

Title: Studies on kinetics and mechanism of electron transfer reactions in colloidal systems

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Abstract: Kinetic studies are expected to provide information on how the electron transfer event is affected by the hydrophobic and electrostatic interactions in the organized media. Electron transfer processes in micellar systems can be considered as models to get insight in electron transport occurring in biological phenomenon. Organized media such as micelles, micro-emulsions, liposomes, etc are compartmentalized liquids, which may show special performance towards reaction equilibria and reaction dynamics. In order to characterize this effect in the most straight forward way, we have thus chosen to study redox reactions where one reagent is uncharged. Kinetics is the study of rate of rate processes such as chemical reactions, diffusion and the flow of charge in an electrochemical cell. Organic chemists use kinetic studies to find out the mechanism of the organic reactions. Biochemists use kinetics to study the rates of enzyme-catalyzed reactions. Chemical engineers use kinetics to calculate how fast the products will be formed and use thermodynamics to predict the equilibrium composition of the reaction mixtures. Polymer chemists use kinetics to investigate the kinetics of the polymerization.

Manganese shows variable oxidation state in their compounds and this ability is certainly related to the redox function of the metal ion in biological system. Permanganates are the broad range oxidants, in synthetic as well as analytical chemistry and also act as disinfectant. During the oxidation it is evident that permanganate is reduced to various oxidation states in acidic, alkaline and neutral media. The extent of oxidation of organic substrate by permanganate depends mainly on the acidity of the medium. In alkaline or weakly acidic solution Mn(VII) changes to Mn(IV), while in strongly acidic medium Mn(VII) is further reduced, forming ultimately Mn(II). During this valence change of manganese almost every conceivable intermediate ion was suggested as participating as an oxidant. But the species having the main role as potential oxidant depend on the nature of the substrate and on the pH of the medium. Mechanistic studies of permanganate

oxidation of both organic and inorganic substrates are invariably encumbered by difficulties due to the multitude of oxidation states, which are involved as intermediates in the reduction of manganese. Extensive work has been done to elucidate the mechanisms involved in the permanganate oxidations system of both organic as well as inorganic substrates. The versatility of permanganate as an oxidant is reflected in the different reaction paths, it follows, depending on the structure of the substrate and the acidity of the medium. The formation of soluble form of colloidal Manganese dioxide as detectable intermediate reactions has added a new dimension to this investigation. The studies discussed in this thesis deals with the kinetics and mechanism of electron transfer reactions in colloidal systems of carbohydrates and amino acids in presence of anionic, cationic and non-ionic surfactants by permanganate ions. A series of kinetic runs were carried out by varying the concentrations of oxidants, reductants, surfactants and inorganic salts (MnCl_2 , NaF , $\text{Na}_4\text{P}_2\text{O}_7$, NaBr) to elaborate their role in the formation of intermediate (s), and also by varying temperature to calculate various activation parameters. The values of rate constants were found to be independent of initial concentrations of MnO_4^- showing a first order dependence of the rate on the oxidant concentration. The positive catalytic role of surfactants has been explained in terms of adsorption, association and solubilization of the reactive species of the oxidant and reductant on to the surface of the micelle. It has been established that the rates of the chemical reactions being affected by surfactants are mainly due to compartmentalization/localization, polarity, pre-orientational and counter-ion effects. Three important factors, namely, electrostatic, hydrophobic and hydrogen bonding seems to play an important role in bringing the reactive species together.

In permanganate oxidation of D-glucose in presence of sulphuric acid, it was observed that the reaction proceeds in two stages (a slow step followed by a relatively fast second step). The influence of different parameters was measured i.e., [reactants], [surfactant], [sulphuric acid] and temperature. The association of permanganate with the cationic head group of CTAB was observed.

Cationic surfactant, cetyltrimethylammoniumbromide (CTAB), in benzene and aqueous potassium permanganate solution brought the MnO_4^- from the aqueous phase to the organic phase. The observed effect on the rate constant is catalytic up to a

certain concentration of CTAB; thereafter, a saturation phenomenon is observed with an increased concentration of CTAB.

The effects of different surfactants like cetyltrimethylammonium bromide (CTAB), sodiumdodecyl sulphate (SDS) and Triton X-100 (TX-100) on the oxidative degradation of ethylenediaminetetraacetic acid (EDTA) by MnO_4^- have been studied. It was found that cationic surfactant catalyse the reaction rate while anionic and non-ionic have no effect. The premicellar environment of CTAB strongly catalyse the reaction rate which may be due to the favorable electrostatic binding of both reactants (MnO_4^- and EDTA) with the positive head groups of the CTAB aggregates.

In case of oxidative degradation of tyrosine by permanganate the effect of total [CTAB] on the reaction rate was determined. When [CTAB] was less than its critical micelle concentration (cmc) the rate constants (k_{ψ}) values decreased from 18.5×10^{-4} to $7.2 \times 10^{-4} \text{ s}^{-1}$. As the [CTAB] was greater than the cmc, the k_{ψ} values increases from 7.2×10^{-4} to $15.8 \times 10^{-4} \text{ s}^{-1}$ at room temperature. The presence of $-\text{OH}$ group is responsible for the higher reactivity of tyrosine which easily transfers the proton to MnO_4^- . The premicellar environment of CTAB strongly inhibits the reaction rate where as increase in rate constant ascribed to the incorporation of tyrosine and MnO_4^- in to the Stern layer of CTAB micelles. The reaction has acid-dependent and acid-independent paths and, in the former case, the zero-order kinetics with respect to $[\text{H}_2\text{SO}_4]$ shifted to fractional-order at higher $[\text{H}_2\text{SO}_4]$.

In this case upon the accumulation of permanganate to a solution of tryptophan (Trp), yellow-brown color species appear within the time of mixing of tryptophan in absence and presence of cetyltrimethylammonium bromide (CTAB), which was stable for some days which show the formation of water soluble colloidal MnO_2 as the most stable reduction product of MnO_4^- . For the fast reduction of permanganate carbon-carbon double of indole moiety of Trp is responsible. Sub- and post-micellar catalytic effect of CTAB ascribed to the association/ incorporation/solubilization of both reactants (MnO_4^- and Trp) with the CTAB aggregates and in to the Stern layer of cationic micelles.