Effect of non-ionic micellar aggregates on the kinetics of oxidation of aminoalcohols by N-bromosuccinimide in alkaline medium

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The kinetics of oxidation of aminoalcohols (AA) viz ethanolamine (EA), diethanolamine (DEA) and triethanolamine (TEA) by N-bromosuccinimide (NBS) in alkaline medium have been investigated in absence and in presence of polyoxyethylene (23) lauryl ether (Brij-35), a non-ionic surfactant. The kinetics showed a first order dependence of rate in NBS while the order in each AA and alkali was found to decrease from unity to zero at higher [AA] and [OH⁻], respectively. The presence of small amount of surfactant strongly enhanced the rate of oxidation and the observed rate constants attained a constancy at higher surfactant concentration. The premicellar kinetics have been rationalised in the light of Piszkiewicz's positive cooperativity model. The binding constants between the reactants and the surfactant have also been evaluated using Raghvan and Srinivasan model, which is applicable for a bimolecular micellar catalysed reaction. The binding constants obtained by both the models are in good agreement.

Keywords: Micellar aggregates, oxidation of aminoalcohol, kinetics of N-bromosuccinimide.

IPC Code: C07B 33/00

Several models¹⁻⁶ have been proposed to describe the reactions in presence of micelles. As the binding of the substrate to oligomeric enzyme effects the observed reaction rate, similarly the cooperativity between the substrate and surfactant may account for micellar catalysis.

It has been observed⁷⁻¹² that several redox-reactions are influenced by the hydrophobic and electrostatic forces in micellar media and for a given set of reaction the observed rate depends on the extent of association between the reactants and micellar aggregate.

The rate of oxidation of aminoalcohols by NBS in alkaline medium is strongly enhanced in presence of surfactant (Brij-35), even at below its reported¹³ CMC (9.2 × 10⁻⁵ mol dm⁻³). This observation indicates either substrate induced micellisation or formation of premicellar aggregates. Therefore, the oxidation of AA viz EA, DEA and TEA by NBS in alkaline medium has been investigated in presence of non-ionic micelle namely, Brij-35 and the results are reported in this communication.

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Experimental Procedure

Materials and methods

The reagents employed were ethanolamine, diethanolamine, triethanolamine, N-bromosuccinimide (Thomas Baker, AR), Brij-35 (s.d. Fine Chemicals, India), NaOH, NaClO₄, succinimide (all Analar). Brij–35 was purified¹⁴ till the CMC agreed with the reported value and its solution was prepared in doubly distilled water just before the experiments to avoid ageing. The solution of NBS was prepared afresh and was standardised iodometrically. All other solutions were prepared in doubly distilled water.

Kinetic measurements

Appropriate quantities of solutions of NBS, NaOH and surfactant were placed in 100 mL Jena glass vessel. The requisite amount of doubly distilled water was added so that the total volume of reaction mixture was 50 mL after adding the substrate. The reaction mixture was then placed in thermostat at desired temperature ± 0.1 °C. The reaction mixture was allowed to attain the bath temperature, the reaction was then initiated by adding the requisite amount of aminoalcohol placed separately in same water bath. The progress of reaction was followed by determining NBS iodometrically in aliquots,
withdrawn after regular time intervals. The reaction mixture was homogenous.

**Rate constant determination**

The log [NBS] versus time plots were always found to be linear up to nearly 80% of reaction (Fig. 1). The pseudo-first order rate constants in NBS in both the conditions, i.e. in absence of the surfactant \( k_w \) and in presence of the surfactant \( k_\psi \) have been evaluated from the slopes of these plots. The observed rate constants were reproducible within ±5% in replicate kinetic run.

**Results and Discussion**

**In absence of surfactant**

The observed rate constants \( k_w \) in absence of the surfactant at various initial concentrations of the reactants are given in Table 1. In absence of the surfactant the reaction was first order in NBS. The order of reaction in AA and alkali was found to

![Fig. 1 — Plots of log [NBS] versus time, at 35 °C

[Aminoalcohol] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, [OH^{-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}, [Brij-35] = 8.47 \times 10^{-4} \text{ mol dm}^{-3}.](image)

<table>
<thead>
<tr>
<th>10^2[NBS] (mol dm^{-3})</th>
<th>10^2[AA] (mol dm^{-3})</th>
<th>10^2[OH^{-}] (mol dm^{-3})</th>
<th>10^4[k_{obs}] (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ethanolamine</td>
</tr>
<tr>
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<td>1.0</td>
<td>2.84</td>
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<td>2.50</td>
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<td>4.00</td>
</tr>
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<td>2.0</td>
<td>3.0</td>
<td>6.40</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
<td>4.0</td>
<td>8.00</td>
</tr>
</tbody>
</table>

\( k_w \) = observed rate constant in aqueous medium.

\( k_\psi \) = observed rate constant in presence of [Brij-35] = 8.47 \times 10^{-4} \text{ mol dm}^{-3}, [AA] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, [OH^{-}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}, [NBS] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}

The effect of alkali was studied at a fixed ionic strength \( \mu = 0.04 \text{ mol dm}^{-3} \) maintained by sodium perchlorate.
decrease from unity to zero at higher [AA] and [OH\(^-\)], respectively. The rate of oxidation was accelerated in presence of succinimide at lower [succinimide], while that became independent to succinimide at higher concentrations. The mechanism for the oxidation of AA by NBS in alkaline medium may be proposed as given in scheme 1.

\[
\begin{align*}
\text{NBr} + \text{OH}^- & \xrightleftharpoons[K_1]{H} \text{OBr}^- + \text{NH} \quad \text{(i)} \\
\text{(NBS)} & \\
\text{HOCH}_2\text{CH}_2\text{N} + \text{NBr} & \xrightleftharpoons[K_2]{H} \text{HOCH}_2\text{CH}_2\text{N}^- - \text{BrN} \quad \text{(Fast) (ii)} \\
\text{R}_1 & \\
\text{HOCH}_2\text{CH}_2\text{N}^- - \text{BrN} & \xrightarrow[k]{X} \text{NH} + \text{R}_1\text{R}_2\text{NH} + \text{Br}^- + 2\text{HCHO} \quad \text{(iii)} \\
\end{align*}
\]

**Scheme 1**

where, \(R_1\) and \(R_2\) represent H and H, respectively, in case of EA, H and HOCH\(_2\)CH\(_2\)^--, respectively, in case of DEA and HOCH\(_2\)CH\(_2\)^-- and HOCH\(_2\)CH\(_2\)^--, respectively, in case of TEA.

According to scheme 1, the rate of disappearance of NBS has been obtained as,

\[
\frac{d \text{[NBS]}}{dt} = kK_1 [\text{AA}] \text{[NBS]}_T [\text{Succ.}] [\text{OH}^-]
\]

where, \([\text{NBS]}_T = \text{[NBS]} + [\text{OBr}^-] + [X]

which is in agreement with the experimental results in absence of the surfactant.

**In presence of surfactant**

The log [NBS] versus time plots were also linear in presence of Brij–35 (Fig. 1). Therefore, pseudo-

first order rate constants \((k_\psi)\) at various initial concentrations of reactants have been evaluated from the slopes of these plots and are summarised in Table 1. Nearly same value of \(k_\psi\) at various initial concentrations of NBS further confirmed the first order dependence of rate with respect to [NBS] in presence of Brij-35.

The effect of alkali was studied at a fixed ionic strength maintained by sodium perchlorate. The results of the effect of a change in concentration of AA and alkali were identical. The plots of \(k_\psi\) versus [AA] or \(k_\psi\) versus [OH\(^-\)] showed a deviation from the linearity, while the plots of \(k_\psi^{-1}\) versus [AA]\(^{-1}\) (Fig. 2) and \(k_\psi^{-1}\) versus [OH\(^-\)]\(^{-1}\) (Fig. 3) were linear with intercept suggesting Michaelis–Menten\(^{15}\) behaviour.
These results suggest that the order of reaction for AA and OH– decreases from unity to zero at higher [AA] and [OH –], respectively. A positive effect of succinimide on the observed rate constant at lower [succinimide] has also been observed (Table 2) in presence of Brij-35. The reactions were also studied at different temperatures, viz 35, 40, 45 and 50 °C and evaluated thermodynamic parameters have been calculated (Table 3) using Arrhenius plot and Eyrings equations in both the conditions.

Similar kinetic results and nearly same value of ΔG° in pure aqueous medium and in the presence of Brij-35 show that the same reaction mechanism is operative in both the media. The large negative value of ΔS° in presence of Brij-35 indicates that more ordered activated complex is formed in surfactant media.

The effect of surfactant on the rate of oxidation has been studied at various temperatures, viz 35, 40 and 45 °C. It was observed that \( k_\psi \) increases with an increase in [Brij-35] at lower concentrations.

<table>
<thead>
<tr>
<th>( 10^3 [\text{succ}] )</th>
<th>Ethanolamine</th>
<th>Diethanolamine</th>
<th>Triethanolamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>[mol dm(^{-3})]</td>
<td>( k_\psi \times 10^4 ) (s(^{-1}))</td>
<td>( k_\psi \times 10^4 ) (s(^{-1}))</td>
<td>( k_\psi \times 10^4 ) (s(^{-1}))</td>
</tr>
<tr>
<td>Nil</td>
<td>3.73</td>
<td>20.2</td>
<td>5.11</td>
</tr>
<tr>
<td>1.0</td>
<td>6.14</td>
<td>21.3</td>
<td>5.90</td>
</tr>
<tr>
<td>1.5</td>
<td>6.39</td>
<td>23.9</td>
<td>6.67</td>
</tr>
<tr>
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<td>7.67</td>
<td>27.4</td>
<td>8.08</td>
</tr>
<tr>
<td>3.0</td>
<td>9.59</td>
<td>31.9</td>
<td>10.90</td>
</tr>
<tr>
<td>4.0</td>
<td>12.70</td>
<td>34.6</td>
<td>13.90</td>
</tr>
</tbody>
</table>

\[ \text{[NBS]} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, \quad \text{[AA]} = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, \quad \text{[OH –]} = 1.0 \times 10^{-2} \text{ mol dm}^{-3} \]

The data on variation of the observed rate constant \( k_\psi \) with [Surfactant] have been analysed in terms of reported models for micellar catalysed reaction.

<table>
<thead>
<tr>
<th>In absence of Brij-35</th>
<th>( \Delta E ) (kJ mol(^{-1}))</th>
<th>( \log A )</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( -\Delta S^\circ ) (JK(^{-1}) mol(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>63.8 ± 0.5</td>
<td>7.2</td>
<td>61.0 ± 0.5</td>
<td>107.0 ± 1.5</td>
<td>94.0 ± 1.0</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>69.6 ± 0.5</td>
<td>8.8</td>
<td>67.0 ± 0.5</td>
<td>75.3 ± 1.0</td>
<td>91.5 ± 1.0</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>58.8 ± 0.5</td>
<td>6.5</td>
<td>56.0 ± 0.5</td>
<td>120.6 ± 1.5</td>
<td>94.0 ± 1.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>In presence of Brij-35</th>
<th>( \Delta E ) (kJ mol(^{-1}))</th>
<th>( \log A )</th>
<th>( \Delta H^\circ ) (kJ mol(^{-1}))</th>
<th>( -\Delta S^\circ ) (JK(^{-1}) mol(^{-1}))</th>
<th>( \Delta G^\circ ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanolamine</td>
<td>42.5 ± 0.5</td>
<td>3.8</td>
<td>39.9 ± 0.5</td>
<td>171.7 ± 1.0</td>
<td>94.0 ± 1.0</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>49.5 ± 0.5</td>
<td>5.6</td>
<td>46.7 ± 0.5</td>
<td>137.1 ± 1.5</td>
<td>90.0 ± 1.0</td>
</tr>
<tr>
<td>Triethanolamine</td>
<td>40.2 ± 0.5</td>
<td>3.5</td>
<td>37.6 ± 0.5</td>
<td>177.7 ± 1.5</td>
<td>93.7 ± 1.0</td>
</tr>
</tbody>
</table>
Menger & Portnoy’s model

Several models have been proposed to describe the phenomenon of catalysis of rate in presence of micelle and important among them are those due to Menger & Portnoy \(^2\) as well as Berezin\(^3\). The variation of the rate constant with surfactant is generally treated on the assumptions that substrate ‘S’ is distributed between the aqueous and micellar pseudo phase as given in scheme 2.

\[
S + D_n \quad \overset{K_S}{\underset{k_w}{\rightleftharpoons}} \quad SD_n \quad \overset{k_m}{\rightarrow} \quad \text{Products}
\]

Scheme 2

This model leads to the following relationship for micellar catalysis,

\[
\frac{1}{(k_w - k_m)} = \frac{1}{(k_w - k_m)} + \frac{1}{K_S(k_m - k_w)[D] - \text{CMC}}
\]

where, \(k_w\), \(k_m\) and \(k_\psi\) are rate constants in aqueous phase, micellar medium and observed rate constant, respectively.

The linearity of the plot between \(1/(k_\psi - k_w)\) and \(1/[D]\) suggests the applicability of the model. However, in the present investigations the plot was non-linear, implying that the model is inadequate for the present reaction.

Piszkiewicz’s model

A kinetic model analogous to the Hill model\(^4\), which describes a more accurate dependence of the observed rate constants on surfactant concentration, was developed by Piszkiewicz\(^5\). This model is applicable specially at low surfactant concentration and the data may be treated without reference to CMC. According to this model a substrate (S), and a number \(n\), of detergent molecules (D), aggregate to form critical micelle (D\(_n\)S), which may react to yield product as,

\[
\text{nD} + S \quad \overset{K_D}{\longrightarrow} \quad D_nS
\]

\[
D_nS \quad \overset{k_m}{\longrightarrow} \quad \text{Product}
\]

\[
S \quad \overset{k_w}{\longrightarrow} \quad \text{Products}
\]

Scheme 3

where, \(K_D\) is the dissociation constant of micelle back to its free component and \(k_m\) is the rate of reaction within the micelle.

According to this model, the observed rate constant is expressed as a function of concentration of detergent by,

\[
k_\psi = \frac{k_m[D]^n}{K_D + [D]^n}
\]

and may be rearranged in the form,

\[
\log \left\{ \frac{k_\psi - k_w}{k_m - k_\psi} \right\} = n \log [D] - \log K_D
\]

Thus, a plot of \(\log \left\{ \frac{(k_\psi - k_w)/(k_m - k_\psi)}{(k_m - k_\psi)} \right\} \) versus \(\log [D]\) should be linear with a slope of ‘\(n\)’, i.e. cooperativity index. At \(\log \left\{ \frac{(k_\psi - k_w)/(k_m - k_\psi)}{(k_m - k_\psi)} \right\} = 0\), \(n \log [D] = \log K_D\). Also at \(\log \left\{ \frac{(k_\psi - k_w)/(k_m - k_\psi)}{(k_m - k_\psi)} \right\} = 0\), catalysis by detergent shows one half of its maximum effect on rate constant. The value of \(\log [D]\) at this point has been designated as \(\log [D]_{50}\).

Data represented in Fig. 4 were used to construct plots of \(\log \left\{ \frac{(k_\psi - k_w)/(k_m - k_\psi)}{(k_m - k_\psi)} \right\} \) versus \(\log [\text{Brij-35}]\). \(k_m\) was taken as the maximum rate constant in presence of surfactant. A representative plot is given in Fig. 5 suggesting a fairly linear correlations. Slopes of the double log plots, \(n\) were calculated by least square analysis. The values of \(n\), \(\log [D]_{50}\) and decomposition constant (\(K_D\)) obtained with the help of these plots are summarized in Table 4.

Raghvan and Srinivasan’s model

Raghvan and Srinivasan\(^6\) developed a model, for bimolecular micellar catalysed reactions, which also predict constancy in \(k_{obs}\) values at high detergent concentrations and may be used for evaluating the binding constants of reactants. They proposed the distribution of both reactant and nucleophile in aqueous and micellar phases. The product formation
is assumed to result from decomposition of ternary complex involving substrate, nucleophile and micelle. After analyzing the data on the basis of this model, they concluded that almost all the nucleophile is present in the bulk phase, an idea which parallels the assumption of Romsted\textsuperscript{17} as well as Reeves\textsuperscript{4}. The model is represented in scheme 4.

\[
\begin{align*}
\text{K}_1 & \quad \text{nD} + \text{S} \rightleftharpoons \text{D}_n\text{S} \\
\text{K}_2 & \quad \text{D}_n\text{S} + \text{N} \rightleftharpoons \text{D}_n\text{SN} \\
\text{k}_m & \quad \text{D}_n\text{SN} \rightleftharpoons \text{Products} \\
\text{k}_w & \quad \text{S} + \text{N} \rightleftharpoons \text{Products}
\end{align*}
\]

Scheme 4

where, D, S and N refer to detergent monomer, substrate and the nucleophile, while D\textsubscript{n}S and D\textsubscript{n}SN refer to binary and ternary complexes. The products are assumed to result from the reaction in aqueous medium as well as in surfactant medium. According to this model the observed rate constant in presence of surfactant is given as,

\[
k_w = \frac{k_w + k_m K_1 K_2 [D]^n}{1 + K_1 [D]^n (1 + K_2 [S])}
\]

Table 4 — Pizkiewicz’s cooperativity values

<table>
<thead>
<tr>
<th>Temp</th>
<th>Substrate</th>
<th>‘n’</th>
<th>-log([D]_50)</th>
<th>([D]_50)</th>
<th>(K_D)</th>
</tr>
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<tbody>
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<td>Ethanolamine</td>
<td>2.3</td>
<td>2.72</td>
<td>19.0 \times 10^4</td>
<td>5.62 \times 10^7</td>
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<tr>
<td></td>
<td>Diethanolamine</td>
<td>2.3</td>
<td>2.92</td>
<td>12.0 \times 10^4</td>
<td>1.94 \times 10^7</td>
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<tr>
<td></td>
<td>Triethanolamine</td>
<td>2.1</td>
<td>2.64</td>
<td>22.9 \times 10^4</td>
<td>2.88 \times 10^6</td>
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<tr>
<td>40 °C</td>
<td>Ethanolamine</td>
<td>2.2</td>
<td>2.76</td>
<td>17.3 \times 10^4</td>
<td>8.51 \times 10^7</td>
</tr>
<tr>
<td></td>
<td>Diethanolamine</td>
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<td>3.00</td>
<td>10.0 \times 10^4</td>
<td>1.25 \times 10^7</td>
</tr>
<tr>
<td></td>
<td>Triethanolamine</td>
<td>2.0</td>
<td>2.70</td>
<td>19.9 \times 10^4</td>
<td>3.98 \times 10^6</td>
</tr>
<tr>
<td>45 °C</td>
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<td>2.80</td>
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</tr>
<tr>
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<td>Diethanolamine</td>
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<td>3.04</td>
<td>9.12 \times 10^4</td>
<td>2.50 \times 10^8</td>
</tr>
<tr>
<td></td>
<td>Triethanolamine</td>
<td>1.9</td>
<td>2.76</td>
<td>17.3 \times 10^4</td>
<td>5.75 \times 10^6</td>
</tr>
</tbody>
</table>

\[
\text{Fig. 5 — Plots of log} \left(\frac{(k_w - k_m)}{(k_w - k_m)} \right) \text{ versus log[Brij-35], at various temperatures in case of triethanolamine.} \\
\text{[NBS]} = 2.0 \times 10^{-3} \text{ mol dm}^{-3}, \text{[Aminoalcohol]} = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, \text{[OH]} = 1.0 \times 10^{-2} \text{ mol dm}^{-3}
\]

is assumed to result from decomposition of ternary complex involving substrate, nucleophile and micelle.
This equation is identical to those derived by Martinek et al.18, Berezin 3 and Bunton et al.1c. Further, the equation may be rearranged in the form,

\[
\frac{k_{\psi} - k_w}{k_{\psi}} = K_1 K_2 \left( \frac{k_m}{k_{\psi}} \right) - K_1 \left( 1 + K_2 [S] \right) \]

which predicts a linear relationship between \((k_{\psi} - k_w)/k_{\psi})\) and \((k_m/k_{\psi})\). This model has been applied in the present system, using the value of \(n\), obtained from Piszkiewicz’s cooperativity model (Table 4). The plots of \((k_{\psi} - k_w)/k_{\psi})\) versus \((k_m/k_{\psi})\) were linear (Fig. 6). The values of binding constants, \(K_1\) and \(K_2\) have been evaluated with the help of intercepts and slopes of these plots. The values of intercepts, \(K_1\) and \(K_2\) are reported in Table 5. The values of intercept and \(K_1\) in all cases are almost same in magnitude as \(K_2 [S] \ll 1\). The evaluated \(K_1\) value is in good agreement with the value of \(1/K_D\) (\(K_D\) is the dissociation constant of the micelle back to its free component) obtained by Piszkiewicz’s model.

The above results show that in presence of surfactant the reaction takes place through the formation of an aggregates between the surfactant and the substrate. The lower values of \(K_2\) reveal that only the substrate and not NBS is distributed between the micellar and aqueous phases.

The basic strength of secondry amine is normally greater than that of primary amine. Further on, moving from secondary amine to tertiary amine, the basic strength of amine decreases. The observed kinetic data may be correlated with the basicity of the substrate. The secondary aminoalcohol being more basic than primary or tertiary aminoalcohols, is more reactive. This is supported by the observed high rate constants in case of diethanolamine in presence as well as in absence of the surfactant.

**Acknowledgement**

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References


