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Kinetic investigation of an azo dye oxidation by hydrogen peroxide in aqueous surfactant solution

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Abstract

In this study, the oxidation of resorcinol based an azo dye, 5-methyl-4-(2-thiazolylazo)resorcinol (5-Me-TAR) by hydrogen peroxide has been investigated from kinetic, spectroscopic and thermodynamic point of view to examine the influence of a cationic surfactant such as cetylpyridiniumchloride (CPC). Activation energy (298.15–313.15 K) and entropy (298.15 K) of the reaction were calculated as 67 kJ/mol and -72 J mol^{-1} K^{-1} in borate buffer, respectively. However, the addition of CPC into 5-Me-TAR solutions at different pH values always reduced the intensity of its azo form, the intensity of its hydrazone form increased. The oxidation of dye proceeds via perhydroxyl anion and hydrazone tautomeric form and oxidation rate was accelerated by the presence of CPC either in micellar or premicellar regions.

Keywords: Kinetics; Peroxide; Surfactant; Hydrazo; 5-Methyl-4-(2-thiazolylazo)resorcinol

1. Introduction

Hydrogen peroxide is one of the principal oxidation agents for textile, paper and cosmetics industry for the treatment of witness of fabrics, paper, cosmetic products and industrial wastewater due to its low cost, simple handling, effectiveness in destroying the chromospheres and being a friendly alternative to chlorine.

The oxidation of azo dyes has attracted considerable attention in recent years and a number of publications have been appeared in the literature [1–3]. These publications were generally focussed on three main points: (i) pK_a of dye, (ii) tautomeric form of the dye, (iii) oxidant type. It is known that, azo dyes contain a hydroxyl group that is conjugated with an azo-linkage and present as an equilibrium mixture with azo or hydrazone tautomeric forms in aqueous solutions. Since the hydroxyl groups form common anions in alkaline media, this type of equilibria has also to be considered. Such equilibria are particularly important if one dye species tends to be more reactive than the other species in the solutions. A common conception is that hydrazone form is most easily oxidizing form of the dyes by the attack of perhydroxyl anion of H_2O_2 [2,3].

The tautomeric behaviour of hydroxy azo dyes has been investigated in different solutions by UV–Vis and NMR spectroscopy. Solvent effect on the azo–hydrazo equilibria were found not to correlate with any of the physical parameters of the solvents. Generally, a more polar solvent favors the hydrazone form whereas less polar solvents favor the azo form [4–7].

In previous studies, the observed spectral changes of the *o*-hydroxy and *p*-hydroxy azo dye–surfactant interactions with above and below the critic micelle concentration (cmc) have been explained by the interactions between the surfactant molecules and

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different forms of the dyes. This studies showed that addition of cationic surfactants into a dye solution may result in the formation of hydrazone form of the dyes [8,9].

Only a few studies examined the influence of surfactants on the oxidation of azo dyes in alkaline media and these studies were also overlooked for the influence of surfactants upon tautomeric forms of dye [10–15]. Thus, different results were naturally reported by the researchers for the influence of surfactants on the oxidation of azo dyes.

The oxidation of 5-Me-TAR in the presence and absence of CPC was investigated by means of UV–Vis spectrophotometric measurements. This study examines whether the observed rate enhancements arise from the dye specification. The main objective of this study is to examine whether this oxidation process proceeds with less energy or not. All the oxidation rate experiments were carried out over a wide pH and surfactant concentration range to explore the operating and maintaining of the oxidation process.

2. Experimental

While 5-Me-TAR (97%) and CPC (99%) were purchased from Sigma, $NaHCO_3$, Na_3BO_3, H_2SO_4, dimethylformamide (DMF), methanol, acetonitrile and H_2O_2 (30%) were purchased from Merck.

The concentrations of the reactants were 2.65×10^{-5} M (5-Me-TAR), 3.44×10^{-2} M (H_2O_2) and different concentrations of CPC. Reaction mixtures of H_2O_2 and CPC were freshly prepared and all the solutions were prepared in deionized water.

No changes were observed either in the λ_{max} or ε_{max} in the concentration range of 1×10^{-6}–1×10^{-5} M for 5-Me-TAR. In addition, observing no significant changes in the spectra of dye with the variation of temperature from 298.15 to 313.15 K may indicate that the dye is in its monomeric form in the experimental range of the concentration.

The UV–Vis absorption spectra of 2.65×10^{-5} M dye solutions obtained at different pH values were used in the determination of pK_a values of the dye at 298.15 K according to the procedure found elsewhere [12].

The oxidation reaction was spectrometrically monitored by using a Unicam UV2-100 UV–vis spectrophotometer and pH values were measured by a Jenway 3040 model pH-meter. The pH = 4 and 9 buffer solutions were used for calibration. Temperature control was provided using Grand Ltd. thermo circulator.

Kinetic studies were carried out in buffer solutions of low ionic strength by monitoring the maximum absorbance values as a function of time. Reactants were allowed to reach the reaction temperature before mixing. Experiments were conducted under pseudo first-order, i.e. $[H_2O_2]_T >> [Dye]_T$ where $[H_2O_2]_T$ and $[Dye]_T$ are the total concentrations of peroxide and dye, respectively. Absorbance is directly proportional to the dye concentration, therefore, the rate of change in the absorbance is equal to the rate of oxidation of dye, and thus the rate law is described by,

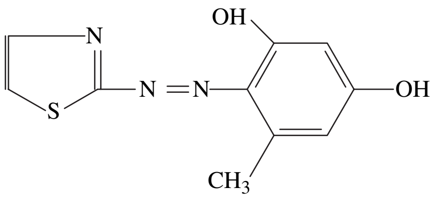
$$-\frac{d[Dye]}{dt} = k_{obs.}[Dye]_T = k_{2obs.}[Dye]_T[H_2O_2]_T \quad (1)$$

The $k_{2obs.}$ is calculated from the time dependence of the absorbance

$$k_{2obs.} = \frac{d(\ln A)/dt}{[H_2O_2]_T} \quad (2)$$

The cmc values of surfactants remarkably change with pH, ionic strength of the solution and chemical structure of dye. Therefore, primary cmc value of the employed surfactant has been determined under the experimental conditions. The absorbance value of hydrazone form of 5-Me-TAR was increased with the addition of CPC at 491 nm wavelength. When the absorbance maxima were plotted versus −log[CPC], the graph shows a break in the linear plot as shown in Fig. 1. This break is considered to be the cmc of CPC corresponding to 9×10^{-4} M concentration.

5-methyl-4-(2-thiazolylazo)resorcinol (5-Me-TAR)



3. Results and discussion

3.1. Spectroscopic studies of 5-Me-TAR

3.1.1. Determination of tautomeric properties of 5-Me-TAR

The UV–Vis spectral behaviour of 5-Me-TAR in a number of different organic solvents were examined and absorbance and λ_{max} values were given in Table 1. The spectral data indicate that the dye exists in azo–hydrazone tautomeric equilibrium in methanol, ethanol, DMSO, DMF solvents, while it is present mainly in the azo form in acetone and water. This tautomerization

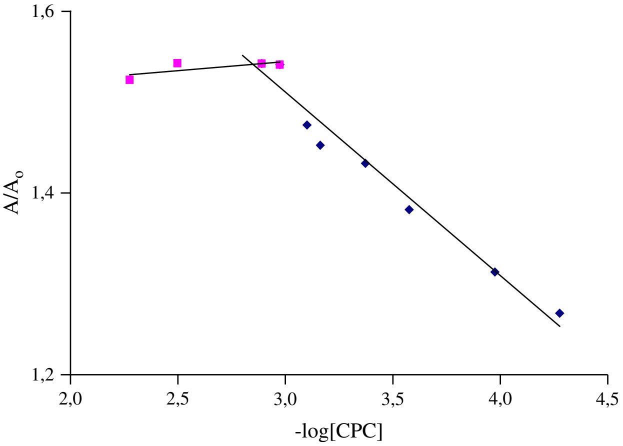


Fig. 1. Plot of A/A_o versus log[CPC] at pH 10 and 298 K.

resulted from the intramolecular proton transfer between nitrogen and oxygen atoms, depending on the solvent polarity and microscopic environment of the dye in the solvent matrix. The proportional relative tautomerization is largely depending on the polarity of the solvent (e.g. DMF, DMSO) and the tendency of the hydrazone form to be stabilizied by H-bonding interaction with the solvent molecules (e.g. methanol and ethanol).

3.1.2. Determination of dye pK_as and effect of CPC on its

The effect of pH on the electronic spectra of 5-Me-TAR of 2.65×10^{-5} M concentration at pH range of 4.0–13.0 was studied in different CPC concentrations below the cmc and free dye solution in low ionic strength. Figs. 2 and 3 show the effect of pH on the absorption spectra of 5-Me-TAR. When the pH of the solution is increased from 4.7 to 6.7, the absorbance of the dianionic dye form is gradually increased at 427 nm wavelength. No significant changes in the absorbance of this band have been observed between pH values of 7.0 and 10.5. When pH value of the solution was increased above 10.5, trianionic form of the dye was appeared in the spectrum at 503 nm wavelength (Fig. 3).

Table 1
λ_{max} (nm) and absorbance values of 5-Me-TARs tautomeric forms in different solvents

Solvent	λ_{max} (nm) of azo form	A of azo form	λ_{max} (nm) of hydrazo form	A of hydrazo form
Acetone	416	0.540	–	–
Water	418	0.535	–	–
Methanol	418	0.459	474	0.641
Ethanol	422	0.460	451	0.584
DMSO	418	0.465	473	0.651
DMF	–	–	496	1.002

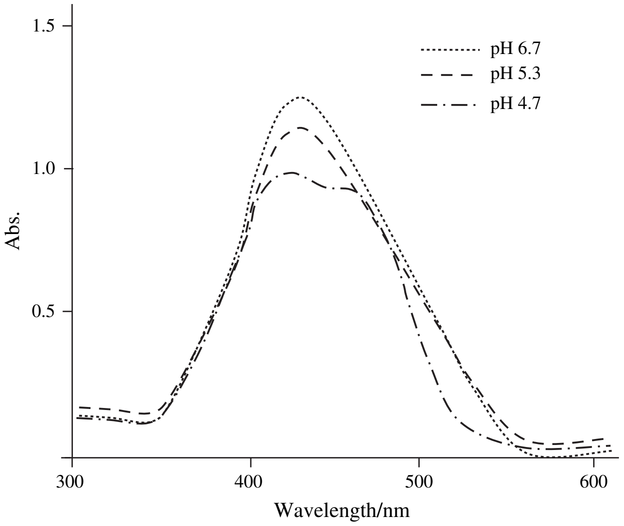


Fig. 2. UV–Vis spectra of 5-Me-TAR between pH 4.7 and 6.7.

5-Me-TAR triprotic acid (H_3D), giving up its first proton in acidic medium, so that dye can be represented as H_2D^-, which process the following equilibria:

$$H_2D^- + H^+ \leftrightarrow HD^{2-} + H^+ \leftrightarrow D^{3-} + H^+ \quad (3)$$

Both pK_2 and the pK_3 values of the dye were calculated from the pH–absorbance relation at $\lambda_{max} = 427$ nm and 503 nm wavelength (Table 2). The CPC affects pK_2 and pK_3 values. For instance, the calculated pK_3 value of the dye with CPC was lower than that of the pK_3 value for free dye, probably due to stabilization of the D^{3-} form of the dye ion pair formation with the surfactant cation before the micelle formation. The organic part of the dye is diffused into the micelles while the ionic or polar groups lie in the

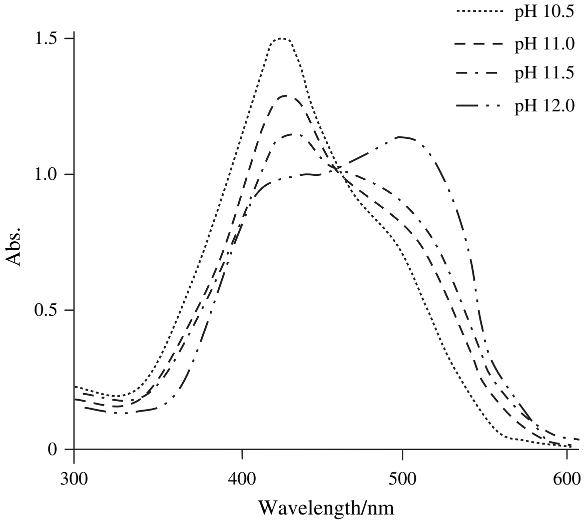


Fig. 3. UV–Vis spectra of 5-Me-TAR between pH 10.5 and 12.0.

Table 2
Surfactant effect on pK_a values of the 5-Me-TAR

Surfactant concentration	pK_2	pK_3
0	5.7	11.8
1.8×10^{-4} M	4.6	10.5
4.5×10^{-3} M	4.0	10.0

Gauy-Chappman layer near the Stern layer. The ionisable protons are oriented and organised at the micelle surface causing a decrease in the pK_3 value due to the attraction of the OH^- or the repulsion of the H^+ ions at the micelle surface by cationic head groups (Figs. 4 and 5).

The absorption spectra of 5-Me-TAR alone and in the varying concentration of CPC in aqueous solution at different pH values are shown in Fig. 6. The spectra of 5-Me-TAR are characterised by two main bands at each pH value. The absorbance of the shorter wavelength maximum shows a decrease with the increasing of CPC concentration until a shoulder appears at higher concentrations. The absorbance of the higher wavelength maximum shows an increase during this process. This behaviour may be interpreted that 5-Me-TAR exists in an azo–hydrazone tautomeric equilibrium in aqueous surfactant solution.

According to the experimental data, the shorter wavelength maximum corresponds to the absorption by the azo form, and the longer wavelength maximum corresponds to absorption by the hydrazone form. Hydrazone form is more polarizable and firmly attached to the head-groups of neighbouring surfactant molecules. Strong interactions between carbonyl group of 5-Me-TAR and the positive charge of pyridinium on the surfactant molecule play important role in the formation of the hydrazone form. The organic hydrophopic part of dye is solubilisied into the micelles core while the hydroxyl and hydrazo groups lie in Stern-Layer oriented near the micelle surface. The vacancies inside of the micelle core may be able to accommodate flexible hydrazo form of the dye.

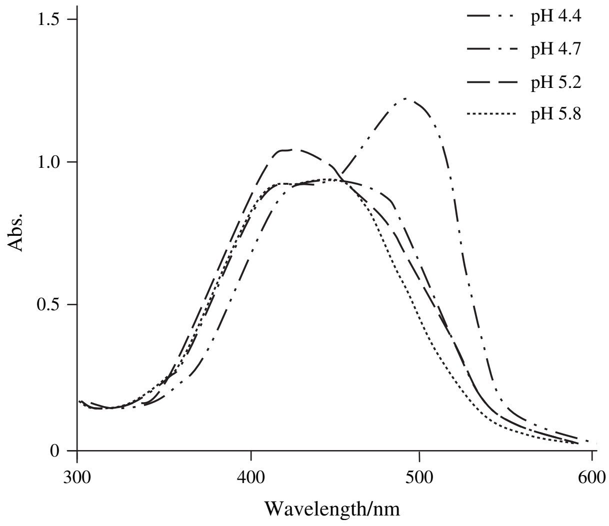


Fig. 4. UV–Vis spectra of 5-Me-TAR in the presence of 1.8×10^{-4} M CPC between pH 4.4 and 5.8.

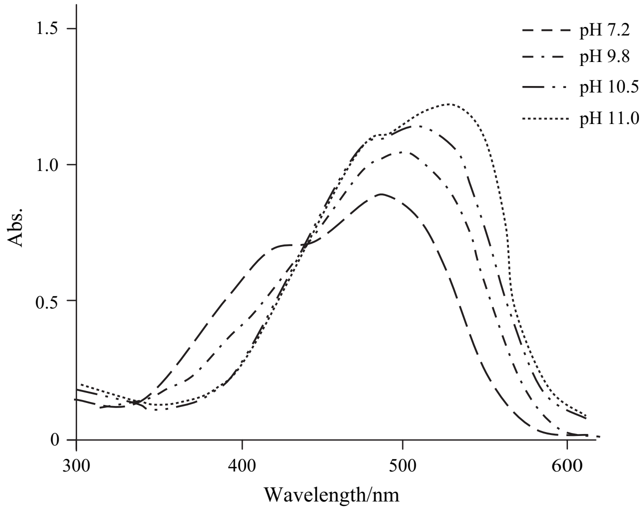


Fig. 5. UV–Vis spectra of 5-Me-TAR in the presence of 1.8×10^{-4} M CPC between pH 7.2 and 12.3.

3.2. Kinetics of 5-Me-TAR oxidation

3.2.1. Oxidation of an azo dye, 5-Me-TAR

The reaction rate was studied in borate buffer at pH 10.0 over temperature range of 298–313 K, above this temperature the decomposition of H_2O_2 occurs. The activation energy change calculated as $\Delta H^{\#} = 67$ kJ/mol agrees with the reported values for H_2O_2 oxidation of phenolphthalein, alizarin, crocetin [16,17]. The close similarity in the activation energy may show that the oxidation of 5-Me-TAR proceeds via attack of the perhydroxyl anion. Peracid anions are well known to react with unsaturated imines, carbon double bonds or carbonyl containing compounds [18–20].

3.2.2. Influence of the CPCs on the kinetics of 5-Me-TAR oxidations

Observed rate constants, $k_{obs.}$, calculated by Eq. (2) for 2.65×10^{-5} M dye as a function of concentration of CPC at pH 10.0 were given in Table 3. Observed rate constants were increased upon the addition of CPCs, reaching a maximum at 9×10^{-4} M CPC then gradually decreased as the cmc is reached and exceeded. The increasing rate constant with CPC concentration suggest that: (i) reactive form of 5-Me-TAR which is hydrazone form and its concentration was increased with addition of CPC. (ii) Decreasing rate constant indicates that there

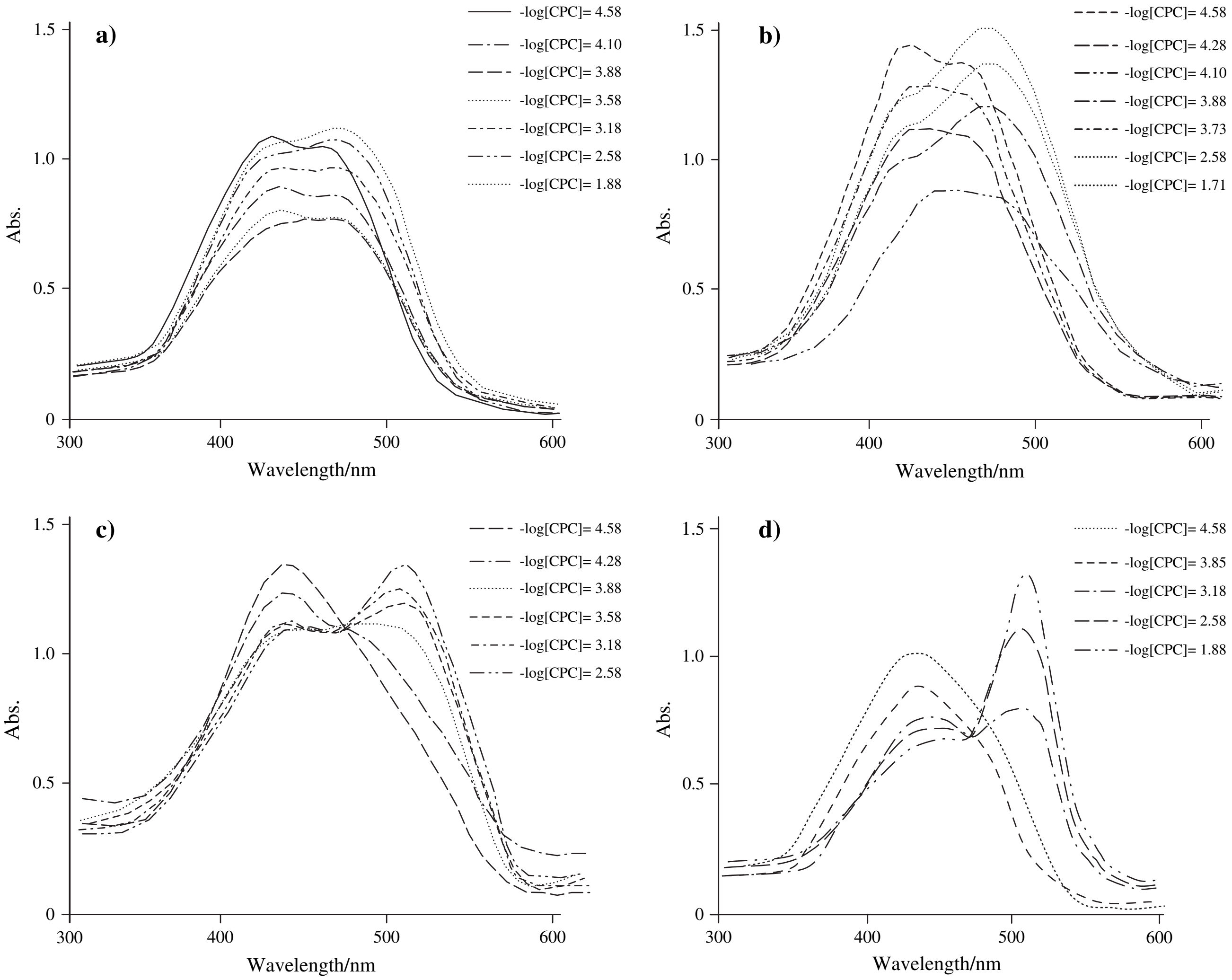


Fig. 6. UV–Vis spectra of 2.65×10^{-5} M 5-Me-TAR as a function of CPC at 298 K (a) pH 3.0 (b) pH 4.7 (c) pH 7.3 (d) pH 10.0.

are two dye environments: one where it is interaction with monomer surfactant molecule in aqueous solution and other where it is incorporated into micelles, where it becomes less reactive to reaction towards H_2O_2 than in solution. Observed rate constants were given for 2.65×10^{-5} M dye as a function of pH in Table 4.

4. Conclusions

We have examined the effect of CPC surfactant on the oxidation of 5-Me-TAR by using H_2O_2. Azo form and common anion are relatively unreactive forms of the dye towards oxidation. The perhydroxyl anion is the active oxidant which initiates oxidation of the hydrazone tautomeric form of the dye. The oxidation rate of dye was accelerated in the presence of CPC and maximum rate is near the cmc. These results may show that the oxidation rate largely depends on the interactions between the dye and surfactant molecules. Surfactant addition may influence the keto–enol tautomerism that is reflected in a change in the absorption bands corresponding to azo–hydrazo forms. This change is due to formation of ion pairs between the dye and surfactant molecules. Not only the oxidation of azo dyes in the presence of surfactants accelerated reaction rate but also surfactant molecules can precipitate the oxidation products and remove the heavy metal ions associated with the dye wastewater up to some extent.

Table 3
Increase in the rate, $k_{2\text{obs.}}$ of oxidation of 2.65×10^{-5} M dye at pH 10.0 and 298 K as function of [CPC]

$-\log[S]$	no	3.97	3.58	3.37	3.28	3.16	3.02	2.74	2.57	2.45	2.35	2.27	2.21	2.15	2.10	2.06
$k_{2\text{obs.}} \times 10^{+2}$ ($M^{-1}\,s^{-1}$)	0.30	0.57	0.80	0.81	0.87	1.08	2.07	1.92	1.80	1.86	1.39	1.54	1.46	1.44	1.06	1.02

Table 4
Effect of pH on $k_{2\mathrm{obs.}}$ for oxidation of 2.65×10^{-5} M dye at 298 K

pH	Buffer	$k_{2\mathrm{obs.}}$ (no CPC)	$k_{2\mathrm{obs.}}$ (1.8×10^{-4} M CPC)	$k_{2\mathrm{obs.}}$ (4.5×10^{-3} M CPC)
8.0	Borate	8.86E-05	4.50E-04	1.34E-04
8.5	Borate	4.68E-04	5.86E-04	5.93E-04
9.0	Borate	8.30E-04	7.54E-04	8.91E-04
9.5	Borate	2.16E-03	4.19E-03	2.48E-03
10.0	Borate	2.99E-03	4.94E-03	3.10E-03
10.5	Carbonate	3.26E-03	4.47E-03	3.74E-03
11.0	Carbonate	5.85E-04	2.66E-03	4.84E-03

References

[1] Oakes J, Gratton P. J Chem Soc Perkin Trans 1998;2:1857.
[2] Bredereck K, Schumacher C. Dyes Pigments 1993;23:1212.
[3] Bredereck K, Schumacher C. Dyes Pigments 1993;21:45.
[4] Bhawat RV, Karambelkar NP, Tiwari A. Indian J Chem 1982;21:419.
[5] Reeves RL, Kaiser RS, Maggio MS, Sylvester EA, Lawton WH. Can J Chem 1973;51:628.
[6] Reeves RL, Kaiser RS. J Org Chem 1970;35(11):3670.
[7] Grasso D, Millefiori S, Fasone S. Spectrochim Acta 1975;31:187.
[8] Dakiky M, Mencova I. Dyes Pigments 2000;44:181.
[9] Reeves RL, Kaiser RS, Mark HW. J Colloid Interf Sci 1973;45(2).
[10] Hamada K, Nishizawa M, Yashida D, Mitsuishi M. Dyes Pigments 1998;36(4):313.
[11] Tokuda J, Ohura R. Textile Res J 1999;69(6):456.
[12] Oakes J, Gratton P, Gordon-Smith T. Dyes Pigments 2000;46:169.
[13] Oakes J, Gratton P. Aatcc Review 2003;3(10):22–6.
[14] Oakes J, Gratton P, Wilkes I, Gordon-Smith T. Coloration Technology 2001;117(2):76–81.
[15] Oakes J. Text Chem Color Am D 2000;32(11):47–52.
[16] Thompson KM, Griffith WP, Spiro M. J Chem Soc Farad Trans 1993;89(22):4035.
[17] Thompson KM, Griffith WP, Spiro M. J Chem Soc Farad Trans 1993;89(8):1203.
[18] Davies DM, Jones P. J Org Chem 1978;43:769.
[19] Robson P. J Chem Soc 1964;5170.
[20] Davies DM, Deary ME. J Chem Soc Perkin Trans 1991;2:1549.