

## MICROEMULSIONS : AN OVERVIEW

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### ABSTRACT

In the past twenty five years, microemulsions have been the focus of extensive research worldwide due to their importance in a variety of technological applications. These applications include enhanced oil recovery, combustion, cosmetics, pharmaceuticals, agriculture, metal cutting, lubrication, food, enzymatic catalysis, organic and bio-organic reactions, chemical synthesis of nanoparticles etc. The basic purpose of this review is intended to provide the most important features of microemulsions and their applications. Emphasis is placed on recent works, however, the reference list is by no means complete. In order to limit the size of the review, a more or less arbitrary selection has been made with respect to examples chosen from literature.

The review is started with a brief introduction and focussed with definition, structure, type, formation characteristics, stability, phase behavior and the effect of additives, pressure, temperature on the phase behavior of microemulsion. In addition, the physicochemical properties, state of water in the micropool, transport (electrical and hydrodynamic) behaviors, thermodynamics of formation, solubilization parameters, and uses and applications of microemulsions have been briefly presented.

## INTRODUCTION

The ancient concept that water and oil do not mix, has undergone modification. If some energy is added on a oil / water system in the form of stirring or other mechanism, a very unstable dispersion of one into the other results, which quickly reverses to the native state if the system is allowed to relax. The increase in interfacial area during dispersion is in conformity with the thermodynamic principle of nonspontaneous formation of surface (or interface). Addition of a third component may either increase or decrease the mutual solubility of two partially miscible liquids.<sup>1</sup> If the third component is a surfactant, it reduces the interfacial tension between the pair of immiscible liquids, enabling them to be dispersed between each other.<sup>2</sup> Depending on the proportion of the components, either water-in-oil (w/o) or oil-in-water (o/w) dispersions are produced (Fig. 1a). These macrodispersions (called emulsions having dimension 0.2-10 $\mu$ m) are turbid and may remain stable for a considerable length of time; they are thermodynamically unstable but kinetically stable.<sup>3</sup> Schulman and Hoar<sup>4</sup> have observed that in presence of short chain alkanols (c.g butanol, pentanol, hexanol, etc), the emulsions transform into solutions having particles of much smaller dimensions (~10nm). They are called microemulsions<sup>5</sup> ( $\mu$ E) which do not, in principle require any mechanical work for their formation. Such preparations are homogeneous, optically isotropic, low viscous and thermodynamically stable dispersions of either oil in water or water in oil (Fig.1b).

The spontaneous formation of  $\mu$ E suggests the free energy change to become negative in accordance with the thermodynamic requirement,

$$-\Delta G = \gamma_{o/w} \Delta A \text{ ----- (1)}$$

where  $\gamma_{o/w}$  is the interfacial tension between oil and water and  $\Delta A$  is the change in surface area due to emulsification. Since  $\Delta A$  is always positive,  $\gamma_{o/w}$  requires to be negative. A very small  $\gamma_{o/w}$  value is also sufficient to form a stable dispersion with slightest agitation; the kinetic energy of the molecules is sufficient to achieve the dispersion. Depending on the nature of the oil, surfactant, cosurfactant and temperature as well as their proportion, the mixture can exhibit the following distinct features proposed and experimentally demonstrated by Winsor<sup>6</sup> (Fig.2).

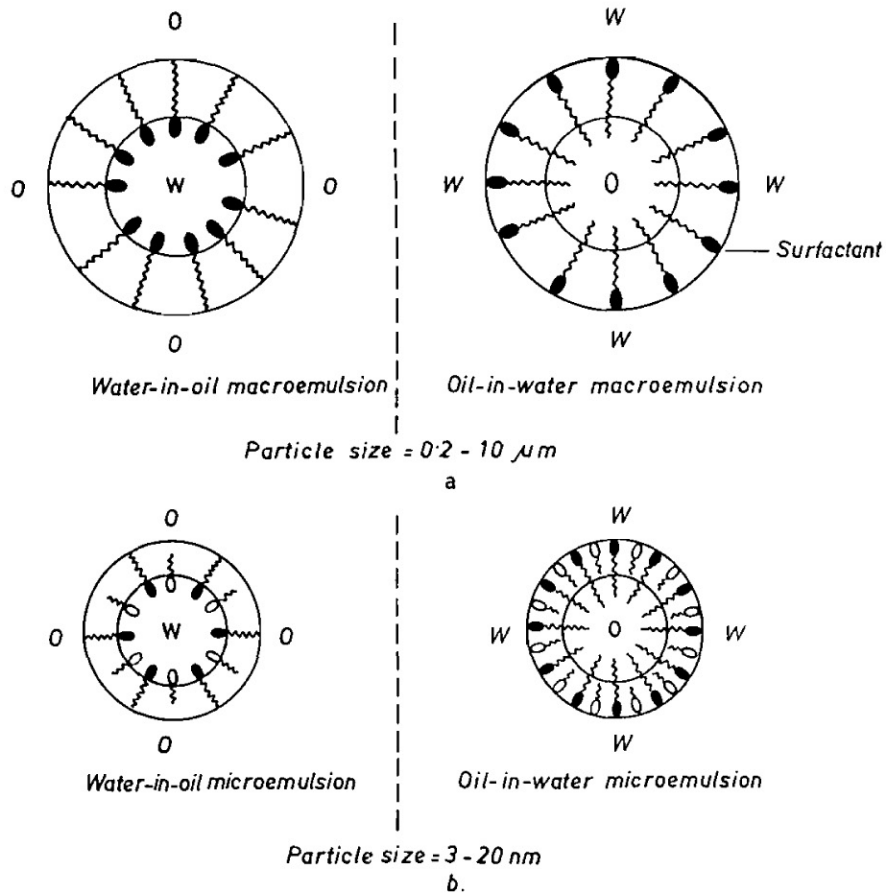


Fig : 1 (a) Structural features and particle size of macroemulsion.

(b) Structural features and particle size of microemulsion.

(1) Two phases, the lower  $\mu E$  phase in equilibrium with the upper excess oil (Winsor type I).

(2) Two phases, the upper  $\mu E$  phase in equilibrium with the lower excess water (Winsor type II).

(3) Three phases, middle microemulsion phase in equilibrium with upper excess oil and lower excess water (Winsor type III).

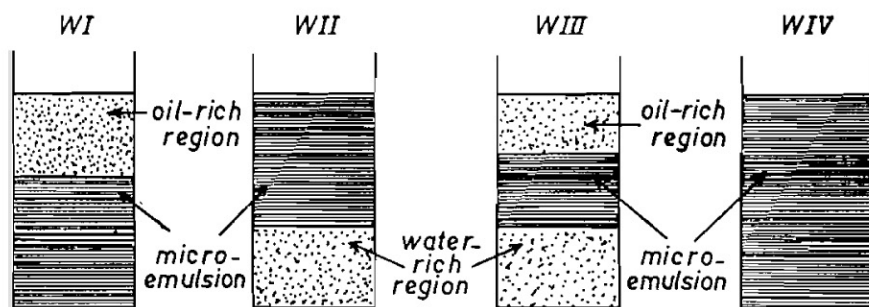


Fig : 2 Winsor classification of the system.

(4) Single phase, oil, water and surfactant are homogeneously mixed (Winsor type IV).

In certain conditions, even a four phase ( $4\phi$ ) solution<sup>7-9</sup> with two microemulsion phase may arise. The interfaces of the multiphase solutions have different tensional characteristics. Special experimental technique (spinning drop method)<sup>10</sup> is required to determine the low interfacial tensions. Healy et al<sup>11</sup>. have used sessile drop technique for such measurements. Depending on the nature of the components and environmental conditions, isotropic lamellar, liquid crystalline and viscous phases may also result.<sup>12-18</sup>

#### Definition and Structure

There has been much debate on the use of the term "microemulsion" ( $\mu E$ ). The term "swollen micelles" and "solubilized micellar solutions"<sup>6,19</sup> have been introduced to describe precisely the same systems as those called microemulsions ( $\mu E$ ) by Hoar and Schulman<sup>5</sup>. The accepted definition reads, a  $\mu E$  is defined as a system comprising mixture of water, hydrocarbons and amphiphilic compounds forming thermodynamically stable, homogeneous (heterogeneous in molecular scale), optically isotropic solutions<sup>3,20-34</sup>. The term amphiphiles makes the definition versatile for small chain alkanols (called cosurfactants) may not be always an essential requirement<sup>35</sup>; for example, the



surfactant aerosol orange T (AOT) may form  $\mu\text{E}$  in absence of a cosurfactant. Detergentless  $\mu\text{E}$ s are also possible; for example hexane, water and 2-propanol<sup>36</sup> or toluene, water and 2-propanol or 2-isobutoxyethanols/water/decane<sup>37</sup> may yield  $\mu\text{E}$  in absence of surfactants.

$\mu\text{E}$  may be contrasted with critical solution. In the latter, two partially miscible liquids completely mix at a higher temperature or at two temperatures, one higher and the other lower called the critical solution temperature (s). In critical solution unlike microdispersions as in  $\mu\text{E}$ , the mixed solvents are molecularly dispersed and complex formation between them may take place. There is no requirement of a third component (normally an amphiphile) for augmenting the processes.

In excess of oil, the  $\mu\text{E}$  is oil continuous and in excess of water it is said to be water continuous. At equiproportion of water and oil the  $\mu\text{E}$  is known as 'bicontinuous'<sup>38-41</sup>. In all the types, the amphiphile molecules reside in the interfacial region between the two liquid domains<sup>42-45</sup>. On incorporation of macroscopic amount of surfactant, the system may become anisotropic and liquid crystalline by the generation of some random globular or tubular structures<sup>46</sup>. The bicontinuous type is a spongelike random network<sup>47</sup>.

#### Type of Microemulsion

$\mu\text{E}$  can be of different categories. Besides normal type, there can be polar oil  $\mu\text{E}$ s<sup>17,48</sup>, polymer oil  $\mu\text{E}$ s<sup>49,50</sup>, biological and other types of  $\mu\text{E}$ s<sup>31-34</sup>. The latter type has been recently reported by Kunieda et al.<sup>51a,b</sup> and Moulik et al.<sup>52</sup> Phase behaviors at different temperatures of water/multisurfactant system (viz homogeneous polyethyleneglycol dodecyl ether,  $\text{R}_{12}\text{EO}_n$  and sucrose fatty acid esters, a biocompatible surfactant) /heptane have been recently investigated by Kunieda et al.<sup>53</sup>. Chemical and biological compounds can be added to suit a specific purpose. Since biological membranes contain proteins, carbohydrates, lipids etc., the addition of such compounds into the  $\mu\text{E}$  has the prospect to develop model biological  $\mu\text{E}$ . By the term biological  $\mu\text{E}$ , we mean systems where ingredients are biologically compatible as well as biologically relevant. They are expected to be used as models for the study of processes of biological relevance. Biological  $\mu\text{E}$ s are important addition in the normal stream. Their formulations

are so far reported by Moulik et al.<sup>52</sup>. keeping wide scope for further research. AOT, sodium deoxycholate and TX 100 were used as surfactants, dextran, gelatin, bovine serum albumin, brine, cholesterol were used as additives and hydrocarbons, vegetable oils including eucalyptus oil, clove oil and cinnamic alcohol were used as oils. It is proposed that homogenisation of vegetable oils with biocompatible amphiphiles may form biological  $\mu$ Es having keen relevance to pharmacy and medicine. Recently Kunieda et al.<sup>51b</sup> studied the phase behavior of polyoxyethylene hydrogenated castor oil (HCO IO, biocompatible and non-toxic oligomer-type non-ionic surfactant) in the oil/water system at different temperatures. Three different oils were used, a polar oil (TEH), hexadecane and n-octane. These type of  $\mu$ Es find applications in pharmaceuticals, cosmetics, toiletries etc. The microemulsification of hydrocarbons by biological amphiphile (lecithin-based  $\mu$ E) was first reported by Shinoda and Kaneko<sup>51c</sup> in 1988. Later on, the phase behavior, and effect of alcohols, temperature and the chloride on it have been reported by several investigators<sup>54</sup>. The microstructure of  $\mu$ E was also investigated from molecular self-diffusion coefficients measurements.  $\mu$ E stabilized by soybean lecithin and ethanol has been characterized by Backlund et al.<sup>55a</sup> with respect to phase behavior, distribution of ethanol cosolvent, conductivities, viscosities and volume fraction of different phases in Winsor III systems. They reported that the reaction yield at 298.5K for enzymatic conversion of cholesterol to cholestenone by cholesterol oxidase performed in lecithin-based  $\mu$ E was low. The structural investigation of water/lecithin/cyclohexane  $\mu$ E by FT-IR spectroscopy has also been reported by Cavallaro et al.<sup>55b</sup>

Quite recently a number of nonaqueous  $\mu$ Es have been reported independently by different groups replacing water by solvents like glycerol, ethylene glycol, propylene glycol, formamide and other amides. For example, Friberg et al. have reported phase diagrams for the systems glycerol/xylene/triethanol ammonium oleate and oleic acid<sup>56</sup>, ethylene glycol/decane/lecithin<sup>57</sup>, glycerol/ alcohol/ surfactant/ oil using various surfactants and oils<sup>58</sup>. Fletcher et al.<sup>59</sup>. have reported a system of glycerol/ heptane/ AOT. Formamide/ butanol/ cyclohexane/CTAB and formamide/ butanol/isooctane/CTAB systems have been reported by Rico et al.<sup>60,61</sup> and they have also prepared

perfluorinated  $\mu\text{E}$ <sup>62</sup> using different perfluorinated alcohols, oils and surfactants. Bergenstahl et al<sup>63</sup> have used various solvents including formamide with an anionic amphiphile. Warnheim and Sjöberg<sup>64</sup> have used formamide with a nonionic amphiphile and Martino and Kaler<sup>65</sup> have used mixture of propylene glycol and glycerol with nonionic amphiphile. Kahlweit et al. have reported nonaqueous  $\mu\text{Es}$  of formamide with nonionic amphiphiles<sup>66,67</sup> and ionic amphiphiles<sup>68</sup>. Lindman et al<sup>69</sup> have presented nonaqueous  $\mu\text{Es}$  of formamide, alcohol and SDS in both the presence and absence of an oil, xylene; the alcohols used were 1-butanol; 1-pentanol, 1-hexanol, 1-heptanol and 1-octanol. Structureless nonaqueous  $\mu\text{Es}$  using N-methylformamide and N,N-dimethylformamide have also been reported. Friberg et al.<sup>70</sup> reported  $\mu\text{E}$  using ammonia as solvent, decane as oil. Phase behaviour of nonaqueous  $\mu\text{E}$  formed from formamide with ethylene glycol, 1,2-propylene glycol, 1,3-butylene glycol, glycerol with cationic, anionic and nonionic surfactants using p-xylene as oil and n-pentanol as cosurfactant have been reported<sup>71</sup>. Recently Dorfler et al.<sup>72</sup> have reported a variety of quaternary and ternary systems of the type, dodecane/aliphatic alcohols/SDS/water or a water-replacing component (viz. formamide, ethylene glycol, propylene glycol, propylene carbonate, DMSO, acetonitrile), and appertaining phase diagrams were plotted and compared with those for aqueous systems. Ray and Moulik<sup>73</sup> have made a detailed investigations on phase behaviors, conductance and viscosity of nonaqueous  $\mu\text{E}$  employing formamide, dimethyl formamide, dimethyl acetamide, ethylene glycol and propylene glycol as polar media, heptane, octane, isooctane, xylene and toluene as oils and AOT as the amphiphile.  $\mu\text{Es}$  with light alkanes (ethane, propane, butane etc.) and nonionic ethoxylated surfactant have also been reported by McFann et al.<sup>74</sup>

#### Formation Characteristics

The characteristics of  $\mu\text{E}$  depends on a number of factors: intra-molecular, intermolecular and environmental, the details of which is only limitedly understood. The main characteristic features of formation are discussed below:

### Emulsifier Selection

#### The Hydrophile-Lipophile Balance (HLB) Scheme

For  $\mu$ E formation, no amount of work may be required when the combination or chemistry is correct and the selection of emulsifier is decisive. In general emulsifier selection for  $\mu$ Es, an emulsifier is matched by its calculated HLB number with the required HLB of the oil to be emulsified<sup>75</sup>. HLB is essentially an empirical property for quantifying the surface activity<sup>76,77</sup> of a species based on its molecular constitution.

The HLB per se has less importance for  $\mu$ Es than for emulsions, but the effects by Graciaa et al.<sup>78</sup> Shinoda et al.<sup>79</sup> and Robbins et al.<sup>80</sup> to establish the relationship between surfactant HLB and  $\mu$ E phase behaviors (Fig. 3) should be noted.

#### Theories of Microemulsions Formation and Stability

Theories of  $\mu$ E formation are classified into three main categories. The interfacial or mixed film theory has been introduced by Schulman et al.<sup>81,82</sup> and Prince<sup>83</sup>. The second theory is the solubilization theory proposed by Shinoda, Friberg and collaborators<sup>29,84</sup>. The third one is the thermodynamic treatment of Ruckenstein et al.<sup>85,86</sup>, Overbeck et al.<sup>87a</sup>, Israelachivilli et al.<sup>87b</sup>

#### Mixed Film Theory

In this theory, the interfacial film is considered as a duplex film having different properties on the water side and the oil side, where tension is,  $\gamma_T = (\gamma_{ow})_a - \pi$ , where  $(\gamma_{ow})_a$  is the o/w interfacial tension in presence of alcohol (cosurfactant hence the subscript a), and  $\pi$  is the spreading pressure of the mixed film.  $\pi$  is attached by the presence amphiphiles and penetration of the oil into the hydrocarbon part of the interface. With the expansion of the interface,  $\pi$  increases and  $\gamma_T$  tends to zero favoring dispersion.

#### Solubilization Theory

In the solubilization concept introduced by Gillberg et al.<sup>23</sup> Shinoda et al.<sup>29,84</sup>,  $\mu$ Es are considered as swollen micellar systems i.e with oil and water solubilized in normal or reverse micelles stemmed from the studies of three and

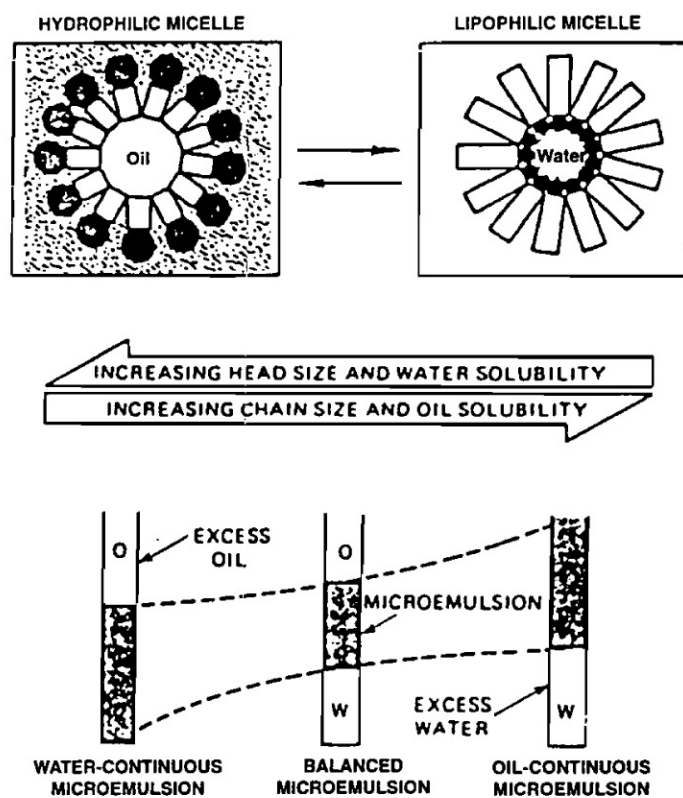


Fig : 3 The transition from a water-continuous to an oil-continuous microemulsion; dependence of interfacial curvature on hydrophile / lipophile ratio and relationship to phase behavior (Ref. 80).

four component phase diagrams on the one hand<sup>25,29</sup> and the solubilization studies of water and hydrocarbons by nonionic surfactants on the other.<sup>84,88</sup>

#### Thermodynamic Theory

The theory of Ruckenstein et al.<sup>83</sup> and of Overbeck<sup>87</sup> although have the same origin but they vary in the details. Ruckenstein et al.<sup>83</sup> treatment considers the free energy of formation of  $\mu E$ ,  $\Delta G_{\mu}$  to consist of 1)  $\Delta G_1$ , an

interfacial free energy term, 2)  $\Delta G_2$ , an energy of interaction between the droplets and 3)  $\Delta G_3$ , an entropy term accounting for the dispersion of the droplets into the continuous medium. The variation of  $\Delta G_m(r)$  with droplet radius  $r$ , and constant volume fraction  $\phi$  of the droplets is given by the relation.

$$\Delta G_m(r) = \Delta G_1 + \Delta G_2 - T\Delta S_m \dots\dots\dots(2)$$

and has been found to follow the transition from instability  $\rightarrow$  kinetic stability  $\rightarrow$  thermodynamic stability. Accumulation of surfactant and cosurfactant at the interface causes significant reduction in the interfacial tension, as well as reduction of their chemical potential in the bulk. The latter reduction may exceed the positive free energy caused by the total interfacial tension to make the overall  $\Delta G$  negative. The treatment of Ruckenstein et al.<sup>86</sup> has also highlighted the role of interfacial tension in the formation of  $\mu E$ . A negative dynamic interfacial tension may be possible, but at equilibrium,  $\sigma/w$  ends up with a small positive value.

Overbeek et al.<sup>87</sup> has also subdivided  $\Delta G_m$  into three contributions :  $\Delta G_1$ , the Gibbs energy of mixing of the constituents;  $\Delta G_2$ , the free energy of the formation of interface and  $\Delta G_3$ , the free energy of droplets into the continuous phase. The  $\Delta G_m$  has been given by the following expression.,

$$\Delta G_m = dA \left[ \gamma_{\text{uncharged}} + \int \Psi_0 d\sigma + \frac{A^2 kT}{12 \pi (n_w V_w)^2} \ln(\phi-1) + \phi \frac{4 - 3\phi}{(1-\phi)^2} \frac{V_0}{V_{hs}} + \ln \frac{V_0}{V_{hs}} \right] \dots\dots(3)$$

Where  $dA$  is the change in the interfacial area,  $\gamma_{\text{uncharged}}$  is the interfacial tension if no double layer is formed and  $\int \Psi_0 d\sigma$  is the electrical contribution to the interfacial tension as a result of formation of an electrical double layer ( $\Psi_0$  being the surface potential and  $\sigma$  the surface charge density). The third term in the brackets is the osmotic contribution due to mixing of  $\mu E$  droplets with the continuous medium with  $\phi$  as the volume fraction of the droplets (treated as hard sphere) and  $V_{hs}$  is their molar volume.

### Phase Behaviors

$\mu E$  systems are complex for their multicomponent composition. The mixed system may be isotropic or mesomorphic solutions and display a variety of complex multiphase equilibria. The understanding of their phase equilibria and demarcation of the phase boundaries are essential aspects of study. The

phase behaviors are recognised by drawing ternary or pseudo ternary phase diagrams on triangular coordinates in two dimensions, where each apex of the equilateral triangle represents one or a mixture of two components. In three dimensions, a four component system may be represented in a tetrahedron, each of four apexes representing one component. Typical examples of such representations are presented in (Fig.4). In this representation, the complex nature of the multicomponent systems is more realistic. For detailed features of various phase diagrams and phase behaviours, the text book of Alexander Findlay is referred<sup>89</sup>.

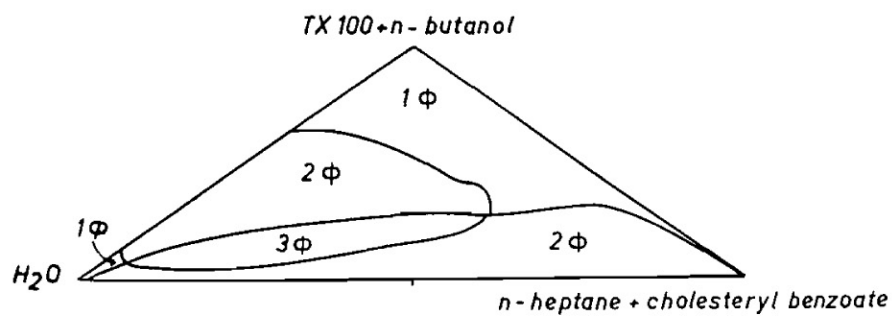
In three component systems, transition from W I to W II can occur through the appearance of an intermediate three phase. This is designated as W III; W III systems should exhibit a tie triangle within the phase diagram whose apexes must touch three  $1\phi$  regions. This ideal situation is hardly achieved in practice, particularly when one of the components is an amphiphile. Pseudo ternary phase diagrams of multicomponent systems may end up with elongated  $3\phi$  region that only touches two  $1\phi$  regions at the two ends.<sup>52,90-92</sup> This has been demonstrated and discussed by Bourrel and Schechter.<sup>93</sup>

The individual phases formed may have different consistencies over a region; thus there may appear a viscous or gel phase with isotropic and nonisotropic characters. A very careful experimentation is, therefore, required for mapping them accurately, which also significantly depends on the environmental conditions, viz, temperature, additives, etc. For working formulations of  $\mu E$ , a detailed phase behavioral study is essential, without which the consistencies and stability of a prepared solutions may become uncertain.

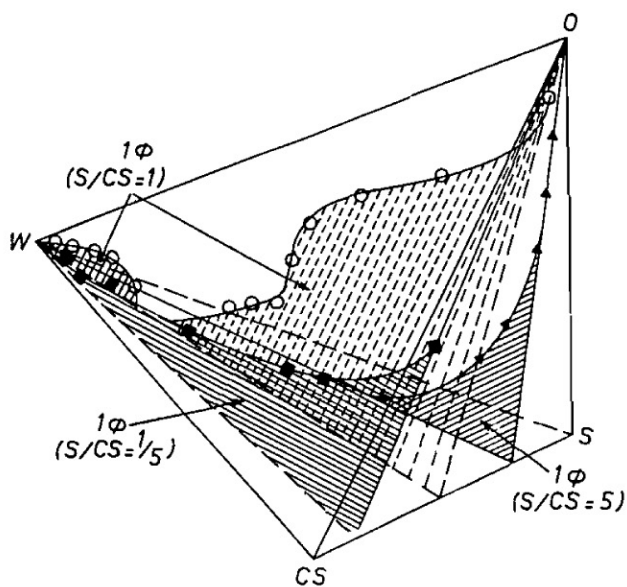
#### Effects of Additives and other Factors on Phase Behaviors

The structure and stability of  $\mu E$ s are greatly influenced by the presence of additives and thereby affecting their thermodynamics. The complex character of the interphase becomes further complex with ionic and nonionic additives.

Salts, especially, NaCl, can significantly affect the phase behaviors and structural properties of  $\mu E$ s.<sup>28,94-100</sup> Such studies have fundamental importance in



a.



b.

Fig : 4 (a) Phase diagram of TX100 + n - butanol, n - heptane + cholesteryl benzoate, water at 303K (Ref. 114a).

(b) Tetrahedral representation of the (cholesteryl benzoate, CB + n - heptane) / (TX100 + n - butanol) / water microemulsion phase at surfactant (S) / cosurfactant (CS) ratios 1:5, 1:1, 5:1 at 303K ( Ref. 114a).



the use of  $\mu$ Es in tertiary oil recovery,<sup>101-105</sup> where NaCl of considerable strength is commonly encountered. The nature of  $\mu$ E droplet may vary with salinity<sup>76,106</sup> and transition from o/w to w/o may occur with increasing salinity via a bicontinuous  $\mu$ E at an optimum salinity in many cases. This is a highly specific and notable effect in the study of  $\mu$ Es.

Bedwell and Gulati<sup>95</sup> have observed that the effects of electrolytes on w/o  $\mu$ Es are opposite to that on o/w; the electrolytes decrease interdroplet attraction rather than increase and it has been supported by time average fluorescence intensity measurements as well as shear viscosity measurements. The effects of lyotropic salts (salts which decrease solubility between water and surfactant, eg. NaCl, KCl etc.) and hydrotropic salts (salts which increase solubility between water and surfactant, eg. NaClO<sub>4</sub>, C<sub>6</sub>H<sub>5</sub>PCI etc.) on the phase behaviors of  $\mu$ Es have been studied in details by Kahlweit et al.<sup>96,107,108</sup> They have found that both types of salt can influence nonionic and ionic  $\mu$ E systems. They have also studied<sup>109a</sup> the phase behaviors of quintinary mixtures (water, oil, a nonionic amphiphile, an ionic amphiphile and salt) and their dependence on temperature, nature of components, ratio between nonionic and ionic amphiphiles and brine concentration. Recently, the effect of mixing surfactants on solubilization in a  $\mu$ E system has been reported<sup>109b</sup> and derived<sup>109c</sup> the theoretical equation to predict the three phase equilibria. Kaheweit et al.<sup>109d</sup> also presented the results on the effect of ionic surfactants on the phase behavior of mixtures of water, oil and nonionic amphiphiles, with the latter being the majority component in the mixture of two surfactants. Nieuwkoop et al.<sup>97</sup> have observed a three phase region in SDS/n-butanol / water (NaCl)/ heptane system and a significant effect of salinity on the size and shape of the three phase region. The effect of salinity on AOT derived systems has been investigated by Ghosh and Miller.<sup>110</sup> Luisi et al.<sup>111a</sup>, Eicke et al.<sup>111b</sup>, Robinson et al.<sup>111c</sup>, studied gelatin solubility in the waterpool of w/o  $\mu$ Es formed by AOT in n-alkanes and  $\mu$ E-based gelatin gels (MBG) were thus formed. The physical characterization of MBG's has been carried out using a variety of techniques including tracer diffusion, electrical conductivity, NMR, X-ray and SANS. According to the concentrations of surfactant / gelatin and water content, different models to describe the microstructure of MBG's were proposed by

them. However, they merged to a common observation that the gels exhibited a high electrical conductivity and suggested that (i) aggregated gelatin molecules in a rigid network surrounded by water channels stabilized by the surfactant (ii) gelatin network as in (i) coexisting with water droplets stabilized by the surfactant, (iii) w/o  $\mu$ Es or reverse micelles containing water and a part of gelatin. The micelles are connected by the rest of the gelatin arranged in helical strands. Skurtveit et al.<sup>112</sup> have investigated didodecyldimethyl ammonium bromide (DDAB)/dodecane/water system with respect to phase behavior and emulsion stability and the effects of added electrolytes (eg NaCl, NaBr and Na<sub>2</sub>SO<sub>4</sub>) and have observed the reduction in stability upon addition of electrolytes.

Moulik et al.<sup>52,113,114</sup> have investigated the phase behaviors of  $\mu$ Es composed of different ionic and nonionic amphiphiles (viz. SDS, AOT, TX 100, CTAB, NaDC/heptane or xylene / butanol / water systems) in presence of additives like NaCl, HCl, CaCl<sub>2</sub>, cholesterol, cholesteryl benzoate, dextran, gelatin, BSA, PEG, urea and polyacrylamide and have observed a variety of phase characteristics and mutual solubility of water and oil. They have also observed<sup>114b</sup> that urea can abstract oils in  $\mu$ E phase by trapping them in the urea channels formed in the aqueous medium. The abstraction of one oil in preference to the other from a mixture by way of microemulsification has a good application prospect.

Little is known about the influence of pressure on the phase behaviors of water/oil/surfactant systems except for the work of Fortland<sup>115</sup>, Kim et al.<sup>116</sup>. Kim and O'connell<sup>117</sup>, Kahlweit et al.<sup>108</sup> and de Loos et al.<sup>118</sup> have investigated independent and combined influence of pressure and the lyotropic electrolyte NaCl on the phase behavior of water/phenyl alkanes/n-alkyl polyglycol ethers C<sub>i</sub>E<sub>j</sub> over a temperature range of 280-365K. It has been shown that at constant temperature, phase transition of the type 2-3-2 occurs with increase of pressure and NaCl. Recently Eastoe et al. have reported phase region for three different  $\mu$ E systems as a function of temperature and pressure<sup>119</sup> and pressure-temperature (P/T) space.<sup>120a</sup> Oils used in this study have been homologs, propane to n-decane (C<sub>3</sub> to n-C<sub>10</sub>). The effect of pressure on the phase behavior of a nonaqueous  $\mu$ E (propylene / water / surfactant) has also been reported.<sup>120b</sup> The

effect of increasing pressure was similar to the effect of reducing temperature or increasing electrolyte concentration, in agreement with a phenomenological model<sup>120c</sup> developed for the phase behavior of amphiphile-water-oil system. Findenegg et al.<sup>121</sup> have studied the phase behavior of three component systems of the type water/hydrocarbon ( heptane / octane ) / poly (oxyethylene) alkyl ether (C<sub>8</sub> E<sub>4</sub> and C<sub>10</sub> E<sub>5</sub> ) at temperatures below the phase inversion and a truncated isotropic channel in the oil-rich region has been established. Shinoda et al.<sup>122</sup> and Lindman et al.<sup>123</sup> have studied systematically the phase equilibria of sodium and calcium (monoxyethylene) sulphates in two or three component systems (decane as oil) and the effect of alkyl chain length and the valency of counterions on the stability of the phases has been evaluated. Abe et al.<sup>124</sup> have reported the results on synthesis, phase behavior and solubilization parameters for a branched tail polyoxyethylene sulphonate surfactants with precise numbers of ethylene oxide moieties with a view to expand the realm of cosurfactant-free  $\mu$ Es into more hostile environments viz, high salinity and low temperature. Several factors that affect transition between different types of  $\mu$ E systems include temperature, salinity, molecular structure of surfactant, nature of oil, oil-water ratio etc.<sup>125-127</sup> A rapid examination of phase behavior of AOT/isooctane or xylene/water  $\mu$ E has been reported by Schelly et al.<sup>128</sup> by flow birefringence technique. Backlund et al.<sup>129</sup> determined the partial phase behavior of quintinary  $\mu$ Es containing water (0.5 M NaCl), SDS, octane and cyclohexane as oil and butanol or pentanol isomers and benzyl alcohol as cosurfactants. The efficiency of cosurfactant for forming  $\mu$ Es has also been discussed in terms of either molecular structure or from its solubilities. The phase behavior and physicochemical properties (viz. conductance, viscosity and adiabatic compressibility) of different  $\mu$ E systems have been studied by Rakshit et al.<sup>130</sup> The effect of salinity, temperature and mixtures of two short chain alcohols (cosurfactants) on the phase diagram of the pseudoternary systems have also been reported. Recently, Backlund et al.<sup>130b</sup> have examined the phase equilibria of the systems hexanoic acid/hexylamine/water. These studies were of complementary nature and contributed to a better understanding of the fatty acid-fatty amine complexation in relation to the properties of cationic surfactants (an amphiphilic compound which contains both a cationic

and anionic surfactant in an equimolar ratio). Strey et al.<sup>131</sup> have elucidated the role of medium chain alcohols in bicontinuous structure of  $\mu$ Es stabilized by nonionic surfactants whereas Kegel and Lekkerkerker et al.<sup>132</sup> have studied phase behavior of cationic emulsions composed of equal volumes of brine and oil and SDS as a function of cosurfactant chain length. They have also reported an experimental study concerning the  $\mu$ Es-lamellar phase competition<sup>133a</sup> as well as the measurement of the interfacial excess concentrations of surfactant (SDS) and cosurfactants (pentanol and hexanol) in mixed monolayers at the oil (cyclohexanol/cosurfactant) - brine interface from surface tension measurements using Gibbs adsorption equation.<sup>133b</sup> La Mesa et al.<sup>134</sup> studied the phase diagram of the system water/hexane/AOT and phase properties were obtained by polarising microscopy, turbidity, <sup>23</sup>Na and <sup>2</sup>H quadrupole splitting, electrical conductance and self diffusion. The experimental findings shed light on the molecular organisation and dynamic properties of the different phases. Earlier Sjoblom and Friberg et al.<sup>135</sup> have reported the relation between the structure of the surfactant/cosurfactant layer adsorbed at the solid surface and that of the layers in the lamellar liquid crystalline (lc) separated from the solution at enhanced surfactant concentrations. The model system they have chosen was SDS/water (with NaCl or without NaCl)/butanol or benzyl alcohol and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as solid adsorbent. Very recently, Strey<sup>136a</sup> has studied symmetric  $\mu$ Es containing equal volume fractions of water / formamide, n-octane and a sufficient amount of n-alkyl polyglycol ether (C<sub>i</sub> E<sub>j</sub>) for various surfactant chain lengths ranging from C<sub>4</sub> E<sub>1</sub> to C<sub>14</sub> E<sub>5</sub> in pure water as well as for given C<sub>4</sub> E<sub>1</sub> with increasing relative amounts of formamide in the water/formamide mixture. He has demonstrated the stability range of  $\mu$ Es with the help of amphiphilicity of surfactants. Tokuoka, et al.<sup>136b</sup> investigated the phase diagrams of hexadecyl polyoxyethylene ether (C<sub>16</sub>POE<sub>10</sub>)/water/synthetic perfume and SDS/water/synthetic perfume ternary systems and the interaction between surfactants and synthetic perfumes in relation to variations in phase regions were discussed. The synthetic perfumes act as oil bearing component. Chhatre and Kulkarni<sup>136c</sup> studied the phase behavior of  $\mu$ E systems containing an anionic surfactant (SDS) as well as a nonionic surfactant (TX 100) along with cosurfactant

(1 - pentanol) and kerosene as an oil phase. The effect of changes in acid concentration and temperature on the phase behavior was also reported.

#### General Physicochemical Properties

Microemulsions exhibit special physical properties such as stability, nature of aggregation, internal structure, droplet size, inter-droplet interaction, dynamics, etc. Depending on the system,  $\mu E$  may be moderately or highly stable with respect to temperature, time, salt environment (normally NaCl destabilises  $\mu E$ s) as well as other additives (polar and nonpolar). Preparations fairly immune to the above environmental effects are, therefore, preferred for their uses in enhanced oil recovery process. A variety of techniques, both direct (static and dynamic light scattering, small angle neutron scattering (SANS), small angle x-ray scattering (SAXS), ultracentrifugation, transmission electron microscopy (TEM), pulse radiolysis, electron spin resonance (ESR) and indirect (self diffusion, fluorescence spectroscopy, NMR, viscosity, conductance, interfacial tensions etc.) are often used to characterize the microstructure of  $\mu E$ , a field of much current research activity.<sup>137-144</sup>

A great deal of self diffusion studies<sup>139,143,146</sup> have been made to find out the nature and dimension of the microdroplets of either oil or water. The existence of a characteristic zone with isotropic  $\mu E$  domain in a continuum has been evidenced by the self diffusion and conductivity studies.<sup>147</sup> The changes in microstructure of  $\mu E$ s (both aqueous and nonaqueous) as a function of temperature, salinity, cosurfactant, additives and mixture of oils has been investigated by the Fourier transform pulsed gradient spin echo NMR method.<sup>148-151</sup> Light scattering study<sup>152-156</sup> of ionic and nonionic  $\mu E$ s has revealed that droplets fit into the hard sphere model amenable to interparticle interactions. It has been revealed that AOT stabilized  $\mu E$ s having spherical<sup>157-159</sup> and nonspherical<sup>160</sup> droplets containing equal volumes of water and oil may not essentially be bicontinuous. The microstructure of cationic  $\mu E$ s stabilised by CTAB with or without additives has been investigated by Lang et al.<sup>161</sup> and Shah et al.<sup>162</sup> by dynamic light scattering method. Electrochemical techniques viz. cyclic voltametry and rotating disc voltametry, have been successfully applied to

characterize o/w  $\mu$ Es and results have been compared with those obtained from quasi-elastic light scattering (QELS) measurements by Qutubuddin et al.<sup>163</sup> Structure and properties of a  $\mu$ E system stabilised by zwitterionic surfactant  $C_{14}$  DMAO, mixture of  $C_{14}$  DMAO and cationic trimethyl tetradecyl ammonium bromide, TTABr and mixture of  $C_{14}$  DMAO and anionic sodium dodecyl sulphate, SDS and sodium tetradecyl sulphate STDS have been investigated by means of light scattering, small angle neutron scattering, electrical conductance, viscosity and interfacial measurements.<sup>164</sup> Dielectric measurements have also been successfully applied to reversed micellar and  $\mu$ E systems to show that the static permittivity is sensitive to geometrical changes of the aggregates and the dielectric relaxation is an indicator on interfacial polarisation, counterion movements in the aggregates and special changes in the domain sizes.<sup>165-169</sup> Dijk et al.<sup>170</sup> have measured the low-frequency permittivity of AOT/water/i-Oc  $\mu$ E at the temperature range 10<sup>o</sup>-45<sup>o</sup>C and as a function of the concentration of water droplets. The results indicate that the droplet shapes are temperature independent, while individual droplets form dimers. Bose et al.<sup>171</sup> have found three different dielectric processes for SDS/toluene or dodecane/butanol or pentanol/water  $\mu$ Es depending upon the frequency used and concluded that the higher frequency process should be attributed to the relaxation of pure water. Sjoblom et al.<sup>172a</sup> have investigated the structural changes in the  $\mu$ E system, didodecyldimethyl ammonium bromide (DDAB)/water/dodecane in presence of NaBr and Na<sub>2</sub>SO<sub>4</sub> by means of dielectric time domain spectroscopy (TDS). Lundsten et al.<sup>172b</sup> investigated the solubility of water in mixtures of aromatic oils (viz. benzene, methylbenzene, mesitylene and p-xylene) and surfactants of alkyl phenyl polyethoxylene types (viz. Berol 02, 268, 223) and mixed with AOT. They elucidated that the different structures were formed (by the addition of water) in the isotropic - oil - surfactant rich phase by means of conductivity, viscosity and light scattering measurements. Recently, Cazabat<sup>173</sup> has observed a negative electric birefringence (negative Kerr effect) for water/benzylhexyl dimethyl ammonium chloride (BHDC)/benzene  $\mu$ Es which he has explained in terms of Mayer's model.<sup>174</sup> However, Koper et al.<sup>175</sup> have presented an alternative interpretation of the results based on separate investigations.<sup>176,177</sup> Lianos et al.<sup>178,179a</sup> have studied the interaction of

polyoxyethylene glycol (molecular wt. 6000) and  $\alpha$ -hydro- $\omega$ -hydroxypoly (oxy-1, 2-ethanediyl) with SDS/cyclohexane /pentanol or toluene  $\mu$ E by dynamic light scattering and luminescence probing technique. Kabalnov et al.<sup>179b</sup> studied the effect of water soluble polymers (viz. dextran of different molecular weights) on the equilibrium of bicontinuous  $\mu$ E, oil and water phases on  $H_2O-C_{12}E_3-C_{10}H_{22}$  system. Eicke has presented valuable informations on dynamic (exchange kinetic) and static (solubilization) properties of w/o  $\mu$ Es (AOT / water / i-Oc) by using ESR spectroscopy<sup>180</sup> and water uptake and its dependance on temperature by small angle laser light scattering technique.<sup>181</sup> Small angle neutron scattering (SANS) and dynamic light scattering techniques have been used by Eastoe et al.<sup>182</sup> for understanding the structure and dynamics of w/o  $\mu$ E.

High resolution  $^1H$ ,  $^2H$ ,  $^{13}C$  NMR technique has been<sup>183,184</sup> used to investigate the intermolecular interaction and rearrangement in the structure of nonionic and anionic  $\mu$ Es. Wade et al.<sup>185</sup> investigated the effect of electrolyte on the structure of cosurfactantless  $\mu$ E by dynamic light scattering and fluorescence polarisation technique. Martino and Kaler<sup>65</sup> studied qualitatively the microstructure of nonaqueous  $\mu$ Es formed with propylene glycol, glycerol, three different alkanes and a nonionic surfactant,  $C_{12}E_3$ , probed with NMR self-diffusion measurements and small angle neutron scattering (SANS). The structure of polymerizable  $\mu$ Es containing styrene, dodecyltrimethyl ammonium bromide (DTAB) and brine was investigated by Full and Kaler<sup>186a</sup> with SANS and quasielastic light scattering (QLS) techniques. They suggested that these  $\mu$ Es consist of a unimodal population of swollen micelles that swell uniformly with the addition of styrene. Chemical polymerization of aniline in an inverse w/o  $\mu$ E medium has been reported by Chan et al.<sup>186b</sup> A number of techniques viz., x-ray photoelectron spectroscopy, (XPS), thermogravimetry (TG) and cyclic voltametry have been employed for characterization of these very small spherical conducting polyaniline particles. The microscopic structure of triglyceride  $\mu$ E (soyabean oil / water-ethanol, 80-20 wt% and polyoxyethylene (40) sorbitol hexaoleates has been studied by Trevino et al.<sup>186c</sup> as a function of concentration and temperature. The results were consistent with a bicontinuous phase in cases of largest aqueous content. In the low aqueous concentration samples, a substantial correlation was found in the spatial distribution of this minority phase.

Almgren et al.<sup>187</sup> have measured the size and polydispersity of water/AOT/octane and dodecane  $\mu$ Es by time resolved fluorescence quenching (TRFQ). Lang et al.<sup>188</sup> have investigated the effect of nature, molecular weight and concentration of the polymer on the droplet size, interdroplet attractive interactions and rate of exchange of material between droplets by TRFQ., Lang et al.<sup>189</sup> have made a systematic study of various parameters [viz. molar concentration ratios  $\omega = [\text{water}]/[\text{surfactant}]$  and  $z = [\text{cosurfactant}]/[\text{surfactant}]$ , nature and length of alkyl chain of the oil, surfactant and cosurfactant, temperature and the nature and concentration of the electrolyte solubilized in the water droplets] on the droplet size, rate constant for exchange materials between colliding droplets and attractive interactions between droplets in w/o  $\mu$ Es. Similar studies using various modern techniques on variety of  $\mu$ Es have been reported.<sup>190</sup> Jain et al.<sup>191</sup> investigated the conformational, structural and microenvironmental transformations in  $\mu$ E systems by positron annihilation spectroscopy.

Schelly et al.<sup>192</sup> have investigated the microenvironment in TX 100 reverse micelles or w/o  $\mu$ Es in cyclohexane or in the mixed solvents of benzene and n-hexane by the use of methyl orange (MO) and 1-methyl-8-oxyquinolinium betaine (QB) as absorption probe by dynamic light scattering and turbidity measurements. The effects of temperature, water content, presence of salts on the aggregation number, surfactant concentration, size and shape of aggregates have been explored by them by controlled partial pressure - vapour pressure osmometry and QELS.<sup>193</sup> A systematic study on the formation, structure, droplet size, inter-droplet exchange rates and the stabilities of w/o  $\mu$ E stabilized by different nonionic surfactants in pure and mixed alkanes has been made by Fletcher et al.<sup>194,195</sup> Abe et al.<sup>196</sup> have reported the changes in the  $\mu$ E microstructure, phase transition mechanism due to changing salinity and quantitative estimation of surfactant in multiphase<sup>197a</sup> sodium octyl sulfate (SOS)/n-hexanol /n-decane/water (brine)  $\mu$ E using dynamic light scattering, interfacial tension, electrical conductivity, fluorescence probe and extraction spectrophotometry techniques. Very recently, Abe et al.<sup>197b</sup> reported the pH-dependence on the zeta-potential and surface charge density of the o/w type  $\mu$ E formed by an amphoteric surfactant, N,N, -dimethyl-N-lauroyllysine (DMLL) in presence of NaCl. They<sup>197c</sup> have also determined the binding constants of sodium and chloride ions and aggregation numbers of the same system by applying a novel numerical analysis.



The interfacial stoichiometric composition of surfactant and cosurfactant in water / SDS / 1-pentanol/hexadecane  $\mu$ E system has been investigated by Rosano et al.<sup>198</sup> and the results have been verified by differential scanning calorimetry (DSC). Findenegg et al. have measured the interfacial tensions in nonionic  $\mu$ Es near three phase region<sup>199</sup> and near phase inversion<sup>200a</sup> by capillary wave spectroscopy. Chen et al.<sup>200b</sup> systematically studied the phase behavior, wetting and nonwetting behaviors as well as the wetting transitions of the system water/n-alkanes/ $C_6E_2$ , the nonionic surfactant (diethylene glycol monoethyl ether) from the measurements of interfacial tension and direct contact angle measurements. The effects of NaCl, temperature and chain length of oil on the above behaviors were discussed. Microstructure and dynamics of w/o  $\mu$ Es stabilised by TX 100 in  $CCl_4$  has been determined from small angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) confirming the oblate spheroidal shape water droplets.<sup>201</sup>

Investigations on the effect of counterions on the structure and properties of w/o  $\mu$ Es are scanty. Eastoe et al.<sup>202</sup> have measured viscosity, electrical conductivity, SANS for w/o  $\mu$ E stabilised by surfactants of the type  $M^{m+}$  (AOT)<sub>n</sub>, where  $M^{m+}$  stands for  $Na^+$ ,  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $Co^{+2}$ ,  $Ni^{+2}$ ,  $Cu^{+2}$ ,  $Zn^{+2}$  and  $Cd^{+2}$  and have observed structural changes depending upon  $\omega$  ( $=$ [Water]/[Surfactant]), charge as well as  $r_{hyd}$  (radius of the counterion). They<sup>203a</sup> have further investigated the effects of replacing the Na<sup>+</sup>-counterion of AOT for  $NH_4^+$  and  $[(C_7H_7)_4N]^+$  on the structure and properties of the  $L_2$  phase in cyclohexane. Rabie and Vera<sup>203b</sup> developed a theoretical model which accurately represented the distribution of cations between a reverse micellar solution of AOT in isooctane and an excess aqueous phase, and in which the specific character of each exchangeable counterion (viz., hydrated size, free energy of hydration and electronic properties) was introduced through a single equilibrium constant. The prediction of the model were in excellent agreement with experimental results. Abuin and Lissi<sup>204</sup> have reported the effects of changing the surfactant counterion (bromide/chloride), the nature as well as composition of the oil ( $CHCl_3$  and  $CHCl_3$ /heptane mixture), salinity of droplets, nature of salt on the solubilization ability of w/o  $\mu$ Es stabilised by CTAB. The structural changes (eg. plastic crystalline phase or liquid to solid transition) of

AOT / cyclohexane continuous phase as a function of pressure and temperature has been investigated by Eastoe et al.<sup>205a</sup> using SANS technique. The surfactant, sodium bis (2-ethylhexyl) phosphate, (NADEHP) is structurally related to the classical AOT and has drawn particular attention for its ability to form reverse micelles in nonpolar solvents,<sup>205b</sup> which is believed to be a key for its utility in metal extraction.<sup>205c</sup> Feng and Schelly<sup>205d</sup> investigated the effect of the difference in head group on aggregation and also on the properties of reverse micelles formed (NAHDEP/benzene/water) by quasiclastic light scattering, controlled partial pressure-vapour pressure osmometry (CPP-VPO), conductance and viscosity measurements. The role of water in the formation of reverse micelles was discussed. Recently, Kurumda et al.<sup>205e</sup> investigated the microstructure of oil-rich  $\mu$ Es composed of NADEHP/water/n-hexane/sodium chloride in the dilute and concentrated regions by small angle x-ray scattering (SAXS), osmotic compressibility, viscosity and electrical conductivity experiments and compared the results with those obtained for AOT/water/n-hexane/NaCl system. Khoshkbarchi and Vera<sup>205f</sup> studied three dialkyl sodium phosphinate surfactants to determine the conditions under which they can form w/o  $\mu$ Es. They have shown that under well-defined condition, these surfactants have the ability to solubilize a considerable amount of water in the isooctane in the form of w/o  $\mu$ Es. The comparative study due to difference in structure of surfactants gave insight into the effect of the surfactant head group on the water uptake of w/o  $\mu$ Es systems.

#### State of Water in the Micropool

The solubilization states of water in reverse micelles and w/o  $\mu$ Es of AOT in apolar solvents (viz. cyclohexane, heptane, isooctane, dodecane, toluene) have been systematically investigated by several authors<sup>206-210</sup> using NMR, ESR, FT-IR, Raman, fluorescence, near-infrared spectroscopic and light scattering techniques. Among the techniques utilized in this study, <sup>1</sup>H NMR has been found to be a convenient tool to distinguish the type of solubilized water. They have proposed two or three states of water i.e water bound to the ionic head group of AOT and water bound to the hydrated ionic groups or bulk like water. Liveri et al.<sup>210</sup> have

investigated the structure of the various water species present in reversed micelles of AOT where the  $\text{Na}^+$ -counterions have been replaced by  $\text{Ca}^{+2}$  and  $\text{Zn}^{+2}$  at very low water content by FT-IR spectroscopy. Halle et al.<sup>211</sup> have investigated the state of water in aqueous  $\mu\text{E}$  droplets in the system AOT/ $\text{D}_2\text{O}$ /isooctane by nuclear spin relaxation study. Thermochemical studies<sup>212,213a</sup> have been made on the dissolution state of water in AOT/isooctane or heptane solutions. The heat capacity and the enthalpy of dilution of  $\mu\text{E}$ s have been measured as a function of the [water]/[AOT] molar ratio,  $R$  and of the weight fraction,  $\phi$  of water plus AOT with a flow type microcalorimeter. Boned et al.<sup>213b</sup> characterized the state of water in water/AOT/oil  $\mu\text{E}$ s by using differential scanning calorimeter (DSC). Moran et al.<sup>213c</sup> presented a combined Raman and infrared spectroscopic study of the hydration of AOT reverse micelle in two solvents (isooctane and cyclohexane) and discussed the molecular processes involved in hydration number of the surfactant head group and compared with findings of earlier investigations using different techniques by other authors. Haandrikman et al.<sup>213d</sup> suggested that the solubilization of water in anionic alkylsulfonate-based surfactant systems, can be described in terms of three steps. Recently, Gu et al.<sup>213e</sup> have pointed out that both the two-state model and the three-state model have some problems. In order to elucidate these problems, they reported calorimetric measurements on sodium dodecylbenzenesulfonate (NADBS)-based system with *n*-pentanol and *n*-heptane as a mixed apolar solvent and found that their thermal behavior is quite different from that of AOT-based systems.

In contrast to AOT as anionic surfactants, information on the solubilized states of water by cationic surfactants is still scarce, probably because of its limited solubility in water. Using  $^1\text{H}$  NMR, fluorescence, and near-infrared spectroscopic techniques<sup>214</sup> and small angle neutron scattering (SANS) technique<sup>215a</sup>, the solubilized states of water for butyldodecyl dimethyl ammonium bromide (BDDAB) in chlorobenzene<sup>214</sup> and didodecyl dimethyl ammonium bromide (DDAB) in cyclohexane w/o  $\mu\text{E}$  systems<sup>215a</sup>, have been examined as a function of molar ratios of [water]/[surfactant],  $R$ , at various concentrations of surfactant. Three types of water exist in varying proportions in the interior of reversed micelles.

Hasegawa et al.<sup>216a</sup> have measured the microviscosity in the waterpool of AOT reversed micelle as a function of R, with the help of viscosity-sensitive fluorescence probe, auramino and have reported that waterpool is highly viscous in the lower R-region; with increasing R,  $\eta_w$  rapidly decreases below R=10 and then gradually decreases until the micellar solution became turbid above R=50. At higher R region, the values of  $\eta_w$  are considerably higher than the viscosity of the ordinary bulk water, indicating that the solubilizing water molecules are tightly bound to the polar head groups of AOT. In continuation of earlier works on the investigation of the microenvironment of the polar core of reverse micelles by using different kinds of absorption and fluorescence probes, Silber et al.<sup>216b</sup> confirmed that there are at least two types of water (structured and bulk) in the reverse micelles from the study of solvatochromic behavior of 1 - methyl - 8 - oxyquinolinium betaine (QB) and  $E_T(30)$  in AOT / n-hexane system.

#### Transport Behaviors

The  $\mu$ Es may exhibit interesting electrical and hydrodynamic properties and for example, the electrical conductivity of  $\mu$ E can be significantly different for different structures. An oil continuous type is very resistant to ion migration, whereas a water-continuous type conducts well; a bicontinuous  $\mu$ E has fair conductance. Increased volume fraction of water in w/o  $\mu$ E system may show a conspicuous effect on conductance, the electrical conductivity suddenly increases (by several orders of magnitude) in a narrow range of addition of water,<sup>217-222</sup> this is known as 'percolation'.<sup>223</sup> This corresponds to the formation of the first infinite cluster of droplets; the number of such clusters increases very rapidly above the 'percolation threshold', giving rise to the observed and other changes of properties (eg. conductivity, permittivity, viscosity etc.). The increase of electrical conductivity above the 'percolation threshold' of volume fraction or temperature<sup>221,223-225</sup> has been attributed to either "hopping" of surfactant ions from droplet to droplet within droplet clusters<sup>218,226</sup> or transfer of counterions from one droplet to another through water channels<sup>225a,227</sup> opening between droplets during 'sticky' collisions or through transient merging of droplets.<sup>227,228</sup> It has been found that cholesterol and cholesterol derivatives (esters) put hindrance to percolation by

rigidifying the interface between water and oil. Such compounds are also known to make the membrane of the living cells rigid.<sup>225,229</sup> Compounds like alkanols, benzyl alcohol, toluene, crown ether, bile salts etc. have been shown to assist percolation.<sup>223,228<sup>a,b</sup></sup> The mechanistic details of these effects have not been worked out and therefore, requires attention.

For liquid crystals, gels or even high viscosity non-Newtonian fluids, the electrical conductivity may exhibit both maxima and/or minima, reflecting the change in the ion mobility caused by variations in viscosity. Winsor<sup>230</sup> has studied a system in which the gel phase has shown maximum and minimum associated with large viscosity. Clause et al.<sup>231</sup> have observed similar complex behavior of electrical conductivities with increasing water-content. In addition to correlating the results with solution viscosity, they have observed a relationship with the type of phase behavior exhibited by micellar solutions. A ternary system containing water (10 mM NaCl), toluene and TX 100 (40 : 40 : 20 wt%), with inversion from a water continuous phase to an oil continuous phase has shown a very drastic change in electrical conductivity, where a marked fluctuation is expected as a sign of dynamics occurring at the boundary.<sup>232</sup>

The percolation behaviour in  $\mu\text{E}$  has been exploited to explore the structural properties of w/o  $\mu\text{Es}$ . From electrochemical measurements and by the application of effective medium theory (EMT), conductometric evaluation of the structural properties has been possible.<sup>217,233,234</sup> The results are comparable with other sophisticated methods viz. NMR, x-ray, neutron scattering, electron microscopy etc. Very recently, the conductance method has been successfully applied by Moulik et al.<sup>235<sup>a,b</sup></sup> to derive microstructural informations on both w/o and o/w  $\mu\text{Es}$  and evaluated the hydration<sup>235<sup>c</sup></sup> of o/w  $\mu\text{Es}$ . The effect of different additives on the percolation behavior in conductance with regard to probable mechanism of conductance has been studied by several workers.<sup>225<sup>a</sup>,236,237<sup>a</sup></sup> Scaling laws are found to obey by some authors.<sup>228,231,233,235</sup> Alexandridis et al.<sup>237<sup>b</sup></sup> and Koper et al.<sup>237<sup>c</sup></sup> reported different thermodynamic models capable of describing as well as quantification of the temperature dependent clustering phenomena occurring in droplet - phase  $\mu\text{Es}$  and compared the results with other authors.<sup>169,170,218,221,222,225,237<sup>a</sup></sup> Recently refractive

index measurements on  $H_2O$  / AOT / heptane  $\mu$ Es have been performed by Liveri et al.<sup>238</sup> and they have suggested that no structural change is involved during the percolation transitions and in percolated  $\mu$ Es the reversed micelles retain their closed structure. Very recently, Hoffmann et al.<sup>239a</sup> have shown from conductance measurements along with flow and electric birefringence methods and pressure jump relaxation techniques that the isotropic  $L_1$ -phase of DDAB / water / dodecane system can be subdivided into an area with interconnected water channels. They have also reported that for a constant O/S ratio and increasing water content, the  $\mu$ Es show a transition in the conductivity from high to low conducting state. This is an area where imagination, concept and mathematical model have ample scope for deriving profitable informations about the structure and dynamics of  $\mu$ Es. The effect of pressure on the percolation phenomenon in the ternary  $\mu$ Es (water / AOT / undecane and glycerol / AOT isooctane) has been reported by Boned et al.<sup>239b</sup> Very recently, Eicke et al.<sup>239c</sup> have further confirmed the nanodroplet model for w/o  $\mu$ Es formed by nonionic and ionic surfactants. They have also shown that the charge transport mechanisms between the clustered nanodroplets is different for ionic and nonionic surfactants.

Similar to conductivity and permittivity, viscosity of  $\mu$ E can also indicate the phenomena of percolation,<sup>211,222,234,237,240-242</sup> although a quantitative theory and explanations are yet to be proposed. Like conductance, viscosity and permittivity may also follow scaling type equations. There may be a change from w/o to o/w with increase of volume fraction of water. The change in structural organisation during the course of water addition may affect viscosity, which has been supported from the measurement of compressibility and specific volume of different  $\mu$ E systems.<sup>114</sup> A viscous solution is expected to be less compressible than a non-viscous one and this may be due to the interparticle association (clustering) in  $\mu$ E. Very recently, D'Aprano and Liveri et al.<sup>243</sup> have compared the viscosity and the electrical conductance with  $\phi$  (volume fraction of the dispersed phase) for AOT/heptane/ $H_2O$  system and have indicated that the processes for momentum and charge transfer, (even if related to the droplet clusters formation) are different. They have further given evidence for viscoelastic phenomena.<sup>244</sup> Bennett et al.<sup>245</sup> have observed two peaks in viscosity with increasing salinity implying the existence of at least three microstructural regions;

one before, one after and the other in between the two peaks. The coincidence of the start of one viscosity maximum with the conductivity percolation threshold supports that the maxima are indicative of the transition from mono- to bicontinuous structure. If the microstructure is ordered, as in liquid crystal or relatively difficult to break, as in a gel; then the viscosity is expected to increase with increasing bicontinuity. The understanding of the structural consistency in  $\mu$ Es has been attempted from viscosity measurements.<sup>222,241</sup> Behaviors like regular solutions have been observed for some systems and some have shown special behavior. However, in most occasions the viscosity influenced conductance behavior of w/o  $\mu$ Es have been observed to be opposite of expectations.<sup>234,235</sup> This phenomenon has been attributed to the unusual mechanism of conductance in  $\mu$ E.

Recently Berg et al.<sup>246</sup> have investigated the effects of droplet clustering on the shear viscosity by comparing the apparent viscosity of AOT / decane / water  $\mu$ Es flowing through thin membrane filters with well-defined pore sizes with the viscosity measured in standard glass capillary viscometers. The apparent viscosity of  $\mu$ Es in pores differed from the viscosity measured in the capillary viscometer by less than 8%-40% depending upon the diameter of the pore. Chen and Warr<sup>247</sup> have investigated the flow of ternary  $\mu$ E composed of DDAB / dodecane / water under shear in both couette and capillary viscometer with an aim to study the relationship between structure and flow behavior. They have studied at different compositions and found to be Newtonian up to very high shear rates ( $\sim 3000 \text{ S}^{-1}$ ), although some indirect evidence for elasticity has been inferred from capillary viscometry. Densities and viscosities of AOT in heptane system containing light and heavy water, as a function of the molar ratio, R ( $R=[\text{H}_2\text{O}]$  or  $[\text{D}_2\text{O}]/[\text{AOT}]$ ) have been measured at different temperatures ( $0^\circ\text{C}$ - $40^\circ\text{C}$ ). The difference in apparent molar volumes and viscosities have been explained in terms of intermicellar interactions mainly governed by hydration of the head groups of AOT.<sup>245</sup>

Although viscosity has been used as a probe in the understanding of the internal structure of  $\mu$ Es at different compositions, quantification of the property in the light of the hydrodynamic equations has been rarely done. The scanty literature may refer to the works of Baker et al.<sup>248</sup> and others. Very recently Ray et al.<sup>249</sup> has made a detailed study on the validities of different viscosity equations on

w/o  $\mu$ Es using various aliphatic and aromatic oils and AOT. Comparison of the established viscosity equations on the basis of the evaluated parameters with references to the nature of the oil has been presented. An attempt on the testing of different viscosity equations on nonaqueous  $\mu$ Es has also been made by Ray and Moulik.<sup>73</sup> Such comprehensive studies are rarely found in literature.

### Thermodynamics of Microemulsion Formation

Although this is a very important field of investigation, it is extremely complex for  $\mu$ E comprises a number of constituents. Theories based on statistical thermodynamics have been proposed<sup>250</sup> but the treatment are far limited. The proposed theories have been shown to be useful to evaluate the free energy and entropy of formation on the basis of droplet dimension and their nature.<sup>251</sup> Their limitations have also been indicated. However, attempts for their verification and modification are only scanty, keeping a wide scope for further study in this potential field, and knowledge on which is essential for understanding of the stability and physicochemical functioning of the preparations.

As to the direct determination of enthalpy of microemulsification, calorimetric method has been successfully employed. Kertes et al.<sup>252</sup> have pioneered in this venture and attempted to develop the topic systematically. Subsequently Stenius et al.<sup>253</sup> and others<sup>254</sup> have also made important contributions by measuring the enthalpy (both partial molar and integral) of solution of various components in binary and ternary compositions. Detailed theoretical analysis have also been made. Very recently, Das and Moulik<sup>255a</sup> have calorimetrically determined the enthalpy of solution of water, into binary and ternary mixtures of heptane + TX 100 and heptane + TX 100 + butanol respectively and the heat capacities of the resultant  $\mu$ Es. Quantitative analysis of the results have also been attempted. Enthalpy of micromulsification of water in AOT / heptane medium has also been studied by Ray et al.<sup>255b</sup> The thermodynamics of clustering of microdroplets during percolation has also been studied by Ray and Moulik,<sup>256</sup> Alexandridis et al.<sup>257b</sup> The calorimetric studies of Liveri et al.<sup>252a</sup>, Goto et al.<sup>253a</sup>, Boned et al.<sup>253b</sup> and Gu et al.<sup>253c</sup> in understanding of the different states of water in the micro waterpool has already been referred in the previous section.



The thermodynamic treatment of the discipline of  $\mu\text{E}$  has an inherent difficulty with regard to the packing restrictions of the particles. Differences in the types of packing of particles of variable shape and size should have unequal say on the measured and derived energetic parameters which is not a problem in regular solution including the cases of critical solution.

#### Solubilization Parameter

The volumes of hydrocarbon and water dissolved in  $\mu\text{E}$  are quantities of considerable practical interest since the oil and water to form a single thermodynamically stable phase is often useful in pharmacy and industry. Denoting  $v_w$  and  $v_o$  as the volume of water and oil dissolved per unit volume of amphiphile, the "solubilization parameters"  $Sp_o$  and  $Sp_w$  has been defined<sup>237</sup> for oil and water respectively as,  $Sp_o = \frac{v_o}{v_s}$  and  $Sp_w = \frac{v_w}{v_s}$ , where  $v_s$  is the volume of surfactant contained in the interphase, normally calculated excluding alcohol or other cosolvents whenever they are present. A typical variation of solubilization parameters as a function of increasing electrolyte concentration (which promotes the classical I  $\rightarrow$  III  $\rightarrow$  II transformations) has been shown by Miller et al.<sup>110</sup> The  $Sp_o$  and  $Sp_w$  curves intersect inside the three phase domain. At that point the micellar phase contains equal volumes of water and oil and the corresponding solubilization is known as "optimal solubilization" ( $Sp^*$ ). It is a parameter that characterizes the solubilizing power of the surfactant. According to this definition, water-oil ratio (WOR)=1, when  $Sp_o = Sp_w = Sp^*$ . These parameters decrease with increasing hydrocarbon chain length. From the plot of solubilization parameters versus water-oil-ratio (WOR) (at a fixed surfactant concentration); it has been shown that a continuous change in composition occurs with increasing WOR, including inversion from an oil continuous to a water continuous  $\mu\text{E}$  at a fixed WOR. The solubilization parameters are dependent on temperature.<sup>238</sup> The variation of the carbon number of a homologous series of oils at a given temperature for a given amphiphile produces a maximum of solubilization parameter at a certain carbon number. For nonionic amphiphiles, this maximum shifts toward higher carbon numbers with rise in temperature and vice versa.

Barakat et al.<sup>259</sup> have correlated the optimal solubilization ( $Sp^*$ ) to the width of the three phase region defined as the range of alkane carbon number (ACN) over which Winsor III systems are observed as follows.  $Sp^* \cdot \Delta ACN = d$ , where  $d$  is a constant characteristic of the class of surfactant under consideration. Values of  $d$  are 5.5, 24.7 and 40.3 for alkyl benzene sulphonates,  $\alpha$ -olefin sulphonates and ethoxylated oleyl sulphonates respectively. In case of ethoxylated alkylphenols, the optimal solubilization parameter ( $Sp^*$ ) has been found to correlate with the reciprocal of the range of surfactant HLB. The solubilization of water into organic phase, cyclohexane by the nonionic surfactant TX 100 is poor, but it is enhanced by the addition of alcohols viz, pentanol, hexanol and octanol.<sup>260</sup> Schelly et al.<sup>261</sup> have investigated the dynamics of the solubilization of picric acid in AOT in benzene reverse micelles by vapour pressure osmometry and spectrophotometric studies. Recently Liveri et al.<sup>262a</sup> have calorimetrically investigated the mechanism of solubilization, degree of hydrophilicity of the solubilizates, their size, structure and steric hindrance, size of the host microregions of some biological compounds (viz. cholesterol, retinol, retinal) and polar compounds in AOT/heptane reversed micelles. Garti et al.<sup>262b</sup> investigated systematically BSO equation (Bansal, Shah and O'Connell) for several systems composed of ethoxylated alcohols (viz., Brij 97 and Brij 76) /  $C_{10}$  -  $C_{16}$  n-alkanes /  $C_2$  -  $C_{12}$  n-aliphatic alcohols / water and significance of this simple equation has been explained in terms of chain length compatibility and natural curvature as well as critical radius of the interface.

### Uses and Applications

Because of their versatile nature,  $\mu$ Es have wide practical applications. Mouth wash, mens' shaving lotion, (transparent oil-in-water  $\mu$ E) and dry cleaning fluid (w/o type  $\mu$ E) can be a few representative examples.  $\mu$ Es find application in paint industry, precious metal recovery, coating technology, advance fuel technology, cosmetics<sup>263</sup>, photochemical and polymerization reactions<sup>263-266</sup>, drug delivery and biomedical applications<sup>267</sup>. They are also prospectively used in agricultural purpose, in pharmaceutical preparations (for uniform dispersion of the active principles, eg. vitamins) as well as in food industry for beverage

preparation. Alcohol free  $\mu$ Es find important applications in pharmaceutical preparations and photochemical studies.<sup>268</sup> The ultralow interfacial tension of  $\mu$ Es is responsible for their potential uses in the enhanced oil recovery<sup>269-272</sup> where capillary forces in the underground rocks prevent smooth flow of flooding fluid of high surface tension. These novel liquids also have uses in the production of chemical energy from water cleavage<sup>273</sup>, metal recovering from liquid - liquid extraction<sup>274-277</sup> and development of potential blood substitutes<sup>278</sup>. Recently prospective attempts have been made to use both o/w and w/o type  $\mu$ Es as liquid membrane for the transport of different solutes (viz. long chain fatty acids, metabolites, drugs etc.) either mediated through a carrier or without carrier.<sup>279-281</sup> Liphophilic materials can be transported and separated employing o/w  $\mu$ Es<sup>279</sup>, whereas w/o type can transport hydrophilic substances.<sup>282,283</sup> Very recently, a successful application has been in the removal of acetic acid and copper ion from aqueous feed phase (both buffered and unbuffered) respectively<sup>284,285</sup>.

Compared with conventional solvents  $\mu$ Es possess novel solvent properties owing to partitioning of the reagents between the different microenvironments available within the  $\mu$ E<sup>286-297</sup> and also because of changes in the molecular environment of the reagents.<sup>298-300</sup> Water dispersed in  $\mu$ E is known to show reduced activity<sup>301</sup>, reduced polarity<sup>302</sup> and reduced translational diffusion<sup>303</sup> in comparison with bulk water.

The chemical reactions may take place at the oil/water interface of microdroplets as well as in the interior of the droplets. Typical examples can be dephosphorylation at high pH, with the nucleophile being an alkoxide ion from the alcohol or an ethylene oxide derived surfactant<sup>296,304</sup>. Mackay et al.<sup>304</sup> have investigated the effect of triphenylphosphine on the incorporation of Cu (II) by tetraphenylporphyrine in benzene - in - water  $\mu$ E containing cyclohexanol and sodium cetyl sulfate as surfactant. The reaction rate of n-hexylamine with 2,4-dinitro chlorobenzene (DNC) is faster in  $\mu$ Es of n-octane, n-hexylamine and CTAB than in water. The rate enhancement in the  $\mu$ E is largely due to an increased concentration of reactants in the droplets.<sup>305a</sup> The effect of  $\mu$ Es on the hydrolysis of bis (4-nitrophenyl) carbonate has been dependent on the water activity in o/w  $\mu$ E droplets, whereas rate constants of decarboxylation of 6-nitrobenzoxazole-3-carboxylate have no direct dependence on water activity

because of its location at the surface of the droplet.<sup>305b</sup> The rate constant for base hydrolysis of ethyl benzoate in oil-in-water (o/w)  $\mu$ E of CTAB / heptane / butanol/ water has been found to be slower than in the corresponding aqueous and acetone-water systems and the rate inhibiting characteristics of the  $\mu$ E are the consequence of the location of the substrate within the microdroplet.<sup>306</sup> Nucleophilic aromatic substitution<sup>304</sup> and deacylation<sup>307</sup> have also been investigated in  $\mu$ E media. Photochemical conversion of diphenyl stilbene from trans-to- cis form in a  $\mu$ E medium composed of SDS, 2-methyl-2-butanol, benzene and water has also been studied.<sup>308</sup> Schomacker et al.<sup>309</sup> have studied the kinetics of alkylation of 2-alkylindan-1, 3-diones and 2-benzyl 1,3-indandiones by benzylbromide in Igepal/heptane/ water  $\mu$ Es and polar organic solvents. In  $\mu$ Es the reaction proceeds at the microscopic water/oil interface. Static fluorescence quenching experiments<sup>310</sup> in the ionic AOT and nonionic Igepal w/o  $\mu$ Es, have shown that compartmentalization occurs in Igepal/cyclohexane system like AOT system but not in water rich Igepal/n-hexane  $\mu$ Es. Pressure jump relaxation method has shown that the rate limiting step of ligand is its binding with surfactant in AOT system, but it is absent in Igepal  $\mu$ E system. Moulik et al.<sup>311</sup> studied the acid-catalyzed inversion of cane-sugar in water/TX 100/1-butanol/ (chloresteryl benzoate + n-heptane)  $\mu$ E medium at constant surfactant / cosurfactant ratio and at different oil / water ratio. The rate of inversion has increased with increase in o/w ratio, brine (2% w/v) and dextran (0.5% w/v) have moderately retarded it; whereas urea has retarded it markedly. The results have been analysed in the light of the polarity of the medium as well as the effective concentration of the catalyst ( $H_3O^+$ ) in the  $\mu$ E. Sanchez et al.<sup>312</sup> have investigated the kinetics of the oxidation of iodide by persulphate in  $\mu$ Es and reverse micelles stabilized by AOT using a number of oils. The rate of reaction has been found to be greater in  $\mu$ E and micellar system than in conventional aqueous medium and depends on the surfactant concentration, the molar ratio R,  $[H_2O]/[AOT]$  as well as on the nature of the organic phase present. Reaction kinetics for the formation of sodium decyl sulfonate in  $\mu$ Es based on nonionic surfactant were investigated by Oh et al.<sup>313</sup> and compared with those in oil-water two phase systems. An equation describing reaction kinetics in the  $\mu$ E system has been derived based on pseudophase model. The use of nonionic surfactant is of more interest from a practical point of view, since they can be easily removed from the product by heating or cooling. Burgess et

al.<sup>314</sup> have studied the rate constants for the dissociation of pyridine derivatives from pentacyanoferrates (II),  $[\text{Fe}(\text{CN})_5(\text{XPy})]^{3-}$  in micellar and in reverse micellar (cationic, anionic, nonionic) media. The reactivity pattern in reversed micelles differs from that of normal micelles.

Synthesis of ultrafine particles using reactions in  $\mu\text{Es}$  was first reported by Boutonnet et al.<sup>315a</sup> when they obtained monodispersed metal particles (in the size range 3 - 5 nm) of Pt, Pd, Rh and Ir by reducing corresponding salts in waterpools of w/o  $\mu\text{Es}$  with hydrazine or hydrogen gas. Since then, there have been several reports<sup>315b</sup> in literature where  $\mu\text{Es}$  have been used for the synthesis of a variety of nanoparticles (viz. metal, alloy, oxides etc.) covering a wide range of applications which includes catalysts, biological stainers, condensers for electron storage in artificial photosynthesis, semiconductors etc. Their structure and properties have also been described. The fundamental characteristics of microemulsion electrokinetic chromatography (MEEKC) have been studied in comparison with micellar electrokinetic chromatography (MEKC) by Terabe et al.<sup>316</sup> using heptane/SDS/butanol/buffer (pH 7.0) system. The  $\mu\text{E}$  has shown a stronger affinity to non-polar compounds than the SDS micelle. Numerous investigations on the acid base behavior and self association of dyes (viz. sulphonethalein, azo, azine derivatives indicators etc) in compartmentalized liquids viz. micelles,  $\mu\text{Es}$  etc. has been made by El Seoud et al.<sup>317</sup> Mackay et al.<sup>318</sup>, Drummond et al.<sup>319</sup>, Robinson et al.<sup>320</sup>, Fletcher et al.<sup>300</sup>, Guo et al.<sup>321</sup>, Luisi et al.<sup>322</sup>, Moulik et al.<sup>323</sup> According to them, the property of a dye depends on its location or the place of residence either at the interface or in the bulk or partitioned between both. Other important reports on the acid-base behaviors may be found in the references cited above.

Rico et al.<sup>324</sup> studied amidation of the olefin by gamma-radiolysis in the bicontinuous phase of a non-aqueous  $\mu\text{E}$  in a formamide containing 1,1,2-trihydroperfluoro-1-decene as oil, potassium 2,2,3,3-tetrahydroperfluoro hexanol as cosurfactant. Candau et al.<sup>325</sup> have also studied reaction in bicontinuous phase of aqueous  $\mu\text{E}$ .

Due to unique properties, reverse micelles or water-in-oil  $\mu\text{Es}$  play an important role in chemical and biochemical reactions<sup>288,326-329</sup>, reverse micellar

enzymology finds applications in such diverse fields as biomimetic chemistry<sup>288,328-330</sup>, cryoenzymology<sup>331</sup>, synthesis of water insoluble compounds<sup>288,332-334</sup>, biotechnology<sup>335-338</sup>, alternate energy sources<sup>339</sup> and analytical chemistry<sup>340</sup>. Researchers have been engaged in the study of enzymatic reactions in reverse micellar (w/o  $\mu$ Es) media under various conditions using AOT, SDS, CTAB, TX 100 as surfactants and n - heptane, isooctane, cyclohexane, n - octane as oils.  $\alpha$ -chymotrypsin<sup>288,327,340-343</sup>, lipase<sup>344,345</sup>, liver alcohol dehydrogenase<sup>346-348</sup>, alkaline phosphatase<sup>349,350</sup>, lysozyme<sup>351</sup>, lipoxigenase<sup>352</sup>, peroxidase<sup>353</sup>, trypsin<sup>331,354</sup>, acid phosphatase<sup>349,350</sup>, ribonuclease<sup>355</sup>, cholesterol oxidase<sup>356</sup> have been used as biopolymers (eg enzymes and proteins). Luisi et al.<sup>357</sup> have found that the rate of formation of water pools of reverse micelles or w/o  $\mu$ Es (AOT/ water / isooctane) is accelerated by the presence of proteins and nucleic acids. Thermodynamic stability of globular proteins (ribonuclease, cytochrome C, lysozyme) in AOT/water/isooctane  $\mu$ E has been also studied by Luisi et al.<sup>358</sup> Mityake et al.<sup>359a</sup> have measured the rates of catalytic hydrolysis of both hydrophilic, acetylsalicylic acid (AA) and hydrophobic (2-naphthyl acetate, NA) substrate both in aqueous solution and w/o  $\mu$ Es formed from AOT in heptane using the enzymes lipase and  $\alpha$ -chymotrypsin, and imidazole has been used as an acid-base catalyst for comparison. He also proposed<sup>359b</sup> reaction model for enzymatic reaction in  $\mu$ Es. Very recently, the hydrolytic splitting of p-nitrophenyl phosphate by alkaline phosphatase has been elaborately studied by Gupta et al.<sup>360</sup> in water/AOT/decane  $\mu$ E. The role of pH, [water] / [amphiphile] mole ratio and polarity of the waterpool have been analysed. Ruckenstein et al.<sup>361</sup> have made theoretical advancement in the field of micellar enzymology and the theoretical results have been found to agree, both qualitatively and quantitatively, with the experimental results available in literature. An extensive study of the interfacial solubilization of zwitterionic amino acids and proteins in AOT reverse micelles /  $\mu$ Es in a Winsor II system has recently been reported by Hatton et al.<sup>360b,362</sup> The effect of pH<sup>363</sup> on amino acid solubilization has been reported. Very recently Hatton et al.<sup>364</sup>, Dekker<sup>365</sup> and Nitsch<sup>366a</sup> have quantified the kinetic behavior associated with protein partitioning in reversed micellar systems. The influence of cosurfactants (a series of alkanols) on the solubilization of amino acid (phenylalanine) in a w/o  $\mu$ E as well as on the kinetics of amino acid mass transfer from an aqueous phase to a

micellar phase was systematically studied by Plucinski et al.<sup>366b</sup> The experimental results were discussed from the view point of the three-step bud mechanism. Earlier they have also investigated the kinetics of interfacial solubilization<sup>366a</sup> of phenylalanine as well as metal ions<sup>366d</sup> in liquid / liquid  $\mu$ E system (Winsor II) and proposed an alternative mechanism to the model of spontaneous aggregation at the interface. Very recently, Adachi et al.<sup>366c</sup> elucidated the mechanism for protein solubilization in a AOT w/o  $\mu$ E, using the two-phase transfer method. In this model, the effect of adsorption of surfactant molecules on the protein has been taken into consideration and it was related with time-dependent solubilization processes. Other group of authors, Hilhorst et al.<sup>366f</sup> investigated various aspects on the extraction of proteins, enzymes using reversed micelles. Different models were proposed. Several fields of applications have been suggested by them for protein containing reversed micelles. Conformational changes of some proteins in micellar and reversed micellar solutions of different charge types have been reported by Takeda et al.<sup>366g</sup>. The reactivity of different anthracene derivatives toward singlet oxygen has been studied in AOT reverse micelles in heptane as a function of the AOT concentration and [Water]/[AOT] molar ratio<sup>367</sup>. Candau et al.<sup>368a</sup> have prepared stable and clear microlattices of uniform size (diameter  $5 \times 10^{-2} \mu\text{m}$ ) through polymerization of acrylamide in AOT/water/toluene and a blend of sequioleate sorbitan and polyoxyethene sorbitol hexaoleate / water / isoparaffinic oil, isopar M  $\mu$ Es. They have also investigated<sup>368b</sup> the influence of various electrolytes (NaAc, NaCl, NaNO<sub>3</sub>, LiNO<sub>3</sub>, LiCl, LiAc, ZnAc, KNO<sub>3</sub>, sodium butyrate and sodium formate) on the stability and conditions of formation of  $\mu$ Es prior to and after polymerization. Candau<sup>368c</sup> in his review article discussed the formulation and various structures of polymerizable  $\mu$ Es. Kinetics and mechanism as well as the physical processes which occur in these systems have been analyzed and compared to the conventional polymerization. Some applications viz. adsorbents for proteins, immobilization of antibodies, drug microencapsulation etc. were proposed. Nevertheless, with diagnostic applications in view, the immobilization of alkaline phosphatase by physical gel entrapment within colloidal particles produced by inverse  $\mu$ E polymerization has been reported by Daubresse et

al.<sup>369</sup> The catalytic activity of the immobilized enzyme has been compared to the enzyme properties in solution.

Gracia Rio et al.<sup>370a</sup> studied the kinetics of the transfer of the nitroso-group from MNTS (N- methyl-N-nitroso-p-toluenesulfonamide) to several amines using wide variety of water /AOT / isooctane  $\mu$ Es as reaction media. The diverse kinetic behavior of the various amines was explained quantitatively on the basis of pseudophase model. Later, the same model was used to study the kinetics of solvolysis<sup>370b</sup> of diphenylmethyl chloride, 4- nitrophenyl chloroformate, benzol chloride, p- amisoyl chloride in the same  $\mu$ E. The rate constants varied widely with [ water ] / [ surfactant ] mol ratio (R), which was surprising in the light of previous results. A different mechanism was proposed considering the changes in the structuredness of the interphase of AOT  $\mu$ Es with [ water ] / [ surfactant ] mol ratio, (R). Tajima et al.<sup>370c</sup> elucidated the reactivity of. reverse micellar AOT with solubilized amine compounds (viz. ethylenediamine and propylene diamine ) in isooctane. A mechanism of aminolysis by diamines was proposed and explained by the concept of intramolecular amine catalysis.

Kulkarni et al.<sup>371</sup> reported a number of works viz. nitration of phenol to o-nitrophenol; Beckmann rearrangement, cyclization and enhanced decarbonylation of D (-) N-carbomoyl phenyl glycine, and enhanced recovery of nicotine from tobacco waste in a suitably prepared  $\mu$ E media.

Rodenas et al.<sup>372</sup> have studied the basic hydrolysis of crystal violet in CTAB /1-hexanol/ water reverse micelles and CTAB/1-butanol or 1-pentanol/cyclohexane w/o  $\mu$ E systems. The reaction rate is mainly related to the amount of water in the system and from the rate constants, the apparent dielectric constants of the water phase has been determined. The cyclohexane incorporation in the system has produced a decrease in the effective dielectric constant of the water phase and also in the specific conductivity.

The use of  $\mu$ Es within the food technology is very limited. However, some attempts (viz. their phase behaviors and structures) in this direction has been reported<sup>373,374</sup>, where different edible oils contain mono-and triglycerides with long hydrophobic hydrocarbon chains mainly C<sub>16</sub>, C<sub>18</sub> and C<sub>20</sub> were used as oils.



Several research groups have investigated the synthesis of mono-, di-, and triglycerides from glycerol and fatty acids as well as enzymatic hydrolysis of triglycerides in  $\mu$ Es. Of these, the contributions of Holmberg et al.<sup>375</sup> are noteworthy. The majority of work reported in the literature is primarily concerned with lipases, since it retains a high intrinsic activity in these high ordered nonpolar solutions ( w/o  $\mu$ Es ). Palm oil was the source of triglyceride. The effect of charge types of surfactant, solvent ( aqueous / nonaqueous ) on enzymatic hydrolysis of palm oil in  $\mu$ E has been reported in detail.

An interesting extension of the use of  $\mu$ Es for synthesis is to use  $\mu$ E-based gels (MBGs) as reaction media. Rees et al.<sup>376a</sup> and Backlund et al.<sup>376b</sup> reported that lipase-containing MBGs have been used to synthesis on a preparative scale, a variety of different esters under mild conditions and both regio- and stereoselectivity have also been demonstrated . The yields and the enantiomeric excesses are slightly higher using an AOT  $\mu$ E-based gelatin gel than using lecithin  $\mu$ E-based gelatin gel. Atay - Guneyman et al.<sup>377</sup> reported the transport of divalent metal ion through the  $\mu$ E-based organo-gel network into a coexisting  $\mu$ E contained a ligand ( murexide ) and a metal ion / ligand complexation reaction was observed.

Recently, several contributions<sup>296,304,378-383</sup> propose the use of compartmentalized liquids (such as micelles, reverse micelles, monolayers, liposomes and  $\mu$ Es) as models for biomimetic systems, photostorage assemblies and photosynthesis and for obtaining highly conducting thin films .

The above presentation clearly evidences versatilities of  $\mu$ Es and their application potentials. The recent review articles in this area by Kon-No et al.<sup>386</sup>, Abe et al.<sup>387</sup>, Luisi<sup>388</sup> Pileni<sup>389</sup>, Maitra et al.<sup>390</sup> and Moulik et al.<sup>391</sup> are worthy addition in  $\mu$ E literature.

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#### REFERENCES

1. W.D. Bancraff, *J. Phys. Chem.*, 1, 414, 647 (1897).

2. W. Clayton, *The Theory of Emulsions and Their Technical Treatment*, 4th ed., p 1, The Blakiston Co., Philadelphia, (1943).
3. L.M. Prince, Ed., *Microemulsions: Theory and Practice*, Academic Press, New York, 1977.
4. C.E. Cooke and J. H. Schulman, *Surface Chemistry*, Munksgaard, Copenhagen, p 231, (1965).
5. T.P. Hoar and J.H. Schulman, *Nature (London)*, 152, 102 (1943).
6. P.A. Winsor, *Trans. Faraday Soc.*, 44. 376 (1948).
7. K. E. Bennett, H.T. Davis and L.E. Scriven, *J. Phys. Chem.*, 86, 3917 (1982).
8. C. Gonzalez, J. Gutierrez, M. Galan, S. Plaja, C. Mans, and J. Costa, *Proc. 6th International Symposium on Surfactants in Solutions, New Delhi, India, Aug. 18-22, p.258 (1986)*.
9. H. Kunieda, H. Asaoka and K. Shinoda, *J. Phys. Chem.*, 92, 185 (1988); S. Yamaguchi and H. Kunieda, *J. Japan Oil Chem. Soc.*, 37, 648 (1988).
10. (a) M. Allen, D.F. Evans, D.J. Mitchel and B.W.Ninham, *J. Phys. Chem.*, 91, 2320 (1987).  
(b) G.J. Verhoeckx, P.L. de Bruyn and J.Th.G. Overbeck, *J. Colloid Interface Sci.*, 119, 409 (1987).
11. R. N. Healy, R.L. Reed and D.G. Stenmark, *Soc. Pet. Eng. J.*, 16, 147 (1976).
12. D. Senatra, *J. Electrostat.*, 12, 383 (1982).
13. S.E. Friberg and Y.C. Liang, *Surfactant Sci. Ser.*, 24 (Microemulsion System), 103 (1987).
14. D.Y. Chao, M. L. Chen and Y. G. Shen, *Surfactant Sci. Ser. 24 (Microemulsions System)*, 211 (1987).
15. H. L. Rosano, J. L. Cavallo and B. Lyons, *Surfactant Sci. Ser. 24 (Microemulsions System)*, 345 (1987).
16. C. Solans, T.G. Dominguez, J.L. Parra, T. Heuser and S.E. Friberg, *J. Colloid Polym. Sci.*, 266, 570 (1988).

17. H. Kunieda and K. Shinoda, *J. Dispersion Sci. Technol.*, **3**, 233 (1982).
18. D. Roux and M. Bellocq, in *Physics of Amphiphiles; Micelles, Vesicles and Microemulsions*; V. Digiorgio and M. Corti, Eds., North-Holland, Amsterdam p. 842 (1985).
19. S.R. Palit, V.A. Moghe and B. Biswas, *Trans. Faraday Soc.*, **55**, 463 (1959).
20. M. Rosoff, in *Progress in Surface and Membrane Science*, Vol. 12, D.A. Cadenhead and J.F. Danielli, eds., Academic Press, New York, p 405 (1978).
21. S.L. Holt, *J. Disp. Sci. Tech.*, **1**, 423 (1980).
22. I.D. Robb, *Microemulsions*, Plenum Press, New York (1982).
23. K. Shinoda, Ed., *Solvent Properties of Surfactant Solutions*, Marcel Dekker, New York, Chapter-I, p 3 (1967).
24. A.W. Adamson, *J. Colloid Interface Sci.*, **29**, 261 (1969).
25. G. Gillberg, H. Lehtinen and S.E. Friberg, *J. Colloid Interface Sci.*, **33**, 40 (1970).
26. P. Ekwall, L. Mandell and M. Larsson, *J. Colloid Interface Sci.*, **33**, 215 (1970).
27. K. Shinoda and H. Kunieda, *J. Colloid Interface Sci.*, **42**, 382 (1973).
28. S.E. Friberg and T. Buraczenska, *Prog. Colloid Polym. Sci.*, **63**, 1 (1978).
29. K. Shinoda and S.E. Friberg, *Adv. Colloid Interface Sci.*, **4**, 281 (1975).
30. E. Sjoblom and S.E. Friberg, *J. Colloid Interface Sci.*, **67**, 16 (1978).
31. I. Danielson and B. Lindman, *Colloids Surf.*, **3**, 391 (1981).
32. K. Shinoda and B. Lindman, *Langmuir*, **3**, 135 (1987).
33. M. Kahlweit, *Science*, **240**, 617 (1988).
34. A.M. Bellocq, in *Complex and Supermolecular Fluids*, S. Safran and N. Clark, Eds., Wiley, New York, p.41 (1987).
35. D.J. Mitchell, B.W. Ninham, *J. Chem. Soc. Faraday Trans.*, **77**, 609 (1981).

36. Y.L. Khmel'nitsky, R. Hilhorst and C. Veeger, *Eur. J. Biochem.*, **176**, 265 (1988).
37. H. Kunieda, *Bull. Chem. Soc., Japan*, **56**, 625 (1983).
38. B. Lindman, *Hepatology*, **4**, 1035 (1984).
39. P. Guering and B. Lindman, *Langmuir*, **1**, 464 (1985).
40. D. Langevin, *Phys. Sc., T 13 (Proc. Gen. Conf. Condens. Matter Div., Eur. Phys. Soc., 6th, p. 252 (1986).*
41. A.de Geyer and J. Tabony, *ibid*, **124**, 357 (1986).
42. E.W. Kaler, K.E. Bennett, H.T. Davies and L.E. Scriven, *J. Chem. Phys.*, **79**, 5673, 5685 (1983).
43. L. Auvray, J.P. Cotton, R. Over and C. Taupin, *J. Phys. Chem.*, **45**, 913 (1984).
44. M. Dvolaitzky, M. Guyot, M. Lagues, J.P. Lepsant R. Ober, C. Sauterey and C. Taupin, *J. Chem. Phys.*, **69**, 3279 (1981).
45. D.J. Mitchell and B.W. Ninham, *J. Chem. Soc. Faraday Trans.*, **77**, 601 (1981).
46. M. Borkovec, H.F. Eicke, H. Hammerich and B. Dasgupta, *J. Phys. Chem.*, **92**, 206 (1988).
47. H.F. Eicke, M. Borkovec and B. Dasgupta, *J. Phys. Chem.*, **93**, 314 (1989).
48. (a) H. Kunieda, *J. Colloid Interface Sci.*, **133**, 237 (1989); H. Kunieda and A Miyajima, *J. Colloid Interface Sci.*, **129**, 554 (1989).  
(b) K. R. Wormuth and E.W. Kaler, *J. Phys. Chem.* **93**, 4855 (1989).
49. H. Katayama, T. Tagawa and H. Kunieda, *J. Colloid Interface Sci.*, **153**, 429 (1992).
50. T. Gulik-Krzywicki and K. Larsson, *Chem. Phys. Lipids*, **35**, 127 (1984).
51. (a) H. Kunieda and K. Shinoda, *Bull. Chem. Soc. Japan*, **56**, 980 (1983); H. Kunieda, K. Yago and K. Shinoda, *J. Colloid Interface Sci.*, **128**, 363 (1989); H. Kunieda, *J. Colloid Interface Sci.*, **116**, 224 (1987).

- (b) H. Kunieda, Y. Hasegawa, A.C. John, M. Naito, and M. Muto, *Colloids Surf.*, **109A**, 209 (1996)
- (c) K. Shinoda and T. Kaneka, *J. Dispersion Sci. Technol.*, **9** 555 (1988)
52. M.L. Das, P.K. Bhattacharya and S.P. Moulik, *Ind.J. Biochem. Biophys.*, **26**, 24 (1989) and *Langmuir*, **7**, 636 (1991); N. Mitra, L. Mukhopadhyaya and S.P. Moulik, *Ind. J. Biochem. Biophys.*, **31**, 115 (1994); N. Mitra, L. Mukhopadhyaya, P.K. Bhattacharya and S.P. Moulik, *Ind. J. Biochem. Biophys.*, **33**,206 (1996)
53. H. Kunieda and M. Yamagata, *Langmuir*, **9**, 3345 (1993); H. Kunieda, N. Ushio, A. Nakano and M. Miura, *J. Colloid Interface Sci.*, **159**, 37 (1993).
54. K. Shinoda, M. Araki, A. Sadaghiani, A. Khan and B. Lindman, *J. Phys. Chem.*, **95** 989 (1991); K. Shinoda, Y. Shibata, B. Lindman, *Langmuir*, **9**,1254 (1993); P. Schurtenberger, R. Scartazzini, L. J. Majid, M.E. Leser and P.L. Luisi, *J. Phys. Chem.*, **94**, 3695 (1990).
55. (a) S. Backlund, M. Rantala and O. Molander, *Colloid Polym. Sci.* **272**, 1098 (1994)
- (b) G. Cavallaro, G. La Manna, V.T. Liveri, F. Aliotta and M. E. Fontanella, *J. Colloid interface Sci.* **176**, 281 (1995)
56. S.E. Friberg and M. Podzimek, *Colloid Polym. Sci.* , **262**, 252 (1984)
57. S.E. Friberg and C.S. Wahn , *Colloid Polym. Sci.*, **263**, 156 (1985) ; S.E. Friberg and P.Liang, *Colloid Polym. Sci.* , **264** , 449 (1986). S.E. Friberg, *Nonaqueous, Microemulsions*, CRC Press, Boca Raton, FL , p.1 (1986)
58. S.E. Friberg and Y.C. Liang, *Colloids Surf.*, **24**, 325 (1987); S.E. Friberg and G. Rong, *Langmuir*, **4**, 796 (1988); K. P. Das, A. Ceglie, B. Lindman and S.E. Friberg, *J. Colloid Interface Sci.*, **116**, 390 (1987). S.E. Friberg and Y.C. Liang, in "Microemulsions : Structure and Dynamics", S.E. Friberg and P.Bothorel , Eds. , CRC , Boca Raton , FL. , ch. 3, p. 79 (1987)
59. P.D. I. Fletcher, M.F. Galal and B.H. Robinson, *J. Chem. Soc. Faraday Trans.1*, **80**, 3307 (1984).
60. I. Rico and A. Lattes, *Nouv. J. Chim*, **8**, 429 (1984); M. Gautier, I. Rico, A.A. Samii, A. Savignac and A. Lattes, *J. Colloid Interface Sci.*, **112**, 484 (1986).
61. A.A. Samii, A. Savignac, I. Rico and. A Lattes, *Tetrahedron*, **41**, 3683 (1985); X. Auvray, C. Petipas, R. Anthore, I Rico, A. Lattes, A.A. Samii, and A.Savignac, *Colloid Polym. Sci.*, **265**, 925 (1987).

62. I. Rico and A. Lattes, *J. Colloid Interface Sci.*, **102**, 285 (1984).
63. B. Bergenstahl, A. Jonsson, J. Sjoblom, P. Stenius, and T. Warnheim, *Prog. Colloid Polym. Sci.*, **74**, 108 (1987).
64. T. Warnheim and M. Sjoberg, *J. Colloid Interface Sci.*, **131**, 402 (1989).
65. A. Martino and E.W. Kalcr, *J. Phys. Chem.*, **94**, 1627 (1990); *Langmuir*, **11**, 779 (1995) and references therein.
66. K.V. Schubert, M. Kahlweit and R. Strey, in *Organised Solution*; S.E. Friberg and B. Lindman, Eds., Dekker, New York, p. 105 (1992).
67. K.V. Schubert, R. Strey and M. Kahlweit, *Prog. Colloid Polym. Sci.*, **84**, 103 (1991) and *Structure and Dynamics of Strongly Interacting Colloids and Supramolecular aggregates in Solution*, S.H. Chen, et al., Eds., K.A.P. Netherlands, pp. 841-844 (1992).
68. K.V. Schubert, G. Busse, R. Strey and M. Kahlweit, *J. Phys. Chem.*, **97**, 248 (1993).
69. K.P. Das, C. Ceglie and B. Lindman, *J. Phys. Chem.*, **91**, 2938 (1987).
70. S.E. Friberg, C. Yang, R. Goubran, and R.E. Partch, *Langmuir*, **7**, 1103 (1991).
71. H.D. Dorfler and E. Nestler, *Tenside, Surfactants, Detergent*, **27**, 168 (1990) (Gr.).
72. H.D. Dorfler and C. Swaboda, *Colloid Polym. Sci.*, **271**, 586 (1993) and references therein.
73. S. Roy and S.P. Moulik, *Langmuir*, **10**, 2511 (1994).
74. G.J. McFann and K. P. Johnston, *Langmuir*, **9**, 2942 (1993).
75. P. Becher, in *Nonionic Surfactants*, M.J. Schick, Ed., Dekker, New York, p.612 (1967).
76. W.C. Griffin, *J. Soc. Cosmet. Chem.*, **1**, 311 (1949).
77. *Surfactant Science and Technology*, Drew Myers, VCH (1988).
78. A. Graciaa, Y. Barakat, R.S. Schechter, W.H. Wade and S. Yiv., *J. Colloid Interface Sci.*, **89**, 217 (1982).

79. H. Kunieda and K. Shinoda, *J. Colloid Interface Sci.*, **75**, 601 (1980).
80. M.L. Robbins and J. Bock, *J. Colloid Interface Sci.*, **124**, 462 (1988) and **124**, 486 (1988).
81. L.M. Prince, *Microemulsion, Theory and Practice*, Academic Press, New York (1977).
82. J.H. Schulman, W. Stoeckentuis and L.M. Prince, *J. Phys. Chem.*, **63**, 1677 (1959).
83. L.M. Prince, *J. Colloid Interface Sci.*, **23**, 165 (1967); L.M. Prince, *J. Cosmet. Chem.*, **21**, 183 (1970).
84. S.I. Ahmed, K. Shinoda and S. Friberg, *J. Colloid Interface Sci.*, **47**, 32 (1974).
85. E. Ruckenstein and J.C. Chi, *J. Chem. Soc. Faraday Trans.*, **71**, 1690 (1975).
86. E. Ruckenstein and R. Krishnan, *J. Colloid Interface Sci.*, **71**, 321 (1979); **75**, 476 (1980); **76**, 188 (1980); **76**, 201 (1980).
87. (a) J.Th.G. Overbeek, P.L. deBruyn and F. Verhoeckx, in *Surfactants*, Th. F. Tadros, Ed., Academic Press, (1985); J.Th.G. Overbeek, F. Verhoeckx, P.L. deBruyn and H.N.W. Lekerkerker, *J. Colloid Interface Sci.*, **119**, 422 (1987).  
(b) J. N. Israelachvili, D.J. Mitchell and B. W. Ninham, *J. Chem. Soc. Faraday Trans. 2*, **72**, 1525 (1976); *J. Phys. Chem.*, **87**, 2996 (1983).
88. S. Friberg and T. Buraszewska, *Prog. Colloid Polym. Sci.*, **63**, 10 (1978).
89. A. Findlay, A. W. Campbell and W.O. Smith, *Dover Publication, Inc., USA 9th Ed.*, (1957).
90. J. Biais, B. Clin, and P.Lalanne, in *Microemulsions : Structure and Dynamics*, S.E. Friberg and P. Bothorel, Eds., CRC, Florida (1987).
91. A.M. Bellocq, J. Biais, P. Bothorel, D. Bourbon, B. Clin, P. Lalane and B. Lamanceau, in *Microemulsions*, I.D. Robb, Ed., Plenum, New York and London, P. 131 (1982).
92. P. Bothorel, in *Physics of Amphiphiles; Micelle, Vesicles and Microemulsions*, V. Digiorgio and M. Corti, Eds., North-Holland, Amsterdam (1985).

93. A.M. Belloq, and R.S. Schechter, *Microemulsions and Related Systems*, Marcel Dekker, New York and Basel, Ch. 4, pp. 130-152 (1988).
94. J. Biais, B. Clin, P. Lalannc and M. Barthe, in *Surfactants in Solution*, K.L. Mittal and B. Lindman, Eds., Plenum, New York, Vol 3, p. 1789 (1984). J. Biais, M. Barthe, M. Bourrel, B. Clin and P.Lalannc, *J. Colloid Interface Sci.*, **109**, 576 (1986).
95. B. Bedwell and E. Gulari, *J. Colloid Interface Sci.*, **102**, 88 (1984).
96. M. Kahlweit, R. Strey and D. Hasse, *J. Phys. Chem.*, **88**, 1937 (1984) and **89**, 163 (1985).
97. J. Nieuwkoop, R.B. de Boer and G. Sonci, *J. Colloid Interface Sci.*, **109**, 350 (1986).
98. V. Chen, D.F. Evans and B.W. Ninham, *J. Phys. Chem.*, **91**, 1823 (1987).
99. H.N. Singh and Sanjeev Kumar, *J. Surf. Sci. Technol.* **5**, 143 (1989).
100. P.L. de Bruyn, J. Th. G. Overbeek and G. J. Verhoeckx, *J. Colloid Interface Sci.*, **127**, 244 (1989).
101. R.L. Healy and R.N. Reed in *Improved Oil Recovery by Surfactant and Polymer Flooding*, D.O. Shah and R.S. Schechter, Eds., Academic Press, Inc., New York, P. 383 (1977).
102. D.O. Shah, Ed., *Surface Phenomena in Enhanced Oil Recovery*, Plenum, New York, (1981).
103. M.K. Sharma and D.O. Shah, in *Macro-and Microemulsions*, D.O. Shah, Ed., ACS, Washington, p. 149 (1985).
104. C.A. Miller and S. Qutubuddin, in *Interfacial Phenomenon in Apolar Media*, G.D. Parfitt and H.F. Eicke, Eds., Marcel Dekkar, Inc., New York, (1986).
105. P. Neogi, in *Microemulsions*, S.E. Friberg and P. Bothorel Eds., CRC Press, Baton Rouge, Louisians, p. 197, (1987).
106. M.L. Robbins, J. Bock and J.S Huang, *J. Colloid Interface Sci.*, **126**, 114 (1988).
107. M. Kahlweit and R. Strey, *Angew. Chem. Int. Ed. Engl.*, **24**, 654 (1985).



108. M. Kahlweit, R. Strey, P. Firman, D. Hasse, J. Jen and R. Schomacker, *Langmuir*, **4**, 499 (1988).
109. (a) M. Kahlweit and R. Strey, *J. Phys. Chem.*, **92**, 1557 (1988).  
(b) H. Kunieda, A. Nakano and M. Akimaru, *J. Colloid Interface Sci.*, **170**, 78 (1995) and references therein.  
(c) M. Angeles and H. Kunieda, *Trends in Phys. Chem.*, **5**, 75 (1995)  
(d) M. Kahlweit, B. Faulhaber and G. Busse, *Langmuir*, **10**, 2528 (1994);  
M. Kahlweit, *J. Phys. Chem.*, **99**, 1281 (1995)
110. O. Ghosh and C.A. Miller, *J. Phys. Chem.*, **91**, 4528 (1987).
111. (a) D. Capitani, A.L. Segre, G. Haering and P.L. Luisi, *J. Phys. Chem.*, **92**, 3500(1988) P. L. Luisi, R. Scartazzini, G. Haering, P. Schurtenberger, *Colloid Polym. Sci.*, **268**, 356 (1990), G. Haering and P. L. Luisi, *J. Phys. Chem.*, **90**, 5892 (1990)  
(b) C. Quellet and H.F. Eicke, *Chimia*, **40**, 233 (1986); C. Quellet, H.F. Eicke and W. Sager, *J. Phys. Chem.*, **95**, 5642 (1991); C. Quellet and H.F. Eicke, R. Gehrke and W. Sager, *Europhys Lett.*, **9**, 293 (1989).  
(c) P. Atkinson, B.H. Robinson, A. M. Howe, R.K. Heenan, *J. Chem. Soc. Faraday Trans.*, **87**, 3389 (1991)  
(d) C. Petit, T.N. Zemb and M.P. Pileni, *Prog. Colloid Polym. Sci.*, **81**, 281 (1990); *Langmuir*, **7**, 223 (1991)
112. R. Skurtveit and U. Olsson, *J. Phys. Chem.*, **95**, 5353 (1991); J. Sjoblom, R. Skurtveit, J.O. Saeten and B.J. Gestblom, *J. Colloid Interface Sci.*, **141**, 329 (1991); R. Skurtveit, J. Sjoblom, J. Bouwstra, G. Georis and M.H. Selle, *J. Colloid Interface Sci.*, **152**, 205 (1992).
113. S.R. Bisal, P.K. Bhattacharya and S.P. Moulik, *J. Surface Sci. Technol.*, **4**, 121 (1988).
114. (a) M.L. Das, P.K. Bhattacharya and S.P. Moulik, *Colloids Surf.* **49**, 247 (1990).  
(b) S. Pal, M.L. Das and S.P. Moulik, *J. Colloid Interface Sci.*, **161**, 101 (1993).
115. P. Fortland, *J. Phys. Chem.*, **91**, 6396 (1987).
116. M.W. Kim, W. Gallagher and J. Bock, *J. Phys. Chem.*, **92**, 1226 (1988).
117. J.D. Kim and J.P. O'Connell, *J. Phys. Chem.*, **92**, 3492 (1988).

118. C.L. Sassen, L.M. Filemon, Th. W. de Loos and J. de Swaan Arnos, J. Phys. Chem., **93**, 6511 (1989).
119. J. Eastoe, B.H. Robinson, D.C. Steytler and J.C. Dore, Chem. Phys. Lett., *ibid.* (1990).
120. (a) J. Eastoe, B.H. Robinson and D.C. Steytler, J. Chem. Soc. Faraday Trans., **86**, 511 (1990); J. Eastoe, B.H. Robinson, D.C. Steytler and D. Thron-Leeson, Adv. Colloid Interface Sci., **36**, 1 (1991).  
(b) E.J. Beckman and R.D. Smith, J. Phys. Chem., **95**, 3253 (1991).  
(c) M. Kahlweit, M. Strey, R. Schomacker and D. Hasse, Langmuir, **5**, 305 (1989).
121. G.H. Findenegg, A. Hirtz, R. Rasch and F. Sowa, J. Phys. Chem., **93**, 4580 (1989).
122. K. Shinoda, H. Kunieda, T. Arai and H. Saijo, J. Phys. Chem., **88**, 5126 (1984); K. Shinoda, M. Mackawea, Y. Shibata, J. Phys. Chem., **90**, 1228 (1986).
123. A. Khan, K. Fontell and B. Lindman, J. Colloid Interface Sci., **101**, 103 (1984); D. Maciewska, A. Khan and B. Lindman, Colloid Polym. Sci., **264**, 909 (1986); A. Khan, B. Lindstrom, K. Shinoda and B. Lindman, J. Phys. Chem., **90**, 5799 (1986); A. Khan, B. Lindman, and K. Shinoda, J. Colloid Interface Sci., **128**, 396 (1989).
124. M. Abe, D. Schechter, R.S. Schechter, W.H. Wade, U. Weerasooriya and S. Yiv, J. Colloid Interface Sci., **114**, 342 (1986), M. Abe, R.S. Schechter, R.D. Selliah, B. Seikh, W.H. Wade, J. Disp. Sc. Technol., **8**, 157 (1987).
125. D.O. Shah, Ed., Macro- and Microemulsions, ACS, Washington, (1985).
126. K. Shinoda and S. Friberg, Emulsions and Solubilization, John Wiley and Sons, N.Y., pp. 24-28 (1986).
127. M. Abe, H. Nishino and K. Ogino, Sekiyu Gakkaishi, **32**, 151 (1989).
128. A.C. Hall, E. Tekle and Z.A. Schelly Langmuir, **5**, 1263 (1989).
129. (a) S. Backlund, G. Bostrom, K.G. Nordli, and T. Warnheim, Prog. Colloid Polym. Sci., **82**, 290 (1990).  
(b) S. Backlund, G. Lundsten, M. Ruths, M. Sjoberg and T. Warnheim, Prog. Colloid Polym. Sci., **88**, 36 (1992).

130. (a) A.C. John and A.K. Rakshit, *Colloids Surf.*, **95A**, 201 (1995); *Langmuir*, **10**, 2084 (1994); S. Ajith, A.C. John and A.K. Rakshit, *Pure and Applied Chem.* **66**, 509 (1994).  
(b) S. Buckland, S. Karlsson and J. Sjoblom, *J. Dispersion Sci. Technol.*, **15**, 561 (1994).
131. (a) R. Strey and M. Jonstroemer, *J. Phys. Chem.*, **96**, 4537 (1992).  
(b) E.J. Beckman and R.D. Smith, *J. Phys. Chem.*, **95**, 3253 (1991).
132. W.K. Kegel and H.N.W. Lekkerkerker, *Colloids Surf. A*, **76**, 241 (1993).
133. (a) W.K. Kegel and H.N.W. Lekkerkerker, *J. Phys. Chem.*, **97**, 11124 (1993).  
(b) W.K. Kegel, G.A. Van Aken, M.N. Bouts, H.N.W. Lekkerkerker, J. Th. G. Overbeck and P.L. deBruyn, *Langmuir*, **9**, 252 (1993).
134. C. La Mesa, L. Coppla, G.A. Ranieri, M. Terenzi and C. Chidichimo., *Langmuir*, **8**, 2616 (1992).
135. J. Sjoblom, A.M. Blokhuis, W.M. Sun and S.E. Friberg, *J. Colloid Interface Sci.*, **140**, 481 (1990).
136. (a) R. Strey, *Bur. Bunsenges Phys. Chem.*, **97**, 742 (1993).  
(b) Y. Tokuoka, H. Uchiyama and M. Abe, *Colloid and Polym. Sci.*, **272**, 317 (1993).  
(c) A.S. Chhatre and B. D. Kulkarni, *J. Colloid Interface Sci.*, **150**, 528 (1992); *J.Chem. Research(S)*, 209 (1992).
137. D. Langeven and J. Meunier, Eds., *Physics of Amphiphilic Layers*; Springer, Heidelberg (1987); *Springer Proc. Phys.*, Vol.21.
138. S.A. Safran and N.A. Clark, Eds., *Physics of Complex and Supermolecular Fluids*, Wiley Interscience ; New York (1987).
139. (a) K.L. Mittal and B. Lindman, Eds., *Surfactants in Solution*, Plenum. New York, Vol 3. pp 1501-1924 (1984).  
(b) U. Olsson and P. Schurtenberger, *Langmuir*, **9**, 5389 (1993).
140. K.L. Mittal and P. Bothorel, Eds., *Surfactants in Solution*, Plenum, New York, Vol. 6, pp. 1137-1484 (1987).
141. H.L. Rosano and M. Clause, Eds., *Microemulsion Systems*, Marcel Dekker, New York, p. 129 (1987).
142. R. Zana, in *Surfactant Solutions: New Methods of Investigation*, Ed., R. Zana, Marcel Dekker, New York, Chapter 5, p. 241 (1987).

143. J. Lang, in *The Structure, Dynamics and Equilibrium Properties of Colloidal Systems*, Eds., D. M. Bloor and E. Wyn-Jones, Kulwer Academic Publishers, Dordrecht, p.1 (1990).
144. S.E. Friberg and P. Bothorel, Eds., *Microemulsions: Structure and Dynamics*, CRC Press, Florida, Chapter 6 and p.119 (1987).
145. B. Lindman, N. Kamenka, B. Brun and P.G. Nilsson, in *Microemulsions*, I.D. Robb, Ed., Plenum, New York, 115 (1982).
146. (a) B. Lindman and P. Stilbs, in *Physics of Amphiphiles, Micelles, Vesicles and Microemulsions*, V. Degiorgio and M. Corti, Eds., North-Holland, Amsterdam, (1984).  
(b) W.O. Parker, C. Genova Jr., and G. Carignano, *Colloids Surf.*, **72A**, 275 (1993).  
(c) R. Skurtviet, J. Sjoblom, S.E. Friberg, C.C. Yang, and A.U. Ahmed, *J. Disp. Sc. Technol.*, **14**, 685 (1993).
147. F. Larche, J. Rouviere, P. Delored, B. Brun and J.L. Dussossoy, *J. Phys. Lett. (Orsay. Fr.)* **41**, 437 (1980).
148. S.E. Friberg and Y.C. Liang, *Surfactant Sci. Ser.*, **24** (Microemulsions System) 103 (1987).
149. B. Lindman, K. Shinoda, M. Jonstromer and A. Shinohara, *J. Phys. Chem.*, **92**, 4702 (1988); K.P. Das, A. Ceglie and B. Lindman, *J. Phys. Chem.*, **91**, 2938 (1987) and *J. Colloid Interface Sci.*, **115**, 115 (1987); U. Olsson, K. Shinoda and B. Lindman, *J. Phys. Chem.*, **90**, 4083 (1986).
150. K.P. Das, A. Ceglie, B. Lindman and S.E. Friberg, *J. Colloid Interface Sci.*, *ibid* (1987).
151. U. Olsson, K. Nagai and H. Wennerstrom, *J. Phys. Chem.*, **92**, 6675 (1988); K. Fukuda, U. Olsson, and U. Würz *Langmuir*, **10**, 3222; M. Jonstromer, U. Olsson, and W. Parker, Jr., *Langmuir*, **11**, 61 (1995); M. Leaver, I. Furo and U. Olsson, *Langmuir*, **11**, 1524 (1995).
152. A.M. Cazabat, D. Langevin and A. Pouchelon, *J. Colloid Interface Sci.*, **73**, 1 (1980).
153. D.J. Cebula, R.H. Ottewill, J. Ralston and P.N. Pusey, *J. Chem. Soc. Faraday Trans. I*, **77**, 2985 (1981).
154. D. J. Cebula, D.Y. Myers and R.H. Ottewill, *Colloid Polym. Sci.*, **260**, 96 (1982).

155. H.M. Cheung, S. Qutubuddin, R.V. Edwards and J.A. Mann Jr., *Langmuir*, **3**, 744 (1987).
156. A.M. Granz and B.E. Boeger, *J. Colloid Interface Sci.*, **109**, 499 (1986).
157. M. Kotlarchyk, *Physica B & C (Amsterdam)* **136**, 274 (1986).
158. A.M. Howe, C. Toprakcioglu, J.C. Dore and B.H. Robinson, *J. Chem. Soc. Farady Trans.1*, **82**, 241 (1986).
159. M.J.Grimson, *Mol. Phys.*, **60**, 179 (1987).
160. J.C. Ravey and M. Buzier, *Surfactants Solution (Proc. Int. Symp.)* 4th, **3**, 1759 (1982), K.L. Mittal and B. Lindman, Eds., Plenum, New York (Pub. 1984).
161. J. Lang, G. Mascola, R. Zana, and P.L. Luisi, *J. Phys. Chem.*, **94**, 3069 (1990) and references therein.
162. P. Ayyub, A.N. Maitra and D.O. Shah, *J. Chem. Soc. Faraday Trans.*, **89**, 3585 (1993).
163. K. Chokshi, S. Qutubuddin and A. Hussan, *J. Colloid Interface Sci.*, **139**, 93 (1990).
164. M. Gradzielski and H. Hoffmann, *Adv. Colloid Interface Sci.*, **42**, 149 (1992).
165. R.H. Cole, G. Delbos, P. Winsor IV, T.K. Bose, and J.M. Moreau, *J. Phys. Chem.*, **89**, 3338 (1985).
166. J. Peyrelasse and C. Boned, *J. Phys. Chem.*, **89**, 370 (1985).
167. J. Sjoblom and B. Gestblom, *J. Colloid Interface Sci.*, **115**, 535 (1987).
168. B. Gestblom and J. Sjoblom, *Langmuir*, **4**, 360 (1988).
169. M.A. Van Dijk, G. Castelleijn, J.G.H. Joosten and Y.K. Levine, *J. Chem. Phys.*, **85**, 626 (1985).
170. M.A. Van Dijk, J.G.H. Joosten, Y.K. Levine and D. Bedeaux, *J. Phys. Chem.*, **93**, 2506 (1989) and references therein.
171. T.K. Bose, G. Delbos and M. Merabet, *J. Phys. Chem.*, **93**, 867 (1989); A. Ponton, R. Nozaki and T.K. Bose, *J. Chem. Phys.*, **97**, 8515 (1992).

172. (a) J. Sjoblom, R. Skurtviet, J.O. Sactan and B. Gestblom, *J. Colloid Interface Sci.*, **141**, 329 (1991).  
(b) G. Lundsten, S. Backlund and G. Kiwilsza, *Prog. Colloid Polym. Sci.*, **97**, 194 (1994); G. Lundsten and S. Backlund, *J. Colloid Interface Sci.*, **169**, 408 (1995).
173. A.M. Cazabat, *Adv. Colloid Interface Sci.*, **38**, 33 (1992).
174. G. Mayer, *Chem. Phys. Lett.*, **168**, 575 (1990).
175. G.J.M. Koper, C.R. Vas and E. Vander Linden, *J. Phys. II France*, **4**, 163 (1994).
176. E. Vander Linden, S. Geiger and D. Bedeaux, *Physica A*, **156**, 130, (1989).
177. E. Vander Linden, D. Bedeaux, R. Hilfiker and H.F. Eicke, *Ber. Bunsenges Phys. Chem.*, **95**, 876 (1991).
178. P. Lianos, S. Modes, G. Staikos and W. Brown, *Langmuir*, **8**, 1054 (1992).
179. (a) D. Papoutsi, P. Lianos and W. Brown, *Langmuir*, **9**, 663 (1993).  
(b) A. Kabalnov, U. Olsson and H. Wennerstrom, *Langmuir*, **10**, 2159 (1994).
180. A. Barelli and H.F. Eicke, *Langmuir*, **2**, 780 (1986).
181. V. Kim, R. Hilfiker and H.F. Eicke, *Colloids Surf.*, **21**, 307 (1986); *J. Colloid Interface Sci.*, **121**, 579 (1988).
182. J. Eastoc, W.K. Young, B.H. Robinson and D.C. Steytler, *J. Chem. Soc. Faraday Trans.*, **86**, 2883 (1990).
183. O.V. Veselova, B.P. Nikolaev and A.M. Shlyakov, *Kolloidn Zh.*, **47**, 1027 (1985).
184. J.S. Guo, M.S. ElAsser, E.D. Sudel, H.J. Yue and J.W. Vanderhoff, *J. Colloid Interface Sci.*, **140**, 175 (1990).
185. A.M. Brun and W.H. Wade, *J. Colloid Interface Sci.*, **139**, 93 (1990).
186. (a) A.P. Full and E.W. Kaler, *Langmuir*, **10**, 2929 (1994).  
(b) H.S. On Chan, L.M. Gan, C.H. Chew, L. Ma and S.H. Seow, *J. Mater. Chem.*, **3**, 1109 (1993).  
(c) S.F. Trevino, R. Joubran, N. Parris and N.F. Berk, *Langmuir*, **10**, 2547 (1994) and references therein.

187. M. Almgren, R. Johannsson and J.C. Eriksson, *J. Phys. Chem.*, **97**, 8590 (1993).
188. M.J. Suarez, H. Levy and J. Lang, *J. Phys. Chem.*, **97**, 9808 (1993) and references therein.
189. J. Lang, N. Lalem and R. Zana, *Colloids Surf.*, **68**, 199 (1992) and references therein.
190. (a) N.P. Rao and R.E. Verrall, *J. Colloid Interface Sci.*, **121**, 85 (1988).  
(b) S. Kato, D. Jobe, N.P. Rao, C.H. Ho and R.E. Verrall, *J. Phys. Chem.*, **92**, 4127 (1988).
191. P.C. Jain, *Adv. Colloid Interface Sci.*, **54**, 17 (1995).
192. D.M. Zhu and Z.A. Schelly, *Langmuir*, **8**, 48 (1992); M. Ueda and Z.A. Schelly, *Langmuir*, **5**, 1005 (1989); D.M. Zhu, X. Wu and Z.A. Schelly, *Langmuir*, **8**, 1538 (1992) and *J. Phys. Chem.*, **96**, 7120 (1992).
193. D.M. Zhu, K.J. Feng and Z.A. Schelly, *J. Phys. Chem.*, **96**, 2382 (1992).
194. P.D.I. Fletcher, *J. Chem. Soc. Faraday Trans. I.*, **83**, 1493 (1987); B.P. Binks, P.D.I. Fletcher and D.I. Horsup, *Colloids Surf.*, **61**, 291 (1991); P.D.I. Fletcher and D. I. Horsup, *J. Chem. Soc. Faraday Trans.*, **88**, 855 (1992).
195. P.D.I. Fletcher and J.F. Holzwarth, *J. Phys. Chem.*, **95**, 2550 (1991).
196. K. Ogino, M. Nakamae and M. Abe, *J. Phys. Chem.*, **93**, 3704 (1989).
197. (a) M. Nakamae, K. Ogino and M. Abe, *Colloid Polym. Sci.*, **266**, 475 (1988).  
(b) M. Abe, A. Kuwabara, K. Yoshihara, K. Ogino, M. J. Kim, T. Kondo and H. Oshima, *J. Phys. Chem.*, **98**, 2991 (1994).  
(c) K. Yoshihara, N. Momozawa, T. Watanabe, K. Kamogawa, H. Sakai and M. Abe, *Colloids Surf.*, **109A**, 235 (1996).
198. H.L. Rosano, A.L. Nixon and J.L. Cavallo, *J. Phys. Chem.*, **93**, 4536 (1989).
199. K. Selcan, K. Kohler and G.H. Findenegg, *Colloid Polym. Sci.*, **266**, 283 (1988).
200. (a) D. Wielebinski and G.H. Findenegg, *Progr. Colloid Polym. Sci.*, **77**, 100 (1988).

- (b) L. J. Chen and M. C. Hsu, *J. Chem. Phys.*, **97**, 690 (1992); **98**, 4830 (1993); L. J. Chen, W.J. Yan, M.C. Hsu and D.L. Tyan, *J. Phys. Chem.*, **98**, 1910 (1994).
201. J. Santhanalakshmi and A. Parameswari, *Ind. J. Chem.*, **31A**, 630 (1992).
202. Eastoe, G. Fragneto, D.C. Steytler, B.H. Robinson and R.K. Heenan, *Physica B*, **180** and **181**, 555 (1992); J. Eastoe, T.F. Towey, B.H. Robinson, J. Williams and R.K. Heenan, *J. Phys. Chem.*, **97**, 1459 (1993).
203. (a) J. Eastoe, G. Fragneto and B.H. Robinson, *J. Chem. Soc. Faraday Trans.*, **88**, 461(1992); J. Eastoe, B.H. Robinson and R.K. Heenan, *Langmuir*, **9**, 2820 (1993).  
(b) H. R. Rabie and J. H. Vera, *Langmuir*, **11**, 1162 (1995) and references therein.
204. E.B. Abuin, M.A. Rubio and E.A. Lissi, *J. Colloid Interface Sci.*, **158**, 129 (1993).
205. (a) J. Eastoe, B.H. Robinson, D.C. Steytler, and J.C. Dore, *Chem. Phys. Lett.*, **166**, 153 (1990); D.C. Steytler, B.H. Robinson, J. Eastoe, K. ibid, J.C. Dore and I. MacDonald, *Langmuir*, **9**, 903 (1993).  
(b) H.F. Eicke and H. Christen, *J. Colloid Interface Sci.*, **46**, 417 (1974).  
(c) R.D. Neuman and S.J. Park, *J. Colloid Interface Sci.*, **152**, 41 (1992).  
(d) K.I. Feng and Z. A. Schelly, *J. Phys. Chem.*, **99**, 17207 and 17212 (1995) and references therein.  
(e) K. Kurumada, A. Shioi and M. Harada, *J. Phys. Chem.*, **98**, 12382 (1994) and references therein.  
(f) M. K. Khoshkbarchi and J. H. Vera, *J. Colloid Interface Sci.*, **170**, 562 (1995).
206. (a) T. Kawai, K. Hamada, N. Shindo and K. Kon-no, *Bull. Chem. Soc. Japan*, **65**, 2715 (1992).  
(b) P.D.I. Fletcher, B. H. Robinson and J.J. Tabony, *J. Chem. Soc. Faraday Trans.*, **1**, **82**, 2311 (1986)  
(c) J.L. Fulton, *J. Phys. Chem.*, **95**, 458 and 1445 (1991)  
(d) M. Belletete and G. Durocher, *J. Colloid Interface Sci.*, **134**, 289 (1990).  
(e) H. Hauser, G. Haering, A. Pande and P.L. Luisi, *J. Phys. Chem.*, **93**, 7869 (1989).
207. G. Giammona, F. Goffredi, V.T. Liveri and G. Vassallo, *J. Colloid Interface Sci.*, **154**, 411 (1992).
208. H.F. Eicke, in *Interfacial Phenomena in Apolar Media*, H.F. Eicke, Ed., Dekker, New York, p. 41 (1987) and references therein.



209. T.K. Jain, M. Varshney and A.N. Maitra, *J. Phys. Chem.*, **93**, 7409 (1989) and references therein.
210. E. Aliotta, P. Migliardo, D.I. Donato, V.T. Liveri, E. Bardez and B. Larrey, *Prog. Colloid Polym. Sci.*, **89**, 1 (1992).
211. G. Carlstrom and B. Halle, *Langmuir*, **4**, 1346 (1988) and *J. Phys. Chem.*, **93**, 3287 (1989).
212. A. D'Aprano, G. D'Arrigo, M. Goffredi, A. Paparelli and V.T. Liveri, *J. Chem. Phys.*, **95**, 1304 (1991); A. D'Aprano, A. Lizzio, V.T. Liveri, *J. Phys. Chem.*, **91**, 4749 (1991); F. Goffredi, V.T. Liveri and G. Vassallo, *J. Colloid Interface Sci.*, **151**, 396 (1992).
213. (a) A. Goto, H. Yoshioka, H. Kishimoto and T. Fujita, *Langmuir*, **8**, 441 (1992); A. Goto, S. Harada, T. Fujita, Y. Miwa, H. Yoshioka and H. Kishimoto, *Langmuir*, **9**, 86 (1993).  
(b) C. Boned, J. Peyrelasse and M. Moha-Quchane *J. Phys. Chem.*, **90**, 634 (1986).  
(c) P.D. Moran, G.A. Bowmaker and R.P. Cooney, *Langmuir*, **11**, 738 (1995)  
(d) G. Haandrikman, G.J.R. Daanc, F.J.M. Kerkhof, N.M. van Os. and L.A.M. Rupert, *J. Phys. Chem.*, **96**, 9061 (1992)  
(e) G. Gu, W. Wang and H. Yan, *J. Colloid Interface Sci.*, **167**, 87 (1994) and references therein.
214. T. Kawai, K. Hamada and K. Kon-No, *Bull. Chem. Soc., Japan*, **66**, 2804 (1993).
215. J. Eastoe, *Langmuir*, **8**, 1503 (1992); J. Eastoe and R.K. Heenan, *J. Chem. Soc. Faraday Trans.*, **90**, 487 (1994).
216. (a) M. Hasegawa, T. Sugimara, K. Kuraishi, Y. Shindo and A. Kitahara, *Chemistry Letters*, 1373 (1992); M. Hasegawa, T. Sugimara, Y. Suzuki, Y. Shindo, *J. Phys. Chem.*, **98**, 2120 (1994).  
(b) N. Mariano Correa, M. Alicia Biasutti and J.J. Silber, *J. Colloid Interface Sci.*, **172**, 71(1995) and references therein.
217. M. Lagues, C. Sauterey, *J. Phys. Chem.*, **84**, 3503 (1980).
218. S. Bhattacharya, J.P. Stokes, M.W. Kim and J.S. Huang, *Phys. Rev. Lett.*, **55**, 1884 (1985).
219. H.F. Eicke, R. Kubik, R. Hasse and I. Zschokke, in *Surfactants in Solution*, K.L. Mittal and B. Lindman, Eds., Plenum, New York, Vol. 3, p. 1533

- (1984); H.F. Eicke, R. Hilfiker and H. Thomas, *Chem. Phys. Lett.*, **125**, 295 (1986); M. Borkovec, H.F. Eicke, H. Hammerich and B. Dasgupta, *J. Phys. Chem.*, **92**, 206 (1988).
220. D. Chatenay, W. Urback, A.M. Cazabat and D. Langevin, *Phys. Rev. Lett.*, **54**, 2253 (1985).
221. M. Moha-Quchane, J. Peyrelasse and C. Boned, *Phys. Rev. A*, **35**, 3027 (1987).
222. J. Peyrelasse, M. Moha-Quchane and C. Boned, *Phys. Rev. A*, **38**, 904 (1988) and **38**, 4155 (1988).
223. H.F. Eicke, S. Geiger, R. Hilfiker, F.A. Sauer and H. Thomas, in *Time Dependant Effects in Disordered Materials*, R. Pyne and T. Riste, Eds., Plenum, New York, (1987).
224. S. Geiger, H.F. Eicke and D. Spiclmann, *Z. Phys. B. Condensed Matter*, **88**, 175 (1987).
225. P.K. Patanjali and A.N. Maitra, *Colloids Surf.*, **27**, 271 (1987); C. Mathew, P.K. Patanjali, A. Nabi and A.N. Maitra, *Colloids Surf.*, **30**, 253 (1988); A.N. Maitra, C. Mathew and M. Varshney, *J. Phys. Chem.*, **94**, 5290 (1990).
226. R. Hilfiker, H.F. Eicke, S. Geiger and G. Furler, *J. Colloid Interface Sci.*, **105**, 378 (1985).
227. A. Jada, J. Lang and R. Zana, *J. Phys. Chem.*, **93**, 10 (1989).
- 228 (a) E. Dutkiewicz and B.H. Robinson, *J. Electroanal Chem.*, **251**, 11 (1988).  
(b) A.C. Lam and R.S. Schechter, *J. Colloid Interface Sci.*, **120**, 43 (1987).  
(c) L. Mukhopadhyay, P.K. Bhattacharya and S.P. Moulik, *Ind. J. Chem.*, **32A**, 485 (1993).
229. C. Tanford, *The Hydrophobic Effect: Formation of Micelle and Biological Membrane*, 2nd. Ed., John Wiley New York.
230. P.A. Winsor, *Faraday Trans. Soc.*, **46**, 762 (1950).
231. M. Clause, J. Heil, A. Zardba and L. Nicolas-Morgantini, *Jornadas del Comete, Espanel de la Detergencia, Tensioactivos Y. Afines, Barcelona* (March 1986).
232. M. Ito, N. Taksawa and K. Shirahama, *J. Phys. Chem.*, **98**, 3726 (1990).

233. J. Fang and R.L. Venable, *J. Colloid Interface Sci.*, **116**, 269 (1987).
234. J. Peyrelasse and C. Boned, *Phys. Rev. A*, **41**, 938 (1990); C. Boned and J. Peyrelasse, *J. Surf. Sci. Technol.*, **7**, 1 (1991).
235. (a). S.R. Bisal, P.K. Bhattacharya and S.P. Moulik, *J. Phys. Chem.*, **94**, 350 (1990);  
(b). S. Pal, S.R. Bisal and S.P. Moulik, *J. Phys. Chem.*, **96**, 896 (1992);  
(c). S.R. Bisal, P.K. Bhattacharya and S.P. Moulik, *J. Phys. Chem.*, **94**, 4212 (1990).
236. M.T. Carver, E. Hirsch, J.C. Wittmann, R.M. Pitch and F. Candau, *J. Phys. Chem.*, **93**, 4867 (1989).
237. (a). L. Mukhopadhyay, P.K. Bhattacharya and S.P. Moulik, *Colloids Surf.*, **50**, 295 (1990) and *Ind. J. Chem.*, **32A**, 485 (1993).  
(b). P. Alexandridis, J.F. Holzwarth and T.A. Hatton, *J. Phys. Chem.*, **99**, 8222 (1995) and references therein.  
(c). G.J.M. Koper, W.F.C. Sager, J. Smeets and D. Bedeaux, *J. Phys. Chem.*, **99**, 13291 (1995)
238. M. Goffredi, V.T. Liveri and G. Vassallo, *J. Soln. Chem.*, **22**, 941 (1993).
239. (a). U. Lenz and H. Hoffmann, *Ber. Bunsengen Phys. Chem.*, **96**, 809 (1992).  
(b). C. Boned, Z. Saidi, P. Xancs and J. Peyrelasse, *Physical Review E (Part A)*, **49** 641, 5295 (1994).  
(c). H.F. Eicke, W. Meier and H. Hammerich, *Langmuir*, **10**, 2223 (1994).
240. R.F. Berg, M.R. Moldover and J.S. Huang, *J. Chem. Phys.*, **87**, 3687 (1987).
241. Z. Saidi, C. Mathew, J. Peyrelasse and C. Boned, *Phys. Rev. A*, **42**, 872 (1990).
242. S. Ray, S.R. Biswal and S.P. Moulik, *J. Surf. Sci. Technol.*, **8**, 191 (1992).
243. A. D'Aprano, G. D'Arrigo, A. Paparelli, M. Goffredi and V.T. Liveri, *J. Phys. Chem.*, **97**, 3614 (1993).
244. G. D'Arrigo, A. Paparelli, A. D'Aprano, I. D. Donato, M. Goffredi and V.T. Liveri, *J. Phys. Chem.*, **93**, 8367 (1989); A. D'Aprano, G.D. Arrigo, M. Goffredi, A. Paparelli and V.T. Liveri, *J. Chem. Phys.*, **95**, 1304 (1991) and *J. Soln. Chem.*, **21**, 323 (1992).

245. K.E. Bennett, J.C Hatfield, H.T. Davis, C.W. Macosko and L.E. Scriven, in *Microemulsions*, I.D. Robb, Ed., Plenum Press, New York and London (1982).
246. D. Ripple and R.F. Berg, *J. Chem. Phys.*, **97**, 7761 (1992).
247. C.M. Chen and G.G. Warr, *J. Phys. Chem.*, **96**, 9492 (1992).
248. R.C. Baker, A.T. Florescence, R.H. Ottewill and Th. F.Tadros, *J. Colloid Interface Sci.*, **100**, 332 (1984); M. Mooney, *J. Colloid Sci.*, **6**, 162 (1950) and J.V. Robinson, *J. Phys. Colloid Chem.*, **53**, 1042 (1949).
249. S. Ray, S.R. Bisal and S.P. Moulik, *J. Surf. Sci. Technol.*, **8**, 191 (1992).
250. C.A. Miller and P. Neogi, *AIChE. J.*, **26**, 212 (1980); S. Mukherjee, C.A. Miller and T. Fort Jr., *J. Colloid Interface Sci.*, **91**, 223 (1983) and C. Huh, *J. Colloid Interface Sci.*, **97**, 201 (1984). A.C. Lam, N.A. Falk and R.S. Schechter, *J. Colloid Interface Sci.*, **120**, 30 (1987).
251. S. Pal and S.P. Moulik, *Ind. J. Chem.*, **34A**, 931 (1995).
252. A.S. Kertes, S. Chaston and W.C. Lai, *J. Colloid Interface Sci.*, **73**, 94 (1980); A.S. Kertes, W.C. Lai, *J. Colloid Interface Sci.*, **76**, 48 (1980); W.C. Lai and A.S. Kertes, *Colloids Surf.*, **4**, 379 (1982) and A.S. Kertes, L. Taimering, N. Garti, *Colloid Polym. Sci.*, **67**, 263 (1985).
253. G. Olofsson, J. Kizhing and P. Stenius, *J. Colloid Interface Sci.*, **111**, 213 (1980).
254. G. Roux-Deagranges, A.H. Roux, J.P.E. Grolier and A. Viillard, *J. Colloid Interface Sci.*, **84**, 636 (1981).
255. (a) S.P. Moulik, M.L. Das and A.R. Das, *Langmuir*, **8**, 2135 (1992).  
(b) S. Ray, S.R. Bisal and S.P. Moulik, *Langmuir*, **10**, 2507 (1994).
256. S.P. Moulik and S. Ray, *Pure and Appl. Chem.*, **66(3)**, 521 (1994); S. Ray, S.R. Bisal, and S.P. Moulik, *J. Chem. Soc. Faraday Trans. I*, **89**, 3277 (1993).
257. M. Bourrel and R.S. Schechter, Ed., *Microemulsions and Related Systems*, Marcel Dekker, New York and Basel, Ch. 4, p. 157 (1988).
258. M. Kahlweit and R. Strey, in *Microemulsion Systems*, H.L. Rosano and M. Clause, Eds., Marcel Dekker, New York & Basel, p. 1 (1987) and M. Kahlweit, R. Strey and P. Firman, *J. Phys. Chem.*, **90**, 671 (1986).

259. Y. Barakat, L.N. Fortney, R.S. Schechter, W.H. Wade and Y. Siv, Proc. Second European Symposium on EOR Techniq., Paris, P. 11 (Nov. 1982) and *J. Colloid Interface Sci.*, **92**, 561 (1983).
260. C. Kumar and D. Balasubramanian, *J. Colloid Interface Sci.*, **69**, 271 (1979).
261. K. Tamura and Z.A. Schelly, *J. Am. Chem. Soc.*, **103**, 1013 (1981) and **103**, 1018 (1981).
262. (a). A. D'Aprano, I.D. Donato, F. Pinto and V.T. Liveri, *J. Solution Chem.*, **19**, 1055 (1990) G. Pitarresi, C. Sbriziolo, M.L.T. Liveri and V.T. Liveri, *J. Solution Chem.*, **22**, 279 (1993) and references therein.  
(b). N.Garti, A. Aserin, S. Ezrahi and E. Wachtel, *J. Colloid Interface Sci.*, **169**, 428 (1995)
263. G. Gillberg, in *Emulsions and Emulsion Technology*, K.J. Lissant Ed., Part 3, p.1, Dekker, New York, (1986).
264. C.A. Jones, L.E. Weaner and R.A. Mackay, *J. Phys. Chem.*, **84**, 1495 (1980).
265. R.A. Mackay, *Adv. Colloid Interface Sci.*, **15**, 131 (1981).
266. C.H. Chew and L. M. Gan, *J. Polym. Sci.*, **23**, 225 (1985).
267. P. Speiser, in *Reverse Micelles*, P.L. Luisi and B.E. Straub, Eds., Plenum, New York, (1984).
268. K.A. Johnson and D.O. Shah, *J. Colloid Interface Sci.*, **107**, 269 (1985).
269. D.O. Shah and R.S. Schechter, Eds., *Improved Oil Recovery by Surfactant and Polymer Flooding*, Academic Press, New York, (1977).
270. M. Bourrel, Ch. Koukounis, R.S. Schechter and W.H. Wade, *J. Disp. Sci. Technol.*, **1**, 13 (1980).
271. C.A. Miller and S. Qutubuddin, in *Interfacial Phenomena in Apolar Media* (H. F. Eicke and G. Parfitt, Eds.), Chap. 4, pp. 117-185, Dekker, New York, (1987).
272. D.O. Shah (Ed.), *Macro- and Microemulsions : Theory and Applications*, Am. Chem. Soc. Symposium Series, Vol. 272, Washington D.C (1985).
273. J. Kiwi and M. Gratzel, *J. Am. Chem. Soc.*, **100**, 6314 (1978).

274. P. Fourre, D. Bauer and J. Lemerle, *Anal. Chem.*, **55**, 669 (1963) P. Fourre and D. Bauer, *Solvent Extr. Ion Exch.*, **1**, 465 (1983).
275. E. Paatero, *The Effects of Amphiphilic Aggregation and Phase Equilibria on Metal Extraction Processes*, Ph. D. Dissertation, Kemisk-tekniska fakulteten, Abo Akademi, (1990).
276. A.G. Gaonkar and R.D. Neuman, *J. Colloid Interface Sci.*, **119**, 251 (1987).
277. M. Boumezioud, A. Derouiche and C. Tondre, *J. Colloid Interface Sci.*, **128**, 422 (1989)
278. G. Mathis and J.J. Dezpuech, French Patent 8022875, (1980); G.Mathis, D.Sc. Thesis, University of Nancy, J. Nancy, France, (1982).
279. C. Tondre and A. Xenakis, *Colloid Polym. Sci.*, **260**, 232 (1982); A. Xenakis and C. Tondre, *J. Phys. Chem.*, **87**, 4737 (1983) and C. Tondre and A. Xenakis, *Proc. Int. Symp. Surfactants in Solution*, K.L. Mittal Ed., Plenum, New York, Vol. 3, 1881 (1983).
280. C. Tondre and A. Deroiche, *J. Phys. Chem.*, **94**, 1624 (1990) ; A. Deroiche and C. Tondre, *J. Chem. Soc. Faraday Trans. I*, **85**, 3301 (1989) ; *Colloids Suf.*, **48**, 243 (1990).
281. A. Xenakis, C. Selve and C. Tondre, *Talanta*, **34**, 509 (1987); M. Ismael and C.Tondre, *J. Membrane Sci.*, **72**, 181 (1992).
282. C. Tondre and A. Xenakis, *Faraday Discuss. Chem. Soc.*, **77**, 1151 (1984).
283. S. Atik, M. Nam and L. Singer, *Chem. Phys. Lett.*, **67**, 75 (1979).
284. J. M. Wiencek and S. Qutubuddin, *Sep. Sci. Technol.*, **27**(10) 1211 (1992).
285. J.M. Wiencek and S. Qutubuddin, *Sep. Sci. Technol.*, **27**(11), 1407 (1992).
286. C. J. O'Connor, T.D. Lomax and R.E. Ramage, *Adv. Colloid Interface Sci.*, **20**, 21 (1984).
287. P.D.I. Fletcher and B.H. Robinson, *J. Chem. Soc. Faraday Trans.1*, **80**, 2417 (1984).
288. J.H. Fendler, *Membrane Mimetic Chemistry*, John Wiley, New York, (1982).
289. M.J. Blandamer, J. Burgess and B. Clark, *J. Chem. Soc. Chem. Commun.*, 659 (1983).

290. J.K. Thomas, *Chem. Rev.*, **80**, 285 (1980).
291. C. Salerno, A. Lucano and D. Fasella, *Biochim.*, **71**, 461 (1989).
292. S.M. Hubig and M.A. Rodgers, *J. Phys. Chem.*, **94**, 1933 (1990).
293. J. Cassado, A. Castro, J.R. Leis, M. Mosquera and M.E. Pena, *J. Chem. Soc. Perkin Trans. II*, 1859 (1985).
294. M.A. Lo'pez-Quintela and J. Cassado, *J. Therm. Biol.*, **139**, 129 (1989).
295. N.F. Borys, S.L. Holt and R.E. Barden, *J. Colloid Interface Sci.*, **71**, 526 (1979).
296. (a) R.A. Mackay, K. Letts and C. Jones, *Micellization, solubilization and Microemulsion*, K.L. Mittal, Ed., Plenum Press, New York, Vol 2, p. 801 (1977).  
(b) C. Hamansky and R.A. Mackay, *Solution Chemistry of Surfactants*, K.L. Mittal, Ed., Plenum Press, New York, Vol. 2, p. 723 (1979).  
(c) R.A. Mackay and C. Hamansky, *J. Phys. Chem.*, **85**, 739 (1981); R.A. Mackay, *J. Phys. Chem.*, **86**, 4756 (1982); R.A. Mackay, *Adv. Colloid Interface Sci.*, **15**, 131 (1981).
297. R. Schomacker, *Progr. Colloid Polym. Sci.*, **81**, 131 (1990).
298. I.V. Berezin, K. Martinek and A.K. Yatsimirski, *Russ. Chem. Rev.*, **42**, 787 (1973).
299. C.A. Bunton, *Pure Appl. Chem.*, **49**, 696 (1977).
300. P.D.I. Fletcher, *J. Chem. Soc. Faraday Trans. I*, **82**, (1986).
301. R. Kubik and H.F. Eicke, *Helv. Chim. Acta*, **65**, 170 (1982).
302. M. Wong, J.K. Thomas and M. Gratzel, *J. Am. Chem. Soc.*, **98**, 2391 (1976).
303. I. Tabony, A. Lior and M. Drifford, *Colloid Polym. Sci.*, **261**, 938 (1983).
304. K. Letts and R.A. Mackay, *Inorganic Chemistry*, **14**, 2993 (1975).
305. (a) C.A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.*, **85**, 3142 (1981).  
(b) C.A. Bunton and F. de Buzzaccarini, *J. Phys. Chem.*, **85**, 3139 (1981).

306. P. Varughese and A. Broge, *J. Ind. Chem. Soc.*, **68**, 323 (1991).
307. C.A. Bunton, D.C. Mckenzie and V. Athaassakis, *J. Phys. Chem.*, **90**, 5858 (1986).
308. B.K. Misra, B.S. Valaulikar, J.T. Kunjappu and C. Monohar, *J. Colloid Interface Sci.*, **127**, 373 (1989).
309. (a) R. Schomacker, K. Stickdom and W. Konche in *Reactions in Compartmentalized Liquids*, W. Konche and R. Schomacker, Eds., Springer-Verlag, Berlin, Heidelberg, p. 31 (1989).  
(b) R. Schomacker, K. Stickdom and W. Konche, *J. Chem. Soc. Faraday Trans.*, **87**, 847 (1991).
310. D. Feustel, F. Runge and G. Ilgenfritz, in *Reactions in Compartmentalized Liquids*, W. Konche and R. Schomacker, Eds., Springer-Verlag, Berlin, Heidelberg, p. 21, (1989).
311. M.L. Das, P.K. Bhattacharya and S.P. Moulik. *Langmuir*, **6**, 1591 (1990).
312. (a) E. Munoz, C. Gomez-Herrera, M. Graciani, M.L. Moya and F. Sanchez, *J. Chem. Soc. Faraday Trans.*, **87**, 129 (1991).  
(b) C. Gomez-Herrera, M. Graciani, E. Munoz, M.L. Moya and F. Sanchez, *J. Colloid Interface Sci.*, **141**, 454 (1991).
313. S.G. Oh, J. Kizling and K. Holmberg, *Colloids Surf.*, **97A**, 169 (1995)
314. J. Burgess and M.S. Patel, *J. Chem. Soc. Faraday Trans.*, **89**, 783 (1993).
315. (a) M. Boutonnet, J. Kizling, P. Stenius and G. Maire, *Colloids Surf.*, **5**, 209 (1982).  
(b) J.H. Fendler, *Chem. Rev.*, **87**, 877 (1987); K. Kandori, K. Kon-No, and A. Kitahara, *J. Colloid Interface Sci.*, **122**, 78 (1988); S. Modes and P. Lianos, *J. Phys. Chem.*, **93**, 5854 (1989); M. Lopaz - Quintela and J. Rivas, *J. Colloid Interface Sci.*, **158**, 446 (1993), M.P. Pileni, *J. Phys. Chem.*, **97**, 6961 (1993) and references therein; C. Petit, P. Lixon and M. P. Pileni, *J. Phys. Chem.*, **97**, 12974 (1993), F. Arriagada and K. Osseo- Asare, *J. Colloid Interface Sci.*, **170**, 8 (1995) and references therein; T. Hirai, S. Shiojiri and I. Komasaawa, *J. Chem. Engg.*, **27**, 590 (1994) and references therein; E. Joselevich and I. Willner, *J. Phys. Chem.*, **98**, 7628 (1994) and references therein; V. Pillai, P. Kumar, M.J. Hok, P. Ayyub and D.O. Shah, *Adv. Colloid Interface Sci.*, **55**, 241 (1995) and references therein; J. Eastoe and A.R. Cox, *Colloids Surf.*, **101A**, 63 (1995) and references therein; U. Natarajan, K. Handique, A. Mehra, J.R.



- Bellare and K.C.Khilar, *Langmuir*, **12**, 2670 (1996) and references therein;  
T. Kawai, A.Fujino, K.Kon-No, *Colloids Surf.*, **109A**, 245 (1996),  
L.M.Gan, K.Zhang and C.H.Chew, *Colloids Surf*, **110A**, 199 (1996).
316. S. Terabe, N. Matsubara, Y. Ishihama and Y. Okada, *J. Chromatography*, **608**, 23 (1992).
317. O.A. El Seoud, A.M. Chinelatto and M.A. Shimizu, *J. Colloid Interface Sci.*, **88**, 420 (1982) and *J. Colloid Interface Sci.*, **95**, 163 (1983); R.C. Vieira and O.A. El Seoud, *J. Colloid Interface Sci.*, **141**, 295 (1991); A.M. Chinelatto, I.T. Okano and O.A. El Seoud, *Colloid Polym Sci.*, **269**, 264 (1991).
318. R.A. Mackay, K. Jacobson and J. Tourian, *J. Colloid Interface Sci.*, **76**, 515 (1980).
319. C.J. Drummond, F. Grieser and T.W. Healy, *J. Chem., Soc. Faraday Trans. 1*, **85**, 521-578 (1989).
320. O. Ortona, V. Vitagliano and B.H. Robinson, *J. Colloid Interface Sci.*, **125**, 271 (1988) and C. Oldfield, B.H. Robinson and R.B. Freedman, *J. Chem. Soc. Faraday Trans.*, **86**, 833 (1990).
321. R. Guo and X. Zhu, *J. Surf. Sci. Technol.*, **7**, 41 (1991).
322. R.E. Smith and P.L. Luisi, *Helv. Chim. Acta*, **63**, 2302 (1980).
323. S.P. Moulik, B.K. Paul and D.C. Mukherjee, *J. Colloid Interface Sci.*, **161**, 72 (1993)
324. I. Rico, A. Lattes, K.P. Das and B. Lindman, *J. Am. Chem. Soc.*, **111**, 7266 (1989).
325. F. Candau, I. Zekhnini and J.P. Durand, *J. Colloid Interface Sci.*, **114**, 398 (1986).
326. P.L. Luisi and B. Straub, Eds., *Reverse Micelles*, Plenum, New York (1984) and P.L. Luisi, *Angew. Chem. Int. Ed. Engl.*, **24**, 439 (1985).
327. (a) P.L. Luisi and L.J. Majid, *CRC Critical Rev. Biochem.*, **20**, 409 (1986).  
(b) P.L. Luisi and R. Wolf, in *Solution Behavior of Surfactants*, K.L. Mittal and J.H. Fendler, Eds., Plenum, Vol. 2, 887 (1982).
328. (a) A.V. Levashov, Y.L. Khmel'nitskii, N.L. Klyachko and K. Martinek; in

- Surfactants in Solution, K.L. Mittal and B. Lindman, Eds., P. 1069, Plenum, New York 1984.
- (b) K. Martinek, A.V. Levashov, N. Klyachko, Y.L. Khmel'nitski and I.V. Berezin, *Eur. J. Biochem.*, **155**, 453 (1986).
- (c) Y.L. Khmel'nitsky, A.V. Kabanov, N.L. Klyachko, A.V. Levashov and K. Martinek, in *Structure and Reactivity in Reverse Micelles*, M.P. Pileni, Ed., Elsevier, Amsterdam, p. 230 (1989).
329. A. Kitahara, *Adv. Colloid Interface Sci.*, **12**, 109 (1980).
330. M. Waks, *Proteins*, **1**, 4 (1986).
331. P. Douzou, E. Keh and C. Balny, *Proc. Natl. Acad. Sci.*, **76**, 681 (1979) and P. Douzou, *Cryobiochemistry: An Introduction*, Academic Press, New York (1977).
332. J.W. Shield, H.D. Ferguson, S. Bommarius and T.A. Hatton, *Ind. Eng. Chem. Fundam.*, **25**, 603 (1986).
333. K. Martinek, I.V. Berezin, Y.L. Khmel'nitskii, N.L. Klyachko and A.V. Levashov, *Collect. Czech. Chem. Commun.* **52**, 2589 (1987).
334. P. Meier and P.L. Luisi, *J. Solid Phase Biochem.*, **5**, 269 (1980).
335. (a) P.L. Luisi, F. J. Bonner, A. Pellegrini, P. Wiget and R. Wolf, *Helv. Chim. Acta*, **62**, 740 (1979).
- (b) P.L. Luisi and C. Laane, *Trends Biotechnol.*, **4**, 153 (1986).
336. R.S. Rahaman, J.Y. Chee, J.M.S. Cabral and T.A. Hatton, *Biotechnol. Prog.*, **4**, 218 (1988).
337. K.L. Kadam, *Enzyme Microbiol. Technol.*, **8**, 266 (1986).
338. K. Martinek, I.V. Berezin, L. Khmel'nitskii, N.L. Klyachko and A.V. Levashov, *Biocatalysis*, **1**, 9 (1987).
339. R. Hilhorst, C. Laane and C. Veeger, *Proc. Natl. Acad. Sci.* **79**, 3927 (1982).
340. (a) A.V. Levashov, Y.L. Khmel'nitskii, N.L. Klyachko, V.Y. Chernyak and K. Martinek, *Anal. Biochem.*, **118**, 42, (1981).
- (b) B. Kelley, R. Rahaman and T.A. Hatton, in *Analytical Chemistry in Organized Media: Reversed Micelles*, W.L. Hinze, Ed., JAI Press, Greenwich (1991).
- (c) T.A. Hatton, in *Surfactant-Based Separation Process*, J.F. Scamehorn and J.H. Harwell, Eds., Dekker, New York, p. 55 (1989).

341. P.L. Luisi, M. Giomini, M.P. Pileni and B.H. Robinson, *Biochim. Biophys. Acta*, **947**, 209 (1988).
342. P.D.I. Fletcher, R.B. Freedman, J. Mead, C. Oldfield and B.H. Robinson, *Colloids Surf.*, **10**, 193 (1984); P.D.I. Fletcher, G.D. Rees, B.H. Robinson and R.B. Freedman, *Biochim. Biophys. Acta.*, **832**, 204 (1985); P.D.I. Fletcher and D. Parrott, *J. Chem. Soc. Faraday Trans. I*, **84**, 1131 (1988).
343. (a) J.W. Shield, H.D. Ferguson, K.K. Gleason and T.A. Hatton, in *Biocatalysis and Biomimetics*, J.D. Burrington and D.S. Clark, Eds., P. 90, Am. Chem. Soc., Washington, DC (1989).  
(b) Q. Mao and P. Walde, *Biochim. Biophys. Commun.*, **178**, 1105 (1991).  
(c) M. Hirai, T. Takizawa, S. Yabuki, R. Kawai - Hirai, M. Oya, K. Nakamura, K. Kobashi and Y. Amemiya, *J. Chem. Soc. Faraday Trans.*, **91**, 1081 (1995).  
(d) S. Christ and P. Schurtenberger, *J. Phys. Chem.*, **98**, 12708 (1994)
344. D. Ham, J.S. Rhee and S.B. Lee, *Biotechnol. Bioeng.*, **30**, 381 (1987).
345. P.D.I. Fletcher, B.H. Robinson, R.B. Freedman and C. Oldfield, *J. Chem. Soc. Faraday Trans. I*, **81**, 2667 (1985).
346. K.M. Larsson, P. Adlercreutz and B. Mattiasson, *Eur. J. Biochem.*, **166**, 157 (1987).
347. G.B. Strambini and M. Gonnelli, *J. Phys. Chem.*, **92**, 2850 (1988).
348. J.P. Samama, K.M. Lee and J.F. Biellmann, *Eur. J. Biochem.* **163**, 609 (1987); K.M. Lee and J.F. Biellmann, *FEBS Letters*, **223**, 33 (1987) and *New. J. Chem.*, **11**, 775 (1987).
349. N.L. Klyachko, A.V. Levashov, A.V. Pshezhetsky, N.G. Bogdanova, I.V. Berezin and K.V. Martinek, *Eur. J. Biochem.*, **161**, 149 (1986).
350. M. Gonnelli and G.B. Strambini, *J. Phys. Chem.*, **92**, 2854 (1988).
351. C. Grandi, R.E. Smith and P.L. Luisi, *J. Biol. Chem.*, **256**, 837 (1981).
352. B. Kurganov, A.V. Levashov, K. Martinek, I.V. Berezin, *Dokl. Akad. Nauk, SSSR*, **282**, 1263 (1985).
353. K. Martinek, A.V. Levashov, Y.L. Khmel'nitskii, N.L. Klyachko, and I.V. Berezin, *Science*, **218**, 889 (1982) and *Biochim. Biophys. Acta*, **657**, 277 (1981).

354. P. Walde, Q. Peng, N.W. Fadnavis, E. Battistel and P.L. Luisi, *Eur. J. Biochem.* **193**, 401 (1988).
355. R. Wolf and P.L. Luisi, *Biochim. Biophys. Res. Commun.*, **89**, 209 (1979).
356. K.M. Lee and J.F. Biellmann, *Bioorganic Chemistry*, **14**, 262 (1986) and *Tetrahedron*, **44**, 1135 (1988).
357. E. Battistel and P.L. Luisi, *J. Colloid Interface Sci.*, **128**, 7 (1989).
358. E. Battistel, P.L. Luisi, *J. Phys. Chem.*, **92**, 6680 (1991).
359. (a) Y. Miyake, T. Owari, K. Matsuura and M. Teramoto, *J. Chem. Soc. Faraday Trans.*, **89**, 1993 (1993); Y. Miyake, T. Owari, F. Ishiga and M. Teramoto, *J. Chem. Soc. Faraday Trans.*, **90**, 979 (1994).  
(b) Y. Miyake, *Colloids Surf.* **109A**, 255 (1996)
360. S. Gupta, L. Mukhopadhyay and S.P. Moulik, *Colloids Surf. B* **3**, 191 (1994); *Ind. J. Biochem. Biophys.* **32**, 261 (1995).
361. P. Karpe and E. Ruckenstein, *J. Colloid Interface Sci.*, **141**, 534 (1991); E. Ruckenstein and P. Karpe, *J. Colloid Interface Sci.*, **139**, 408 (1990).
362. E.B. Leodidis and T.A. Hatton, *J. Phys. Chem.*, **94**, 6400 (1990) and other two papers in the series; R.S. Rahaman and T.A. Hatton, *J. Phys. Chem.*, **95**, 1799 (1991).
363. (a) T. A. Hatton, in *Ordered Media in Chemical Separations*, W.L. Hinze and D.W. Armstrong, Eds., ACS Symp. Ser., Am. Chem. Soc., New York, Vol. **342**, p. 170 (1987).  
(b) E.B. Leodidis and T.A. Hatton, *J. Colloid Interface Sci.*, **147**, 163 (1991).  
(c) M. Dekker, K. Van't Riet, S.R. Weijers, J.W.A. Baltussen, C. Laane and B.H. Bijsterbosch, *Chem. Eng. J.*, **33B**, 27 (1986).
364. S.R. Dungan, T. Bauch, T.A. Hatton, P. Plucinski, W. Nitsch, *J. Colloid Interface Sci.*, **145**, 33 (1991).
365. M. Dekker, K. Van't Riet, B.H. Bijsterbosch, P. Fijneman and R. Hilhorst, *Chem. Eng. Sci.*, **45**, 2949 (1990).
366. (a) W. Nitsch and P. Plucinski, *Ber. Bunsenges Phys. Chem.*, **93**, 994 (1989).  
(b) P. Plucinski and J. Reitmeir, *Colloids Surf.*, **97A**, 157 (1995).

- (c) P. Plucinski and W. Nitsch , *J. Phys. Chem.* , **97**, 8983 (1993).
  - (d) P. Plucinski and W. Nitsch , *J. Colloid Interface Sci.* , **154**,104 (1992); *Langmuir*, **10**, 371 (1994).
  - (e) M. Adachi and M. Harada , *J. Phys. Chem.* , **97** , 3631 (1993) ; *J. Colloid Interface Sci.* , **165** , 229 (1994) ; K. Kawakami , M. Harada , M. Adachi, A. Shioi , *Colloids Surfs.* ,**109A** , 217 (1996).
  - (f) R. Hilhorst , in *Structure and Reactivity of Reversed Micelles* , M.P. Pileni , Ed., Elsevier , Amsterdam , pp. 323-341 (1989) . R. Hilhorst , P. Fijnemann , P. Heering, R.B.G. Wolbert , M. Dekker , K. Van't Reit and B.H. Bijsterbosch, *Pure and Appl. Chem.*, **64**, 1765 (1992) ; R.M.D. Verhaert , R. Hilhorst , M. Vermue, T.J. Schaafsma and C. Veeger , *Eur. J. Biochem.* , **18** , 59 & 73 (1990).
  - (g) K.Takeda, K. Harada, K. Yamaguchi and Y. Moriyama, *J. Colloid Interface Sci.*, **164**, 382 (1994) and references therein.
367. M.A. Rubio and E.A. Lissi, *J. Colloid Interface Sci.*, **128**, 458 (1989).
368. (a) F. Candau in *Encyclopedia of Polymer Science and Engineering*, John Wiley, New York, Vol. 9, p. 718 (1987).
- (b) C. Holtzscheler and F. Candau , *J. Colloid Interface Sci.* , **125** , 97 (1988).
  - (c) F. Candau , in *Polymerization in Organised Media* , C.M. Paleous , Ed. , Gordon and Breach Science Pubs., Philadelphia , PA , Ch. 4 (1992).
369. C. Daubresse , C. Grandfils , R. Jerome and P. Teyssie , *J. Colloid Interface Sci.* , **168**, 222 (1994)
370. (a) L. Garcia-Rio , J.R. Leis , M.E. Pena and E. Iglesias , *J. Phys. Chem.* , **97**, 3437 (1993).
- (b) L. Garcia-Rio , J.R. Leis and E. Iglesias , *J. Phys. Chem.* , **99** , 12318 (1995) and references therein.
  - (c) K. Tajima , Y. Imai , A. Nakamura and M. Koshinuma , *J. Colloid Interface Sci.*, **164** , 444 (1994).
371. A.S. Chhatre , R.A. Joshi and B.D. Kulkarni , *J. Colloid Interface Sci.* ,**158**, 183 (1993); B.K. Jha , A.S. Chhatre and B.D. Kulkarni , *J. Chem. Soc. , Perkin Trans.2* , 1383 (1994) ; B.K. Jha , A.S. Chhatre , B.D. Kulkarni , R.A. Joshi , R.R. Joshi and U.R. Kalkote , *J. Colloid Interface Sci.*, **163**, 1 (1994); A.S. Chhatre , N.K. Yadav and B.D. Kulkarni , *Sep. Sci. , Technol.* , **28** , 1465 (1993) .
372. M. Valiente and E. Rodenas, *J. Phys. Chem.*, **95**, 3368 (1991) ; *Colloid Polym. Sci.*, **271**, 494 (1993).

373. (a) M. Nokaly and D. Conell, Ed., *Microemulsions and Emulsions in Foods*, ACS Symposium Series 448, ACS, Washington DC (1991).  
(b) L. Moberger and K. Larsson, *J. Dispersion Sci. and Technol.*, **8**, 207 (1987).
374. (a) A. Gaonkar, *Proc. Int. Symp. on Industrial Applications of Microemulsion Technology*, New Delhi (1993).  
(b) L. Engstrom, *Proc. 15th Scandinavian Symposium on Lipids*, V.K.S. Shukla and G. Holmer, Eds., Rebild Bakker, Skorping, Denmark (1989).
375. K. Holmberg, *Adv. Colloid Interface Sci.*, **51**, 137 (1994) and references therein.
376. (a) G.D. Rees, T.R.J. Jenta, M.V. Nascimento, M. Catauro, B.H. Robinson, G.R. Stephenson and R.D.G. Olphert, *Ind. J. Chem.*, **32B**, 30 (1993) and references therein.  
(b) S. Backlund, F. Ericksson, L.T. Kanerva and M. Rantala, *Colloids Surf.*, **4B**, 121 (1995) and references therein.
377. N.Z. Atay-Guneyman, F. Atadinc and Y. Kozluca, *J. Colloid Interface Sci.*, **169**, 246 (1995).
378. J.K. Thomas, *The Chemistry of Excitation at Interfaces*, ACS Monograph 181, ACS, Washington DC (1984).
379. K. Kalyanasundaran, *Photochemistry in Microheterogeneous Systems*, Academic press, New York (1987).
380. M. Gratzel and K. Kalyanasundaran, Eds., *Kinetics and Catalysis in Microheterogeneous Systems*, Marcel Dekker, New York (1991).
381. J.H. Fendler, *J. Phys. Chem.*, **89**, 2730 (1985); *Chem. Rev.*, **87**, 877 (1987).
382. R.C. Ahuja, D. Mobius and M. Matsumoto, *J. Phys. Chem.*, **96**, 1855 (1992) and *Thin. Solid Films*, **210-211**, 60 (1992).
383. M.H. Gehlon and F.C. De Schryver, *Chem. Rev.*, **93**, 199 (1993) and references therein.
- 384 (a) E. Bardez, E. Monnier, B. Valcur, *J. Colloid Interface Sci.*, **112**, 200 (1986).  
(b) M. Panda, P.K. Behara, B.K. Mishra and G.D. Behara, *Ind. J. Chem.*, **34A**, 11 (1995).

385. B.K. Paul , D.C. Mukherjee and S.P. Moulik , J. Photochem. Photobiol., A. Chem, **94**, 53 (1996).
386. K. Kon-No, in Surface and Colloid Science, E. Matijevic, Ed., Plenum, New York, Vol. **15**, Ch. 3, pp. 125-151 (1993).
387. K. Ogino and M. Abe, in Surface and Colloid Science, E. Matijevic, Ed., Plenum, New York, Vol. **15**, pp. 85-123 (1993).
388. P.L. Luisi, in Kinetics and Catalysis in Microheterogeneous Systems, M. Gratzel and K. Kalyanasundaran, Eds., Marcel Dekker Inc., New York, pp. 115-134 (1991).
389. M.P. Pileni, J. Phys. Chem., **97**, 6961 (1993).
390. Tapas De and Amarnath Maitra , Adv. Colloid Interface Sci. , **59** , 95 (1995).
391. S. P. Moulik and K. Mukherjee , Proc. Natl. Sci. Acad. , **62A** , 215 (1996).