CHAPTER VI

EFFECTS OF ANIONIC SURFACTANTS ON THE KINETICS OF ACIDIC HYDROLYSIS OF ACETOHYDROXAMIC ACID

The acid-catalyzed hydrolysis of acetohydroxamic acid (AHA) in nitric acid solution has been studied spectrophotometrically in absence and presence of some anionic surfactants, (sodium dodecyl sulphate (SDS), dodecylbenzenesulfonic acid sodium salt (SDBS), dodecyl lithium sulphate (DLS) and 1-octane sulphonic acid sodium salt). First order dependency on the hydronium ion concentration was observed in the acid catalyzed reaction. The kinetics for the hydrolysis of the acetohydroxamic acid in nitric acid solution in the presence of anionic surfactants fit the pseudo-first-order condition. The variation of the rate constant with respect to the increasing concentration of anionic surfactant was examined. It was observed that the anionic micelles accelerate the rate of reaction for hydrolysis of AHA in nitric acid. Activation parameters at different temperature were also evaluated.

Part of this work has been published in J. Ind. Chem. Soc., 2011, 88, 193-197.
CHAPTER VI: EFFECTS OF ANIONIC SURFACTANTS ON THE KINETICS OF ACIDIC HYDROLYSIS OF ACETOHYDROXAMIC ACID

6.0 INTRODUCTION

Hydroxamic acids are naturally occurring compounds of great importance in analytical, biological and medicinal fields [1-4]. These compounds have been used as excellent spectrophotometric and gravimetric reagents, with current interest focused on their reduction/complexation chemistry with metals [5, 6]. It is reported that hydroxamic acid-metal complex is a promising DNA cleaving agent [7]. The acetohydroxamic acid (AHA) is salt free, hydrophilic organic compounds (RCONHOH, R = CH₃) which act as bidentate O,O donor ligands and hence have higher affinities for hard cations such as Fe³⁺, Np⁴⁺ and Pu⁴⁺. On the basis of this interaction, numerous microorganisms developed hydroxamate type metal sequestering siderophores for the uptake, storage, and transport of metal ions with biological relevance [8-9]. In past decade, our research groups have made important contributions in the field of acid/base catalyzed reactions of hydroxamic acids in absence/presence of micellar media [10-16]. Compartmentalized liquids such as aqueous micelles, vesicles and microemulsions droplets have found potential uses and applications in various fields related to chemistry and biology. Rates of numerous organic and inorganic reactions [17-25] are affected by micelles in aqueous solutions.

Acetohydroxamic acid (AHA) is utilized as drug for hepatic coma and DNA scission agent [26]. In addition to the reduction and complexation ability of AHA, it is also noteworthy to mention that under acidic conditions, AHA is unstable and undergoes hydrolysis [27-31]. The acidic hydrolysis of AHA is an irreversible destructive process resulting in formation of acetic acid and hydroxylamine as degradation products.

Over the recent years, increasing interest in micellar reaction media have attracted considerable attention as means of controlling the rate of reactions that are chemical,
industrial and biological interest. Anionic micelles which accelerate reaction between hydrophobic substrates and cations (notably acid hydrolysis in which the reactive cation is \( \text{H}^+ \)) have been used in relatively few detailed studies [32-40]. In the present chapter an attempt has been made to study the effect of anionic surfactants on the acidic hydrolysis of acetohydroxamic acid.

### 6.2 REVIEW OF THE EARLIER WORK

Most important contribution made by Bunton [41], Menger [42], Rodenas [43] toward the hydrolysis of esters, phosphate esters, amides, acetals and other carboxylic acid derivatives under micellar environment. Over the past several years, kineic investigation of acidic and alkaline hydrolysis of hydroxamic acids have been widely studied in absence and presence of micellar media [10, 44].

The rate of acidic hydrolysis of a series of meta and para substituted benzohydroxamic acids in aqueous solution with sodium, 1-dodecanesulfonate as surfactant were studied by Berndt group [45]. The substitution effect indicate specific micellar influences on the rates and a difference in mechanism between the bulk aqueous phase and the micellar phase. Berndt et al. have [46] also investigated the rates of acidic hydrolysis of some N-aryl and N-alkylhydroxamic acids in aqueous perfluoro-octanoic acid, a reactive counterion surfactant system.

Iglesias et al. [47] have studied the solvent isotope effect on the kinetics of acid denitrosation of \( \text{N-methyl-N-nitroso-p-toulenesulfonamide} \) (MNTS) in the presence of sodium dodecyl sulphate micelle. They observed that anionic micelle accelerate the rate of reaction for the hydrolysis of MNTS under acidic conditions. Taylor et al. [48] have investigated that hydrolysis of formo- and acetohydroxamic acids complexants (FHA, AHA) with nitric acid in the presence of non-oxidizing metal ions such as \( \text{Fe}^{3+}, \text{Np}^{4+}, \text{Pu}^{4+} \) by UV-visible and near IR spectrophotometric methods. Chung et al. [49] studied that the
reduction of Np (VI) by acetohydroxamic acid in nitric acid solution. They observed that the reduction of Np (VI) by acetohydroxamic acid is rapid and first order with respect to both [Np (VI)] and [AHA]. Ghosh et al. [10-16] have studied that the acidic and alkaline hydrolysis of hydroxamic acids with different types of acids in absence and presence of anionic, cationic and zwitterionic surfactants.

6.3 PRESENT INVESTIGATIONS

This chapter deals with the acid catalyzed hydrolysis of acetohydroxamic acid with anionic micelles by spectrophotometric method. We have used different anionic surfactants viz., sodium dodecyl sulphate (SDS), dodecylbenzenesulfonic acid sodium salt (SDBS), dodecyl lithium sulphate (DLS) and 1-octane sulphonic acid (Scheme 6.1) to study the reaction of acetohydroxamic acid (AHA) in the presence of nitric acid. The variation of the rate constants with respect to the increasing concentration of anionic surfactants was examined. Activation parameters have also been calculated.

\[
\begin{align*}
\text{Sodium dodecyl sulphate (SDS)} & \quad \begin{aligned}
\text{Dodecylbenzenesulfonic acid sodium salt} \\
\text{(SDBS)}
\end{aligned} \\
\text{Dodecyl lithium sulphate (DLS)} & \quad \begin{aligned}
\text{1-octanesulphonic acid sodium salt (OSA)}
\end{aligned}
\end{align*}
\]

\text{Scheme 6.1}
6.4 EXPERIMENTAL

6.4.1 Materials

The acetohydroxamic acid (AHA), sodium dodecyl sulphate (SDS), dodecylbenzene sulphonic acid sodium salt (SDBS), dodecyl lithium sulphate (DLS), and 1-octane sulphonic acid sodium salt (OSA) were procured from Sigma/Aldrich. The nitric acid was procured from of Moly Chem and used without further purification. The iron (III) chloride solution used in the spectrophotometric method was prepared by dissolution of anhydrous ferric chloride (SM, LR, 44g) in triple distilled water (1L) containing concentrated HCl (10 ml). All the solutions were prepared in triple distilled water.

6.4.2 Method

The rate of hydrolysis of acetohydroxamic acid is determined spectrophotometrically by following the decrease in the characteristic absorption of acid catalyzed reaction in which a purple iron (III) acetohydroxamic acid complex is produced. The acetohydroxamic acid (0.013gm -0.015gm) under experiment is mixed with aqueous and surfactant in a reaction vessel. In other reaction vessel, diluted catalyzing acid of certain molarity is taken. After thorough shaking, 2ml aliquot of the reaction mixture is periodically transferred to a test tube containing 2ml ferric chloride (acidic) and 6ml water in case of acidic hydrolysis. These serve the double purpose, one is quenching of the reaction and the other is the color development. A purple color is developed due to formation so 1:1 Fe$^{3+}$ acetohydroxamic acid complex. Absorbance of the purple colored complex is measured at 500nm, using reference solution containing 2ml of ferric chloride and 6ml water in acidic hydrolysis. As the reaction proceeds, there is a decrease in the absorbance of the solution. The rate of hydrolysis is calculated from this decrease in absorbance. First order rate constants were calculated from the standard equation and graphically from the plot of log(a-x) against time (t). As Beers law is applicable to all the ferric acetohydroxamic acid complex, the concentration of reacting species is proportional to absorbance.
6.5 RESULTS AND DISCUSSION

6.5.1. Hydrolysis of AHA in the Absence of Surfactants

Pseudo-first order rate constants have been measured for the hydrolysis of acetohydroxamic acid (AHA) by nitric acid (HNO₃) in absence/presence of anionic micellar media. Table 6.1 shows the kinetic hydrolysis of AHA with varying concentration of nitric acid (0.5 - 3.0 M) at different temperatures (27 ºC, 37 ºC, 47 ºC and 57 ºC). At low acidity increase in concentration of acid causes an increase in the rate of hydrolysis of AHA. Fig. 6.1 shows that the rate of reactions linearly increase with increasing acid concentration.

![Fig. 6.1 Rate acidity profiles for acid catalyzed hydrolysis of acetohydroxamic acid.](image)
Table 6.1 Rate constants on the hydrolysis reactions of acetohydroxamic acid with varying concentration of nitric acid at different temperatures.

<table>
<thead>
<tr>
<th>[HNO₃] (M)</th>
<th>Temp. (°C)</th>
<th>$k_\Psi (10^3 \text{ s}^{-1})$</th>
<th>$k (\text{M}^{-1}\text{s}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>27</td>
<td>1.02</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>3.90</td>
<td>7.80</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>7.60</td>
<td>15.2</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>18.0</td>
<td>46.8</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>2.30</td>
<td>21.0</td>
</tr>
<tr>
<td>1.0</td>
<td>37</td>
<td>8.70</td>
<td>8.70</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>15.8</td>
<td>15.8</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>38.0</td>
<td>56.7</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>4.40</td>
<td>2.30</td>
</tr>
<tr>
<td>2.0</td>
<td>37</td>
<td>15.5</td>
<td>77.5</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>35.0</td>
<td>18.7</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>85.0</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>6.80</td>
<td>3.10</td>
</tr>
<tr>
<td>3.0</td>
<td>37</td>
<td>27.5</td>
<td>9.10</td>
</tr>
<tr>
<td></td>
<td>47</td>
<td>52.2</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>57</td>
<td>130</td>
<td>33.4</td>
</tr>
</tbody>
</table>

5.2 Effects of Anionic Surfactants

The influence of anionic surfactants on the kinetic hydrolysis of AHA (0.01 M) has been studied with the fixed concentration of HNO₃ (0.5 M). Different anionic surfactants i.e. SDS, SDBS, DLS, 1-octane sulfonic acid sodium salt and their kinetic rate effect are shown in Table 6.2. The concentration of the anionic surfactants viz. SDS, SDBS and 1-octane sulfonic acid sodium salt used were in the range of (0.005-0.0208 M).
Table 6.2 Kinetic rate data for acidic hydrolysis of acetohydroxamic acid in presence of anionic surfactants.

<table>
<thead>
<tr>
<th>[Surf], mM</th>
<th>10^4 k_{obs} (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[SDS]</td>
</tr>
<tr>
<td>0.0</td>
<td>7.6</td>
</tr>
<tr>
<td>0.5</td>
<td>8.0</td>
</tr>
<tr>
<td>1.0</td>
<td>9.2</td>
</tr>
<tr>
<td>1.7</td>
<td>10.8</td>
</tr>
<tr>
<td>3.4</td>
<td>13.5</td>
</tr>
<tr>
<td>6.9</td>
<td>9.3</td>
</tr>
<tr>
<td>10.5</td>
<td>7.9</td>
</tr>
<tr>
<td>12.0</td>
<td>-</td>
</tr>
<tr>
<td>13.8</td>
<td>7.6</td>
</tr>
<tr>
<td>16.0</td>
<td>-</td>
</tr>
<tr>
<td>18.0</td>
<td>-</td>
</tr>
<tr>
<td>20.8</td>
<td>7.3</td>
</tr>
</tbody>
</table>

Fig. 6.2 shows that first-order-rate constants increase with increasing concentration of anionic surfactants and go through a maxima and then decreases, with higher concentration of SDS, SDBS, DLS and 1-octane sulfonic acid sodium salt. Iglesias et al. [41] presented the effect of rate acceleration on the acid catalyzed hydrolysis of esters. A micelle offers several binding sites for substrate; these include the hydrophobic core and hydrophobic binding sites located in the Stern layer. The Stern layer is particularly flexible in binding molecules as it contains the highly hydrophobic surfactant tails as well as water molecules. The negatively charged head groups facilitates the passage of H^+ ions of HNO_3 by means
Effect of Anionic Surfactants on the Kinetics of Acidic Hydrolysis of…………..

of electrostatic attraction in the Stern layer containing water soluble substrates thereby enhancing the rate of reaction. The rate increases gradually from SDS, SDBS, DLS and 1-octane sulphonic acid sodium salt in the Stern layer thereby lesser neutralization of charge and greater availability of protons occurs in the zone. The counter ions in such cases prefer to remain in the Gouy-Chapman layer. At low concentration of acid, the catalytic efficiency of surfactants is greater. By working at lower concentrations of acid, strong catalyzing capacity of anionic surfactants is confirmed.

![Fig. 6.2 Pseudo-first order rate constants for the acid hydrolysis of AHA as a function of anionic surfactant.](image)

6.5.3 Effect of Counterions

Added anionic surfactant increases the relative concentration of AHA and H⁺ in the Stern layer and ascending branch of the curve is observed. At sufficient higher concentration of anionic surfactants increases more Na⁺ and Li⁺ ions are available in the Stern layer which in turn, competes with the concentration of H⁺ ions. As a result, the rate of reaction at the specific sites in the Stern layer decreases. Observed rate increases with
increasing concentration of anionic surfactants and further decreases the rate constant. Nevertheless, the micellar pseudo-first-order condition confirms the dominant influence of the concentration effect, which is completely responsible for the observed rate acceleration in the presence of anionic surfactants.

### 6.5.4 Effect of Temperature

To investigate whether differences of this kind between the state of the proton in water and the micellar phase might be responsible for the observed differences in the reaction rates, we studied the influence of temperature on the reaction rate in the presence and absence of anionic micellar media within temperature range 47 to 57°C. The activation parameters are listed in Table 6.3. A possible explanation of the difference in activation entropy between the non-micellar and micellar phases is that, the mobility of the transition state at the micellar surface is restricted by interaction between negative charged micelle sulfate heads and the positive charge of counterion. This restriction of mobility lowers the entropy of the transition state, but there is no parallel effect on the reagents or for the reaction in water. Hence the negative value of entropy of activation increases in the micellar media as compare to non-micellar media.

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>$E_a$ (kJ mol$^{-1}$)</th>
<th>$\Delta S^{\neq}$ (JK$^{-1}$mol$^{-1}$)</th>
<th>$\Delta H^{\neq}$ (kJ mol$^{-1}$)</th>
<th>$\Delta G^{\neq}$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nil</td>
<td>76.0</td>
<td>-50.9</td>
<td>60.6</td>
<td>98.2</td>
</tr>
<tr>
<td>OSA</td>
<td>63.9</td>
<td>-85.2</td>
<td>49.3</td>
<td>76.9</td>
</tr>
<tr>
<td>DLS</td>
<td>54.3</td>
<td>-114.1</td>
<td>48.9</td>
<td>86.1</td>
</tr>
<tr>
<td>SDS</td>
<td>55.0</td>
<td>-118.2</td>
<td>48.0</td>
<td>86.5</td>
</tr>
<tr>
<td>SDBS</td>
<td>43.4</td>
<td>-153.8</td>
<td>48.9</td>
<td>99.0</td>
</tr>
</tbody>
</table>
6.6 CONCLUSIONS

The kinetics of the acid-catalyzed hydrolysis of acetohydroxamic acid in nitric acid solutions were studied spectrophotomerically in the absence and presence of different anionic surfactants. The anionic micelles accelerate the rate of reactions for hydrolysis of AHA in nitric acid. Anionic surfactant shows catalytic effect. Activation parameters were obtained by different temperature and observed the reaction was slower in the micellar pseudophase than in the absence of surfactant.
6.7 REFERENCES