

## Notes

### A Fixed Time Kinetic and Spectrophotometric Method for the Determination of [C<sub>16</sub>TAB]

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*Received April 19, 2002*

**Key Words :** Surfactants, C<sub>16</sub>TAB, Methylene violet, Dye-surfactant interaction

Surfactants are potential anthropogenic pollutants. Surfactants enter waters and wastewaters mainly through the discharge of aqueous waters from household and industrial laundering and other cleaning operations. Ionic surfactants make up about two thirds of the total surfactants used, and nonionics about one third. Dye-surfactant interactions have been widely studied by a number of spectrophotometric methods for the determination of surfactants.<sup>1,2</sup> A bathochromic shift of the absorption maxima is an indication of its interaction in the micellar medium. This is attributed to the localization of the dye in bulk aqueous medium due to electrostatic repulsion of the cationic micellar surface and to increased delocalization of the pi electron in the conjugated bond system, thus leading to a change in the excited energy states. Methylene violet is a water-soluble dye of phenazine class,<sup>3</sup> has a sharp absorption peak in visible region and exhibits a bathochromic shift of 20 nm with C<sub>16</sub>TAB. Therefore, an analytical method for determining trace amounts of C<sub>16</sub>TAB has been designed. Furthermore, the oxidative depletion of MV<sup>+</sup> by chloramine-T<sup>4</sup> abbreviated as CAT is specifically and selectively catalyzed by C<sub>16</sub>TAB. Thus, based on the MV<sup>+</sup>-CAT reaction as an indicator reaction, a fixed time kinetic analytical method for the trace determination of a C<sub>16</sub>TAB is also proposed, whereas the kinetics and mechanism of this reaction are discussed elsewhere.<sup>5</sup>

#### Experimental Section

The chemicals used were of high purity (Aldrich, B.D.H.), and double distilled water was used throughout to prepare the solutions.

1) Chloramine-T solution. A stock solution of  $1.0 \times 10^{-2}$  mol dm<sup>-3</sup> CAT (E. Merck) was prepared by dissolving 0.2817 g in 100 mL of water.

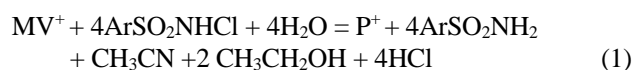
2) Methylene Violet solution. A stock solution of  $1.0 \times 10^{-3}$  mol dm<sup>-3</sup> MV<sup>+</sup> was prepared by dissolving 0.0379 g of

methylene violet (Aldrich) in 100 mL water. Working solutions were prepared by appropriate dilution of the stock solution.

3) C<sub>16</sub>TAB. The 100 mL stock solution of  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> the detergent (BDH) was prepared by dissolving 0.0364 g of C<sub>16</sub>TAB in 50% acetic acid (v/v).

4) Perchloric acid. A stock solution of  $1.0 \times 10^{-1}$  mol dm<sup>-3</sup> HClO<sub>4</sub> was prepared by diluting the previously standardized acid.

**Kinetic Procedure.** In all the experiments the pseudo-first-order kinetics with respect to methylene violet were monitored at 560 nm, using a systronix UV-VIS spectrophotometer. Beer's law was valid for the measurement under the experimental conditions considered. No interference from the reagents, intermediates or products was observed at 560 nm. The total initial volume of the reaction mixture was 10 mL at (25.0 ± 0.1 °C). In all the experiments, the reactions were monitored up to two half lives. Constant ionic strength of the reaction mixture was maintained by adding the required amount of sodium sulphate solution.



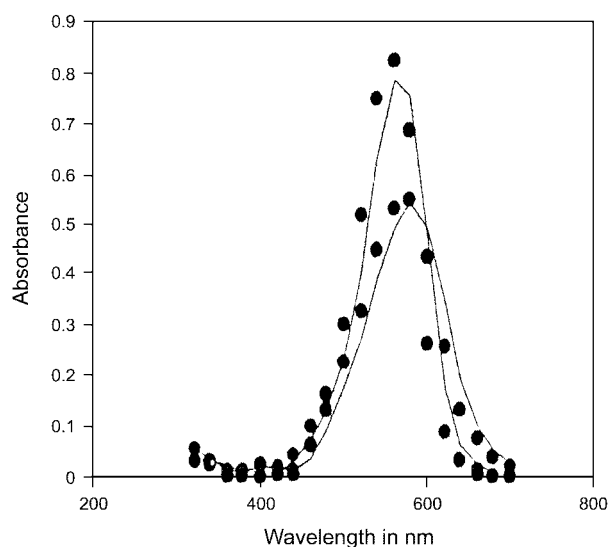
P<sup>+</sup> = 7-amino-9-phenyl quinoxaline-2,3-dicarboxylic acid.<sup>5</sup>

#### Results and Discussion

The addition of C<sub>16</sub>TAB to the dye solution shifts its absorbance maxima from 560 nm to 580 nm (Figure 1). The calibration curve [Table 1] exhibits linearity for the range of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> to  $7.0 \times 10^{-4}$  mol dm<sup>-3</sup>. Beyond this range linearity was not obtained. This is obviously because of the fact that the MV<sup>+</sup>-surfactant interactive species is solubilized near the critical micelle concentration (cmc) of the detergent. The reported cmc of C<sub>16</sub>TAB is  $9.1 \times 10^{-4}$  mol dm<sup>-3</sup>.

**Scope as kinetic-catalytic indicator reaction.** To find a still lower limit of determination, and considering the substantial catalytic effect [Table 2] of C<sub>16</sub>TAB on the MV<sup>+</sup>-CAT reaction, a fixed time method was tested. The scope of the title reaction as the catalytic indicator reaction was very

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**Figure 1.** Repetitive Scan and shifting of absorbance maxima.

**Table 1.** Dye-surfactant interaction ( $[MV^+] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$ ; Temperature 25 °C)

$[CTAB]/10^{-4} \text{ mol dm}^{-3}$	Absorbance*
Nil	0.512
1.0	0.620
2.0	0.634
3.0	0.645
4.0	0.630
5.0	0.663
6.0	0.678
7.0	0.683

\*Mean of duplicate experiments.

**Table 2.**  $C_{16}TAB$  Catalyzed Reaction ( $[MV^+] 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[H^+] 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; [chloramine-T]  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ; Temperature 25 °C)

$[C_{16}TAB] \times 10^{-5} \text{ mol dm}^{-3}$	$*k_0' \times 10^{-2} \text{ s}^{-1}$
Nil	2.35
1.0	3.15
2.0	6.35
3.0	9.36
4.0	12.70
5.0	18.11
6.0	20.70

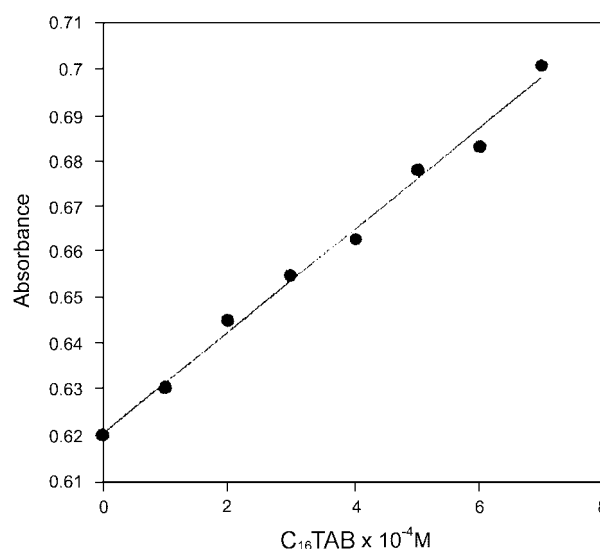
\*Mean of duplicate runs.

promising. In this fixed time method the lowest determination limit fell to the  $5.0 \times 10^{-6} \text{ mol dm}^{-3}$  range. The plot of log Abs (for a fixed time) versus  $[C_{16}TAB]$  yields a good straight line. Reagent solutions were mixed in the order of 2.0 mL each of methylene violet and perchloric acid. Water, bringing the total volume to 10.0 mL, plus catalyst or other reagents were used when necessary. A separately thermostatted solution of CAT 2.0 mL was added to commence the reaction. After vigorous mixing, the solution was transferred to a spectrophotometer cell. A fixed time procedure was

**Table 3.** Absorbance values of methylene violet at fixed time for  $[C_{16}TAB]$  variation ( $[MV^+] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[H^+] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ ;  $[CAT] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ; Temperature 25 °C)

$[CTAB]/10^{-5} \text{ mol dm}^{-3}$	Absorbance* 300s
–	0.784**
0.05	0.762
0.07	0.729
0.09	0.671
1.0	0.687
2.0	0.551
3.0	0.462
4.0	0.325
5.0	0.276
6.0	0.207

\*Mean of triplicate runs. \*\*Not taken for plot.



**Figure 2.** Calibration curve, direct complexation.

**Table 4.** Tolerance ratio of Interferents ( $[MV^+] 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ;  $[H^+] 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ ; [chloramine-T]  $2.0 \times 10^{-4} \text{ mol dm}^{-3}$ ; Temperature 25 °C)

Cation	Tolerance ratio
W(VI), Ce(IV), Se(IV)	10000*
Ca(II), Ba(II), Ru(III), Os(VIII)	1000
Ni(II), Co(II), Mn(II), Fe(III), Cu(II), Pd(II)	100

\*Maximum ratio tested.

used to plot the calibration curves. Kinetic runs were carried out at  $(25.0 \pm 0.1 \text{ °C})$  in duplicate with fixed initial concentrations of  $MV^+ = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $H^+ = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$  and  $CAT = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$  and varied concentrations of  $C_{16}TAB$  in the range of  $1.0 \times 10^{-5}$  to  $6.0 \times 10^{-5} \text{ mol dm}^{-3}$ . The absorbance at 580 nm was measured at the fixed time of 300 s (Table 3). Figure 2 illustrates the log Abs at 300 s versus  $[C_{16}TAB]$ , which is a good straight line with  $r^2 = 0.998$ .

**Interference studies.** In the direct complexation method there was no interference of anions, such as chloride,

bromide, iodide and nitrite, but the kinetic method suffers with the interferences of these ions. Sublation is required, therefore, to get rid of the non-surfactant impurities. The addition of various cations did not interfere in either case. The presence of sodium dodecylsulfate, an anionic surfactant, did not cause interference in the direct interaction, nor did it exhibit any catalytic effect on the oxidation reaction in the chosen range. The effects of the presence of various potential interfering cations were investigated. Synthetic mixtures containing various concentrations of numerous individual metal cations and  $[C_{16}TAB] 1.0 \times 10^{-5} \text{ mol dm}^{-3}$  were prepared. None of the cations tested interference. Table 4 summarizes the tolerance ratios for the presence of each individual species. The analytical results summarized in Table 4, clearly show that the proposed kinetic-catalytic methods have far higher tolerance limits.

### Conclusion

The  $C_{16}TAB$  catalyzed oxidation of methylene violet by

acidic chloramine-T reaction can be effectively used to determine cationic detergent as low as 0.73 mg/L to 6.06 mg/L. Non-surfactant impurities can be easily removed from the real sample by sublation. The direct interaction of the dye and the detergent provides a calibration curve with which  $C_{16}TAB$  can be determined in waste water after sublation up to as low as 36 mg/L. Most of the other cations studied had negligible influence on  $C_{16}TAB$  determination.

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