Inhibition Effect of {Surfactant-Substrate} Aggregation on the Rate of Oxidation of Reducing Sugars by Alkaline Hexacyanoferrate(III)

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ABSTRACT: The effect of cationic (cetyltrimethylammonium bromide, CTAB), anionic (sodium lauryl sulfate, NaLS), and nonionic (Brij-35) surfactants on the rate of oxidation of some reducing sugars (xylose, glucose, and fructose) by alkaline hexacyanoferrate(III) has been studied in the temperature range from 35 to 50°C. The rate of oxidation is strongly inhibited in the presence of surfactant. The inhibition effect of surfactant on the rate of reaction has been observed below critical micelle concentration (CMC) of CTAB. In case of NaLS and Brij-35, the inhibition effect was above CMC, at which the surfactant abruptly associates to form micelle. The kinetic data have been accounted for by the combination of surfactant molecule(s) with a substrate molecule in case of CTAB and distribution of substrate into micellar and aqueous pseudophase in case of NaLS and Brij-35. The binding parameters (binding constants, partition coefficients, and free-energy transfer from water to micelle) in case of NaLS and Brij-35 have been evaluated with the help of Menger and Portnoy model reported for micellar inhibition. © 2007 Wiley Periodicals, Inc. Int J Chem Kinet 39: 595–604, 2007

INTRODUCTION

Micelles are known to affect the rate of reaction by partitioning the substrate between aqueous and micelle pseudophase and also by perturbing the thermodynamic parameters of the reaction [1-6]. Micellar as well as premicellar catalysis in various redox reactions is reported in the literature [7–12]. In some cases, premicellar aggregation has also been observed. In preliminary studies, it has been observed that a small amount of cationic surfactant (even at below of its critical micelle concentration, CMC), viz. cetyltrimethylammonium bromide (CTAB) retarded the rate of oxidation of reducing sugars by hexacyanoferrate(III), which is a well-known one-electron oxidant [13] in alkaline medium. The retarding effect of anionic (sodium lauryl



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sulfate, NaLS) and nonionic (Brij-35) surfactants on the rate of oxidation of reducing sugars by hexacyanoferrate(III) has also been observed but above CMC of the surfactants. Therefore, in order to observe the micellar effect on the reaction mechanism, the detailed kinetics of oxidation of some reducing sugars, viz. xylose (aldopentose), glucose (aldohexose), and fructose (ketohexose) by alkaline hexacyanoferrate(III) in the presence of NaLS, CTAB, and Brij-35 has been investigated, and the results are reported in the present communication.

EXPERIMENTAL

Material

Solution of hexacyanoferrate(III) was prepared by dissolving potassium ferricyanide (GR grade; Loba, Mumbai, India) in doubly distilled water. Freshly prepared solutions of glucose (AR; s.d. fine, Mumbai, India), fructose (AR; Thomas Baker, Mumbai, India), and xylose (AR; Qualigens, Mumbai, India) in doubly distilled water were used throughout the experiments. The surfactants CTAB (AR; Thomas Baker), NaLS (AR; s.d. fine), and Brij-35 (AR; Thomas Baker) were purified until the CMC agreed with their reported CMC as 9.8×10^{-4} mol dm⁻³, 8.0 \times 10⁻³ mol dm⁻³, and 9.2 \times 10⁻⁵ mol dm⁻³ of CTAB [14a], NaLS [14b], and Brij-35 [14c], respectively. The solutions of surfactants were prepared in doubly distilled water just before the experiment to avoid the aging. All other reagents, viz. NaOH, NaClO₄, and potassium ferrocyanide used were of AR grade, and their solutions were prepared in doubly distilled water.

Method

To a reaction mixture containing appropriate quantities of solutions of hexacyanoferrate(III), NaOH, and surfactant, required amount of doubly distilled water was added so that the total volume of mixture was 50 mL after adding substrate (reducing sugar). The reaction mixture was then placed in a water bath maintained at desired temperature $\pm 0.1^{\circ}$ C. The reaction mixture was allowed to attain the bath temperature, and the reaction was then initiated by adding requisite amount of sugar solution placed separately in the same bath. The rates were measured by monitoring the absorbance due to hexacyanoferrate(III) as a function of time at 420 nm (λ_{max} of hexacyanoferrate(III)). The absorbance due to hexacyanoferrate(II), substrate, and the surfactant was negligible at this wavelength. The concentration of hexacyanoferrate(III) solution was kept within the limits of Beer's law.

RESULTS

Stoichiometry and Product Analysis

The stoichiometry of the reactions between sugar and hexacyanoferrate(III) in the absence as well as in the presence of surfactants has been studied. The reaction mixtures containing a known excess of hexacyanoferrate(III) over reducing sugar in alkaline medium were kept for 72 h at 40°C until the reaction was complete. Estimation of unreacted [Fe(CN)₆⁻³] showed that 1 mol of reducing sugar (xylose, glucose, or fructose) consumes nearly 2 mol of ferricyanide. The results may be represented by the following stoichiometric equations:

$$\begin{split} \text{RCHOHCHO} + 2\text{OH}^- + 2\text{Fe}(\text{CN})^{3-}_{6-} &\rightarrow 2\text{Fe}(\text{CN})^{4-}_{6-} \\ &+ \text{H}_2\text{O} + \text{RCHOHCOOH} \\ \text{RCOCH}_2\text{OH} + 2\text{OH}^- + 2\text{Fe}(\text{CN})^{3-}_{6-} &\rightarrow 2\text{Fe}(\text{CN})^{4-}_{6-} \\ &+ \text{H}_2\text{O} + \text{RCOOH} + \text{HCHO} \end{split}$$

The presence of corresponding aldonic acid as the oxidation product of aldose was identified by the spot test [15]. The presence of formaldehyde as the oxidation product in case of fructose was identified by forming its 2,4-dinitrophenyl-hydrazone and comparing it with an authentic sample [16]. The results are in agreement with the earlier reported oxidation products of reducing sugars [17–19].

Determination of Rate Constants

The reactions were studied at different initial concentrations of reactants in the absence as well as in the presence of surfactants. Absorbance versus time plots (Fig. 1) were found to be good a straight line upto 85% of the reactions, suggesting a zero-order dependence of rate with respect to hexacyanoferrate(III). Therefore, the pseudo-zero-order rate constants in hexacyanoferrate(III) (k_{ψ}) have been evaluated from the slopes of these straight lines. The reported rate constants data, represented as an average of duplicate runs, were reproducible to within $\pm 5\%$.

Kinetic Results in the Absence of Surfactant

The kinetics of oxidation of the reducing sugars by alkaline hexacyanoferrate(III) in the absence of the surfactant is reported in the literature [17,18]. The reaction followed a first-order dependence of rate with



Figure 1 Plots of absorbance versus times (min) at 35°C. [Fe(CN)₆⁻³] = 10.0 × 10⁻⁴ mol dm⁻³, [substrate] = 10.0 × 10⁻³ mol dm⁻³, [CTAB] = 0.55 × 10⁻⁴ mol dm⁻³, [OH⁻] = 1, 2, 3, 4, 6, and 8 × 10⁻³ for a, b, c, d, e, and f, respectively, $\mu = 0.8 \times 10^{-2}$ mol dm⁻³ maintained by NaClO₄.

respect to each OH^- and reducing sugars and a zeroorder dependence of rate with respect to an oxidant. A mechanism involving the formation of an intermediate enediol anion of sugar in a slow and rate-determining step and its subsequent reaction with ferricyanide in a fast step to give product have been proposed for the oxidation process.

Similar kinetic results have also been observed for the oxidation of reducing sugars in the absence of the surfactant during present investigations and, therefore, have not been provided in the present communication.

Kinetic Results in the Presence of Surfactants

The observed rate constants in the presence of each surfactant (k_{ψ}) at various $[Fe(CN)_6^{3-}]_0$ remained identical (Table I), confirming an independent nature of the rate with respect to hexacyanoferrate(III).

The plot of k_{ψ} versus [substrate] was linear in the absence of the surfactant, whereas that in the presence of each surfactant deviated from linearity at higher concentrations of the substrate, suggesting that in the presence of surfactant the order of reaction in substrate decreases at higher [substrate]. A plot of $1/k_{\psi}$ versus 1/[substrate] in the presence of the surfactant (Fig. 2) was linear with a positive intercept, which further confirmed the suggested Michaelis–Menten-type kinetic behavior.

The effect of alkali was studied at fixed ionic strength maintained by NaClO₄. The results of effect of alkali on the rate of oxidation were identical in the absence and in the presence of each of the surfactant. The plot of k_{ψ} versus [OH⁻] (Fig. 3) was linear passing through the origin in each case, suggesting a first-order dependence of rate with respect to [OH⁻].

Addition of hexacyanoferrate(II) and sodium perchlorate upto $(0.002 \text{ mol } \text{dm}^{-3} \text{ and } 0.04 \text{ mol } \text{dm}^{-3}, \text{ re$ $spectively})$ in a reaction mixture had a negligible effect on the rate of oxidation in the presence of surfactant.

The activation parameters $(E_{act}, \Delta H^{\#} \text{ and } \Delta S^{\#})$ in the presence as well as in the absence of the surfactant have been evaluated using Arrhenius and Eyring equations and are reported in Table II. The large values of E_{act} and $\Delta H^{\#}$ in the presence of surfactants in comparison to those in aqueous medium are consistent with the accepted view that the slow reaction (in the presence of surfactant) would require a higher $E_{\rm act}$ or $\Delta H^{\#}$. A comparison of $\Delta S^{\#}$ values in aqueous medium and in the presence of surfactants shows that the entropy of activation in the presence of the surfactants is less negative. The observed positive change in entropy of activation in the presence of surfactant is in contrast with the trend in the energy of activation. In the absence of the surfactant, a negative value of $\Delta S^{\#}$ indicates that the activated complex in the transition state has a more ordered or more rigid structure than the reactants in the ground state. In the presence of the surfactant, a positive change in entropy of activation (less negative $\Delta S^{\#}$) suggests that the reactants become

$[Fe(CN)_6]^{-3} \times 10^4$ (mol dm ⁻³)	$k_{\rm \psi} \times 10^7 ({ m mol}{ m dm}^{-3}{ m s}^{-1})$									
	Fructose (a)				Glucose (b)	Xylose (c)			
	СТАВ	NaLS	Brij-35	СТАВ	NaLS	Brij-35	CTAB	NaLS	Brij-35	
6.0	2.5	2.7	3.0	1.7	2.0	2.0	2.8	2.9	2.9	
8.0	2.6	2.7	3.1	1.7	2.1	2.2	2.8	2.9	2.7	
10.0	2.5	2.8	3.0	1.7	2.1	2.0	2.8	2.7	2.9	
12.0	2.5	2.8	3.0	1.8	2.2	2.0	2.7	2.9	2.9	

Table I Effect of [Hexacyanoferrate(III)] on the Rate Constant at 35°C

 $[Substrate] = 10.0 \times 10^{-3} \text{ mol } dm^{-3}, [OH^{-}] = 2.0 \times 10^{-3} \text{ mol } dm^{-3} \text{ for fructose; } 4.0 \times 10^{-3} \text{ for glucose and xylose; } [CTAB] = 0.55 \times 10^{-4} \text{ mol } dm^{-3}, [NaLS] = 13.86 \times 10^{-3} \text{ mol } dm^{-3}, and [Brij-35] = 16.0 \times 10^{-5} \text{ mol } dm^{-3}.$



Figure 2 Plots of $1/k_{\psi}$ versus 1/[substrate] at 35°C. [Fe(CN)₆⁻³] = $10.0 \times 10^{-4} \text{ mol dm}^{-3}$, [OH⁻] = $2.0 \times 10^{-3} \text{ mol dm}^{-3}$ for a; $4.0 \times 10^{-3} \text{ mol dm}^{-3}$ for b and c, [CTAB] = $0.55 \times 10^{-4} \text{ mol dm}^{-3}$, [NaLS] = $13.86 \times 10^{-3} \text{ mol dm}^{-3}$, [Brij-35] = $16.0 \times 10^{-5} \text{ mol dm}^{-3}$. Plots a, b, and c represent fructose, glucose, and xylose, respectively.

relatively more rigid, which is not surprising in view of the binding/association of the reactants (reducing sugar) to the surfactant.

The effect of each surfactant on the rate of oxidation has been studied at four different temperatures, viz. 35, 40, 45, and 50°C, and results are reported in the form of the plots of k_{ψ} versus [surfactant] (Fig. 4). The representative rate constants at different temperatures for all the three reducing sugars in the absence of surfactant (i.e., when [surfactant] = 0) are also given in Fig. 4 in order to compare the inhibition action of the surfactant on the rate. It is observed from these plots that k_{ψ} decreases on increasing the [surfactant]. The retarding effect of CTAB on the rate of oxidation (k_{ψ}) has been observed even at below CMC (9.8 × 10⁻⁴ mol dm⁻³). It was also observed that at very high [surfactant], k_{ψ} attains a constant value (not shown in Fig. 4). The intercepts of the plot of k_{ψ} versus [surfactant]



Figure 3 Plots of k_{ψ} versus [OH⁻] at 35°C. [Substrate] = 10.0×10^{-3} mol dm⁻³. Other conditions are the same as in Fig. 2.

Substrate	Surfactant	$E_{\rm act} \pm 0.5 (\rm kJ \ mol^{-1})$	$\Delta H^{\#} \pm 0.5 \; (\mathrm{kJ} \; \mathrm{mol}^{-1})$	$-\Delta S^{\#} \pm 1.0 (\mathrm{J}\mathrm{K}^{-1}\mathrm{mol}^{-1})$
Fructose	Absent	88.0	85.4	86.1
	CTAB	91.8	89.2	70.9
	NaLS	93.8	91.2	66.9
	Brij-35	89.9	87.3	78.9
Glucose	Absent	72.5	70.1	138.9
Glucose	CTAB	76.5	73.9	119.7
	NaLS	99.5	96.9	52.2
	Brij-35	95.7	93.0	63.8
Xylose	Absent	91.8	89.2	75.5
11,1000	CTAB	99.5	96.8	52.4
	NaLS	95.7	93.1	63.8
	Brij-35	93.8	91.2	69.3

Table IIActivation Parameters for the Oxidation of Reducing Sugars in the Absence as well as in the Presenceof Different Surfactants

(Fig. 4) match with the observed rate constants at [surfactant] = 0.

At high [CTAB], turbidity in the reaction mixture was observed and, therefore, the rate constant (k_{ψ}) at above CMC of CTAB could not be determined. It was also observed that a small inhibition effect of NaLS and Brij-35 was started even below of their CMC, but it was more pronounced at above CMC of the surfactants. There was also no turbidity in the reaction mixture at high concentrations of the surfactant in these cases. Therefore, in the case of NaLS and Brij-35, the kinetics has been studied above the CMC of the surfactants.

A first-order dependence of the rate with respect to each alkali and reducing sugar in the absence of surfactant and observed first-order dependence of the rate with respect to OH^- in the presence of surfactants indicate the enolization of reducing sugar as the ratedetermining step. In alkaline medium, the formation of enediol anion of monosaccharides takes place as follows:



In the absence of other reactants, these anions undergo epimerization and isomerization to form a mixture of aldoses and ketoses (the Lobry de-Bruyn-Alberda Van Ekenstien transformation). Aldoses and ketoses generally yield a mixture of Z- and E-enediols, the proposition of which differ from sugar to sugar and experimental conditions, viz. strength and nature of alkali and temperature. In the presence of an oxidant or a catalyst, the enediol anion has been considered as the reactive species of the reducing sugar. The faster rate of fructose enolization has been explained [20] on the basis of an easy attack on the two active primary H-atoms at C-2 of aldoses. It has been observed that an aldohexose (glucose) reacts more slowly than an aldopentose (xylose). A large group of aldohexose on C-5 may retard the tendency of sugar to enolize.

A comparison of the k_{ψ} for various reducing sugars under the similar experimental conditions (Table III) indicate the reactivity of the order of

$$k_{\psi}(\text{fructose}) > k_{\psi}(\text{xylose}) > k_{\psi}(\text{glucose})$$

Thus, the observed reactivity order, i.e. fructose > xylose > glucose, also confirms the enolization of reducing sugar as the rate-determining step.

Table III k_{ψ} for Different Reducing Sugars ur	nder Similar Experimental Conditions
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Surfactant	Fructose	Glucose	Xylose
$\overline{[\text{CTAB}]} = 0.55 \times 10^{-4} \text{ (mol dm}^{-3}\text{)}$	5.5	1.7	2.8
$[NaLS] = 13.86 \times 10^{-3} \text{ (mol dm}^{-3}\text{)}$	5.8	2.1	2.7
$[\text{Brij-35}] = 16.0 \times 10^{-5} \text{ (mol dm}^{-3}\text{)}$	6.0	2.0	2.9

 $[OH^{-}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}, [substrate] = 10.0 \times 10^{-3} \text{ mol dm}^{-3}, [Fe(CN)_{6}^{-3}] = 10.0 \times 10^{-4} \text{ mol dm}^{-3}, and temperature = 35^{\circ}C.$



Figure 4 Plots of k_{ψ} versus [surfactant] at different temperatures. Other conditions are the same as in Figs. 2 and 3.

The retarding effect of the surfactant on the rate of oxidation and the observed Michaelis-Menten behavior during the substrate effect in the presence of the surfactants clearly indicate the binding/association of the reducing sugar with surfactant and inactiveness of the bounded/associated species toward the oxidant, i.e. $Fe(CN)_6^{3-}$. The inhibition effect by CTAB below the CMC may be caused by the interaction between the substrate and submicellar aggregates of the surfactant that stabilize the initial state, or the substrate might promote micellization of the surfactant by the formation of molecular complex between the substrate and surfactant [21]. There is also evidence [22] for the formation of small complexes between surfactant molecules and substrate at the concentration of the surfactant below CMC. In such instances, catalysis or for that matter inhibition occurs at the surfactant concentration lower than that for CMC.

To confirm association or complexation between reducing sugar and surfactant, the spectrum of various freshly prepared samples was analyzed on UV-double beam spectrophotometer (SYSTRONICS-2203). When the spectrum of the solution consisting of 1.0 \times 10⁻³ mol dm⁻³ fructose was analyzed in the range 200-400 nm, no peak was observed in the spectrum. Again no peak was observed in the spectrum of the solution consisting of 1.0×10^{-3} mol dm⁻³ fructose and 5.5×10^{-4} mol dm⁻³ CTAB. When the solution consisting 1.0×10^{-3} mol dm⁻³ fructose and 1.0 \times 10⁻² mol dm⁻³ OH⁻ was analyzed, a peak was observed at 206.4 nm. Furthermore, on adding 5.5 \times 10⁻⁴ mol dm⁻³ CTAB in the above solution, the peak shifted from 206.4 to 211 nm. An increase in the absorbance of the solution on adding CTAB was also noted. A shift in the peak and an increase in the absorbance on addition of CTAB in the solution of reducing sugar in the presence of OH⁻ clearly indicate the interaction between enediol anion of sugar and surfactant.

On the basis of above facts and kinetics results, a common mechanism for the oxidation of reducing sugars by hexacyanoferrate(III) in the presence of surfactants is proposed in Scheme 1.

$$\begin{array}{ccc} S + OH^{-} & \underline{k_{1}} & S^{-} + H_{2}O \text{ (slow)} \end{array} \quad (i)$$

$$S^{-} + Fe(CN)_{6}^{3-} \xrightarrow{k_{2}} Fe(CN)_{6}^{4-} + Product (fast) (ii)$$

S^{*} + Surfactant $K_s = k/k$. (iii) Scheme 1 In the absence of surfactants, considering steps (i) and (ii) and by applying steady-state conditions with respect to $[S^-]$, the rate of disappearance of $Fe(CN)_6^{3-}$ may be given as

$$-\frac{d\left[Fe(CN)_{6}^{3-}\right]}{dt} = k_{2}[S^{-}]\left[Fe(CN)_{6}^{3-}\right]$$
$$= \frac{k_{1}k_{2}[S][OH^{-}]\left[Fe(CN)_{6}^{3-}\right]}{k_{-1}[H_{2}O] + k_{2}\left[Fe(CN)_{6}^{3-}\right]}(1)$$

Again, $k_2[\text{Fe}(\text{CN})_6^{3-}] \gg k_{-1}[\text{H}_2\text{O}]$ may be taken as suitable approximation (step (ii) in fast step), the rate law (1) reduces to

$$-\frac{d\left[Fe(CN)_{6}^{3-}\right]}{dt} = k_{1}[S][OH^{-}]$$
(2)

The experimental results, i.e. the zero-order dependence of rate with respect to oxidant and a first-order dependence of rate with respect to each substrate and OH^- in the absence of surfactants, are in agreement with the rate law (2). Observed negligible salt effect supports the involvement of a neutral species in the rate-determining step.

It is also observed that the rate of reaction depends upon the formation of enediol anion of the reducing sugar.

In the presence of surfactants, step (iii) should also be considered. According to step (iii),

$$[X] = K_S[S^-][surfactant]$$

If $[S^-]_0$ and $[surfactant]_0$ are the total concentration of enediol anion and surfactant, respectively, then,

$$[S^{-}]_{0} = [S^{-}] + [X] \text{ or } [S^{-}] = [S^{-}]_{0} - [X]$$

and

$$[surfactant]_0 = [surfactant] + [X]$$
$$[surfactant] = [surfactant]_0 - [X]$$

Therefore, [X] becomes

or

$$[X] = K_{s} \{ [S^{-}]_{0} - [X] \} \{ [surfactant]_{0} - [X] \}$$

where $K_s = k/k_-$. Therefore, the value of [S⁻], i.e. concentration of enediol anion at any time, may be obtained as

$$[S^{-}] = \frac{[S^{-}]_{0}\{k_{-} + k[S^{-}]_{0}\}}{k_{-} + k[surfactant]_{0} + k[S^{-}]_{0}}$$
(3)

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where $k[X]^2$ term has been neglected in comparison to other terms.

Furthermore, $k_{-}[S^{-}]_{0} \gg k[S^{-}]_{0}^{2}$ may be taken as suitable approximation and therefore, Eq. (3) reduces to

$$[S^{-}] = \frac{k_{-}[S^{-}]_{0}}{k_{-} + k[\operatorname{surfactant}]_{0} + k[S^{-}]_{0}}$$
(4)

According to Eq. (4), the formation of enediol anion at any time will be affected by the total concentrations of surfactant and enediol anion. Since the rate of reaction depends upon formation of enediol anion that is proportional to {[reducing sugar] [OH⁻]}, the order of reaction in the substrate at higher [substrate] will decrease (due to binding/association of substrate with surfactant), which is expected from Eq. (4). The retarding effect of surfactant on the rate of reaction can also be explained on the basis of Eq. (4). A decrease in order of reaction in OH⁻ is also expected from Eq. (4), although it has not been observed experimentally because the concentration of OH⁻ was very low $(10^{-3} \text{ mol dm}^{-3})$ under the experimental conditions.

The binding constant between the micelle and the substrates in case of NaLS and Brij-35 has been calculated by the Menger and Portnoy model [23] reported for miceller inhibition. According to the Menger and Portnoy model, the substrate "S" is distributed between the aqueous and micellar pseudophase as given in Scheme 2.

In the scheme, k_{ω} , $k_{\rm m}$, and k_{ψ} are rate constants in aqueous phase, micellar media, and observed rate constant, respectively; $K_{\rm s}$ is the binding or association constant of substrate with surfactant. $D_{\rm n}$, S, and $SD_{\rm n}$ represent micellar surfactant, free substrate, and associated substrate, respectively.

According to Scheme 2, the observed rate constant k_{ψ} may be given as

$$k_{\psi} = \frac{k_{\omega} + k_{\mathrm{m}}K_{\mathrm{s}}\{[D] - \mathrm{CMC}\}}{1 + K_{\mathrm{s}}\{[D] - \mathrm{CMC}\}}$$

The above equation may be rearranged in the form





This equation has been observed to hold good for continuous inhibition in various reactions. The values of $k_{\rm m}$ and $K_{\rm s}$ can be evaluated with the help of slope and intercept of the plot.

The binding constant (K_s) of the substrate with surfactant can be related [24–27] to the partition coefficient (P) by relation

$$K_{\rm s} = P \bar{V}$$

where \bar{V} is the partial molar volume of the surfactant monomer and the partition coefficient $P = [substrate]_{micelle}/[substrate]_{water}$.

The molar volume [28] of the surfactant has been calculated using the relation

$$\bar{V} = \frac{x_1 M_1 + x_2 M_2}{d}$$

where x_1 and x_2 are mole fraction of surfactant and water (solvent), respectively and M_1 and M_2 are their molecular weights.

The binding constant is also related to standard transfer free energy per mol $(\Delta \mu^{\circ})$ of a solute from water to micelle [29,30] by the following equation:

$$\Delta \mu^{\circ} = -RT \ln(55.5K_s)$$

The validity of the Menger and Portnoy model in case of NaLS and Brij-35 has been tested by the plot of $1/(k_{\omega}-k_{\psi})$ versus 1/([D] - CMC). The observed linearity in the $1/(k_{\omega}-k_{\psi})$ versus 1/([D] - CMC) plots (Fig. 5) indicates the applicability of the Menger and Portnoy model in the systems. The value of k_m and binding constant (K_s) were obtained and are reported in Table IV. The value of partition coefficients and $\Delta \mu^{\circ}$ have also been evaluated in each case and are reported in Table V.

Micellar aggregation/binding between the surfactant and the substrate is well reported in the literature. The effect of organized structure on the rate of chemical reactions has been attributed to the hydrophobic as well as electrostatic interactions. The electrostatic surface potential at micellar surface can attract or repel the reaction species, and hydrophobic interactions can bring about the incorporation into the micelle even of the reagent that bears the same charge or neutral as ionic micelle. Thus, the rate and mechanism of chemical reactions may be affected by means of electrostatic and/or hydrophobic interactions.

The retardation of the rate of disappearance of ferricyanide with an increase in surfactant concentration indicates the inactiveness of the bounded/associated (surfactant–substrate) species toward the oxidant, i.e.,



Figure 5 Plots of $1/(k_{\omega} - k_{\psi})$ versus 1/([D] - CMC) at different temperatures in case of NaLS and Brij-35. Other conditions are the same as in Figs. 2 and 3.

			$K_{\rm s} \times 10^2$				$k_{\rm m} \times 10^7 \; ({\rm mol} \; {\rm dm}^{-3} \; {\rm s}^{-1})$			
Surfactant	Substrate	35°	40°	45°	50°	35°	40°	45°	50°	
NaLS	Fructose	2.3	2.0	1.5	1.0	2.4	4.1	7.1	11.4	
	Glucose	3.0	2.6	1.8	0.8	1.9	2.2	4.1	7.3	
	Xylose	2.8	2.2	1.0	0.5	2.2	2.3	2.6	5.2	
Brij-35	Fructose	175	160	150	75	2.3	4.6	6.8	9.8	
0	Glucose 300 250 220 125 1.6 2	2.2	4.7	9.9						
	Xylose	350	275	150	50	2.5	2.6	4.3	5.2	

Table IVBinding Constants (Ks) and Rate Constants in Micellar Media (k_m) at Different Temperatures

Table V Partition Coefficients (P) and Free-Energy Transfer from Water to Micelle $(-\Delta \mu)$ at Different Temperatures

Surfactant		Р				$-\Delta\mu \ (kJ \ mol^{-1})$			
	Substrate	35°	40°	45°	50°	35°	40°	45°	50°
NaLS	Fructose	9.2	8.3	6.2	4.1	24.1	24.2	23.8	23.1
	Glucose	12.3	10.7	7.2	3.0	24.8	24.9	24.2	22.3
	Xylose	11.3	8.3	4.1	2.0	24.6	24.2	22.7	21.2
Brij-35	Fructose	878	803	753	376	35.3	35.6	36.0	34.7
	Glucose	1506	1255	1104	627	36.6	36.7	37.0	36.1
	Xylose	1757	1318	753	251	37.0	37.0	36.0	33.6

 $Fe(CN)_6^{3-}$. When surfactant is present in the reaction mixture, it incorporates/binds the substrate by hydrophobic interactions, leading to a decrease in the concentration of the substrate in aqueous phase, and thus a retarding effect of the surfactant on the rate of reaction is observed.

There are no electrostatic interactions with polar head groups of nonionic surfactant, i.e. Brij-35. The poly(oxyethylene) head groups of nonionic surfactant play a significant role in favoring the incorporation or solubilization of the substrate in the micelle. The high values of K_s and P in case of Brij-35 are in favor of the absence of the electrostatic forces.

In the case of NaLS, the electrostatic repulsion between negatively charged substrate (enediol anion of sugar) and ionic surfactant opposes the binding between the micelle and substrate. Thus, in case of NaLS, the hydrophobic interactions favor the binding whereas the electrostatic repulsion opposes it. Consequently, the binding between the micelle and substrate should be much less. The low values of K_s and P are in favor of domination of electrostatic repulsions in case of NaLS.

In the case of CTAB, the electrostatic attraction between negatively charged substrates (enediol anion of sugar) and positively charged surfactant favors the binding between the surfactant and substrate in addition to hydrophobic interactions. The domination of electrostatic attractions may be responsible for the association of CTAB and substrate even below CMC of the surfactant. Since the Menger and Portnoy model is applicable for the binding of the substrate with micelle, it has not been applied in case of CTAB, where the substrate is associated with surfactant molecule(s) and not with the micelle.

The transfer of free-energy charge per mole from water to micelle $(\Delta \mu^{\circ})$ in case of NaLS and Brij-35 is also in accordance with the above result. A decrease in the value of K_s or P on increasing the temperature suggests that the binding is an exothermic process.

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