Redox behaviour of chromium(VI) towards D-mannose in the presence and absence of micelles and inorganic salts

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The kinetics and mechanism of the oxidation of D-mannose by chromium(VI) in the absence and presence of sodium dodecyl sulfate(SDS) and polyoxylethylene t-octylphenol(TX-100) micelles have been investigated. Under pseudo-first-order conditions the reaction rate is of fractional- and first-order, respectively, in D-mannose and oxidant. The reaction is catalyzed by the micelles which is due to favourable electrostatic/thermodynamic/hydrophobic/ hydrogen bonding between the reactants and anionic/nonionic micelles. From the observed kinetic data micelle-chromium(VI) binding constants($K_s$) and micelle-D-mannose binding constants($K_M$) were calculated to be 86, 84 mol$^{-1}$ dm$^3$ and 58, 75 mol$^{-1}$ dm$^3$ for SDS and TX-100, respectively. The reaction is retarded by addition of inorganic salts (NaBr, LiBr, NH$_4$Br) which is attributed to competition between salt cations and H$^+$ from the reaction sites in the SDS micelles.

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Although kinetics of the oxidation of aldo sugars by transition metal ions have been studied$^{1-7}$ data in the presence of ionic- and non-ionic surfactants are scanty. As we know, micelles, microemulsions, liposomes, etc., are compartmentalized liquids which may show special performance toward reaction dynamics and reaction equilibria$^{8-10}$. The concentration of reactants into a small volume through electrostatic and/or hydrophobic interactions is the main factor involved in the kinetic micellar effects on bimolecular reactions$^{11-13}$.

Chromium(VI), known to show mutagenic and carcinogenic effects$^{14}$, reduces to lower states with a wide variety of naturally occurring cellular reductants$^{15,16}$. In case of oxidative degradation of carbohydrates by chromium(VI), the general conclusion is that the reactions exhibit a characteristic one-step two-electron oxidation. On the other hand, the works of Sala$^5$ and Sen Gupta$^6$ suggest that the reduction involves formation of chromium(IV) as an intermediate.

As part of our program on the redox chemistry of organic acids$^{17}$ and carbohydrates$^{18}$ in the presence of ionic and non-ionic surfactants we set out to elucidate the electron transfer behaviour of D-mannose by chromium(VI). This study may be of interest in the biochemistry of carbohydrates related to metabolic problems. Therefore, the present work was undertaken to confirm the path of chromium(VI) reduction by D-mannose in the presence and absence of manganese(II) and ionic/non-ionic micelles. The use of manganese(II) is an useful tool to determine the involvement of chromium(IV) as an intermediate$^{19,20}$. It acts as a catalyst/inhibitor in many redox reactions of chromium(VI)$^{20,21}$.

**Experimental Section**

D-Mannose (reductant, s.d.fine, India, 99%), potassium dichromate (oxidant, Merck, India, 99%), perchloric acid (Merck, India, 70% solution), manganese(II) sulfate-1-hydrate (Merck, India, 99%), TX-100 (Fluka, Switzerland, 99%), cetyltrimethylammonium bromide (CTAB, Fluka, Switzerland, >99%), SDS (Fluka, Switzerland, >98%), and inorganic salts (NaBr, LiBr, NH$_4$Br) were used as received. The water used as solvent was subjected to deionization followed by distillation (specific conductance: ($1\sim2$) $\times 10^{-6}$ S cm$^{-1}$).

**Kinetic measurements.** The reaction was initiated by adding the requisite quantity of pre-equilibrated D-mannose solution to a thermally equilibrated mixture of chromium(VI), perchloric acid and other reagents.
(when required). The progress of the reaction was followed by measuring the absorbance of remaining chromium(VI) at known time intervals at 360 nm using a Bausch & Lomb Spectronic-20 spectrophotometer. At this wavelength neither chromium(III) nor the oxidized products has any appreciable absorbance. The pseudo-first order conditions were maintained with a large excess of reductant over oxidant concentration. The kinetic runs were carried out up to ca. 80% completion and the pseudo-first-order rate constants were obtained from the slopes of log (A) versus t plots. The results were reproducible to within ±4% with average linear regression coefficient, r ≥ 0.998. The experimental second-order rate constants (k"1) were calculated from the relationship: k"1 = kₕₒₑᵦ/[D-mannose]. Other details are described elsewhere.\(^17,18\).

Stoichiometry and product analysis. Several reaction mixtures with \([\text{chromium(VI)}] > [\text{D-mannose}] (5 \times 10^{-4} \text{ mol dm}^{-3} \text{ oxidant: 0.5 to 4.5 } \times 10^{-4} \text{ mol dm}^{-3} \text{ reductant})\) at fixed \([\text{H}^+] (0.58 \text{ mol dm}^{-3})\) were prepared and kept for several days at room temperature. After completion of the reaction, the unconsumed oxidant was determined spectrophotometrically. In all cases the reaction stoichiometry was found to be 1:2 (chromium(VI):D-mannose). The exact stoichiometry equation is difficult to predict due to the autoacceleration nature of the reaction (vide infra).

To characterize the reduction product of chromium(VI) (i.e., chromium(III)), [D-mannose] = 30 \times 10^{-3} \text{ mol dm}^{-3}, [\text{chromium(VI)}] = 4 \times 10^{-4} \text{ mol dm}^{-3}, and \([\text{HClO}_4] = 0.58 \text{ mol dm}^{-3}\) were mixed at 60 °C. Spectra of the mixture were recorded at different time intervals. Figure 1 (Set A), shows that, as the reaction progresses, the 360 nm peak decreases. Under the experimental kinetic conditions and when all the chromium(VI) has reacted, the spectrum did not show any maximum (Figure 1, Set A). However, the spectra of the reaction mixture, recorded with higher [chromium(VI)] (Figure 1, Set B), show two sharp peaks (410 and 570 nm) which are indicative of the presence of aqua-chromium(III) species\(^23\) in the reaction mixture.

For organic products, qualitative analysis of the oxidized reaction mixture in the presence of HClO₄ was performed. After ensuring the completion of reaction, the oxidized reaction mixture was treated with alkaline hydroxylamine solution. The presence of lactone in the reaction mixture was tested by FeCl₃ - HCl blue test\(^22\). On the other hand, when barium carbonate was added into the reaction mixture to make it neutral\(^39\), FeCl₃ solution that had been coloured violet with phenol when added to the reaction mixture gave a bright-yellow colouration, indicating that aldonic acid is formed in the oxidation of D-mannose\(^50\). Apparently, lactone, which is formed in the rate-determining step, is hydrolysed to aldonic acid in neutral medium in a fast step\(^56\). At higher pH, the [lactone] is reduced because of the formation of aldonic acid anion that shifts the equilibrium away from lactone\(^23\).

**Polymerization studies.** Upon addition of acrylonitrile to a reaction mixture ([D-mannose] = 30 \times 10^{-3} \text{ mol dm}^{-3}, [\text{chromium(VI)}] = 4 \times 10^{-4} \text{ mol dm}^{-3}, \([\text{HClO}_4] = 0.58 \text{ mol dm}^{-3}\), temp. = 60 °C), polymerization (white precipitate formation) started quickly while blank experiments with either chromium(VI) or D-mannose gave no detectable precipitate. The observations demonstrate that the reaction of D-mannose with chromium(VI) proceeds via free radicals.
Results and Discussion

A. Kinetics in the absence of surfactants

The results can be summarized as follows:

(i) Under the experimental conditions of [D-mannose] > [chromium (VI)], the first-order plots were non-linear indicating two step-oxidation behaviour (cf. Figure 2), i.e., induction and autoacceleration periods. The values of pseudo-first-order rate constants for the induction period are summarized in Table I. The independence of $k_{obs}$ over a range of [oxidant]$_r$ is in agreement with the first-order dependence on [Cr(VI)]$_r$.

(ii) The rate increased with increase in [HClO$_4$] and it was also observed that the induction period decreased with increase in the acid content. At higher [HClO$_4$] (≥ 0.93 mol dm$^{-3}$), the induction period was completely eliminated (Figure 2). Therefore, all the kinetic runs were performed at fixed [HClO$_4$] (= 0.58 mol dm$^{-3}$). The plot of log $k_{obs}$ versus log[HClO$_4$] was linear with slope = 1.7 ($r = 0.970$) indicating a complex dependence on the concentration of H$^+$. (Figure 3).

(iii) The reaction rate increased with increase in [D-mannose] (range: $5.0 \times 10^{-3}$ to $50.0 \times 10^{-3}$ mol dm$^{-3}$) and the order in D-mannose was found to be fractional (Figure 3).

(iv) The rate increased with increase in [Mn(II)] (Table II). For example, under the conditions [D-mannose]$_r$ = $30 \times 10^{-3}$ mol dm$^{-3}$, [Cr(VI)]$_r$ = $4 \times 10^{-4}$ mol dm$^{-3}$ and [H$^+$] = 0.58 mol dm$^{-3}$ at 60°C, a 4-fold rate increase from 4.4 x $10^{-4}$ to 17.9 x $10^{-4}$ S$^{-1}$ was observed when [Mn(II)] was increased from 0.005 to 0.05 mol dm$^{-3}$. At lower [Mn(II)] ($5 \times 10^{-3}$ to $20 \times 10^{-3}$ mol dm$^{-3}$), the $k_{obs}$ increased marginally (from 4.3 x $10^{-4}$ to 5.3 x $10^{-4}$ S$^{-1}$) but fast thereafter. The order with respect to [Mn(II)] was determined from the plot of log $k_{obs}$ against log[Mn(II)] only for the higher [Mn(II)] range which was found to be 1.01. The

![Figure 2](image-url)

**Figure 2 — Plots of log(absorbance) vs. time for the oxidative degradation of D-mannose (3.0 x $10^{-3}$ mol dm$^{-3}$) by chromium(VI) (4.0 x $10^{-4}$ mol dm$^{-3}$) at 60°C; [HClO$_4$] = (a) 0.11, (b) 0.23, (c) 0.34, (d) 0.46, (e) 0.58, (f) 0.69, (g) 0.93, and (h) 1.16 mol dm$^{-3}$).**

<table>
<thead>
<tr>
<th>$10^4$[Cr(VI)] (mol dm$^{-3}$)</th>
<th>$10^3$[D-mannose] (mol dm$^{-3}$)</th>
<th>$10^4$[HClO$_4$] (mol dm$^{-3}$)</th>
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* [SDS] = $26.0 \times 10^{-3}$ mol dm$^{-3}$, [TX-100] = $50.0 \times 10^{-3}$ mol dm$^{-3}$.
Figure 3 — $k_{\text{obs}}$ vs. [mannose] (a) and $1/k_{\text{obs}}$ vs. 1/[mannose] (b) plots; [Cr(VI)] = $4.0 \times 10^{-4}$ mol dm$^{-3}$, [HClO$_4$] = 0.58 mol dm$^{-3}$, and temp. = 60°C.

<table>
<thead>
<tr>
<th>$10^3$ [Mn(II)] (mol dm$^{-3}$)</th>
<th>Temperature ($^\circ$C)</th>
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<td>13.4</td>
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$E_\text{a}$ (kJ mol$^{-1}$) 47 41 36
$\Delta H$ (kJ mol$^{-1}$) 44 38 33
$\Delta S$ (JK$^{-1}$mol$^{-1}$) -299 -297 -296

[a] [Cr(VI)]$_T$ = $4.0 \times 10^{-4}$ mol dm$^{-3}$, [d-mannose]$_T$ = $30.0 \times 10^{-3}$ mol dm$^{-3}$, [HClO$_4$]$_T$ = 0.58 mol dm$^{-3}$, [SDS] = $26.0 \times 10^{-3}$ mol dm$^{-3}$, [TX-100] = $50.0 \times 10^{-3}$ mol dm$^{-3}$
The increase in the reaction rate with increase in 
\([H^+]\) may be explained by considering the equilibria 
between chromium(VI) species (Cr2O7^2- + H2O \rightleftharpoons 2HCrO4^-; HCrO4^- + H^+ \rightleftharpoons H_2CrO_4) and that, under our 
experimental conditions of \([HClO_4] = 0.58 \text{ mol dm}^{-3}\), 
the \(H_2CrO_4\) species being the reactive one. Also, the 
aqueous solution of sugar is an equilibrium mixture of 
\(\alpha\) and \(\beta\)-sugars. Polymethylenealdehyde 
which has the same configuration as that of glucose 
extcept for the configuration at C-2. In equilibrium, 
D-mannose mainly consists of \(\alpha\)-monomer having 
the epimeric \(H\) in equatorial position. The ratio of the \(\alpha\)- 
and \(\beta\)-pyranose forms has been estimated from NMR 
studies at 30°C to be 64:36 for D-mannose^{24}. 

It has been established in the oxidation of aldoses 
by metal ions that the anomer having OH-1 equatorial 
undergoes faster oxidation than the corresponding 
anomer having OH-1 axial^{23,25,26}. Therefore, the 
reaction is presumed to follow the ‘chromate-ester’ 
formation between the chromium(VI) and 
equatorial anomeric OH-1 of \(\beta\)-pyranose^{27} (\(\alpha\)-anomer’s axial 
OH-1 is less exposed so less accessible to chromium(VI)). The chromate-ester formation is 
similar to the oxidation of alcohols/\(\alpha\)-hydroxy 
acids/carboxylic acids by chromium(VI)^{2,17,18,28}. In the 
determination step, the chromate-ester breaks 
leaving to the formation of chromium(IV) and 
lactone. After the slow two-electron step (3), reactions 
(4) to (6) may follow (thus the overall reaction 
becomes a three-electron process) (Scheme I).

The positive catalytic role of manganese(II) (vide 
supra) rules out the formation of chromium(IV) as 
an intermediate^{19,20}. Therefore, the oxidation of D-
mannose by chromium(VI) is presumed to be via a 
one-step, three-electron transfer mechanism in 
presence of Mn(II) (Scheme II); the third electron 
being supplied by Mn(II). In the mechanism, the first 
step is envisaged to be the formation of a complex 
between Mn(II) and D-mannose (step 7) which is then 
oxidised by Cr(VI) via the ester formation (steps (8) 
and (9)).

The possibility of MnO2 formation is ruled out as 
no turbidity appeared and the solution remained 
colourless at the end of the reaction. Furthermore, 
attempts to monitor the reaction utilizing 470 nm 
wavelength (characteristic of Mn(III)^{29}) failed 
imindicating no buildup of Mn(III) (this is understandable 
in view of the fact that disproportionation 
reaction (10) is fast^{29}).

Considering Schemes I and II, the respective rate 
laws can be written as Eqns (13) and (15),

\[
-k\frac{\partial}[\text{Cr(VI)}]_T}{\partial t} = \frac{kK_{cs}K_{a}[H^+]_T[D \text{- mannose}]_T[\text{Cr(VI)}]_T}{(1 + K_a[H^+] + K_{cs}K_a[H^+]_T[D \text{- mannose}]_T)}
\]  

or

\[
k_{\text{obs}} = \frac{kK_{cs}K_{a}[H^+]_T[D \text{- mannose}]_T}{(1 + K_a[H^+] + K_{cs}K_a[H^+]_T[D \text{- mannose}]_T)}
\]

and

\[
k_a = \frac{k_{cs}K_a[H^+]_T[D \text{- mannose}]_T[Mn(II)]_T}{(1 + K_a[H^+] + K_{cs}K_a[H^+]_T[D \text{- mannose}]_T)}
\]

and

\[
k_{\text{obs}} = \frac{k_{cs}K_a[H^+]_T[D \text{- mannose}]_T[Mn(II)]_T}{(1 + K_a[H^+] + K_{cs}K_a[H^+]_T[D \text{- mannose}]_T)}
\]

Eqn (13) explains all the experimental observations 
and is coherent with the fractional- and first-order 
dependencies found for the rate of the reaction on the 
[D-mannose] (Figure 3) and [Mn(II)] (of course, at 
higher concentrations of Mn(II)), respectively. Taking 
its reciprocal, we get

\[
\frac{1}{k_{\text{obs}}} = \frac{(1 + K_a[H^+]_T)}{b_1[D \text{- mannose}]_T} + b_2 \quad \ldots (16)
\]

where \(b_1 = kK_{cs}K_a[H^+]_T\) and \(b_2 = 1/k_a\). It is clear from 
Eqn (16) that the plot of \(1/k_{\text{obs}}\) versus \(1/[D \text{- mannose}]_T\) 
at constant \([H^+]\) should be linear; such Michaelis-
Menten reciprocal plot was indeed obtained with an 
intercept on y-axis. From the intercept and slope 
values the rate constant \((k = 8.7 \times 10^{-2} \text{ s}^{-1})\) and 
‘chromate ester’ formation constant \((K_{cs} = 431 \text{ mol}^{-1} \text{ dm}^3)\) were evaluated.

Table III summarizes the values of second-order-
rate constants \((k_1^{nl}, \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1})\) for the reactivity 
of D-mannose towards different oxidants. We see that 
the oxidation by chloramine-T takes place only in
highly alkaline medium. Therefore, the reactivity of D-mannose can not be compared with chloramine-T. Though all other values of $k^H_1$ are for acidic conditions, comparison is not possible as well because different mineral acids (H$_2$SO$_4$, HClO$_4$, HCl) or buffer (sodium picolinate - picolinic acid) were used; that too at different temperatures. However, a comparison of $k^H_1$ under identical conditions using Cr(VI) as oxidant can be made which reveals the sequence: L-arabinose > D-fructose > D-mannose > D-xylene towards their reactivity (the associated rate constants being 8.3, 6.3, 5.6 and 2.1 x 10$^{-3}$ mol$^{-1}$ dm$^3$ s$^{-1}$)$^{17}$. This trend shows that the oxidation by Cr(VI) seemingly depends on the number of available primary -OH
Scheme II

Table III — Values of second-order rate constants ($k^b$) for the oxidation of D-mannose by different oxidants

<table>
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<tr>
<th>Oxidant</th>
<th>Medium (mol dm$^{-3}$)</th>
<th>Temperature (°C)</th>
<th>$10^3 k^b$ (mol$^{-1}$ dm$^{3}$ s$^{-1}$)</th>
<th>Ref.</th>
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</thead>
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<td>Ce(IV)$^a$</td>
<td>H$_2$SO$_4$ (0.5)</td>
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<td>3a</td>
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<td>V(V)$^b$</td>
<td>HClO$_4$ (5.7)</td>
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<td>4.1</td>
<td>30</td>
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<tr>
<td>Mn(III)$^c$</td>
<td>Buffer (pH 6.1)</td>
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<td>0.23</td>
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<tr>
<td>chloramine-$T^d$</td>
<td>NaOH (0.10)</td>
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<tr>
<td>bromamine-$T^*$</td>
<td>HCl (0.51)</td>
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<tr>
<td>Cr(VI)$^f$</td>
<td>HClO$_4$ (0.75)</td>
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<td>(0.58)</td>
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$^a$[oxidant] = 2.5 (a), 2.0 (b), 0.25 (c), 2.0 (d), 2.2 (e), 0.8 & 0.4 (f) × 10$^{-3}$ mol dm$^{-3}$; [D-mannose]$_T$ = not specified (a), 10 (b), 30 (c), 2 (d), 4 (e), 1.6 & 3 (f) × 10$^{-2}$ mol dm$^{-3}$

groups, the stereochemistry, and the chelating ability of the monosaccharide.

Kinetics in the presence of surfactants

It was observed that a reaction mixture containing CTAB (=1.4 × 10$^{-4}$ mol dm$^{-3}$) and HClO$_4$ (=0.58 mol dm$^{-3}$) became intense turbid at room temperature (~30 °C); it did not become clear even after raising the temperature. Obviously, CTA perchlorate is formed which is known to be very insoluble. However, no precipitation occurred with anionic SDS or nonionic TX-100 surfactants; therefore, the kinetic experiments
Table IV — Effect of [SDS] and [TX-100] on the pseudo-first-order rate constants \((k_p)\) for the reaction of chromium(VI) with D-mannose

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<td>7.0</td>
</tr>
<tr>
<td>30</td>
<td>6.4</td>
<td>7.2</td>
</tr>
<tr>
<td>35</td>
<td>6.7</td>
<td>7.4</td>
</tr>
<tr>
<td>40</td>
<td>6.9</td>
<td>7.7</td>
</tr>
<tr>
<td>45</td>
<td>7.3</td>
<td>8.0</td>
</tr>
<tr>
<td>50</td>
<td>7.4</td>
<td>8.3</td>
</tr>
<tr>
<td>60</td>
<td>7.7</td>
<td>9.6</td>
</tr>
<tr>
<td>67</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\([\text{Cr(VI)}]_t = 4.0 \times 10^{-4} \text{ mol dm}^{-3}; [\text{D-mannose}]_t = 30.0 \times 10^{-3} \text{ mol dm}^{-3}; [\text{HClO}_4]_t = 0.58 \text{ mol dm}^{-3}; \text{ temp.} = 60 ^\circ\text{C}\)

were carried out only with SDS and TX-100 surfactants.

Effect of [SDS] and [TX-100]. The effect of varying the surfactant concentrations on the reaction rate \((k_p)\) was studied keeping other variables constant \([[\text{Cr(VI)}]] = 4 \times 10^{-4} \text{ mol dm}^{-3}, [\text{D-mannose}] = 30 \times 10^{-3} \text{ mol dm}^{-3}, [\text{H}^+] = 0.58 \text{ mol dm}^{-3}, \text{ temperature} = 60 ^\circ\text{C}\). The results (Table IV) are illustrated in Figure 4 as \(k_p\) - [surfactant] profiles, which clearly demonstrate the surfactants' catalytic effects not only above but even below cmc, i.e., micellar as well as submicellar catalyses are observed. Micelles are not fixed entities but have a transient character. Surfactant monomers rapidly join and leave micelles and the aggregation number represents only an average over time. According to the multiple equilibrium model, therefore, the distribution of surfactant \((D_i)\) between various states of aggregation is controlled by a series of dynamic association-dissociation equilibria:

\[
D_1 + D_1 \rightleftharpoons D_2 \\
D_2 + D_1 \rightleftharpoons D_3 \\
\vdots \\
D_{n-1} + D_1 \rightleftharpoons D_n
\]

The catalysis below cmc (i.e., submicellar catalysis) is not new and conforms to various available results. The feasibility can be sought in the fact that small aggregates of the surfactant (dimers, trimers, tetramers, etc.) exist below the cmc; these small submicellar aggregates can interact physically with the reactants forming catalytically active entities.

Effect of other variables

In order to confirm whether or not the same mechanism operates in micellar medium, the \(k_p\)
values were determined as functions of variations in [D-mannose], [Cr(VI)], [H⁺], [Mn(II)] and temperature at fixed [SDS] or [TX-100] (Tables I, II and IV), we can see that the same pattern is being followed, i.e., fractional-order in [D-mannose], complex-order in [H⁺], and first-order in [Cr(VI)]. The effect of varying [Mn(II)] on the rate was also the same, namely, the $k_w$-values increased with increase in [Mn(II)]. These observations establish that the mechanism of redox behaviour of chromium(VI) towards D-mannose in presence of surfactant micelles of SDS and TX-100 remains the same as in the absence of surfactants.

**Binding constants and rate constants in the micellar media**

The binding ($K_5$ and $K_M$) and the rate constants ($k_m$) in the micellar media can be determined by considering the micellar pseudo-phase kinetic model proposed by Menger and Portnoy\(^9\) as modified by others\(^9,36\). This model considers the micelles and aqueous as two separate phases and that the reaction occurs in both the phases (Scheme III).

\[
\begin{align*}
(Cr(VI))_w + Dn & \quad \xrightarrow{K_S} \quad (Cr(VI))_m \\
(mannose)_w + Dn & \quad \xrightarrow{K_M} \quad (mannose)_m
\end{align*}
\]

**Scheme III**

The method for calculation of constants by the use of non-linear least squares technique has been detailed earlier\(^8\). The best fit values are summarized in Table V. For comparison, the $k_{\text{eq}}$ (Table IV) values were obtained by substituting the $k_w$, $K_S$, $k_m$, $K_M$ and [D₃] in the relevant equation. The agreement between the calculated and observed values provides supporting evidence for the method of calculation.

**The reaction site.** Despite uncertainty of the exact reaction site of the micellar-mediated reactions, locations of the reactant molecules can at least be ascertained with some degree of reliability. The chromium(VI) (H₂CrO₄) has neither hydrophobic nor electrostatic interactions with the anionic headgroups of SDS micelles but the catalytic effect of this surfactant clearly indicates the localization of H₂CrO₄ into the Stern layer (the site of most ionic micelle mediated reactions). In acidic medium, the pH of the anionic micellar surface is decreased by ca. 2 units due to the electrostatic interaction/exclusion of Na⁺ by H⁺\(^37\). Under our experimental conditions of [HClO₄] ≥ 0.58 mol dm⁻³, chromium(VI) (H₂CrO₄) gets converted to HCrO₄⁺ (H₂CrO₄ + H⁺ → HCrO₄⁺ + H₂O)\(^38\). Thus, anionic headgroups (-OSO₃⁻) of SDS micelles form ion-pairs with HCrO₄⁺. On the other hand, association of D-mannose molecules (due to possessing 5-OH groups) cannot be ruled out\(^39\). The micelle thus helps in bringing the reactants together which may now orient in a manner suitable for the ester formation (a characteristic feature of the mechanism of chromium(VI)-organic substrate reactions\(^28\)).

Regarding catalysis in presence of TX-100, hydrogen bonding between oxyethylene and/or -OH of non-ionic TX-100 micelles and the reactants

**Table V — Values of binding constants ($K_5$ and $K_M$) and rate constants ($k_m$ and $k_w^{k2}$) for the reaction of chromium(VI) with D-mannose**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Aqueous</th>
<th>SDS</th>
<th>TX-100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^3 k_w$ (s⁻¹)</td>
<td>15.0</td>
<td>9.8 (8.2)$^b$</td>
<td>(0.3)$^b$</td>
</tr>
<tr>
<td>$10^3 k_m$ (s⁻¹)</td>
<td>7.0</td>
<td>3.15</td>
<td></td>
</tr>
<tr>
<td>$K_S$ (mol⁻¹ dm³⁻¹)</td>
<td>86</td>
<td>58</td>
<td></td>
</tr>
<tr>
<td>$K_M$ (mol⁻¹ dm³⁻¹)</td>
<td>84</td>
<td>75</td>
<td></td>
</tr>
<tr>
<td>$10^3 k_2^{k2}$ (mol⁻¹ dm³⁻¹ s⁻¹)$^c$</td>
<td>9.8</td>
<td>21.4</td>
<td></td>
</tr>
</tbody>
</table>

$^a[Cr(VI)]_T = 4.0 \times 10^{-4}$ mol dm⁻³, [D-mannose]ₜ = 30.0 $\times 10^{-3}$ mol dm⁻³, [HClO₄]ₜ = 0.58 mol dm⁻³, [SDS]ₜ = 26.0 $\times 10^{-3}$ mol dm⁻³, [TX-100] = 50.0 $\times 10^{-3}$ mol dm⁻³


$^c$Second-order rate constants ($k_2^{k2}$) are based on the relation: $k_2^{k2} = k_w \cdot V_w$, $V_w = 0.14$ dm³ mol⁻¹ for SDS\(^1\) and 0.68 dm³ mol⁻¹ for TX-100\(^3\)
seems to play an important role. Due to this, concentration of both the reagents into the small volume of the hydrophilic part of the TX-100 micelles takes place. Perusal of Figure 3 reveals that not only the overall rate enhancement is higher in TX-100 in comparison to SDS, the former is more effective even at low concentrations which suggests that hydrogen bonding is more important than ionic interaction. There are no electrostatic interactions with the polar head groups of TX-100, but this non-ionic surfactant could stabilize an undissociated H$_2$CrO$_4$ relative to the more hydrophilic HCrO$_4^-$ and glucose through hydrogen bonding. Thereafter, the associated D-mannose and H$_2$CrO$_4$ with the non-ionic TX-100 micelles (through hydrogen bonding) seemingly facilitate formation of the chromate-ester.

The effect of salts

Addition of electrolytes, in general, is responsible for rate inhibition of micellar mediated reactions due to the exclusion of the reagent(s) from the micellar pseudo-phase. Figure 5 shows that the kinetic electrolyte effect is negative for all the added electrolytes (NaBr, LiBr, NH$_4$Br) for the oxidation of D-mannose by chromium(VI) in presence of SDS micelles. Also, the observed rate constants depend on the nature of the cation. Thus, the excess monopositive cations seem to exclude H$^+$ from the reaction site (which, in turn, means reduction in the effective [HCrO$_4^-$]) and the inhibitory power decreases in the order NH$_4^+<$Li$^+<$Na$^+$. The behaviour is as expected according to their increasing hydrophobicity (Na$^+<$Li$^+<$NH$_4^+$) and polarising power.

Activation parameters

Comparison between the activation parameters in SDS and TX-100 with that in aqueous medium (Table 11) clearly indicates that the micelle acts as catalysts and provide a new reaction path with lower values of $E_a$. Furthermore, though a change in temperature is known to produce changes in the size, shape, surface charge, etc., of the micelles, equally good fit of the observed data ($k_{obs}$ and $k_q$) to the Eyring equation (both in the absence as well as presence of surfactants) shows that the micelle structural sensitivity to temperature is kinetically unimportant. Similar conclusions had been drawn earlier also.

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**References**

11 (a) Bunton C A, Cat Rev Sci Eng, 20, 1979, 1; (b) J Mol Liq, 72, 1997, 231.