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Reverse Microemulsions as a Novel Reaction Media

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ABSTRACT

Microemulsions are psuedohomogeneous mixtures which may show special performance towards reaction equilibria, nanoscale synthesis and reaction dynamics. Rate of reaction are most often accelerated in microemulsion media compared to that in water. This study is an effort to review some important reaction kinetics measured in reverse micro emulsion media. In the same time some pioneering research works concerned with the synthesis of nanoscale material in inverted (w/o) microemulsion have also been reviewed.

Key words: Microemulsions, Reaction equilibria, Media.

INTRODUCTION

When water is mixed with an organic liquid immiscible with water and an amphiphile, generally a turbid milky emulsion is obtained which separates after some time into an aqueous and an organic phase. Schulman[1-2], for the first time, observed that these turbid unstable emulsion can be converted into optically transparent and thermodynamically stable mixtures by alcohol. He was the first to use the term 'microemulsion' for these mixture containing two components which are not miscible by themselves i.e. water and oil.

Microemulsions are transparent optically isotropic and thermodynamically, stable mixture of oil and water stabilized by surfactants. They are droplet-type dispersion either of oil-in-water (o/w) or water in oil (w/o). Four component systems of surfactant, cosurfactant (low molecular mass alcohols), oil and water are the most studied microemulsion system. The reason being the introduction of cosurfactant greatly extends isotropic solution region, especially with single chain ionic surfactants o/w microemulsions can be thought of as swollen micelles containing a large volume of water and w/o microemulsions are swollen reversed micelles containing large volume of oil. W/o microemulsions contain aqueous microdrops trapped in a film of surfactant and dispersed in a low polarity bulk solved[3-5]. w/o type of microemulsion having [water]/[amphilphile] mole ratio, less than 3 are termed as reverse micelle. Actually reverse micelles and w/o microemulsions are two different names of the same species[6]. But, because of their specific physico-chemical features this distinction of nomenclature is used.

One of the widely studied model microemulsion system is a three component oil continuous system containing water, a hydrocarbon and sodium bis (2-ethylhexyl) surlfoscuccinate (commonly known as Aerosol orange T or AOT). In this system cosurfactant is not needed in microemulsion formulation. This most extensively studied microemulsion and reverse micelles system for measuring reaction kinetics is AOT / isoactane / water system. This is because isooctane has the structure similar to the tail structure of AOT and thus has the best penetration into AOT tails[7].

In recent years interest appears to have strikingly shifted towards W/o microemulsions. The main reason for this is probably the opportunity to investigate the structure of water in the hydrocarbon environment in the presence of surfactant. The discovery of a remarkable catalytic activity has considerably fostered the research on this type of emulsion. The interest in the structure of water in microemulsion is due to its possible impact on the reactivity of dissolved molecules and the possible applications of these simple systems as models of complex biological structures containing trapped water. From the viewpoint of chemical reactivity, owing to the existence of large internal interfaces and the unusual state of water in the droplets, the reverse microemulsions have attracted great interest because they can be used as substitutive novel media capable of significantly altering the rates of chemical and biochemical reactions compared with their rate is bulk water.

w/o. Microemulsions as a novel reaction media

There have been interesting reports on the kinetics of chemical reactions in w/o microemulsion but only few of these studies have been quantitative in contrast with kinetics in normal micelles. In microemulsions three different compartments are available for localization of small solutes : (a) the internal water pool (b) the micellar interface formed by a monolayer of surfactant molecules with their polar head groups oriented towards the water pool (c) external organic phase.

Chemists in all fields of activity studied chemical reactions in microemulsions. One of the earliest pioneering work in catalysis by reverse micelles is the hydrolysis of p-nitrophenyl laurate in hexanol / water system containing catyltrimethylammonium bromide of different composition. The rate constant showed a pronounced increase when reversed micelles were formed in the system, giving evidence of a catalysic effect of reversed micelles. In an another study acid catalysed inversion of cane sugar has been reported in water / poly (oxyethylene) iso-octylphenyl either / l-butanol / (cholesteryl benzoate + n-heptane) microemulsion medium at a constant surfactant / cosurfactant ratio and at-different oil / water ratio (o/w). Increasing the o/w ratio increased the rate, 0.5% (w/v) dextrin and 2% (w/v) brine moderately retarded the reaction[9]. The results are analysed in the light of the polarity of the medium as well as the effective concentration of the catalyst in the microemulsions.

Gupta et. al.[10] investigated the alkaline phosphatase catalysed hydrolysis of p-nitrophenyl phosphate in aqueous carbonate bicarbonate buffered medium as well as buffered water / AOT / decane microemulsion. Enhancement of reaction rate has been found in microemulsion which depends on water/AOT mole ratio w with a maximum at w = 18.6. The kinetics has a maximum at pH = 10.2, the effect being sharper in microemulsion. Behera and coworkers[11] studied the hydrolysis of Schiff bases in acidic, alkaline and neutral medium in mciroemulsion involving cetyltrimethylammonium bromide (CTAB) / sodium do decyl sulphate (SDS) – hexane isobutanol – water system. Rate of hydrolysis of the Schiff bases have been carried out in o/w and w/o microemulsion and under different conditions and are found to be higher in acidic and neutral medium in SDS microemulsion than in CTAB microemulsion respectively.

Utilizing the versatile surfactant AOT Garcia – Rio *et al.,* carried out solvolysis of substituted benzoyl chloride in AOT / Isooctane / Water microemulsions[12]. The benzoyl chlorides are found distributed between the isooctane and the interface, where they react with its hydration water. For dissociative pathway the rate constant k_i decreases together with w whereas for associative pathway the rate constant k_i increases as w decreases. In all cases the solvolysis rate at the interface of the microemulsion is lower than in pure water. In an another study Athanssakis at el. applied pseudophase ion-exchange model for the reaction of 2, 4-dinitrofluorobenzene (DNF) with OH^- in microemulsions of n-octane, tert. amyl alcohol and CTAB and in the micelles of CTAB and tert. amyl alcohol. The second order rate const in microemulsion or micelle droplets were greater than that in water, but smaller than those in moist tertiary alcohol.[13]

Nucleophilic aromatic substitution between glutathione and 2, 4-dinitrochlorobenzene has been studied by Lion *et al.,*[14] in reversed micellar systems composed of limited amount of water, a surfactant and the organic solvent isooctane. A two fold increase in second order rate constant was observed using cationic surfactant where positive charge is contained in aromatic ring. On the other hand, the rate of reaction increased by three fold using neutral polar head groups. The rate enhancement was supposed to be due to stabilization of meisenheimer s-complex by the positively charged polar head and the weak aromatic ring's electric quadruple interactions of the surfactants. In one another study Moya *et al.,* reported rate constants for the oxidation of iodide ions by persulfate in AOT / decane / water microemulsions. The reaction rate is higher in microemulsion than when it takes place in conventional aqueous medium. Results show that when AOT concentration remains constant, the reaction rate decreases by increasing w[15].

Blagoera *et al.,*[16] applied pseudophase model for the kinetic investigation of 1-octane bromination in AOT-isooctane – water microemulsions. Bromination occurs in an aquous microenvironment. Reasonable values for the coefficients of reagents partition between the interface and the two microphases and for the local bromination rate constants are obtained from the kinetic equation derived from the pseudophase model. Garcia Rio *et al.,*[17] reported kinetics of the transfer of the nitroso group from N-melthyl-N-nitroso-p-toluene sulfona mide to seven secondary amines using a variety of water / AOT / isooctane microemulsions as reaction media. The reaction was observed to take place at the interface. The order of reactivity parallels the bascity of the amines, except for dimethylamine.

In one of the important kinetic investigation Moulik and coworkers[18] studied kinetics of alkaline fading of crystal violet in aqueous and ethylene glycol media as well as in water / AOT / decane, water / AOT / isooctane, and ethylene glycol / AOT / isooctane microemulsino media. Both elthylene glycol and its microemulsion have shown rate accelerating effects compared with other environments. The rate of reaction in microemulsion medium is inversely proportional to the water / AOT or elthylene to the water / AOT or elthylene glycol / AOT mole ratio.

In an novel research work Leis and coworker[19] carried out Diets – Alder reaction in water / AOT / isooctane microemulsion system. The rate of reaction is found to be higher in microemulsion as compared to isooctane. The efficiency is found to be maximum for w = 3 to 35.

Ghosh and co-worker[20] in an innovative research studied the acidic hydrolysis of N-hydroxyphalimide in microemulsion of AOT / isooctane / water at 328 K. She effect of w (water / AOT mole ratio) and AOT concentration were also analysed in this study. The reaction rate is higher in microemulsion than in concentrated aqueous solution. In all cases pseudofirst order kinetics were observed and the rate constant was found to be much higher compared to the same reaction in aqueous medium. Same group also studied the kinetics of acid catalysed hydrolysis of salicylhydroxamic acid (SHA) in AOT / isooctane / water microemulsion at 328 K[21]. Enhancement of reaction rate has been found which depends on w with a maximum at w = 10.7. The effect of AOT concentration on reaction rate has been studied. The pseudofirst order rate constant decrease with [AOT] at constant w = 12.3. The results are discussed in terms of chemical properties of the water molecules encased in the microemulsion droplets.

Microemulsions as nanoreaction for the synthesis of nanoparticles

w/o or reverse microemulsion serves as a microreactor for the systhesis of several types of metal nanoparticles and quantum dots. Haung *et al.,*[22] reported a novel simultaneous in situ synthesis of Cds and Pbs quantum dots via single reversed microemulsion nanoreactor consisted of cyclohexane (oil), poly (oxy ethylene), and nonyl phenyl either.

Some researchers have also successfully utilized o/w microemulsion for the synthesis of nanosized particles. sanchez-Dominguez[23] and coworker adopted a novel and straight forward approach based on o/w microemulsion for the synthesis of inorganic and organic nanoparticles at ambient conditions. It implies the use of nanometallic precursor dissolved in nanometer scale oil droplets of o/w microemulions. Addition of reducing or oxidising agents results in formation of metallic or metallic oxide nanoparticles. Non-ionic o/w microemulsions chosen and several key compositions were selected for nanoparticle synthesis at 25°C. These nanoparticles were confirmed by diffraction technique. In an another study Srivastava *et al.,*[24] Synthesized gold hanorods using conc. AOT in hexane and its application as catalyst for reduction of eosin. The shape of size of nanoparticles synthesized in this case of being controlled by w (water / oil mole ratio).

Recently Becerra *et al.,*[25] used the droplet phase of reversible microemulsion formed by the surfactant cetyltrimethylammonium ferrocyanide as a matrix to synthesize nanoparticles of nicked hexacyanoferrate by adding just a solution of $NiCl_2$ to the microemulions media. The result obtained by dynamic light scattering and transmission electron microscopy show that the size and shape of coordination compound nanoparticle correspond with the size and shape of the droplets, suggesting that the presented system constitute an alternative method to synthesis of metal hexacynanofenate nanoparticles Carlos Garcia *et al.,*[26] reported recently the synthesis of hydroxyapatite nanoparticle using the hydrothermal microemulsion technique with calcium nitrate tetrahydrate and diammonium hydrogen phosphate as precursor. The advantage of this technique over other technique is that particles with controlled size and morphology can be obtained with a new microemulsion with CTAB / toluene / n-butanol / water as a nanorerctor.

CONCLUSION

Reverse micelles and w/o microemulsions are more and more frequently used as microreactor for performing reactions in constrained, taking advantage of reagent compartmentalization and of the particular properties of encased water. The presence of droplet can enhance or retard chemical reaction rates by large factors. In recent years, microemulsions, therefore have found increasing uses as potential reaction media both for kinetic, synthetic and equilibrium studies.

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