

Catalytic effect of CTAB reverse micelles on the reduction of toluidine blue by ascorbic acid

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The kinetics of the reduction of toluidine blue by ascorbic acid has been studied in the presence of CTAB/CHCl₃/hexane/water reverse micelles. In the absence of added acid, the reaction obeys simple first order kinetics with respect to both the reactants. The second order rate constant in the presence of reverse micelles, k_w ($0.027 \text{ M}^{-1} \text{ s}^{-1}$) was found to be about sixty times greater than that in aqueous medium, k_0 ($4.50 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) under identical experimental conditions. The significant increase is attributed to the concentration effect in the reverse micelles, and, lower micro-polarity due to the reverse micelles, which facilitates the reaction between oppositely charged ions. The effect of variation of W ($= [\text{H}_2\text{O}]/[\text{CTAB}]$) at constant [CTAB] and variation of [CTAB] at fixed W has been studied. The kinetics at $W < 6$ is explained on the basis of the special properties of the entrapped water, while the kinetics at $W > 10$ is explained on the basis of ionic strength.

Keywords: Kinetics, Toluidine blue, Ascorbic acid, Water pools, CTAB, Micelles, Reverse micelles

Reverse micelles and microemulsions are the subject of increasing interest as reaction rates, reaction pathways and equilibrium positions are greatly altered in these systems as compared to conventional solvents¹⁻³. This is particularly true in the case of enzyme catalysed reactions where water droplets provide a unique microenvironment for proteins and serve as powerful models for biological systems⁴. Reverse micelles, which are nanosized aqueous droplets encapsulated by surfactant molecules existing at various compositions, are used widely in the synthesis of many types of nanoparticles⁵.

When surfactants aggregate in non-polar solvents, their polar or charged groups are located in the interior or core of the aggregate while their

hydrocarbon tails extend into the bulk solvent. Thus, water is readily solubilised in the polar core, forming a water pool and this solubilised water exhibits peculiar properties characterised by a parameter W ($= [\text{H}_2\text{O}]/[\text{Surfactant}]$)⁶. When the reactants are in the water pool they are concentrated and act as a nano-reactor leading to a concentration effect in the micellar pseudo-phase. At low water contents where $W \leq 5$, the water is structured due to interactions with the polar head groups and counter ions. When $W > 12$ unstructured 'free' water appears in the water pools. The properties of the structured water are different from those of free water and these properties alter the reactions rates. For example, the solubilising capacities of the two pseudo-phases are different; the structured water has comparatively lower dielectric constant, lower mobility and a high ionic strength due to the counter ion in the case of ionic surfactants.

Systematic studies on the kinetics of electron transfer reactions in the presence of CTAB/CHCl₃/hexane/water reverse micelles are limited. In our previous work, we have studied the aquation of tris-2, 2'-bipyridyl iron(II)⁷, base hydrolysis of tris-1,10'-phenanthroline iron(II)⁸ and oxidation of iodide by V(V)⁹ in the presence of CTAB reverse micelles. The kinetics of toluidine blue-ascorbic acid reaction in the presence of CTAB and SDS aqueous micelles has been studied^{10,11}. In order to investigate further the influence of these unique properties of the water pools on kinetics of electron transfer reactions, we have taken up a kinetic study of the reduction of toluidine blue by ascorbic acid in the presence of CTAB reverse micelles.

Experimental

All the reagents used were of analytical reagent grade and solutions were prepared in doubly distilled water. Toluidine blue (TB) (3-amino-7-dimethyl amino-2 methyl phenazathionium chloride) and ascorbic acid (H₂A) were purchased from Aldrich and were used as received. Stock solutions of toluidine blue $6.36 \times 10^{-3} \text{ M}$ and ascorbic acid 0.6 M were prepared by dissolving the appropriate amounts of these compounds in doubly distilled water. Cetyl trimethyl ammonium bromide (CTAB) received from Merck (India) was used without further purification. Hexane and chloroform were distilled before use.

A 0.1 *M* solution of CTAB was prepared by dissolving appropriate amount of CTAB in a chloroform-hexane (3:2 *v/v*) mixture.

A typical experiment was carried out as follows: Small quantities of aqueous solutions of toluidine blue (0.022×10^{-3} L) were injected into 10×10^{-3} L of CTAB solution using a micro pipette. Ascorbic acid (0.025×10^{-3} L) was then added to initiate the reaction. The mixtures were shaken sufficiently to obtain a transparent and apparently homogenous solution that can be regarded as a reverse micellar system. In all the experiments, the molar ratio of [Water] to [CTAB], i.e., *W* was varied in the range 0.870 – 25.0 (corresponding to 0.047×10^{-3} L – 0.45×10^{-3} L of water).

Although the reverse micellar systems are heterogeneous on the molecular scale, they are macroscopically homogeneous and isotropic. Since they are optically transparent, a change in the concentration of the reactant/product can be followed spectrophotometrically. The reduction kinetics of toluidine blue (TB^+) with ascorbic acid (HA^-) was carried out under pseudo-first order conditions, i.e., $[HA^-] \gg [TB^+]$, by taking the initial concentration of toluidine blue as 1.4×10^{-5} *M* and that of ascorbic acid in the range 1.1×10^{-3} – 2.5×10^{-3} *M*. The reactions were monitored by measuring the decrease in absorbance of TB^+ at 625 nm using a Shimadzu UV-1800 spectrophotometer. The temperature was maintained at 302.0 ± 0.1 K in the reaction cell of the spectrophotometer with a thermostatic bath. The observed first order rate constants were calculated by a linear least squares method from the relationship $\log(A_t/A_\infty)$ versus time. The kinetic data are the averages from triplicate runs with reproducibility less than $\pm 5\%$.

Results and discussion

In the studies on reactions in reverse micelles involving water-soluble reactants, the reactivity in the aqueous droplets of the reverse micelle is usually compared with that in bulk aqueous medium. In the case of first order reactions the measured rate constants may be compared directly in both the systems. However, in the case of bimolecular processes, the calculation of the second order constant involves consideration of the concentration of the species in the reverse micelle. Also, the question arises as to whether the overall concentration or the concentration in the entrapped water, i.e., the effective concentration, should be taken into account. In the present reaction, the reduction of toluidine blue by

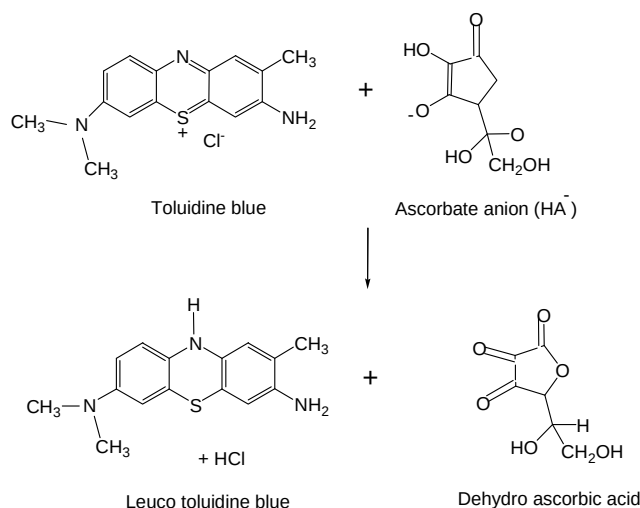
ascorbic acid has been investigated in neutral medium. In the neutral medium, the negatively charged species of ascorbic acid, i.e., HA^- , is the dominant species^{10,11,12} ($pK_{a1} = 4.17$, $pK_{a2} = 11.57$). Since both the reactants, i.e., HA^- and TB^+ , are ionic, they cannot exist in the oil phase and are constrained to the solubilised water only. Therefore, their effective concentrations are considered for calculation of k_2 . For the calculation of second order rate constant, the effective concentration of a reactant in the water pool is calculated by dividing the overall concentration by the volume fraction (*f*) of solubilised water¹³. The volume fractions lie in the range $(4.70-45.0) \times 10^{-3}$ L for 10×10^{-3} L of 0.1 *M* CTAB, and therefore, there is a 212.7-22.20 fold increase in concentration. For example, if the concentration of CTAB is 0.1 *M*, *W* = 4.61, *f* = (0.083/10) and $[HA^-]_{\text{overall}} = 1.5 \times 10^{-3}$ *M* then $[HA^-]_{\text{effective}} = \{[HA^-]_{\text{overall}}/f\} = \{1.5 \times 10^{-3}/0.0083\} = 0.181$ *M*. Herein, the subscript 'o' is used to represent overall concentrations and subscript 'e' to represent effective concentration.

The reaction between TB^+ and HA^- in CTAB/ $CHCl_3$ /hexane/water mixtures obeys first order kinetics with respect to TB^+ as observed by the linear plots of $\log(\text{absorbance})$ versus time, under the condition of $\{[HA^-]_o \gg [TB^+]_o\}$. The pseudo-first order rate constant is directly proportional to $[HA^-]$, indicating first order kinetics with respect to the $[HA^-]$ (Table 1). The reaction is shown in Scheme 1.

The second order rate constant, k_2 , has been determined over a wide range of *W* (0.870–25.0) at constant [CTAB] and also at varying [CTAB] (Table 2). At constant [CTAB], k_2 increases with *W* but in the range of *W* = 0.870–6.61, the increase in k_2 is much less compared to the increase in k_2 in the range 10.0 – 25.0. In the lower *W* range, the confined water is utilised to solvate the ionic surfactant head groups and counter ions, and therefore, the reaction can be considered to take place at the interface. The water is highly structured in this low *W* range and

Table 1—Effect of varying $[HA^-]$ on the observed rate constants (*k*). $\{[TB^+] = 1.4 \times 10^{-5}$ *M*; $[CTAB]_o = 0.1$ *M*; *T* = 302.0 K}

$10^3 \times [HA^-]_o$ (<i>M</i>)	<i>W</i> = 5.61		<i>W</i> = 25.0	
	$10^2 \times [HA^-]_e$ (<i>M</i>)	$10^3 \times k'$ (<i>s</i> ⁻¹)	$10^3 \times [HA^-]_e$ (<i>M</i>)	$10^3 \times k'$ (<i>s</i> ⁻¹)
1.1	11.0	4.80	24.0	6.60
1.5	15.0	6.30	33.0	9.20
1.7	17.0	6.90	37.0	9.90
2.1	21.0	8.30	46.0	1.25
2.5	25.0	1.02	55.0	1.43



Scheme 1

is associated with special properties like lower micro- polarity. The reaction, being a cation-anion reaction, is facilitated by the lower micropolarity of the structured water at the interface. With increase in $\mathbf{W}$, the micropolarity increases, resulting in decrease in rate. At the same time, with increasing $\mathbf{W}$, the ionic strength decreases, and therefore, k_2 should increase since lower ionic strength favours a cation-anion reaction. In the case of ionic surfactants, the value of $\mathbf{W}$ regulates the concentration of polar heads of the surfactant (CTA^+) and its counter ions (Br^-) in the aqueous water pool, and therefore, $\mathbf{W}$ gives the value of ionic strength¹⁴. For example, at $\mathbf{W} = 5.61$ and $[\text{Br}^-]_e = \mu$ and $[\text{Br}^-]_o/f = 0.1/0.01009 = 9.91 \text{ M}$. For a change in $\mathbf{W}$ from 0.870 to 25.0, the ionic strength ($= [\text{Br}^-]_e$) changes from 63.8 M to 2.22 M. The combined effect of these two factors results in a small overall increase in k_2 indicating a slight predominance of ionic strength effect over polarity effect.

At higher $\mathbf{W}$ ($= 10.0\text{--}25.0$), the increase in k_2 is much more pronounced. In this range, the special properties of water become extinct and it is no longer micropolar. Thus, the polarity effect on k_2 is not significant. The acceleration of the reaction is due to decrease in ionic strength with increase in $\mathbf{W}$. Under these conditions, the reaction can be considered to have two components, one at the interface and other in the water pool. With increase in $\mathbf{W}$, the latter component becomes increasingly important. At high $\mathbf{W}$ ($\mathbf{W} > 10$) the entrapped water behaves like bulk water and assuming that only ionic strength effect is present, the effect of $\mathbf{W}$ has been

Table 2—Observed first order (k') and second order rate constants (k_2) for the reduction of toluidine blue by ascorbic acid. $\{[\text{HA}^-] = 1.5 \times 10^{-3} \text{ M}; [\text{TB}^+] = 1.4 \times 10^{-5} \text{ M}; T = 302.0 \text{ K}\}$

$[\text{CTAB}]_0$ (M)	$[\text{Br}^-]_e$ (M)	$10^3 \times f$ (vol. fraction)	$\mathbf{W}$	$10^3 \times k'$ (s ⁻¹)	$10^3 \times k_2$ (M ⁻¹ s ⁻¹)
0.1	21.3	4.70	2.61	7.9	24.74
	15.4	6.50	3.61	7.2	31.20
	12.1	8.30	4.61	6.9	39.20
	9.91	10.0	5.61	6.3	42.00
	8.41	11.9	6.61	5.9	46.82
	5.55	18.0	10.0	7.6	91.23
	3.71	27.0	15.0	8.5	154.4
	2.77	36.0	20.0	9.2	226.2
	2.22	45.0	25.0	9.5	287.9
0.2	41.7	4.70	1.30	8.8	27.60
	21.3	9.39	2.61	6.9	43.26
	15.4	12.9	3.61	6.7	57.70
	12.1	16.5	4.61	5.8	63.73
	9.91	20.2	5.61	5.1	68.64
	8.41	23.8	6.61	4.9	77.80
	5.55	36.0	10.0	5.9	140.4
	3.71	54.0	15.0	7.0	250.0
	2.77	72.0	20.0	7.4	360.6
	2.22	90.0	25.0	7.6	420.0
0.3	63.8	4.70	0.87	9.0	28.20
	41.7	7.20	1.30	8.4	40.33
	21.3	14.1	2.61	5.1	47.93
	15.4	19.5	3.61	4.6	59.74
	12.1	24.9	4.61	4.2	69.73
	9.91	30.3	5.61	3.9	79.20
	8.41	35.7	6.61	3.7	88.10
	5.55	54.0	10.0	5.1	189.0
	3.71	81.0	15.0	5.7	308.1
	2.77	108	20.0	5.9	427.5
	2.22	135	25.0	6.2	563.6

assessed in terms of ionic strength relating the rate constant k_2 (Eq. 1),

$$k_2 = k_2^0 \frac{\gamma_{\text{HA}^-} \gamma_{\text{TB}^+}}{\gamma_{\#}} \quad \dots(1)$$

where γ_{HA^-} , γ_{TB^+} and $\gamma_{\#}$ are the activity coefficients of HA^- , TB^+ and the transition state and k_2^0 is the rate constant at zero ionic strength. According to Guggenheim equation¹⁵, the activity coefficient γ_i of an ion is related to ionic strength (μ) (Eq. 2),

$$-\log \gamma_i = \frac{A Z_i^2 \mu^{1/2}}{1 + \mu^{1/2}} - \sum_j B_{i,j} C_j \quad \dots(2)$$

where A is equal to 0.5, Z_i is the charge on the ions and the summation extends over all ions of concentration C_i . In the present case, the relevant specific interactions are between positively charged micellar surface (M) and HA^- and TB^+ and Br^- , represented respectively by the specific interaction terms B_{M,HA^-} , B_{TB^+,Br^-} . The specific interactions between ions whose concentrations are very small as compared to the concentration of Br^- have been neglected. Using Eqs (1) and (2), it can be shown that

$$\log k_2 = \log k_2^0 - \frac{A\mu^{1/2}}{1+\mu^{1/2}} + B_{M,HA^-} - [M]_e \quad \dots(3)$$

$$+ B_{TB^+,Br^-} - [Br^-]_e$$

and $[M]_e$ is equal to $[CTAB]_e/N$ where N is the aggregation number and $[Br^-]_e$ is equal to $[CTAB]_e$ since the source of Br^- is only CTAB.

$$\log k_2 = \log k_2^0 - \frac{A\mu^{1/2}}{1+\mu^{1/2}} + B_{M,HA^-} - \{[Br^-]_e/N\} \quad \dots(4)$$

$$+ B_{TB^+,Br^-} - [Br^-]_e$$

$$\log k_2 = \log k_2^0 - \frac{A\mu^{1/2}}{1+\mu^{1/2}} + b[Br^-]_e \quad \dots(5)$$

where

$$b = (B_{M,HA^-}/N) + (B_{TB^+,Br^-}) - (B_{\#,Br^-})$$

The ionic strength of the water pool at $W = 5.61$ has been calculated to be 9.91 M and at $W = 25.0$, it is 2.22 M . It is known that at high ionic strengths, variation of the second term in Eq. (2) with can be neglected in comparison with the third term¹⁴. If this is true, a plot of $\log k_2$ versus $[Br^-]_e$ should be linear. Interestingly, the Guggenheim plots are linear and parallel to each other for data at different $[CTAB]$ (Fig. 1). The specific interaction effect is included in the value of 'b' in Eq. (5), which is equal to the slope of the plot between $\log k_2$ versus $[Br^-]_e$. The value of 'b' includes the interaction effect of both the interface and water pool components and was found to be -0.125, -0.121, -0.124 for 0.1, 0.2 and 0.3 M [CTAB] respectively.

With increase in CTAB concentrations at constant W , the second order rate constant increases. This study has been carried out in a detailed manner at low W (5.61) where the entrapped water is highly structured and is associated with lower micro polarity compared to bulk water. It has been reported that the Berezin pseudo-phase model is applicable to reactions taking place in reverse micellar media^{16,17} and according to this model, the second order rate constant k_2 is given by Eq. (6),

$$k_2 = \frac{k_m P_{HA^-} P_{TB^+} CV + k_w(1-CV)}{(1+K_{HA^-}C)(1+K_{TB^+}C)} \quad \dots(6)$$

$$k_2 = \frac{k_m P_{HA^-} K_{TB^+} C + k_w(1-CV)}{(1+K_{HA^-}C)(1+K_{TB^+}C)} \quad \dots(7)$$

where k_m is the rate constant of the reaction at the interface, k_w is the rate constant of the entrapped water, C is the concentration of CTAB, V is the molar volume of surfactant and P_{HA^-} , P_{TB^+} are the partition coefficients of ascorbic acid and toluidine blue respectively. K_{TB^+} , K_{HA^-} are the binding constants of toluidine blue, ascorbic acid and $K_{TB^+} = P_{TB^+}/V$ and $K_{HA^-} = P_{HA^-}/V$.

Neglecting CV in comparison with 1 and if $1 \geq (K_{HA^-}C)$ and $(K_{TB^+}C)$, Eq. (7) becomes Eq. (8).

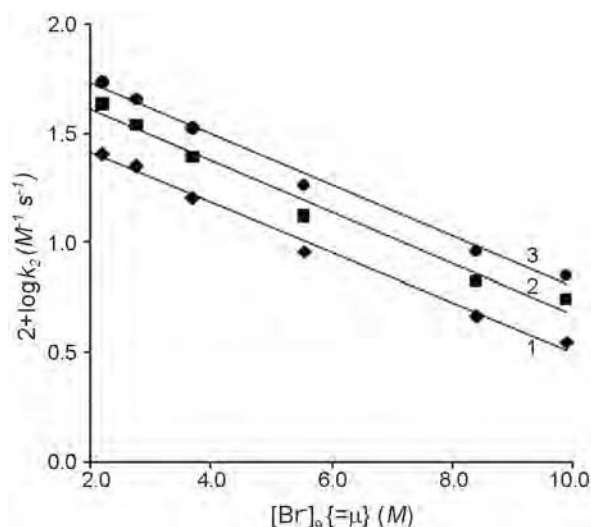


Fig. 1—Effect of ionic strength (μ) (= effective bromide ion concentration $[Br^-]_e$) on reduction of toluidine blue by ascorbic acid, [1, 0.1 M CTAB; 2, 0.2 M CTAB; 3, 0.3 M CTAB].

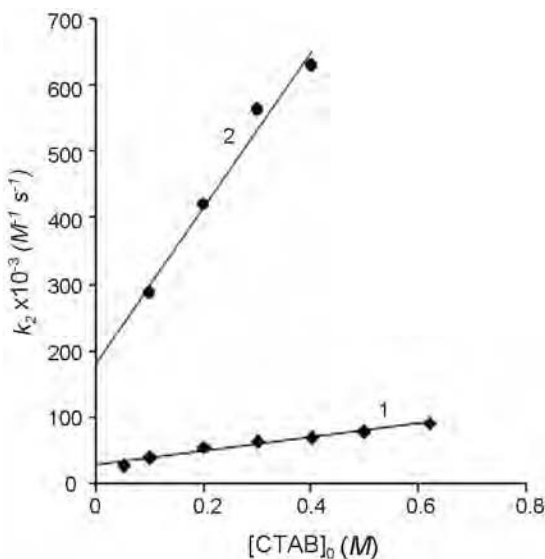


Fig. 2—Effect of [CTAB] at varying water:CTAB ratio on the reduction of toluidine blue by ascorbic acid. [1, 0.1 M CTAB; 2, 0.2 M CTAB].

$$k_2 = k_m P_{HA^-} K_{TB^+} C + k_w (1 - CV) \quad \dots(8)$$

In the present case, a plot of k_2 versus C is linear with a positive intercept (Fig. 2) supporting the assumption, $1 \gg (K_{HA^-})C$ and $(K_{TB^+})C$. The slope corresponds to $k_m P_{HA^-} k_{TB^+}$ and intercept gives the rate constant (k_w) for the reaction in the entrapped water. The value of k_w ($0.027 \text{ M}^{-1} \text{ s}^{-1}$) is about 60 times greater than the rate constant of the reaction in aqueous medium in the absence of surfactant k_0 ($4.5 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$) and bromide ion. The value of k_0 should have been much smaller at this ionic strength i.e., $\mu = 9.91 \text{ M}$ (at $W = 5.61$), but this high ionic strength cannot be achieved in aqueous medium to determine the value of k_0 under identical conditions. This large increase of rate in the reverse micelles illustrates the special properties of entrapped water, i.e., micro-polarity at low W . The Berezin pseudo-phase model has been applied to the data corresponding to higher W also ($W = 25.0$) and the plot of k_2 versus $[\text{CTAB}]_0$ is linear with a positive intercept. The value of k_w ($0.185 \text{ M}^{-1} \text{ s}^{-1}$) is very close to the rate constant of the reaction in aqueous medium at the same ionic strength in the absence of surfactant,

k_0 ($0.230 \text{ M}^{-1} \text{ s}^{-1}$). This shows that the properties of the free, unstructured water at $W = 25.0$ are very similar to that of the bulk water in the aqueous medium.

The present study shows that the reduction of toluidine blue by ascorbic acid is around 60 times faster in the CTAB/ CHCl_3 /hexane/water reverse micellar medium compared to conventional aqueous medium. The significant increase is attributed to the concentration effect produced in the reverse micelles and lower micro-polarity of the reverse micelles, which facilitates the reaction between oppositely charged ions.

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