Acceleration of Hydrolysis of Acetylsalicylic Acid in AOT/Supercritical Ethane Reverse Micelles

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In situ UV-vis spectroscopy has been applied to study the hydrolysis of acetylsalicylic acid, as a model reaction, in sodium bis(2-ethylhexyl)sulfosuccinate (AOT)/supercritical ethane reverse micelles in the presence of imidazole as a catalyst. A 55-fold increase in the rate constant was observed in AOT/supercritical ethane micelles compared to the reaction carried out in aqueous buffer medium. The promotion of hydrolysis in the micelles as compared to aqueous solution has originated from compartmentalization of water-soluble reactant and the catalyst in the aqueous core of micelles.

Reverse micelles are formed by adding a small quantity of water to a surfactant solution usually in hydrocarbon (oil) solvents.[1] Thermodynamically stable and optically transparent reverse micelles solution is composed of water droplets surrounded by a layer of surfactant dispersed in continuous oil phase.[2] Because of the presence of different polarity domains, reverse micelles are known as universal solvents which can solubilize hydrophilic, hydrophobic and amphiphilic solutes.[3] Therefore, they have potential as reaction media for both organic[4] and inorganic synthesis,[5] and are also used in extraction[6] and separation[7] processes. Depending upon the nature of reactant, the reaction can occur inside the aqueous core of micelles, at the interface or in the continuous oil phase. For water soluble reactants the core of micelle can act as a nanoreactor and the size of core can be adjusted by changing the water content of micelles which can have profound effect on the kinetics of reactions. In 1987, the existence of reverse micelles in supercritical (SC) ethane and propane was observed[8] since then much attention has been focussed on these high pressure micelles as supercritical continuous phase that has liquid-like density and gas-like diffusivity and viscosity.[9] In this article, we find out if supercritical fluid micelles have the potential as the medium for chemical reactions. To this end, we have selected a model reaction, the hydrolysis of acetylsalicylic acid carried out in AOT/SC ethane micelles in presence of catalyst imidazole and compared with the reaction carried out in aqueous buffer solution. The contribution of water content of micelles and pressure effect of ethane have also been reported.

The reaction was conducted in a high pressure UV cell consisted of a cylindrical stainless steel block fitted with a pair of sapphire windows and had an internal volume of 2.2 ml. The temperature of the reaction was controlled within ±0.2 °C with a temperature controller attached to the cell. Sample preparation was done by loading AOT, acetylsalicylic acid, imidazole, and water into the high pressure cell and after closing the cell micelles solution was obtained by introducing pre-cooled ethane to a desired pressure inside the cell. The reaction mixture was stirred continuously during the measurement by a Teflon-coated bar driven by an outside magnet attached to the high pressure UV cell. The concentration of AOT, acetyl salicylic acid, and imidazole was taken as 0.1, 2.5×10^{-4} and 2.5×10^{-2} M, respectively. For rate constant determination, the time-course of the reaction was monitored at 298.6 nm, the band of the product salicylic acid, with a Jasco V-570 spectrometer. The conversion rate (%) was determined by recording the UV absorption spectrum of the product at various reaction time. 100 mM phosphate buffer was used to adjust the water content (W_0) of micelles and also as an aqueous reaction medium. W_0 is the molar ratio of water-to-AOT. In all the measurements temperature was kept constant at 310 K. The pressure of AOT/SC ethane micelles was varied in the range of 27 to 44 MPa, while the reaction in aqueous buffer were carried out at ambient pressure.

The pseudo first order rate constants for the hydrolysis of acetylsalicylic acid under various conditions are shown in Figure 1. The introduction of AOT/SC ethane micelles in the presence of imidazole catalyst has enhanced greatly the reaction rate as compared to the reaction carried out in aqueous buffer solution. The addition of imidazole in the aqueous solution has no influence on the reaction rate whereas the incorporation of imidazole in micelles has increased the reaction rate remarkably. Figure 1 also shows that increasing water content (W_0) of micelles containing imidazole decelerates the reaction. In a separate experiment of conversion rate (%) of acetylsalicylic acid to salicylic acid vs the reaction time in presence of imidazole, it was found that in the initial 33 min of reaction time 100% conversion was obtained in micelles of $W_0 = 1$ at 40.2 MPa pressure of ethane, while in aqueous solution it took 61 longer hrs to complete the reaction. The above findings could be explained on the basis of compartmentalization of water-soluble imidazole catalyst and acetylsalicylic acid within the aqueous core of micelles rather existence of a diluted solution of these solutes in aqueous buffer medium. Because of the increase in concentration of the water-soluble catalyst and substrate in the compartmentalized aqueous

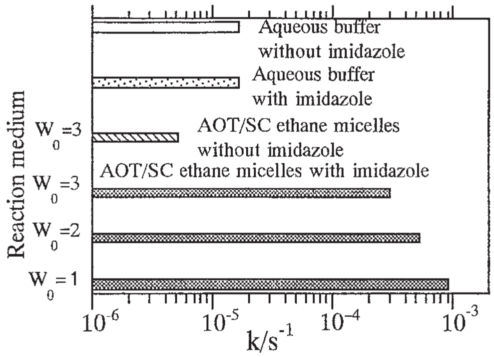

Figure 1. Hydrolysis rate constant of acetylsalicylic acid in AOT/SC ethane micelles (P = 40.2 MPa) and in aqueous buffer at 310 K.

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domain of micelles, the enhancement of the reaction rate and shorter reaction time were noticed. Increasing amount of water in micelles decreases the concentration of reactants in the core of micelles, which results in the lowering of the values of rate constant. The effect of concentration on the reaction kinetics was also studied in micelles and aqueous buffer solution; in both the systems the rate constant increased with increasing the concentration of catalyst and substrate proportionately (Figure 2) which further proves that the compartmentalization of the water-soluble reactants in the aqueous domain of micelles is indeed the reason for acceleration of the reaction in micelles. A comparison of the rate constants was made in AOT/SC ethane (40.2 MPa) and AOT/isooctane micelles at 310 K for $W_0 = 1$. The rate constant was found 1.3 times higher in AOT/SC ethane micelles attributed to the higher diffusivities of the reactants in SC ethane phase. The hydrolysis of acetylsalicylic acid using the imidazole catalysis is a generally acid and base catalyzed reaction with the generation of hydroxide ions followed by the transfer of proton from protonated imidazole in the transition state.[10] The effect of pressure on the hydrolysis of acetylsalicylic acid in AOT/SC ethane micelles has also been investigated (Figure 3). Increasing the pressure of ethane has no influence on the kinetics of the reaction, which is contrary to the pressure dependence observed in normal AOT/octane micelles for enzyme catalysed hydrolysis reactions[11] attributed to the stability of the enzyme in structurally ordered micelles at higher pressures of octane. In contrast to the large sized enzyme molecules which are in contact to the micellar interface most efficiently, the samller sized imidazole molecule located inside the core of micelles, where it does not experience any change thus rendering no pressure dependence on the reaction rate at high pressures of the system. Pressure dependence has also been observed for the reactions carried out in carbon dioxide[12,13] in the near-critical region. The maximum reaction yield obtained in the near-critical region has been attributed to the increased solubility and diffusivity of reactants in this region. In the present reaction, the supercritical state of ethane continuous phase of micelles has been maintained throughout the reaction. Also, the system containing catalyst imidazole and acetylsalicylic acid existed in a single homogeneous solution, as confirmed by looking across the windows of high pressure UV cell, at all the pressures therefore, the solubility and diffusivity of the solutes have not contributed to the kinetics of the reaction and thus no pressure dependence of the reaction was noticed.

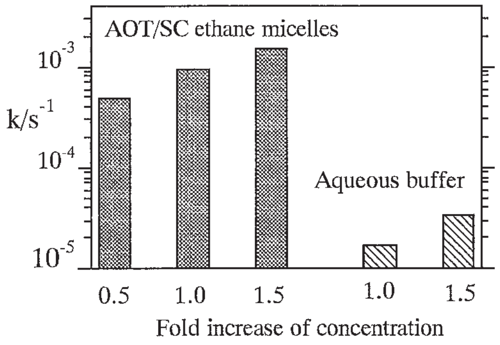

Figure 2. Rate constant vs fold increase in concentration of imidozole and acetylsalicylic acid in micelles ($W_0 = 1$, P = 35.6 MPa, T = 310 K) and in aqueous buffer at 310 K. One fold of imidazole and acetylsalicylic acid is 2.5×10^{-2} and 2.5×10^{-4} M, respectively.

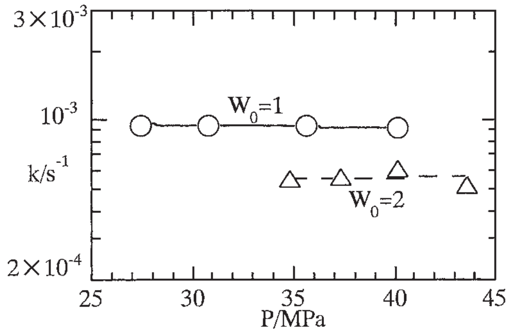

Figure 3. Pressure dependence of the rate constant of hydrolysis of acetylsalicylic acid in AOT/SC ethane micelles at 310 K.

In this work, we demonstrated that in supercritical fluid micelles a greater enhancement of catalytic activity was noticed as compared to aqueous buffer medium. The enhancement of the reaction rate in micelles and the influence of water content have been confirmed to be attributed to compartmentalization of the water-soluble imidazole and acetylsalicylic acid in aqueous core of micelles. No influence of increasing pressure of supercritical ethane was observed on the kinetics of the reaction, and reaction can be carried out efficiently in lower pressure region of ethane.

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