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ORIGINAL CONTRIBUTION

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Effect of cationic and anionic surfactants on the addition–elimination-type interaction between *o*-toluidine and D-glucose

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Abstract The kinetics of the *o*-toluidine–D-glucose reaction has been studied as a function of [*o*-toluidine], [D-glucose], [acetic acid], and temperature by UV–visible spectrophotometry at 630 nm in the absence and presence of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). The reaction follows second-order kinetics, being unity in each of the reactants in both media. The effect of added surfactants has also been investigated. The model of micellar catalysis, such as the Menger–Portony model modified by Bunton, is applied to explain the catalytic role of CTAB and SDS micelles. The association/incorporation constants (K_s and K_n), the rate constant in micellar media (k_m), and the activation parameters of this system have been calculated and discussed. The value of the rate constant is found to be higher in SDS than in CTAB. Hydrophobic and electrostatic interactions are responsible for higher reaction rates in SDS. From all observed facts, a reaction mechanism involving a nucleophilic addition–elimination path has been suggested.

Keywords Kinetics · Micellar catalysis · *o*-Toluidine · D-glucose · CTAB · SDS

Introduction

Micellar catalysis and inhibition have received considerable attention in view of analogies drawn between micellar and enzyme catalyses [1–3]. Micelles increase rates of bimolecular reactions by concentrating both reactants at their surfaces. Three factors may account for the rate enhancement of an organic reaction in aqueous solution when the reactants are incorporated into or onto a micelle: approximation effects, electrostatic effects, and medium effects. Due to these facts, a significant amount of systematic kinetic results has been reported on the effect of micelles on various organic reactions during the past few decades [1–6].

o-Toluidine was originally used by Hultman [7] as an analytical reagent for the determination of glucose concentrations in the blood and urine with high specificity. It has been established that this reaction takes place only in the presence of acetic acid [8], which acts as a solvent and/or a proton source. In order to determine other suitable solvents for this reaction, Hartel and Lang [9] used organic solvents containing a hydroxy group and found that glycolic acid, lactic acid, malic acid, or citric acid could be substituted for acetic acid in the *o*-toluidine reagent. Several modifications have also been made by a large number of investigators to avoid the use of acetic acid or to decrease acetic acid content [10–14]. *o*-Toluidine is the most specific reagent of nonenzymatic methods used for glucose estimation. The reaction between *o*-toluidine and glucose (other aldoses/sugars) is well characterized in aqueous media [8–13]. A rate-limiting step involves the nucleophilic attack of the -NH_2 group of *o*-toluidine and the carbonyl group of glucose. This is followed

by the formation of an intermediate, which eliminates water molecules (1):

$$\text{o} - \text{toluidine} + \text{glucose} \rightleftharpoons \text{glycosylamine} \rightarrow \text{green chromogens} + H_2O. \quad (1)$$

Micelles normally permit water-insoluble compounds to solubilize in aqueous solutions. Rate studies can provide information on how the mechanism of a reaction is affected by hydrophobic, electrostatic, and hydrogen bonding interactions between micelles and reagents.

The purpose of this investigation is to determine the effect of surfactants on the kinetic parameters of *o*-toluidine–glucose reaction in order to understand clearly the nature of this reaction in the absence and presence of ionic surfactants. Two surfactants—one cationic [cetyltrimethylammonium bromide (CTAB)] and one anionic [sodium dodecyl sulfate (SDS)]—have been used for this purpose.

Experimental

Materials

D-glucose (Merck, India), *o*-toluidine (Qualigens, India), glacial acetic acid (Merck), SDS (Fluka, Switzerland), and CTAB (Fluka) were of AR-grade and used without further purification. All solutions were prepared based on molarity using doubly glass-distilled, deionized, and CO_2-free water.

Kinetic measurements

Requisite volumes of D-glucose, acetic acid, and water (for dilution), except *o*-toluidine, were placed in the reaction vessel fitted with a double-wall spiral condenser to check evaporation. The reaction vessel was placed in an oil bath thermostat. When the temperature of the reaction mixture became constant (±0.1°C), the *o*-toluidine solution thermostated at the same temperature was instantly transferred to the reaction vessel as the last addition. Zero time was taken when half of the *o*-toluidine solution had been added. The progress of the reaction was followed by measuring the absorbance of the product at 630 nm using a spectronic-21 D spectrophotometer (the absorption coefficient was calculated to be 1,480 $dm^3\ mol^{-1}\ cm^{-1}$). For this purpose, aliquots of the reaction mixture were taken out at definite intervals and cooled in an ice bath to quench the reaction before each measurement. At this wavelength, the reactant species have no absorbance. Pseudo-first-order rate constants (k_{obs}, s^{-1}) were calculated by plotting log $(A_\infty - A_t)$ vs time, where A_t is the absorbance at time t and A_∞ is the final absorbance. The values of absorbance at infinite time (A_∞) for each kinetic run were obtained as follows. At the end of each kinetic run, 10 cm^3 of the solution (in a standard volumetric flask) was heated at 70°C for 2 h. It was then cooled to room temperature and, after adding water to compensate for any volume loss, absorbance was recorded. The rate constants were reproducible within ±3%. Other details of the kinetic procedure were the same as described previously [15, 16].

Critical micelle concentration determination

The critical micelle concentration (CMC) values of CTAB and SDS in the absence and presence of *o*-toluidine and glucose have been determined at break points of nearly two straight-line portions of specific conductivity-vs-concentration plots. The CMC values were found to be 7.6×10^{-4} and 6.0×10^{-3} mol dm^{-3}, respectively, for CTAB and SDS in the presence of *o*-toluidine (2.0×10^{-4} mol dm^{-3}) and D-glucose (2.0×10^{-3} mol dm^{-3}). The corresponding values in aqueous solutions at 50°C are 5.0×10^{-4} mol dm^{-3} (CTAB) and 5.0×10^{-3} mol dm^{-3} (SDS) [17].

Results and discussion

Reaction in the absence of surfactants

1. Figure 1 shows examples of kinetic curves from which pseudo-first-order rate constants were estimated. The plot of log $(A_\infty - A_t)$ vs time was linear (Fig. 1a), indicating first-order dependence on [*o*-toluidine]. Inspection of Fig. 1 clearly suggests that the reaction has complicated kinetic features [plots of log $(A_\infty - A_t)$ vs time deviate from linearity, which depends on experimental conditions; i.e., [D-glucose], [acetic acid], and temperature]. The plots of log $(A_\infty - A_t)$ vs time were linear at lower [acetic acid], [D-glucose], and temperature. Surprisingly, as these variables increased from low to high, deviations in plots of log $(A_\infty - A_t)$ vs time were observed. One possibility can be the involvement of other side reactions, which, at higher [reactant], cannot be ruled out.
2. *o*-Toluidine is slightly soluble in water but is completely miscible in all organic solvents at lower temperatures [18]. *o*-Toluidine concentration varied in the range of 1.6×10^{-4} to 2.2×10^{-4} mol dm^{-3} under constant [D-glucose] (2.0×10^{-3} mol dm^{-3}), [acetic acid] (8.7 mol dm^{-3}), and temperature (70°C). k_{obs} values were found to be $3.8\pm0.1\times10^5$ s^{-1} at [*o*-toluidine] values of 1.6, 1.8, 2.0, 2.2, and 2.4×10^{-4} mol dm^{-3} in aqueous media. The reaction follows first-order kinet-

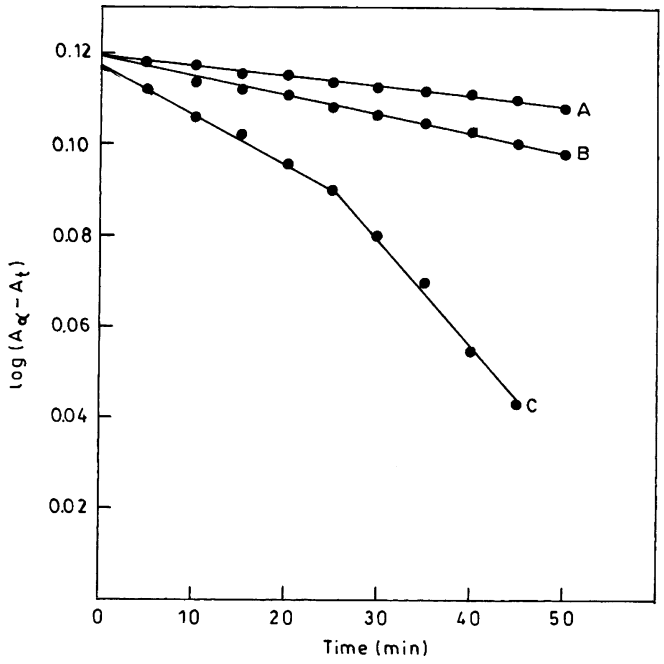


Fig. 1 Plots of log $(A_\infty - A_t)$ vs time for the reaction of D-glucose with *o*-toluidine. *Reaction conditions*: [D-glucose]=2.0×10^{-3} mol dm^{-3}; [*o*-toluidine]=2.0×10^{-4} mol dm^{-3}; [acetic acid]=8.72 mol dm^{-3}; temperature 50°C (**a**), 60°C (**b**), and 70°C (**c**)

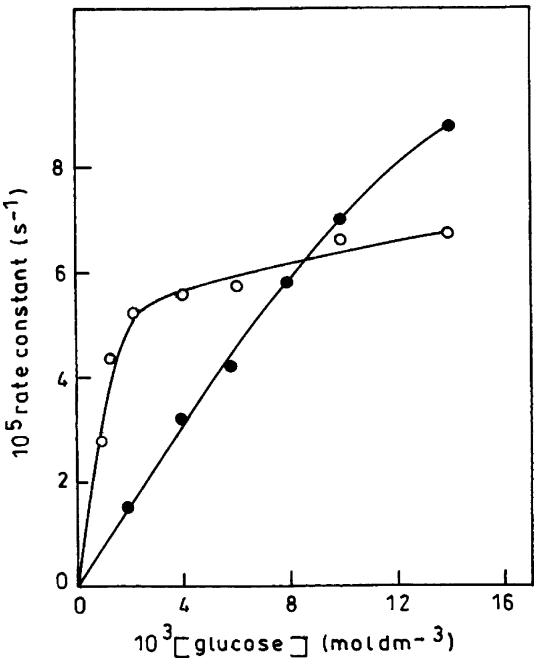


Fig. 2 Plots of rate constant vs [D-glucose] in the absence (•) and presence (○) of CTAB. *Reaction conditions*: [*o*-toluidine]=2.0×10^{-4} mol dm^{-3}; [acetic acid]=8.7 mol dm^{-3}; [CTAB]=20.0×10^{-4} mol dm^{-3}; temperature=70°C

ics with respect to [*o*-toluidine]. The rate law is, therefore, represented by Eq. 2:

$$\frac{d[\text{product}]}{dt} = k_{obs}[o-\text{toluidine}]. \quad (2)$$

3. The concentrations of acetic acid and *o*-toluidine were kept constant, and [D-glucose] varied from 2.0×10^{-3} to 14.0×10^{-3} mol dm^{-3} at 70°C. The k_{obs} values are summarized in Table 1. The plot of rate constants vs [D-glucose] is nonlinear, passing through the origin (Fig. 2), indicating that the reaction follows complex-order kinetics with respect to [D-glucose]. On the other hand, the plot of 1/rate constant vs 1/[D-glucose] is linear at constant [CH_3COOH], with a positive intercept and a positive slope (Fig. 3). Such a plot is indicative of Michaelis–Menten behavior (kinetic proof for complex formation between *o*-toluidine and D-glucose).
4. The reaction of *o*-toluidine with D-glucose has been studied at four different temperatures (Table 2). The

Table 1 Effect of [D-glucose] on pseudo-first-order rate constants (k_{obs} or k_ψ) for the reaction of *o*-toluidine (2.0×10^{-4} mol dm^{-3}), D-glucose, and acetic acid (8.7 mol dm^{-3}) in the absence and presence of CTAB (20.0×10^{-3} mol dm^{-3}) and SDS (16.0×10^{-3} mol dm^{-3}) at 70°C

10^3 [D-glucose] (mol dm^{-3})	$10^5 k_{obs}$ or k_ψ (s^{-1})		
	Aqueous	CTAB	SDS
1.0	–	5.7	5.0
1.5	–	4.4	5.4
2.0	1.5	5.3	6.4
4.0	3.2	5.5	6.9
6.0	4.2	5.7	7.3
8.0	5.8	–	7.5
10.0	7.0	6.5	8.0
14.0	8.7	6.7	8.5

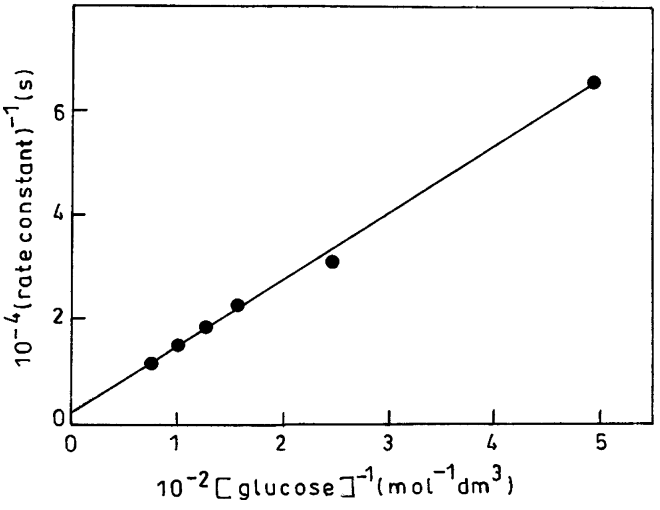


Fig. 3 Plot of rate constant^{-1} vs [D-glucose]$^{-1}$. Reaction conditions are the same as in Fig. 2

Table 2 k_{obs} or k_{ψ} as a function of temperature, activation parameters, and other parameters for the reaction of *o*-toluidine (2.0×10^{-4} mol dm^{-3}), D-glucose (2.0×10^{-3} mol dm^{-3}), and acetic acid (8.7 mol dm^{-3}) in the absence and presence of CTAB (20.0×10^{-3} mol dm^{-3}) and SDS (16.0×10^{-3} mol dm^{-3})

Variable	$10^5 k_{obs}$ or k_{ψ} (s^{-1})		
	Aqueous	CTAB	SDS
Temperature			
50°C	0.8	1.9	2.3
60°C	1.9	3.1	3.8
70°C	3.8	5.3	6.4
80°C	13.0	16.5	17.2
E_a (kJ mol^{-1})	96	86	58
$\Delta H^{\#}$ (kJ mol^{-1})	93	83	55
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−51	−77	−157
$10^3 k_m$ (s^{-1})		1.2	3.4
K_s (mol^{-1} dm^3)		72	46
K_n (mol^{-1} dm^3)		68	60

activation energy (E_a) and other parameters ($\Delta H^{\#}$ and $\Delta S^{\#}$) of this system were evaluated from Arrhenius (log k_{obs} vs $1/T$; Fig. 4) and Eyring (log k_{obs}/T vs $1/T$) plots. The results are given in Table 2. A useful explanation of $\Delta H^{\#}$ and $\Delta S^{\#}$ is not possible because k_{obs} does not represent a single elementary reaction; it is a complex function of the ionization of *o*-toluidine, the equilibrium constant between *o*-toluidine and D-glucose, and true rates. However, the large negative value of $\Delta S^{\#}$ shows that the transition state is well structured and highly solvated.

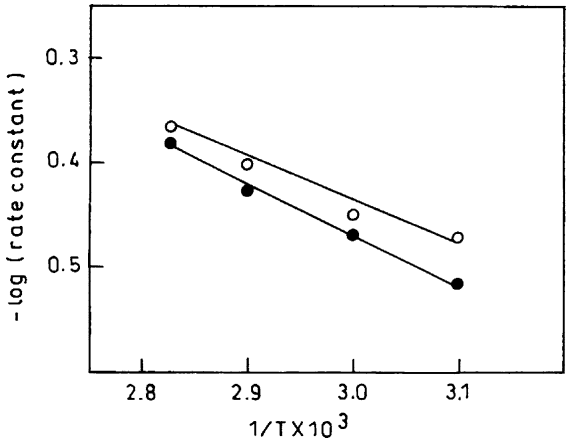


Fig. 4 Arrhenius plots for the reaction of D-glucose with *o*-toluidine in the absence (•) and presence (○) of CTAB. Reaction conditions are the same as in Fig. 3, with [acetic acid]=8.7 mol dm^{-3}

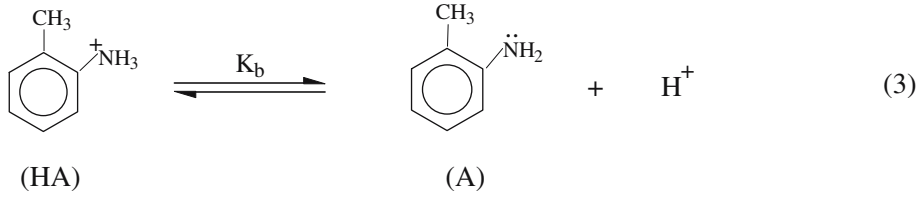
Mechanism

Before proposing the mechanism of the reaction, it is necessary to discuss the reactive species of *o*-toluidine and D-glucose in the working reaction mixture. In our experimental conditions, [acetic acid] ≥3.8 mol dm^{-3}, with *o*-toluidine existing in the following acid–base equilibrium:

From the above relation, we may write the expression (4):

$$pK_b = pH + \log\frac{[HA]}{[A]}. \quad (4)$$

At higher [H$^+$], *o*-toluidine exists mainly as HA; as [H$^+$] decreases, the percentage of unprotonated species of *o*-toluidine (A) increases, which, in turn, increases the reaction rate. It has been established [19, 20] that this reaction proceeds through the attack of the lone pair of electrons of *o*-toluidine nitrogen on the carbonyl group of D-glucose. For nucleophilic addition reaction, the presence of a lone pair of electrons on nitrogen is necessary [21]. Thus, we may safely conclude that the unprotonated species of *o*-toluidine (A) is the reactive species. On the other hand, in aqueous solutions, carbohydrates exist mainly as cyclic hemiacetals, which are in dynamic equilibrium with acyclic forms. D-glucose exists in equilibrium between α-pyranose and β-pyranose forms, with free aldehyde forms as intermediates [22]. Experimental results suggest that, in experimental conditions, the reaction proceeds through the nucleophilic addition–elimination path, leading to the formation of a Schiff base. In light



(3)

of the above observations, the proposed addition–elimination-type mechanism is (Scheme 1):

which gives

$$\frac{d[P]}{dt} = \frac{k_1 K_{es1}[H^+][o-toluidine]_T[D-\text{glucose}]}{(1 + K_b[H^+] + K_{es1}[D-\text{glucose}])} \quad (5)$$

or

$$k_{obs} = \frac{k_1 K_{es1}[H^+][D-\text{glucose}]}{(1 + K_b[H^+] + K_{es1}[D-\text{glucose}])}. \quad (6)$$

Equation (5) can be rewritten as Eq. (7):

$$\frac{1}{k_{obs}} = \frac{(1 + K_b[H^+])}{k_1 K_{es1}[H^+][D-\text{glucose}]} + \frac{1}{k_1[H^+]}. \quad (7)$$

The plot of $1/k_{obs}$ vs 1/[D-glucose] at constant acidity shows an expected linear relationship. Equation (7) also indicates that both the intercept and the slope of such a plot should be dependent on $[H^+]$.

Reaction in the presence of surfactants

In order to check whether *o*-toluidine reacts with the surfactants (CTAB and SDS) in our kinetic conditions, *o*-toluidine (2.0×10^{-4} mol dm^{-3}) and surfactants, and CTAB (20.0×10^{-3} mol dm^{-3}) and SDS (16.0×10^{-3} mol dm^{-3}), respectively, were mixed and kept for 1 h at 70°C. The CMC values of the respective mixtures were then measured. No change in the observed and reported values of CMC (*vide supra*) for the surfactants ruled out the possibility of any reaction between them:

1. The effects of CTAB and SDS concentrations were studied at 2.0×10^{-3} mol dm^{-3} D-glucose, 2.0×10^{-4} mol dm^{-3} *o*-toluidine, and 8.7 mol dm^{-3} acetic acid at 70°C. The results (Table 3) are illustrated in Fig. 5 as rate constant–[surfactant] profiles. The plot of k_ψ against [CTAB] or [SDS] shows a gradual increase in rates that is nearly twofold and fourfold the increase in [CTAB] and [SDS], respectively. This behavior may be attributed to increasing solubilization of the reactant species with increasing surfactant concentration. However, after this optimum concentration, the reaction rate decreases with increasing [surfactant].

Scheme 1

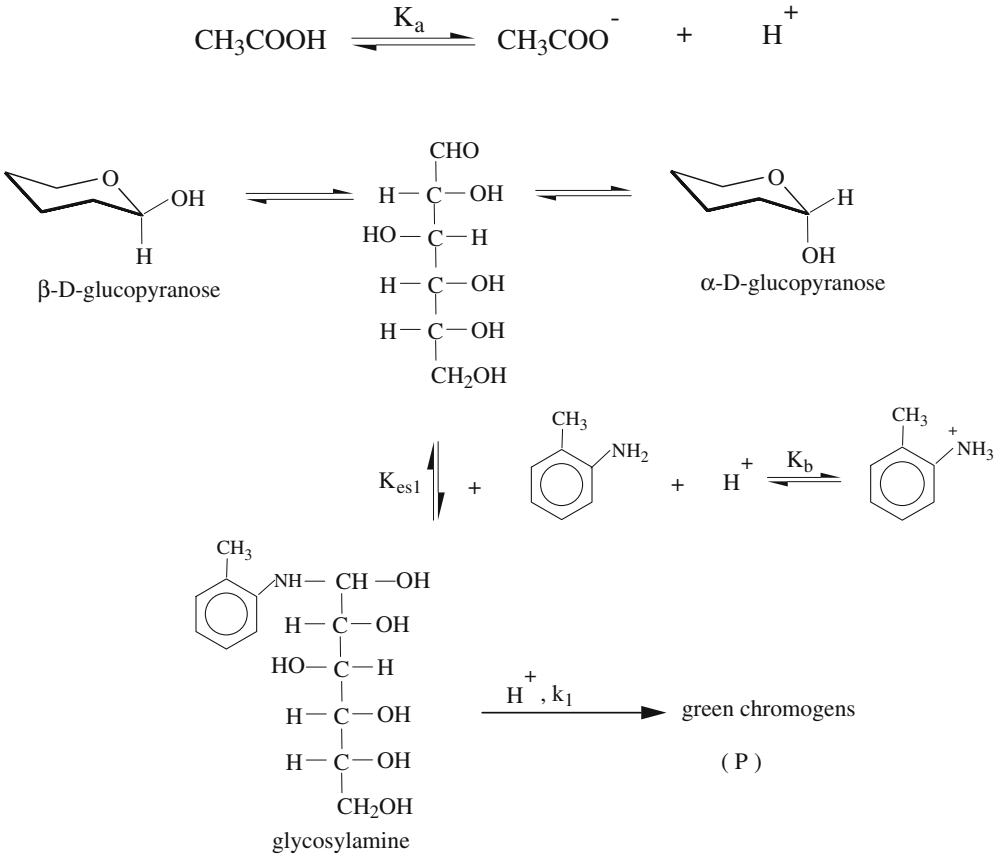


Table 3 Effect of [CTAB] and [SDS] on pseudo-first-order rate constant (k_ψ) for the reaction of *o*-toluidine (2.0×10^{-4} mol dm^{-3}), D-glucose (2.0×10^{-3} mol dm^{-3}), and acetic acid (8.7 mol dm^{-3}) at 70°C

10^3 [Surfactant] (mol dm^{-3})	$10^5 k_\psi$ (s^{-1})		$10^5 k_{\psi cal}$ (s^{-1})	
	CTAB	SDS	CTAB	SDS
0.0	1.5	1.5	1.5	1.6
4.0	1.7	2.7	1.6	2.8
8.0	2.1	4.2	2.0	4.1
12.0	2.3	5.0	2.3	5.1
16.0	3.8	6.4	3.7	6.3
20.0	5.3	4.6	5.4	4.6
24.0	3.7	4.2	3.6	4.2
28.0	3.1	–	3.2	–

The decrease in k_ψ at higher [CTAB or SDS] could be due to *dilution effect*: a continuous increase in [CTAB or SDS] produces micelles and, progressively, more and more *o*-toluidine gets incorporated into the micellar phase. Segregation deactivates the substrate since *o*-toluidine in one micelle cannot react with D-glucose. A point worth noting is that even at [CTAB or SDS]=28.0×10^{-3} mol dm^{-3}, k_ψ values are still higher than those observed in bulk water (Fig. 5); this process proves beyond doubt that CTAB or SDS is still playing its role in catalyzing the reaction.

2. In order to confirm whether or not the same mechanism operates in micellar media, k_ψ values were determined as a function of variations in [*o*-toluidine], [D-glucose] (Fig. 2), and temperature (Fig. 4) at fixed [CTAB] and [SDS] (Tables 1 and 2). We can see that the same pattern is being followed (i.e., first order each in [*o*-toluidine] and [D-glucose]). These observations undoubtedly show that the reaction mechanism in the presence of cationic CTAB micelles and anionic SDS remains the same as that in homogeneous aqueous media. A comparison between the E_a values in aqueous and miceller media (Table 2) indicates that the CTAB and SDS micelles act as catalysts and provide a new reaction path with a lower value of E_a.
3. The observed micellar catalytic results are consistent with reactions 8, 9, 10 and 11, where *o*-toluidine in water associates with micellized surfactants D_n, forming (*o*-toluidine)$_m$ with an association constant K_s:

$$(o-toulidine)_w + D_n \overset{K_s}{\rightleftharpoons} (o-toluidine)_m \qquad (8)$$

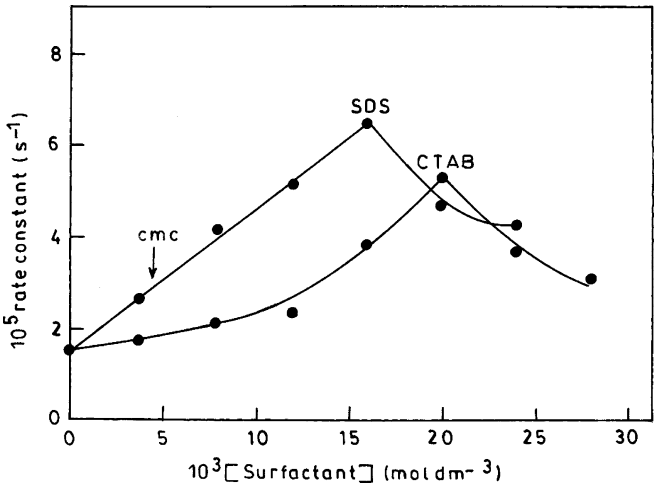


Fig. 5 Plots of rate constant vs [surfactant]. *Reaction conditions*: [*o*-toluidine]=2.0×10^{-4} mol dm^{-3}; [D-glucose]=2.0×10^{-3} mol dm^{-3}; [acetic acid]=8.7 mol dm^{-3}; temperature=70°C

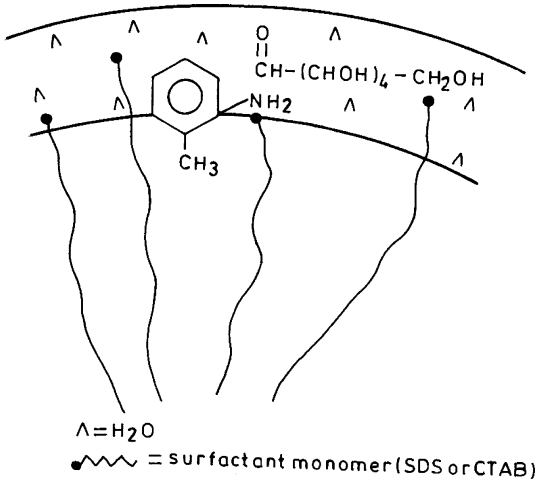
$$(\text{glucose})_w + D_n \overset{K_n}{\rightleftharpoons} (\text{glucose})_m \qquad (9)$$

$$(o-toluidine)_w + (\text{glucose})_w \xrightarrow{k'_w} \text{Product} \qquad (10)$$

$$(o-toluidine)_m + (\text{glucose})_m \xrightarrow{k'_m} \text{Product} \qquad (11)$$

Similarly, glucose in water solubilizes in micelles with association constant K_n. The reaction occurs in aqueous

S



Scheme 2

phases and micellar pseudo-phases with the first-order rate constants k'_w and k'_m, respectively. Application of the Menger–Portony model to reactions 8, 9, 10 and 11 considers the micelles and aqueous solutions as two separate phases [23]. The assumptions involved in this model, the advantages, and the disadvantages are critically discussed by Bunton [24, 25] and Cerichelli et al. [26]. As both reactants are considered to be incorporated into the micellar phase, k_ψ is the first-order rate constant for the overall reaction. k_ψ is given in Eq. (12):

$$k_\psi = \frac{k_w[glucose]_T + (K_s k_m - k_w) M_A^S [D_n]}{(1 + K_s[D_n])} \tag{12}$$

where $k_w = k_w^{'} / \left[(o - toluidine)_w\right]$ and $k_m = k'_m \mathrm{M}_\mathrm{A}^S$; k_w and k_m are the second-order rate constants and M_A^S (being the mole ratio of glucose bound to the micellar head group) is given as:

$$M_A^S = \left[(glucose)_m\right] / D_n. \tag{13}$$

In order to calculate the value of K_s, K_n, and k_m, the nonlinear least squares technique has been used, as detailed earlier [27, 28]. The best-fit values are given in Table 2. For comparison, the $k_{\psi\, cal}$ values were obtained by substituting the k_w, K_s, K_n, k_m, and $[D_n]$ values in the relevant equation (12). The agreement between the calculated and observed values provides supporting evidence for the method of calculation (Table 3).

The results (Table 3) are illustrated in Fig. 5 as rate constant–[surfactant] profiles, which clearly demonstrate the SDS catalytic effect not only above but also below the CMC (i.e., micellar as well as premicellar catalyses are observed). Micelles are not fixed entities but have a transient character [29]. 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_1) between various states of aggregation is controlled by a series of dynamic association–dissociation equilibria:

$$\begin{aligned} D_1 + D_1 &\rightleftharpoons D_2 \\ D_2 + D_1 &\rightleftharpoons D_3 \\ &\vdots \\ D_{n-1} + D_1 &\rightleftharpoons D_n \end{aligned}$$

The catalysis below CMC (i.e., submicellar catalysis) is not new and conforms to various available results [2, 5, 30]. Feasibility can be sought in the fact that small aggregates of the surfactant (dimmers, trimers, and tetramers) exist below the CMC; these small submicellar aggregates can interact physically with the reactants, forming catalytically active entities.

Micellar surfaces are water-rich and do not provide a uniform reaction medium because a micelle is a porous cluster with a rough surface and deep-water-filled cavities [31]. Water activity at the surface of ionic micelles is not different from water activity in the aqueous pseudo-phase or at the interface between micellar and bulk water solvents. It has been assumed that rate enhancements of bimolecular reactions are due to the association/incorporation of both the reactants through hydrophobic/electrostatic interactions in the small volume of the micellar pseudo-phase. In micelle-mediated reactions, it is not possible to precisely locate the exact site of the reaction but, at least, localization of reactants can be considered. The rate of the *o*-toluidine–glucose reaction is catalyzed by anionic micelles of SDS, as well as by cationic micelles of cetyltrimethlyammonium bromide (Table 3) at constant [acetic acid]. The catalysis of the reaction by both micelles could be rationalized in terms of hydrophobic effect. In both micelles, *o*-toluidine gets incorporated hydrophobically into the palisade layer. On the hand, D-glucose may be assumed to be totally present in the Stern layer because there is no degree of hydrophobicity due to the presence of 5-OH groups, thus closing the reactants in small volume and resulting in the observed catalysis. It can now be stated confidently that the interaction between *o*-toluidine and glucose occurs in the palisade–Stern region of SDS and CTAB micelles. *o*-Toluidine might be expected to partition significantly between the palisade–Stern layer of the micelle and its interior. A complete understanding of micellar effect is not possible because a number of different interactions, including those associated with the head group of the surfactant, are involved. A possible arrangement (although highly schematic) could be that as shown in Scheme 2, which clearly indicates that the probable reaction site is the palisade–Stern layer's junctural region.

Interestingly, as compared to CTAB micelles, the reaction rate is higher in SDS micelles (Table 3). This may be due to the fact that the positive charge on *o*-toluidine nitrogen in the presence of acetic acid (≥8.7 mol dm^{-3}) seems to play a significant role, as there will be strong electrostatic association with the negative head group of SDS micelles, which, in turn, increases the effective concentration of *o*-toluidine in SDS micelles. Due to the electrostatic repulsion between protonated *o*-toluidine and the positive head group of CTAB micelles, less amount of *o*-toluidine can be distributed into the micellar phase.

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