Title of research project : "Kinetics and Mechanism of Micellar Catalysed Oxidation Reactions of Aliphatic acid Hydrazides"

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The ability of polar portion of surfactant molecule to increase the solubility of non- polar side chain can be used to estimate the contributions of solute and solvent to the observed bulk properties. The most characteristic property of a surfactant solution is the self association of solute within a narrow concentration range in dilute solution to form high molecular weight aggregates known as Micelles

At extremely low concentration of surfactant, the true crystalloidal solutions are formed, but above a fairly distinct concentration ,the solutions become colloidal due to aggregation of surfactant molecules.. The micelle formation is favoured by addition of salts as they reduce the repulsion between ionized particles.

The Thermodynamics of micelle formation shows that the entropy change of micelle formation is positive .The hydrazides selected for the kinetic study, belong to a homologous series, so that the effect of chain length on the reaction rate and on the mechanism of the reaction can be established.

It may be noted that the first order kinetics of reaction refers to change in concentration of V(V) and observed rate constant (k) stands for first order rate constant, because the reaction was studied under pseudo-first order condition in which concentration of hydrazide was in excess as compared to that of ammonium metavanadate.

SUMMARY OF RESULTS :

1) The oxidation of hydrazides is first order with respect to oxidant.

2) The oxidation of hydrazides follows Michealis Menten type of kinetics.

3) The various thermodynamic parameters were determined by studying the reaction at five different temperatures.

4) The effect of acid on the reaction was also studied and was used to predict the possible active species of reactants. It is observed that the reaction is faster in H_2SO_4 than in $HClO_4$.

5) The intervention of free radicals was established by using acrylonitrile in presence of which copious precipitation due to free radical polymerisation was observed.

6) The oxidation products identified in these reactions were corresponding acids and nitrogen.

Micellar catalysis and inhibition have received considerable attention in view of the analogies drawn between micellar and enzyme catalysis. Micelles are formed in aqueous solutions by surfactants. This may account for the rate enhancement of an organic reaction in aqueous solution when the reactants are incorporated into or onto a micelle: approximation effects, electrostatic effects, and medium effects. The aliphatic acid hydrazides oxidation by vanadium(V) (H_2SO_4) has been carried out in anionic surfactants, namely sodium lauryl sulphate (SLS). The reaction rate increases with increasing [SLS] up to $45.0x10^{-3}moldm^{-3}$ and remains constant at higher [SLS]. This may be due to the dilution effect. The role of SLS micelles in catalysis can be explained by incorporation = solubilizition of vanadium(V)- acid hydrazide system in the Stern layer of SLS micelles through electrostatic and hydrophobic interactions. These results are in good agreement with our previous observations

CONCLUSION

A perusal of literature revealed that anionic species are stabilized by cationic micelles, cationic species by anionic micelles and neutral molecules by nonionic micelles accordingly exhibit catalytic effect. Micelles may catalyze or inhibit a reaction. In this study we have used an anionic surfactant, SLS, which has a catalytic effect i.e. the rate of oxidation of aliphatic acid hydrazide by vanadium(V) in presence of SLS has been enhanced. The micellar catalysis is due to the ability of micelles to concentrate both reactants at their surface.