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Physicochemistry and Applications of Microemulsions

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Abstract — Microemulsions are a class of microheterogeneous systems having unique features of stability, solubilization capacity, structural morphology, physical property and applicability. Depending on the types of oil and amphiphile, and environmental conditions, microemulsion systems of varied categories, consistencies and internal structures may result. The essentials of microemulsion systems are thus controlled by external factors and internal chemistry. The underlying physicochemical principles controlling their formation, phase behaviour and related properties supplemented with experimental observations need time to time assessment and appraisal to scientists and technologists. This review aims at such a purpose and makes a concise presentation of the physicochemistry and applications of microemulsions to bring the readers up-to-date with the present state of knowledge on the subject. The features that will be presented in some details are the theory of microemulsion formation, general procedure for their preparation, phase forming behaviour of mixed water, amphiphile and oil systems, viscosity and conductance behaviour in relation to internal consistency and structure. Important applications of microemulsions in enhanced petroleum recovery, biotechnology, pharmaceuticals, nanoparticle preparation, corrosion inhibition, etc. will also be discussed.

Keywords : *Microemulsion, theory, preparation, phase behaviour, structure, properties, viscosity, conductance , application.*

INTRODUCTION

It is established that microemulsions are amphiphile aided thermodynamically stable oil in water (o/w) or water in oil (w/o) dispersions [1]. They have stability for long

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duration. Normally, an oil-water interface has high interfacial energy (or tension) so that the free energy of formation of the interface is highly positive. The addition of amphiphilic compounds can bring the interfacial tension to a very low value, leading to spontaneous formation of one dispersion into the other, i.e., forming a microemulsion. The difference between emulsions (some times called macroemulsions) and microemulsions is in terms of stability. The former has comparatively higher interfacial tension and is kinetically stable (requiring occasional stirring or agitation), whereas the latter is thermodynamically stable. Thus, emulsions are weakly or moderately stable systems and with time separate into water and oil. The droplet sizes of the dispersions in microemulsions range between 10–100 nm; for emulsions the size may be greater than 10^5 nm. Systems with sizes ranging between 10^2 to 10^5 nm are termed as miniemulsions. They also are not thermodynamically stable.

It is well known that in the presence of water, surfactants can form reverse micelles in non polar organic media. A completely dry organic medium does not allow reverse micelle formation. A w/o microemulsion droplet is also a reverse micelle. In the reverse micelle, the amount of water present is low and is limited to the maximum capacity of hydration of the hydrophilic head group of the surfactants; hence, the pool water is rigid. In a w/o microemulsion, when the amount of water exceeds the hydration requirement of the surfactant headgroups, both bound and free water prevail in the pool. The rigidity and the bend of the interfacially bound water layer affect the structure and physicochemical behaviour of the microemulsion. A term w defined as $[\text{water}]/[\text{surfactant}]$ has been taken as a criterion as to whether a reverse micelle or a microemulsion has been formed. It has been suggested that when $w < 10$ it is a reverse micellar system and when $w > 10$ it is a microemulsion [2]. However, some evidence exists that the cut-off point may be $w = 15$ [3]

Though historically microemulsions have been studied for a long time, their importance was not acknowledged until the work of Schulman in 1943 with his definition of the system [1]. Physicochemically speaking, a microemulsion is an amphiphile stabilized low viscous, isotropic, and thermodynamically stable dispersion of either w/o or o/w. The importance of microemulsions lies in the varied formulation possibilities and numerous applications. The characteristics of microemulsions have been ascertained by different physical methods. It has been found that microemulsions generally have low viscosity and are conveniently formed in the presence of short chain alcohols or amines (called cosurfactants), which help to reduce the interfacial tension to a very low value. But surfactants like Aerosol OT (AOT) can conveniently form microemulsions without employing a cosurfactant.

THEORY

Because of very high interfacial free energy at the oil/water interface, the two components do not mix. However, the presence of surfactants and cosurfactant can bring down this interfacial energy (or tension) to a low value, resulting in the spontaneous dispersion of one liquid into the other. Energetically, the following relation holds

$$\Delta G = \Delta H - T\Delta S + \gamma\Delta A \quad (1)$$

where, ΔG , ΔH and ΔS are free energy, enthalpy and entropy change associated with the formation of ΔA extent of interface having interfacial tension γ at a temperature T . To make the dispersion process spontaneous (i.e., with a negative ΔG), the magnitude of the $T\Delta S$ term should be greater than the sum total of the contributions of ΔH (a small positive quantity) and $\gamma\Delta A$. Reduction of the interfacial tension γ by concerted actions of the surfactant and the co-surfactant allow very easy dispersion of one liquid (oil or water) into the other (water or oil). Hence, increasing the entropy term $T\Delta S$ makes its value either very close to or greater than $(\Delta H + \gamma\Delta A)$ so that very little agitation or practically no agitation results in the formation of a microemulsion. The required agitation may be provided by the thermal energy of the system. In the above balance, a required small positive free energy change can be supplied by the thermal energy of the system making it thermodynamically stable.

For large droplets, $\gamma\Delta A$ is not a small value and ΔG is not negative. This condition leads to emulsion formation with agitation. Slowly over time, the $T\Delta S$ quantity decreases by the Ostwald ripening process ultimately leading to phase separation. For microemulsions, the interfacial tension γ is required to be very low (0.02 mN m^{-1} or less) which is the main driving force [4] to derive a large surface area by way of numerous droplets associated with a large change in entropy. A pure surfactant does not generally provide low interfacial tension (IFT). Generally, the γ value becomes constant at the critical micelle concentration where the surfactant forms a monolayer at the oil/water interface. A mixed system (two surfactants or a mixture of surfactant and co-surfactant) can reduce the IFT to a very low value. The surface excess can be calculated by using Gibbs adsorption equation. For two components, the equation can be written as

$$\partial\gamma = -\sum\Gamma_i d\mu_i = -\sum\Gamma_i RT d\ln C_i \quad (2)$$

$$\therefore \gamma - \gamma_0 = -RT \left[\int_0^{C_1} \Gamma_1 d\ln C_1 - \int_0^{C_2} \Gamma_2 d\ln C_2 \right] \quad (3)$$

where, Γ_1 and Γ_2 are the surface excesses of the components, 1 and 2 respectively.

In other words, the co-surfactant (if it does not undergo any interaction with the surfactant) also helps to decrease the interfacial tension. The effect of a surfactant at the oil/water interface and the nature of the interface have been discussed in literature [5,6]. A mixed monolayer of the mixed surfactant at oil/water interface can exert a two dimensional surface pressure. The crowding of the mixed amphiphiles at the interface produces stress in the system and releases it. The interface bends with the expansion of the film on one side, to maintain a balance with the other side until the surface pressure on both sides of the interface becomes constant. For o/w microemulsions, the bending occurs on the water side and for w/o microemulsion the bending is on the oil side. A schematic diagram of the film bending is shown below (Fig. 1).

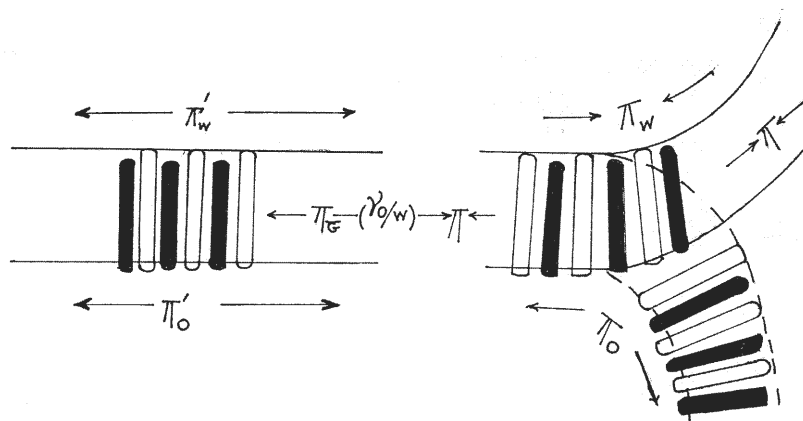


Fig. 1. A schematic representation of film bending.

Preparation of Microemulsion and Phase Behaviour

Microemulsions are spontaneously formed dispersions of either water-in-oil or oil-in-water. Generally, water (1), surfactants and cosurfactants (2) are placed together in a container and the mixture is then titrated with an oil (3) until turbidity is visually observed. Alternatively, a mixture of water and oil can be titrated with a surfactant until turbidity disappears. Also, a mixture of surfactants and oil can be titrated with water. The weight percent compositions at the end points of all these 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 representing microemulsions and other types of entities as shown in Fig. 2. When a cosurfactant is used as more often than not, for a particular pseudo-ternary phase diagram, the surfactant and the cosurfactant are taken in a definite ratio

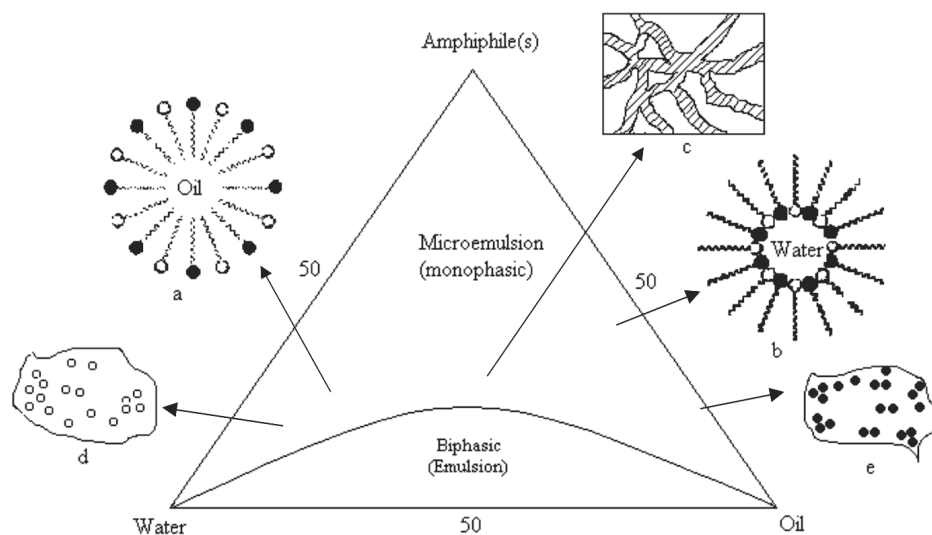


Fig. 2. A comprehensive ternary phase diagram depicting various structures a) o/w microemulsion; b) w/o microemulsion; c) bicontinuous microemulsion; d) and e) various dispersions.

considering the mixture as a single component.

It should be noted that the phase diagrams might be more complicated than shown in the figure. Viscous solution, lamellar liquid crystals, thin or thick gels, single phase, two phase and three phase regions are observed depending upon the surfactant, the co-surfactant, the oil, and their concentrations as well as the temperature. The structures of microemulsions can be very complex and different [7-9]. Four different types of situation may arise by mixing water, oil and amphiphiles as shown by Winsor [10]. In the first, the spherical oil droplets are dispersed in water continuum and such a phase is in equilibrium with oil (Winsor I or W I). Similarly, spherical water droplets dispersed in oil and in equilibrium with water is the second possibility (Winsor II or W II). In these cases the concentrations of dispersed oil and water are low. In W II system, the requirement of surfactant is low. As it increases, it distorts the droplets. At a ratio of 1:1(v/v) oil/water, the distorted droplets get attached to one another leading to a state of continuous water and oil phases and form a bicontinuous structure that remains in equilibrium with both the oil and water phases. This is referred to as (the Winsor III or W III) system. It has been suggested that the bicontinuous microemulsion structures have the physical appearance of a 'fractal' though is not yet conclusively proven [7, 11, 12]. Besides these three types, a final type of totally homogeneous single phase may arise. Such a system is known

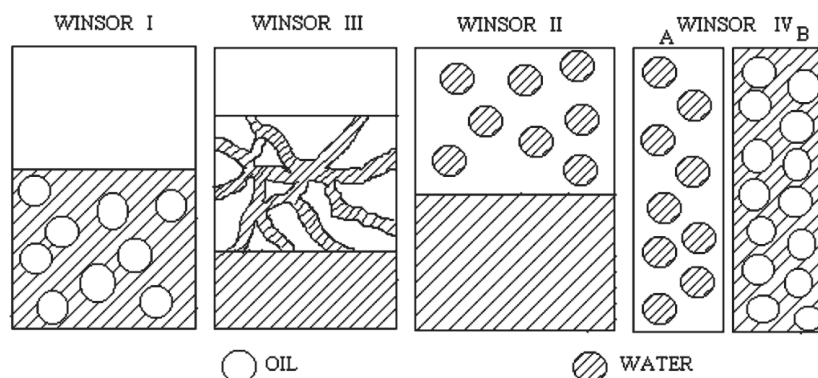


Fig. 3. Different phase forming situation for water-surfactant-oil mixtures.

as Winsor IV or W IV. A schematic representation of all these four types is shown in Fig. 3. There are also reports on the formation of four phases (two microemulsion phases, water and oil) arising out of certain water/amphiphile/oil combinations (ref. 13-15 in ref.7). Such studies are very limited.

The mixed water-oil-amphiphile systems have complex phase variations and it can be difficult to identify these various forms. The nature of the surfactant and the cosurfactant influence the phase diagram. In Fig. 4, a collaged comparison of four different pseudo phase diagrams with water, chloroform (as oil) and various different surfactants are presented. As seen, that the diagrams differ from one another in respect of type and size.

These surfactants have different characteristics e.g., cetyltrimethylammonium bromide (CTAB) is a cationic surfactant, whereas Triton X-100 (TX100) is a nonionic surfactant. Besides the type of surfactant, the diagrams also vary in their hydrophilic lipophilic balance (HLB) number. A lower HLB number indicates a lower hydrophilicity of the molecule. Systems with a low HLB [3-6] generally forms w/o microemulsions. Systems with high HLB [8-18] form o/w microemulsions. This criterion is also true for emulsion formation.

In addition to HLB, phase inversion temperature (PIT) and cohesive energy ratio (CER) have been used to predict the possibility of microemulsion formation. The surfactant hydrophobic group should match the oil structure: the better the match, the higher the possibility of a microemulsion formation. The phase inversion temperature (PIT) can be used to determine the type of oil, nature of microemulsion, etc. The HLB number of surfactant is a function of temperature, and at a particular temperature o/w microemulsion may change over to w/o microemulsion. This

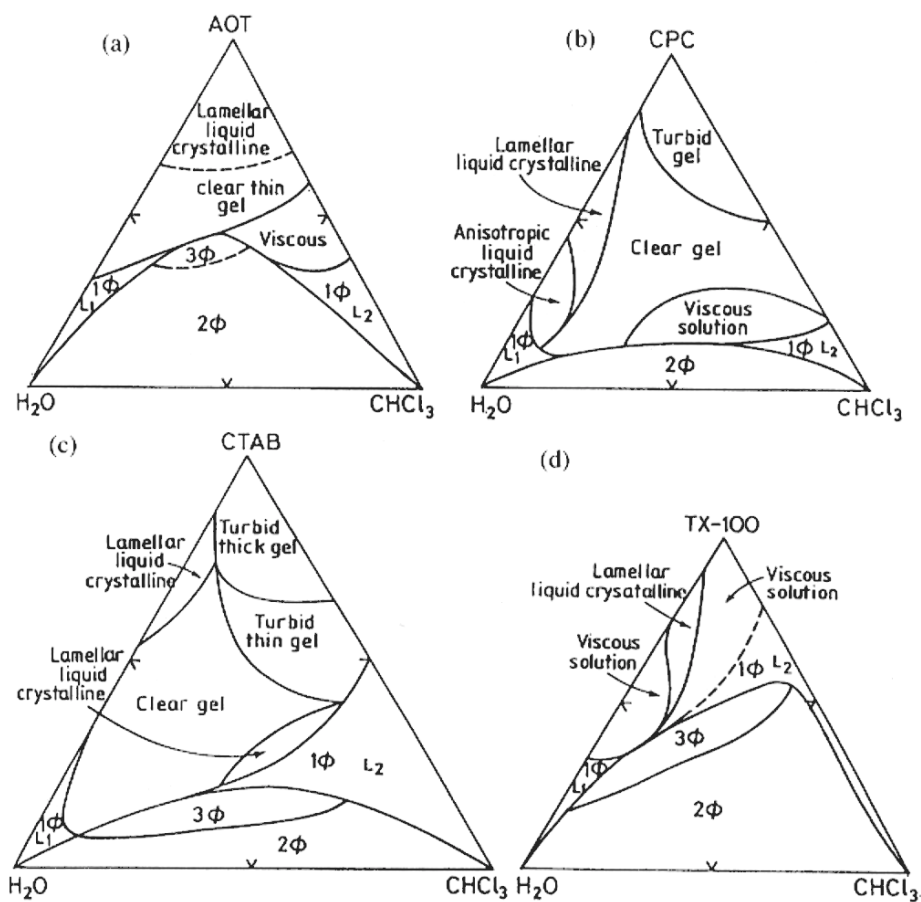


Fig. 4. Ternary phase diagram for a) H₂O-AOT-CHCl₃; b) H₂O-CPC-CHCl₃; c) H₂O-CTAB-CHCl₃ and d) H₂O-TX-100-CHCl₃ systems at 303 K. 1φ, single phase; 2φ two phase; and 3φ three phase. (Fig. 3 A, Ref 7).

transition temperature, called the PIT [4,13] provides an idea about the chemical type of emulsifier needed to match a given oil [4]. The HLB and PIT values correlate with each other and an increase in HLB means an increase in PIT though the relation is not linear [14].

The cohesive energy ratio (CER) is another criterion, which may determine the type of microemulsion formed. If the interaction parameters between the lipophilic group and oil, and the hydrophilic group and water are represented by C_{LO} and C_{HW} respectively [17], then when C_{LO}/C_{HW} > 1, a w/o microemulsion is formed. For an

o/w microemulsion, the ratio is less than 1. If the cohesive energy 'd' has the contributions from polar group (δ_p), hydrogen bonding (δ_h) and dispersion energy (δ_d) it satisfies the relation,

$$\delta^2 = \delta_d^2 + 0.25\delta_p^2 + 0.25\delta_h^2 \quad (4)$$

Winsor [16] suggested a 'R' criterion, which is the above C_{L0}/C_{HW} ratio. The CER concept has been used in the formulation of polymerization microemulsion [17]. Recently [18], it has been shown that by using HLB and mass balance equations, the starting and the end points of the three phase regions can be calculated. The shorter the carbon chain length of the oil and longer the carbon chain length of the alcohols, the higher the solubilization capacity of the microemulsion. It has further been shown [19] that liquid or supercritical CO_2 swell potassium carboxylate perfluoropolyether cylindrical micelles in water to produce novel CO_2 -in-water microemulsion. This microemulsion has been found to solubilize both lipophilic and fluorophilic substances simultaneously. It has also been reported that water-in- CO_2 microemulsion and emulsion can both be formed [20]. Cationic double chain molecules like didecyldimethylammonium bromide (DeDAB) are an important class of surfactants. The phase behaviour of water/DeDAB/dodecane system [21] has been depicted (Fig. 5).

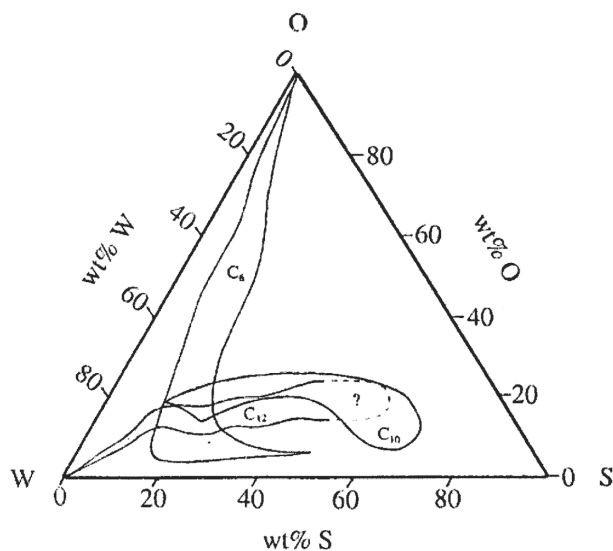


Fig. 5. The extension of microemulsion regions in the DeDAB/hydrocarbon/water system at 25°C. (Fig. 1, Ref 20)

PROPERTIES OF MICROEMULSIONS

Viscosity

Microemulsions are o/w or w/o dispersions, stabilized with amphiphiles. Although low, their viscosities have characteristic features. Essentially their viscosity is a function of composition. The presence of salt can affect the viscosity. For example, the viscosity of a water/Brij 35-propanol/heptane microemulsion system increased with the addition of NaCl [22]. For NaCl-water/ SDS-propanol/ cyclohexane system, an increasing amount of water increased the viscosity of the system. With the addition of water, the diameter of the dispersed water droplets increased, aggregation induced conduits were formed and there was an adequate amount of amphiphiles to result in the formation of a bicontinuous structure [21]. The observed maxima in the viscosity versus water content profiles of *microemulsion* forming systems indicated a structural transition from w/o to o/w types [23, 24]. The hydrophobicity of the oil and the salinity of the system may show antagonistic behaviour. Thus, in the water/ Brij 35-propanol/heptane system, replacement of heptane by nonane decreases the viscosity, whereas in the presence of NaCl the viscosity increases [22].

This replacement has also a similar effect on cloud point. The cloud point of nonane-based microemulsion was less affected than a heptane-based microemulsion. Addition of oligomers like PEG 400 increased the viscosity of the cetyltrimethylammonium bromide (CTAB) contained microemulsion system and Frenkel-Eyring equation has been used to compute the activation energy for the viscous flow measured at different temperatures [25].

It has been shown that in the microemulsion systems, the empirical Walden rule (i.e., the constancy of the product ηL where η and L are the viscosity coefficient and the equivalent conductance respectively) does not hold [26]. Rakshit *et al.* have also observed such behaviour [22,23]. The cationic surfactant (didodecyldimethylammonium bromide, DDAB) has been used to form a microemulsion with different alkanes in which both viscosity and conductance increased. Thus, the Walden product rule was found not to be obeyed [27].

Moulik *et al.* [28,29] studied both viscosity and conductance of a biological microemulsion consisting of water-AOT-hexylamine-saffola and have shown the invalidity of the Walden product relation. Of course, the applicability of the Walden rule can be questioned by the Curie-Prigogine principle [30], which states that forces and fluxes of different elements of symmetry cannot be coupled. Thus, the inverse proportional relationship between conductance and viscosity, as suggested by Walden Rule, is not thermodynamically valid. The Walden product constancy seems to be fortuitous, at least for microemulsion systems.

In microemulsion systems, unlike any other fluid system, increasing temperature may increase viscosity by way of clusters of droplets, which lead to network formation. The viscosity of microemulsion may also show two types of percolation processes. A water continuous microemulsion changes into a bicontinuous system with increasing oil content (with $\sim 20\%$ (w/w) oil percolation threshold) and afterwards at $\sim 80\%$ (w/w) of oil, the bicontinuous structure may change into an oil continuous structure. At both these points, the viscosity can suddenly change because of the structural transformation from o/w through bicontinuous to w/o microemulsions. A viscosity percolation process can be seen here. The viscosity of microemulsion obeys scaling laws. Thus,

$$\eta = A(\phi - \phi_p)^m \quad (5)$$

$$\eta = A'(\phi_p - \phi)^{-s} \quad (6)$$

where, ϕ is the volume fraction of the dispersed phase and ϕ_p is its percolation threshold; m and s are scaling exponents; A and A' are constants. The equations (5) and (6) are obeyed if $\phi > \phi_p + \delta'$ and $\phi < \phi_p + \delta''$ respectively where δ' and δ'' are the respective crossover regimes. A plot of $\log \eta$ vs $\log(\phi - \phi_p)$ helps determine the cross over regime [31]. It has generally been observed that the hard sphere model can fairly describe the viscosity of microemulsions [32-34]. In this model, the flow is expected to be controlled by viscous interaction and Brownian motion. Einstein's relation, $\eta/\eta_0 = 1 + 2.5\phi$ is obeyed by a dilute microemulsion. At higher concentration, due to many body interactions, Einstein's relation is not obeyed. There is no accurate theory yet [34]. However, several semi-empirical relations have been suggested. These are [35,36]

$$\text{a) Krieger and Dougherty : } \frac{\eta}{\eta_0} = \left(1 - \frac{\phi_{HS}}{\phi_m}\right)^{-[\eta]\phi_m} \quad (7)$$

$$\text{b) Quemada : } \frac{\eta}{\eta_0} = \left(1 - \frac{\phi_{HS}}{\phi_m}\right)^{-2} \quad (8)$$

In the above equations ϕ_m is an empirical constant and $[\eta]$ is the intrinsic viscosity. ϕ_{HS} is the partial molal volume of hard sphere (HS). Some researchers have calculated that the value of $\phi_m \gg 0.63$, which is very close to the volume fraction of a close packing of hard sphere, i.e., 0.64. However, other recent studies have indicated that this value should be around 0.58 [37, 38].

The viscosity study has been used to estimate water pool diameter and

aggregation for the system made up of surfactants, isooctane and water [39]. The surfactants used were AOT (sodium bis(2-ethylhexyl) sulfosuccinate) and SDEHP (sodium di (2-ethylhexyl) phosphate) mixtures. The volume of the reverse micelle, V_{rm} and that of the water pool, V_{wp} were considered to be

$$V_{rm} = \frac{\pi \left[\left(\frac{6V_{wp}}{\pi} \right)^{1/3} + 2L_s \right]^3}{6} \quad (9)$$

$$\text{and } V_{wp} = \frac{V_w \cdot C_w \cdot n_{ag}}{C_s}$$

where, V_w , C_w and C_s are the volumes of water molecule, water concentration and surfactant concentration respectively, and n_{ag} is aggregation number (a constant quantity). The droplets were assumed to be spherical and the diameter of reverse micelle d_{rm} and diameter of water pool d_{wp} were as follows

$$d_{rm}^3 = \frac{6V_{rm}}{\pi}; \quad d_{wp}^3 = \frac{6V_{wp}}{\pi}; \quad d_{rm} = d_{wp} + 2L_s$$

where L_s is the length of the surfactant molecule or chain.

Among the viscosity equations used to describe the microemulsion systems, the relations of Vand, Mooney, Eiler, Thomas and Moulik may be mentioned. A unified relationship has been reported by Moulik to be fairly valid for microemulsions. An elaborate discussion on the above relations and their validity and limitations can be found in an earlier review article [7]. The measurement of intrinsic viscosity of microemulsion has been shown to be capable of deriving useful information on the droplet geometry and their solvation [40]. It may be mentioned that the w/o dispersions are mostly spheroidal in nature. The dispersions of formamide, ethylene glycol and dimethyl formamide in isooctane in the presence of AOT have been also found to be spheroidal in shape with negligible solvation. Such waterless microemulsions have been found to obey the above-mentioned equations [7].

Conductance

Microemulsions can show striking conductance behaviour. 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. For w/o systems, conductance may suddenly change (like viscosity) at a particular temperature for a given composition or at a particular water concentration for a given

temperature. This phenomenon is called percolation and the threshold temperature and threshold water concentration associated with the process are called percolation thresholds. In these situations, the systems change from insulators to conductors. The conductance change has been explained by inter droplet interaction leading to the transfer of the charge carriers from one drop to another. The presence of additives can have striking effect on percolation, and various different additives including polymers have demonstrated different characteristics [41-43]. Dynamic light scattering studies of a polymer-reverse micelle indicated that the spherical droplet structure is preserved in presence of the polymer [43]. The effect of various alkylamines on the percolation phenomenon of water/AOT/isooctane microemulsion has also been studied and the ability of the amines to associate with AOT film has been suggested as the reason for the percolation [44]. Dogra *et al.* [42] have discussed the effect of the presence of various alcohol cosurfactants on conductance and percolation in a mixed-surfactant microemulsion system. The conductance percolation also obeys scaling equations, 10 and 12.

$$s = P (f - f_t)^m \quad (10)$$

$$s = P' (q - q_t)^s \quad (11)$$

for volume percolation and temperature percolation respectively, where s is the conductance, f_t is the threshold volume fraction of the dispersed phase, q is the temperature of the system, q_t is the threshold temperature of the process, P and P' are appropriate constants. m and s have the same significance as discussed in connection with equations, 5 and 6.

These equations have been tested, and their coefficients and exponents have been evaluated. Equation 11 has been observed to significantly deviate from the prediction. Equations other than the scaling forms have been also proposed by different authors where clustering of droplets in different forms has been considered. For detailed discussion on this and related issues, the review article of Moulik and Paul [7] may be consulted.

Structural Features

Freeze fracture electron microscopy (FFEM) has been used to study a ternary water-*n*-octane- $C_{12}E_5$ system varying in water to *n*-octane ratio [45]. Liquid ethane was used to freeze the temperature-controlled microemulsion. The surfactant concentration was so chosen that the composition of the sample was at the point of highest efficiency, i.e., where the three and one phase regions meet. The images observed clearly indicated that for this system even at the highest water or oil content, the elements of bicontinuous microstructure were present [45]. It has been shown that the bicontinuous structure was present from a very low oil content (volume fraction 0.1)

to a high oil content (volume fraction 0.9) with pivotal point at $j = 0.5$.

Estoe et al. [46] have made photo-responsive microemulsions by adding a photo-destructible surfactant, sodium 4-hexylphenylazosulfonate to AOT solubilized water in heptane phase. UV light affected the phase stability and droplet size because of the break down of sodium 4-hexylphenylazosulfonate.

By component-resolved NMR diffusion studies, the microstructure of microemulsions have been studied. It was observed that the microemulsion becomes bicontinuous upon decreasing water content until the appearance of a definite discontinuity occurring at a definite concentration (citations 167-175 in ref.7). Rigidity of the interfacial monolayer is an important criterion for microemulsion stability. Electrical deformation or temperature deformation is also important. Recently, Bisceglia et al. [47] have studied the temperature dependence of the elastic rigidity of the AOT-water-isooctane microemulsion. Both static and dynamic electric birefringence was measured at various temperatures. The rigidity of the nano droplets of the above microemulsion in the static condition appreciably differed from the dynamic state over the whole temperature range and the modulus of rigidity in the dynamic condition was lowered by an order of magnitude from the static one.

By the phase gradient spin echo NMR (PGSE-NMR) measurements self diffusion coefficient of a $C_{18:1} E_{10}$ /oil/water system were determined. The oil was a mixture of 1 : 1 miglyol 812 and retinyl palmitate (the retinoids play very important role in the field of dermatology [48]). The ternary phase diagram was constructed. In the o/w microemulsion, retinyl palmitate was located in the core of the medium chain triglyceride, and a swelling effect on the microemulsion droplet was observed. The hydrodynamic radius was found to increase with increasing oil content. The surfactant concentration in the system was very high, much higher than the cmc value. The o/w microemulsion was found to be significantly structured. The diffusion coefficient values decreased with increasing oil content suggesting micellar growth. The phase inversion temperature (PIT) was found to be $>57^{\circ}\text{C}$ depending on the oil content. Thus, the microemulsion has potential for topical vitamin delivery at room temperature.

Recently, Li et al. [49] reviewed the formation of microemulsion using cationic surfactants which was first reported by Bourrel et al. [50]. In this type of surfactant system, a cosurfactant (like small chain alcohols, etc.) is essential. In its absence, lamellar liquid crystals or precipitates are formed. Bourrel et al. [50,51] studied a mixture of tetradecyltrimethylammonium bromide and sodium octylsulfonate using *i*-pentanol as the co-surfactant to obtain a three phase W III system. Interestingly, they found that a mixture of cationic and anionic surfactants could form a bicontinuous microemulsion. Li et al. [52,53] have studied the effect of weight percents of the alcohol to surfactant as well as cationic to anionic surfactant ratio

on the phase behaviour and solubilization of microemulsions. The mixing of anionic and cationic surfactants favoured the formation at the high level of water and oil. Increasing surfactant concentration increased the solubilizing capacity. Silas et al. [54] have shown that the amphiphiles like didodecyldimethylammonium bromide can behave as a booster to increase the solubilization potential of nonionic surfactants using silicone oil. Similar boosting effects of sucrose distearate on nonionic surfactants for solubilization have been reported by Aramaki et al. [55].

Recently, Yagmur et al. [56] have shown that propylene glycol, ethylene glycol and ethanol can be effective solubilizers of both oil and water. Food grade surfactants like Tweens (polyoxyethylene sorbitan- laurate, -palmitate, - stearate, - olate) were compared with non food grade surfactants (such as ethoxylated nonionic surfactants). R(+)-limonene was used as a food grade solvent to improve solubilization properties compared to other hydrocarbons and triglyceride based oleic phases. The solubilization was explained in terms of spontaneous curvature and film flexibility and it was found that the Bansal, Shah, O'Connell (BSO) equation [57] is not always applicable. Food grade microemulsions, containing polyols with compatible structures of oil and surfactants can be prepared that can be conveniently diluted with both oil and water. It has been also shown that solubilization capacity of such microemulsions increase with increasing chain length of the alcohol, and is the highest with carbon number 4 [57].

Bumajdad et al. [58] studied the structure and film properties of a zwitterionic surfactant (1,2-n-octanoyl-sn-glycero-3-phosphocholine, PC₈)-alcohol system. It was observed that the maximum water solubilization in w/o decreased with increase in carbon chain length in alcohol. This was due to the fact that the solubility of alcohol increased with increasing chain length of n-alkane, whereas its solubility decreased in water. For PC₈-C₅OH system, when the cosurfactant solubility was lowest in oil, there was the highest alcohol adsorption and hence highest water uptake. This was proved by small angle neutron scattering (SANS) studies [58].

Yagmur et al. [59] have studied a five component microemulsion system consisting of polyoxyethylene(10)oleyl alcohol, i.e., Brij 97, R(+)-limonene, propylene glycol, ethanol and water. It was shown that by changing the water and propylene glycol amount, one could obtain a w/o microemulsion to change from a bicontinuous to an o/w type. Differential scanning calorimetric studies at subzero temperatures were done to differentiate between various types of water, i.e., bound water, non freezable water, etc. It was found that no free water was present; in other words, the water was interacting with the surfactant and other ingredients present at the interface. This seems to be a reasonably good method in differentiating between various forms of water present in the system. From both batch and titration calorimetric measurements, the states of pool water in w/o microemulsion under normal environmental condition

has been investigated. Both two and three states of water in the pool have been reported [60,61]. From isothermal microcalorimetric (ITC) measurements, Moulik et al. [62] have shown that the water which dissolves in the AOT/oil system to form microemulsion may exist in three different states. The first transition occurs virtually at $w=1.0$. Maitra [63] has also discussed the presence of different states of water in microemulsion.

APPLICATIONS

Microemulsions have found numerous applications in different fields, and in this respect they are among the most useful microheterogeneous systems. A concise account of a number of important applications and uses of microemulsions is presented.

Liquid Membrane

Microemulsions can function as a liquid membrane. Both the W I (o/w) and W II (w/o) types have been considered as dispersed liquid membranes which facilitate the transfer of solutes by convenient uptake and release. Tondre et al. [64,65] have studied various separation processes with the help of microemulsions. Acetic acid has been separated from water by using a microemulsion [66]. However, one needs to consider cell design, choice of solutes, amphiphiles, additives, etc. [66].

Microemulsions have also been found to be efficient in the extraction of heavy metals (e.g., Hg) involving oleic acid [67] from contaminated water. They have been used in chromatography, e.g., microemulsion electrokinetic chromatography. By this method solute hydrophobicity can be obtained. Al^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Mn^{2+} ions have been estimated by using microemulsions which are useful as spectral shift reagents, intensity amplification agent, as media, etc [68]. Selective transport of aminoacids, e.g., tryptophane and *p*-iodophenylalanine through AOT containing microemulsion (WII) liquid membrane, has been investigated. The microemulsion used was AOT/isooctane/aqueous phosphate buffer (0.1 M). The two amino acids have different hydrophobicities but their partition coefficients between water and microemulsion have no direct relation to their transport properties. The selectivity seems to depend upon AOT concentration in the microemulsion [69].

Biotechnology

Microemulsions have been used for selective protein extraction from fermenter liquids. The proteins and enzymes have been found to retain their normal activities [70-72]. The pH, ionic strength, salt type, temperature, solvent concentration, etc. affect the partition of protein. This has been discussed thoroughly in a few recent articles [73,74]. Moreover, it has been shown that the chiral epoxide can be produced by using mycobacterium in w/o microemulsion. This is important because many biotransformation processes are difficult to carry out because of the poor water

solubility of the substrate or product. If microemulsions are used, such problems can potentially be overcome [75]. *Candida rugosa* lipase has been immobilized on gelatin containing AOT microemulsion based organogels (MBGs) as well as on silica gel. Lipase containing MBGs is a better immobilization system than silica gel [76]. This was shown by the synthesis of esters at various concentrations. Tyrosinases are copper oxidases which catalyses the hydroxylation of monophenols and oxidises the diphenols to quinones. The activity of tyrosinases was studied both in aqueous phosphate buffer solution as well as in AOT/water/isooctane w/o microemulsion for oxidation of 4-butylcatalchol to 4-butylquinone. In aqueous solutions AOT activates the enzyme at low concentrations but reduces the activity at higher concentrations. The same is true in w/o microemulsion [77]. The enzyme, candida lipolytical lipase (CL) has been used in the esterification of octanoic acid with octanol and the kinetics of the esterification process in the w/o microemulsion (water/AOT/isooctane) has been studied. The reaction seems to follow Ping-Pong Bi Bi mechanism and becomes inhibited by excess 1-octanol. For two reactants- two products enzyme kinetic processes, if a product is released before all the substrates are added, and the reactants do not interact with one another on the surface of the enzyme, then such reactions are called Ping-Pong-Bi-Bi reactions. This lipase could be immobilized in gelatin containing AOT microemulsion (organogels, MBGs) where lipase catalytic activity was preserved. It has recently been shown that the enzymatic reactions are affected by the concentration of the surfactant. The initial reaction rates of oxidation of *t*-butyl catalchol and 4-methyl catalchol in presence of organic solvent resistance tyrosinase (OSRT) decrease when the AOT concentration in isooctane in water/AOT/isooctane microemulsion system is increased. However, below 2 mM concentration, AOT does not activate OSRT in the above microemulsion [78]. These are novel solid phase enzyme catalysts which can be used in apolar organic solvents [79]. Enzymatic activity of horseradish peroxidase in a mixed cationic surfactant (SDS+DTAB) reverse (w/o) microemulsion was studied recently. Enzymatic superactivities were observed for system where DTAB was almost 15% of the surfactant mixture. In pure DTAB microemulsion system, the enzymatic superactivity is not observed when DTAB concentration is over 3% [80]. It has been reported that the enzyme organophosphorous hydrolase degrades organophosphorous pesticides in water/Tween 85+isopropanol/hexane microemulsion system. Kinetic and stability studies showed the partitioning of the enzyme between the micelle surfactant layer and aqueous core [81].

Enhanced Petroleum Recovery

Microemulsions have been suggested to be used in the enhanced tertiary oil recovery. Approximately 20% of difficult-to-recover underground oil can be recovered by this method. Because of high interfacial tension (IFT) between crude oil and brine, the

oil remains trapped in the fine pores of the geological oil reservoirs. By decreasing IFT to a very low value ($\sim 10^{-3}$ mN m⁻¹), a large amount of the crude oil can be recovered [82]. This is known as the Surfactant-Polymer flooding process.

Fuel, Lubricant and Corrosion Inhibitors

Microemulsions can be used as fuels with less formation of soot. This also creates less heat and requires a lower combustion energy. These benefits are significant as environmental regulations require the emission rates of nitrogen oxides (NOX) and carbon monoxide to decrease. Microemulsions seem to increase the octane number of gasoline and cetane number of diesel oil [83]. A detergentless microemulsion system containing 1-butanol, diesel oil and water has also been suggested to be a good addition [84]. The microemulsions are used as effective lubricants, cutting oils and corrosion inhibitors. The systems have thermodynamic stability, and the surfactants help in corrosion inhibition and higher water content (i.e., higher heat capacity which provides advantage in their uses as cutting oils). Corrosive agents get solubilized in microemulsion, surfactants get adsorbed on metal surface, and hence the corrosion is reduced [85].

Coatings and Textile Finishing

Microemulsions are also used in industrial coatings and textile finishing. They are used in coatings because they produce microdispersions (a) by using microemulsified monomers, (b) by making non water soluble polymers into water- soluble polymers, and (c) by polymerization in w/o system and getting specific effect. Dyeing of nylon 6,6 with an azodye using a microemulsion system gives greater homogeneity in dying than conventional systems [86]. Siloxane containing microemulsions produce finely dispersed finishes. Microemulsions are better than emulsions for these purposes because of a) higher stability, b) good product distribution, c) high internal softness, d) good washing performance, and e) increased abrasion resistance and good surface smoothness.

Detergency

Microemulsions are good for detergency. It does contain both polar and nonpolar liquids and hence can dissolve both polar (e.g., salt, pigment, protein) and nonpolar (e.g., grease, oil, etc) substances. Microemulsion, particularly the middle phase microemulsion, is good for detergency for effective soil removal from textiles, wool and also for skin degreasing. Details can be obtained from the literature [87]. Microemulsions are efficient colour remover from textile waste-water. The effect of cosurfactants in the microemulsion on the efficiency of colour removal process was studied. It was observed that in the presence of isoamyl alcohol as cosurfactant, the ionic surfactants were somewhat more efficient in colour removal than the n-butyl alcohol or n-octyl alcohol. Various different colours were used, e.g., procion yellow

H-E4R (CI Reactive Yellow 84); Procion Blue H-ERD (CI reactive blue 160), etc. [88].

A detergent formulation of dioctylsulfosuccinate, alkyldiphenyloxide disulfonate and sorbitan monooleate was used in the detergency of two highly hydrophobic oil, hexadecane and motor oil. Maximum detergency was found in WIII as well as in supersolubilization region WI. It has been seen that the oil removal in the rinse step is very high, almost as high as in the wash step for both WI and WIII regions. The very low interfacial tension (IFT) in microemulsion inhibits complete oil removal. However IFT increases in the rinse step and due to “roll up” mechanism the oil removal becomes high [89]. Verma et al. have shown earlier that the measurement of interfacial tension alone is not a good criterion for a prediction on possible detergency [90]. A good amount of information can be obtained from a recent book [91].

Cosmetics

Cosmetics represent another field in which microemulsions are being used. It is believed that skin easily adsorbs cosmetics that are based on microemulsions. Because some amphiphiles are not suitable for use in personal health care products, this is most true in scenarios in which cost and safety are the most important criteria. Sodium alkyl sulfate, tetraethyleneglycolmonododecylether, lecithin, dodecyl-oligoglucoside, alkyldimethylamine oxide, propanol, hexadecane and isopropyl myristate are used in skin care microemulsion formulations [92]. Fragrance and flavored oils can be added as required. Microemulsion based hair care products and silicone oil based cosmetic microemulsions have been formulated. For cosmetic use of microemulsions, the study of the vapor pressure of the fragrance over time and temperature is important and various systems like water/Brij 30/phenylethyl alcohol, water/Brij 30/linalol, etc. have been studied [93].

Agrochemicals

The agrochemical industry is very important for the world economy. This is because the agricultural products provide the basis for the economic growth and hence the use of pesticide is integral to many economies. Microemulsion formulation of pesticides is, therefore, a major tool for pesticide delivery. This use also decreases the use of smelly solvents. It has been shown that o/w microemulsions of organic, water insoluble phenoxy herbicides dissolved in a hydrocarbon solvent show appreciably more effectiveness than the corresponding emulsions in the control of plant growth. Water-in-oil microemulsions are used to enrich the mineral deficient crops with respect to trace metals such as iron, because the oil portion of the microemulsion can hold the element in contact with the leaves for sufficient time to allow the metallic element to be adsorbed.

Most agrochemicals are water insoluble. However, in microemulsion formulation the droplets are very small with higher penetrability, larger contact area and a more even distribution. It is said that thermodynamic stability and a large concentration of surfactant used in these formulations are advantageous. It has been suggested that herbicide penetration depends upon the known relationship between the herbicides and surfactant structure [85].

Pharmaceuticals

Drug manufacture is another very important field where microemulsions are being used. Microemulsions are favoured over other microheterogeneous systems because of stability, large solubilization capacity and ease of spontaneous formation. The dispersed phase can act as potential drug reservoir and the drug then is partitioned between disperse phase and dispersion medium and can get transported through the membrane, e.g., skin, mucous membrane, etc. The other important point about using microemulsions is the fact that the same medium could be used both for hydrophilic and lipophilic drugs. Moreover, injection formulations have been made as the microemulsions have low viscosity and are easily miscible with blood. In microemulsions, proteins are not denatured and they have low immunoreactions. Total dose of a drug can be decreased and the side effects are generally low. However, toxicity, bioincompatibility and high concentrations of amphiphile, temperature stability, effect of salinity, etc. need be considered before its use [94]. Microemulsions have been used as drug delivery systems in controlled drug release for topical, ocular, transdermal, and parenteral administration [85]. The advantages associated in these processes are enhanced adsorption of drugs, modulation of kinetics of drug release and low toxicity. Mathematical models for the drug release from microemulsions have been suggested [95]. Use of microemulsions in cutaneous drug delivery have also been discussed [95].

Nanoparticle Synthesis

Microemulsions are being used in the synthesis of nanoparticles, and in altering the morphologies of the particles. For example, it has been shown recently that the molecular sieve aluminium phosphite number 5 ($\text{AlPO}_4\text{-5}$) could be obtained by microwave heating of water in toluene microemulsion which had the reactants. The surfactant and cosurfactant used were CTAB and *n*-butanol. On changing the microemulsion composition, it was found that the crystal morphology got modified. Many interesting and somewhat novel crystal shapes were obtained [96,97]. Fibers with novel morphology of AlPO_4 [98] were also synthesized. Interestingly CuS nanoparticles have been synthesized in water-in- CO_2 microemulsions [99]. Similarly, spherical magnetic alginate microparticles (25-60 nm in diameter) were prepared from a microemulsion where 1-pentanol was taken as the organic phase. These

microparticles were useful as magnetic affinity adsorbents for specific purification of the enzyme α -amylase [100]. Atik and Thomas [101] have synthesized a divinylbenzene-styrene copolymer in a microemulsion stabilized by CTAB and hexanol. Kaler and his colleagues [102] have done a series of studies on microemulsion polymerization of styrene, *n*-hexyl methacrylate, *n*-butyl methacrylate and so on. Significantly small supermagnetic Ni particles were prepared by reducing NiCl_2 with hydrazine in CTAB/*n*-hexanol derived microemulsion [103]. Maitra et al. [104] studied the formation of unusual nanostructured TiO_2 by hydrolysis of TiCl_4 in w/o microemulsion. Ultrafine particles of Rh were prepared in polymer matrix using microemulsion [105]. Photochemically important nanoparticles of tungstic acid were prepared in TX 100-alkanol stabilized water-in-heptane microemulsion [106]. Very recently, fairly uniform and low sized semi-conducting nanoparticles of PbS have been prepared in water/AOT/heptane w/o microemulsion in our laboratory [107]. It is generally believed that the size of the water pool in the microemulsion is responsible for the size of the nanoparticles. However, recently Kimizima *et al.* [108] have shown that the particle size and growth rate of AgCl nanoparticle in a reverse micelle system of polyoxyethylene(6)nonylphenylether/ water/cyclohexane are dependent on the solubility of the solid and the diffusivity of reverse micelle and not upon the size of the water pool. It is also interesting to note that by reducing $\text{Cu}(\text{NO}_3)_2$ in Triton X100 w/o microemulsion by γ -irradiation, a monodisperse Cu_2O octahedron nanocrystals of less than 100 nm size can be prepared where the edge length of the octahedron shaped nanocrystals varies as a function of the irradiation dose rate [109]. Fractal porous silica has been synthesized by the hydrolysis of tetraethoxy silane($\text{Si}(\text{OC}_2\text{H}_5)_4$) in a bicontinuous microemulsion containing polyoxyethylenedodecyl ether, isooctane and water [110]. Recently, Holmberg [111] has discussed nanomaterial synthesis by using microemulsion in details. A review of Pileni [112] in this field may be cited for details. An interesting new method to prepare nanostructured materials should also be mentioned here. In this method gold microemulsion was flame sprayed on silicon wafers and gold nanoclusters of well-defined sizes were obtained. Air/acetylene flame was used [113].

Microemulsion method has also been applied to synthesize nanostructured Pt-M/C catalysts. Such catalysts have much higher electrochemically active surface area than those made by high temperature route. They show improved catalytic activity towards oxygen reduction compared to pure Pt. Pt-Co/C catalyst prepared by microemulsion method shows the best performance with maximum catalytic activity. Moderate heating (at $\sim 200^\circ\text{C}$) makes the catalyst better active because of the cleaning of the surface [114].

Analytical Chemistry and Remediation processes

The uses of microemulsion for soil remediation purposes have been reasonably well

documented [115]. Polycyclic aromatic hydrocarbons (PAH) and polychlorinated biphenyls (PCB) have been extracted from soils with the help of rapeseed methyl ester containing microemulsion. Both the middle phase bicontinuous and o/w microemulsions have been used and it was found to be almost 100% efficient in bicontinuous microemulsion, and o/w microemulsion also has reasonably good efficiency. This is sufficient because ground water contamination is becoming a problem all over the world. By using chlorinated hydrocarbons and various different types of hydrophilic surfactants (e.g., sodium dialkylsulfosuccinate, ethylene oxide containing surfactants, alkyl benzene sulfonates, tweens, etc.) these contaminants can be removed as micromulsions [116]. Microemulsions (both o/w or w/o) have been used for detoxification of mustard compounds and pesticides and remove surface-active impurities by extraction in the microemulsion phase [117]. Polycyclic aromatic hydrocarbon at a low level of 309 ng ml⁻¹ can be detected by measurement of phosphorescence at room temperature using microemulsion medium [118].

Food Science

Another significant use of microemulsions is in the area of food chemistry and food preservation. Maillard reactions are nonenzymatic and very complex reactions between reducing sugars and free amino acids and proteins. This is very important in the food industry as it produces flavour, taste and color in cooked food. A thermal reaction between cysteine and furfural is a model Maillard reaction, and it seems that the generation of aromas is affected by the fluids used. Garti et al. [119] have studied such reaction in microemulsion media where the microemulsion was composed of sucrose ester, water, dodecane, and alcohol. Sucrose stearate and sucrose laurate were used as esters with medium chain alcohols. In aqueous system 2-furfurylthiol (FFT) is obtained as a product whereas in this w/o microemulsion they obtained 2-(2-furfuryl)-thiazolidine and *N*-(-mercaptovinyl)-2-(2-furfuryl)-thiazolidine besides FFT.

Microreactors for Chemical Reactions

Microemulsion are microheterogeneous systems where the dispersed medium may behave as a chemical reactor. Formation of nanoparticles, which has been mentioned earlier, is a good example of these systems acting as chemical reactors. Polymerization reaction as well as photochemical, electrochemical, electrocatalytic and organic syntheses have been carried out in microemulsion. Moreover, processes like photosensitized electron transfer, photodimerization and photoisomerization have been carried out in microemulsion medium. Photoisomerization of trans-stilbene has been investigated in H₂O/SDS/benzylalcohol microemulsion medium. The yield of the reaction in this medium was found to be much larger than in pure benzyl alcohol. With the increase in water concentration, the increase in the yield of the reaction product was high. However, the yield was inversely related with the benzyl alcohol concentration [120]. The transfer of electronic excitation energy from Rhodamine 6G

to thionine has been studied in an anionic microemulsion system where the concentrations of both Rhodamine 6G and thionine were high ($\sim 10^{-3}$ M). The energy transfer in this case was found to be both radiative and nonradiative. The nonradiative energy transfer was suggested to be due to Forster type long-range dipole-dipole interaction. This study is useful to explain the enhanced efficiency of the photogalvanic cell based on thionine-iron system in anionic microemulsion by the presence of auxiliary absorber [121]. The o/w microemulsion has been used as reaction medium for electrochemical analysis. The electrochemical synthesis of polyparaphenylenes and the dehalogenation of vicinal dihalogen compounds in microemulsion medium have been reported. Cyclic voltametric study has also been done in a bicontinuous microemulsion medium. Various types of chemical reactions have been studied in microemulsions and they have been found to end up with enhanced reaction rates [122]. Moreover, synthesis of macrocyclic lactones, nitration of aromatics, Diels-Alder reaction, H_2O_2 oxidation, reduction of carbonyl compounds, acylation and deacylation reactions have been carried out in microemulsion media [85]. Bunton and Romsted have recently reviewed the reactions in microemulsion medium [123]. The Diels-Alder reaction seems to be faster in non-aqueous microemulsion medium. Hager et al. [124] studied a substitution reaction in microemulsion medium by phase transfer catalysis. AOT/methylene chloride/water w/o microemulsion was used as a microreactor to control the regioselectivity in the photocycloaddition of 9-substituted anthracene. Potential advantage of enzyme reactions in w/o microemulsions may be mentioned. Catalysis of a variety of reactions by enzymes has been studied [122]. The aqueous environment in the micro water pool has been found to have important say on the process [125].

Oxidation of azodyes is important from environment point of view. Microemulsion media were used in studying reactions where immiscibility is a problem. Hager et al. [126] studied the oxidation of azodyes (methyl orange and amaranth) by hydrogen peroxide catalyzed by manganese porphyrins in nonionic surfactant containing o/w microemulsions. The mechanism of a reaction can also be studied. Nitration of aromatic compounds was recently studied in microemulsion medium and compared with the results with a two-phase system where there was no surfactant. It was almost selective para nitration in microemulsion and almost equal mixture of ortho and para nitro products were obtained in the biphasic system. The rate of reaction was also high in microemulsion and dilute nitric acid was sufficient for nitration process, which was not the fact in biphasic system [127]. It should also be mentioned here that recently a combination of microemulsion with pervaporation process has been used for dark singlet oxygenation of hydrophobic substances like α -pinene [128].

Microporous solids with very high surface area of ~ 70 m²/g has been prepared

by polymerizing the organic phase of a bicontinuous microemulsion stabilized with didodecyldimethylammonium bromide. SAXS has been used to characterize the polymer wherein it was observed that the original microemulsion characteristics were retained in the polymerization process. The same characteristics got destroyed only at the time of detergent extraction and drying [129].

CONCLUSIONS

Because of their high degree of dispersion (and their very low size), microemulsions are a unique class of colloidal systems having novel properties. Both traditional and emerging techniques are required for their characterization and property elucidation. The numerous applications of microemulsions mean that these microheterogeneous systems will continue to be a rich field for exploration for scientists and will continue to create interest among industrial technologists.

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