C.I. Reactive Orange 16-dodecylpyridinium chloride interactions in electrolytic solutions

Halide Akbaş*, Çiğdem Kartal

Department of Chemistry, Faculty of Sciences and Letters, Fen-Edebiyat Faculty, Aysekadin, Trakya University, 22030 Edirne, Turkey

Abstract

The effect of electrolytes on the interaction between an anionic dye and a cationic surfactant was investigated spectrophotometrically in submicellar concentration range at certain temperature. The spectral change of the azo dye C.I. Reactive Orange 16 (RO16) exhibits a high sensitivity to the polarity of dye's environment. Dodecylpyridinium chloride (DPC) affects the electronic absorption spectra of dye solution that is dye–surfactant interaction results formation of complex and therefore a decrease in maximum absorption spectra (1.577 at 494 nm). The electrolyte cations cause an increase of the absorbance of DPC–RO16 ion-pair complex in the following order: $Ca^{2+} > Na^+ > NH_4^+ > K^+ > Mg^{2+}$, also for electrolyte anions $Br^- > Cl^- > SO_4^{2-}$. Furthermore, this order can be changeable with increasing electrolyte concentration. The increase on absorbance value with increasing electrolyte concentration is explained as charge screening. The increase or decrease on absorption spectra of RO16–DPC solution depends on concentration range of the electrolyte added. As an increase on absorbance value with increasing electrolyte concentration is explained as charge screening, a decrease in this value for higher concentration of electrolyte is attributed as the charge of micelle shape.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Spectrophotometry; Effect of electrolyte; Dye–surfactant interaction; Anionic dye; Cationic surfactant

1. Introduction

Dye–surfactant interactions are subjects of numerous investigations. Surfactants are used as solubilizer for water insoluble dyes, to break down dye aggregates in order to accelerate absorption processes on fiber, as auxiliaries in most textile finishing processes such as wetting dispersing, dyeing and finishing [1–5]. Dyes are extensively used in dyeing processes in textile industry but the majority of textile dyes belong to the structure class of azo dyes. [6,7]. Different methods were used to investigate the dye–surfactant interactions; potentiometry [8], conductometry [9,10], tensiometry [11], voltammetry [12], and other methods, but most widely used are spectroscopic methods [13–16].

Dye molecules with phenyl groups can adopt a planar structure and readily tend to form intermoleculer interaction that facilitates permanent aggregation under some experimental condition. The spectral change of the azo dye exhibits a consid-

erable sensitivity to the polarity of the dye's environment and therefore spectrophotometry has been widely used to study the complexation equilibria between dye and surfactant in solution. We have used this dependence of absorption wavelength on microenvironment to investigate the ion-pair complex formed from electrostatic interaction of cationic surfactant with anionic dye in electrolytic solution. In the previous studies, by spectrophotometric method we were concerned with an anionic dye (RO16)–surfactants (anionic, cationic and non-ionic surfactants) interaction in mixture of ionic and non-ionic surfactants. We also discussed optimum conditions for surfactants and temperatures used in colour-fastness of anionic dye [17,18].

In the present paper, spectrophotometry was used to investigate the effect of the kind and concentration of strong electrolytes on the interaction of an anionic dye C.I. Reactive Orange 16 (RO16) with a cationic surfactant dodecylpyridinium chloride (DPC) in aqueous submicellar solution at certain temperature (303 K). Surfactants are able to affect the electronic absorption spectra of solution of many dyes. The interaction of RO16 with DPC results in decrease the maximum absorption spectra (1.577 at 494 nm). This decrease is due to the ion-pair complex formed

---

by the dye and the surfactant molecules. This complex is stable at ambient temperature but become unstable with addition of electrolytes. The aim of the study reported here was to determine the influence of the kind and concentration of electrolyte on the RO16–DPC interaction.

2. Materials and method

2.1. Anionic dye

C.I. Reactive azo dyes RO16 (commercial product, a gift from DyStar, İstanbul, Turkey) was used as received. It exhibits a maximum absorption band (1.577) at 494 nm and 298 K. Its chemical structure is shown in Fig. 1. A stock solution of 1.0×10^{-3} mol dm^{-3} RO16 was prepared dissolving in distilled water. The solution was stored under cold and dark conditions and the stability was checked by absorption spectra in the visible region.

2.2. Cationic surfactant

Dodecylpyridinium chloride $CH_3(CH_2)_{10}CH_2N^+(CH)_5Cl^-$ (DPC) was supplied by Merck, re-crystallized from acetone three times and dried at 323 K in vacuum. The purity of the surfactant was checked by measuring that there was no minimum on the surface tension versus surfactant concentration curve in the vicinity of CMC.

2.3. Electrolytes

As inorganic electrolytes, sodium chloride, bromide and sulphate, potassium chloride, bromide and sulphate, and calcium, magnesium and ammonium chloride were used. All electrolytes were purchased from Merck and Aldrich and used as received.

Water used in the measurement was distilled twice from dilute alkaline permanganate solution; its conductivity was about 1.0×10^{-6} Ω^{-1} cm^{-1} and the air/water tension was equal to 71–72 mN m^{-1} at 298 K.

2.4. Absorbance measurements and analyses

Absorption spectra over the range of 350–650 nm were recorded at 303 K on a Shimatzu UV-160 A spectrophotometer with a two quartz cells (10.0 mm in light pass length). While surfactant concentration was chosen to bracket the CMC value
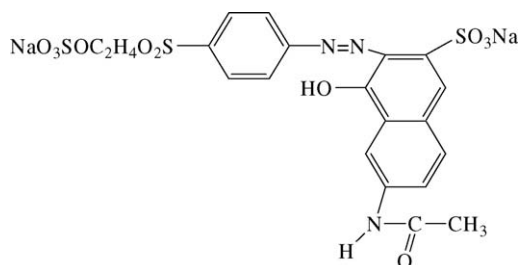
Fig. 1. Chemical structure of C.I. Reactive Orange 16.

$(1.0 \times 10^{-2}$ M), RO16 concentration in all cases was held constant at $(1.0 \times 10^{-4}$ M).

3. Results and discussion

The position of the long-wavelength absorption band of azo dyes is sensitive to medium effect; therefore they can be used as solvatochromic micro polarity reporter molecules. The visible absorption spectrum of RO16 $(1.0 \times 10^{-4}$ mol dm$^{-3})$ in aqueous solution exhibits an absorption maximum at 494 nm at 298 K as shown as Fig. 2. The dye molecules are able to form in solution aggregates and these aggregates will react with molecules of surfactant to form the complex. Upon addition of dodecylpyridinium chloride to dye RO16, the UV–vis absorption spectrum rapidly decreases in intensity as shown Fig. 2. These spectral changes can be attributed to the formation of a complex between dye and surfactant molecules [19]. The ion-pair complex of dye and surfactant is likely arranged with an orientation of the hydrophobic surfactant tail about the chromophore to effect a partial replacement of the solvating water molecules [20]. It is concluded that loss in intensity of the UV–vis absorption spectra results from the formation of insoluble complexes. These complexes are due to strong electrostatic interaction between sulfonate groups of dye and head groups of cationic surfactant and short-range non-coulombic interaction, which are mainly hydrophobic and disperse [21,22]. As both surfactant and dye possess an aromatic ring, π–π electronic interactions and Van der Waals interactions can also be expected. In order to find out the effect of an electrolyte on the absorption spectra of RO16–DPC mixture system the experiments similar to the previous one were performed, adding NaCl, NaBr, Na$_2$SO$_4$, KCl, NH$_4$Cl, MgCl$_2$ and CaCl$_2$. Fig. 3 shows that the influence of a kind of inorganic cations (Na$^+$, K$^+$, NH$_4^+$, Ca^{2+} and Mg^{2+}) at the 0.05 M concentration on absorption spectrum for solution of
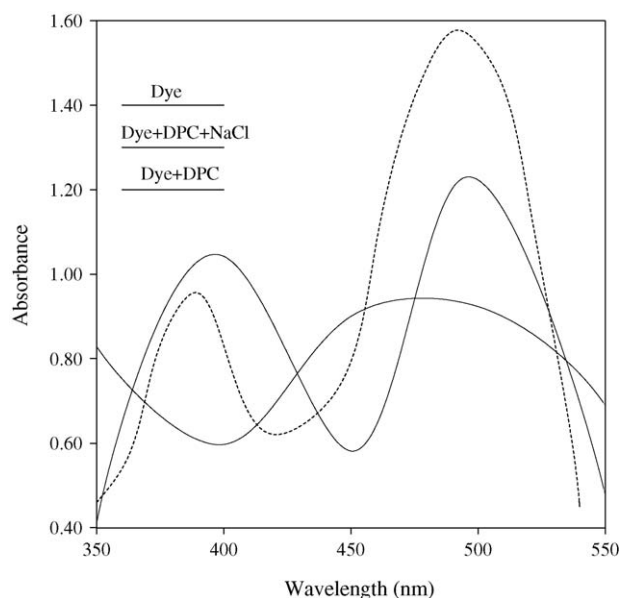

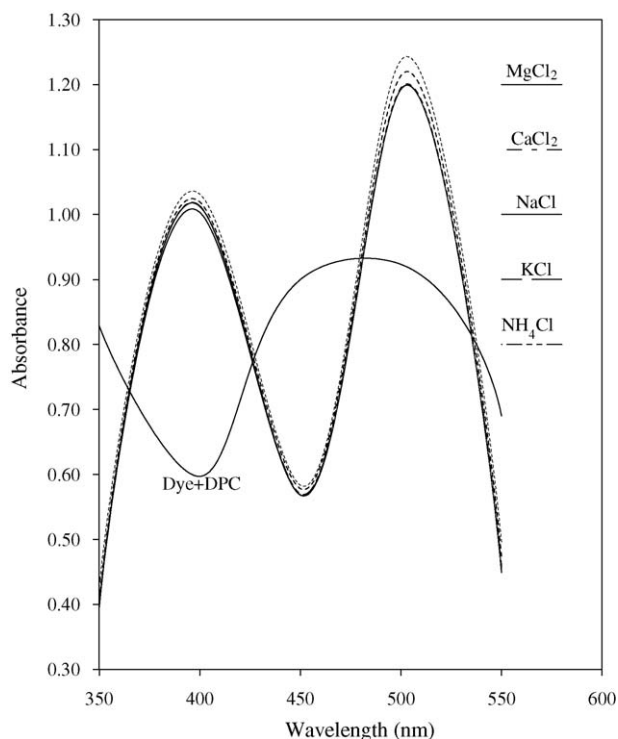Fig. 2. Absorption spectra of aqueous solutions only RO16, RO16 + DPC with and without electrolyte.

Fig. 3. Effect of electrolyte cations on the absorbance of RO16–DPC mixture system.

Fig. 4. Effect of electrolyte anions on the absorbance of RO16–DPC mixture system.

RO16–DPC mixture system. Upon addition of an electrolyte to mixed solution of dye and surfactant induces screening of the charge on dye and surfactant ions by electrolyte ions. Therefore, the attraction of oppositely charged ions by electrostatic force diminishes. However, it is compensated to a great extent by hydrophobic interaction. It is observed from Fig. 3 that the electrolyte cations cause a decrease on complex occurrence or an increase in the absorbance of RO16–DPC ion-pair complex in the lower electrolyte concentration (0.05 M) in the following order: $Ca^{2+} > Na^+ > NH_4^+ > K^+ > Mg^{2+}$. The decrease on complex occurrence or an increase in the absorbance of RO16–DPC ion-pair complex may be due to less stronger interaction between dye and surfactant. We note that the Na^+ ion is smaller than the K^+ ion and the NH_4^+ and K^+ ions are less hydrated than the Na^+ ions. Therefore, the NH_4^+ and K^+ charges are less screened than the Na^+ charges. The diameters of Ca^{2+} and Na^+ are almost identical but Ca^{2+} is more heavily hydrated than Na^+. The Mg^{2+} ions are the best hydrated among the ions studied here but their effective ionic charge is the greatest. Therefore, according to the effective ionic charge, cations cause a decrease on complex occurrence in above order. The effective ionic charge of K^+ and Mg^{2+} is the greatest from among the cations studied and therefore, cationic effect on complex occurrence appears at very low electrolyte concentration. As seen from Fig. 6, in the presence of potassium and magnesium electrolytes, the value of absorbance decrease especially drastically in comparison with the decrease in absorbance in the presence of sodium electrolyte at 0.01 M electrolyte concentration.

Also Fig. 4 shows that the influence of a kind of inorganic anions (Cl^-, Br^- and SO_4^{2-}) on absorption spectrum
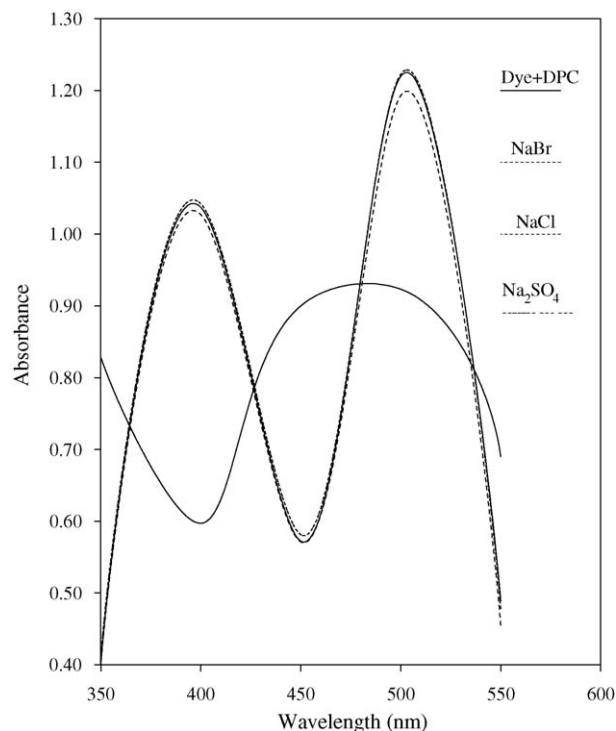
for solution dye–surfactant with 0.05 M electrolyte concentration. The electrolyte anions have a much smaller effect on absorbance values than the cation's effect and this effect is shown in the lower electrolyte concentrations in the following order: $Br^- > Cl^- > SO_4^{2-}$. This order may be changeable in the higher concentration ($Br^- = Cl^- > SO_4^{2-}$ at 0.10 M concentration). The difference in solution properties of Br^- and Cl^- is that Cl^- counterions are more hydrated. The observed micellar growth is significantly different for NaCl and NaBr that is the nature of the condensation of counterions on the micellar surface is different for Cl^- and Br^- [23]. The counterion concentration is more effective to neutralize the charge on the micellar surface when the hydrated size is small. The Br^- anions have much larger affinity to the interface than Cl^- anions that can be explained in terms of a larger repulsion of chloride anions from the interface due to their excess polarizability [24]. This is in agreement with our observations. In the presence of divalent SO_4^{2-} counterions, the loss in intensity of the UV–vis absorption spectra is highest because SO_4^{2-} counterions neutralize the surface charge of adsorbed surfactant head group more effectively than monovalent counterion.

The effect of ionic strength of the solutions on the absorption spectra of RO16–DPC was studied in detail with whole electrolytes at different concentrations (0.01, 0.05, 0.1, 0.3 and 0.5 M) and this effect is shown in Fig. 5 only for NaCl solutions. It can be seen from the figure, as the absorbance value is increasing at the lower ionic strength, this values are decreasing at higher concentration. That is, the increase or decrease on absorption spectra of RO16–DPC depends on the concentration range of the electrolyte added. For sodium electrolyte, the value
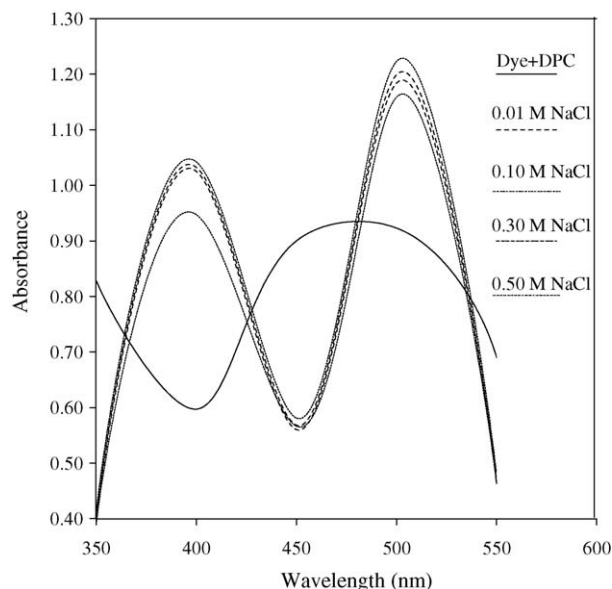
Fig. 5. Effect of the NaCl concentration on the absorbance of RO16–DPC mixture system.

of absorbance at first increased, reached a maximum and then decreased. The increase on absorbance value with increasing electrolyte concentration can be explained either by increased charge screening [25] or by micelle growth in the presence of the electrolyte added. Such a growth of micelles would result in decrease in the micelle charge density and, consequently, the liberation of counterion. A decrease in this value for higher concentration of sodium electrolyte is attributed as the change of micelle shape. The micelles formed at the CMC are spherical.
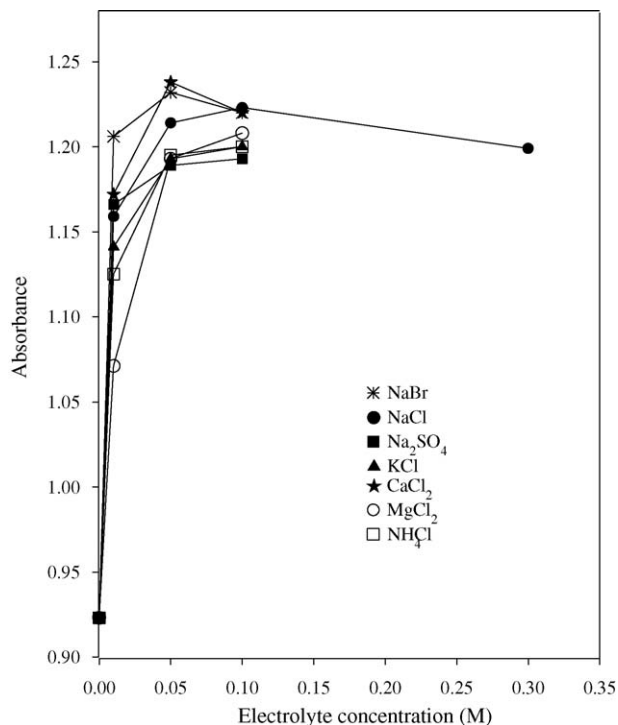

Fig. 6. Effect of the different electrolyte concentrations on the absorbance of RO16–DPC mixture system.

With increasing concentration or ionic strength of micellar solutions, micelle shapes are changed. Micelles usually grow along one of the axial direction of the micelles. The growths of the micelles along other two axial directions is restricted by the length of the surfactant molecule to avoid the energetically unfavorable any empty space or water penetration inside the micelle [26,27]. A decrease in absorbance value observed for higher concentration of sodium electrolyte precedes micelle transition from the spherical forms to rodlike ones, which according to Ref. [28] takes place at 0.4 mol dm^3 Na$^+$ ions.

Fig. 6 represents the effect of electrolytes studied on the absorbance of RO16–DPC with increasing electrolyte concentrations. As seen from the figure, the greatest effect on the absorbance change is presence for calcium electrolyte. Also, the minimum effect on the absorbance change appears for sulphate anions. Consequently, these results indicate that electrostatic effects are important in the interaction of anionic dye (RO16)–cationic surfactant (DPC). The effect of kind and concentration of electrolytes added causes changes on the absorbance of complex, which occurred due to effect between anionic dye and cationic surfactant.

4. Conclusion

Very strong synergism in mixed micelle formation exists in the anionic dye–cationic surfactant system investigated. The formation of the dye–surfactant complex is consequence of mutual influences of long-range and short-range interaction. It is concluded that loss intensity of the UV–vis absorption spectra results from the formation of insoluble complex, due to strong electrostatic interactions between sulphate groups of dye and head group of surfactant. The electrolyte anions and cations cause a change in the UV–vis absorption spectra. The changes of absorbance of ion-pair complex have shown to depend on the kind and concentration of the electrolyte added. The electrolyte cations cause an increase on the absorbance values of complex in the following order: $Ca^{2+} > Na^+ > NH_4^+ > K^+ > Mg^{2+}$, also for electrolyte anions $Br^- > Cl^- > SO_4^{2-}$. Further more, this order can be changeable with increasing electrolyte concentration.

References

[1] H. Akbaş, M. İşcan, Turkish J. Chem. 18 (1994) 80.
[2] J. Ribe, J. Cegarra, L. Aizgurua, J. Soc. Dyers Colour 99 (1983) 374.
[3] E.A. Sudbeck, P.L. Dubin, M.E. Curran, J. Skelton, J. Colloid Interface Sci. 142 (1991) 512.
[4] A.M. Misselyn-Bavduin, A. Thibaut, J. Grandjean, G. Broze, R. Jerome, Langmuir 16 (2000) 4430.
[5] B. Simoncic, J. Span, Dyes Pigments 36 (1998) 1.
[6] S. Borros, G. Barbara, J. Biada, N. Agullo, Dyes Pigments 43 (1999) 189.
[7] M. Stylidi, D.I. Kondarides, X.E. Verykios, Appl. Catal. B: Environ. 40 (2003) 271.
[8] B. Simoncic, J Span, Dyes and Pigments 46 (2000) 1.

[9] S. Bracko, J. Span, Dyes Pigments 45 (2000) 97.

[10] T.X. Zhang, H.Z. Liu, J.Y. Chen, Colloids Surf. A 162 (1999) 259.

[11] L.N. Guo, I. Arnaud, M.P. Ramel, R. Gautheir, C. Monnet, P.L. Perchec, Y. Chavalier, J. Colloid Interface Sci. 163 (1994) 334.

[12] A. Navarro, F.J. Sanz, J. Colloid Interface Sci. 237 (2001) 1.

[13] M. Sarkar, S. Poddar, J. Colloid Interface Sci. 221 (2000) 181.

[14] M. Khamis, B. Bulos, F. Jumean, A. Manassra, M. Dakiky, Dyes Pigments 66 (2005) 179.

[15] Yu.V. Malyukin, S.L. Efimova, K. Kemnitz, J. Lumin. 94–95 (2001) 239.

[16] S. Göktürk, M. Tunçay, Spectrochim. Acta A 59 (2003) 1857.

[17] H. Akbaş, Ç. Kartal, Spectrochim. Acta A 61 (2005) 961.

[18] Ç. Kartal, H. Akbaş, Dyes Pigments 65 (2005) 191.

[19] D.M. Stevensen, D.G. Duff, D. Kirkwood, J. Soc. Dyers Colour 97 (1981) 13.

[20] R.K. Dutta, S.N. Bhat, Bull. Chem. Soc. Jpn. 66 (1993) 2457.

[21] K. Ogino, T. Kusuya, M. Abe, Colloid Polym. Sci. 266 (1988) 539.

[22] R. Sagaster, G. Robisch, Dyes Pigments 13 (1990) 187.

[23] D. Varade, T. Joshi, V.K. Aswal, P.S. Goyal, P.A. Hassan, P. Bahadur, Colloids Surf. A 259 (2005) 109.

[24] P.K. Weissenborn, R.J. Pugh, J. Colloid Interface Sci. 184 (1996) 550.

[25] P.C. Shanks, E.I. Frances, J. Phys. Chem. 96 (1992) 1794.

[26] V. Degiorgin, M. Conti, Physics of Amphiphiles: Micelles, Vesicles and Micro-emulsion, North-Holland, Amsterdam, 1985.

[27] J.N. Israelachvili, Intermolecular and Surface Forces, Academic Press, New York, 1992.

[28] E. Dutkiewicz, A. Jakubowska, J. Phys. Chem. B 103 (1999) 9898.