, the model consists of monodisperse microdroplets, which are randomly distributed in the continuous phase. The theory postulated the factors which are responsible for the stability of these systems which includes van der Waals attraction potential between the dispersed droplet, the repulsive potential from the compression of the diffuse electric double layer, entropic contribution to the free energy from the space position combinations of the dispersed droplets along with the surface free energy. The van der Waals potential was calculated by Ninham-parsegian approach, however, the energy of the electric double layer was estimated from the Debye-Huckel distribution. Accordingly the highest and lowest limit of entropy has been estimated from the geometric considerations. The calculations depicted that the contribution from the van der Waals potential is negligible in comparison to the other factors contributing to the free energy.

It has been suggested (Rehbinder & Shchukin, 1972) that when the interfacial tension is low but positive, the interface may become unstable due to a sufficiently large increase in entropy by dispersion. The entropy change decreases the free energy and overpowers the increase caused by the formation of interfacial area and therefore net free energy change is negative. Along with this Murphy (Murphy, 1966) suggested that an interface having a low but positive interfacial tension could nevertheless be unstable with respect to bending if, the reduction in the interfacial free energy due to bending exceeds the increase in free energy due to the interfacial tension contribution. He also concluded that this bending instability might be responsible for spontaneous emulsification. Based upon these conclusions, Miller and Scriven interpreted the stability of interfaces with electric double layer (Miller & Scriven, 1970). According to them the total interfacial tension was divided into two components

$$\gamma_T = \gamma_p - \gamma_{dl} \tag{3}$$

where γ_T is total interfacial tension which is the excess tangential stress over the entire region between homogenous bulk fluids including the diffuse double layer. γ_p is the phase interphase tension which is that part of the excess tangential stress which does not arise in the region of the diffuse double layer and - γ_{dl} is the tension of the diffuse layer region. Equation 3 suggests that when γ_{dl} exceeds $\gamma_{p,}$ the total interfacial tension becomes negative. For a plane interphase the destabilising effect of a diffuse layer is primarily that of a negative contribution to interfacial tension. Their results confirm that the double layer may indeed affect significantly the interfacial stability in low surface tension systems. However, the thermodynamic treatment used by Ruckenstein and Chi also included the facts that

along with free energy of formation of double layers, double layer forces and London forces were also taken in consideration. For evaluating entropy of the system, the ideality of the system was not assumed.

The theory also predicts the phase inversion that can occur in a particular system. According to the calculations, the free energy change ΔG_m is the sum of changes in the interfacial free energy (ΔG_1), interaction energy among the droplets (ΔG_2) and the effect caused by the entropy of dispersion ($\Delta G_3 = T\Delta S_m$). The antagonism among these different factors mainly predicts the formation of microemulsions. The variation of ΔG_m with the radius of droplet, R, at constant value of water/oil ratio can be determined using $\Delta G_m(R) = \Delta G_1 + \Delta G_2 - T\Delta S_m$. R* is stable droplet size for a given volume fraction of the dispersed phase that leads to a minimum in G_m^* (Fig. 5). R* can be obtained from

$$\frac{d\Delta G_m}{dR_{R=R^*}} = 0 \tag{4}$$

if the condition, $(d^2\Delta G_m/dR^2)_{R=R^*} > 0$ is satisfied. In order to determine the type of microemulsion and the phase inversion, the values of ΔG^*_m for both types of microemulsions have to be compared at same composition. The composition having more –ve value of Gibbs free energy will be favoured and the volume fraction for which the values of ΔG^*_m are same for both kinds of microemulsion are said to undergo phase inversion.

The quantitative outcome of the model for the given free energy as a function of droplet size has been shown in Fig. 5. The free energy change is positive for B and C i.e., only emulsions, the free energy change is positive. Hence, only emulsions which are thermodynamically unstable are formed in the case C. However, kinetically stable emulsions may be produced that too depending upon the energy barrier. The free energy change is negative within a certain range of radius (R) of dispersed phase in the case A, this means that droplets having a radius within this size range are stable towards phase separation and microemulsions formed are thermodynamically stable. The calculations show that at specific composition and surface potential, the transformation of curves from C to A can take place by decreasing the specific surface free energy.

As obvious from the above explanation, the assessment of the stability of microemulsions has been carried simultaneous by various groups after it was first triggered by Schulman and his collaborators. Simultaneously, Gerbacia and Rosano measured the interfacial tension at the interphase in the presence of an alcohol that is present in one of the phase (Gerbacia & Rosano, 1973). The presence of alcohol lowered the interfacial tension to zero as the alcohol diffuses to interface. This observation lead to the conclusion that for the formation of microemulsion, the diffusion of surface active molecules to the interface is mandatory and also the formation depends on the order in which the components are added.

The concept that interfacial tension becomes zero or negative for spontaneous formation of microemulsions has been later modified (Holmberg, 1998). It is believed that a monolayer is formed at the oil/water interphase which is responsible for a constant value of interfacial tension, which can be estimated using Gibbs equation.

$$\partial\gamma = -\Sigma\Gamma_i d\mu_i = -\Sigma\Gamma_i RT d\ln C_i \tag{5}$$

where Γ, , μ, C_i are Gibbs surface excess, chemical potential, and concentration of i^{th} component. The presence of cosurfactant in the system further lowers this value.

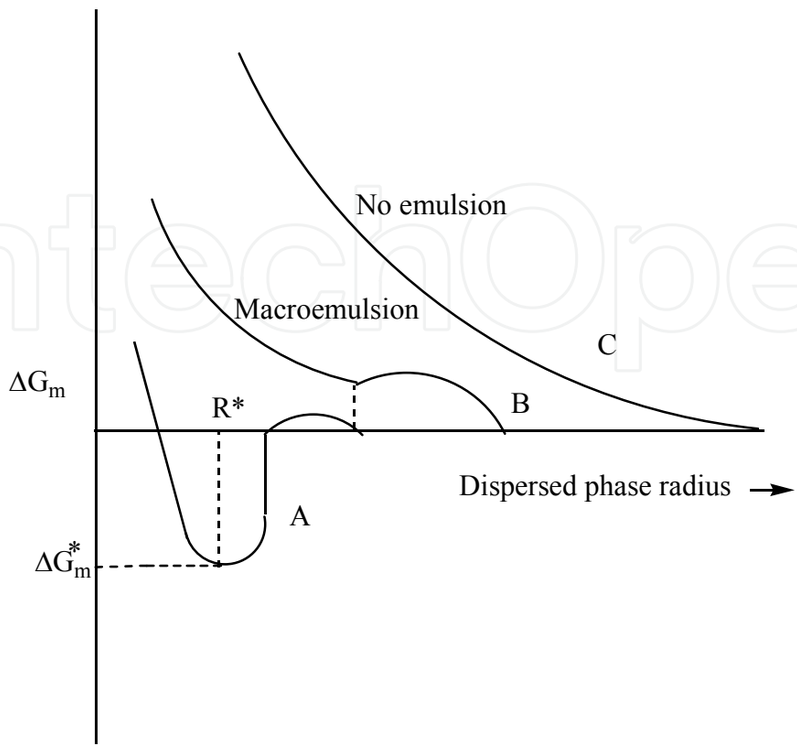


Fig. 5. Diagrammatic illustration of free energy as a function of droplet size

During 1980s the "dilution method" was well adopted by many, to extract energetic information for different combinations along with the understanding of their structural features (Bansal et al., 1979; Birdi, 1982; Singh et al., 1993; Bayrak, 2004; Zheng et al., 2006; Zheng et al., 2007), after it was first introduced by Schulman group (Bowcott & Schulman, 1955; Schulman et al., 1959). Basically, this method deals with the estimation of distribution of cosurfactant (k_d) and hence, determines the composition of interphase which is in turn responsible for the formation and stability of microemulsions. From the value of k_d (equilibrium constant), the Gibbs free energy of transfer of alcohol from the organic phase to the interphase can be obtained from the equation

$$\Delta G^{o}_{transfer} = -RT \ln K_d \tag{6}$$

Using this method, the different thermodynamic parameters such as entropy or/ and enthalpy of transfer can also be obtained. A polynomial fitting between $\Delta G^{o}_{transfer}$ and the temperature (T) was used to obtain $\Delta S^{o}_{transfer}$ from its first derivative

$$\frac{\Delta G^{o}_{transfer}}{\Delta T} = -\Delta S^{o}_{transfer} \tag{7}$$

From the knowledge of $\Delta G^{o}_{transfer}$ and $\Delta S^{o}_{transfer}$, the enthalpy of transfer was calculated according to the Gibbs Helmoltz equation

$$\Delta H^{o}_{transfer} = \Delta G^{o}_{transfer} + T\Delta S^{o}_{transfer} \quad (8)$$

Apart from the understanding of the composition of interphase, the "dilution method" also helps in the estimation and determination of structural aspects of the microemulsion system like droplet size, number of droplets, etc.

3. Percolation phenomenon

The integrity of the monolayer is often influenced by the events occurring upon collision between microemulsion droplets. One expects various changes of the properties of the microemulsions, when the volume fraction of the dispersed phase ϕ is increased. The electrical conductivity is especially sensitive to the aggregation of droplets. This is indeed observed in several reported studies (Lagues, 1978, 1979; Dvolaitzky et al., 1978; Lagues & Sauterey, 1980; Lagourette et al., 1979; Moha-Ouchane et al., 1987; Antalek et al., 1997) in aqueous microemulsions. The paper of 1978 by Lagues is the first to interpret the dramatic increase of the conductivity with droplet volume fraction for a water-in-oil microemulsion in terms of a percolation model and termed this physical situation as stirred percolation, referring to the Brownian motion of the medium. This was, however, soon followed by several investigations. According to most widely used theoretical model, which is based on the dynamic nature of the microemulsions (Grest et al., 1986; Bug et al., 1985; Safran et al., 1986), there are two pseudophases: one in which the charge is transported by the diffusion of the microemulsion globules and the other phase in which the change is conducted by diffusion of the charge carrier itself inside the reversed micelle clusters. According to this theory, two approaches (static and dynamic) have been proposed for the mechanism leading to percolation (Lagourette et al., 1979). These are being governed by scaling laws as given in equations 9 and 10.

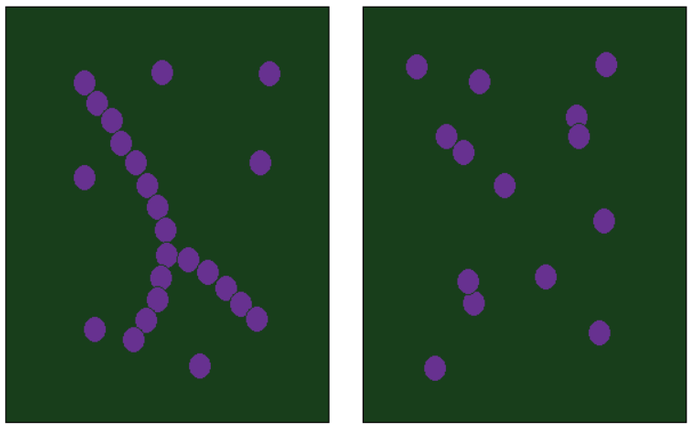
$$\sigma = A(\phi_c - \phi)^{-s} \qquad \text{pre-percolation} \quad (9)$$

$$\sigma = B(\phi - \phi_c)^{t} \qquad \text{post-percolation} \quad (10)$$

where σ is the electrical conductivity, ϕ is the volume fraction, and ϕ_c is the critical volume fraction of the conducting phase (percolation threshold), and A and B are free parameters. These laws are only valid near percolation threshold (ϕ_c). It is impossible to use these laws at extremely small dilutions ($\phi \rightarrow 0$) or at limit concentration ($\phi \rightarrow 1$) and in the immediate vicinity of ϕ_c. The critical exponent *t* generally ranges between 1.5 and 2, whereas the exponent *s* allows the assignment of the time dependent percolation regime. Thus, $s > 1$ (generally around 1.3) identifies a dynamic percolation (Cametti et al., 1992, Pitzalis et al., 2000; Mehta et al., 2005). The static percolation is related to the appearance of bicontinuous microemulsions, where a sharp increase in conductivity, due to both counter – ions and to lesser extent, surfactant ions, can be justified by a connected water path in the system. The dynamic percolation is related to rapid process of fusion- fission among the droplets. Transient water channels form when the surfactant interface breaks down during collisions or through the merging of droplets (Fig. 6). In this latter case, conductivity is mainly due to the motion of counter ions along the water channels. For dynamic percolation model, the overall process involves the diffusional approach of two droplets, leading to an encounter pair (Fletcher et al., 1987).

In a small fraction of the encounters, the interpenetration proceeds to a degree where the aqueous pools become directly exposed to each other through a large open channel between the two compartments, created by the rearrangement of surfactant molecules at the area of mutual impact of the droplets. The channel is probably a wide constriction of the monolayer shell between the two interconnected compartments. Due to the geometry of the constriction, the monolayer at that site has an energetically unfavorable positive curvature, which contributes to the instability of the droplet dimmer. The short lived droplet dimmer than decoalesces with a concomitant randomization of the occupancy of all the constituents and the droplets re-separate. Thus, during the transient exchange of channels, solubilizate can exchange between the two compartments. This offers an elegant approach to study the dynamic percolation phenomenon. However, another approach depicts a static percolation picture which attributes percolation to the appearance of a "bicontinuous structure" i.e formation of open water channels (Bhattacharaya et al., 1985).

The conductivity of the microemulsion system is very sensitive to their structure (Eicke et al., 1989; Kallay and Chittofrati, 1990; Giustini et al., 1996 ; D'Aprano et al., 1993, Feldman et al., 1996). The occurrence of percolation conductance reveals the increase in droplet size, attractive interactions and the exchange of materials between the droplets. The percolation threshold corresponds to the formation of first infinite cluster of droplets (Kallay and Chittofrati, 1990). Even before the occurrence of percolation transition the change in conductivity indicates the variation of reverse micellar microstructure. The conductivity is closely related to the radius of the droplet but other factors like the composition of the microemulsions system, presence of external entity, temperatures etc. Under normal conditions, water in oil microemulsions represent very low specific conductivity (ca.10^{-9} – 10^{-7} $\Omega^{-1}cm^{-1}$). This conductivity is significantly greater than it would be if we consider the alkane, which constitutes the continuous medium and is the main component of the water in oil microemulsions (~10^{-14} Ω^{-1} cm^{-1}). This increase in the electrical conductivity of the microemulsions by comparison with that of the pure continuous medium is due to the fact that microemulsions are able to transport charges.



(a) Static droplet fusion (b) Dynamic droplet fusion

Fig. 6. Dynamics of droplet fusion

When we reach a certain volume of the disperse phase, the conductivity abruptly increases to give values of up to four orders of magnitude, which is greater than typical conductivity of water in oil microemulsions. This increase remains invariable after reaching the maximum value, which is much higher than that for the microemulsion present before this

transition occurs. Similar behavior is observed with variation in water content, temperature or volume fraction for the fixed composition of the microemulsion. This phenomenon is known as *electric percolation*, (Hamilton et al., 1990, Garcia-Rio et al., 1997, Hait et al., 2001, Borkovec et al., 1988, Papadimitriou et al., 1993, Mehta et al., 1995, 1998, 1999, 2000, 2002) the moment at which an abrupt transition occurs from poor electric conductor, system (`10^{-7} Ω^{-1} cm^{-1}) to the system with fluid electric circulation (10^{-3} Ω^{-1} cm^{-1}). As a consequence of ion transfer it yields a sigmoidal $\sigma - \theta$ and $\sigma - \phi$ profile. The point of maximum gradient of the $d\log\sigma/d\theta$ or $d\log\sigma/d\phi$ profile corresponds to the transition of the percolation process and is designated as the threshold volume fraction (ϕ_c) or the threshold temperature (θ_c), characteristic feature of a percolating system.

Moulik group (Hait et al., 2001) has proposed the sigmoidal Boltzmann equation (SBE) to determine the threshold characteristics of microemulsion systems. In conductance percolation, the equivalent equation can be written as

$$\log\sigma = \log\sigma_f\left[1+\left(\frac{\log\sigma_i-\log\sigma_f}{\log\sigma_f}\right)\{1+\exp(\theta-\theta_c)/\Delta\theta\}^{-1}\right] \tag{11}$$

where i, f and c are the initial, final and percolative stages. The composition of the system and other environmental conditions such as pressure and presence of additives control the threshold values.

The specific conductance of the system is calculated with the help of *droplet charge fluctuation model* (Eicke et al., 1989). In this model which is valid for the free diffusing species, it is assumed that the net charges of a droplet around an average net zero charge and its transport is associated with the free diffusive process of single droplets. Using this model the final result of the conductivity of a dilute microemulsion is

$$\sigma = \frac{\varepsilon_o\varepsilon k_B T}{2\pi\eta}\frac{\phi}{r_n^3} \tag{12}$$

However, in order to arrive at this expression, consider a nanodroplet composed of N_1 negatively charged surfactant molecules and N_2 positively charged counterions. For electroneutrality the average values are equal $\langle N_1\rangle = \langle N_2\rangle = N$. However, due to spontaneous fluctuations in these numbers the droplet will carry can excess charge

$$z = N_2 - N_1 \tag{13}$$

in units of the elementary charge e. Even though the valency of a droplet z will fluctuate in time, the conductivity of microemulsion and a dilute electrolyte solution containing different ions can be evaluated in an entirely equivalent manner. This is because only the mean square valency of the ions (or droplets) determines the conductivity. The conductivity σ of a dilute electrolyte solution of different ions i, with a valency z_i, radius r_n (taken as independent of i for simplicity), number density ρ_i, is given (Berry et al., 1980) by

$$\sigma = \frac{e^2}{6\pi\eta r_n}\sum_i z_i^2\rho_i \tag{14}$$

where η is the viscosity of the solvent and i runs over all different ionic species in the solution. In case of microemulsion droplets, it is more convenient to write equation 14 as

$$\sigma = \frac{\rho e^2}{6\pi\eta r_n}\langle z^2\rangle \tag{15}$$

where ρ is the number of droplets per unit volume and $\langle .....\rangle$ is the canonical average over all droplets. Note that due to electroneutrality $\langle z\rangle = 0$.

The quantity of interest is the mean square charge $\langle z^2\rangle$ of a droplet. It can be expressed in the terms of the mean squared fluctuations of the number of ions residing on a droplet $\delta N_i = N_i - \langle N_i\rangle$ by

$$\langle z^2\rangle = \langle \delta N_2^2\rangle - 2\langle \delta N_2 \delta N_1\rangle + \langle \delta N_1^2\rangle \tag{16}$$

Such averages are related to derivatives with respect to the conjugated thermodynamic forces (Callen, 1960)

$$\langle \delta N_i \delta N_j\rangle = k_B T\left(\frac{\partial N_i}{\partial \mu_j}\right)_{T,\mu_{k\neq j}} \tag{17}$$

where μ_j is the chemical potential of the j^{th} component (j=1,2), T is the absolute temperature and k_B is the Boltzman constant.

To evaluate $\langle z^2\rangle$ explicitly, one need a model for the chemical potential μ_i of the ion residing on a droplet. One may write

$$\mu_i = \mu_i^o + k_B T \log N_i + \mu_i^{(ex)} \tag{18}$$

where first two terms on the right hand side represents the chemical potential for an ideal solution while $\mu_i^{(ex)}$ is the excess chemical potential

$$\mu_i^{(ex)} = \left(\frac{\partial G^{(ex)}}{\partial N_i}\right)_{T,N_{k\neq j}} \tag{19}$$

Here a simple model is adopted to identify the electrostatic work required to charge a droplet in the solvent with the excess Gibbs free energy, i.e.

$$G^{(ex)} = \left(\frac{z^2 e^2}{8\pi\varepsilon_o \varepsilon r_n}\right) \tag{20}$$

where z is given in equation 13, ε_o is the dielectric permittivity of the vacuum, and ε is the dielectric constant of the solvent. The excess Gibbs free energy (eqn no. 20) is also the basis of Born's theory of ionic solvation (Berry et al., 1980).

Now the calculation of $\langle z^2\rangle$ explicitly, using equations 18-20, the 2X2 matrix with the elements $(\partial\mu_i / \partial N_j)_{N_{k\neq j},T}$ was calculated and it was found

$$k_B T\begin{bmatrix} 1/N_1+\alpha & -\alpha \\ -\alpha & 1/N_2+\alpha \end{bmatrix} \tag{21}$$

The abbreviation $\alpha = e^2/(4\pi k_B T \varepsilon_o \varepsilon r_n)$ has been introduced. The derivatives $(\partial N_i / \partial \mu_j)_{\mu_{k\neq j},T}$ required in equation 15 can be obtained most easily by noting the fact that

the matrices with the elements $(\partial\mu_i / \partial N_j)_{N_{k\neq j},T}$ and $(\partial N_i / \partial \mu_j)_{\mu_{k\neq j},T}$ are related by simple matrix inversion (Callen, 1960). Inverting the matrix in equation in 21 and using equation 16 and 17, it gives

$$\langle z^2 \rangle = \frac{2N}{1+2N\alpha} \tag{22}$$

There are two limiting cases to consider.

For $\alpha << 1$ the second term in the denominator of equation 22 is negligible, and therefore $\langle z^2 \rangle = 2N$. This is the limiting case of ideal behavior where the mean-square fluctuations are essentially given by the number of ions residing on the droplet. As N>>1, the realistic case corresponds to the second limit where $\langle z^2 \rangle = 1/\alpha$. This means that it is determined by the ration of coulomb and thermal energies. Inserting $\langle z^2 \rangle = 1/\alpha$ into equation 15, we obtain the final result for the conductivity of a dilute microemulsion i.e. equation no. 12.

ρ has been replaced with the volume fraction of the droplet ϕ by using the relation $\phi = 4\pi r^3 \rho / 3$. Equation 12 predicts that the specific conductivity of microemulsion (σ/ϕ) should be constant and for a given solvent and temperature, depend on the radius of the droplet only $\propto r_n^3$. this result is independent of the charge of the ions in question.

However the phenomenon of percolation process (Peyrelasse et al., 1988) was also assessed using permittivity studies by Peyrelasse et al. From a very general point of view the complex permittivity ε* of a heterogeneous binary system may be represented by a relationship of the form $\varepsilon^* = G(\varepsilon_1^*, \varepsilon_2^*, \phi, p_k)$ in which ε_1^* and ε_2^* are the complex permittivities of the constituents 1 and 2, ϕ is the volume fraction and p_k represents the parameter, which enable the function G to contain all the information on the geometry of the dispersion and on the interactions, which takes place within the system. The models, which enable a approximation of the function G, are often based on effective and mean field theories. Satisfactory results are generally obtained when the interactions within the mixtures are weak, which is often the case when the volume fraction of one of the constituents is small, and as long as the dispersion can be considered macroscopically homogenous. But when the dispersed particles are no longer isolated from each other, in other words, when clusters of varying sizes form, the conventional models no longer apply and the concept of percolation can be successfully used. The general relationship for complex permittivity (Efros & Shklovskii, 1976; Stroud & Bergman, 1982) is

$$\frac{\varepsilon^*}{\varepsilon_1^*} = |\phi - \phi_c|^t f\left[\frac{\varepsilon_2^* / \varepsilon_1^*}{|\phi - \phi_c|^{t+s}}\right] \tag{23}$$

where ε*, ε^*_1, ε^*_2 are the complex permittivities of microemulsion and the components, ϕ is the volume fraction of dispersed phase ϕ_c is the percolation threshold. Similar to the conductivity, permittivity also obeys the characteristic scaling laws. The function f(z) in which z is a complex variable satisfies the following asymptotic forms

$$\phi > \phi_c, |z| << 1, f(z) = C_1 + C_1' z \tag{24}$$

$$\phi < \phi_c, |z| << 1, f(z) = C_2 z \tag{25}$$

$$z >> 1 \forall \phi, f(z) = Cz^{t(t+s)} \tag{26}$$

If it is assumed that the two components are dielectric conductors of static permittivities ε_{1s} and ε_{2s} and the conductivities σ_1 and σ_2, then one obtains

$$\varepsilon_1^* = \varepsilon_{1s} - j\frac{\sigma_1}{\varepsilon_o \omega}, \ \varepsilon_2^* = \varepsilon_{2s} - j\frac{\sigma_2}{\varepsilon_o \omega}, \ \omega = 2\pi\upsilon \tag{27}$$

in which υ is the frequency of the electric field applied, ε_o i.e. the dielectric permittivity of a vacuum and $j^2 = -1$. The heterogeneous system built from components 1 and 2 presents static permittivity ε_s and conductivity σ. The following relations are obtained
when $\phi < \phi_c, |z| << 1$,

$$\varepsilon_s = C_2 \varepsilon_{2s} (\phi_c - \phi)^{-s} \tag{28}$$

$$\sigma = C_2 \sigma_2 (\phi_c - \phi)^{-s} \tag{29}$$

But when $\phi > \phi_c, |z| << 1$

$$\varepsilon_s = C_1' \varepsilon_{2s} (\phi - \phi_c)^{-s} [1 + \frac{C_1 \varepsilon_{1s}}{C_1' \varepsilon_{2s}} (\phi - \phi_c)^{(t+s)}] \tag{30}$$

$$\sigma = C_1 \sigma_1 (\phi - \phi_c)^t [1 + \frac{C_1' \sigma_2}{C_1 \sigma_1} (\phi - \phi_c)^{-(t+s)}] \tag{31}$$

As (t+s) are positive $\varepsilon_{1s} / \varepsilon_{2s}$ does not tends towards infinity, while ϕ is close to ϕ_c we have

$$\varepsilon_s = C_1' \varepsilon_{2s} (\phi - \phi_c)^{-s} \tag{32}$$

So when ϕ is close to ϕ_c, $\varepsilon \alpha |\phi - \phi_c|^{-s}$ on either side of ϕ_c. Moreover, of $\sigma_2 / \sigma_1 << 1$ (for example, with a perfect insulator $\sigma_2 = 0$), close to the percolation threshold one can still have

$$\frac{\sigma_2}{\sigma_1} << |\phi - \phi_c|^{(t+s)} \tag{33}$$

One consequently obtains

$$\sigma = C_1 \sigma_1 (\phi - \phi_c)^t \tag{34}$$

It will be noted that equations 29 and 34 indicate that the derivative $(1/\sigma)(d\sigma / d\phi)$ tends towards infinity at percolation threshold. It should also be observed that equations 28-34 are only valid if z <<1. For conductivity this implies that $\frac{\sigma_2}{\sigma_1} << (\phi - \phi_c)^{(t+s)}$. These are not valid in the neighbourhood of ϕ_c in which $z \to \infty$. In fact, experimentally, there is a continuous transition with in an interval of width (Δ) in the immediate neighbourhood of ϕ_c. The width of this transition interval (the cross over regime) is of the order of

$$\Delta = s_1 + s_2 = (\frac{\sigma_2}{\sigma_1})^{1/(t+s)} \tag{35}$$

The above discussion leads to asymptotic relationships for conductance as

$$\sigma\alpha(\phi - \phi_c)^t \text{if} \phi > \phi_c + s_1 \tag{36}$$

$$\sigma\alpha(\phi_c - \phi)^{-s} \text{if} \phi < \phi_c - s_2 \tag{37}$$

Finally one obtain the equations in the form of equation 9 and 10.

In terms of permittivity, when in equation (23) $\left[\frac{\varepsilon_2^* / \varepsilon_1^*}{|\phi - \phi_c|^{t+s}}\right]$ is much smaller than 1,

$$\varepsilon_s = A'(\phi_c - \phi)^{-s} \qquad \text{pre-percolation} \tag{38}$$

$$\varepsilon_s = B'(\phi - \phi_c)^t \qquad \text{post-percolation} \tag{39}$$

where ϕ is the volume fraction, and ϕ_c is the critical volume fraction of the conducting phase (percolation threshold), and A and B are free parameters. These laws are only valid near percolation threshold (ϕ_c).

The study of microemulsions provides a characteristic insight in to its structural features. However, in the dilute limit and for Newtonian behavior, the microemulsions are said to obey well-known Einstein relation

$$\eta_r = \frac{\eta}{\eta_o} = 1 + 2.5\phi \tag{40}$$

According to the relation, the dispersed particles in the liquid are in the form of rigid spheres, which are larger than the solvent molecules. However, on account of complex interaction between the particles and solvent, the relation no longer remains linear when the concentration is increased (ϕ volume fraction >0.05). Ward and Whitemore have found that η_r is a function of size distribution and is independent of the viscosity of the suspending liquid and the absolute size of the spheres at a given concentration (Ward & Whitemore, 1950). According to Roscoe and Brinkman the viscosity of solutions and suspensions of finite concentration with spherical particles of equal size (Roscoe, 1952; Brinkman, 1952) is given by

$$\eta_r = (1 - 1.35\phi)^{-2.5} \tag{41}$$

For large volume fractions one must, on the one hand, account for hydrodynamic interactions between the spheres and on the other hand, for direct interactions between the particles that are, e.g., of a thermodynamic origin. However, there is no accurate theory to explain the viscosity of microemulsions but several semiempirical relations are used for the purpose (Saidi et al., 1990). When the composition of microemulsion is subjected to change it subsequently changes its viscosity profile yielding different structural organisations. Further, in order to understand the percolation phenomena viscosity studies are

successfully employed. With time the viscosity increases and at time t_c a molecule of infinite length is formed. t_c corresponds to the gelation point and scaling laws can be written as follows

$$\eta\alpha(t_c - t)^{-s} \text{ pre percolation} \tag{42}$$

$$E\alpha(t - t_c)^{\mu} \text{ post percolation} \tag{43}$$

where E is the elastic modulus. However, the critical exponent obtained for η can have various values. It depends on the experimental conditions which suggest the existence of different growth mechanism.

4. Energetics of droplet clustering

Various studies (Peyrelasse et al., 1989; Peyrelasse & Boned, 1990; Mathew et al., 1991) have shown that conductivity percolation in microemulsions is the result of droplet clustering. This is being depicted in Fig. 7. At low ϕ, individual droplets maintain a low conductivity. As ϕ increases, the conductivity also increases as droplets assemble in the clusters and ion diffusion or exchange of droplet content is facilitated and an infinite percolating droplet network is eventually formed at ϕ_c. The droplets clustering process has been estimated utilizing the values of dispersed phase volume fraction (ϕ_c) at the percolation threshold (Ray et al., 1993; Alexandridis et al., 1995). It has been postulated that the threshold of electrical percolation corresponds to the formation of first open structure of an infinite cluster (Eicke et al., 1989; Riddick & Bunger, 1970).

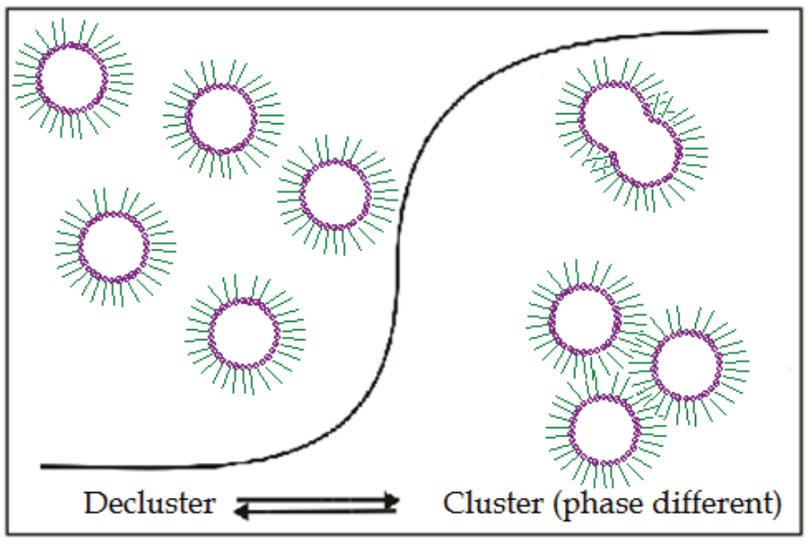


Fig. 7. Schematic representation of droplet cluster formation and the course of electrical conductivity with varying temperature and composition

Organodiselenide	S=[Oil]/[AOT]	$-\Delta G^{o}_{cl}$ (kJ mol^{-1})	ΔH^{o}_{cl} (kJ mol^{-1})	ΔS^{o}_{cl} (JK^{-1}mol^{-1})
Without	5	21.67,24.36	64.34, 67.49	130.80, 131.24
	7	22.30,25.41		
	9	23.14,26.35		
	15	24.93,28.33		
$C_{12}H_{16}N_6Se_2$	5	21.25, 24.48	74.59, 82.36	162.63,175.34
	7	22.39, 25.66		
	9	23.23, 26.60		
	15	25.04, 28.40		
$C_8H_4N_4Se_2Cl_2$	5	25.84,24.21	61.33,68.82	133.95,134.24
	7	26.84, 25.26		
	9	27.77, 27.84		
	15	29.74, 28.84		
Nap_2Se_2	5	25.36,24.57	68.62,69.22	131.50,132.24
	7	26.36,25.87		
	9	27.25,27.62		
	15	29.23,30.59		
$(Ph_2CHSe)_2$	5	24.36,24.30	67.29, 69.68	133.36,137.48
	7	25.41,25.47		
	9	23.26,26.34		
	15	24.95,28.95		
$C_{10}H_6N_2Se_2Br_2$	5	28.70, -----		
	15	32.70, 33.02		
$C_{10}H_4N_2Se_2Br_4$	5	28.90, 35.40		
	15	-------, 42.50		

Table 1. Energetics of droplet clustering, ΔG^{o}_{cl} for water-induced percolation for AOT/isooctane/water and Lecithin+AOT/isooctane/water for different organodiselenide at various concentrations

The microemulsion droplet above the percolation threshold, aggregated in clusters, are considered to be phase different than that of nonpercolating droplets, with distinct physical properties such as conductivity. This is comparable to psuedophase concept used for modeling the formation of micelles in solutions of amphiphillic molecules (association model). Dilution of clustered (percolating) microemulsion system upon addition of an apolar solvent at constant droplet size lowers the conductivity rapidly until the clusters dissociate into individual droplets below percolation threshold ϕ_c. This phenomenon is comparable to the process of demicellization occurring when the surfactant concentration is lowered below the critical micellar concentration. In the light of the concept of droplet association, the Gibb's free energy of droplet clustering (standard free energy change for the transfer of 1 mole of droplets from an infinitely diluted solution to the percolating cluster), ΔG_{cl}^{o} is calculated from the relationship

$$\Delta G_{cl}^{o} = RT \ln X_p \tag{44}$$

where R is the gas law constant, T is the absolute temperature, X_p is the mole fraction of the microemulsion droplets corresponding to percolation threshold (ϕ_c) at constant temperature T. The Xp value is obtained from the relation

$$X_p = \frac{n_d}{(n_d + n_o)} = A_t R_w M_o / [A_t R_w M_o + 3 V_o \rho_o N] \tag{45}$$

where, n_d and n_o are the number of moles of droplet and oil, respectively. A_t is the total cross-sectional area of the surfactant, V_o, ρ_o, M_o are the volume, density and molar mass of the oil, respectively. N is the Avogadro number, R_w is the water pool radius is obtained from

$$R_w = 3[M_s + rM_{cs} + \{(W_w + W_{cs}) / W_s\} M_s / \{N\rho_d (A_s + rA_{cs}\}] \tag{46}$$

where M stands for molar mass, W is the weight fraction and subscript c and cs represents for surfactant and cosurfactant respectively. ρ_d, A and N are the density of the dispersed phase, cross-sectional area and Avogadro number, respectively. $r = (N_{cs} / N_s)$ is called structural ratio (ratio between the number of molecules of s and cs at the droplet interface) However, in the absence of cosurfactant equation 46 becomes

$$R_w = 3[M_s + (W_w + W_s)] / N\rho_d a_s \tag{47}$$

Further, the enthalpy of clustering ΔH_{cl}^{o} can also be obtained from Gibbs Helmoltz equation

$$d(\Delta G_{cl}^{o} / \theta_{cl}) / d(1 / \theta_{cl}) = \Delta H_{cl}^{o} \tag{48}$$

The entropy change of the process is obtained from

$$\Delta S_{cl}^{o} = (\Delta H_{cl}^{o} - \Delta G_{cl}^{o}) / \theta_t \tag{49}$$

The energetics of the clustering have been well utilized during all these years for different microemulsions with and without additives. The dynamics of percolation and thereafter energetics of the clustering have been extensively investigated in our group for various

cationic, anionic and non-ionic microemulsions (Mehta et al., 2006, 2007, 2009). The data for energetics of the clustering of AOT/isooctane/water and Lecithin+AOT/isooctane/water microemulsion in presence of different additive i.e., glycols, aminopyridines, modified aminoacids and organodiselenide have been tabulated in Tables (1-3) (Mehta et al., 2007, 2009).

Anti-tuberculosis drug	$-\Delta G^{o}_{cl}$ (kJ mol^{-1})
Tween 80/ oleic acid/ ethanol/phosphate buffer	
without	4.35
rifampicin	5.17
isoniazid	5.17
pyrazinamide	5.17
Brij 96/Ethyl Oleate/butanol/water	
without	48.8
rifampicin	46.04
isoniazid	48.80
pyrazinamide	42.97

Table 2. Energetics of droplet clustering, ΔG^{o}_{cl} for water-induced percolation for different non-ionic microemulsion with and without the presence of anti-tuberculosis drugs (rifampicin, isoniazid and pyrazinamide)

	S = [Oil]/[AOT]	Conc. (mM)	$-\Delta G^{o}_{cl}$ (kJ mol^{-1})	ΔH^{o}_{cl} (kJ mol^{-1})	ΔS^{o}_{cl} (JK^{-1}mol^{-1})
Glycols					
Without	5	15	20.0	61.2±7.5	264.6
	7	15	21.0		
	9	15	22.0		
PG	5	15	20.0	69.4±5.9	291.4
	7	15	21.2		
	9	15	22.0		
BG	5	15	19.8	55.1±5.8	226.4
	7	15	21.1		
	9	15	21.9		

PMG	5	15	19.8	49.0±5.8	226.4
	7	15	20.9		
	9	15	21.8		
Aminopyridines					
Without		-	21.68	55.40±5.2	243.00
2-Ampy	9	50 30 15 5	20.86 21.13 21.55 21.74	48.45±4.8	220.00
3-Ampy	9	50 30 15 5	20.65 21.00 21.47 21.55	48.31±3.6	219.70
2-Am-4-mpy	9	50 30 15 5	21.20 21.40 21.54 21.61	54.53±4.2	239.69
2-Am-6-mpy	9	50 30 15 5	21.13 21.48 21.55 21.61	53.74±1.5	237.33
Modified Aminoacids					
Without	9	5 7 9 15	20.08 21.54 22.35 24.37	47.99	220.4
NAG	9	5 7 9 15	20.33 21.68 22.41 24.81	45.20	209.27
NAA	9	5 7 9 15	20.27 21.61 22.49 24.66	45.64	211.75
NAC	9	5 7 9 15	20.43 21.82 22.62 22.44	43.16	203.6

Table 3. Standard free energy values (kJ mol^{-1}) for volume induced percolation for Glycol, Aminopyridines and Modified Aminoacids (MAA) in AOT/isooctane/water microemulsion

5. Conclusions

Microemulsions are thermodynamically stable, transparent, low viscosity mixtures of oil and water stabilized by a monolayer of surfactant. The chemistry of microemulsions is at an incredibly exciting stage of development. The advent of systems that are easy to handle allows those without specialist knowledge of the field to use them for the first time. Because of its versatility and thermodynamic stability, the microemulsion systems find potential applications in pharmaceutical, oil recovery, as food additives and as reaction media, etc. There are different theories which have been developed over the course of time relating to the formation of microemulsions. Most acceptable among them are interfacial, solubilization and thermodynamic theories, etc. The spontaneity of formation of microemulsion involves change in the free energy of formation of microemulsion, ΔG_m, which mainly consists of interfacial energy and energy of clustering droplets. Irrespective of the mechanism, the reduction of the interfacial free energy is critical in facilitating microemulsion formulation. Alongwith the stability, the size of droplets in microemulsions can also be adjudged using the thermodynamic approach.

The unique solvent properties of microemulsion compared to conventional organic solvents, indicate that the novel micro-heterogeneous media can be efficiently used as reaction media for various biocatalytic reactions. Presence of different domains of variable polarity due to compartmentalization in microemulsions makes them particularly useful in the area of drug delivery. Microemulsion media finds several applications ranging from drug delivery to drug nanoparticles templating due to its ability to enhance solubility, stability and bioavailability. To thoroughly understand the drug delivery potential of microemulsion, it is necessary to know the possible phase transitions occurring in the system and the influence of drug on its microstructure. Apart from being used as a carrier, microemulsions also act as template for synthesis of nanoparticles. In its pharmaceutical applications, attempts are being made to synthesize drug nanoparticles for controlled release.

This chapter deals with different theories and models developed during the course of time using various approaches to interpret the formation, stability and structure of microemulsion systems which offers application and adaptability in multiple fields.

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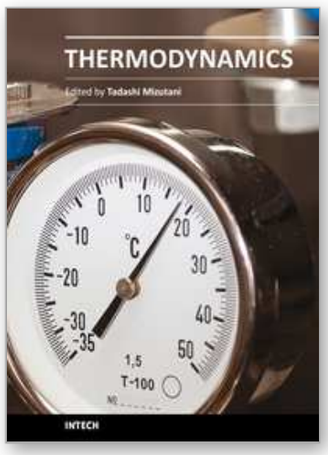
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