CHAPTER- 5

MICELLAR CATALYSED OXIDATION
OF DICARBOXYLIC ACIDS
BY
VANADIUM (V)

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One of the fundamental characteristics of micellar catalysed reaction is the nature of dependence of reaction rate on the micelle – substrate interaction. The exact mechanism may not be independent of chemical nature of oxidant used in the study. Vanadium (V) is a point oxidizing agent and has been used in the oxidation of several organic and inorganic compounds [1, 2, 3, 4, 5, 6, 7, 8] in acidic medium. Micellar effect on Vanadium (V) ion oxidation in sulphuric acid has been reported [9, 10, 11].

As a part of proposed work the micellar effect on oxidation of dicarboxylate ions, first we have studied the micellization of sodium lauryl sulphate in presence of substrates in order to obtain information related to interactions present between the chemical species.

In the second part, the kinetic studies on oxidation of oxalate, malonate and succinate ions were carried out in presence of sodium lauryl sulphate (SLS) micelle by Cerium (IV) in sulphuric acid medium. The nature of substrates and surfactants obtained in micellization has been utilized in the kinetic study.

It is evident from literature that no work has been reported with micellization studies of surfactants in presence of substrates used in oxidation process. The purpose of investigation is to test and confirm the influence of substrates on micellization with influence of micelles on rate of oxidation.

In presence of sodium lauryl sulphate the rate of oxidation of dicarboxylate ions by Cerium (IV) has a catalytic effect, the rate increases with increase in concentration of sodium lauryl sulphate below its critical micelle concentration. In order to compare the above findings, we have undertaken the kinetic study of these ions by Vanadium (V) in the presence of sodium lauryl sulphate as proposed in the initial stage of the work. The oxidation of dicarboxylate ions by Vanadium (V) under the same experimental conditions as used in the oxidation by Cerium (IV), not possible. Hence, the oxidation of carboxylic acids were undertaken in place of carboxylate ions namely oxalic acid and succinic acid.

The postulates considered in the study are summarized below in brief.
(I) In aqueous solution, a strong binding for bivalent ions like $\text{VO}^{2+}$ is a general phenomenon regardless of the nature of micelles, provided that the charge sign of the solute is opposite to that on the micellar surface [12].

(II) Vanadium (V) forms different types of ions in sulphuric acid medium depending upon the concentration of the acid which are designed as $\text{VO}^{2+}$, $(\text{VO}.\text{H}_2\text{O}.\text{SO}_4)^+$, $\text{V}$(OSO$_3$H)$_3$,$^2+$, $\text{V}$(OH)$_3\text{HSO}_4^+$, $(\text{VO}_2.\text{H}_2\text{O}.\text{H}_2\text{SO}_4)^+$ and $(\text{VO}_2.2\text{H}_2\text{SO}_4)^+$ [13].

(III) In the ESR measurement on vanadyl ion, $\text{VO}^{2+}$ in aqueous solution of sodium lauryl sulphate have reported that virtually all $\text{VO}^{2+}$ ions become attached to surfactant at concentration slightly above the cmc [14].

(IV) The oxidation of dicarboxylate ions was not feasible in presence of sulphuric acid by Vanadium (V) whereas the oxidation takes place with the carboxylic acids. It can be mentioned here that the stability of dicarboxylate ions in presence of acid is much higher in comparison to towards oxidation is favored by the more positively charged sites through resonance.

(V) The Piszkiewicz model is applicable for the oxidation of dicarboxylate ion by Cerium (IV) which justifies the interactions of dicarboxylate ions towards surfactant of low concentration.

(VI) The formation of aggregate by dicarboxylate ions is also confirmed in this study in chapter 3.
(VII) The oxidation behaviour of malonate ion and succinate ion is similar in nature. Hence, the oxidation studies of oxalic acid and succinic acid can give the results based on interaction behavior of substrate.

(VIII) Before starting the oxidation study of carboxylic acid, it is justified to test the solution behavior of dicarboxylate ion in aqueous sulphuric acid which can support the non-feasibility of the oxidation of dicarboxylate ion by Vanadium (V).

(IX) Sulphuric acid and carboxylic acids are the solute which behaves as structure maker in water but B-coefficient for oxalic acid in aqueous solution of sulphuric acid has negative value [8].

(X) The oxidation of glycolic acid [15], lactic acid[16], malic acid [17], tartaric acid [18], citric acid [19], and oxalic acid [20,21], by Vanadium (V) have been reported in aqueous sulphuric acid.

(XI) The anionic character of the carboxylate ions favours the formation of the thick/hard solvation layer around the anion in water [22].

5.1. Experimental

All the solutions were prepared using the chemicals mentioned in the list of materials and by the methods described in chapter-2. The studies were carried out with the instruments according to the methods described in chapter-2.

5.2. Results

5.2.1. Conductance study

The specific conductance of dicarboxylate ions was measured at different concentration in the range 0.01 to 0.04 mol dm$^{-3}$ at constant concentration of sulphuric acid 0.05 mol dm$^{-3}$.

The results obtained are given in Table 5.1, and plot between specific conductivity versus concentration of dicarboxylate ion are illustrated in Figure 5.1A, 5.1B and 5.1C. The analysis of the data and nature of the plots indicates that the specific conductivity decreases with increase in concentration of
dicarboxylate ion. It can be concluded that the sulphuric acid forms complex ion with dicarboxylate ion. This also proves the non-feasibility of the oxidation of dicarboxylate ion as found in our preliminary study.

Table 5.1
Effect of dicarboxalate ions on specific conductance of 0.05 mol dm$^{-3}$ sulphuric acid at 298 K

<table>
<thead>
<tr>
<th>S. No.</th>
<th>[Substrate] mol dm$^{-3}$</th>
<th>Specific conductance mS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>oxalate</td>
<td>malonate</td>
</tr>
<tr>
<td>0</td>
<td>0.00</td>
<td>1.62</td>
</tr>
<tr>
<td>2</td>
<td>0.01</td>
<td>1.45</td>
</tr>
<tr>
<td>3</td>
<td>0.02</td>
<td>1.35</td>
</tr>
<tr>
<td>4</td>
<td>0.03</td>
<td>1.26</td>
</tr>
<tr>
<td>5</td>
<td>0.04</td>
<td>1.15</td>
</tr>
</tbody>
</table>
Fig. No. 5.1A

\[ y = -11.3x + 1.592 \]

\[ R^2 = 0.984 \]
Fig. No. 5.1B

\[ y = -20.11x + 1.589 \]
\[ R^2 = 0.973 \]
Fig. No. 5.1C

\[ y = -23.16x + 1.579 \]

\[ R^2 = 0.990 \]
5.3. Dependence of rate on initial [reactants]

The pseudo-first order rate constant with respect to vanadium (V) was calculated from the kinetic data obtained at different initial concentration of the reactants namely Vanadium (V), sulphuric acid, substrate and SLS for both the substrate, oxalic acid and succinic acid keeping concentration of other reactant constant. The values of rate of oxidation for each reactant are summarized in Table 5.2.
Table 5.2

Effect of initial concentration on rate of oxidation of dicarboxylic acids by vanadium (V) at 298 K

<table>
<thead>
<tr>
<th>[H$_2$SO$_4$] mol dm$^{-3}$</th>
<th>[V(V)] mol dm$^{-3}$</th>
<th>[SLS] mol dm$^{-3}$</th>
<th>[substrate] mol dm$^{-3}$</th>
<th>$10^4k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Oxalic acid</td>
</tr>
<tr>
<td>6.16</td>
<td>0.002</td>
<td>-</td>
<td>0.04</td>
<td>0.73</td>
</tr>
<tr>
<td>6.16</td>
<td>0.003</td>
<td>-</td>
<td>0.04</td>
<td>0.74</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>0.71</td>
</tr>
<tr>
<td>6.16</td>
<td>0.005</td>
<td>-</td>
<td>0.04</td>
<td>0.72</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>0.60</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.05</td>
<td>0.69</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.06</td>
<td>0.78</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.07</td>
<td>0.88</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>-</td>
<td>0.08</td>
<td>1.01</td>
</tr>
<tr>
<td>5.16</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>1.08</td>
</tr>
<tr>
<td>5.66</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>0.73</td>
</tr>
<tr>
<td>6.66</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>0.46</td>
</tr>
<tr>
<td>7.16</td>
<td>0.004</td>
<td>-</td>
<td>0.04</td>
<td>0.36</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>0.0001</td>
<td>0.04</td>
<td>1.37</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>0.0002</td>
<td>0.04</td>
<td>1.27</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>0.0003</td>
<td>0.04</td>
<td>1.19</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>0.0004</td>
<td>0.04</td>
<td>1.15</td>
</tr>
<tr>
<td>6.16</td>
<td>0.004</td>
<td>0.0005</td>
<td>0.04</td>
<td>1.00</td>
</tr>
</tbody>
</table>
5.4. Mechanism and Discussion

The results of the kinetic study of the dicarboxylic acids by Vanadium (V) in sulphuric acid are given below:

(a) The rate of the disappearance of [V(V)] at any given concentration always followed first order kinetics in presence and absence of surfactant.

(b) The effect of varying the initial concentration of carboxylic acid was studied over the range 0.04 to 0.08 mol dm$^{-3}$. The plots between $k_{\text{obs}}$ and [carboxylic acid] were found to be linear having intercept value nearly zero. The plots are given in Fig. 5.2A and 5.2B. It indicates the reaction is first order with respect to substrate.
$y = 0.001x + 2 \times 10^{-5}$
$R^2 = 0.993$

Fig. No. 5.2A
Fig. No. 5.2B

\[ y = 0.001x + 0.000 \]

\[ R^2 = 0.978 \]
The $k_{\text{obs}}$ were measured at different initial concentration of sulphuric acid. It was noted that for both the carboxylic acid the $k_{\text{obs}}$ decrease with increase $[\text{H}_2\text{SO}_4]$. An analysis of the results indicated that there exist a linear correlation between $k_{\text{obs}}$ and $1/[\text{H}_2\text{SO}_4]^2$. It indicates the inverse second order dependence of rate on sulphuric acid. The plots are illustrated in Fig.5.3A and 5.3B.
Fig. No. 5.3A

\[ y = 0.003x - 4 \cdot 10^{-05} \]
\[ R^2 = 0.974 \]

\[ 1/[\text{H}_2\text{SO}_4]^2 \]

Oxalic acid
Fig. No. 5.3B

\[ y = 0.010x - 9 \times 10^{-5} \]
\[ R^2 = 0.008 \]
In absence of surfactant the following scheme for the oxidation may be considered.

**In the absence of surfactant:**

\[
\begin{align*}
S + H_2SO_4 &\xrightarrow{K_1} S\cdots H_2SO_4 \quad \ldots(5.2) \\
V(V) + H_2SO_4 &\xrightarrow{K_2} V(V)\cdots H_2SO_4 \quad \ldots(5.3) \\
S + V(V) &\xrightarrow{k_1} \text{Free radical} + \text{V(IV)} \quad \ldots(5.4)
\end{align*}
\]

\[
\text{fast} \quad \text{Free radical} \xrightarrow{} \text{Product} \quad \ldots(5.5)
\]

\[
-d[V(V)] \\
\quad \quad = \quad k_1 \quad [S] \quad [V(V)] \quad \ldots(5.6)
\]

\[
dt
\]

V(V) and substrate can exist in free state and in complex action with sulphuric acid. Hence,
\[\frac{-d[V(V)]_T}{dt} = \frac{k_1[S]_T[V(V)]_T}{(1+K_1[H_2SO_4])(1+K_2[H_2SO_4])} \quad \text{...(5.7)}\]

When \([H_2SO_4] \gg 1\), the rate expression can be given by equation 5.8.

\[\frac{-d[V(V)]_T}{dt} = \frac{k_1[S]_T[V(V)]_T}{K_1K_2[H_2SO_4]^2} \quad \text{...(5.8)}\]

5.5. **Micellar catalysis**

The reaction was studied at different concentrations of surfactant. A plot of \(k_{obs}\) versus [SLS] has maxima as illustrated in Fig 5.4.
Fig. No. 5.4

[SLS]

Succinic acid
The rate increases initially and then decreases with the increase of surfactant concentration. This behavior is an agreement with the micellar catalysis of organic molecular type. It can be concluded that the sten layer of micelle increases rapidly with surfactant concentration and organic substrate relatively. On the basis of the experimental results in the presence of surfactant following steps may be considered.

\[
\begin{align*}
    nD & \quad \xrightleftharpoons{} \quad Dn \\
    Dn & \quad + \quad S \quad \xrightarrow{\text{slow}} \quad SDn \\
    SDn & \quad + \quad V(V) \quad \rightarrow \quad \text{Free radical} \quad + \quad V(IV) \\
    \text{Free radical} & \quad \rightarrow \quad \text{Product}
\end{align*}
\]

The results of kinetic study have been applied to the Piszkiewicz model. A plot of log \((k_{\text{obs}} - k_0) / (k_m - k_{\text{obs}})\) values log D is linear with slop n and intercept \(-\log K_D\), which justified the applicability of the model. The value of n < 1 (0.82) for succinic acid, which proves the retardation of the oxidation in presence of SLS. Whereas for oxalic acid n > 1 (1.94). In case of oxalic acid the probable region of the retardation may be attributed to the nature having only electrostatic interactions in the medium. The negative cooperativity for succinic acid is justified because it has both electrostatic and hydrophobic
interaction due to the presence of CH$_2$ groups. The representative plots are given in Fig 5.5A and 5.5B.
\[ y = -1.9472x - 6.3489 \]

\[ R^2 = 0.9824 \]

Fig. No. 5.5A
$y = -0.8262x - 2.7332$
$R^2 = 0.934$

Fig. No. 5.5B
The values of $-\log K_D$ for oxalic acid is 6.34 and for succinic acid is 2.73, which justify the higher rate of oxidation of succinic acid in comparison to oxalic acid. The finding of the study have similar characteristic up to certain limits reported for micellar catalyzed reactions [23].

**Conclusion-**

There was no report till date on micellization of surfactant in micellar catalysis, in which the influence of substrate has been studied on micellization in aqueous solution. Hence, in the present work the micellization study has been taken up with a view of investigating the interactions between surfactant and substrate.

The present studied showed variation in specific conductance of surfactant at two concentrations: first corresponds to critical aggregation concentration and second corresponds to critical saturation concentration for oxalate malonate and succinate ions. The dicarboxylate ions are bound to the micelles in aqueous solutions.

The experimental results obtained for oxidation for dicarboxylic acids, correlated reasonably well by the Piszkiewicz model of molecular catalysis. It has been found that dicarboxylate ions have a strong tendency to interact with sulphuric acid. The micellar catalyzed oxidation of carboxylic acids by Vanadium (V) have distinct feature from the oxidation of dicarboxylate ions by Cerium (IV) because the oxidation of the acids inhibited by the increasing concentration of the surfactant. The rate of oxidation followed the following oxalate ion > malonate ion > succinate ion.

This study tries to achieve and to predict the physisibility of micellar catalysis in pre or post micellar concentration range and can be used as model in Journal in the study related to micellar catalysis.
References:


<table>
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<tr>
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