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Microemulsions as an emerging technology

From petroleum recovery to nanoparticle synthesis of magnetic materials and superconductors

Since the discovery of microemulsions by Schulman and co-workers in the early 1940's [1], the applications of microemulsions have extended to numerous technological areas from tertiary oil recovery to nanoparticle synthesis. The availability of high interfacial area, combined with thermodynamic stability and the ability to solubilize otherwise immiscible liquids have led to the use of microemulsions in cosmetics, pharmaceutics, lubrication, food technology, agricultural sprays, coatings, environmental remediation, cleaning, combustion, chemical synthesis, microporous media synthesis, enhanced reaction kinetics, and chemical analysis. This paper discusses the potential applications of microemulsions in emerging technologies.

Seit ihrer Entdeckung in den frühen 40er Jahren durch Schulman et al. haben Mikroemulsionen ein weites Anwendungsspektrum in zahlreichen technischen Bereichen gefunden, von der tertiären Erdölförderung bis hin zur Synthese von Nanopartikeln. Ihre Eigenschaften – eine große Grenzfläche in Verbindung mit thermodynamischer Stabilität und der Fähigkeit, Flüssigkeiten zu lösen, die normalerweise nicht mischbar sind – führten zu ihrer Anwendung in Kosmetika, Pharmazeutika, Schmiermitteln, landwirtschaftlichen Sprays, Coatings, in der Lebensmitteltechnologie, der Umweltsanierung, Reinigungstechnologie, Verbrennung, Chemischen Synthese von mikroporösen Stoffen, als Reaktionsbeschleuniger, und in der Chemischen Analyse. Diese Arbeit befaßt sich mit Anwendungsmöglichkeiten von Mikroemulsionen in neu entstehenden Technologien.

1 Introduction

Microemulsions are thermodynamically stable, optically isotropic dispersions of aqueous and hydrocarbon liquids that are stabilized by an interfacial film of surfactant molecules [2–6]. Microemulsions are generally described as monodispersed spherical droplets (50–1000 Ångstroms in diameter) of water in oil or oil in water depending upon the nature of the surfactants and the composition of the microemulsion. Microemulsions can be readily distinguished from macroemulsions on the basis of optical transparency as shown in Fig. 1. The optical transparency is a direct function of droplet

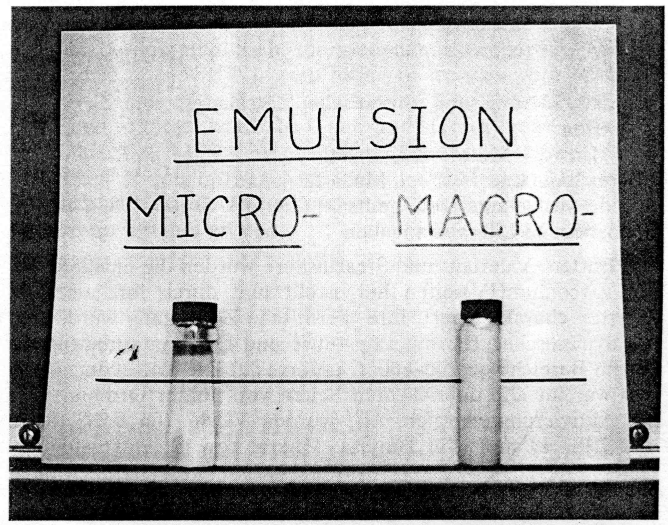

Fig. 1. Comparison of the optical transparency of micro- and macroemulsions. Note that the dark line is visible through the microemulsion solution

size. Microemulsions are larger than molecular and micellar solutions, but they have a smaller droplet size than either colloidal dispersions or macroemulsions as illustrated in Fig. 2. In order to form microemulsions, surfactants must be selected to decrease the oil/water interfacial tension to 10^{-3}–10^{-5} mN/m. Under certain conditions, however, bicontinuous [7, 8] or cubic [9] structures have been reported.

2 Microemulsions in enhanced oil recovery

The efficient production and utilization of natural resources have been established as important objectives by the petroleum industry over the past thirty years. Geological evolution

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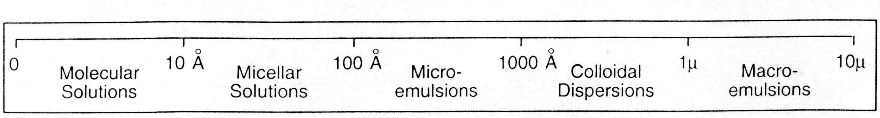

Fig. 2. Comparison of size ranges of various dispersed systems

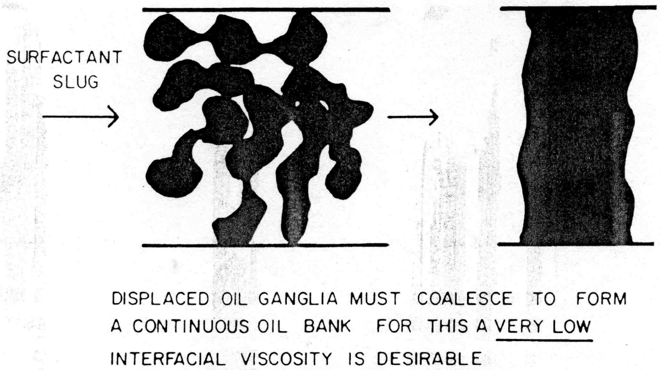

Fig. 3. Addition of surfactant to increase coalescence of oil ganglia via very low interfacial viscosity

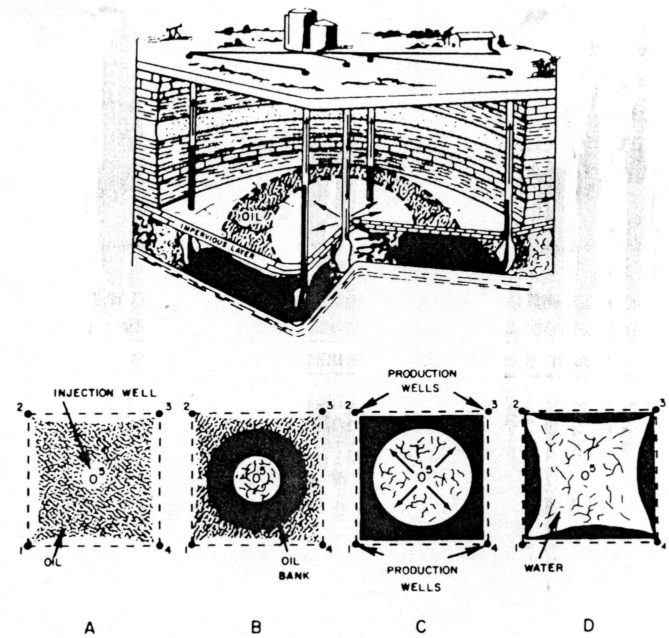

Fig. 4. Displacement of oil in petroleum reservoirs by water or chemical flooding (five spot pattern)

has been kind to the industry in so far as producing high pressure oil reserves in which primary oil recovery methods can achieve close to 35 % production efficiency. The unrecoverable oil which remains in the reservoir has provided an engineering challenge. This area has been known as tertiary or enhanced oil recovery (EOR). Initial areas of research brought about by the oil shortages of the 1970's concentrated on the importance of reducing the interfacial tension (IFT) of the oil/water interface with the use of surfactants [10]. The petroleum industry seized this concept as a method to increase oil production through modified water flushing strategies.

Enhanced oil recovery techniques which can produce ultra-low IFT can collect the diffuse oil ganglia in the rock (Fig. 3), mobilize it, and propagate some portion of the trapped oil to the production wells (Fig. 4). Reduction in interfacial tension was in fact found to lessen the capillary forces responsible for oil entrapment within porous media [11]. In addition, *Wilson* and *Brandner* [12] identified petroleum sulfonates as being useful in producing these ultra-low interfacial tensions (10^{-3} mN/m) in homologous series of hydrocarbons.

Such promising results led to fundamental research directed to better understanding the water/surfactant/oil interface, and the identification of the existence and importance of a middle-phase emulsion ahead of the drive water [13–15]. Notice the migration of the surfactant from the oil phase on the left (top solution layer) to the water rich phase on the right (bottom layer of solution) (Fig. 5). The identification of additional parameters to attain ultra-low IFT led to work in the areas of critical micelle concentration (c. m. c.) [16, 17], oil chain length and the degree of surfactant partitioning in the oil and water phases [17]. The effect of the c. m. c. on the interfacial tension for varying salt and surfactant concentrations, as well as the effect of oil chain length on interfacial tension are shown in Fig. 6. The concept of optimal salinity and its effect on IFT, the formation of middle-phase microemulsions and the efficiency of oil displacement processes were investigated by several researchers [17, 18–20]. The

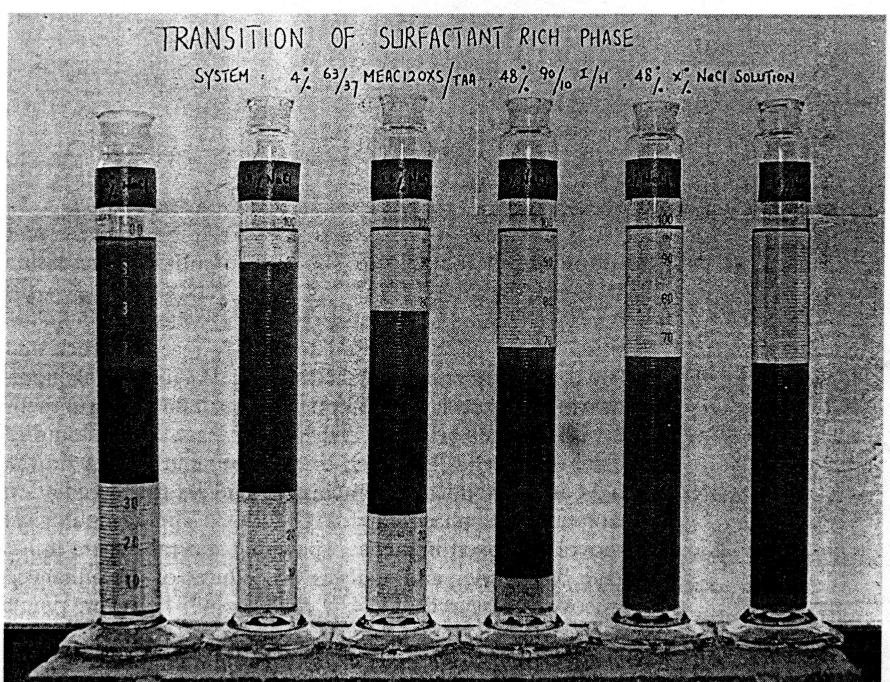

Fig. 5. Transition of Surfactant Rich Phase. Cylinder content: oil/surfactant/water + salt. Salt (NaCl) concentration decreases from right to left: 2 %, 1.8 %, 1.6 %, 1.4 %, 1.2 %, 1 %

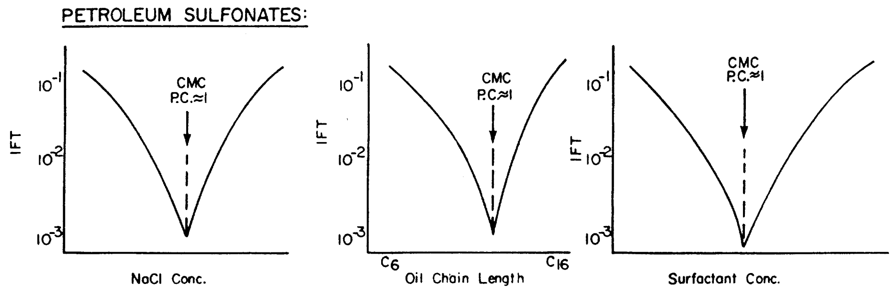

Fig. 6. The effect of salt concentration, oil chain length and surfactant concentration on interfacial tension

effect of salinity on various process parameters is presented in Fig. 7. The middle-phase microemulsion and ultra-low IFT were achieved with the addition of short chain alcohols [21–23] as well as a change of other parameters (Fig. 8).

Addition of polymer to the chase water was introduced to help maximize the viscosity of the water front [24, 25]. The additional costs, problems of mechanical shear, chemical and microbial stability, chemical reactivity, and microemulsion mobility all became factors in these complex systems. Even with the development of more stable and controllable microemulsion interfaces, industrial applications of such interfaces were limited due to the necessity of the high yields required to justify the added costs associated with polymer additions.

Studies in the area of surfactant concentration [20] and the effects of surface charge [26, 27] provided a greater insight into oil displacement processes in porous media using microemulsions. Results in this area showed that the interfacial tension was a function of three factors as illustrated in Fig. 9. Each of the parameters (i. e. surfactant concentration, charge density, and water/oil solubilization) are shown relative to the magnitude of their influence on interfacial tension. These chemical interactions combined with thermal instability of the emulsion systems [28] as well as disappointing reservoir permeability in the emulsion/polymer systems seemed to limit production efficiency for such emulsion systems.

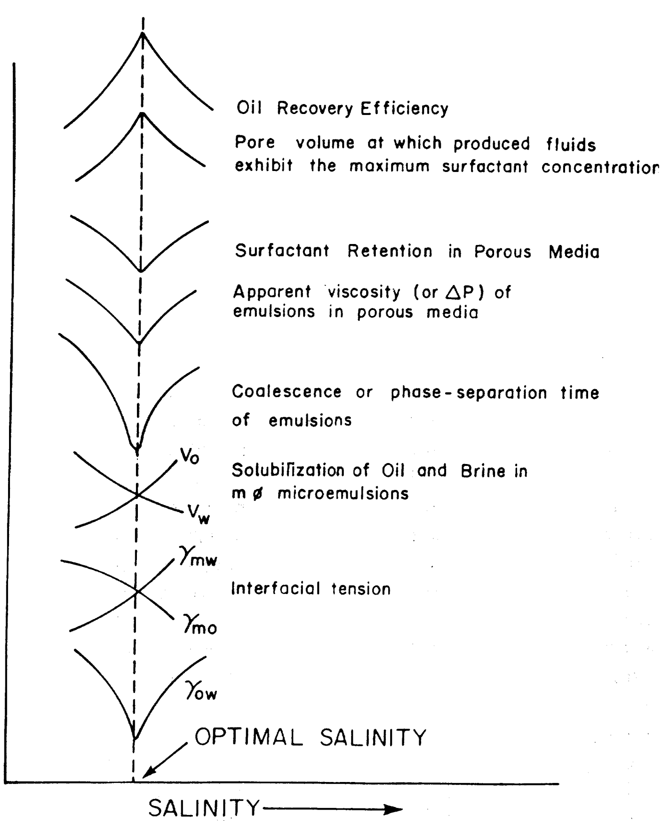

Fig. 7. Various phenomena occurring at the optimal salinity in relation to enhanced oil recovery by surfactant flooding

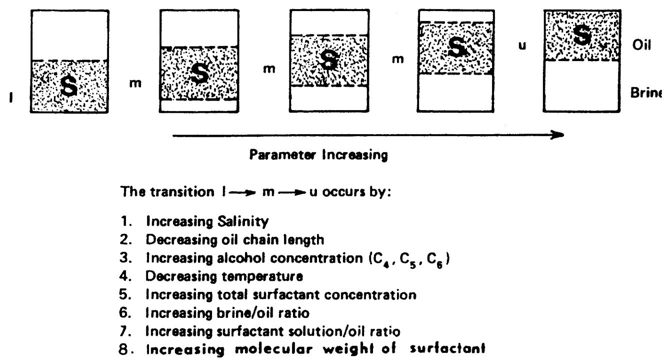

Fig. 8. The transition of lower to middle to upper phase in microemulsions

Although the microemulsion systems had been successful, chemical conditions such as the presence of reactive clays and physical problems such as gravitational override and decreased permeability had economically limited the microemulsion application. Foam systems appeared to be a promising alternative due to decreased gravitational override and increased permeability. Originally proposed in 1958 by *Bond* and *Holbrook* [29] for oil recovery, foam has the potential of attaining a viscosity higher than either of its components (i. e. the gas or the surfactant solution). The actual mechanics behind the process, however, remained, a topic of debate into the 1980's [30–33]. In addition to the research directed toward the physical understanding of the foaming systems, it was found that breakthrough time and fluid displacement were closely related to surface properties and molecular packing at interfaces. Researchers showed that chain length compatibility in mixed surfactant systems resulted in minimized surface tension, maximized surface viscosity [34–36], and higher levels of oil recovery. Additional work with steam-produced foams also showed potential in increasing oil well productivity [37–39].

Another technique to enhance recovery has been alkaline flooding where acids are used to modify reservoir rock and improve porosity and permeability [40]. Again, the economics surrounding such a technique did not allow for competition with low oil prices of the Middle East. The passing of the late 1980's did, however, bring continued interest in the area as an economically competitive process for remediation of non-aqueous phase liquids (NAPLs). The technological crossover has been immense, spawning several papers utilizing the discoveries and analysis procedures of the enhanced oil recovery research [41, 42]. *Baviere* [43] however, points out that with cheaper production of many of the commonly used surfactants, polymers, alkalis and the continued refinement of mixed recovery system techniques [44], enhanced oil

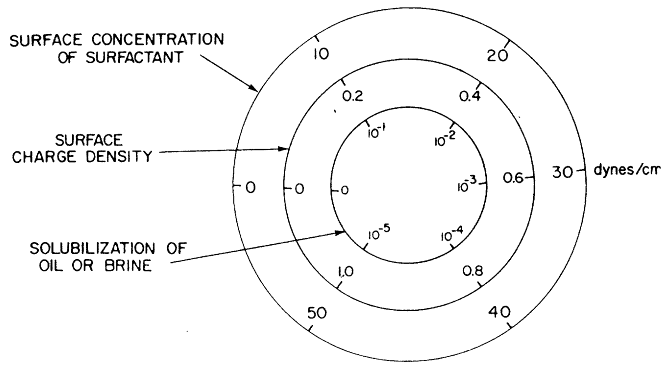

Fig. 9. The three components of interfacial tension and their respective contributions to IFT [20]

recovery is becoming an affordable method of industrial oil production [45]. The advancement in computational processing has also ensured longevity to the area through fine tuned modeling and numerical simulation [46, 47]. Additional advancement in equipment, allowing for studies of interfacial systems at high temperature and pressure [48], also promises to greatly expand the viability of EOR and the industrial application of microemulsions.

On a more contemporary note, bacteria and biosurfactants have recently shown signs of being low cost analogues to mixed chemical systems. Bacteria appear to 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 [28, 49]. Some of these bacteria actually appear to mass produce surface active agents and could be used in-situ to alter surface charge of the interface as they migrate [50, 51].

The field of enhanced oil recovery has received a great deal of effort over the last thirty years building a strong foundation for future use. The insight and information produced during these years has not only increased oil production but has led to further advancement in microemulsion applications that extend into many areas of technological interest, including nanoparticle synthesis.

3 Microemulsions in nanoparticle synthesis

Nanophase ceramics with an average grain size of less than 100 nm have generated considerable scientific interest recently because of the improvements in a variety of properties that are expected to result from size reduction to the nanometer scale. A variety of interesting effects are observed when the particle dimensions are reduced to below certain characteristic distances such as coherence or correlation length, mean free path, wavelength (of elementary excitations), etc. [52]. Because of their ultrafine sizes, and high surface area, these particles can easily overcome conventional restrictions of phase equilibria and kinetics, leading to lowering of sintering temperature and solid-state reaction and increasing the sintering rates of metal complexes. The large fraction of atoms residing at the surfaces and grain boundaries of these materials also leads to materials with novel properties. These nanoparticles have important technological applications in areas such as (a) catalysis (b) lowering of the sintering temperature and increasing the sintering rate (c) controlling the microstructure in ceramic materials (d) micro-electronic devices, and (e) high density magnetic recording materials [53–55]. Other nanoparticles such as polymer latex particles are of considerable importance in paints, paper coatings, biomedical applications and textiles.

It has been reported that the use of powders, consisting of unagglomerated submicron particles with narrow size distributions, as starting material in the processing of ceramics gives rise to a reduction of sintering time and temperature and improves considerably the properties of the final products [56, 57]. These potential technological applications have led to the development of several new techniques for the synthesis of various types of nanoparticles in recent years. These include gas-phase techniques such as gas evaporation, laser vaporization and laser pyrolysis [58–62]; vacuum synthesis techniques such as sputtering, laser ablation, and ionized beam deposition [63–66]; precipitation [67, 68], thermal decomposition [69], aerosol production [70–73], sol-gel processing [74], etc.

Water-in-oil microemulsions are a particularly attractive reaction medium for preparing particles of submicron dimensions. Reverse micelles, water-in-oil microemulsions or vesicles can be used as microreactors to carry out chemical reactions in confined geometries [75, 76]. 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.

Due to the dynamic nature of the microdroplets in microemulsions there is continual exchange between the droplets. The exchange mechanism involves coalescence and fusion of the droplets upon collision, which then disintegrate into droplets. This exchange process occurs continuously in the microemulsion [75, 77]. If two reactants, A and B, are dissolved in the aqueous core of two identical water-in-oil microemulsions I and II, upon mixing they will form a precipitate, AB. It was proposed that the growth of these particles in microemulsions involves interdroplet exchange and nuclei aggregation [78]. A schematic diagram for the preparation of TiO_2 particles in microemulsion is shown in Fig. 10.

Synthesis of nanoparticles using reactions in microemulsions was first reported by *Boutonnet* et al. [79] when they

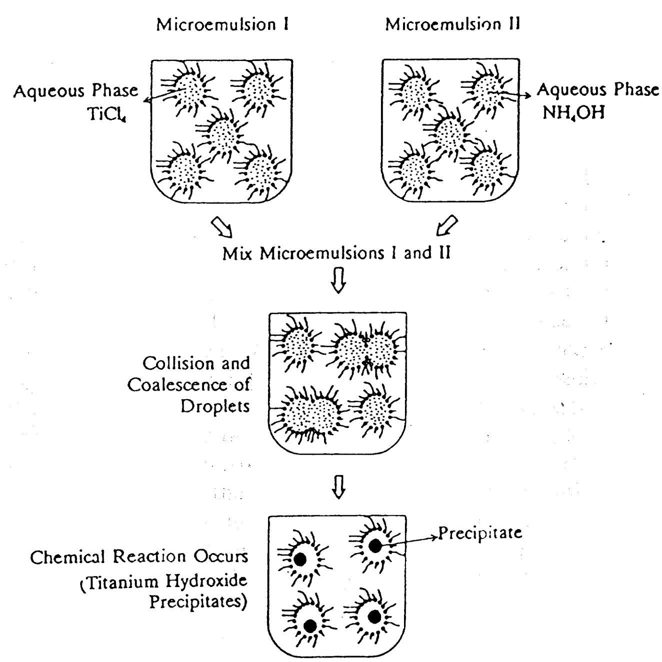

Fig. 10. Schematic diagram for the preparation of TiO_2 particles in a microemulsion

produced monodispersed metal particles of Pt, Pd, Rh and Ir by reducing corresponding salts in water micropools of water-in-oil microemulsions with hydrazine or hydrogen gas. Since then, there have been several reports in literature where microemulsions have been used for the synthesis of a variety of nanoparticles.

Metallic nanoparticles and metal clusters have a wide range of applications, including their use in catalysis and magnetic fluids. *Touroude* et al. [80] synthesized bimetallic particles of platinum and palladium by reduction of H_2PtCl_6 and $PdCl_2$ in a microemulsion. Colloidal silver and gold particles have potential applications as condensers for electron storage in artificial photosynthesis. These particles have been successfully prepared by several researchers [81–83].

Colloidal semiconductor particles, especially cadmium sulfide, are of great interest due to their unique photochemical and photophysical properties. It has been observed that these properties are very much size dependent. Several researchers have therefore synthesized such nanoparticles using microemulsions. *Meyer* et al. [84] have generated platinized colloidal cadmium sulfide *in situ* in AOT based microemulsions. Several studies have recently been published on the synthesis and growth of cadmium sulfide [86–89], lead sulfide [90], and cadmium selenide particles [91]. Recently *Chang* et al. [92] have developed a new synthetic methodology for preparing 40–300 nm silica-cadmium sulfide nanoparticles, a new material with potential for nonlinear optics.

Colloidal particles of calcium carbonate, stabilized by surfactants, constitute an important class of additives for oils used in lubrication for internal combustion engines. This has been exploited for the synthesis of calcium carbonate [93–95] and barium carbonate particles [96] by carbonation of their respective salts or hydroxides in the aqueous cores of water-in-oil microemulsions.

Using the aqueous core of water-in-oil microemulsion droplets as microreactors, several authors reported the preparation of various other particles having technological importance. A group in Belgium led by *Nagy* [97] prepared ultrafine particles of different insoluble metal compounds (particularly borides), which have application in heterogeneous catalysis. $Al(OH)_3$ particles are reported by *Matson* et al. [98]. The particle size was found to be considerably larger than the micellar diameter. This has been attributed to the partial coalescence of precipitated nuclei due to rapid exchange of electrolytes of the micellar core. *Hirai* et al. [99] reported the mechanism of formation of CdS and ZnS nanoparticles in AOT reverse micelles, which they investigated using UV spectra. It was observed that in the beginning the particle coagulation rate constant was dependent on the intermicellar exchange rate. However, as the particle diameter approached to that of the water core, the coagulation depended on micellar size. *Kitahara* et al. [100] used surfactant containing organic media to produce and disperse magnetic particles. Silica nanoparticles have been prepared via base catalyzed hydrolysis of tetraethoxy-silane [101]. It has been shown that more monodispersed particles are formed on addition of benzyl alcohol as a cosurfactant. Ultrafine SiO_2 particles were also prepared by hydrolysis of tetraethoxy-silane [102]. The conditions of the drying and calcination process were found to influence the purity of the final product. Nanosized silver crystallites have been synthesized in AOT reverse micelles [103]. The study describes the dependence of various parameters such as micellar structure and the nature of the reducing agent on the size of particles.

In the recent years, a variety of nanoparticles have been sucessfully synthesized in our laboratories using various microemulsion systems. These materials are described in the following sections.

3.1 Magnetic particles

Finely divided magnetic nanoparticles are widely used in high density magnetic recording media. The magnetic oxides commonly used for magnetic recording are γ-Fe_2O_3, Fe_3O_4, cobalt modified Fe_3O_4, cobalt modified Fe_2O_3 and CrO_2 for longitudinal recording, and hexagonal ferrites such as $BaFe_{12}O_{19}$ for high density perpendicular recording. We showed for the first time that the concentration of the salt affects the size of the particles and the amount of γ-Fe_2O_3 in the final compound [2]. Recently we have shown that the yield of γ-Fe_2O_3 prepared through microemulsions depends on the size of the microemulsion droplets in which precursor has been precipitated as well as calcination temperature [104]. We have also reported the preparation of nanophase barium ferrite particles using aqueous as well as nonaqueous microemulsions [105–107].

3.2 High T_c superconductors

It is well recognized that the properties of high temperature superconductors are critically dependent on the microstructure of the sample. Control of particle size, size distribution and morphology of precursor particles are critical to obtaining a desired microstructure. One can achieve a better level of homogeneity and smaller particle sizes if the chemical reactions are carried out in constrained nanosize reactors, such as the aqueous cores of water-in-oil microemulsions. We have used water-in-oil microemulsions for the synthesis of Y-Ba-Cu-O (123) [2, 108] and Bi-Pb-Sr-Ca-Cu-O (2223) [109] superconductors. $YBa_2Cu_3O_{7-x}$ superconductor was synthesized by the co-precipitation of oxalates of yttrium, barium and copper in the aqueous cores of water/cetyl trimethyl ammonium bromide/1-butanol/octane microemulsion. Two microemulsions (each consisting of 29 wt.% surfactant + cosurfactant phase, 60 wt.% hydrocarbon phase and 11 wt.% aqueous phase), one containing aqueous solution of yttrium, barium and copper nitrates in the molar ratio 1:2:3 and the other containing ammonium oxalate solution as the aqueous phase, were mixed. This led to the precipitation of the oxalate precursors within the aqueous cores of the microemulsion. In order to compare the results we also prepared yttrium-barium-copper oxalate in bulk aqueous medium. The oxalate precursor thus formed was calcined and then sintered to produce 123 superconductor. We found that the microemulsion mediated superconductor had a superconducting transition temperature (T_c) of 93 K and showed 90% of Meissner shielding. The sintered disk had 98% theoretical density, which is due to the ability of nanoparticles to pack closely with very few voids. Upon sintering, these well packed particles are able to form large grains (15–50 mm) with very low porosity. On the other hand, the bulk coprecipitated sample showed a T_c of 91 K and a Meissner shielding of 14%. This can be explained by the fact that this sample was more porous (lower density) than the microemulsion synthesized sample due to the large size of precursor particles which resulted in smaller grains (0.5–2 mm) in the sintered pellets. SEM pictures of $YBa_2Cu_3O_{7-x}$ sintered pellets synthesized by conventional and microemulsion mediated reaction are shown in Fig. 11.

Recently, we have also used water-in-oil microemulsions for the synthesis of Bi-Pb-Sr-Ca-Cu-O (2223) superconductors [109]. A nonionic surfactant Igepal CO-430 or nonyl-

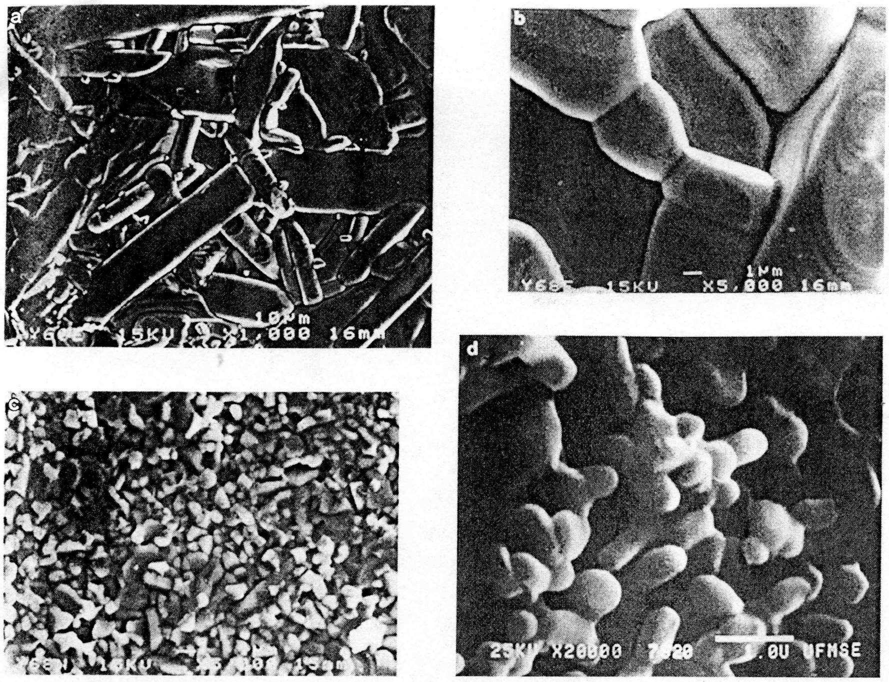

Fig. 11. Scanning electron micrographs showing the microstructure of sintered $YBa_2Cu_3O_{7-x}$ pellets synthesized by the microemulsion-mediated reaction (a, b) and the conventional aqueous reaction (c, d). The magnification used were (a) 1000 (b) 5000 and (d) 20000

phenoxypoly (ethyleneoxy) ethanol was used for the formation of microemulsions with cyclohexane as the oil phase. The aqueous phase in the first microemulsion was a solution of salts of Bi, Pb, Sr, Ca, Cu in the molar ratio 1.84:0.34:1.91:2.03:3.06 dissolved in a 50/50 (v/v) mixture of acetic acid and water. The aqueous phase in the second microemulsion was a solution of oxalic acid in a 50/50 (v/v) acetic acid and water mixture. Both the microemulsions consisted of 15 grams of surfactant, 50 ml of oil and 10 ml of aqueous phase. Mixing of these two microemulsions led to the formation of the oxalate precursor within the aqueous cores of the microemulsion. These precursors were in the range of 2–6 nm as shown in Fig. 12. These oxalate particles were calcined at 800 °C for 12 hrs and then pressed into a pellet and sintered in air for 96 hours at 850 °C. The sintered disk had very low porosity and had a density corresponding to 97 % of the single crystal density value.

Thus, we have shown that nanoparticles of superconductors precipitated through microemulsion mediated systems are superior to those synthesized by most wet chemical methods.

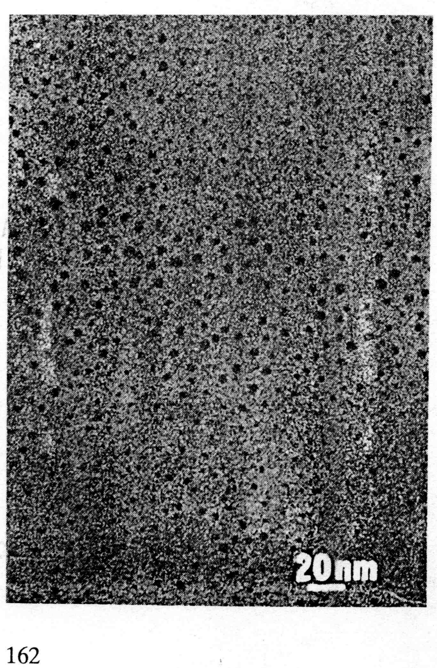

Fig. 12. Transmission electron micrograph of oxalate precursor powder

3.3 Silver halides

Nanoparticles of silver halides are extremely important for applications in photographic emulsions. It is however, difficult to obtain nanosize, monodispersed particles of silver halides by conventional methods. Nanoparticles of AgBr [110] and AgCl [111] have been synthesized ***in-situ*** using water/AOT/alkane microemulsion systems. It has been found that an increase in alkane chain length results in (a) higher growth rate for AgCl particle formation, and (b) decrease in the stability of microparticulate dispersion. The growth rate was found to increase with a decrease in alcohol chain length.

3.4 Electronic or semiconductor materials

A new process for the synthesis of ZnO [112] using microemulsions has been developed. The optimized microemulsion system consisted of the surfactant cetyltrimethyl ammonium bromide, 1-butanol as cosurfactant, n-octane as continuous oil phase, and aqueous solution as the dispersed phase. The ultrafine precursor powders result in highly dense zinc oxide nanoparticles with narrow size distribution. A comparison of properties of ZnO specimens produced (using same purity of material) by chemical, conventional and microemulsion routes showed that the microemulsion synthesis yields zinc oxide particles with the largest surface area, highest density and highest conduction at a particular voltage.

3.5 Paint and photocatalytic materials

Recently we prepared nanophase TiO_2 particles [113] using water/Tx-100/hexanol/cyclohexane microemulsion. It has been shown that attenuation of ultraviolet radiation decreases as the calcination temperature increases (or particle size decreases) as shown in Fig. 13. We have also shown that only the anatase form of TiO_2 particles acts as photocatalyst for photodegradation of phenol and the rutile form is totally inactive for this reaction as shown in Fig. 14.

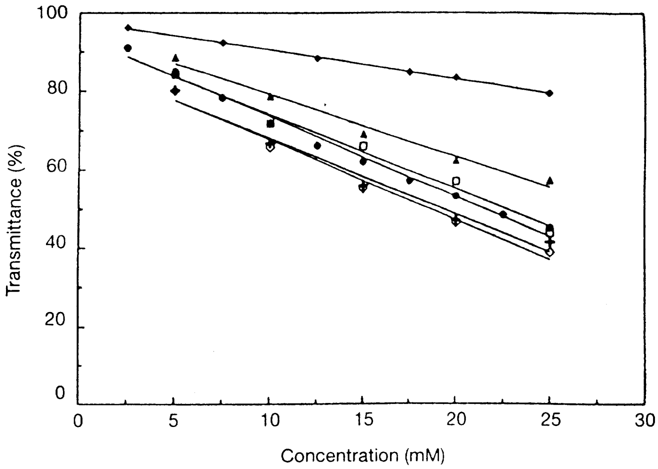

Fig. 13. UV transmittance measurements of solutions with suspended TiO_2, particles calcined at different temperatures: (◇) precursor, (+) 200, (□) 400, (●) 600, (▲) 800, and (◆) 1000°C

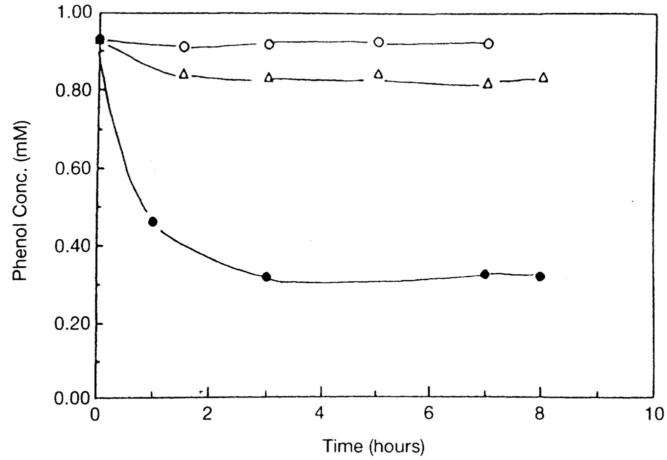

Fig. 14. Photodegradation of phenol (1 g/l of phenol solution, 0.02 % w/v in water) in the presence of (○) rutile TiO_2 particles, (●) anatase TiO_2 particles and (△) TiO_2 particles without catalyst

3.6 Latex nanoparticles

In the past, emulsions have been used to produce polymer latex particles for use in applications such as paints, paper coatings, biomedical applications and textiles. However, microemulsions offer several advantages over emulsions in the production of latex particles such as higher surface area due to smaller droplet size, higher stability, smaller particles and optical transparency. The property of optical transparency, which results from the small microemulsion droplet size, allows latex particles to be synthesized using photochemically induced polymerization. The small size of latex particles produced in microemulsions may also be useful for drug delivery systems in which it is believed that smaller latex particles (10–20 nm) may be effective [114]. Microemulsions have been used to produce polystyrene, methyl methacrylate, and other functionalized microlatex particles [115–117].

4 Microemulsions in other technologies

4.1 Pharmaceutical and cosmetic technology

In the past, micellar solutions and emulsions have been widely used in pharmaceutical and cosmetic products. The disadvantage for micellar solubilization is the limited solubilization capacity. The major disadvantage of emulsions is their instability. Until the early 1980s, despite the many new potential applications for microemulsions in the fields of science and technology, very few researchers have explored the possibilities of using microemulsions for pharmaceutical and cosmetic applications. In 1981, *Jayakrishnan* and coworkers [118] successfully produced a microemulsion using only pharmaceutically acceptable surfactants and hexadecane oil. Since then, microemulsions have been used in place of emulsions. Some of the advantages that microemulsions have over emulsions are their higher surface area, thermodynamic stability (i.e. infinite shelf-life), ease of preparation and higher diffusion and absorption rates through skin. Because of the small droplet size and biocompatibility of the components, immunoreactions or fat embolisms should not be a problem [119].

One example of the current research on the use of microemulsions in pharmaceuticals is oral delivery of therapeutic peptides [120, 121]. Oral dosage form is the most preferred method for most patients. However, bioavailability (the fraction of drug that actually reaches the systemic circulation intact) is very low by this method and therefore higher dosage is necessary which results in higher toxicity and higher cost to the patients. Formulations using microemulsions can lead to higher clinical potency and decreased toxicity [122]. One such use is in the formulation of cyclosporin, an immunosuppressant peptide. A preliminary study by *Drewe* and coworkers [123] showed that the microemulsion formulation has 49 % higher absorption than the maize oil in a soft gelatin capsule formulation. Another study on the same formulation showed that the influence of fat-rich meals on the rate and extent of absorption is less pronounced [124]. Another application is in the optimization of blood substitutes. Microemulsions were used to solubilize highly hydrophobic fluoroalkanes which are used as plasma substitutes [125].

In most cosmetic applications such as skin lotions, emulsions are widely used with water as the continuous phase. It is believed that microemulsion formulations will result in faster uptake into the skin. However, *Friberg* [126] has shown that the rate of uptake into the skin is not dependent on the initial state of the formulation. It is dependent on the structural form as the water evaporates from the skin.

4.2 Chemical reactions

Polymerization of styrene and other water insoluble monomers in microemulsions are described in the section under nanoparticles. The focus of this section is the use of microemulsions in biochemical reactions, electrochemical and electrocatalytic reactions and organic reactions. Enzymes are used as biocatalysts in many technological processes because of their catalytic activity and substrate specificity. Many researches have shown that these reactions can be carried out in microemulsions [127–131]. By dissolving the enzyme in water-in-oil microemulsions, the enzyme is protected from the denaturing effects of the organic solvents (oil). Other advantages of a microemulsion system are its unique solubilizing power and high interfacial area. Microemulsions provide an opportunity to study enzymatic reactions using substrates which are oil soluble (or commonly not soluble in water). In this case, the reaction takes place at the oil/water interface of the water droplets. Enzymatic reactions in water-in-oil microemulsions have also been used for the production of monoglycerides [132] and steroids [133], and for the esterification of butterfat [134].

Bicontinuous microemulsions of surfactant/oil/water have been used in the study of decomposition of polychlorinated biphenyl (PCBs) by electrochemical catalysis. In electrochemical catalysis, a rapid mass transfer of the materials to the electrodes is essential. Bicontinuous microemulsions are excellent fluids for mass transport in this type of reaction because the "molecules and ions travel along the respective oil and water conduits in the network" [135]. The study shows that catalytic electrolytic dechlorination with bicontinuous microemulsions is technically feasible but cost is a factor.

One of the big advantages of using microemulsions in organic reactions is in the reaction of a water-soluble reactant with a water-insoluble reactant. Microemulsions allow both of these components to be solubilized simultaneously so that vigorous mechanical agitation is not necessary. It has been used as the media for many types of organic reactions such as oxidation/reduction and nitrations of aromatics [136].

4.3 Cleaning technology

The basic properties of microemulsions that lead to enhanced oil recovery also apply to oil removal from fibrous materials. The large interfacial area and ultra-low interfacial tensions found in microemulsions make them ideal for removing oil from fibrous materials such as clothing. In one study, results showed that a microemulsion consisting of water, pentanol, sodium hexadecyl sulfate and the oil solubilized from soiled cotton leads to a cleaning effect that was approximately 15% better than other surfactant systems that did not form microemulsions [119]. It has been reported that the use of microemulsions also results in less redeposition than conventional surfactant solutions [137]. Microemulsions are particularly attractive cleaning agents for heavily soiled sections of material, where high solubilization is required and redeposition is more likely to occur. Also, microemulsions may provide a more environmentally-acceptable alternative to some of the currently applied solvent cleaners.

4.4 Environmental remediation and detoxification

Research has shown that microemulsions are very effective in environmental remediation. Microemulsions can be used to remove toxic hydrocarbon substances from soils in the same way as additional oil is extracted from oil reservoirs as mentioned previously in the enhanced oil recovery section of this paper. Other uses for microemulsions in remediation include detoxification of mustard compounds. *Menger* and *Elrington* [138] have shown that half-mustard can be oxidized to nontoxic sulfoxides by hypochlorite in 15 seconds using an oil-in-water microemulsion made from water, heptane, Aerosol-OT, and 1-butanol. Other research in this area shows the usefulness of microemulsions in detoxifying pesticides in a continuous-flow, two-phase microemulsion reactor. *Komives* et al. [139] have recently shown that a continuous centrifugal reactor can be used with either a Windsor I (microemulsion in equilibrium with a lighter bulk organic phase) or a Windsor II (microemulsion phase in equilibrium with a heavier bulk water phase) system to degrade pesticides. This technique has the potential for application in a number of related fields that currently utilize membrane-type extraction/reaction systems [139].

4.5 Combustion technology

Water in fuel microemulsions have been sucessfully used to reduce soot formation [140]. It is believed that the presence of microdroplets of water in the flame results in rapid water vaporization and the formation of free radicals that contribute to more effective burning of the hydrocarbon fuel. As a result of the more efficient burning, the soot formation is reduced. Other research indicates that microemulsions in fuels improve air-fuel contact and increase the flash point of the fuel [141]. Other research in this area has resulted in two patents [142, 143].

4.6 Food technology and agricultural sprays

Microemulsions have a variety of applications in the food and agricultural industries. In the agricultural industry microemulsions can be used to apply herbicides [144] as well as pesticides [145]. The use of microemulsions allows excellent dispersion of the pesticides and herbicides as well as excellent spreading onto plant surfaces due to low surface and interfacial tensions. Recent research also shows that microemulsions of carnauba wax form better protective coatings on citrus fruit than shellac, wood resin, oxidized polyethylene or mixtures of these substances with carnauba wax [146]. The protective coatings minimize weight loss as well as internal oxidation. Also, the fruit coated with the microemulsion of carnauba wax maintains a better appearance than other coatings after washing and drying [146]. Microemulsions have also been used to produce glycerides for application in food products [132, 147]. Although considerable research has been conducted to show the usefulness of microemulsions in edible food products using edible surfactants, the application of this technology will likely require additional research [148].

4.7 Corrosion and cutting oil technologies

Reverse micellar solutions or microemulsions have been used as corrosion inhibitors for several decades. Surfactants such as petroleum sulfonates are dissolved in motor oil so that they can solubilize corrosive oxidation products and keep them from corroding engine parts. The metal surface is also coated with a hydrophobic surfactant film which also keeps it from corroding. It is reported, however, that solubilization is selective and in some cases, other mechanisms might play a role in corrosion prevention [137]. Since water has a much higher thermal conductivity, addition of water to mineral oils leads to a solution with higher heat capacity than mineral oil alone. Such formulations can be used in cutting oil where two effects are desired: the oil lubricates the cutting surface and the water helps to remove the frictional heat generated in the cutting process. For both of these applications microemulsions have been used instead of macroemulsions because of their higher stability.

4.8 Coatings and textile finishing

Water-based emulsion paints and coatings are desirable because they are environmentally friendly. Researchers have been looking at the possibility of using microemulsions instead of emulsions as coating media. Due to their stability and small droplet size, microemulsions are ideal for this type of application where stability and homogeneity of the finished product is desired. Paint formulations using microemulsions showed higher scrub resistance, better color intensity and more stain resistance than those prepared by emulsions [149].

Barni and colleagues [150] studied the dyeing of nylon-6,6 with an azo dye using a microemulsion system and concluded that greater homogeneity in dyeing was achieved when compared with conventional dyeing aids. More importantly, homogeneity increased at lower dyeing temperatures and thus energy consumption was less. Another application is the use of microemulsions to prepare finely dispersed finishes. Using microemulsion prepared finishes containing siloxane, *Agster* [151] has shown that the resulting properties are much better than those prepared by conventional methods. Some of the improved properties are higher stability, better surface smoothness and increased abrasion resistance.

4.9 Analytical applications

Microemulsion applications have extended to the field of analytical techniques. Water-in-oil microemulsions as the mobile phase in normal liquid chromatography has recently been investigated because of their unique solubility capability [152, 153]. They have shown that selectivity could be achieved but only with poor efficiencies. *Berthod* and *De Carvalho* [154] also explored the use of oil-in-water microemulsions as the mobile phases in reverse-phase liquid chromatography. Again, the selectivity is good but efficiency is low. In addition, microemulsions have been studied as a possible solvent for laser-excited multiphoton photoionization spectroscopy. The drawback of the current use of polar liquid solutions as the solvents is the high noise level. It has been shown that a microemulsion system can improve the root-mean-square noise level by as much as 30 times [155]. However, the desired signal is also reduced due to an unknown mechanism. Despite the signal reduction, it was reported that for test compounds, significant improvements in linearity and precision were achieved with the microemulsion system. Finally, microemulsions are used in an effort to characterize solute hydrophobicity by electrokinetic chromatography [156]. Microemulsion electrokinetic chromatography (MEEKC) provides a quick and reproducible method to obtain hydrophobic parameters for solutes and possibly for biological hydrophobic parameters as well.

4.10 Microporous media synthesis

The unique properties of microemulsions have been utilized to produce microemulsion-gel glasses and microporous media with high surface areas. Using a sol-gel type process that utilizes a microemulsion, organic additives can be dispersed homogeneously throughout a final glass product [157]. Glass products developed in this manner have potential applications as solid-state dye-laser materials, luminescent solar concentrators and particle detectors [157]. Using bicontinuous microemulsions made using didodecyldimethylammonium bromide, which has a large bicontinuous phase stability region, polymerization reactions have produced a relatively continuous medium with marginal success [158]. In another study, a microporous calcium phosphate material was synthesized using a bicontinuous microemulsion [159]. These polymeric, microporous media may be useful in filtration and absorption applications.

5 Conclusions

The uses of microemulsions range from enhanced oil recovery to nanoparticle synthesis. The number of applications for microemulsions is increasing at a rapid pace due to their unique properties. This paper provides only a glimpse at the possible applications of microemulsions as an emerging technology with numerous proven uses and countless opportunities.

Acknowledgments

The authors wish to express their thanks and appreciation to Alcon Laboratories, Inc., The Procter & Gamble Company, Kraft Corporation, General Foods Corporation, Kimberly-Clark Corporation, National Science Foundation Grants (CPE 8005851, and CTS 9215384), National Science Foundation-Engineering Research Center (Grant No. 9402989) at the University of Florida, and to all former students and post-doctoral associates who carried out the research that is presented in this paper. It should also be noted that the enhanced oil recovery research was supported by the National Science Foundation, the U.S. Department of Energy and a consortium of the following companies: 1) Alberta Research Council, Canada, 2) American Cyanamid Co., 3) Amoco Production Co., 4) Atlantic-Richfield Co., 5) BASF-Wyandotte Co., 6) British Petroleum Co., England, 7) Calgon Corp., 8) Cities Service Oil Co., 9) Continental Oil co., 10) Ethyl Corp., 11) Exxon Production Research co., 12) Getty Oil Co., 13) Gulf Research and Development Co., 14) Marathon Oil Co., 15) Mobil Research and Development Co., 16) Nalco Chemical Co., 17) Phillips Petroleum Co., 18) Shell Development Co., 19) Standard Oil of Ohio Co., 20) Stepan Chemical co., 21) Sun Oil Chemical Co. 22) Texaco, Inc., 23) Union Carbide Corp., 24) Union Oil Co., 25) Westvaco, and 26) Witco Chemical Company.

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