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Micellar effects and reactant incorporation in reduction of toluidine blue by ascorbic acid

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Abstract

The kinetics of the reduction of toluidine blue by ascorbic acid was studied both in the absence and presence of hydrochloric acid as a function of cetyltrimethylammonium bromide concentration. The pseudo-first order rate constant was calculated from the decrease in the absorbance of toluidine blue. The results are analyzed according to pseudophase model of micelles. The reaction is catalyzed by cetyltrimethylammonium bromide micelles in the absence of hydrochloric acid but retarded in the presence of hydrochloric acid. This opposing effect of cetyltrimethylammonium bromide micelles may be explained by the changing species of reactants in acidic pH.

To find a correlation between micellar effect on the rate constants and incorporation of the reactants to the micelles, separate spectrophotometric experiments were performed and binding constants for the association of reactants with micelles were determined using the Benesi–Hildebrant equation.

Keywords: Toluidine blue; Ascorbic acid; Cetyltrimethylammonium bromide; Micellar catalysis; Micellar binding constant

1. Introduction

The modification of chemical reactions by incorporating reactant molecules to micelles has received considerable attention [1–3]. Chemical reactivity, equilibria, and stereochemistry of the reactants have been significantly affected by micelles. Micellar catalysis of reactions is important because of the parallel behaviour of macro-molecules and enzymes.

Micellar catalysis of reactions in aqueous solution is generally explained in terms of distribution of reactants between water and micelles, with reactions occurring in both media. Therefore it is possible to treat the rate-surfactant profiles in terms of the concentrations of reactants in the aqueous and micellar pseudophases and the rate constants in each pseudophase [4].

Toluidine blue, TB^+ (3-amino-7-dimethyl-amino-2-methyl phenazathionium chloride), a phenothiazine blue dye, is generally used as polymerization inhibitor, complexing agent, biological sensitizer and stain [5]. The redox reactions of phenothiazine dyes may be exploited for the storage of solar energy using photo galvanic cells. The low toxicity and high water solubility of TB^+ with an intense absorption peak in the visible region makes it a suitable substance to monitor the depletion kinetics using other reactants. A number of reduction reactions of TB^+ forming the basis of analytical methods have been reported earlier [5–10]. The influence of various surfactants upon the oxidation of an azo dye by hypochlorite has been studied and the result discussed by means of specific dye–surfactant interaction [11]. It was shown previously that selenosulfide reduction of

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methylene blue (3,7-bis-dimethylamino-phenothiazine), also a phenothiazine blue dye, is accelerated by the presence of cetyltrimethylammonium bromide (CTAB) at the concentrations in the micellar region, giving rise to a catalytic–spectrophotometric method of increased sensitivity for Se (IV) determination [12].

The oxidation of L-ascorbic acid, AA, which is a well-known bioactive reducing agent, to L-dehydroascorbic acid has received a great deal of attention because of the important role that the redox chemistry of AA plays in human nutrition [13,14]. Photoreaction between TB^+ and AA has been studied by Cooper et al. [15]. Wen et al. [16] reported that the antioxidant activity of AA was enhanced in micellar systems in their study on the anodic oxidation of AA and its lipophilic derivatives in the presence of micelles.

The aim of this work was to determine the influence of CTAB micelles on the oxidation of AA using the reduction reaction with TB^+. The reduction of TB^+ by AA has been investigated in acidic medium by Safavi and Fotohui [17] for the kinetic-spectrophotometric determination of low levels of AA in some fruits and vegetables. It is interesting to study the effect of CTAB micelles on the reaction between TB^+ and AA in the absence and presence of hydrochloric acid (HCl) since species of both reactants varies with the pH of the media.

The present study deals with the effect of the cationic surfactant CTAB at various concentrations on the rate constant of the TB^+–AA reaction with and without HCl. Also, to interpret the results, the interaction of AA and TB^+ with CTAB micelles in the absence and presence of HCl was studied separately, since incorporation of the reactants to micelles is a prerequisite for micellar catalysis.

2. Experimental

2.1. Materials

All the chemicals were of analytical reagent grade. The cationic dye TB^+, AA and HCl were supplied by Merck. CTAB was obtained from Aldrich. All solutions were prepared in double distilled water.

2.2. Procedures

The spectroscopic measurements were carried out with a Hitachi 220-A UV–Vis spectrophotometer equipped with thermostatic cuvette holder. The pH values of the solutions were measured using a Metrohm Herisau pH-meter.

The onset of enhancement in the absorption maxima of TB^+ or AA with addition of the surfactant was considered as the critical micelle concentration (CMC) of CTAB under each experimental condition [18–20,22,23].

2.2.1. Micellar binding

The binding constant, K_B, of TB^+ and AA to CTAB micelles was separately determined spectrophotometrically in the absence and presence of 0.1 mol dm^{-3} HCl. The absorption spectra of TB^+ and AA solutions containing various concentrations of CTAB (10^{-4}–10^{-2} mol dm^{-3}) were recorded at 25 ± 0.2 °C over the range of 500–700 nm and 190–300 nm, respectively [24,25]. The reproducibility of duplicate λ_{max} determination was ±0.2 nm. The reactant concentrations were 6.54×10^{-5} mol dm^{-3} for TB^+ and 1.41×10^{-4} mol dm^{-3} for AA, and kept constant during the study.

2.2.2. Kinetic measurements

The kinetics of the reduction reaction of TB^+ with AA in acidic medium was originally studied by Safavi and Fotohui [17]. According to them, the orders of the reaction with respect to AA, TB^+ and HCl were 1, 1 and 0.5, respectively. In this work, the initial concentrations of TB^+ and AA were 2.35×10^{-5} mol dm^{-3} and 1.14×10^{-3} mol dm^{-3}, respectively, so the reduction kinetics of TB^+ was performed with at least 48-fold excess of AA and excessive acid, producing pseudo-first order conditions with respect to TB^+ [10,11,21].

The rate of reduction of TB^+ was obtained by following the decrease in the absorbance at 630 nm in the absence and presence of 0.1 mol dm^{-3} HCl using the UV–Vis spectrophotometric technique. The absorption band of TB^+ vanishes gradually without showing any change in its shape and position.

The influence of CTAB concentration on the rate of this reaction was examined for different surfactant concentrations, in the range of 1×10^{-5}–1×10^{-2} mol dm^{-3}. An aliquot of the reaction mixture was transferred to a thermostated cell at 25 ± 0.2 °C and the absorbance change of the solution was recorded at 1 min intervals and absorbance at infinity A_∞ was read when equilibrium was reached.

The observed first order rate constants were calculated by a generalized least-squares method from the relationship $\ln(A_t - A_\infty)$ versus time, and absorbance values were averages of two to four runs with standard deviation less than 1%. These plots were satisfactory straight lines, with correlation coefficients, $r \geq 0.9993$ for all kinetic runs indicating first order kinetics with respect to TB^+.

3. Results and discussion

Micelles can change the reaction rate in several ways. One of the dominant factors responsible for the observed micellar effect on the reaction rate is the substantial change in the local concentration of the reactants upon their binding to the micelles. Therefore, incorporation of reactants to CTAB micelles was studied separately in the absence and presence of 0.1 mol dm^{-3} HCl.

3.1. Binding of solutes to micelles

The visible absorption spectrum of TB^+ (6.54×10^{-5} mol dm^{-3}) in aqueous solution exhibited an absorption maximum at 630 nm and a shoulder at 590 nm at 25 ± 0.2 °C. In the presence of 0.1 mol dm^{-3} HCl, the peak at 630 nm diminished, whereas the one at 590 nm was enhanced. The molar absorptivity of TB^+ at 630 nm (concentration range: 1.962×10^{-5}–8.175×10^{-5} mol dm^{-3}) in aqueous solution in the absence and presence of 0.1 mol dm^{-3} HCl was calculated as $(29.8 \pm 0.02) \times 10^3$ dm^3 mol^{-1} cm^{-1} and $(22.6 \pm 0.02) \times 10^3$ dm^3 mol^{-1} cm^{-1} at 25 ± 0.2 °C, respectively. In the absence of acid, TB^+ is in equilibrium with protonated species of toluidine blue, TBH^{2+}, whereas TB^+ concentration decreased and TBH^{2+} increased toward lower pH ($pK_a = 7.2$) [10]. The absorption spectrum of AA (concentration range: 5.67×10^{-6}–1.293×10^{-4} mol dm^{-3}) in aqueous solution in the absence and presence of 0.1 mol dm^{-3} HCl exhibited absorption maxima at 265 nm and 245 nm with molar absorptivities, ε, of $(11.6 \pm 0.04) \times 10^3$ dm^3 mol^{-1} cm^{-1} and $(9.9 \pm 0.05) \times 10^3$ dm^3 mol^{-1} cm^{-1} at 25 ± 0.2 °C, respectively. In the case of AA ($pK_{a1} = 4.17$, $pK_{a2} = 11.57$) [26], in acidic pH, mono protonated and negatively charged species, HA^-, is dominant but, HA^- concentration decreases and undissociated species H_2A concentration increases steeply with increasing HCl concentration. Each relation between absorbance and concentration of TB^+ or AA was linear ($r > 0.9997$), indicating the validity of Beer's law within the concentration range studied. As seen from the results, λ_{max} and molar absorptivity of both TB^+ and AA were different in the presence of HCl compared to its absence. Toluidine blue has a conjugated structure in neutral medium, and this structure gives rise to charge-transfer transitions in the visible range in addition to the less sensitive $n \rightarrow \pi^*$ transitions, responsible for the high molar absorptivity observed at $\lambda = 630$ nm. However in acidic medium, the lone electron pair on the side N-atoms is used to coordinatively bind to a proton, i.e., $N{:}H^+Cl^-$, and thus $n \rightarrow \pi^*$ transitions disappear, together with a rearrangement of alternating double bonds in the conjugated structure. In the presence of HCl, species of ascorbic acid changes, too. Thus, completely different structure of toluidine blue and ascorbic acid have different absorption maximum wavelengths and molar absorptivities in acidic medium.

The absorption spectra of TB^+ in neutral medium with and without CTAB are shown in Fig. 1. The absorbance of TB^+ is substantially constant at the CTAB concentrations below the CMC but above a certain concentration corresponding to the CMC, the absorbance increased as the CTAB concentration increased both in the absence and presence of HCl. In other words, CTAB caused an absorbance increase without changing the general shape of the TB^+ spectrum only at concentrations above the CMC. In the presence of CTAB micelles, increased extinction coefficient can be interpreted as due to the incorporation of TB into the micelles. The absorption spectra of AA in neutral medium with and without CTAB are shown in Fig. 2. In the absence of HCl the absorbance of AA decreased at the concentrations below the CMC, indicating complex formation between AA and CTAB molecules and above the CMC, absorbance increased gradually. It was observed that presence of CTAB at the concentrations below and above the CMC, had no influence on the absorbance of AA in the presence of HCl, indicating lack of interaction between undissociated species of AA and CTAB molecules and micelles.

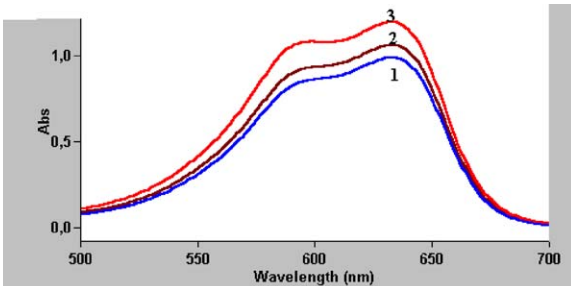


Fig. 1. Visible absorption spectra of TB^+ (3.35×10^{-5} mol dm^{-3}) at various selected concentrations of CTAB at 298 K. [CTAB] mol dm^{-3}: (1) 0.0; (2) 1.0×10^{-2}; (3) 2.0×10^{-2}.

Binding of solute to micelles can be assumed to follow the equilibrium reaction as

$$S + M \overset{K_B}{\rightleftharpoons} SM \tag{1}$$

where S, M, SM and K_B represent the substrate, micelle, substrate–micelle complex and binding equilibrium constant, respectively. K_B is given by

$$K_B = \frac{[SM]}{[S][M]} \tag{2}$$

The extent of micellar binding can be seen readily from the fraction of bound solute, f, defined as $f = [S_m]/$

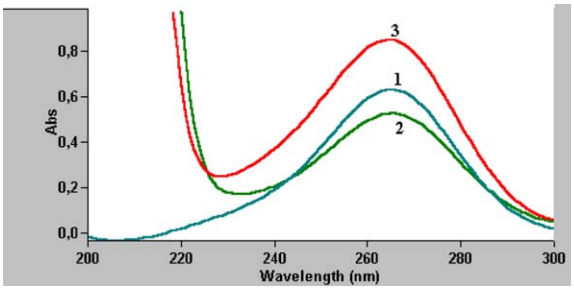


Fig. 2. Visible absorption spectra of AA (5.00×10^{-5} mol dm^{-3}) at various selected concentrations of CTAB at 298 K. [CTAB] mol dm^{-3}: (1) 0.0; (2) 5.0×10^{-4}; (3) 1.0×10^{-2}.

$[S_t]$, where S_m is the concentration of solute in the micellar pseudophase and S_t is the total concentration [18,27]. Provided that the spectra of the fully micellar incorporated solute can be measured, the value of f can be directly calculated from experimental data using the following equation:

$$f = \frac{A - A_0}{A_m - A_0} \tag{3}$$

where A_0, A and A_m are the absorbances of the substrate in the absence of surfactant, in the presence of surfactant, and when the substrate is completely micellar bound, respectively [4,28,29].

The values of f obtained by using Eq. (3) are shown in Fig. 3 for AA and TB^+ in the absence and presence of HCl as a function of CTAB concentration. It is seen that the values of f reached a plateau for AA but did not reach a plateau value for TB^+ with increasing CTAB concentration.

For the determination of the binding constant, K_B, the modified equation of Benesi–Hildebrand [30–32] was used

$$\frac{[S_t]}{(A - A_0)} = \frac{1}{(\varepsilon_m - \varepsilon)} + \frac{1}{K_B(\varepsilon_m - \varepsilon)C_m} \tag{4}$$

where ε_m and ε are the molar absorptivities of the substrate in the micelle-associated and free states, respectively, and C_m is the concentration of micellized surfactant (total concentration of surfactant, CMC). CMC is the critical micelle concentration of CTAB in the experimental medium, obtained from the onset of absorption enhancement [22,23].

The plot of $S_t/A - A_0$ vs $1/[C_m]$ was found to be linear $r \geq 0.9998$ in all cases confirming 1:1 complex formation between micelle and substrate, as seen in Fig. 4. The K_B and ε_m values of TB^+ and AA calculated from the slope and intercept of the plots shown in Fig. 4 are compiled in Table 1. Table 1 also summarizes CMC values determined by absorbance method [33,34]. The presence of AA and HCl reduced CMC values due to the known effect of added electrolyte.

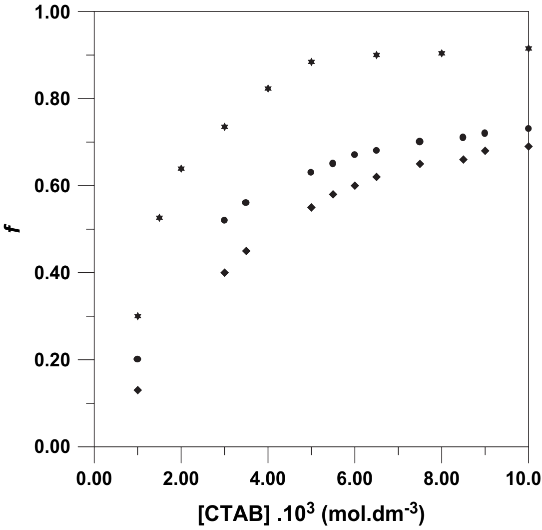


Fig. 3. Fraction of the substrate associated to micelle as a function of CTAB concentration. (●) TB^+ without HCl, (✱) HA^- without HCl, (◆) TBH^{2+} in 0.1 mol dm^{-3} HCl.

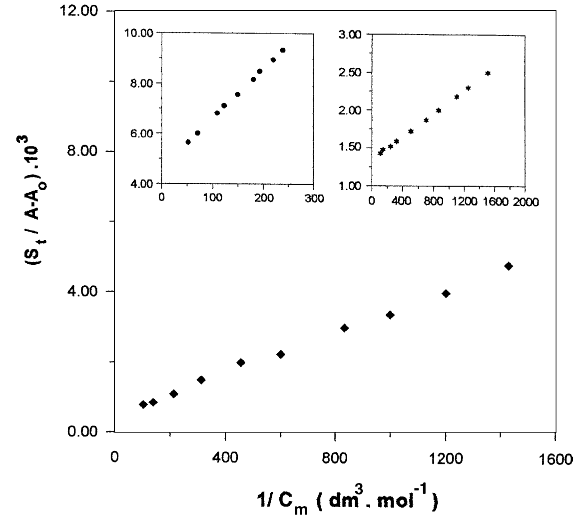


Fig. 4. Relation between $S_t/\Delta A$ and $1/C_m$ according to Eq. (4). (●) TB^+ without HCl, (✱) HA^- without HCl, (◆) TBH^{2+} in 0.1 mol dm^{-3} HCl.

Results indicated that TB^+, which is a cationic dye, was incorporated into the cationic micelles by hydrophobic attraction, which is sufficiently intense to overcome electrostatic repulsion between dyes and micelles of similar charge. This is in agreement with the finding of Taniguchi and Iguchi for incorporation of four cationic dyes to cationic micelles [33], with the results of Reddy and Katiyar for the binding of cationic ethyl violet carbonium ion to cationic micelles [35], and also with the results of Sabate et al. for binding of pinacyanol chloride to cationic micelles [32]. In the study of association between anionic dyes to different types of surfactants, a similar interaction was also observed between anionic micelles and anionic dyes in spite of electrostatic repulsion [36].

The binding constant of TB^+ to CTAB micelles decreased in the presence of 0.1 mol dm^{-3} HCl. Therefore, the smaller binding constant obtained for TBH^{2+} than that of TB^+ is due to the increased electrostatic repulsion between TBH^{2+} and CTAB micelles which is related to the increased positive charge on TBH^{2+}.

AA was found to have a higher binding constant to CTAB micelles than TB^+ in the absence of HCl, but in the presence of HCl, no interaction was observed. Lack of interaction between H_2A and CTAB micelles can be expected since H_2A has no hydrophobic structure and is also uncharged in acidic pH.

The effect of micelles on the dissociation constants of various dyes and acid–base indicators has been studied [24,37,38]. The shifts in the pK_a have been attributed to

Table 1
Interaction parameters of toluidine blue and ascorbic acid with CTAB micelles in the presence and absence of HCl

	ε_m[a] (M^{-1} cm^{-1})	CMC[b] (mol dm^{-3})	K_B (dm^3 mol^{-1})	f[c]
TB^+ without HCl	30,016	9.0×10^{-4}	153.5 ± 1.0	0.730
TB^+ in 0.1 mol dm^{-3} HCl	24,592	3.0×10^{-4}	146.2 ± 0.5	0.690
HA^- without HCl	12,348	8.4×10^{-4}	1706 ± 0.5	0.915

[a] ε_m calculated from ($\varepsilon_m - \varepsilon$) since ε values separately determined, error limit in ε_m is ±1%.
[b] Obtained from absorbance measurements at 25 °C (CMC in pure water is 9.2×10^{-4} mol dm^{-3} [20]).
[c] Calculated in the presence of 1.0×10^{-2} mol dm^{-3} CTAB.

electrostatic and polarity effect of micelles and also to monomeric surfactant head groups. The observed effect of CTAB micelles can also be rationalized in terms of micellar effects upon the apparent dissociation constants of TB^+ and AA.

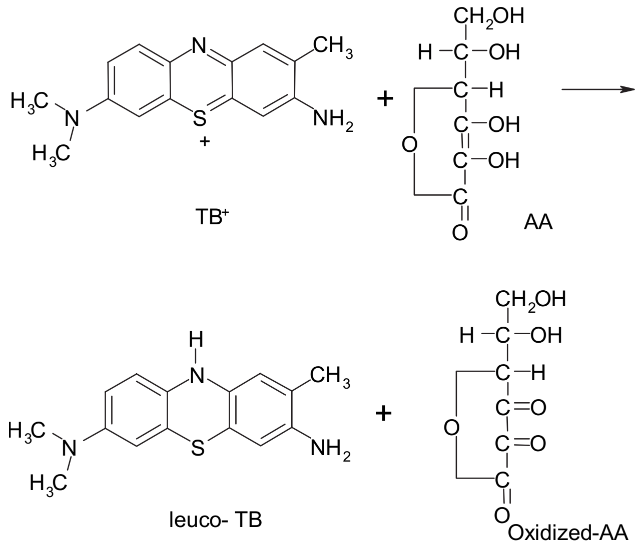
3.2. Kinetics of reduction of TB^+ in the absence of CTAB

The reduction of TB^+ to colourless leuco compound involves two single electron transfer steps, i.e. TB^+ gains two electrons [5,39]. The stable oxidation product of AA is dehydroascorbic acid. The oxidation of AA to dehydroascorbic acid also involves transfer of two electrons, i.e. AA loses two electrons [40]. The reaction scheme may be proposed as follows:

$TB^+ + AA \rightarrow$ leuco-TB + oxidized-AA

$TB^+ + 2\,e^- \rightleftarrows$ leuco-TB

AA - $2\,e^- \rightleftarrows$ oxidized-AA



The observed pseudo-first order rate constant, k_0, was obtained from plots of $\ln(A_t - A_\infty)$ against time using the equation [41]:

$$\ln(A_t - A_\infty) = -k_0 t + \ln(A_0 - A_\infty) \quad (5)$$

where A_t, A_0 and A_∞ are the absorbances at time t, 0, and equilibrium, respectively. The observed pseudo-first order rate constants in the absence and presence of 0.1 mol dm^{-3} HCl calculated from the slope of the straight lines between $\ln(A_t - A_\infty)$ and time are given in Table 2.

The kinetics of this reaction in the presence of HCl was studied by Safavi and Fotouhi [17], therefore we report here a brief summary of our results including the ones obtained in the absence of HCl for comparison with those obtained in micellar media.

The increase in k_0 with the presence of HCl can be attributed to the change in the concentration of the protonated species of reactants in solution. The species of toluidine blue and ascorbic acid changes with the variation of pH. In the presence of 0.1 mol dm^{-3} HCl, TBH^{2+} and H_2A are the only species present in solution. One would expect that reduction of TB^+ would be slower in the presence of HCl as the negative charge on the AA is decreased. Our results showed the opposite effect of acidic medium, i.e. the reaction rate increased in agreement with previous finding of Safavi and Fotohui [17]. This result may indicate that H_2A is more reactive than HA^- and TBH^{2+} more reactive than TB^+.

3.3. Kinetics in the presence of CTAB

The kinetics of this reaction was studied for different CTAB concentrations, in the range of 1×10^{-5}–1×10^{-2} mol dm^{-3}. In the absence of HCl and CTAB micelles, the reaction proceeds very slowly, the absorption band does not vanish, but there is an almost 50%

Table 2
Kinetic parameters of the reduction reaction of toluidine blue with ascorbic acid in the presence of CTAB micelles using the micellar pseudophase model

	Absence of HCl	In 0.1 mol dm^{-3} HCl
k_0 (min^{-1})	0.149 ± 0.008	0.302 ± 0.006
k_ψ (min^{-1})[a]	0.265 ± 0.005	0.194 ± 0.003
k_m (min^{-1})	0.345 ± 0.004	0.112 ± 0.004
K_B^1 (dm^3 mol^{-1})	141.4 ± 0.4	130.8 ± 0.5

[a] Calculated in the presence of 1.0×10^{-2} mol dm^{-3} CTAB.

loss in intensity. On the other hand, in the presence of CTAB micelles, the reaction is accelerated and the absorption band for TB^+ completely vanishes. The electrostatic attraction between oppositely charged TB^+ and HA^- for effective reaction in aqueous medium is not observed, presumably because of the solvation effect. The extent of solvation is reduced through the use of micellar environment. The complete reduction of micelle bound TB^+ occurs at high micelle concentrations.

The reduction rate of TB^+ in the presence of CTAB with or without HCl showed some striking differences. Pseudo-first order rate constant increased with increase in CTAB concentration in the absence of HCl and contrarily decreased in the presence of HCl. The variation of the observed pseudo-first order rate constants, k_ψ, for the reduction of TB as a function of CTAB concentration in the absence and presence of $0.1\ \mathrm{mol\,dm^{-3}}$ HCl is depicted in Fig. 5. The plot of k_ψ against CTAB concentration $[C]$ above the CMC can be fitted to the following equation:

$$k_\psi = -1223[C]^2 + 26.104[C] + 0.12 \qquad \text{(I)}$$

A similar mathematical model between k_ψ and CTAB concentration $[C]$ above the CMC was also developed from the data shown in Fig. 5 in the presence of HCl, as:

$$k_\psi = 308.87[C]^2 - 14.59[C] + 0.31 \qquad \text{(II)}$$

The lines in Fig. 5 were drawn according to these equations.

The kinetics are discussed in terms of micellar pseudophase model, which assumes that reaction can take place both in aqueous and micellar pseudophases. It should be possible therefore to treat the rate-surfactant profiles in terms of the concentrations of reactants in each pseudophase. Use of the pseudophase model also allows comparison of the rate constants in the pseudo-micellar phase and in the bulk [35,42,43].

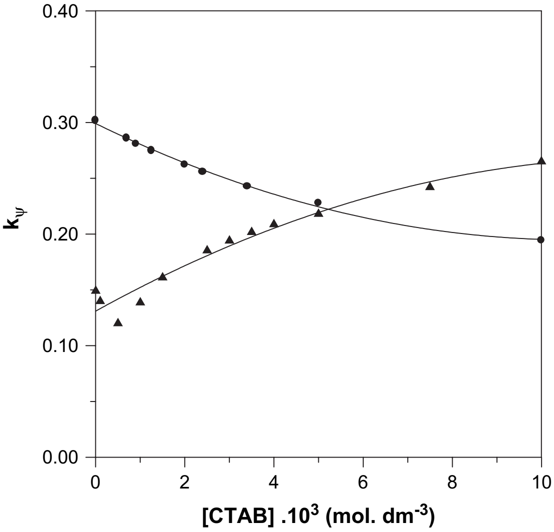
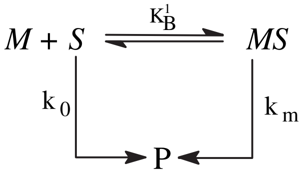


Fig. 5. Variation of the pseudo-first order rate constant of the reaction of TB^+ with HA^- as a function of CTAB concentration. (▲) without HCl, solid line is fitted to Eq. (I), (●) in $0.1\ \mathrm{mol\,dm^{-3}}$ HCl, solid line is fitted to Eq. (II).

In this work, reduction reaction of TB^+ with AA in the presence of cationic CTAB micelles is applied to the Michaelis–Menten type kinetics [33,43]. This pseudophase model treats overall rate constants as the sum of rate constants in two pseudophases. The pseudophase model predicts that overall first order rate constants, k_ψ, for a spontaneous micellar-accelerated reaction should increase monotonically until all the substrate is micellar-bound. Conversely, for an inhibited reaction, k_ψ decreases monotonically to a constant value [44,45]. The reaction proceeds in both phases depicted as



(6)

The substrate (S) forms a complex with micelle (M) and k_0 and k_m are the rate constants for the reaction in the aqueous and micellar pseudophase, respectively. This behaviour is fitted to Eq. (7)

$$k_\psi = \frac{k_0 + k_m K_B' C_m}{1 + K_B C_m} \qquad (7)$$

It can be rearranged into

$$\frac{1}{k_0 - k_\psi} = \frac{1}{k_0 - k_m} + \frac{1}{(k_0 - k_m) K_B^1 C_m} \qquad (8)$$

where K_B^1 represents the binding constant of a given reactant in the reaction media. As predicted the plots of $1/(k_0 - k_\psi)$ vs $1/C_m$ are linear at high concentrations of CTAB micelles ($r \geq 0.9997$) as seen in Fig. 6. The line in Fig. 6 in the absence of HCl was drawn according to the equation given below:

$$\frac{1}{k_0 - k_\psi} = -0.03615 \frac{1}{C_m} - 5.133 \qquad \text{(III)}$$

The line in the presence of HCl was drawn according to the equation given below:

$$\frac{1}{k_0 - k_\psi} = 0.04019 \frac{1}{C_m} + 5.261 \qquad \text{(IV)}$$

k_m and K_B^1 values obtained from the slope and intercept of the plots shown in Fig. 6 and the observed pseudo-first order rate constants obtained in the absence of CTAB (k_0) and in the presence of $1.0 \times 10^{-2}\ \mathrm{mol\,dm^{-3}}$ CTAB (k_ψ) are listed in Table 2.

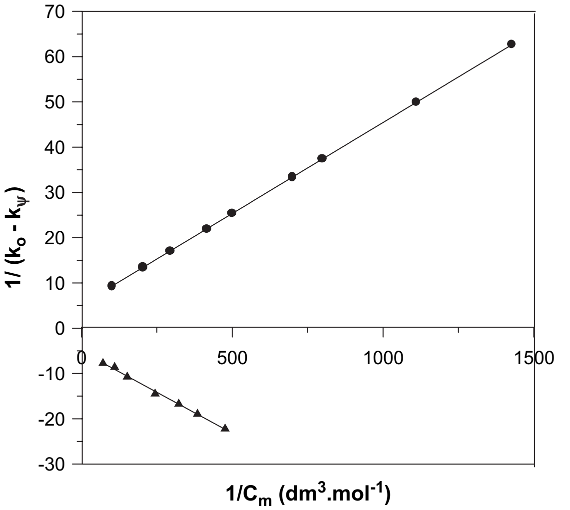


Fig. 6. Plots of $(1/k_0 - k_\psi)$ vs $1/C_m$ according to Eq. (8). (▲) without HCl, solid line is fitted to Eq. (III), (●) in 0.1 mol dm^{-3} HCl, solid line is fitted to Eq. (IV).

The binding constants of TB^+ to the CTAB micelles estimated from binding and kinetic data can be compared with the values listed in Tables 1 and 2, respectively. The K_B values obtained from binding studies in the absence of any additive were higher than the K_B^1 values obtained under the reaction conditions, i.e. in the presence of the other reactant, which competes with TB^+ for the micelles. These results are in agreement with the findings of Kabir-ud-Din et al. [42]. Though the values differ, the kinetically determined K_B^1 values are pertinent for the reason that they belong to the actual experimental conditions. It can be concluded that both binding constants, K_B and K_B^1 decreased with the presence of 0.1 mol dm^{-3} HCl.

The reduction of TB^+ with HA^- in the absence of HCl, which proceeds very slowly, was catalyzed by CTAB micelles. The two primary physicochemical factors responsible for the change in the observed first order rate constant were: the change in the reactivity of the reactants on transfer from water to the pseudo-micellar phase and increased encounter probability of reactants in the micellar phase. In the absence of HCl, TB^+ was bound to CTAB micelles by hydrophobic interaction and HA^- was bound to the micelles by electrostatic interaction. In other words, both reactants were bound to the CTAB micelles, i.e., concentrated in a small volume and their reactivities might also be changed so that the reaction was accelerated, since the rate constant of this reaction in the pseudo-micellar phase, k_m, was about twice the value of k_0.

On the contrary, reduction of TBH^{2+} with H_2A in the presence of HCl was retarded by CTAB micelles. The value of rate constant in the micellar phase, k_m, was less than that in the bulk phase, k_0. The reduction of TBH^{2+} is inhibited about 3-fold in micelles in the presence of HCl. The decrease of pseudo-first order rate constant, k_ψ, as a function of CTAB concentration is as expected for the situation where H_2A is almost entirely in aqueous phase and TBH^{+2} is partially bound to the micelles. It is worthwhile to note that the reaction rate between H_2A in the bulk and TBH^{+2} associated with CTAB micelles is smaller than its rate in aqueous solution. This effect is not difficult to interpret by using results of binding studies which indicate that there is no interaction between H_2A and CTAB micelles in the presence of HCl. It must also be remembered that exclusion of the H^+ ions from micellar surface can also be responsible for the smaller value of k_m obtained in the presence of HCl. Although we have not calculated the apparent pK_a values of TB^+ and AA in the micellar pseudophase, it is well known that micelles almost certainly shift the apparent pK_a values [37,38].

4. Conclusions

The data presented show that in the absence of HCl, the reduction rate of TB^+ with AA is accelerated as the concentration of CTAB increased. The rate enhancement is derived largely from reactants being concentrated into a small volume of the micellar pseudophase. However, in the presence of HCl, the rate is greatly retarded, because uptake of TB^+ to micelles lowers its concentration in the aqueous phase. Changing species of TB^+ and AA in acidic pH, must be responsible for this opposing effect of CTAB micelles.

The effect of CTAB micelles on the reaction rate in the absence and presence of HCl, is well described by pseudophase model. Binding of TB^+ and AA to CTAB micelles has been calculated separately in order to interpret the micellar effects on the reaction rate. TB^+ incorporated in or on the cationic CTAB micelles by hydrophobic attraction. The binding of TB^+ to CTAB micelles decreased in acidic pH due to the increased positive charge on TB^+. AA was found to have the highest binding constant to CTAB micelles in the absence of HCl, whereas no interaction was observed in the presence of HCl where undissociated species of ascorbic acid is dominant.

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