Kinetics of oxidation of non-ionic surfactants (Triton X-100 and Brij-35) by KMnO₄ in H₂SO₄ medium

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The kinetics of oxidation of non-ionic surfactants, viz. polyoxyethylene(10)octylphenol (Triton X-100) and polyoxyethyleneglycol dodecylether (Brij-35) by potassium permanganate in aqueous H₂SO₄ medium have been investigated in temperature range 35-45°C. The reactions show first order dependence of rate with respect to [MnO₄⁻]. The order of reaction in surfactant and H₂SO₄ decreases from unity at higher [surfactant] and [H₂SO₄], respectively. Probable reaction mechanism involving an intermediate between surfactant and active species of the oxidant is proposed and constants involved in the rate law have been evaluated.

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The study of electron transfer processes in organized molecular assemblies (i.e., micelles) has added a new dimension to biochemical research. The stability and degradability of non-ionic surfactants is important from industrial viewpoint. The kinetics of a variety of chemical reactions in non-ionic micellar medium, i.e. in presence of surfactants has been investigated to understand role of micelles as catalysts. However, only a few reports are available to reveal, how a surfactant behaves when it interacts with an oxidant. The oxidation of non-ionic surfactants (viz., Tween-80 and Triton X-100) by chromium(VI) and cerium(IV) in H₂SO₄ and HClO₄ medium is known. We report herein the oxidation of two non-ionic surfactants, viz. polyoxyethylene(10)octylphenol (Triton X-100) and polyoxyethyleneglycol-dodecylether (Brij-35) by KMnO₄ in H₂SO₄ medium.

Experimental
The solutions of KMnO₄ (A.R., Ranbaxy) were prepared by customary procedure using double distilled water and standardized against standard oxalic acid. The surfactants, viz. Triton X-100 and Brij-35 (each A.R., S.D. Fine) were used as received. However, their purities were ascertained by determining critical micelle concentration (CMC) from (surface tension) versus log [surfactant] plots. The CMC values were found to be same as reported: 1.7×10⁻⁴ mol dm⁻³ and 9.2×10⁻⁵ mol dm⁻³ in case of Triton X-100 and Brij-35, respectively. All other reagents used were of A.R. grade and their solutions were prepared in double distilled water.

Appropriate quantities of solutions of surfactant and H₂SO₄ were placed in 100 cm³ jena glass vessel. The requisite amount of double distilled water was added so that total volume of reaction mixture was 50 cm³ after adding the KMnO₄ solution. After equilibration at desired temperature (±0.1°C), the reaction was initiated by adding requisite amount of KMnO₄ solutions placed separately in the same water bath. The rates were measured by monitoring the absorbance due to KMnO₄ as function of time at 527 nm (observed λmax of KMnO₄ in presence of sulphuric acid) on a spectrophotometer (Toshniwal TVSP 25, India).

Stoichiometry and products
The stoichiometry of the reactions between MnO₄⁻ and surfactants has been studied. The reaction mixtures containing a known excess of [MnO₄⁻] over [surfactant] were kept in the presence of sulphuric acid at 40°C for 24 h. Estimation of unreacted MnO₄⁻ shows that 1 mole of surfactant consumes nearly 2 moles of MnO₄⁻. The results may be represented by:

\[
RCH₂OH + 2 MnO₄⁻ + 2H⁺ \rightarrow RCHO + 2 MnO₂ + 2H₂O + O₂
\]

where

\[
R = \begin{array}{c}
\text{OCH₃CH₂–} \\
\text{CH₂CH₂O₃–}
\end{array}
\]

in case of Triton X-100

\[
H₂C₃O₃–CH₂–CH₂–[C₃H₄O₂]₂–O–CH₂–
\]

in case of Brij-35

The presence of aldehyde group in the product was detected by forming a yellow precipitate on treating the reaction mixture with 2,4 dinitrophenyl hydrazine solution. The aldehyde as the oxidation product of the above surfactants with other oxidants is also reported.

Results and discussion
The reaction was studied at various initial concentrations of the reactants. To maintain the
pseudo condition, [surfactant] was always kept in large excess, i.e. at least eight times to that of KMnO₄. The log (absorbance) versus time plots were linear up to 80% of the reactions, suggesting a first order dependence of rate with respect to [MnO₄²⁻]. Therefore, the pseudo-first order rate constants (k(obs)) in permanganate have been evaluated from the slopes of these plots. The observed rate constants (k(obs)) at different initial [MnO₄²⁻] were nearly identical (Table 1) conforming a first order dependence of the rate with respect to MnO₄²⁻.

The effect of each surfactant on the rate of reaction has been studied over a wide range of the [surfactant] and at different temperatures, viz. 35, 40 and 45°C. The values of k(obs) at different initial concentrations of the surfactants at three temperatures are given in Table 2. It was observed that k(obs) increased linearly with [surfactant] at low concentrations of the surfactant. However, a deviation from linearity was observed at high [surfactant]. Further, a plot of (1/k(obs)) versus 1/[surfactant] was linear with an intercept in each case, suggesting that order of reaction in surfactant decreases from unity at higher [surfactant].

The effect of H⁺ on the rate was studied by varying [H₂SO₄] in the reaction mixture, keeping fixed ionic strength (0.20 mol dm⁻³, maintained by NaClO₃). The results of effect of H⁺ on the rate were similar as observed in case of surfactant effect. A deviation from linearity at higher [H⁺] was observed in the plot of k(obs) versus [H⁺] in each case.

The effect of ionic strength variation on the rate was negligible. The rate constants (k(obs)) have also been measured at different temperatures, viz. 35, 40 and 45°C. The activation parameters have been evaluated using Arrhenius and Eyring plots. The values of ΔE#, ΔH#, ΔS# and ΔG# were obtained as 75.3±0.5 kJ mol⁻¹, 72.5±0.5 kJ mol⁻¹, −62.7±1.0 J mol⁻¹ K⁻¹ and 92.4±0.5 kJ mol⁻¹, respectively in case of Triton X-100 and 40.8±0.5 kJ mol⁻¹, 38.3±0.5 kJ mol⁻¹, −174.2±1.0 J mol⁻¹ K⁻¹ and 92.8±0.5 kJ mol⁻¹, respectively in case of Brij-35.

It has been observed that the reaction rate increases with an increase in [H⁺], tending to a limiting value at high [H⁺]. This non-linear variation of order of reaction in [H⁺] indicates the involvement of protonated species of MnO₄²⁻. Permanganic acid (HMnO₄) has been considered as a more powerful oxidant than the MnO₄²⁻. The following rapid equilibrium may be considered for the protonation of MnO₄²⁻:

\[
\text{MnO}_4^{2-} + H^+ \rightleftharpoons HMnO_4
\]

The value of the equilibrium constant for protonation of MnO₄²⁻, i.e. K₁ is reported as 3.05×10² ± 0.6×10¹ dm³ mol⁻¹ at 25°C. The value of K₁ is also in agreement with the pK value of HMnO₄, as reported earlier.

It is well understood that an aqueous solution of surfactant is in dynamic equilibrium among three components, i.e. surfactant monomer in aqueous solution, micellar aggregates and monomer at the interface. The micelles disappear and reform at a fairly rapid rate, in the range of milliseconds.

| Table 1 — Effect of [MnO₄²⁻] on the rate constants at 35°C |
|------------------------|------------------------|
| Triton X-100            | Brij-35                |
| [MnO₄²⁻] x 10⁴ (mol dm⁻³) | k(obs) x 10⁴ (s⁻¹) | [MnO₄²⁻] x 10⁴ (mol dm⁻³) | k(obs) x 10⁴ (s⁻¹) |
| 2.0                    | 4.9                    | 1.6                    | 5.7                    |
| 3.0                    | 4.9                    | 2.4                    | 5.7                    |
| 4.0                    | 4.8                    | 3.2                    | 5.6                    |
| 6.0                    | 4.8                    | 4.0                    | 5.6                    |

[H⁺] = 10.0×10⁻² mol dm⁻³; [TritonX-100] = 4.0×10⁻¹ mol dm⁻³; [Brij-35] = 2.4×10⁻¹ mol dm⁻³

| Table 2 — Effect of surfactant on the k(obs) at different temperatures |
|------------------------|------------------------|
| Triton X-100            | Brij-35                |
| [TritonX-100] x 10²     | k(obs) x 10⁴ (s⁻¹) at  | [Brij-35] x 10³        | k(obs) x 10⁷ (s⁻¹) at |
|                         | 35°C  40°C  45°C       |                         | 35°C  40°C  45°C       |
| 1.0                    | 1.3  4.6  6.7         | 0.8                    | 2.0  2.8  3.8         |
| 2.0                    | 3.0  6.1  9.5         | 1.6                    | 4.7  5.7  6.7         |
| 3.0                    | 3.8  7.5  12.4        | 2.4                    | 5.7  7.6  9.5         |
| 4.0                    | 4.9  9.2  14.3        | 3.2                    | 7.6  9.5  11.5        |
| 5.0                    | 5.3  10.7 16.3        | 4.0                    | 9.5  13.4 15.3        |
| 6.0                    | 5.7  12.6 18.2        | 4.8                    | 10.5 15.3 17.2        |
| 8.0                    | 6.1  14.5 20.1        | 6.0                    | 12.4 16.3 21.1        |

[MnO₄²⁻] = 4.0×10⁻⁴ mol dm⁻³; [H⁺] = 10.0×10⁻² mol dm⁻³
Therefore, the oxidant may oxidize both the monomeric surfactant as well as aggregated units.

The mechanism of oxidation of non-ionic surfactants by cerium(IV) and chromium(VI) has been suggested\textsuperscript{13,14} to proceed via formation of an intermediate free radical to give aldehyde as the end products. To confirm the presence of free radical in reaction mixture, in solution consisting of oxidant, surfactant(s) and sulphuric acid, the acrylamide was added. Polymerization was shown by gelification after 12 h at 35°C. This indicates the presence of free radical during oxidation process.

On the basis of experimental results and reported literature, a common mechanism for the oxidation of non-ionic surfactants, viz. TritonX-100 and brij-35 is proposed as given in Scheme 1.

\[
\begin{align*}
\text{MnO}_4^- + H^+ & \xrightleftharpoons{K_1} \text{H}_2\text{MnO}_4 \quad \text{(fast) (i)} \\
\text{RCH}_2\text{OH} + \text{H}_2\text{MnO}_4^- & \xrightarrow{K_2} [\text{R} - \text{CH}_2\text{O} - \text{MnO}_3^-] + \text{H}_2\text{O} \quad \text{(ii)} \\
\text{X}_T + \text{H}_2\text{O} & \xrightarrow{k_1} \text{RCH}_2\text{O}^- + \text{HMnO}_4^- + \text{H}^+ \quad \text{(rds) (iii)} \\
\text{RCH}_2\text{O}^- + \text{HMnO}_4^- & \xrightarrow{k_2} \text{HMnO}_4^- + \text{RCHO} + \text{H}^+ \quad \text{(radical) (iv)} \\
2\text{HMnO}_4^- + 2\text{H}^+ & \xrightarrow{(\text{fast}) (v)} 2\text{MnO}_2 + 2\text{H}_2\text{O} + \text{O}_2
\end{align*}
\]

According to Scheme 1, the rate of disappearance of $[\text{MnO}_4^-]$ may be given as:

\[
-\frac{\text{d}[\text{MnO}_4^-]}{\text{dt}} = 2k_1[X_T][\text{H}_2\text{O}] \quad \text{(1)}
\]

Considering steps (i) and (ii) of Scheme 1, we get:

\[
[\text{HMnO}_4] = K_1[\text{MnO}_4^-][\text{H}^+] \quad \text{(2)}
\]

and

\[
[X_T] = K_2[\text{Surfactant}][\text{HMnO}_4]
\]

\[
= K_1K_2[\text{MnO}_4^-][\text{H}^+][\text{Surfactant}] \quad \text{(3)}
\]

The total concentration of MnO$_4^-$, i.e. $[\text{MnO}_4^-]_T$, at any time is given by:

\[
[\text{MnO}_4^-]_T = [\text{MnO}_4^-] + [\text{HMnO}_4] + [X_T] \quad \text{(4)}
\]

On substituting the value of $[\text{HMnO}_4]$ and $[X_T]$ from Eqs (2) and (3), respectively in Eq. (4) and solving it in terms of $[\text{MnO}_4^-]_T$, the value of $[X_T]$ at any time is given as:

\[
[X_T] = \frac{K_1K_2[\text{MnO}_4^-][\text{H}^+][\text{Surfactant}]}{1 + K_1[H^+][1 + K_2[\text{Surfactant}]]} \quad \text{(5)}
\]

Thus, the rate law (1) becomes:

\[
-\frac{\text{d}[\text{MnO}_4^-]}{\text{dt}} = \frac{2k_1K_1K_2[\text{MnO}_4^-][\text{H}^+][\text{Surfactant}]}{1 + K_1[H^+][1 + K_2[\text{Surfactant}]]} \quad \text{(6)}
\]

Fig. 1 — Plots of $1/k_{obs}$ versus $1/[\text{Surfactant}]$ at different temperatures ($[\text{MnO}_4^-] = 4.0\times10^{-4} \text{ mol dm}^{-3}$; $[\text{H}^+] = 10.0\times10^{-2} \text{ mol dm}^{-3}$).
The rate law (6) explains all experimental results, i.e. first order dependence of rate with respect to oxidant, MnO$_4^-$ and a decrease in order of reaction in each surfactant and acid at higher concentrations of surfactant and acid, respectively.

Further, the rate of disappearance of HMnO$_4$ may be written as:

\[
\frac{d[MnO_4^-]}{dt} = k_{obs}[MnO_4^-] \quad \text{... (7)}
\]

Therefore, from relations (6) and (7), we get:

\[
k_{obs} = \frac{2k_1K_1K_2[H^+][Surfactant]}{1 + K_2[H^+] + K_1K_2[H^+]\text{[Surfactant]}}
\]

or

\[
\frac{1}{k_{obs}} = \frac{1}{2k_3K_2[H^+]} + \frac{1}{2k_3} \quad \text{... (8)}
\]

According to Eq. (8), a plot of $1/k_{obs}$ versus $1/[\text{surfactant}]$ should be linear with a positive intercept which has been observed experimentally (Fig. 1). From the intercept, the values of $k_3$ can be calculated. With the help of intercepts and slopes of these plots, the values of $K_2$ have also been evaluated using $K_1$ (3.05×10$^2$ mol dm$^{-3}$) as reported at 25°C. The values of $k_3$, $K_1$, $K_2$ [surfactant] and [H$^+$] were used to calculate rate constant ($k_{cal}$) from Eq. (8) at 35°C. $k_{cal}$ values are in excellent agreement with observed value of rate constant, i.e. $k_{obs}$ (Table 3). However, slight variation in $k_{obs}$ and $k_{cal}$ may be due to the reason that the value of $K_1$ used in calculation was given at 25°C while the experiment was performed at 35°C. The data confirm the validity of rate law (6) and the proposed mechanism.

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**References**