Oxidation of Alcohol Component of Microemulsion by Lipophylic Cr(VI)

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CERTIFICATE

This is to certify that the dissertation entitled "**Oxidation of Alcohol Component of Microemulsion By Lipophylic Cr(Vi)**" being submitted by **Mr. Santosh Kumar Behera** to the Department Of Chemistry, National Institute Of Technology, Rourkela-769008, for the award of the degree of Master Of Science in Chemistry, is a record of bonafide research carried out by him under my supervision and guidance. The dissertation report has reached the standard fulfilling the requirements of the regulations relating to the nature of the degree.

I further certify that to the best of my knowledge Mr. Behera bears a good moral character.

NIT-Rourkela **Sabita Patel**

Date:

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Date: 05.05.2011 Name: Santosh Kumar Behera

CONTENTS

1. INTRODUCTION AND LITERATURE REVIEW

The concept of microemulsion was first introduced by Hoar and Schulman in 1943.[1] They prepared the first microemulsions by dispersing oil in an aqueous surfactant solution and adding an alcohol as a co-surfactant, leading to a transparent, stable formulation. "A microemulsion is a system of water, oil, and amphiphilic compounds (surfactant and co-surfactant) which is a transparent, single optically isotropic, and thermodynamically stable liquid". Microemulsions are formed when and only when (i) the interfacial tension at the oil/water interface is brought to a very low level and (ii) the interfacial layer is kept highly flexible and fluid.[2] These two conditions are usually met by a careful and precise choice of the components and of their respective proportions, and by the use of a "co-surfactant" which brings flexibility to the oil/water interface.[2]

These systems are currently of interest due to its application in the following fields.[3]

- Microemulsions in enhanced oil recovery**.**
- Microemulsions as fuels
- Microemulsions as lubricants, cutting oils and
- corrosion inhibitors
- Microemulsions as coatings and textile finishing
- Microemulsions in detergency
- Microemulsions in cosmetics
- Microemulsions in agrochemicals
- Microemulsions in food

- Microemulsion in pharmaceuticals as drug delivery systems
- Microemulsions in environmental remediation and
- Detoxification
- Microemulsions in analytical applications
- Microporous media synthesis (microemulsion gel technique)
- Microemulsions as liquid membranes
- Microemulsions in biotechnology

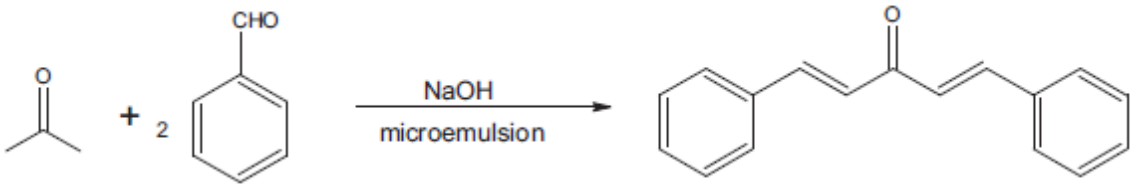
Furthermore microemulsions are gentle solvents for extraction of proteins without altering their enzymatic or functional properties although the process can readily be scaled by conventional liquid–liquid extraction techniques. Therefore this can also be used for bioseparations.

Due to varied consistencies and microstructures, microemulsions have been used as a reaction media for a variety of chemical reactions such as synthesis of nanoparticles,[4] polymerization,[5,6,7] photochemical, electrochemical and electrocatalytic and organic synthesis.

Zhou et al.[8] have investigated the bicontinuous microemulsions made from dodecane, water, and didodecyldimethylammonium bromide (DDAB) as media for the catalytic reduction of trans- 1,2-dibromocyclohexane (DBCH) and for S_N2 reactions of n-alkyl bromides with electrochemically generated Co(1) complexes. Macrocyclic complexes vitamin B 12 (a cobalt corrin) and Co(salen) resided in the water phase, while the alkyl bromides resided in the oil phase of the microemulsion. Rates of DBCH reduction is 40-fold larger in the bicontinuous fluid than in a water-in-oil microemulsion which is attributed to the larger interfacial area of the bicontinuous

system. Formal potentials in the microemulsion depended on specific interactions, such as those of [Col(salen)]- with cationic surfactant head groups or the influence of water phase pH on vitamin B12.

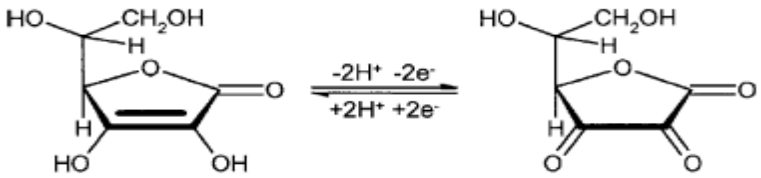
Shrikhandea et al.[9] have studied the condensation between benzaldehyde and acetone in a cationic o/w microemulsion prepared from the combination of n-butanol as co-surfactant, n-hexane as oil and cetyltrimethylammonium bromide (CTAB) as the cationic surfactant (Scheme 1). They have also determined the hydrodynamic diameters of the oil droplets in the o/w microemulsion at different compositions using dynamic light scattering. Various parameters influencing the formation of microemulsions, like oil content, surfactant content, oil and co-surfactant ratio were varied and their corresponding effects on the solubilization of reactants and rate of a condensation reaction were studied. A direct correlation between the droplet size of the microemulsion and rate of the reaction is observed. The changes in solubility of benzaldehyde in the microemulsion affect the reaction rate while the composition of the oil phase does not influence the rate of the reaction.



Scheme-1

From this study they have concluded the that, the solubilization capacity of benzaldehyde is decreased with the increase in oil + co-surfactant and the surfactant content, indicating that the aldehyde is solubilized at the interface rather than the core of the droplet. Further from the decrease in observed reaction rate constants on variation in oil + co-surfactant and surfactant content further indicate that the reaction takes place at the interface.

The atmospheric and electrochemical oxidation of AA(Ascorbic acid) in the SDS micellar solutions and in the microemulsions pentanol/water stabilized by SDS have been studied by Szymul et al.[10] (Scheme-2). They found that the hydrophilic vitamin C readily dissolves in water and O/W microemulsions as well as undergoes the irreversible two-electron oxidation reaction and the atmospheric oxidation of AA is accelerated by the SDS up to the CMC and inhibited in the concentrated SDS solutions. They also found that the rate of atmospheric oxidation of ascorbic acid is higher in the water-in-oil (W/O) than in the oil-in-water (O/W) microemulsions and increases with the increasing oil content. The influence of the SDS on the electrochemical behavior of vitamin C was also studied. The general conclusion emerging from this investigation is that the increasing surfactant concentration shifts the ascorbic acid oxidation potential to higher values whereas the corresponding peak current values diminish. In the microemulsions the AA oxidation is slowed down by increasing the pentanol amount in the system.



L-ascorbic acid L-dehydroascorbic acid

The oxidation reaction of L-ascorbic acid

Scheme-2

Sathishkumar et al[11] were synthesized *n*-Hexyl-β-d-glucopyranoside (HGP) through the β-glucosidase-catalyzed condensation of glucose and hexanol in an aqueous-organic bicontinuous microemulsion system with both water and oil as continuous

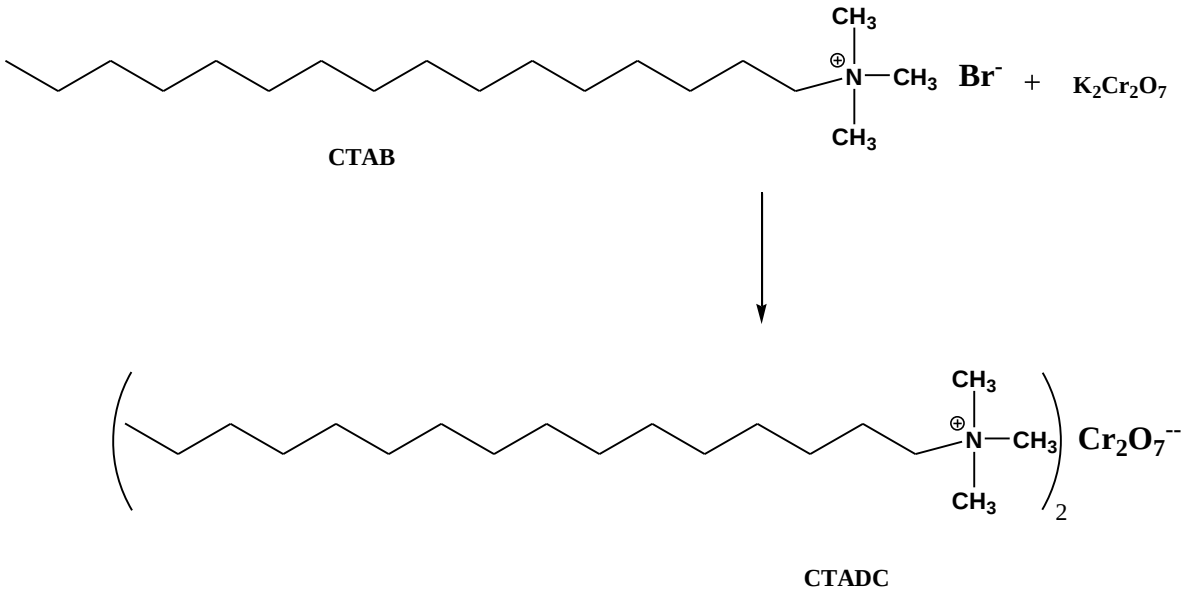
phases. Methodology for separation of HGP from the microemulsion system for analysis by gas chromatography was developed. Various factors influencing the synthesis of HGP like reaction time, enzyme concentration and temperature were optimized experimentally. Reverse reaction (hydrolysis) occurred was also studied. Comparison of the rate of the reaction between synthesis and hydrolysis showed the latter to be faster, suggesting that bicontinuous microemulsion system is more applicable to the enzymatic hydrolysis. Degradation of enzyme in bicontinuous microemulsion system was very negligible.

2. EXPERIMENTAL

Synthesis of Cetyltrimethylammonium dichromate (CTADC)

CTADC was prepared (Scheme-1) by adding aqueous solution of $K_2Cr_2O_7$ (0.037mol) in small portions to the flask containing aqueous solution of cetyltrimethylammonium bromide (CTAB) (0.2mol) with stirring.Yellow precipitate appeared immediately. It was filtered, washed properly till the filtrate in free from trace of dichromate and bromide. It was dried and kept in sample bottle.

The prepared yellow solid was characterized using CHN, IR and NMR analytical data. M.Pt. 212 ^{o}C, yield: 98%.Elemental analysis: C,58.14; H, 10.65; N, 3.54; Cr, 13.11. C38H84O7N2Cr2 requires C, 58.16; H, 10.71; N, 3.57; Cr, 13.26. IR (cm_1): 771, 879, 933, 1467, 2850, 2921, 3028, 3471. NMR (CDCl3, 300MHz): d 0.86 (t, 6H), 1.29 (m, 48H), 1.67 (m, 4H), 1.74 (m, 4H), 3.42 (s, 18H), 3.51 (m, 4H) (Scheme-3).



(Scheme 3)

Oxidation of Butanol by CTADC

Different microemulsions were prepared using Surfactant(TX-100,CTAB and SDS),Cosurfactant (n-Butanol),Oil(Chloroform),Water in Acetic acid medium. Phase diagrams were drawn for different systems. The microemulsions are used to study the oxidation of alcohol by CTADC at varying concentrations of oxidant, butanol, surfactant, acid etc to unveil the reaction mechanism in this medium. The product was found to be butanal.

The kinetics of the oxidation reaction was studied using UV-Vis spectrophotometer by monitoring the change in absorbance of CTADC at 350 nm. Pseudo first order condition was maintained throughout the experiment. The observed rate constant k_{obs} was calculated using 1^{st} order rate expression as follows.

Where OD_0 , OD_t, OD_∞ and t refers to optical density of CTADC at 350 nm before the commencement of the reaction, optical density at any time t, optical density at infinite time or after completion of the reaction and reaction time respectively. A representative time scan spectra is given in figure. 1.

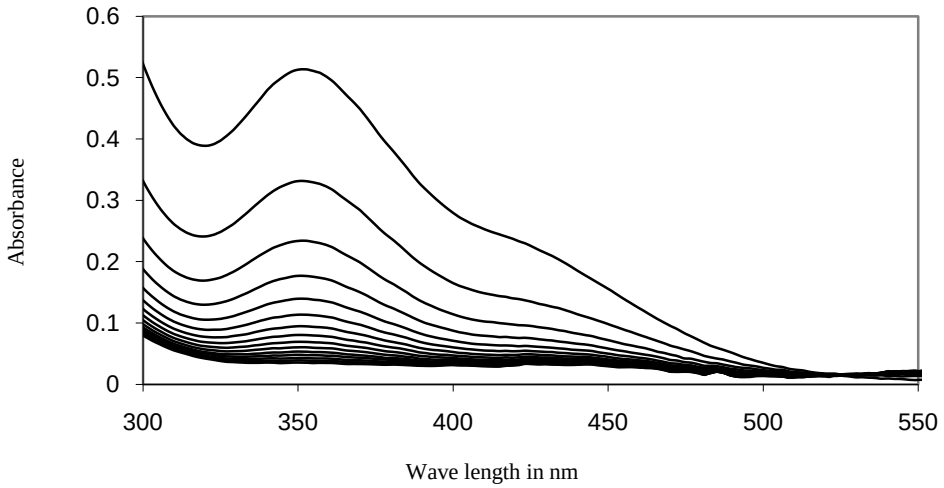


Figure 1: representative UV-Vis time scan plot for the oxidation of butanol by CTADC in microemulsion medium

3. RESULTS AND DISCUSSION

Cr(VI) is known for its versatility the oxidation reaction. It can oxidise a variety of substrates alkane, alcohol, aldehyde, thiols etc. For the oxidation process it generally requires a high concentration of concentrated sulphuric acid. For which it is very difficult to undertake reactions in milder conditions for acid sensitive compounds. Further the insolubility of potassium dichromate in non-aqueous solvents makes the oxidation process difficult and tedious for water insoluble organic substrates. To overcome these difficulties different Cr(VI) oxidants are explored with counter ions like ammonim, phosphonium etc.

An onium ion, as the counterion for anionic oxidants, makes a lot of difference in oxidation potential of the oxidant as well as to the oxidizing system.[12] A large number of Cr(VI) oxidants with onium ions have been reported. [12]

In a continuation of our efforts to explore some biomimetic oxidants to oxidize organic substrates in organic solvents, we have reported the oxidation behavior of cetyltrimethylammonium dichromate (CTADC) toward various organic substrates. This reagent is water insoluble and stable at room temperature for more than a year when kept in sealed bottle. It absorbs around 353-383 nm. Exists as a tight ionpair and forms monolayer on water surface with area/molecule 51 Å2.[13] Although Cr(VI) is undisputedly carcinogenic, the insolubility in water reduces contamination of Cr(VI) in aqueous medium, and the compound thus can be used as a green reagent. Further, CTADC is devoid of an acidic proton and thus is relatively milder than other Cr(VI) oxidants. In the absence of acid, CTADC exhibits some bizarre reactions with

nonconventional products. Aromatic amines are found to yield corresponding diazo compounds,[14] and arylaldoximes yielded corresponding nitriles.[15]

In an oxidation reaction of cholesterol with CTADC, Patel et al.[16] have observed that 7-dehydrocholesterol is obtained instead of usual product cholestenone. This dehydrogenation is a rare event in Cr(VI) oxidation studies, and it is explained through remote functionalization mechanism where the cetyltrimethylammonium ion provides a favourable environment for proper orientation of the dichromate group so that the removal of hydrogen from 7^{th} and 8^{th} position becomes easier.

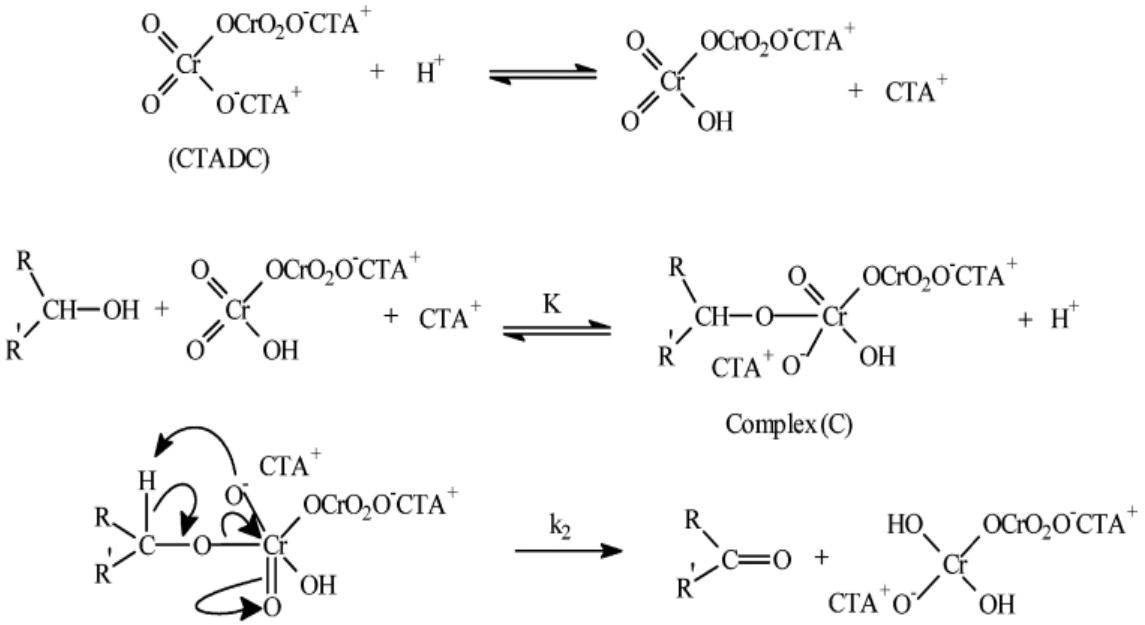
Owing to the applicability of CTADC as biomimetic oxidant, present project aims at the oxidation of different substrates in microemulsion medium which is mimicking the cell structure. We have chosen butanol as the substrates for the oxidation process.

Oxidation of alcohol by CTADC in nonaqueous medium has benn studied extensively by Patel and Mishra[17]. A Michaelis- Menten type kinetics was reported by them with change in substrate concentration (Figure 2). From the dependence of rate with various factor and order with respect to all the reactants the following rate expression (eq 3) and mechanism has been proposed (Scheme 4).

$$\text{alcohol} + \text{CTADC} \underset{k_{-1}}{\overset{k_{+1}}{\rightleftharpoons}} [\text{complex}] \qquad (1)$$

$$[\text{complex}] \xrightarrow{k_2} \text{product} \qquad (2)$$

$$\frac{1}{k_{obs}} = \frac{1}{k_2 K[Alcohol]} + \frac{1}{k_2} \qquad \textbf{(3)}$$



(Scheme 4)

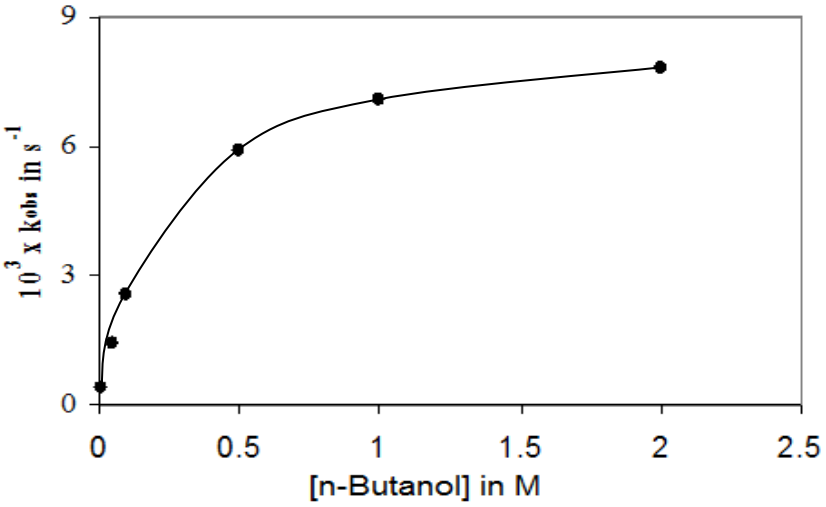
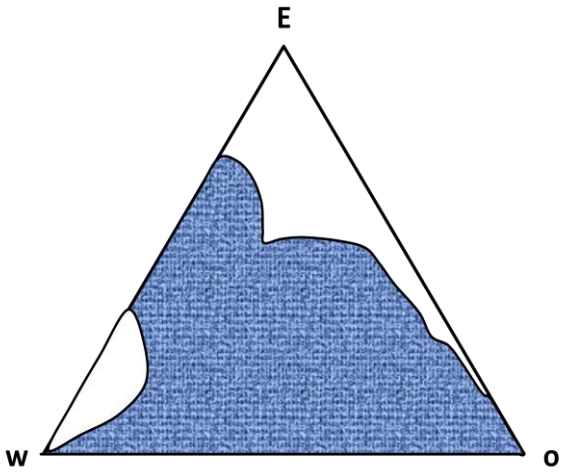


Figure 2

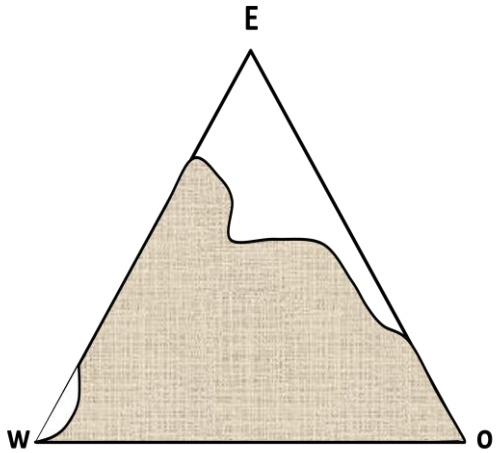
To study the oxidation reaction in microemulsion medium, we have constructed the phase diagrams with varying concentration of the components (Figure 8). In all the phase diagrams chloroform is used as oil phase because of the solubility of CTADC in chloroform. The surfactants used are Triton X-100 (TX100) a non-ionic surfactant, Cetyltrimethylammonium bromide (CTAB) a cationic surfactant and sodium

dodecylsulphate (SDS) an anionic surfactant with different composition with the cosurfactant n-butanol. Acetic acid is used as catalyst for the oxidation process.



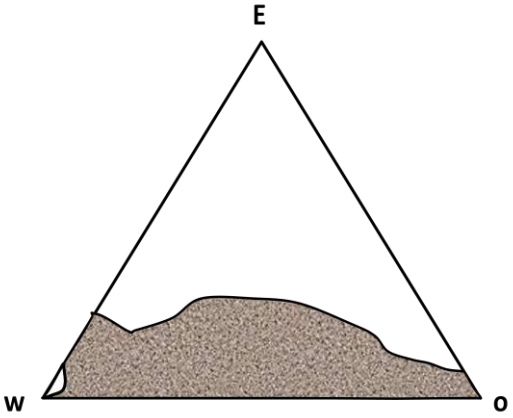
CTAB: nBuOH(1:6.5),Chloroform,Water

Fig-3a



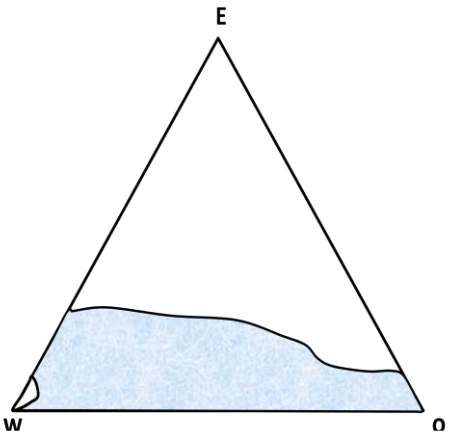
CTAB: nBuOH (1:6.5), Chloroform,CTADC,Water

Fig-3b



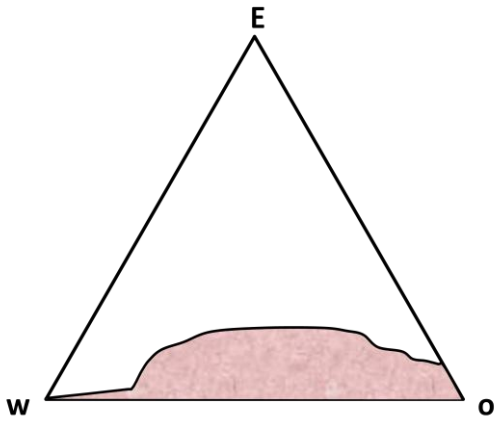
SDS:nBuOH(3:1),Chloroform,Water

Fig-3c



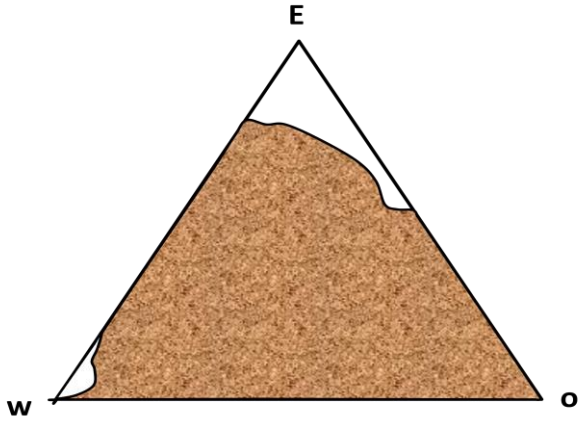
SDS:nBuOH(3:1),Chloroform,Water

Fig-3d



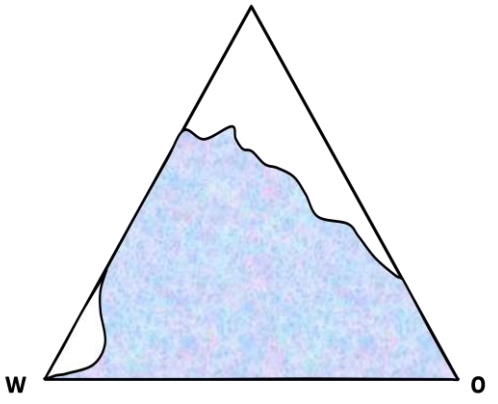
SDS:nBuOH(3:1),Chloroform,CTADC,AcOH,Water

Fig-3f



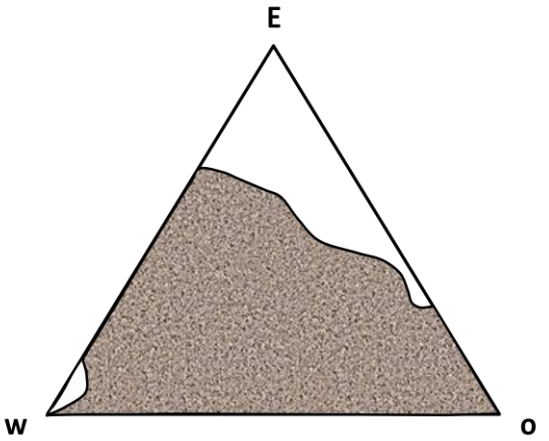
TX-100:BuOH(1:4),Chloroform,Water

Fig-3g



TX-100:nBuOH(1:4),Chloroform,CTADC,Water

Fig-3h



TX-100:nBuOH(1:4),Chloroform,CTADC,AcOH

Fig-3i

Figure 3 (a-i): represents the Pseudo-ternary phase diagram of the microemulsion system at different S/CS ratios. E, W and O in all the plots represents 100% emulsifier, 100% water and 100% oil respectively. The shaded regions in the diagrams represent turbid zone and the rests are clear domain.

From these pseudoternary phase diagram it is seen that microemulsion in presence of CTAB have less clear region than that of the anionic surfactant such as SDS. In SDS microemulsion the clear region that is the Winsor-IV domain is larger in presence of

CTADC.This may be due to the participation of CTADC as surfactant in the formation of isotropic microemulsion.

The oxidation of CTADC in various microemulsion medium can be determined by monitoring the depletion of the CTADC at 350 nm. The observed rate constants are tabulated in Table 1.

Table 1: Change in k_{obs} with Variation of TX-100 concentration for the oxidation of butanol by CTADC in microemulsion.[CTADC]=5 X 10^{-5} [Butanol]=1.8 X 10^{-1}[Acetic acid]=1.45 X 10^{-1}Temp= 25 ^{o}C.

SL.NO.	**[TX-100] 10^3 (mol)**	**k_{obs} x10^4 (sec^{-1})**
1	6.0	6.1
2	12.12	6.5
3	18.2	6.7
4	24.26	8.1
5	30.32	9.6

From the table it is clear that with increase in surfactant concentration rate constant increases, hence rate increases. This may be attributed to the higher solubility of CTADC and n-butanol in micellar region which increases the amount of reactants in close proximity which in turn increases the rate of the reaction.

Table 2: Change in k_{obs} with Variation of CTADC concentration for the oxidation of butanol by CTADC in microemulsion. [Butanol]= 1.8 X 10^{-1}, [Acetic acid]= 1.45 X 10^{-1} , Temp. = 25 ^{o}C

SL.NO.	[CTADC] x 10^{5}(mol)	K_{obs} x 10^{4}(sec^{-1})
1	0.83	3.6
2	1.66	4.9
3	3.33	5.5
4	5.0	5.6

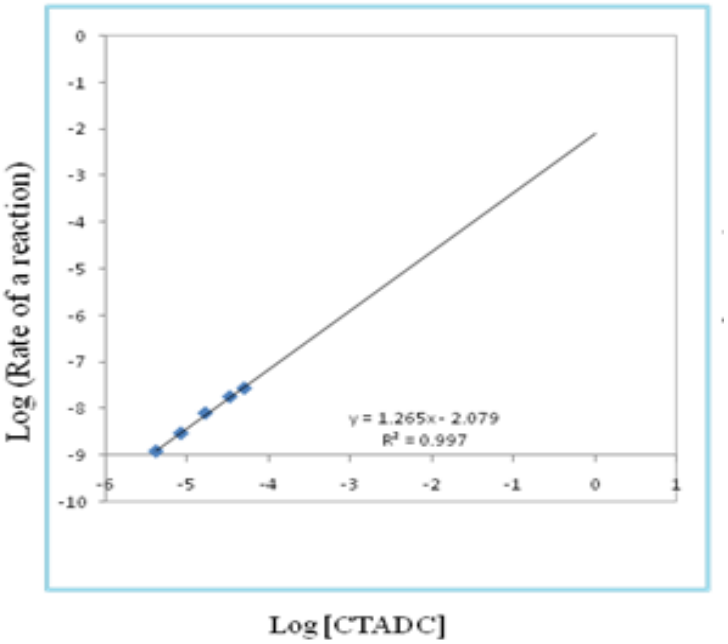


Figure 4: Plot of Log (rate) vs. Log[CTADC] for the oxidation of butanol in microemulsion formed by TX 100.

Table 3: Change in k_{obs} with Variation of Acetic acid concentration for the oxidation of butanol by CTADC in microemulsion.[CTADC]= 2 X 10^{-5}, [Butanol]= 1.8 X 10^{-1},[Acetic acid]= 1.45 X 10^{-1} Temp.= 25 ^{o}C.

SL.NO.	[AcOH] x 10^{1}(mol)	k_{obs} x 10^{4} (sec^{-1})
1	3.5	4.0
2	6.72	7.2
3	10.11	8.4
4	12.9	12.3
5	15.88	23.4

From this data in table 4 it is seen that with increase in CTADC concentration rate of the reaction increases. From the plot of log[rate] vs. log[CTADC] (figure 4) the order with respect to CTADC is found to be 1. With increase in acetic acid concentration the rate increases with an uncatalytic rate 1.1 x 10^{-4}.

Table 4: Change in k_{obs} with Variation of butanol concentration for the oxidation of butanol by CTADC in microemulsion. [CTADC]= 2.5 X 10^{-5} [Acetic acid]= 1.45 X 10^{-1},Temp.= 25 ^{o}C

SL.NO.	[Butanol] x 10^{5} (mol)	K_{obs} x 10^{4}(sec^{-1})
1	3.64	9.6
2	7.28	11.5
3	10.92	23.0
4	14.57	38.38
5	18.2	22.03
6	21.85	8.1
7	25.5	6.9
8	29.13	5.8

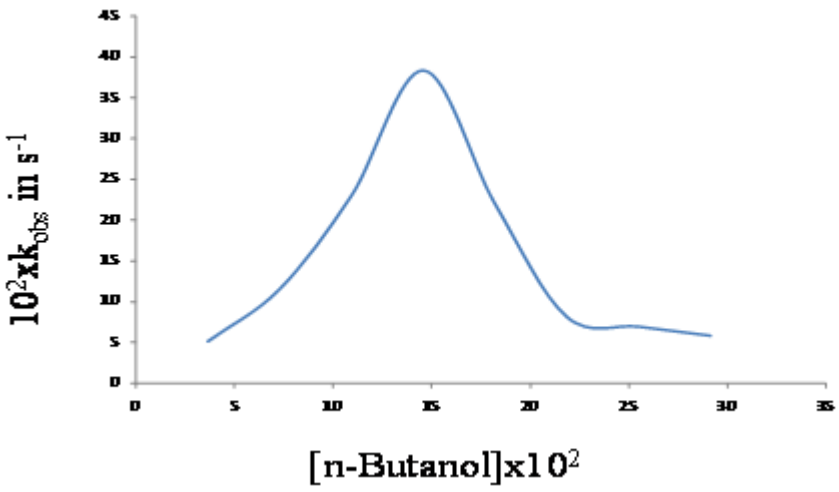


Figure5: Plot of k_{obs} versus [n-butanol] in the oxidation of butanol by CTADC in microemulsion medium.

With increase in butanol concentration in the mixture, the rate of a reaction increases up to the concentration of 14.57 x 10^{-4} of butanol then it sharply decreases (figure.5). This may be attributed to the structural change accompanied at higher concentration of butanol. As the n-butanol concentration increases in the micellar interface, replaces the CTADC. CTADC gets penetrated towards the micellar core as the solubility is higher in the non-polar medium. So the availability of CTADC in the interface region decreases. Hence protonation of H^+ with dichromate ion decreases. At higher butanol concentration, due to the increase partition of the reactants H^+, CTADC and n - butanol in different medium the rate of the reaction decreases.This phenomenon is shown in the following figure. 6.

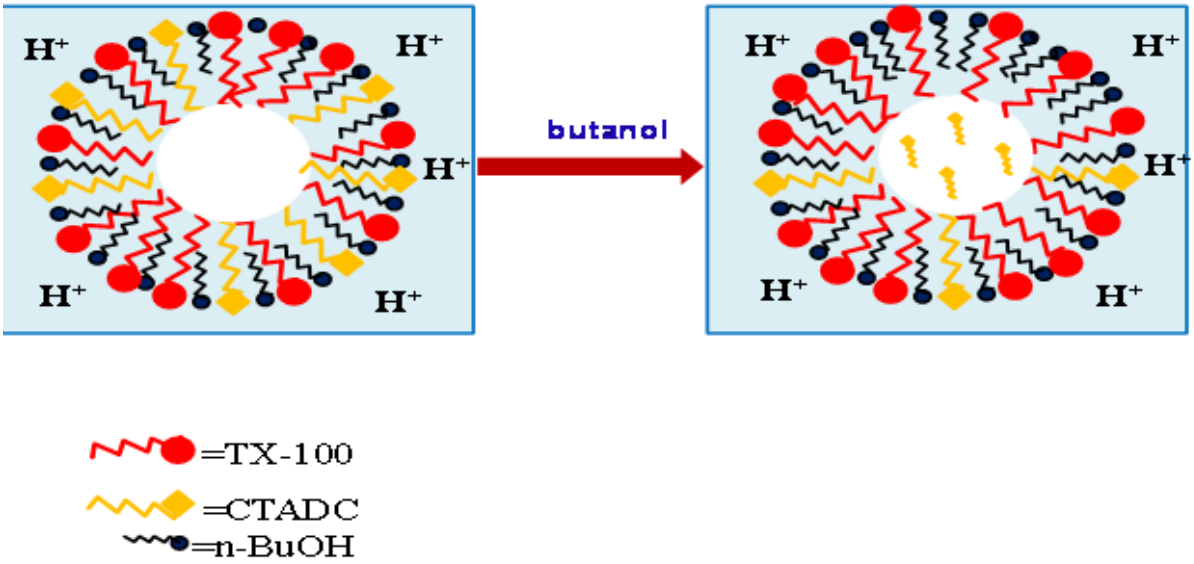


Figure 6: Schematic representation of partition of butanol and CTADC in microemulsion with increase in butanol content

4. Conclusion

Oxidation of butanol in microemulsion by CTADC (Lipophylic oxidation) has been undertaken. The reaction is 1st order with respect to the oxidant CTADC. With increase in surfactant concentration and acid concentration rate of the reaction increase.With increase in n-Butanol concentration rate increases up to $15x10^{-2}$M and the order with respect to butanol is found to be1. After $15x10^{-2}$M concentration of n-butanol rate decreases due to structural change.

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