Uses and applications of microemulsions

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Since the discovery of microemulsions, they have attained increasing significance both in basic research and in industry. Due to their unique properties, namely, ultralow interfacial tension, large interfacial area, thermodynamic stability and the ability to solubilize otherwise immiscible liquids, uses and applications of microemulsions have been numerous. The objective of this review is to present briefly the possible applications of the novel compartmentallized systems of microemulsions.

IT is well established that large amounts of two immiscible liquids (e.g. water and oil) can be brought into a single phase (macroscopically homogeneous but microscopically heterogeneous) by addition of an appropriate surfactant or a surfactant mixture. This unique class of optically clear, thermodynamically stable and usually low viscous solutions, called 'microemulsions'[1], have been the subject of extensive research over the last two decades primarily because of their scientific and technological importance. Microemulsions can have characteristic properties such as ultralow interfacial tension, large interfacial area and capacity to solubilize both aqueous and oil-soluble compounds. For detailed information one can consult several books and review articles[2–5].

The essential distinction between normal emulsion and microemulsion is their particle size and stability; the former is 'kinetically stable' whereas the latter is 'thermodynamically stable'. The stability of the microemulsion can be influenced by addition of salt, other additives, temperature or pressure. Normal emulsions age by coalescence of droplets and Ostwald ripening (transfer of material from small droplets to larger ones), since these processes lead to a decrease in the free energy of dispersion (the system is inherently thermodynamically unstable). Thermodynamic stability of the microemulsions has been proposed by Ruckenstein and Chi[6] who considered that the free energy of formation comprises interfacial free energy, interaction energy between droplets and entropy of dispersion. The interaction energy between droplets has been shown to be negligible and the free energy of formation can be zero or even negative if the interfacial tension is of the order of 10^{-2}–10^{-3} mN/m. The concept of hydrophilic–lipophilic balance temperature (HLBT) or phase inversion temperature (PIT) at which maximum solubilization of oil in water and ultralow interfacial tensions are achieved has been also introduced[6,7].

Microemulsions can be prepared by controlled addition of lower alkanols (butanol, pentanol and hexanol) to milky emulsions to produce transparent solutions comprising dispersions of either water-in-oil (w/o) or oil-in-water (o/w) in nanometer or colloidal dispersions (~ 100 nm). The lower alkanols are called cosurfactants, they lower the interfacial tension between oil and water sufficiently low for almost spontaneous formation of the said microheterogeneous systems. The miscibility of oil, water and amphiphile (surfactant plus cosurfactant) depends on the overall composition which is system specific. Ternary and quaternary phase diagrams can describe the phase manifestations and are essential in the study of microemulsions.

The knowledge on the phase manifestations of the pseudo-ternary (water/amphiphile/oil) or explicitly quaternary (water/surfactant/cosurfactant/oil) mixtures has been systematized. At low surfactant concentration, there is a sequence of equilibria between phases, commonly referred to as Winsor phases[8], they are Winsor I: with two phases, the lower (oil/water, o/w) microemulsion phase in equilibrium with the upper excess oil; Winsor II: with two phases, the upper microemulsion phase (water/oil, w/o) in equilibrium with excess water; Winsor III: with three phases, middle microemulsion phase (o/w plus w/o, called bicontinuous) in equilibrium with upper excess oil and lower excess water; Winsor IV: in single phase, with oil, water and surfactant homogeneously mixed. Inter-conversion among the above-mentioned phases can be achieved by adjusting proportions of the constituents. Simultaneous presence of two microemulsion phases, one in contact with water and the other in contact with oil is also possible[9]. This may be considered as an extension of Winsor's classification forming the fifth category. A composite representation of the above-mentioned features of microemulsion forming systems are depicted in Figure 1 *a*. A quaternary phase diagram of a specific system is also presented in Figure 1 *b*. The extents of formation of w/o, o/w and bicontinuous microemulsions can be understood from the phase equilibrium studies. Such

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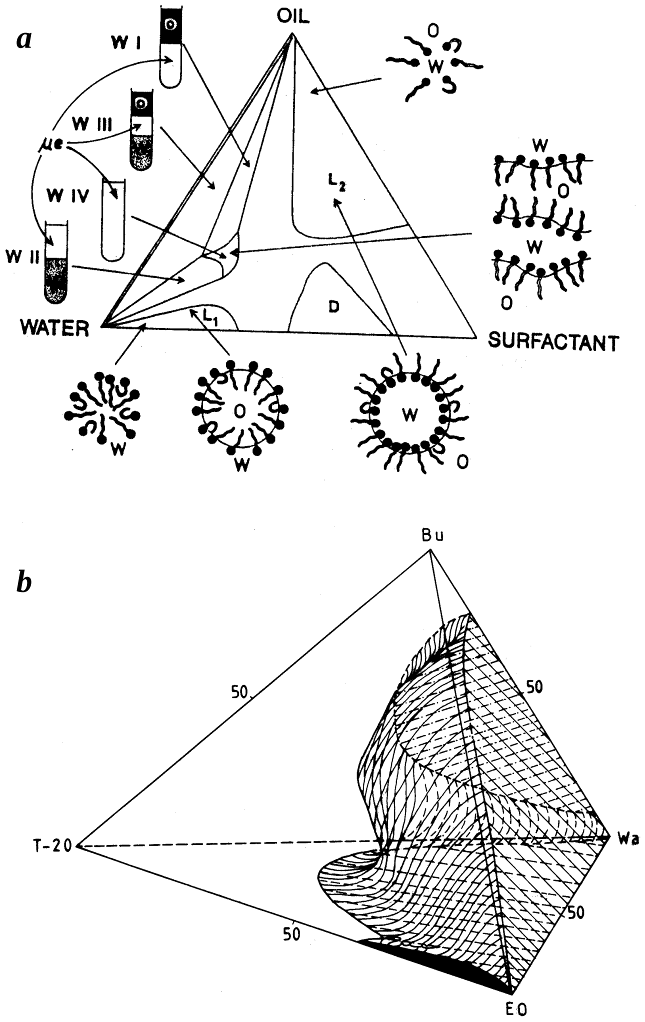

Figure 1. ***a***, Schematic ternary phase diagram of water–oil–surfactant mixtures representing Winsor classification and probable internal structures. L_1, a single phase region of normal micelles or oil-in-water (o/w) microemulsion; L_2, reverse micelles or water-in-oil (w/o) microemulsions; D, anisotropic lamellar liquid crystalline phase. The microemulsion is marked by μE, oil by O and water by W (see ref. 57); ***b***, Composite tetrahedral representation of the phase behaviour of Eucalyptol/Tween 20/Butanol/Water system at 30°C. The surface planes represent the behaviour of the associated ternary system. The clear area represents monophasic zone, and the dark and the shaded areas represent biphasic zones in different surface planes. Bu, butanol; T-20, Tween 20; Wa, Water; and EO, Eucalyptus Oil. (see ref. 58).

studies may often become complex with the appearance of tiny or extended additional zones of viscous gel and liquid crystalline phases[10], the establishment of their boundary demarcations is time consuming and laborious.

Microemulsions have been studied using a variety of techniques. Due to their complexity, namely, the variety of structures and components involved in these systems, as well as the limitations associated with each technique, the characterization of microemulsions is rather difficult. Therefore, complementary studies using a combination of techniques are usually required to obtain a comprehensive view of the physicochemical properties and structure of microemulsions. Most commonly used methods and techniques to acquire information on the particle dimension and shape, their diffusion coefficient and polydispersity, aggregation and dynamics of coalescence, state of the water pool, thermodynamics of formation, etc. of the compartmentalized systems of microemulsion are related to conductance, viscosity, ultrasound, static and dynamic light scattering, neutron and low angle X-ray scattering, nuclear magnetic resonance, dielectric relaxation, time resolved fluorescence quenching, transmission electron microscopy, calorimetry, etc. This area has been covered in comprehensive reviews[11,12].

Applications of microemulsions

There has been a revolution in the last two decades in the utilization of microemulsion systems in a variety of chemical and industrial processes. A brief account of processes and applications is presented here in order to demonstrate their significance and potential.

Microemulsions in enhanced oil recovery

The understanding of the mechanisms of enhanced oil recovery (EOR) using surfactant and microemulsion flooding has been attempted[13–15]. Roughly 20% of the otherwise unrecoverable underground oil can be obtained by the EOR process. The oil remains trapped in the reservoir because of high interfacial tension (about 20–25 mN/m) between the crude oil and reservoir brine. If the interfacial tension can be reduced to around 10^{-3} mN/m, a substantial fraction of the residual oil in the porous media in which it is trapped can be mobilized. Low interfacial viscosity of the system is also advantageous.

In surfactant–polymer flooding process, a surfactant formulation is injected into the porous media in the petroleum reservoir. Upon mixing with the reservoir oil and brine, the surfactant produces the middle-phase microemulsion *in situ* between excess oil and excess brine that propagates through the petroleum reservoir. In the surfactant (microemulsion)–polymer flooding process, salinity can induce precipitation of charged surfactants, with a concomitant destabilization of the microemulsion system. The multivalent ions can pose a problem. The concept of optimal salinity and its effect on the interfacial tension (IFT), the formation of middle-phase microemulsion and the efficiency of the oil displacement processes using short chain alkanols have been investigated.

According to recent reports, bacteria and biosurfactants have shown signs of being low cost analogues of mixed chemical systems. They have the ability to physically modify solid surfaces, emulsify through adherence to hydrocarbons and lower oil viscosity while multiplying within the porous bed's capillaries. Surface active agents are produced in mass scale by some of these bacteria and have the potential for use in EOR. EOR is becoming an affordable method for industrial oil production due to cheaper production of many of the commonly-used surfactants, polymers, alkanols and the continued refinement of mixed recovery techniques and advancement in the equipment to monitor IFT at high temperature and pressure[14].

The specific requirements for successful application of EOR from North Sea together with the development of adequate model system have been recently evidenced. The potential of the EOR has been very recently reviewed by Shah[15].

Microemulsions as fuels

One of the direct advantages of microemulsion-based fuels is the presence of water in a stable microemulsion and they are successfully used to reduce soot formation. When the water is vapourized during the combustion, this will lower the heat released and the combustion temperature. As a direct consequence, the emission rate of gases like nitrogen oxides (NO_x) and carbon monoxide (CO) will decrease.

The presence of water is also supposed to cause improved fuel atomization, minimization of particulate emission and sooting, and improved fuel economy in terms of price and miles/volume of the fuel. Another interesting feature of microemulsion-based fuel is their capacity to increase the octane number of gasoline and the corresponding octane number for diesel oils. Octane number improvers include formamide, glycols, urea, etc. In diesel fuels, many problems are overcome due to the high combustion temperatures (160–325°C). It is normal that diesel microemulsions contain water-soluble cetane number improvers[16]. Microemulsions in fuels are also found to improve air–fuel contact and increase the flash point of fuel. A variety of microemulsions designed as fuel systems have been reported along with detergentless systems consisting of 1-butanol, diesel and water[17].

Microemulsions as lubricants, cutting oils and corrosion inhibitors

Microemulsions or reverse micellar solutions are in use as lubricants, cutting oils and corrosion inhibitors for several decades[18]. The presence of surfactant in microemulsion causes corrosion inhibition and the increased water content compared to pure oil leads to higher heat capacity. On one hand the corrosive agents, because of solubilization in microemulsion cannot react with the metal surface and on the other, the metal surface is protected by the adsorbed hydrophobic surfactant film. However, solubilization is selective, and in some cases, other mechanisms might play a role in corrosion prevention.

In microemulsions, water with much higher thermal conductivity, imparts higher heat capacity to the system. Such formulations can be used in cutting oil; the oil lubricates the cutting surface, and the water helps to remove the frictional heat generated during the cutting process. Because of their thermodynamic stability, microemulsion systems have been used instead of macroemulsions.

Microemulsions as coatings and textile finishing

The coating application area is a very promising and rapidly-growing field of microemulsion technology, because the microemulsified resins overcome many of the shortcomings of the more traditional water-based systems without creating the health and pollution problems and flammability hazards of the solvent-based coatings. Due to their stability and small droplet size, microemulsions are ideal, where stability and homogeneity of the finished product is desired. Paint formulations using microemulsions have shown higher scrub resistance, better colour intensity and more stain resistance than those prepared by emulsions. In principle, three different possibilities of using microemulsions exist for coating applications: (1) for producing microdispersions by using microemulsified monomers, (2) for transferring non-water-soluble polymers into water, and (3) for obtaining specific effects by polymerization in w/o system. An example of such a system is acrylate lattices stabilized by isothiouronium groups, which have been successfully polymerized to yield particle sizes of 0.08 μm. Atik and Thomas[19] have polymerized (light induced reaction) a divinyl-benzene-styrene copolymer in a microemulsion stabilized by CTAB and hexanol. The microemulsions of the vinyl resins can be produced by converting them to ionomers in the presence of carefully selected solvent and co-solvent systems. Average particle sizes of about 0.02–0.14 μm are formed depending on the system.

Many auxiliary agents used in textile finishing are of amphiphilic nature. Barni *et al.*[20] have studied the dying of nylon-6,6 with an azodye using a microemulsion system (Ethofor-dioctadecyl dimethyl ammonium bromide/octanol/water) and have concluded that greater homogeneity in dying can be achieved compared to conventional dying aids. Microemulsions containing siloxane have been observed to produce finelydispersed finishes. The following advantages can be obtained using microemulsion in comparison with normal emulsion: (1) higher emulsion stability, (2) excellent product distribution on and in the substrate, (3) pronounced breaking effect, (4) very high internal softness, (5) excellent surface smoothness, (6) increased abrasion resistance and (7) high washing permanence.

Microemulsions in detergency

Due to their characteristic properties, microemulsions are promising systems for detergency purposes over traditionally-used organic solvents, as they can solubilize polar (e.g., salt, pigment, protein) and non-polar soil components (e.g., grease, oil). They have low interfacial tension (between aqueous and oil phases) and can spontaneously form when the components are brought together. The uses of microemulsions in washing/cleaning processes with reference to mechanism of soil removal have been discussed in literature[21,22].

Various additives such as synthetic zeolites improve the properties, e.g. viscosity and secondary washing performance. The effects of non-ionic surfactant and temperature on the efficacy of the textile detergency have been studied. The most salient feature of these investigations has been the correlation between the highest level of soil removal and the phase inversion temperature (PIT) of the corresponding washing solution/soil system. The phase transitions that are observed in anionic surfactant systems with salinity are similar to those of nonionic surfactants with temperature. Azemar *et al.*[23] have studied the effect of addition of several lyotropic electrolytes in depressing the optimum detergent temperature, which is essentially guided by the ‘salting-in’ and ‘salting-out’ properties of the electrolytes. Fabric detergent studies have been performed using pure triolein as a model for triglyceride soils, basic components in oily laundry soil (sebum). The phase behaviours of systems with nonpolar oils, are now well understood. In water/nonionic surfactant/triglyceride systems, two types of three-liquid phase regions exist; the observation of four phases and coexistence of two microemulsion phases in three component systems is remarkable. The middle phase microemulsion is a better medium for detergency. Microemulsions are effective in soil removal from textile fabrics, in wool scouring, and in skin degreasing.

Microemulsions in cosmetics

In many cosmetic applications such as skin care products, emulsions are widely used with water as the continuous phase. It is believed that microemulsion formulation will result in a faster uptake into the skin. Cost, safety (as many surfactants are irritating to the skin when used in high concentrations), appropriate selection of ingredients (i.e. surfactants, cosurfactants, oils) are key factors in the formulation of microemulsions. Microemulsions as skin care products have been reported[24]. In these formulations, sodium alkyl sulfate, tetraethylene glycol monododecyl ether, lecithin, dodecyl oligoglucoside, alkyl dimethyl amine oxide, propanol, hexadecane, isopropyl myristate have been used as surfactants, cosurfactants and oils respectively. Unique microemulsions as hair care products have been prepared. They contain an amino-functional polyorganosiloxane (a nonionic surfactant) and an acid and/or a metal salt. Solubilization of fragrance and flavoured oils can be achieved in microemulsions. Cosmetic microemulsions (transparent and translucent) of silicone oils, produced by emulsion polymerization have been reported. They are, however, not thermodynamically stable products because of low solubility of silicone oil in the surfactants.

Ultrafine emulsions prepared by condensation method have some advantages in cosmetic and medical products, as they have excellent stability and safety and their droplet size can be readily controlled. Ultrafine emulsions can be regarded as thermodynamically unstable microemulsions, as they are o/w emulsions with droplet size similar to microemulsion. Cosmetic formulations for skin care products using commercial nonionic surfactants and oils usually used in cosmetics are also investigated. There are patents on the formulation (by dispersion method) of skin care cosmetic products using ionic surfactants. Silicone oil ultrafine emulsions have been reported. Tokuoka *et al.*[25] have studied the solubilization of several systems consisting of water, surfactant and synthetic perfumes (viz. d-limonene, α-ionone, benzyl accetate, linalol, eugenol and α-hexylcinnamaldehyde), clarifying (a) the influence of fragrance structure on the phase regions in a water/nonionic surfactant systems, (b) the distribution co-efficient between micelles and the bulk phase, and (c) the partition between dissolved and solubilized perfume components on their volatility. In this regard, the phase equilibria in water, lecithin, soybean oil and vanillin have been studied. The conditions of preparation-related function of a fragrance in a personal care product have been studied and this field has been reviewed[26]. According to them, the variation of the fragrance vapour pressure over time is an essential factor both for consumer acceptance and economic point of view. The systems are water/AOT/cyclohexane, water/Brij 30/phenethyl alcohol, water/Brij 30/linalol.

Microemulsions in agrochemicals

Microemulsions have a variety of applications in agrochemical industry, of which pesticide-containing systems are relatively old[18]. To minimize the side effects of excessive use of agrochemicals on the ecosystem, chemicals with greater specificity and less persistence are developed. The ease of handling and lower requirement of smelly solvents go in favour of the use of microemulsions. However, increased efficacy of insecticides when applied as ‘microcolloidal aqueous emulsion’ instead of microemulsions has also been demonstrated. O/W microemulsions of organic, water-insoluble phenoxy herbicides optionally dissolved in a hydrocarbon solvent have been shown to be appreciably more effective than the corresponding emulsions in the control of plant growth. Microemulsions formulated with a hydrotope solubilizing the herbicide can be promising. The choice of hydrotope and the emulsifier could be largely determined by the water solubility of the herbicides. W/O microemulsions have been suggested to enrich the mineral-deficient crops with respect to trace metals such as iron. The oil medium of the microemulsion can hold the element in contact with the leaves even during moist conditions, until the trace element is adsorbed.

Tadros[22] has reviewed the formulation of agrochemicals using surfactants in detail. He has discussed the discovery and development of effective agrochemicals that can be used with maximum efficiency and minimum risk (i.e. enrichment of biological efficacy) to the user with the optimization of their transfer to the target during application. Controlled release of the formulations in reduced amounts is the most promising route. Most agrochemicals are not water soluble and become deactivated with water. Their formulation in o/w microemulsion is advantageous. The much finer droplet size of the microemulsion leads to higher penetrability, much larger contact area of the active substance to the treated surface and a much more even distribution during application. The infinite stability of the microemulsion and the high concentration of surfactants generally needed for a formulation are advantageous. A definite relationship exists between herbicides and surfactant structures for mixed herbicide penetration.

Microemulsions in food

Certain foods contain natural microemulsions. Microemulsions as a functional state of lipids have been, therefore, used in the preparation of foods. Microemulsions form in the intestine during the digestion and absorption of fat. The possibility of producing microemulsion on purpose and using them as tools in food production is, however, a neglected field in food technology. Excellent component solubilization, enriched reaction efficiency and extraction techniques have considerable potential in the area of food technology. The major differences between food and other microemulsions are in the composition of the oil component and food grade surfactants. In foods, the oil is a triglyceride, whereas in other microemulsions the oil is a hydrocarbon, often a mineral oil. The triglyceride molecule is itself surface active, which in turn implies that triglycerides are not capable of forming separate oil domain in an amphiphile–water system in the same way as mineral oils. Therefore, the composition range in the oil–water–surfactant systems that allows microemulsions to form when the oil is a triglyceride is much smaller than the range allowing microemulsion formation when the oil is a hydrocarbon. Food grade surfactants, viz. phosphatidycholine (lecithin), AOT and sorbatin monostearate/ monolaurate (Tweens) have been extensively studied with regard to the formation of o/w and w/o microemulsions[27]. Although microemulsion have a host of promising application in the food industry, there are still very few reports in the literature[28]. Recently, Dungan[22] reviewed current information on o/w and w/o microemulsion formed using food-grade materials, complex food mixture (liquid crystal, gels), possibilities of incorporating food ingredients (such as flavour, preservatives and vitamins) within microemulsions, reactions carried out in microemulsions media and potential of microemulsions for extracting food components from a complex mixture. Larsson *et al.*[29] have focused on the cereal and edible lipid systems that form microemulsions and their potentialities. Recent research has shown that microemulsions of carnauba wax form better protective coatings on citrus fruit than shellac, wood resin, oxidized polyoxyethylene or mixtures of these substances with caranuba wax. The protective coatings minimize weight loss as well as internal oxidation. The fruit coated with the microemulsions of caranauba wax maintains a better appearance than other coatings after washing and drying. Microemulsions have also been used to produce glycerides for application in food products. An important application of microemulsion is to provide improved antioxidation effectiveness because of the possibility of a synergistic effect between hydrophilic and lipophilic antioxidants. It is known that soybean oil is effectively protected when contained within an L_2-phase produced by the addition of monoglycerides (sunflower oil monoglycerides) to water. An approximately 1 : 5 ratio of monoglycerides to triglycerides is needed to get enough water into the L_2-phase (about 5 wt%). In such a system, 200 ppm of tocopherol in the oil and 5% ascorbic acid in the reverse micelles give a dramatic antioxidant effect compared to conventional methods of dissolving or dispersing antioxidants in oils. In fish oils, the same microemulsion-based method to achieve an antioxidant protective effect has also been used. Glycerol has been used instead of water for further improvement of the protectivity. The effect of adding various lipids and propylene glycol to monoolein (a common food emulsifier)–water system and the cubic liquid crystal thus formed undergoing a transition to a sponge or L_3-phase have been reported. The structure of the spongy cubic phase has been described as a 'melted' bicontinuous cubic phase. Although considerable research has been conducted to show the usefulness of microemulsions in foods, the application and technology require further work.

Microemulsion in pharmaceuticals

Liquid crystalline, miceller and emulsion forming systems are widely used in pharmaceutical preparations. Low solubilization capacity of micelles and instability of emulsions are disadvantageous. The easy formation, remarkable environment independent stability, excellent solubilization capacity, etc. favour microemulsions to be a better proposition over other compartmentalized systems. The dispersed phase, lipophilic or hydrophilic (o/w or w/o type) can act as a potential reservoir of lipophilic or hydrophilic drugs that can be partitioned between the dispersed and the continuous phases. Coming in contact with a semipermeable membrane, such as skin or mucous membrane, the drug can be transported through the barrier[22]. Both lipophilic and hydrophilic drugs can be administered together in the same preparation. Low viscous formulations using microemulsions with suitable protein compatible surfactants can be used as injection solutions, for they are miscible with blood in any ratio. In contrast to emulsions, microemulsions cause minimum immuno reactions or fat embolism. Proteins are not denatured in microemulsions although they are unstable at high or low temperatures. The total dose of the drug can be reduced when applied through the microemulsion route and thus side effects can be minimized. Toxicity, bioincompatibility of surfactants and cosurfactants, requirement of high concentrations for formulations and other relevant factors such as maintenance of thermodynamic stability in the temperature range between 0° and 40°C, salinity, constant pressure during storage, low solubilizing capacity for high molecular weight drug (and oil), etc. limit the uses of microemulsions in the pharmaceutical and medicinal fields.

An interesting and specific practical application of o/w microemulsion in the pharmaceutical industry is the use of strongly hydrophobic fluorocarbons (as oils) to produce short-time blood plasma substitutes to maintain the supply of oxygen in the living systems. The components to be used must have low allergic potential, good physiological compatibility and high biocompatibility. The biocompatibility requirements of the amphiphiles are fulfilled by lecithins, non-ionic surfactants (Brijs, Arlacel 186, Spans, Tweens and AOT). Microemulsions are promising delivery systems[21,22,30–32] to allow sustained or controlled drug release for percutaneous, peroral, topical, transdermal, ocular and parenteral administration. Enhanced absorption of drugs, modulation of the kinetics of the drug release and decreased toxicity are several advantages in the delivery process. Garcia-Celma[22] has reviewed microemulsions as drug delivery systems for different types of drugs, viz. antineoplastics/antitumour agents (doxorubicin, idarubicin, tetrabenzamidine derivative), peptide drugs (cyclosporine, insulin, vassopressin), sympatholytics (bupranolol, timolol, levobunolol, propanolol), local anesthetics (lidocaine, benzocaine, tetracaine, heptacaine), steroids (testosterone, testosterone propionate, testosterone enanthate, progesterone, medroxyprogestorane acetate), anxiolytics(benzodiazepines), anti-infective drugs(cloitrimazole, ciclopirox olamine, econazole nitrate, tetracycline hydrochloride), vitamins(menadione, ascorbic acid), anti-inflammatory drugs(butibufen, indomethacin), and dermological products(tyrocine, azelaic acid, octyl dimethyl PABA, 2-ethyl hexyl *p*-methoxy cinnamate). Enzyme doped silica nanoparticles (ceramic drug carrier) in the aqueous core of reverse micelles and microencapsulation of diospyrin, a plant-derived bisnapthoquinol of potential chemotherupic activity have been very recently reported[32].

Microemulsions in environmental remediation and detoxification

Research has shown that microemulsions are very effective in environmental remediation. In conventional soil washing, organic pollutants are detached from the soil particle by mechanical energy input. This causes increased absorption of contaminants at the fine grain fraction, which must then be deposited or burnt. Washing with water in presence of surfactants, can be another technique, where solubilization process is involved in the washing mechanism. A microemulsion intensifies the advantages of surfactant solution, such as decreasing interfacial tension and increasing wettability of soil and acting as an excellent solvent for polar and nonpolar organic substances. The additional solubility of the pollutant in the oil component of the microemulsion enhances its uptake. Further, the wettability of the soil particles is substantially increased due to the very low interfacial tensions provided by microemulsions, so that the fine grain fraction also becomes accessible for washing. The extraction of polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB) and other organic substances, from the fine grain fraction of a real soil sample using different extraction media has been reported. The systems studied are aqueous solution of $C_{12}E_4$ at a concentration below and above the critical micelle concentration (cmc), a ternary mixture of water/alkyl polyglycoside (PAG) and rapeseed oil. The latter has shown about 70% of the extraction yield compared to pure toluene. The components of these systems have been chosen to be biodegradable in soil and waste water. An alternative technique for soil extraction is the application of supercritical CO_2 which is cost effective.

Very recently, Haegel *et al.*[33] have reviewed soil remediation with microemulsions through different separation procedures including solid/liquid separation, liquid/liquid extraction and liquid/liquid separation for removal of the contaminant and reuse of the microemulsions.

Bicontinuous microemulsions with 39–45% of rapeseed oil methyl ester (RME) and o/w microemulsions with <1% RME content have been used to extract polycyclic aromatic hydrocarbon (PAH) or polychlorinated biphenyls (PCB) from soils. Extraction is complete with bicontinuous microemulsions and is fairly good with o/w microemulsions. Baran (Jr.) *et al.*[34] have reviewed the remediation of groundwater contaminations by nonaqueous phase liquids (NAPLs, chlorinated hydrocarbons) via microemulsion formation using more hydrophilic surfactants, e.g. sodium dialkylsulfosuccinates, ethylene oxide and propylene oxide containing surfactants, alkyl benzene sulfonates, tweens, spans, alkyl glucamides, alkyl polyglycosides, etc.

Other uses of microemulsions in remediation include detoxification of mustard compounds. Half-mustard can be oxidized to nontoxic sulfoxides by hypochlorite in 15 s using an o/w microemulsion made from water, heptane, AOT and 1-butanol. Microemulsions are useful in detoxification of pesticides in a continuous flow, two phase microemulsion reactor. A centrifugal reactor can be used with either a Winsor I (microemulsion in equilibrium with a lighter bulk organic phase) or a Winsor II system (microemulsion in equilibrium with a heavier bulk water phase) to degrade pesticides. This technique has the potential for application in a number of related fields that currently utilize membrane-type extraction/reaction systems.

Microporous media synthesis (microemulsion gel technique)

The unique properties of microemulsions have been utilized to produce microemulsion-gel glasses and microporous media with high surface area[35,36]. The preparation of titanium oxide gels and glasses using w/o microemulsion and the potential of microemulsions to serve as vehicles to incorporate inorganic water-soluble salts in glass have been reported. Microemulsion/gel glasses doped with organic laser dyes, silica supported spinel $LiMn_2O_4$, combination materials with organic polymers, and bioactive materials have good formation possibilities. These gels are reported to be obtained by the traditional sol/gel method with an increase in the viscous and elastic response by several orders of magnitude at gelation. Microemulsion gels are important *per se* as an alternative to gelation of microemulsions using collagen or lecithin. Microporous calcium phosphate material using a bicontinuous microemulsion can be synthesized. These polymeric microporous media may be useful in filtration and absorption application. Nonaqueous microemulsions have also been used to prepare gels in order to evaluate the influence of the polarity of the medium on the properties of the final gel. The formation of broad size distribution of clusters has been claimed as predicted by both percolation and kinetic theories.

Microemulsions in analytical applications

Applications of microemulsions have been extended to the field of analytical techniques, viz. chromatography, laser-excited photoionization spectroscopy, etc. The characterization of solute hydrophobicity by microemulsion electrokinetic chromatography (MEEKC) has been attempted[37], which provides a quick and reproducible method to obtain hydrophobic parameters for solvents.

Microemulsions are able to enhance analytical spectroscopic techniques by functioning as solubilized media, spectral shift reagents, intensity amplification agents, etc. The utilization of microemulsion media in analytical spectroscopy and the analytical sensitivities of the three systems o/w, w/o and bicontinuous microemulsion have been assessed. A series of studies have been reported on the determination of aluminium, zinc, copper, cadmium, manganese ions using both microemulsion and mixed microemulsion systems. These studies are mostly published in the journals published by the Chinese Chemical Society. This field has also been recently reviewed[21,38].

Microemulsions as liquid membranes

Two liquids placed across a middle liquid or porous support form a liquid membrane system. Transport of materials through the middle phase (membrane) depends on the way (complexation or entrapment with suitable agents) the solute is transferred from one side called the ‘source phase’ (S) to the other called the ‘receiving phase’ (R). Microemulsions of Winsor I (o/w) and Winsor II (w/o) types can be used as liquid membranes that can facilitate the transfer of solutes (oil soluble compounds by Winsor I and water soluble compounds by Winsor II) across it by trapping them in the microdroplets for convenient uptake and subsequent release. Winsor I and Winsor II microemulsions are called ‘bulk liquid membranes’. The use of liquid membrane for separation is an established and potent field in chemistry and biology.

'Bulk liquid membrane' is a recent addition in the field of separation science and technology, and major works for its introduction, function and prospects in practical field have been done[29,39,40]. It has also been extended towards the separation of different metal ions (Ni^{2+}, Co^{2+} and Cu^{2+}). The o/w microemulsions have been also used as liquid membranes for the transport of lipophilic compound (viz. pyrene, perylene and anthracene). Mechanisms have been proposed for the transfer of hydrophilic and lipophilic substances by microemulsion liquid membranes. Different mathematical equations have been proposed and tested under varied experimental conditions for the transport of lipophilic materials through o/w microemulsions.The transfer of salted water from an external aqueous phase to AOT reverse micelles has been examined. A membrane separated two-component cell has been used to measure the transfer of salt that has been monitored by conductivity measurement.

The emulsion liquid membranes (ELMs) technique[40] works by forming a surfactant stabilized emulsion between two immiscible phases. The solute (i.e. the chemical species desired) is selectively transported from a feed phase across a thin liquid film of immiscible phase and enriched in the receiving phase. The phases involved are stabilized by forming an emulsion of the membrane and one of the other phases using appropriate surfactants. ELMs for the separation of acetic acid under a variety of experimental conditions have been tested. The removal of mercury as Hg (II) from water is possible by this technique. The microemulsion liquid membrane containing sulphuric acid as the receiving phase is able to reduce mercury from 460 ppm to 0.8 ppm within 20 min, with most of the separation completed in less than 1 minute. This compares favourably to an equilibrium extraction control that resulted in final concentration of 20 ppm. However, difficulty in demulsification poses a problem and separate studies are required for the recovery. Electrostatic coalescence and butanol addition have been evaluated as potential demulsification techniques for recovery of the components of mercury-rich microemulsions.

Microemulsions in biotechnology

Many biocatalytic and enzymatic reactions are conducted in aquo-organic or pure organic as well as in biphasic media (i.e. polar media solubilizing enzymes and nonpolar media solubilizing apolar substituents). Their use is seriously limited, as they can inactivate or denature the biocatalysts. Recently, interest on microemulsions is being focused for various applications in biotechnology, viz, enzymatic reactions, immobilization of proteins and bioseparation. Microemulsions are advantageous over other multiphase equilibrium systems because of simultaneous solubilization of polar and nonpolar reactants in the same solution, shifting of the equilibrium position of the reaction and the separation of products by physical means.However, bioincompatibility of the amphiphiles used poses a serious limitation in the advancement of this field. The prospects of biotechnological applications have also been reviewed[22,29,41,42]. Enzyme reactions (catalysis) in microemulsion media have widely been studied. The use of microemulsion for enzyme catalysis is not arbitrary for enzymes under *in vivo* condition function in the cell as well as at the interface of hydrophobic and hydrophilic domains of cell and tissue containing lipids and other natural amphiphiles.

Enzymatic reactions in microemulsions: The potential advantages of employing enzymes in media of low water content, i.e. w/o microemulsions are: (i) increased solubility of nonpolar reactants; (ii) possibility of shifting thermodynamic equilibria in favour of condensation; (iii) improvement of thermal stability of the enzymes, enabling reactions to be carried out at higher temperature. Catalysis by a large number of enzymes in microemulsion media has been studied for a variety of reactions, such as synthesis of esters, peptides and sugar acetals; transesterifications; various hydrolysis reactions; glycerolysis; oxidation and reduction and steroid transformation. The conformation and activity of an enzyme depend on ω ([water]/[surfactant]); the enzyme is thus sensitive to amount of surrounding water. Gomez-Puyon has written an excellent review of the behaviour of enzymes in microemulsions[43].

Immobilization of protein in microemulsion: In the field of protein immobilization, microemulsion medium has been found to be a good proposition. Immobilization of a variety of proteins on suitable solid surfaces using microemulsion media has been successfully achieved[44].

Microemulsions for bioseparations: The possibility of microemulsions to extract biopolymers (proteins and enzymes) from an aqueous phase has been explored. Microemulsions are gentle solvents for extraction of proteins without altering their enzymatic or functional properties although the process can readily be scaled by conventional liquid–liquid extraction techniques. The pH, ionic strength, type of salt, concentration of solvent and temperature influence the partition of a protein. For the merits and demerits of conditions and environment with reference to physicochemical principles and specification of systems, the readers may consult references[45,46].

Biomolecules other than proteins, such as amino acids because of their structure and properties have been separated using w/o microemulsions of Winsor II type. For the solubilization and extraction of amino acids in a liquid–liquid system as well as in the organic phase, the electrostatic interaction is considered to be the main driving force; the hydrophobic interaction is the other important factor. From the free energy of transfer (between water and surfactant shell) of different amino acids a new hydrophobicity scale has been proposed[46]. In the separation of amino acids by the microemulsion technique, the size of the droplet plays a vital role because it controls the core hydrophilicity and the interfacial hydrophobicity. The amino acids that preferentially solubilize in the shell of the w/o microemulsion are expelled from the interface with increasing curvature, i.e. with decreasing droplet size. The process can also be achieved by changing ionic strength, solvent type, etc. The interfacial properties of a microemulsion droplet depend on the amphiphilic type and the presence/absence of a cosurfactant. This important aspect for microemulsion extraction and separation has been only limitedly explored.

Influence of microemulsions on chemical reactions

Due to varied consistencies and microstructures, microemulsions have been considered as useful reaction media for a variety of chemical reactions. The major types of reactions studied in microemulsions comprise formation of inorganic particles (nanoparticles), polymerization, photochemical, electrochemical and electrocatalytic and organic synthesis. These are emerging as technologies of considerable current interest with a large number of publications. Individual types are briefly described below.

Synthesis of nanoparticles: Kizling *et al.*[47] reported the synthesis of nanoparticles Pt, Pd, Rh and Ir by reducing corresponding salts in the water micropools of w/o microemulsions with hydrazine or hydrogen gas. W/o microemulsions are particularly attractive reaction media for the preparation of monodisperse solid particles of submicron dimensions through a complex process. It involves a delicate interplay between nucleation, microcrystal formation, intermediate growth, coagulation and flocculation. Precipitation reactions in microemulsions offer a novel technique for the synthesis of a wide variety of nanophase materials. It also offers a unique method to control the kinetics of particle formation and growth by varying the physicochemical characteristics of the microemulsion system.

Five aspects are to be taken into consideration for particle synthesis in microemulsions; phase behaviour and solubilization, average concentration of the reacting species in the aqueous domains, intramicellar interactions, water/surfactant ratio and structure and properties of the solubilizing water, and dynamic behaviour of the microemulsion. The average number of ions per droplet can be calculated by determining the droplet size in a microemulsion system, and the distribution follows Poisson's law. Interactions within a droplet can also decisively influence the particle size and two factors have been found responsible for this phenomenon. Firstly, the activity of an ion can be significantly changed in such a droplet as compared to a pure aqueous phase, and secondly, the reaction process can be significantly influenced by the localization of a species, e.g. at the interface. This effect can be very specific for different ions.

A large variety of particles having different technological applications (such as surface chemical, photochemical, catalysis, magnetic materials, paint materials, superconductors, semiconductors, vehicles polymer, *in vivo* drug carriers, ultramodern molecular devices, etc.) have been prepared in microemulsions (aqueous and non aqueous). These include catalytically active transition metals and their alloys, silver, silver halogenides, gold, nickel, cobalt and iron borides, cadmium sulphide, copper, lead and indium sulphides, cadmium selenide, titanium dioxide, zinc sulphide, molybdenum sulphide, magnetite and polymer coated magnetite, cadmium and barium carbonates, silica particles, tin oxide, sulphates of calcium and barium, zirconium dioxide, bioceramic hydroxyapatite, nanocomposite powders (SiO_2–CuO, Ag_2S/CdS, Ag/SiO_2, etc.), superconducting salts and semiconductor materials. Recently the formation and physicochemical behaviours of molecular aggregates of $Cu_2[Fe(CN)_6]$, in water/AOT/*n*-heptane microemulsion have been reported[48]. The enthalpy of formation of the complex salt formed in aqueous and microemulsion media has been measured microcalorimetrically. Tungstic acid and lead chromate have been in synthesized w/o microemulsions and characterized.

Preparation of ultrafine particles of oxide materials, metals, metal borides, superconductors and magnetic materials in microemulsions has been reviewed[21]. A few studies on the synthesis of nanometer and micrometer sized metal oxide and metal sulfide particles in supercritical fluid microemulsions have also been reported. Formation, characterization and drug loading and targeting of polymeric nanoparticles using microemulsions have been reviewed[49]. Preparations of polymeric nanoparticles in the aqueous compartment of w/o microemulsions have been successfully attempted.

Polymerization: Polymerization in microemulsions has received much attention. Preparation of spherical latex particles of diameters between 20 to 40 nm using an o/w microemulsion consisting of CTAB, styrene and hexanol in water has been reported. The problem of phase separation was encountered during such a preparation. The polymerization and co-polymerization of systrene, methyl methacrylate (MMA) and other water-insoluble monomers in microemulsions have yielded monodisperse lattices. The monodisperse microlattices obtained from microemulsions are useful as a seed for emulsion polymerization or as a carrier for pharmaceuticals. The details of the experimental procedure, etc using the example of styrene, methylmethacrylate, etc. have been reviewed[21,50,51].

Photochemical, electrochemical and electrocatalytic reactions: Microemulsions have been used in the photodegradation of chlorophyll using fluorescent probes, flash photolysis of various acceptor systems and steady state photolysis. Photosensitized electron transfer, photodimerization and photoisomerization, photoreduction and ion transport by utilising the quenching of triple state excited pyrene tetrasulphonic acid (PTSAT) in microemulsion systems have been found to be prospective.

Electrochemistry often faces the problem of finding a solvent that simultaneously dissolves an organic substrate and a sufficient amount of conducting electrolyte. The uses of o/w microemulsions as reaction medium for electrochemical analysis and catalysis have been reported. The electrochemical synthesis of polyparaphenylenes or the dehalogenation of vicinal dihalogen compounds are interesting new synthesis paths. Reports on the cyclic voltametry studies (electrochemical, diffusion and kinetic) in bicontinuous microemulsion systems (didodecyldimethylethyl ammonium bromide, DDAB/water/dodecane or tetradecane) are available in literature. Bicontinuous microemulsions are observed to be excellent fluids for mass transport for the study of decomposition of polychlorinated biphenyl (PCB) by electrochemical means. Electrochemical reactions using micelles and microemulsions have been recently reviewed[52].

Organic reactions: Organic reactions in microemulsion media have been widely investigated mainly focussing on the kinetics. A few investigations have only considered the synthetic aspects; consideration of detailed kinetic and synthetic aspects are rare. There are a good number of reports on the reactions between esters and nucleophiles, and hydrolysis of esters in microemulsion media. Various organic reactions with reactants such as acids, bases, cyanide, bromide, iodide, hypochlorite, permanganate, $NaBH_4$, etc. in microemulsions have also been reported. Enhancement in the reaction rates in microemulsions is usually larger than in the micellar media.

In addition to reactions with ionic reactants, synthesis of macrocyclic lactones, the Diel–Alder reaction, oxidation with H_2O_2, nitrations of aromatics, nitrosation, reduction of carbonyl compounds, catalytic reductions and oxidations and deacylation as well as acylation have been carried out. The nitration of phenol in an AOT-based microemulsion system has been performed; 80% ortho product in microemulsion in comparison to 35% in aqueous system has been observed. Regioselectivity of product has been established in microemulsion media. The kinetics of various reactions, for example, inversion of cane sugar, fading of crystal violet, hydrolysis of phenyl acetate and reaction between hexacyanoferrate(III)-iodide, etc. have been studied[53]. Comprehensive information on chemical reactions (organic and inorganic) in microemulsions can be found in recent reviews by Sjoblom *et al.*[52] and Bunton and Romsted[21].

The use of waterless microemulsions (formamide or other nonaqueous solvents instead of water) for investigations of Wacker process and Diel–Alder reactions has been shown to be prospective; the reactions are faster in these media than in water.

Novel crystalline colloidal arrays as chemical sensor materials

Microemulsions as novel compartmentalized liquids have wide applications. Scientists are also in search of other novel self-organizing colloidal systems for important physico-chemical applications. The crystalline colloidal arrays (CCA) are new findings in this direction, which are prospective novel chemical sensors. The field is only very limitedly studied. A brief summary of the work so far done on CCA is herein included as a supplementary addition to the main issue.

Over the last decade intelligent photoionic crystalline colloidal array self assemblies have been developed[54], which can have use in medicine, environmental chemistry, process control and remote sensing. These are mesoscopically periodic fluid materials, that diffract light satisfying the Bragg condition. The crystalline colloidal array self assemble into either face centered or body centered cubic form. Just as atomic crystals diffract X-rays that fulfill the Bragg condition, CCAs diffract ultraviolet, visible and near-infrared light, depending on the lattice spacing. Colloidal particles of inorganic materials, such as silica or organic polymers, such as poly (*N*-isopropylacrylamide) have been synthesized having periodicity of the order of ~200 nm. Asher *et al.*[55] and Holtz *et al.*[56] have developed a novel sensing material from a polymerized crystalline colloidal array (PCCA) which is a mesoscopically periodic crystalline colloidal array of spherical polystyrene colloids within a thin, intelligent polymer hydrogel film. They have fabricated a sensor, utilizing a crown ether as the recognization agent that can detect Pb^{2+} in the 0.1 μM–20 mM (~20 ppb – ~ 400 ppm) concentration range. The sensors for glucose and galactose utilising glucose oxidase or *b*-D-galactosidase as the recognization entities have been developed. Besides sensing glucose, this sensor can estimate dissolved oxygen concentration in the presence of constant glucose concentration. Development of thermally tunable photonic crystal of poly (*N*-isopropylacrylamide) (PNIPAM), a novel CCA photoionic crystals with variable sphere sizes and variable array periodicity and sensors that change volume in response to nonionic molecular recognition processes such as antibody/antigen interactions have been attempted.

Conclusions

The large variety of applications (from enhanced oil recovery to nanoparticle synthesis) as well as the steadily increasing number of research workers engaged in studies on microemulsions due to their unique properties, have made significant contributions to many branches of chemistry and technology, and suggest that the potential of microemulsions as novel compartmentalized liquids will be even more significant in future.

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