

Influence of a Crown Ether on the Spectral Properties of Triarylmethane Dyes in Aqueous and Micellar Environments

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This study demonstrates the spectral data for two triarylmethane dyes, malachite green and crystal violet, at room temperature. Effects of micellar environment and crown ether addition on the spectral behaviour of these dyes are studied using absorption spectroscopic method. The dye-anionic surfactant interactions in micellar media are investigated. The chosen surfactants with different alkyl chain length are SOS, STS, SHS and SDS. Effect of a crown-ether (*i.e.* aza-15-crown-5) addition on the absorption spectra and decolorization of the dyes is also studied at room temperature. Moreover, effect of crown ether addition on the micellar properties of the media is studied and compared. Spectroscopic analysis shows that the dye decolorization can be accelerated in presence of the crown ether. Conversely, the decolorization process can be inhibited in the micellar media. The nature of decolorization process is interpreted in terms of direct and indirect mechanisms of crown-ether and the dye interactions.

Keywords: Triarylmethane dyes, Dye-surfactant interactions, Crown ether addition, Decolorization

INTRODUCTION

Dye-surfactant interaction is important from theoretical and practical viewpoints and has been of particular interest. Studies of the interactions between oppositely charged dyes and surfactants give useful information for industrial and scientific applications. The effect of surfactant on the absorption spectra of a wide variety of dyes has been studied by many researchers [1-10]. Surfactants are among the most important amphiphilic materials owing to their specific molecular structure, *i.e.* containing both hydrophobic and hydrophilic part (polar group) in their structure [11]. It is well reported that ionic surfactants can alter the solution properties of dyes, which have an opposite charge. For the oppositely charged dye and surfactant, the attractive forces (electrostatic and hydrophobic forces) between dye and surfactant lead to the formation of dye-surfactant complexes in aqueous solution.

Malachite green, MG, and crystal violet, CV, are cationic triarylmethane dyes, which have a variety of industrial and medical applications [12,13]. The photochemical and photophysical properties of this group of dyes have been demonstrated by several authors [14-19]. One of the earliest publications of spectroscopic properties of CV in aqueous

solutions was that of Mandel and co-workers [20]. The effect of solvents on the electronic spectra of some triarylmethane dyes has been reported by Lewis and Indig [21]. The significant role of solute-solute (dye aggregation and ion pair formation) on the spectroscopic properties of crystal violet has been reported by Oliveira and co-workers [22]. They have demonstrated that in solvents with small dielectric constant the formation of ion pairs represents a major contribution to the shaping of the dye spectra, while, solvent-solute interactions is more favorable in solvents with the higher dielectric constant. Recently, the pre-micellar and micellar solvations of the triphenylmethane dyes have been reported by Gohain and co-workers [23]. Their works provides appreciable information and refer to relevant publications in this field.

Among the various forms of environment, the micellar media can be the best choice to reach a deeper understanding of dye-media interactions as compared to the other solvation systems. From practical and scientific aspects, the studies in this area are still important and interesting. Therefore, the present study was undertaken to have a deeper understanding on the media effect on the photo-physical behavior of the investigated dyes.

Crown ethers, as cyclic oligomer additives, exhibit interesting properties. Interest in gaining deep knowledge

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about this group of matter is strongly stimulated by possibility of their applications in many scientific and technological fields. The photophysical of the electron donor aza-15-crown-5 and its derivatives has been investigated by several investigators [24-26].

In the present work, the authors have studied the spectral behavior and cationic dye-anionic surfactant interactions of the triarylmethane dyes (MG and CV) in pre- and post-micellar media and in presence of a cyclic oligomer additive. Therefore, the spectral changes of MG and CV with a series of anionic surfactants having different alkyl chain length such as SOS, STS, SHS and SDS were investigated. Additionally, spectral variations due to interactions between aza-15-crown-5 ($C_{10}H_{21}NO_4$) with the chosen dyes were studied and reported. Finally, effect of crown ether on absorption spectra and decolorization process of the dyes in micellar medium was also explored.

EXPERIMENTAL

Material

Malachite green oxalate, MG, and crystal violet chloride, CV, were obtained from Merck (pro-analysis) and used without further purification as solutes. The chemical structures of the dyes are shown in Fig. 1a.

Sodium octyl-1-sulfonate (SOS) and Sodium dodecyl sulfate (SDS) were purchased from Lobachem and Merck, respectively. Sodium-1-tetradecyl sulfonate (STS), and Sodium-1-hexadecyl sulfonate (SHS) were obtained from Fluka. Surfactants were 8, 12, 14 and 16 carbonic organic compounds. The chemical structures and critical micelles concentration (cmc) are shown in Table 1. The temperature for preparing the solutions and recording absorption spectra

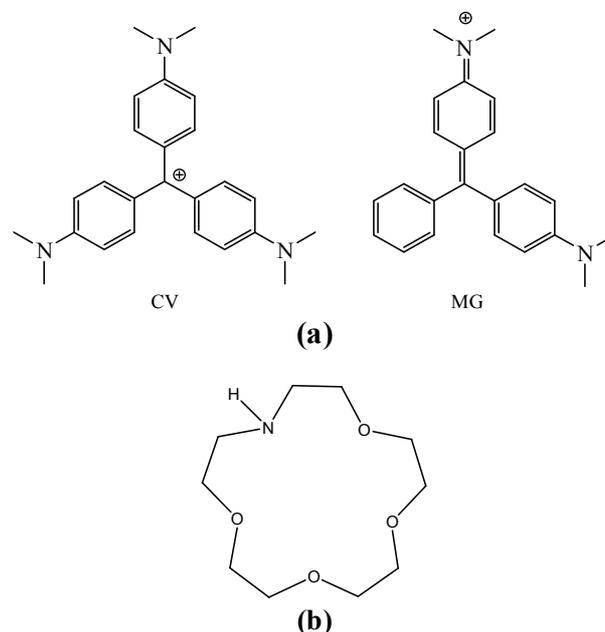


Fig. 1. The molecular structure of a) triarylmethane dyes; b) crown ether (aza-15-crown-5).

was 308.2 K for STS and 323.2 K for SHS, because of their high Krafft points [27], whereas it was about 298.2 K for SOS and SDS.

The chemical structure of the specific solvent, crown ether (1-aza-15-crown-5, 97%) is shown in Fig. 1b. Distilled water was prepared in our laboratory and used throughout all experiments. Samples used in these experiments were prepared fresh and changed daily.

Absorption Spectra

The absorption spectra of the dyes in solutions were scanned on a Cary UV-Vis double-beam spectrophotometer

Table 1. Selected Physical Properties of the Surfactant Used in This Work and Their Molecular Structures. The Data Were Taken from Ref. [28]

Surfactant	Molecular structure	Krafft point (°C)	cmc (M)
SOS	$CH_3-(CH_2)_7-SO_3Na^{\ominus}$	25	0.16
STS	$CH_3-(CH_2)_{13}-SO_3Na^{\ominus}$	35	0.0021
SHS	$CH_3-(CH_2)_{15}-SO_3Na^{\ominus}$	40	0.0001
SDS	$CH_3-(CH_2)_{11}-SO_4Na^{\ominus}$	25	0.00823

(Model 100). The samples were mounted in a thermostatted holder. Absorption measurements were carried out for each one of dye-solvent systems. The surfactant concentrations varied from 0.125 to 10 cmc. The concentration of MG was chosen at 2×10^{-4} M, while two concentrations were chosen for CV (2×10^{-5} M- 2×10^{-4} M). It is assumed that there is a mainly single monomer-dimer equilibrium, since the dye concentrations used in this work were below the concentration at which noticeably higher aggregates occurs.

RESULTS AND DISCUSSION

Dye-Surfactant Interactions in Absence of Crown Ether

The spectral data of CV and MG in aqueous surfactant solutions, at four different surfactant concentrations ranging from 0.125 cmc to 4 cmc, were recorded at room temperature. Figures 2a and 2b show the spectral behavior of CV and MG at fixed dye concentration (2×10^{-4} M) in water and in aqueous solution of the surfactants (SOS, STS, SHS and SDS) at a high surfactant concentration (4 cmc). As seen, there are observable changes in the spectral characteristics of the dyes on going from the aqueous solution to amphiphilic environment. Particularly, a reduction in shoulder intensity of CV spectrum in the micellar media can be observed in Fig. 2a. At high concentrations of the surfactants, far above the cmc, the micelles formed by the surfactant molecules increase the solubility of the dye in solutions.

The photo-physical behavior of the dye depends on several factors including the structures of the dye and surfactant. In the presence of the surfactant molecules, strong association might take place through the long-range electrostatic and short-range hydrophobic interactions between the dye and the surfactant molecules. Below the critical micelle concentration (in pre-micellar medium), a spectral change indicates the formation of complex between dye and surfactant while above the cmc the spectral change might be due to incorporation of dye into the micellar structure.

The maximum absorption wavelength of CV in the aqueous surfactant solutions is red-shifted as compared to the dye spectrum in aqueous solution. Summary of spectral data are listed in Table 2. The red shift observed for the dye-surfactant systems indicates interactions between the cationic

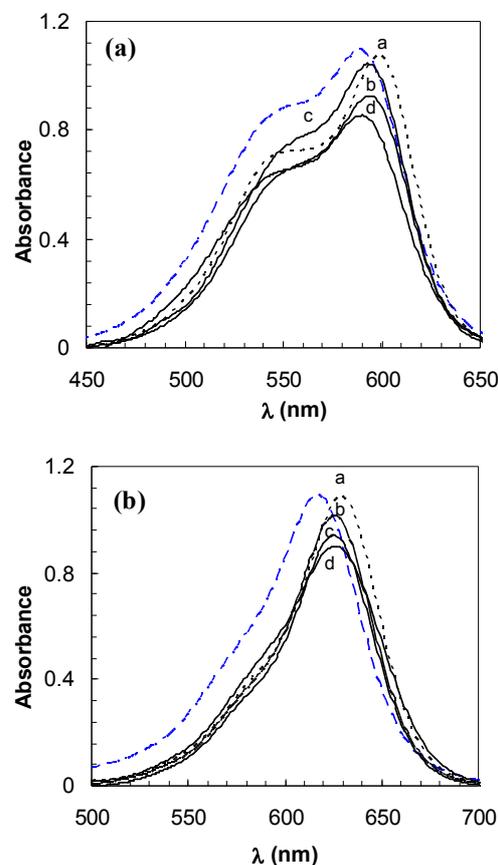


Fig. 2. Effect of hydrophobic group of surfactants on the absorption spectra of the dyes; a) CV, b) MG, above the cmc point; (a) SOS, (b) SDS, (c) STS and (d) SHS (dashed spectrum is the absorption of the dyes in water).

dye and the anionic surfactant molecules. Selected spectral data for the other triarylmethane dye have been also listed in Table 3. It should be noted that, both the electrostatic and hydrophobic interactions (between dye and surfactant) change the spectral characteristics of the dyes. SOS has shorter alkyl chain and the contribution of hydrophobic interactions to the association is supposed to be smaller. Since, CV is a cationic dye it is expected to have strong interactions with anionic surfactants (long-range electrostatic and short-range hydrophobic interactions). The hydrophobic part of the dye is solubilized into micellar core, while the hydrophilic-amino group lie near the micelle surface.

Table 2. Spectroscopic Parameters of CV (2×10^{-4} M) in Water and Aqueous Solution of Surfactants

CV in	$\lambda_{\text{shoulder}}$	λ_{max}	$A_{\text{shoulder}}/A_{\text{max}}$	$\Delta\nu$ (cm^{-1})
water	538	593	0.76	1724
SOS				
1/4 cmc of SOS	538	594	0.92	1752
1/2 cmc of SOS	540	597	1.15	1768
2 cmc of SOS	543	599	0.66	1720
4 cmc of SOS	541	601	0.65	-
SDS				
1/4 cmc of SDS	538	605	1.20	2058
1/2 cmc of SDS	541	600	0.88	1816
2 cmc of SDS	543	597	0.67	1664
4 cmc of SDS	543	597	0.66	1664
STS				
1/4 cmc of STS	534	626	1.15	2752
1/2 cmc of STS	539	601	0.94	1912
2 cmc of STS	543	596	0.67	1636
4 cmc of STS	543	596	0.66	1636
SHS				
1/4 cmc of SHS	537	593	0.72	1758
1/2 cmc of SHS	536	593	0.70	1794
2 cmc of SHS	540	601	0.96	1880
4 cmc of SHS	540	601	0.95	-

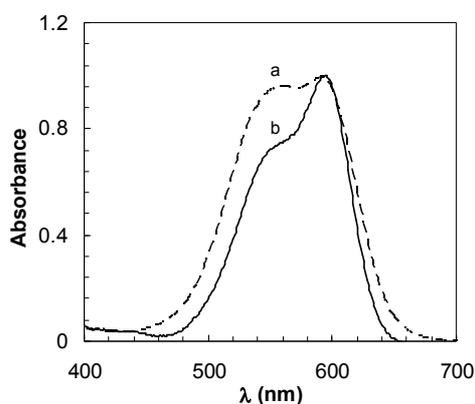
It is noted that the temperature has an important role on spectral characteristic of the dye-SHS system. It is due to the solubility problem of SHS in water at 25 °C (the cmc value for SHS is 0.0001 M at 50 °C). Although the SHS concentration was above the cmc, micelles did not form because the temperature was below the krafft point, *i.e.* the temperature that the solubility of a surfactant increases sharply. At this temperature, the solubility of the surfactant becomes equal to the critical micelle concentration. The absorption spectra of CV-SHS system (4 cmc) above and below the krafft point are shown in Fig. 3.

The Surfactant Concentration Effect

The visible spectra of CV and MG typically possess an intense absorption band (λ_{max}), which is neighbored by a shoulder at shorter wavelengths ($\lambda_{\text{shoulder}}$). However, they appear to exist almost in their monomeric form in dilute aqueous solutions. The origin of the two absorption bands in the monomer spectra could be due to the existence of two ground states. For example, the existence of different ground state structures of crystal violet (the propeller structure and the pyramidal structure) was suggested and interpreted by the earlier researchers [14]. Unlike CV, MG has only two out of

Table 3. Spectroscopic Parameters of MG (2×10^{-4} M) in Water and Aqueous Solution of Surfactants

MG in	$\lambda_{\text{shoulder}}$	λ_{max}	$A_{\text{shoulder}}/A_{\text{max}}$	$\Delta\nu$ (cm^{-1})
water	568	618	0.42	1424
SOS				
1/4 cmc of SOS	571	620	0.41	1384
1/2 cmc of SOS	577	625	0.45	1330
2 cmc of SOS	577	630	0.33	1458
4 cmc of SOS	578	630	0.34	1428
SDS				
1/4 cmc of SDS	584	633	0.71	1324
1/2 cmc of SDS	582	630	0.54	1308
2 cmc of SDS	575	627	0.33	1442
4 cmc of SDS	575	627	0.32	1442
STS				
1/4 cmc of STS	584	631	0.68	1274
1/2 cmc of STS	581	632	0.55	1388
2 cmc of STS	575	627	0.33	1442
4 cmc of STS	575	627	0.32	1442
SHS				
1/4 cmc of SHS	572	618	0.45	1301
1/2 cmc of SHS	573	618	0.54	1271
2 cmc of SHS	578	628	0.42	1377
4 cmc of SHS	579	629	0.45	1373

**Fig. 3.** Visible absorption spectra of CV (2×10^{-4} M) in presence of SHS at two different temperatures; (a) 25 °C, (b) 50 °C.

three phenyl rings substituted with dimethylamino groups. The third aromatic ring is not entered into the resonance structure. Compared to the CV spectrum, the λ_{max} of MG is shifted to the longer wavelengths in the visible region of the spectrum.

The spectroscopic studies were extended to obtain information about the influence of the surfactant concentrations on the absorption profile of the dyes in water and in the surfactant aqueous solutions (Tables 2 and 3). As an example, Fig. 4 shows the spectral changes of CV (the initial dye concentration in aqueous solution was M) in water and in SOS surfactant solutions (The SOS concentration varied from 0 to 4 cmc). The spectral shape is concentration dependent, *i.e.* an increase of the surfactant concentration initially develops the shoulder band intensity ($\lambda_{\text{shoulder}}$) and

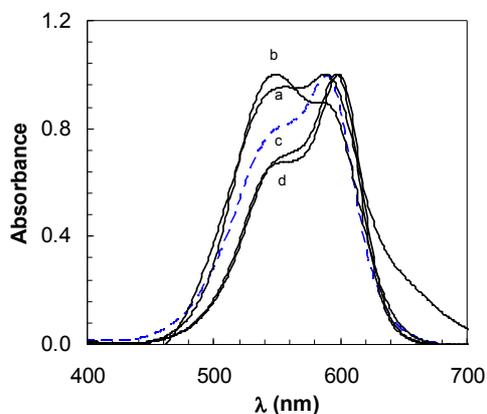


Fig. 4. Visible absorption spectra of CV (2×10^{-4} M) in presence of SOS at different concentrations; a) 0.25 cmc, b) 0.5 cmc, c) 2 cmc, d) 4 cmc (dashed spectrum is the absorption of CV in water).

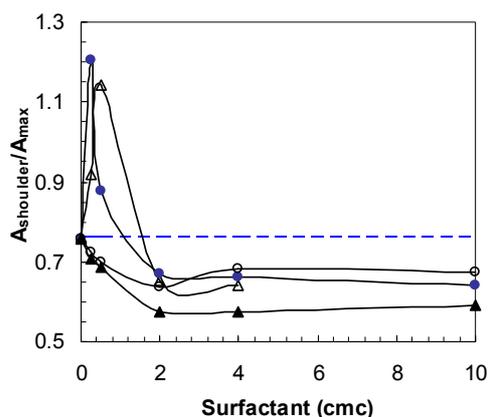


Fig. 5. Dependence of the ratio of the intensity of the shoulder maximum to the monomer maximum, $A_{\text{shoulder}}/A_{\text{max}}$, for CV (2×10^{-4} M) on the concentration in different environments; (Δ) SOS, (\bullet) SDS, (\blacktriangle) STS, (\circ) SHS (dashed line is the $A_{\text{shoulder}}/A_{\text{max}}$ of CV in water).

then decrease it. The visible spectra presented in Fig. 4 clearly shows that at low SOS concentration, below the cmc, the shoulder intensity increases, indicating formation of the dye aggregates in the pre-micellar medium. At high SOS concentration, 4 cmc, shoulder intensity of the CV spectrum is noticeably reduced in SOS solution, and therefore, the dye molecules appear to exist almost completely in its monomeric

form into micelles. It should be noted that, at high surfactant concentration, far from the cmc, the micelles formed by the surfactant molecules increase the solubility of the dye in solution.

Figure 5 shows the ratio of the intensity of the shoulder maximum to monomer maximum, and influence of the surfactant structure and concentration on absorption spectra of CV (2×10^{-4} M). As shown in Fig. 5, the value of $A_{\text{shoulder}}/A_{\text{max}}$ for CV initially increases with increasing the surfactant concentration, and then a gradual reduction occurs up to cmc. The value of $A_{\text{shoulder}}/A_{\text{max}}$ for the dye in presence of surfactants, far above their cmc, is almost independent of the surfactant concentration. At extremely low surfactant concentrations, the anionic surfactants reduce the electrostatic repulsion between dye molecules, and in turn facilitate the aggregate formation of the dye. However, increase of the anionic surfactant concentration lead to solubilization of CV in surfactant micelles, and decrease the dye aggregation.

Comparing to the CV (containing three $-N(\text{CH}_3)_2$ groups), the MG is a dye with less hydrophilic nature (containing two $-N(\text{CH}_3)_2$ groups). Therefore, higher aggregate formation is observed for CV in aqueous solution. CV and MG are cationic dyes, thus relatively strong electrostatic and hydrophobic interactions with the anionic surfactants are expected. Therefore, different values are obtained for the band splitting [$\Delta v = (\bar{\nu}_{\text{shoulder}} - \bar{\nu}_{\text{max}})$] between the dye molecules in presence of anionic surfactant as compared to aqueous solutions.

Spectral Behavior and Decolorization of the Dyes in Presence of Crown Ether

Figure 6 illustrates the absorption spectra of CV in the pure aza-15-crown-5 together with that of water. It is interesting to notice the observed red shift (about 11 nm) in the absorption maxima on going from water to crown ether. It might be attributed to different solute-solvent interactions in crown ether and water media. The red shift observed for CV in the pure CE medium cannot be explained based on solvent polarity. However, origin of the observed shifts can be partially due to the dye-CE interactions.

Effect of addition of aza-15-crown-5 on the spectral characteristic of aqueous solution of MG and CV was also studied. The samples were prepared by addition of the crown ether (10 μl) in aqueous solutions of known dye concentration

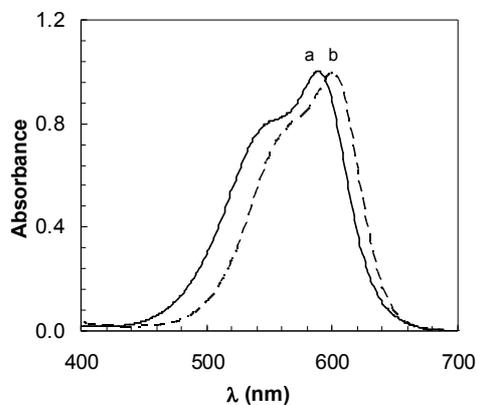


Fig. 6. Absorption spectra of CV (a) in aqueous solution and (b) in the pure crown ether (aza-15-crown-5).

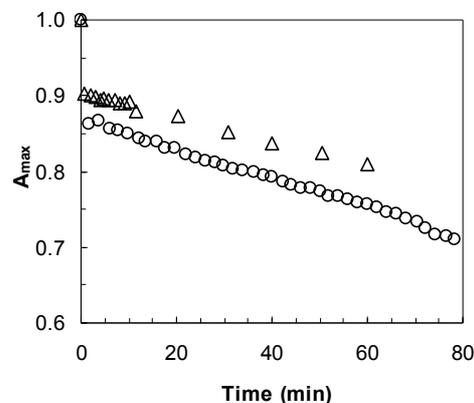


Fig. 8. Effect of the initial CV concentration ((Δ) 2×10^{-4} M and (\circ) 2×10^{-5} M) on the dye decolorization.

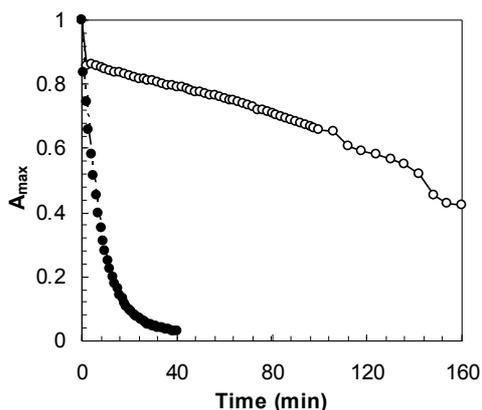


Fig. 7. Decolorization of the dyes ((\circ) CV and (\bullet) MG) using aza-15-crown-5.

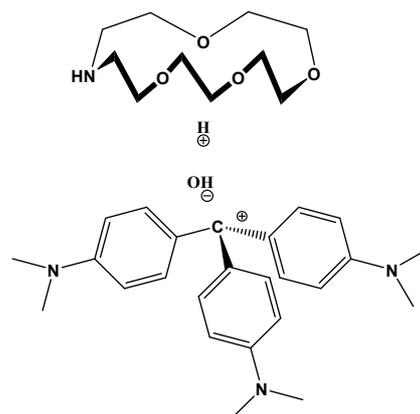


Fig. 9. Possible molecular interaction between the crown ether and CV molecules.

for various duration of the time. Both dyes can be reductively decolorized. In the present study, decolorization of CV and MG by the crown ether was investigated. Fresh solutions of the dyes were prepared and experiments were performed at 25 °C. After adding of the crown ether to the dye solutions, the absorbance at 618 nm (malachite green) or 593 nm (crystal violet) was measured, at 2 minutes intervals. Time dependence of absorbance of CV and MG in presence of the crown ether at 25 °C is presented in Fig. 7. Figure 8 shows the absorbance of CV in presence of the crown ether (10 μ l) at two different dye concentrations (*i.e.* 2×10^{-4} and 2×10^{-5} M). As a result, analysis of the spectroscopic data shows that the dye

decolorization can be accelerated in presence of the crown ether.

The size of the cavity of the aza-15-crown-5-ether moiety is not large enough to accommodate CV and/or MG. It seems that the addition of the crown ether destroys the conjugation between the aromatic rings in the triarylmethane dyes and results in the formation of colorless compounds. It should be noted that in the case of CV, the central carbon atom is in conjugation with three benzene rings. The positive charge is strongly delocalized. Therefore, the triphenylmethyl cation possesses several resonance structures. A possible molecular arrangement between the crown ether and CV molecules is

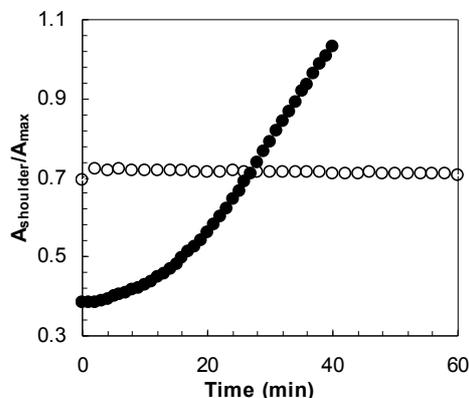


Fig. 10. Dependence of the ratio of intensity of the shoulder maximum to the monomer maximum, $A_{\text{shoulder}}/A_{\text{max}}$, for the dyes (2×10^{-4} M) on the time of presence of aza-15-crown-5.

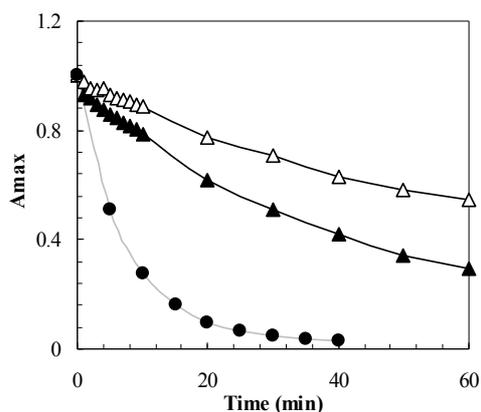


Fig. 11. Absorbance of aqueous solution of MG in presence of crown ether ($10 \mu\text{l}$) at the two different SDS concentrations; (\blacktriangle) 0.25 cmc, (\triangle) 2 cmc, (\bullet) the absorbance of aqueous solution of MG in presence of crown ether without surfactant.

shown in Fig. 9. As seen, a pyramidal structure for the CV may be obtained [14]. The main explanation highlights the possible role of alkaline media on the changes in the structure of the dyes in solution. As an extreme case, the crown ether may provide an electron rich moiety for the proton from aqueous media and the remaining hydroxide ion reacts with the CV cation and decolorizes it. However, the

decolorization process through this mechanism may have partial contribution. Another explanation might be due to the direct interaction of the CE and the CV cation.

Time dependence of $A_{\text{shoulder}}/A_{\text{max}}$ of CV and MG in presence of the crown ether at room temperature is presented in Fig. 10. As seen, the value of $A_{\text{shoulder}}/A_{\text{max}}$ is independent of CV aqueous solution (2×10^{-4} M) in presence of CE ($10 \mu\text{l}$) at various duration of the time. As shown in Fig. 10, this value for MG aqueous solution in the same condition increases sharply as the time goes on.

Finally, the role of the crown ether in the decolorization of MG in presence of an anionic surfactant, SDS, was studied (the initial dye concentration in aqueous solution was $C_0 = 2 \times 10^{-4}$ M). Figure 11 shows the absorbance of MG in presence of crown ether ($10 \mu\text{l}$) and an ionic surfactant (SDS) at two different concentrations (0.25 times of cmc and 2 times of cmc). As seen, MG decolorization is inhibited with increasing the surfactant concentration.

CONCLUSIONS

Our investigation shows that the interactions of the two triarylmethane dyes with surfactant molecules is dependent on various factors such as the dye molecular structures, the type of surfactant and the hydrophobicity of alkyl chain, which is responsible for hydrophobic interactions, the concentration of the surfactants, especially pre- and post-micellar regimes. It can be concluded that the maximum absorption wavelength (λ_{max}) of the dyes can be affected by strong dye-surfactant interactions.

The absorption spectrum of CV in pure crown ether (electron donor) shows a red shift about 11 nm, indicating a relatively strong solute-solvent interaction between the dye and the CE molecules. Effect of addition of aza-15-crown-5 on the spectral feature of aqueous solution of the dyes was also studied. Both dyes can be reductively decolorized. The spectral properties of the dyes in aqueous solution vary with the molecular structure of the dye and also in presence of the CE. Our experimental result shows that the dye decolorization depends on time duration and the dye concentration. However, MG-CE system has a higher tendency for decolorization as compared to the CV-CE system. MG decolorization can be inhibited in the presence of SDS. The

decolorization spectroscopic analysis of the dyes shows that MG decolorization depends on an interaction between the dye and the surfactant.

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