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Effect of Microemulsion Microstructure on Efficiency of Chemical Reactions

Pravin Kumar Srivastava

Department of Chemistry, Sanjay Gandhi (P.G.) College, Meerut, INDIA

Abstract: Organic syntheses are often faced the problem of reacting water-soluble inorganic reactants with water-soluble organic reactants. In microemulsion high concentration of both water-soluble and water-insoluble compounds dissolved simultaneously. Microemulsion acts as reaction media for various organic reactions with reactants such as acids, bases, cyanide, bromide, hypochlorite or permanganate.

Keywords: Microemulsion, oxidation, reduction and polymerization.

1.1 INTRODUCTION:

The chemistry of colloids is well known and getting importance in catalysis and biological reactions. Colloids may be defined as suspension of finely divide particles of one material in a dispersing medium that do not separate on long standing.[1,2] colloidal properties are dominated by their surface due to their small size.[2,3]Materials which fall under the classification of colloid[4] include foams, emulsions, fogs, aerosols, smokes, miscelles and macromolecules including polymers[1,2,5,6] Surfactants micelles and microemulsions are other types of colloids that have been investigated as sites for catalysis.[7]

1.2 Microemulsions:

Microemulsions are optically transparent, thermodynamically stable isotropic liquid mixtures of surfactants, water and oil (non –polar solvent), with or without addition of a co-surfactant (a low molecular weight alcohol). These systems are heterogeneous on a microscopic scale and consist of microscopic domains of water and oil separated and stabilized by a monolayer of surfactant molecules. In most cases, depending on the experimental conditions, microemulsions can be regarded as dispersion of either water droplets in oil continuous phase (W/O) or oil droplets in water continuous phase (O/W), each droplets being surrounded by the surfactant monolayer. Figure 1, 2 The size of oil droplets in (O/W) systems or water droplets in (W/O) systems is small i.e. 50-500A^0.The presence of a cosurfactants is critical in reducing the interfacial tension between the droplets and the continuous phase to near zero. In the absence of cosurfactant at the droplets interphase, the emulsions become milky and unstable owing to the much stable droplets. There are number of publications on microemulsion and they attained increasing significance both in basic research and in industry.

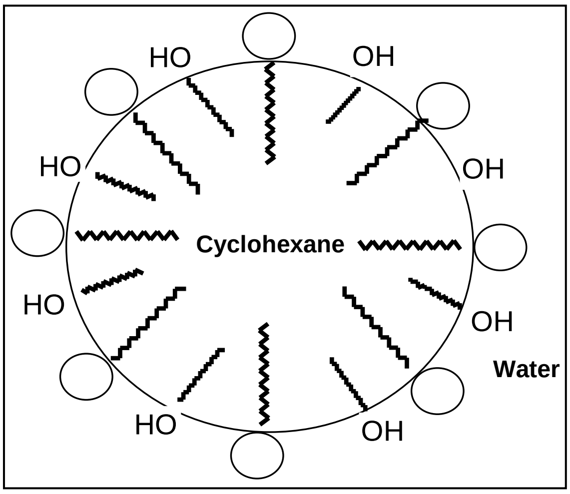

Figure 1. Oil –In-Water Microemulsion

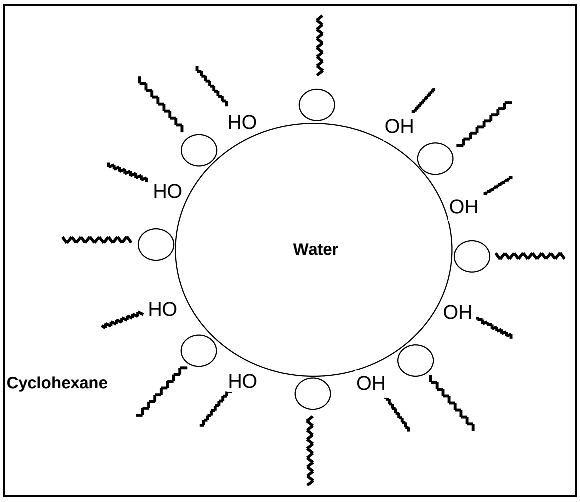

Figure 2. water–In-Oil Microemulsion

So there are three types of surfactant (anion, cationic and non-ionic) which were used to make the micromulsion, sorption of anionic surfactant aerosol-OT (SDS or AOT),Cetyltrimethyl ammonium bromide (CTAB), and Brij-96 (a long chain polyoxyethylene ether) respectively.

Certain surfactants in the concentration range of 10^{-5} to 10^{-3} m, in non-polar solvent form liner aggregates. These linear aggregates in the concentration range of 10^{-3} to 10^{-2}m solution form cyclic aggregates with polar groups pointing towards interior of circle.

Sodium bis-(2'-ethyl-hexyl) sulphosuccinate (AOT)-isooctane reverse micelles are the simplest and well characterized model membrane systems. Surfactant, sodium bis-(2'-ethyl-hexyl) sulfosuccinate (AOT) dissolved in non-polar solvents from spheroidal aggregates called reverse mivelles. They can be formed both in the presence and in the absence of water. If the medium is completely free of water, the aggregates are very small and polydispersed. The presence of water is necessary to form large surfactant aggregates. Water is readily solubilised in the polar core, forming so called water pool characterized by the water-surfactant molar ratio (W0= [H_2O/[S]).

The dimension and shape of unified micelles formed by AOT have been characterized by different spectroscopic technique such as FTIR, NMR, Neutron scattering measurement and Photon correlation spectroscopy etc. cetyltrimethyl ammonium bromide (CTAB) is a cationic surfactant which forms reverse micelles in the presence of cosurfactants.

Selected incompatibles lipids also form reverse mecelles in organic solvents. The lecithin reverse micelles are well characterized and have been used for solubilisation of biopolymers. Due to their small size (in the 1-10 nm range) the reverse micelles aggregates are subjected to Brownian motion. They colloid continuously, and a small fraction of droplets exist on short –lived dimmers with exchange of the coalescence and decoalescence sequence, polar molecule solbulized in the water pool are redistributed over the micellar population. The average location of solute in the reverse micellar solution may be at the interphase or at the polar volume depending upon molecular geometry of the solute. Because of the exchange processes between droplets, reverse micelles can be used to synthesize size-controlled crystallites by carryout coprecipitaion or chemical reaction in the water pool. In these past few years several groups studied the formation of various types of clusters such as semiconductors, metallic clusters, carbonate aggregates, magnetite particles or colloidal alumina in reverse micelles.

1.3 Chemical Reactions in Microemulsions:

Organic syntheses are often faced the problem of reacting water-soluble inorganic reactants with water-soluble organic reactants. In these cases it is general practice to bring the reactants together to react with aid of polar aprotic solvents, phase transfer catalysis or just by intensive mechanical mixing. However, in microemulsion high concentration of both water-soluble and water-insoluble compounds dissolved simultaneously. This has been recognized in the past 40years by several groups who used these solutions as reaction media for various organic reactions with reactants such as acids, bases, cyanide, bromide, hypochlorite or permanganate. In addition to reactions with ionic reactants there were also some other reactions which carried out in a very good yield.

In this review paper an attempt has been made to include various chemical reactions in microemulsions and its comparison with other reaction media.

1.3.1 Hydrolysis:

The use of microemulsions as a reaction media for various acids and alkaline hydrolysis reactions can be understood. For this purpose the model substate p-nitrophenyl diphenyl phosphate (PNDP) was selected which follows many mechanistic route that. Which upon hydrolysis was implicitly assumed to produce only two organic products, the diphenyl phosphate anion (DPP) and p-nitrophenoxide.[8-13] Figure 3 Mackay and Hermansky[14] studied the hydroxide and fluoride assisted hydrolysis of DNDP and suggested that the sole phosphate product of hydrolysis of PNDP in a microemulsions composed of hexadecane in water, stabilized by CTAB and n-butanol, is n-butyl diphenyl phosphate. Gellman, Petter and Breslow[15] reported that diphenyl phosphate was the major product but that p-nitrophenyl phenyl phosphate (PNDP) in aqueous acetonitrile and in Brij 35 micellar solution R.A.Mackay reported that diphenyl phosphate anion and p-nitrophenylphenyl anion (PNPP) are major hydrolysis products of PNDP in CTAB microemulsion. Based on these assumptions, R.A. Mackay et al[16] examined the 2-Iodosobenzoic acid (IBA) catalyzed hydrolysis of 4-nitrophenyl diphenyl phosphate (PNDP) in a hexadecane/water microemulsion stabilized by cetyltrimethyl ammonium bromide CTAB and 1-bitanol; same reaction in the absence of IBA was also examined by same group[17].in this catalyzed reaction rate in CTAB microemulsion is approximately thrice than the value in water. Moreover, not only rate of reaction but the mechanism of the hydrolysis in microemulsion is different from that wether the reaction was catalyzed or uncatalyzed.[18-20]

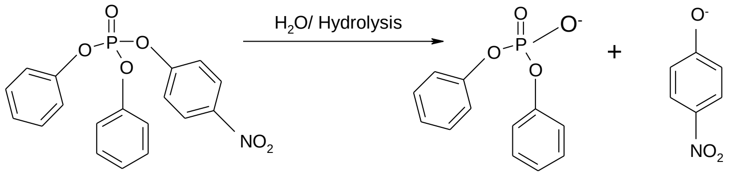

Figure.3. Hydrolysis of p-nitrophenyl diphenyl phosphate (PNDP) in hexadecane in water microemulsion

Later C.A.Bunton[21] et al observed the micellar effects upon reaction of OH$^-$with p-nitrophenyl diphenyl phosphate or 2, 4-dinitro-1-chloronaphthalene with cetylammonium surfactants (CTOX, X= Cl,Br,$(SO_4)H_2$. Figure 4

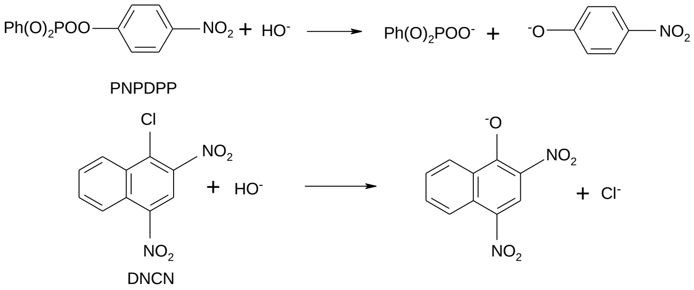

Figure 4.Hydrolysis of p-nitrophenyl diphenyl phosphate (PNPDPP) and 2, 4-dinitro-1-chloronaphthalene (DNCN) in cetylammonium surfactant

The rate is enhanced when the substrates are the nucleophilic anions at the micellar surface. The anion concentrations at micellar surfaces depend upon nonspecific coulombic and specific interactions.

In all the uncatalyzed microemulsion media (containing no IBA) the major product of the hydrolysis of PNDP is DPP observed at a 75% yield in CTAB pH 12 and 77% in CTAB and PNPP at 13% and 12% in CTAB pH 12. Butyl diphenyl phosphate (BDPP) can also be observed in the CTAB pH 9 and tha CTAB 12 microemulsions.[22]

The complexity of the reaction mixture is due primarily to the BDPP which from PNDP by butoxide (OBu$^-$) attack. BDPP (4) is subject to nucleophilic attack by either OH$^-$ or OBu$^-$ to form DPP (2), BPP (5) and DBPP (6) is shown in scheme I. However the formation of DPP is by OH- attack on 4 is not favourable, and therefore DPP is formed predominantly from PNDP. Only 6 were found to undergo further nucleophilic attack, potentially forming involves loss of OBu$^-$, this pathway is not favorable. Compounds 2,5 and 7 remain stable to any further hydrolysis.

When PNDP is incubated in an IBA-catalyzed CTAB pH microemulsion for 17 days, a high yied, 90.5% of DPP, 7%PNDP, 2% BDPP and no BPP. This suggests the conversion of BDPP into BPP is strongly dependent on OH$^-$ since the yield of BPP in CTAB pH 12 is 8% and BDPP is absent after 17 days.

G. Lamaty et al. studied the acid- catalyzed hydrolysis for series of para-substituted benzaldehyde diethyl acetals in the presence of reverse micelles prepared from water, heptanes and aerosol-OT (AOT).[23]The reaction is taking place near the surfactant head groups. They also shown that the hydrolysis of enantiomeric pairs of activated amino acid esters takes place in the mesophase structure, formed by the surfactant monolayer surrounding the aqueous core.

P. Varughese[24] et al reported the alkaline hydrolysis of ethyl benzoate in microemulsions which were formulated from combinations of heptanes, 1:5 (W/W) KBr-H_2O solution (W) and 1.23:1 (W/W) mixture of CTAB and 1-butanol.

$$C_6H_5COOCH_2CH_3 + HO^- \longrightarrow C_6H_5COO^- + CH_3CH_2OH$$

1.3.2 Oxidations:

The use of microemlsion as a reaction medium is essential for the generation and the stabilization of catalytically active species. These systems hold promise in performing catalytic reactions such as alkene oxidation. C. Larent[25] et al described the first example of the catalytic oxidation of alkanes in water-oil reverse microemulsion. These microemulsions systems offer many advantages over homogeneous catalysis; 1. No ligands or solvent degradation; 2. Stabilization of reactive intermediates within the swollen micelles.[26, 27]

When oxidation of cyclooctane is performed in microemulsion system consisting of water-hydrocarbon-anionic surfactant (AOT) with 30% H_2O_2 and Fe (II) or Fe (III) salts in aqueous droplets cyclooctane gave cyclooctanone. The catalytically active species is generated within the aqueous microdroplets. This system is similar to homogeneous iron-pyridine –acetic acid system (Gig system) Figure 5

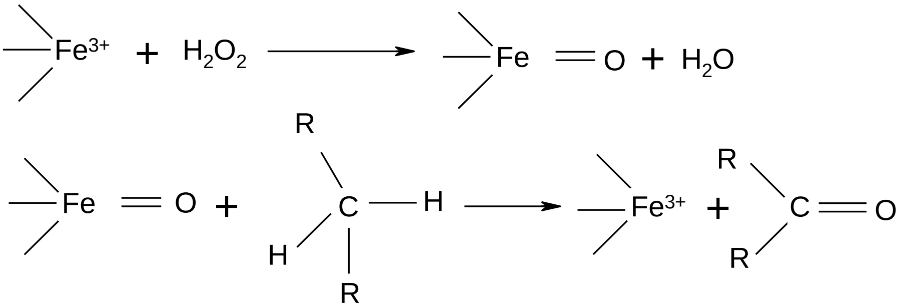

Figure 5. Oxidation mechanism by Fentons type reagent

When the substrate contains both tertiary and secondary carbons (e.g. in cis- or trans-decaline) the oxidation leads to a mixture of ketones and tertiary alcohols. Here the mechanism of formation of products is different from Fenton type reagent[28] but is more analogus to homogeneous from catalyst-oxidant systems for which the intervention of an iron (V) oxone intermediate has been proposed.(equation 2). Such iron (V) oxone species is produced within the confined aqueous droplets having Fe (III) and H_2O_2.F.P. Cavasino[29] et al showed by kinetic studies that the iron (III) oxidation of ferrocene and its 1, 1'-dimethyl and 1, 1'-dibutyl derivatives (B) takes place in the water pool and at the surfactant/water interface.

$$Fe^{3+} + B = Fe^{2+} + B^{+}$$

Bis(salicyclidine)ethylenediamine cobalt (II) solubilized in a micellar system formed by 3% aqueous sodium dodecylsulphate catalyzes the oxygenation of indole at high dilution. The high rate and selectivity in the oxygenation of indole derivatives are obtained due to condensation and distribution effect of micelles.[30-32]

Although the oxidation reactions catalyzed by metalloporphyrins are common in homogeneous medium, but only few examples are reported in microemulsion. The biomimetic oxidation of N-nitrosodibenzylamine[33] with molecular oxygen catalyzed by water soluble anionic manganese (III) 5,10,15,20-tetraphenyl porphyrine acetate/ sodium dithionate in aerosol-OT (AOT), under phase transfer conditions with AOT concentrations higher than 10^{-3}m, gave moderate yields of benzaldehyde, benzyl alcohol and benzyl amine. The oxidation of indole-3-acetic acid (IAA)[34] with H_2O_2 in the presence of $Cl_8TPPS_4Fe(III)(OH)_2$ in AOT reverse micelles at pH4.0 and water to surfactant ratio (W_0=14) gave high yield of indole-3-carboxyaldehyde(AI) and indole-3-carbinol(IC) in moderate yield.

1.3.2.1 Oxidation of hetero atoms containing compounds:

Microemulsion can also be used for the detoxification of mustard, a chemical war fare agent. Mustards are environmentally persistent cytotoxic alkylating agents that can be manufactured with low technology and used in chemical weaponry. Their detoxification is hampered by an extreme insolubility in the solvent where they are potentially more reactive, hence they can remain in a water surface unchanged for months even exposed to sunlight and oxygen. The problems as biological threat can be removed using microemulsion. Menger et al [35-37] oxidized mustard simulants (e.g. half-mustards) to non toxic sufoxide on a reasonable scale using microemulsions. The oxidation of half-mustard (Figure 6) in 15 ml microemulsion made up of (by weight) 3% cyclohexane in 82% water stabilized by 5% SDS and 10% n-butanol with 5% hypochlorite gives sulfoxide rapidly (i.e. in less than 1.5 second). The product formation is identified by NMR spectroscopy. Mustard present in the environment can, in contrast, persists for months. Microemulsions formulated with non-alcoholic cosurfactants were not very active. Therefore, the reactivity depends on an alkyl hypochlorite forming at the oil /water interface where the alcohol is known to reside subsequent oxidation of the half mustard then proceeds either in or on the oil droplets. As high as 1ml of sulfide can be oxidized in oil droplets of 15ml of oil/water microemulsions and from this it is obvious that large amount of water-insoluble reactants can be solubilized in microemulsions. Since the reaction mixtures are homogeneous, no stirring is necessary which a distinct advantage for application.

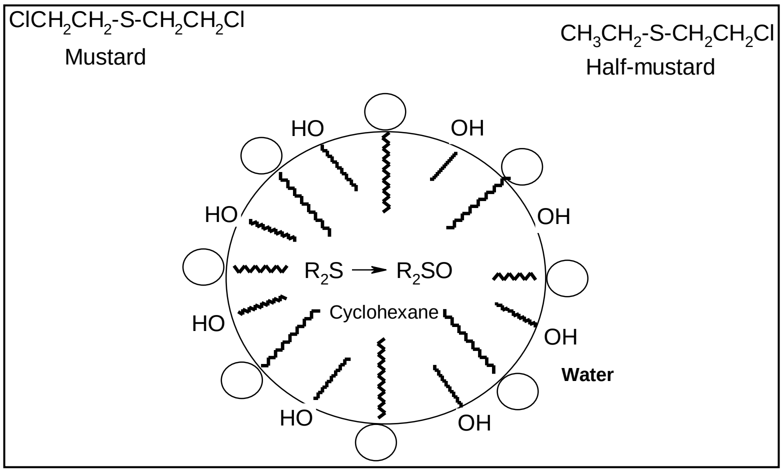

Figure6. Oxidation of Mustard to non-toxic sulfoxide in microemulsion

1.3.2 Reduction:

Microemulsions containing sodium borohydride are useful for the reduction of moano- and di carbonyl compounds. David A Jaeger[38] et al used the microemulsionsformulated by hexanes (O), 50:1 (W/W) solution (W) of 0.1 M KOH-$NaBH_4$ and 1.23:1 (W/W) mixture (S) of hexadecyltrimethylammonium bromide (HTABr) and 1-Butanol. The borohydride reduction of mono carbonyl compounds like benzphenone(1a), benzaldehyde (2a), acetophenone (3a), and 1-phenyl-1-octadecanone (4a) gave benhydrol (1b), benzyl alcohol (2b), 1-phenylethanol (3b), and 1-phenyloctadecanol (4b), respectively. Figure.7

R= C_6H_5, H, CH_3,n-$C_{17}H_{35}$

Figure 7 Borohydride reduction of carbonyl compounds

Microemulsions A and B of composition (60:35:5 and 20:10:70 S: W: O respectively) were used for reduction at 26^0C and aqueous 2-propanol solutions were used. The initial molar ratio of sodium borohydride to substrate was 2:1 or 1:2. An α,β- unsaturated ketones (6a) and diketone (7a) were reduced regioselectively with borohydride in microemulsions (the molar ratio of NaBH4 to 6a was 2:1 or 1:2), both 1,2- and 1,4-reduction can be occoured to yield enol (6b) and ketones (6c) respectively[39]the formation of alcohol 6d can be explained by 1,4-reduction because 6c was undetectable due to it's very rapid reduction to 6d as demonstrated. Figure 8 Nicles and Sukenik[40] have performed a similar study with enone 6a in aqueous miceller HTABr found 13% and 21% 1, 4-reduction under non miceller and miceller conditions, respectively.

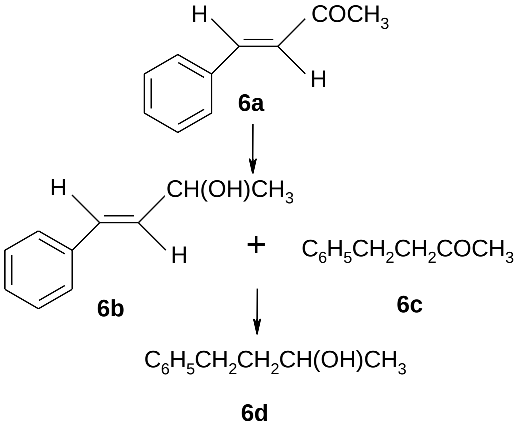

Figure 8 Regioselective reduction of α,β-unsaturated ketones with borohydribe in microemulsion

Reduction of diketones 7a with $NaBH_4$ gave ketol 7b, ketol 7c and diol 7d with a molar ratio of 4:1:1were obtained. Figure.9 it is possible to reduce selectively one carbonyl group of a diketone of this group is preferentially solubilised in the interphase on a time averaged basis. The aromatic carbonyl group of 7a may prefer the interphase as a solubilisation site more does the aliphatic carbonyl groups, it has been demonstrated [42, 43] with other systems that aromatic groups absorb at miceller water interphases. Therefore the reactivity of the aromatic carbonyl group relative to that of the aliphatic carbonyl groups was enhanced by a factor of about two in the microemulsion.A comparison of the borohydride reduction of above reaction with those performed under phase transfer condition with typical quaternary ammonium and phosphonium salts[44] indicates that the former was much faster and 6a underwent complete reduction in 20 minutes in microemulsion, whereas under phase transfer condition with triethylmethylammonium chloride in benzene /water system at room temperature 2-octanone reduced only 80% in 390 minutes. Therefore, for the sodium borohydride reduction of ketones, microemulsion catalysis is more effective than phase transfer catalysis. Furthermore, microemulsion are especially more attractive media for the reduction of relatively more non-polar substarte.

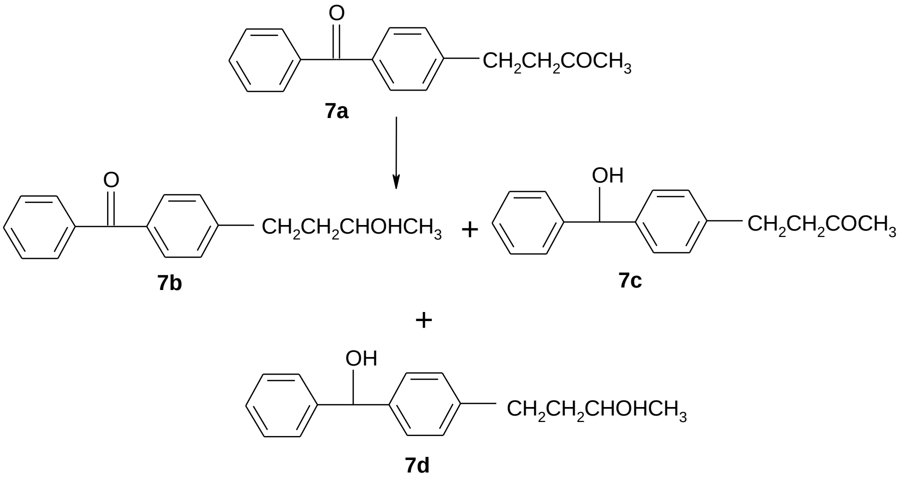

Figure 9. Selective reduction of diketones with $NaBH_4$ in microemulsion

1.3.4. Diels-Alder reactions:

Though aqueous microemulsions are having wide applications in synthetic organic chemistry their more widespread use has been limited by inadequate substrate solubility in water. A. Lattes[48-50] et al have reported that it is possible to prepare microemulsions by replacing water with saturated solvent like formamide. They also reported that such a non-aqueous microemulsions can be used as reaction media for Diels-Alder addition of methyl acrylate to cyclopentadiene, which is highly sensitive to the polarity of the reaction media[51] in microemulsions having iso-octane as oil, 1-butanol as cosurfactant and cetyl trimethylammonium bromide (CTAB) as surfactant and formamide. Figure.10. As we known that ENDO/EXO selectivity increases with increasing polarity of the solvent like water.[52,53] When a protic solvent N-methyl acetamide was used as a medium, the selectivity was less than in water or formamide. Breslow[53-55] suggested that their might be solvophobic type of interactions would play an important role. Formamide which strongly favors solvophobic interaction.[55]Therefore, formamide is an excellent medium for Diels-Alder reactions, especially at high concentrations.

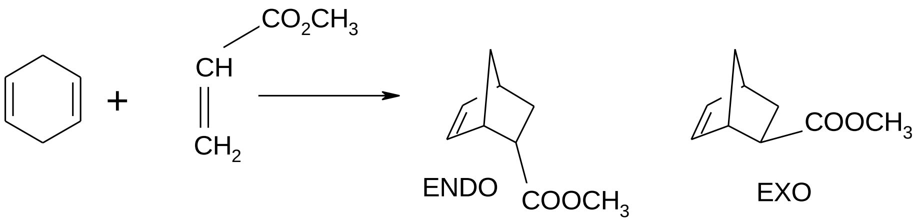

Figure 10. Reaction of methyl acrylate to cyclopentadiene

A. Latted et al obtained improved stereselectivities at high concentration, over those obtained by Breslow[56] (for C=0.30 mol/lt, ENDO/EXO=5.3 for water and 6.3 for formamide). In water the reaction takes place heterogeneously, whereas in formamide the reaction takes place homogeneously with significantly improved yield i.e. 85% whereas in water only 40%. Therefore, Diels Alder reaction is a valuable probe reaction for the study of formamide microemulsions. Formamide microemulsions can also be used as a media for others reactions like photoamidation[57], polymerization[58], Wacker process[59] as a media.

1.3.5 Polymerization:

The performance of polymerization reactions in microemulsions can be used to obtain very small polymer particles on the order of the primary micelle size. Candu and Leong et al first reported polymerization of acrylamide in inverse microemulsion.[60-63]Atik and Thomas polymerized styrene in oil/ water microemulsion [64, 65]and obtained narrowly distributed latex particles with diameters of the order of 20-30 nm. Their system however is based on hexanol as a cosurfactant, and it is known that the stability of such microemulsions is limited by the solubility of the formed polymer in the cosurfactant.[66]Turro and El-Assar et al examined the photoinitiated polymerization of styrene in microemulsion, using pentanol as a cosufactant and toluene as a mediator.[67]They found that the latex size is slightly larger than the droplets of the corresponding microemulsion and almost independent of the initiation rate. Jayakrishana and shah first demonstrated the polymerization of styrene in microemulsion can be performed with surfactant and without a cosurfactant.[68]Later Thomas et al also performed polymerization in microemulsion without a cosurfactant. M.Antonietti et al used polymerization in microemulsions for the controlled synthesis of spherical micogels.[68-71]The microemulsion in which these polymerizations can be carried out containing higher surfactant concentrations than the formations of technically performed emulsion polymerizations. The controlled synthesis of ultrafine latex particles or microgels (15<d<100nm), are having widespread technical and medical applications. Kaler[72] et al give a good survey of polymerizations in microemulsions and demonstrate in detail the experimental procedure using the example of styrene polymerization.

1.3.6 Enzyme catalyzed reactions:

During the studies with enzymes in non-polar solvents Martinek found that α-chymotrypsin can be solublised in the water droplets of microemulsions without the activity being lost.[73] These observation by Martinek initiated a great number of studies with various enzymes, which were summarized in reviews by Luisi[74,75] If hydrophobic substrate were added to the enzymes containing microemulsions , It was observed that the enzymes dissolved in the aqueous domains converts the substrate dissolved in hydrocarbon. Since enzymes are entrapped in the water pools of microemlsions, it seems that the behavior of the reaction strongly depends on the locus of the substrate. The catalytic hydrolysis of the surface active substrate, 2-naphthyl acetate, has also been measured both in aqueous and in water-in-oil microemulsions formed by di (2-ethyl hexyl) sodium sulphosuccinate (AOT) in heptanes. The catalysts used were lipase, α-chymotrypsin and imidazole. It is suggested that the reactions with these catalyst proceeds at the interfacial region of microemulsion. For the imidazole catalyzed reaction, if the imidazole exits preferentially at the interface, the rate constant is independent of W0, but the value was 0.2 times that in the aqueous phase. Enzymes catalyzed synthesis with water insoluble substrates in microemulsion can be carried out[76-80] by selecting the components for preparing the microemulsions so that no inhibition or denaturation of the enzymes occurs.[81]An interesting study of an enzyme catalyzed reactions including enzymes recovery by extraction from the reaction solution is described by Larrson[76]. This studies show reaction control, product isolation and enzyme recovery from the microemulsion are possible of the phase diagram of the system used is well known.

The isolation of the protein from the aqueous solution by liquid liquid extraction with a microemulsion can be regarded as a mature technique.[82]. By varying the pH values, ionic strength, or temperature, the distribution coefficient of a protein can be adjusted between a water /oil microemulsion and the co-existing aqueous phase so that the protein can be absorbed in or released from the microemulsion.[83] Structural and catalytic properties of cutinase were studied in bis-(2-ethylhexyl)-Na-sulfo-succinate (AOT)-isooctane microemulsion systems. The effect of water content of the microemulsion on the cutinase activity of the esterification reaction of lauric acid with pentanol showd that cutinase followed a bell shaped profile presenting a maximum at W_0 9, with $W_0=[H_2O]/AOT$

1.3.7 Electrochemical reactions:

A. Dehalogenation of polyhaloalkanes:

Last 20-30 years many new applications of surfactants in electrochemistry were observed. Dehaolgenation of aryl and alkyl halides were used as model reactions in surfactant media. Aryl halides like toxic polychlorinated biphenyls (PCBS), chlorodioxins and polyhaloalkanes (pesticides) are mostly insoluble and often found persistent in aquatic sediments.[84]These non-polar compounds to surfactant aggregates and thus are excellent substrates for attempting rate enhancements. Electrochemical catalytic dehalogenation is an attractive[85, 86] route to reduction of polyhaloalkanes and sodium naphthalide or borohydride were widely used as photocatalytic reduction. Electrochemical catalysis in surfactant media does not require excess chemical reagents. Electrochemistry often faces the problem of finding a solvent which simultaneously dissolves an organic substrate and a sufficient amount of conducting electrolyte. The uses of O/W microemulsions are reaction medium often very interesting new possibilities of electrochemical analysis and catalysis.[87, 88]Vicinal dihalides such as ethylene bibromide are suspected carcinogens that had been used as agricultural fumigants. Reduction of vicinal dihalides to less toxic alkenes is catalyzed by vitamin B12 or a CO (II) comin complex. J.F. Rusling et al[89] studied the same reactions in a W/O microemulsions of Aerosol-OT (AOT/Water/Isooctane) in which vitamin B12 resides entirely in water pools. The substrates EOB, 1, 2-dibromobutane and trans-1, 2 dibromocyclohexane (t-DBC) are mainly in the isooctane.[90]This are an example in which reactants are spatially separated in the two phases of the microemulsions.

B. The electrochemical synthesis of polyparaphenylenes:

Electrochemical synthesis in microemulsions is a promising approach to environmentally friendly methods for producing fine chemicals. Polyparaphenylenes (PPP) is having its chemical applications for its stability towards air oxidation and easy convertibility into n-and p-type obatinig PPP films through electrodeposition has been plagued with problems in obtaining homogeneous coherent films and high molecular mass. K.L.N. phani et al synthesized these electrodeposited PPP films in oil in water microemulsion of the type benezene/concn.H_2SO_4/dodecylsulfate (SDS). The electropolymerization can be carried out either galvanostatically and potentiostatically at +950 mV/Hg/Hg_2SO_4 (MSE) at room temperature. As the polymerization proceeds in the microemulsion the droplets reach the electrode by diffusin rather than by electrophoresis, since there is no driving force for the latter process.

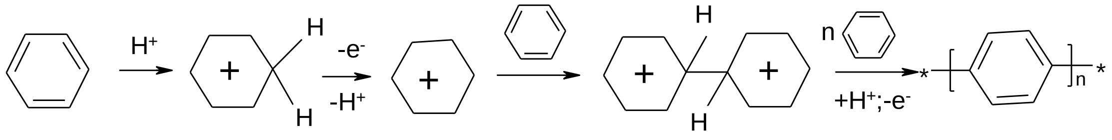

Figure 11 Electrochemical syntheses of polyparaphenylenes

The PPP films can be deposited on indium-tin oxide (ITO) glass (4cm^2) are Pt (4cm^2), when platinum plate (10 cm^2) was used as the counter electrode, the size that the polymer can grow to be controllable by the size of the droplet cores. Much better film of defined molecular size can be achieved by using more conventional methods of polymerization. Figure 11

1.3.8 Formation of metalloporphyrins

The metalation of free base porphyrins is governed by substituents present in the porphyrine ring, types of metal salts and reaction media.[91]The metallation of 5, 10, 15, 20-tetraaryl porphyrins with metal salts and complexes in hot dimethyl formamide is an important method and it is interpreted on the basis of an associative mechanism.102 The micellar media effect the solbulization of free base porphyrins in organic phase and distributin of metal ions in the stern layer of the micelles. The relative rate of metallation of 5, 10, 15, 20-tetraarylporphyrin with different metal ions are as follows $Cu^{2+}>Zn^{2+}>Cd^{2+}$ in miceller media and it is higher than the homogeneous media during the metallation of 5, 10, 15, 20-tetraaryl porphyrins.[92] The reactivity of picket fence potphyrins towards the metallation with Cu(II) and Zn(II)indicate enhancement in rate in aqueous anionic SDS surfactant micelle and AOT reverse micelles compared to homogeneous N,N-dimethyl formamide (DMF) solution. The rate vary systematically as a function of chain length of N-alkyl substituents and more significantly on the atropisomer configuration.[93]

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