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Effect of hydrophobicity on micellar binding of carminic acid

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Abstract

The effect of hydrophobicity on micellar binding of carminic acid (CA), an anionic dye, with various cationic surfactants; dodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), cetyltrimethylammonium bromide (C_{16}TAB) cetylpyridinium bromide (C_{16}PBr) and cetylpyridinium chloride (C_{16}PC) has been studied spectrophotometrically in submicellar and micellar concentration range. Going from aqueous solution to the more hydrophobic micellar environment the maximum absorbance of CA shifted a higher wavelength in its absorption maxima.The binding constant (K_c) values of CA to cationic micelles were calculated by means of Benesi–Hildebrand Equation and the binding of CA followed the order as:

$$C_{16}PB > C_{16}PC > C_{16}TAB > C_{14}TAB > C_{12}TAB$$

The K_c values and the absorption maxima of CA in the presence of micelles showed that hydrophobic interaction plays a major role in binding process of CA to cationic micelles.

Keywords: Carminic acid; Binding constant; Hydrophobic interaction; Micelles; Cationic surfactants

1. Introduction

The nature of the interactions between dyes and surfactants is one of the basic information for understanding the process of dyeing and finishing of textile material. Although a lot of research work has already been done into dye–surfactant interactions, the studies in this area are still important and interesting for the theory and technology of dyeing. The studies on different type of dyes in aqueous surfactant solutions can give useful information about the mechanism according to which surfactants operate as leveling agents and about the influence of dye–surfactant interactions on the thermodynamics and kinetics of dyeing process [1–10].

The dye–surfactant interactions have also been the subject of many studies in view of the fact that they mimic many biological processes taking place between the large organic molecules and biomembrane and can act as a model redox system [11–14].

Spectrophotometry has been widely used to study the complexation equilibria between a dye and surfactants in solution. Thus, spectroscopic techniques based on either the absorption or emission of light from a dye are used to determine certain physicochemical properties of micelles and vesicles [15,16]. Surfactants (above or below their critical micelle concentration (CMC)) affect the electronic absorption spectra of solutions of many dyes [4–6,15] and a similar effect is produced by the interaction between dyes and phospholipid membranes [8,17,18]. Literature survey indicates, beside the electrostatic interactions, the hydrophobic interactions are also very important for the binding between the oppositely charged dyes and surfactants. The electrostatic interaction combined with the classical hydrophobic interactions act concurently bringing about the largest changes, as shown for anionic dye–cationic surfactant complexes by Savvin et al [19] or for metalchelate-cationic surfactant species by Sanz-

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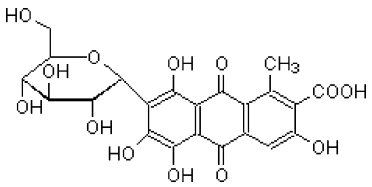

Scheme 1. Structure of Carminic Acid.

Medel et al [20]. There is multiplebinding in these associated micellar species: evidence has been produced indicating that hydrophobic interaction, not charge compensation, plays the main role in binding between dyes and surfactants. Chiang and Lukton [21] report that their results on the interaction between 2-*p*-toluidinylnaphtalene-6-sulphonate and sodium dodecylsulphate (NaDDS) micelles suggest that the binding force is hydrophobic. Analogusly, Birdi et al. [22] claim that the interaction of NaDDS micelles with 1-anilinonaphtalene-8-sulphonate is hydrophobic in nature. The objective of this paper is to understand and characterize the role of the hydrophobicity on the interaction between oppositely charged dye and surfactant in aqueous solutions.

Carminic acid (7-α-D-glycopyranosyl)-9,10-dihydro-3,5,6,8-tetrahydroxy-1-methyl-9,10-dioxo-2-anthracenecarboxylic acid) contains two distinct moieties, a chromophore and a pendant glucose group (Scheme 1) and exists in four forms viz., H_4CA, H_3CA^-, H_2CA^{2-} and HCA^{3-} [23]. The data has been presented here the region at pH 5.7 that contains H_2CA^{2-} form of CA.

In this work, the interaction of CA, an anionic dye, with various cationic surfactants was studied both at the concentration below the CMC and micellar region in aqueous media. Benesi–Hildebrand Equation was applied to calculate the binding constants of CA to cationic micelles.

The effect of alkyl chain length on hydrophobic interaction was compared by studying a series of alkyltrimethylammonium bromide (C_nTAB) i.e. dodecyltrimethylammoniumbromide(C_{12}TAB), tetradecyltrimethylammoniumbromide (C_{14}TAB), cetyltrimethylammonium bromide (C_{16}TAB) and the effect of counter ion was compared by studying cetylpyridinium bromide (C_{16}PBr) and cetylpyridinium chloride (C_{16}PC) having the same hydrophobic group (C_{16}) with pyridinium ring but different counter ion.

2. Materials and Method

All the chemicals were of analytical reagent grade. C_{12}TAB, C_{14}TAB, C_{16}TAB, C_{16}PBr and C_{16}PC were used of Sigma products. CA was obtained from Fluka. The solvents methanol (MeOH), ethanol (EtOH), 1-propanol (PrOH), 1-butanol (BuOH), pentanol (PenOH), 1-hexanol (HexOH) and 1-octanol (OctOH) used were spectroscopic grade products from E. Merck. Doubly distilled conductivity water was used for solution preparation. Visible absorption spectra were recorded with UV-vis Spectrophotometer (UV-1601 Shimadzu) with a matched pair of cuvets of 1 cm optical length placed in a thermostated cell holder, at 25 °C (±0.1). All solutions were prepared at a constant CA concentration of 1.10^{-5} mol dm^{-3} during the whole process since this concentration is sufficiently low that no dye aggregation or other cooperative effects could be detected. The absorption spectra of 1.10^{-5} mol dm^{-3} CA solution containing cationic surfactants in the concentration range from 1.10^{-5} mol dm^{-3} to 4.10^{-2} mol dm^{-3} were recorded and the reproducibility for λ_{max} of the spectra was ±0.1 nm.

All measurements were done at least in triplicate during the study.

3. Results and discussion

In aqueous solutions 1.0×10^{-5} mol dm^{-3} CA exhibited an absorbance maximum (λ_{max}) at 492 ±1 nm. The molar extinction coefficient of CA (ε_0) at 492 nm was calculated as 8.09 (±0.01) × 10^3 mol^{-1}dm^3 cm^{-1} at 298 K (±0.1). An excellent correlation ($r^2 > 0.999$) indicated that the Beer–Lambert Law was obeyed in the CA concentrations ranges of interest. The effect of cationic surfactants at concentrations varied from 1.0×10^{-5} to 4.0×10^{-2} mol dm^{-3} on the absorption spectrum of CA at fixed concentration of 1.0×10^{-5} mol dm^{-3} from premicellar to micellar region was studied. Under working conditions at pH 5.7 CA bears a net negative charge and H_2CA^{2-} is dominant form. The absorbance change of 1×10^{-5} mol dm^{-3} CA (below and above the CMC) with the concentration of C_{12}TAB, C_{14}TAB, C_{16}TAB, C_{16}PB and C_{16}PC were shown in Fig. 1. The absorbance of CA initially decreased with increasing the surfactant concentrations well below the CMC and reached a minimum value and then increased again with further increasing of surfactant concentrations above the CMC. The concentration at the observed minimum is considered as CMC in the presence of 1.0×10^{-5} mol dm^{-3} CA for each surfactant [24]. As seen in Table 1, CMC values of all surfactants determined spectrophotometrically were different from their CMC in pure water (Table 1). The increase in λ_{max} and decreasing absorbance values can be assumed due to some sort of association or complex formation between dye and surfactant monomers [4,7,8,25–27]. The complex formation of the dye–surfactant is a consequence of mutual influences of electrostatic and hydrophobic interactions.

The increase in absorbance of CA above the CMC is generally attributed to the increase in the amount of solubilized CA in the micelles. The absorbance and the values of λ_{max} reached the limiting value with further increase of surfactant concentration above the CMC indicates that all dye molecules are compartmentalized into micelles [27–30] i.e. the amount of solubilized CA reach saturation. In 0.02 mol dm^{-3} surfactant concentration the solubilization of CA in the micelles is practically completed and further addition of surfactants failed to bring about any spectral change. Fig. 2 presents

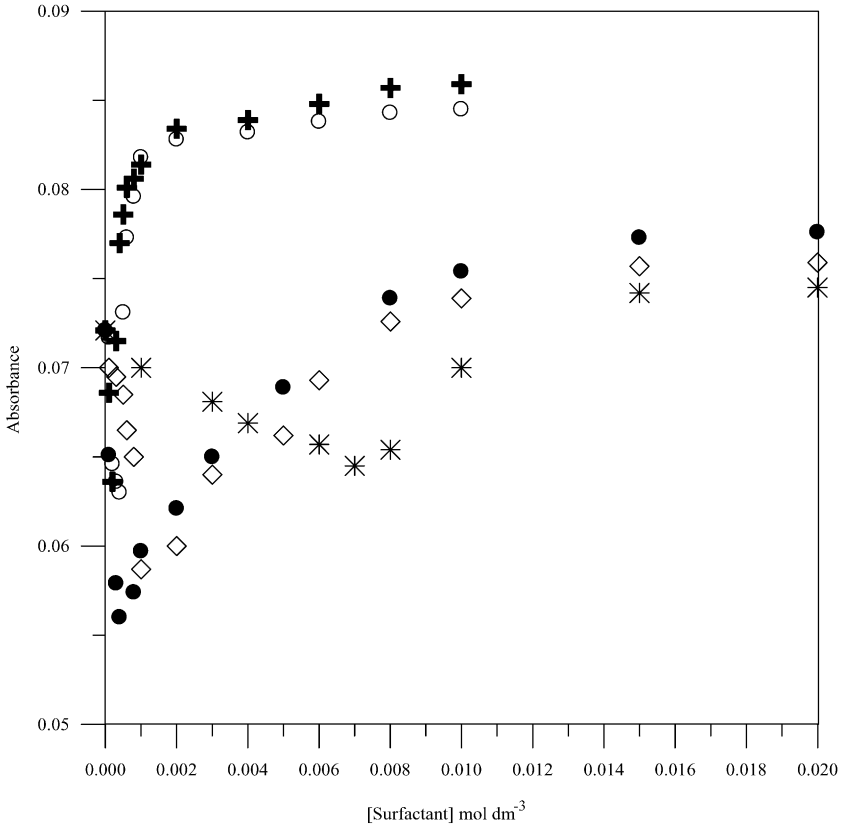

Fig. 1. The absorbance change of 1×10^{-5} mol dm^{-3} CA (below and above the CMC) with the concentration of C_{12}TAB (✳), C_{14}TAB (◇), C_{16}TAB (●), C_{16}PC (◯) and C_{16}PB (✚).

the absorption spectra of 1×10^{-5} mol dm^{-3} CA in various types of cationic micelles and, for the sake of comparison, also in water. Table 1 shows the observed λ_{max} shift values of CA in the presence of micelles. The red shift is a clear indication for the incorporation of CA with five cationic micelles and increased with increasing hydrophobicity of cationic surfactants. Going from aqueous solution to the more hydrophobic micellar environment the maximum absorbance of CA shifted a higher wavelength in its absorption maxima and the shift increased with the surfactant chain length for C_{12}TAB, C_{14}TAB, C_{16}TAB and the most significant shift was observed in the presence of C_{16}PB and C_{16}PC.

3.1. Determination of binding constant

Change of absorption spectra of CA due to incorporation into cationic micelles allows obtaining the binding constants.

The equilibrium for the incorporation of the dye (D) into micelles (M) can be assumed to follow as

$$D + M \overset{k_c}{\rightleftarrows} DM$$

where D, M, DM and K_c represent the dye, micelle, dye–micelle associate and binding constant (K_c) respectively. The binding constant, K_c, and molar extinction coefficient

Table 1
Physical parameters of (1.0×10^{-5} mol dm^{-3}) CA in different cationic surfactants at 298 K

Surfactants	CMC[a] (mol dm^{-3})	CMC[b] (mol dm^{-3})	λ_{max}[c] (ε_c)	K_c[d] (mol^{-1} dm^3)	f_{mic}[e]
C_{12}TAB	1.6×10^{-2}	7.0×10^{-3}	508 (8377)	120	0.706
C_{14}TAB	3.5×10^{-3}	1.50×10^{-3}	538 (8546)	287	0.852
C_{16}TAB	9.2×10^{-4}	4.0×10^{-4}	543 (8674)	650	0.929
C_{16}PC	9.0×10^{-4}	3.50×10^{-4}	544 (9435)	1228	0.960
C_{16}PB	6.86×10^{-4}	2.0×10^{-4}	546 (9569)	1520	0.970

[a] The CMCs were taken from literature [34].
[b] The CMCs were obtained from spectrophotometric determination in the presence of 1.0×10^{-5} mol dm^{-3} CA.
[c] λ_{max} is in nm and ε_c is in mol^{-1} dm^3 cm^{-1}; error limit in ε_c is ±1%.
[d] Error limit in K_c is ±5%. The correlation coefficients are 0.9970, 0.9980, 0.9991, 0.9976, 0.9938 for C_{16}PB, C_{16}PC, C_{16}TAB, C_{14}TAB and C_{12}TAB, respectively.
[e] f_{mic} values, at the concentrations of 0.02 mol dm^{-3} for C_{16}PB, C_{16}PC, C_{16}TAB, C_{14}TAB, C_{12}TAB.

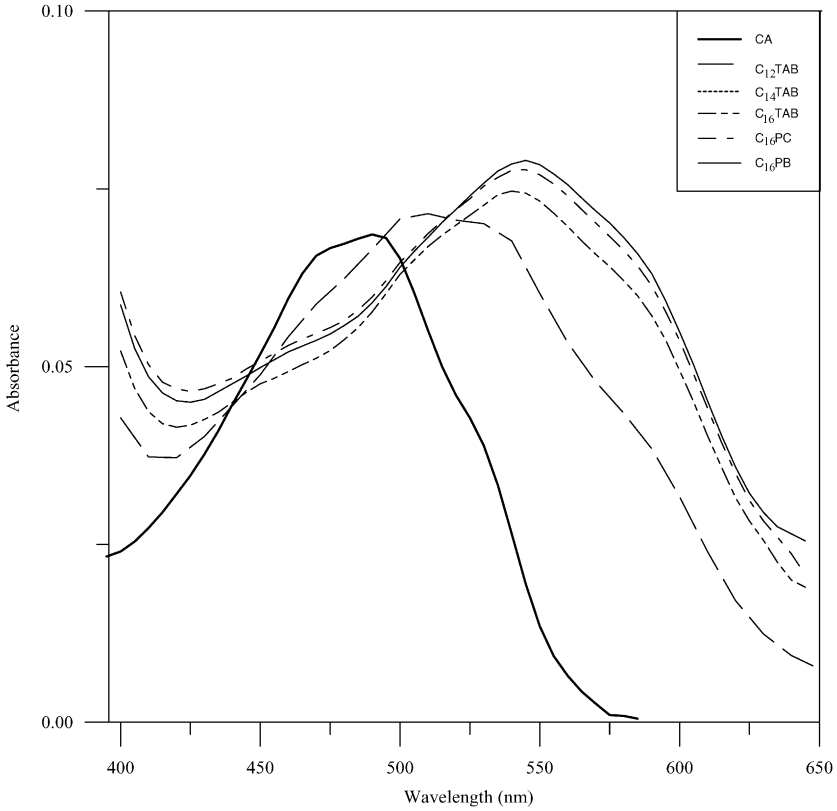

Fig. 2. Visible absorption spectrum of 1.0×10^{-5} mol dm^{-3} CA in the absence and presence of 0.02 mol dm^{-3} C_{12}TAB, C_{14}TAB, C_{16}TAB, C_{16}PC and C_{16}PB, respectively.

ε_c can be determined using the Benesi–Hildebrand Equation [31] which is valid for high surfactant concentrations [5,32,33] in the following modified form

$$\frac{[D]l}{d - d_0} = \frac{1}{\varepsilon_c - \varepsilon_0} + \frac{1}{K_c[S_m](\varepsilon_c - \varepsilon_0)} \quad (1)$$

where D and S_m (S_m = total surfactant concentration—CMC) are the initial molar concentrations of CA and the micellized surfactant concentration respectively, l is the optical path length of the solution. d and d_0 are the absorbances of CA in the presence and absence of surfactants, respectively. ε_c is the molar extinction coefficient of the dye fully bound to micelles determined in large excess of the micelles. The plot of $(D)l/d - d_0$ against $1/S_m$ was found to be linear in all cases. The extent of CA-surfactant interaction in the aqueous medium K_c and ε_c was calculated from the slope and intercept.

The binding constants, K_c, presented in Table 1 shows that the surfactants yield different affinities which follow the order as:

$$C_{16}PB > C_{16}PC > C_{16}TAB > C_{14}TAB > C_{12}TAB$$

The order of K_c may represent the trend of the effect on CA produced by the surfactant micelles. This indicates that the interaction of CA with cationic micelles not only depends on the hydrocarbon chain length but also on the head group of surfactant. The values of K_c of CA with C_{12}TAB, C_{14}TAB, C_{16}TAB was found to be much lower than that of both C_{16}PC and C_{16}PB. The very high binding constants for C_{16}PB and C_{16}PC showed that strong interactions occur between anionic dye CA and cationic surfactants with pyridinium ring. It is possible that π–π electronic interactions occur between dye and surfactants with a pyridinium ring which do not exist in quaternary ammonium surfactants. Weaker interactions could also be the result of steric hindrance arising from the tetrahedral structure of the quaternary ammonium ion. As shown in Table 1 C_{16}PB is more effective than C_{16}PC on binding of CA that can be explained with the difference in head groups, C_{16}PC has Cl^- and C_{16}PB has Br^- [34] i.e.Br^- is more effective than Cl^- as expected from hydophilicity of the head group.

The results in Table 1 show that K_c values vary directly with the band shift and are indirectly proportional with CMC. Comparison of the binding degree of CA to micelles indicates a direct correlation between K_c and hydrophobicity. Also, the CMC values obtained in the presence of CA has a direct relation with the hydrophobicity of the surfactants. A linear relationship between the K_c versus 1/dCMC (dCMC = CMC_0 − $CMC_{induced}$) was obtained for C_{12}TAB, C_{14}TAB, C_{16}TAB (Fig. 3). The linear relation between K_c and 1/dCMC can be fitted to the following equation (R^2 = 0.9947).

$$K_c = \frac{3.480}{\text{dCMC}} - 362.60 \quad (2)$$

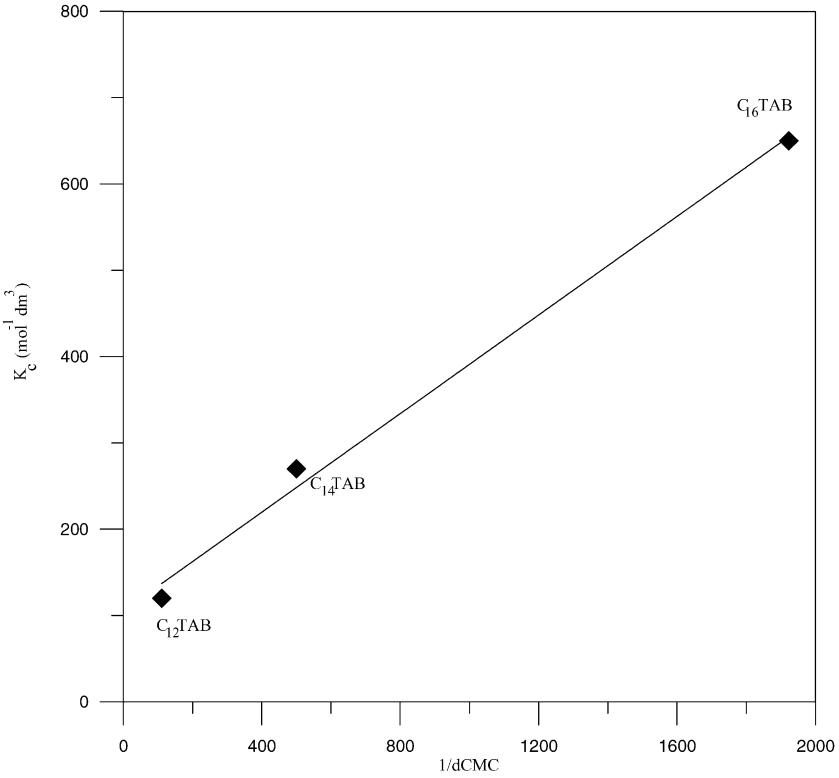

Fig. 3. The plot of the linear relation between K_c and 1/dCMC for C_{12}TAB, C_{14}TAB and C_{16}TAB.

Comparison of K_c values for C_{16}TAB, C_{16}PC and C_{16}PB shows that the molecular structure (having pyridinum ring) plays a fundemental role on the hydrophobic interacton and could represent its degree of hydrophobicity.

A comparison of the efficiency of cationic micelles on holding CA can be made also from f_{mic} values. Once the K_c value is determined the fraction of micellized CA (f_{mic}) can be calculated using the following equation [6,35].

$$f_{mic} = \frac{K_c M}{1 + K_c M} \quad (3)$$

The values of f_{mic} of CA calculated for 0.02 mol dm^{-3} surfactant concentration are listed in Table 1. The fraction of bound CA to micelles followed the same order as;

$C_{16}PB > C_{16}PC > C_{16}TAB > C_{14}TAB > C_{12}TAB$

The standard free energy change ΔG^0 can be calculated from the values of K_c, as follows [28,36]: $\Delta G^0 = -RT \ln K_c$.

ΔG^0, which is an indication of the tendency of the binding of CA to micelles, shows that CA interacts with C_{16}PC and C_{16}PB more easily and strongly than with alkyltrimethylammonium bromides at the same conditions. As seen in Table 2 the ΔG^0 values increased with increasing hydrophobicity of cationic surfactants.

Table 2
Values of standard free energy changes for the interaction of CA with cationic micelles

Surfactants	C_{12}TAB	C_{14}TAB	C_{16}TAB	C_{16}PC	C_{16}PB
ΔG (kJ/mol)	−11.86	−14.02	−16.05	−17.62	−18.15

3.2. Effect of medium polarity

As mentioned earlier CA exhibits a maximum at 492 nm under the working conditions the increase in absorbance with red shift caused from incorporation of CA to cationic micelles.

In order to gain further insight about the localization of CA into the various cationic micelles it has been monitored the dependence of CA absorption on the solvent medium (a series of *n*-aliphatic alcohols). The λ_{max} shift of CA in *n*-aliphatic alcohols of decreasing polarity was plotted against the corresponding dielectric constant (ϵ). Fig. 4 shows that the reduction of polarity involved a red shift and that the relationship between λ_{max} (nm) and dielectric constant (ϵ). As the shifts produced by surfactants were outside the range obtained with these *n*-alcohols, the dielectric constant values characteristics of surfactants were calculated by Eq. (4) derived from Fig. 4 (Table 3).

$$\mathrm{Ln}(\lambda) = \mathrm{Ln}\,553.97 - 0.035\epsilon \quad (4)$$

The location in micelles depends upon the structure of dye which may penetrate deeply into the nonpolar hydrocarbon core or remain adsorbed at relatively polar surface of micelle [27,29]. It has previously found that in the presence of cationic surfactants, aromatic compounds with carboxylic

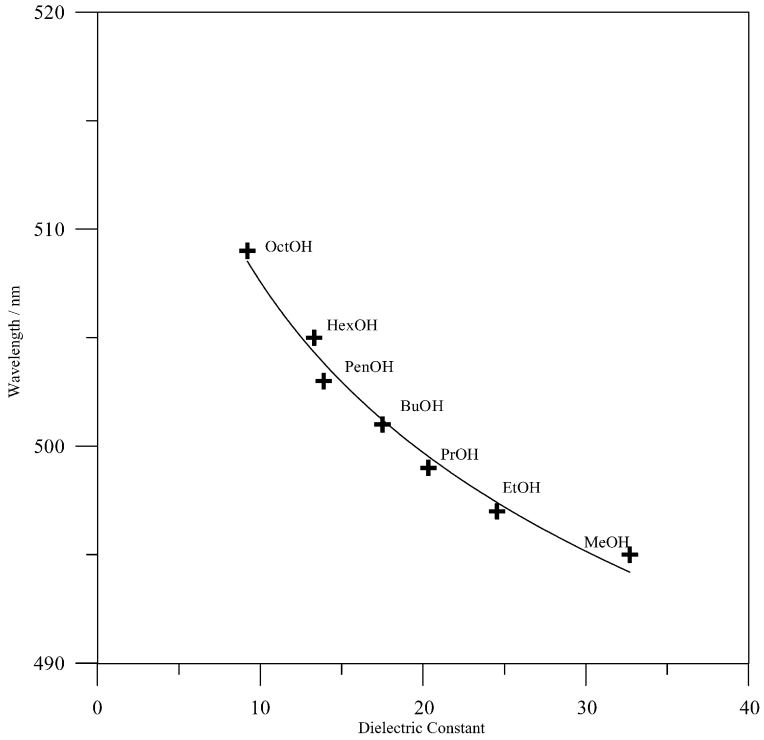

Fig. 4. λ_{max} values for 1.0×10^{-5} mol dm^{-3} CA in a series of *n*-alcohols (MeOH, EtOH, PrOH, BuOH, PenOH, HexOH, OctOH) as a function of the dielectric constants of the media at 298 K.

acid groups [37] are incorporated into the water-rich Stern layer of the micelle in a sandwich arrangement. This permits not only the hydration of the hydrophilic –COO^- group but also the solvation of the aromatic ring of the dye by the –$N^+(CH_3)_3$ group and the participation of Van der Waals interactions between adjacent surfactant chains and the dye organic moiety (hydrophobic forces). In this situation the microenvironment of the chromophore has clearly changed from that existing in the bulk phase and this change is the cause of the spectral shift observed. Micelles are characterized by three distinct regions: a nonpolar core formed by hydrocarbon tails of the surfactant, a compact Stern layer having the head groups and a relatively wider Gouy–Chapman Layer that encompasses majority of counter ions. Depending on the nature of the solute and micelle, a solute molecule may take place either to the non-polar core of micelles or to the micelle–water interfaces [38,39]. The micellar surface is less polar than water and the ionic micelles have a polarity near to that of pure ethanol even at the Stern layer [40,41]. In this context, it is worth mentioning the importance of the presence of a –COO^- group in CA. In the aromatic system with a –COO^- group the negative charge is delocalized and distributed over the terminal –COO^- group and the aromatic ring of CA; thus the cationic end of the surfactant will tend to interact electrostatically less with the –COO^-. The –COO^- group will therefore be buried deeper in the micelle leading to diminished electrostatic interaction between the –COO^- groups and the charged head-groups of the surfactant [8,42].

Table 3
Shift of the maximal absorption of 1×10^{-5} mol dm^{-3} CA in the presence of micelles, the corresponding apparent dielectric constant and the transition energies

Surfactant	$\Delta\lambda_{max}$	Dielectric constant	$\Delta E_T \times 10^5$ (joule)
C_{12}TAB	12	13	7.47
C_{14}TAB	46	3.35	2.60
C_{16}TAB	51	2.80	2.35
C_{16}PC	52	2.72	2.30
C_{16}PB	53.5	2.53	2.23

Dielectric constant of the medium derived from Eq. (4) and electronic transition energy corresponding to the red shift calculated from $\Delta E_T = hc/\Delta\lambda_{max}$, where $\Delta\lambda_{max} = \lambda_{max}$(CA–surfactant)$- \lambda_{max}$(CA–water) were listed in Table 3. Comparing the red shift ($\Delta\lambda_{max}$) values in the presence of cationic micelles it is seen that the red shift increased with decreasing medium polarity.The parallelism between polarity of the medium and electronic transition energies demonstrate the significant influence of hydrophobic interaction on localization as well as micellar binding degree. It can be concluded that CA molecules penetrate deeper towards the hydrocarbon core with increasing hydrophobicity of the surfactants.

4. Conclusions

Based on the study of the binding of CA to cationic micelles the following conclusions can be drawn.

1. The λ_{max} value of CA shifted to high wavelength in the presence of cationic micelles studied. The magnitude of this shift increased with increasing hydrophobicity of cationic surfactants. The magnitudes of these red shifts are comparable and indicate a decrease in polarity around the chromophore of CA molecule.
2. The K_c values of CA increased with the hydrophobicity of cationic surfactants indicate that hydrophobic interaction plays a major role in solubilization. It was observed that the CMC values of cationic surfactants decreased in the presence of CA has a direct relation between hydrophobicity of surfactants. It is evident from Table 1 the binding constant values are smaller for alkyltrimethylammonium bromide than for CPC and CPB. The marked increase in red shift in the presence of C_{16}PC and C_{16}PB indicates deeper localization of CA towards the micellar core in comparison to C_{12}TAB, C_{14}TAB and C_{16}TAB.
3. The K_c values and the λ_{max} value of CA in the presence of micelles and solvents are in conformity with the current view that the more hydrophobic character of the surfactants, the deeper is CA penetration to the interior of the micelle.

References

[1] S. Bracko, J. Span, Dyes and Pigments 50 (2001) 77.
[2] Y. Nemoto, H. Funahashi, J. Colloid Interface Sci. 80 (2) (1981) 542.
[3] A.K. Mandal, M.K. Pal, Spectrochim. Acta A 55 (1999) 1347.
[4] M. Sarkar, S. Poddar, J. Colloid Interface Sci. 221 (2000) 181.
[5] M. Sarkar, S. Poddar, Spectrochim. Acta A 55 (1999) 1737.
[6] R. Sabate, M. Gallardo, A. de la Maza, J. Estelrich, Langmuir 17 (21) (2001) 6433.
[7] B. Simoncic, J. Span, Dyes and Pigments 36 (1998) 1.
[8] M.E. Diaz Garcia, A. Sanz-Medel, Talanta 33 (1986) 255.
[9] B. Simoncic, M. Kert, Dyes and Pigments 54 (2002) 221.
[10] G. Nowicka, W. Nowicki, J. Chim. Phys. 91 (1994) 247.
[11] V.B. Gawandi, S.N. Guha, K.I. Priyadarsini, H. Mohan, J. Colloid Interface Sci. 242 (2001) 220.
[12] R.K. Dutta, S.N. Bhat, Colloids Surf. A 106 (1996) 127.
[13] S.S. Shah, R. Ahmad, S.W.H. Shah, K.M. Asif, K. Naem, Colloids Surf. A 137 (1998) 301.
[14] A.K. Chibisov, V.I. Prokhorenko, H. Gomer, Chem. Phys. 250 (1999) 47.
[15] R. Sabate, M. Gallardo, J. Estelrich, J. Colloid Interface Sci. 233 (2001) 205.
[16] P.M. Nassar, L.E. Almeida, M. Tabak, Biochim. Biophs. Acta 1328 (1997) 140.
[17] T. Handa, M. Nakagaki, K. Miyajima, J. Colloid Interface Sci. 137 (1990) 253.
[18] P. Kaschny, F.M. Goni, J. Colloid Interface Sci. 160 (1993) 24.
[19] S.B. Savvin, I.N. Marov, R.K. Chernova, S.N. Shtykov, A.B. Sokolov, Zh. Analit. Khim. 36 (1981) 850.
[20] A. Sanz-Medel, J.I. Garcia Alonso, E. Blanco Gonzalez, Anal. Chem. 57 (1985) 1681.
[21] H.-C. Chiang, A. Lukton, J. Phys. Chem. 79 (19751935).
[22] K.S. Birdi, H.N. Singh, S.V. Dolsager, J. Phys. Chem. 83 (1979) 2733.
[23] L. Dewitt, G.J. Blanchard, E. LeGoff, M.E. Benz, J.H. Liao, M.G. Kanatzidis, J. Am. Chem. Soc. 115 (1993) 12158.
[24] C. Samsonoff, J. Daily, R. Almog, D.S. Berns, J. Colloid Interface Sci. 109 (1986) 325.
[25] W. Caetano, M. Tabak, J. Colloid Interface Sci. 225 (2000) 69.
[26] P.F. Tavcer, J. Span, Text. Res. J. 69 (4) (1999) 278.
[27] M.J. Minch, S.S. Shah, J. Org. Chem. 44 (18) (1979) 3252.
[28] S.S. Shah, M.S. Khan, H. Ullah, M.A. Awan, J. Colloid Interface Sci. 186 (1997) 382.
[29] S.S. Shah, G.M. Laghari, K. Naeem, Thin Solid Films 346 (1999) 145.
[30] M.A. Awan, S.S. Shah, Colloids Surf. A 122 (1997) 97.
[31] H.A. Benesi, J.H. Hildebrand, J. Am. Chem. Soc. 71 (1949) 2703.
[32] R.K. Dutta, S.N. Bhat, Can. J. Chem. 71 (1993) 1785.
[33] Z. Yuan, M. Zhu, S. Han, Anal. Chim. Acta 389 (1999) 291.
[34] M.J. Rosen, Surfactants and Interfacial Phenomenon, Wiley, New York, 1978.
[35] L. Sepulveda, J. Colloid Interface Sci. 40 (3) (1974) 372.
[36] S.S. Shah, K. Naeem, S.W.H. Shah, G.M. Laghari, Colloids Surf. A. 168 (2000) 77.
[37] C.A. Bunton, M.J. Minch, J. Phys. Chem. 78 (1974) 1490.
[38] K. Bhattacharyya, B. Bagchi, J. Phys. Chem. A. 104 (2000) 10603.
[39] A. Datta, D. Mandal, P.S. Kumar, S. Das, K. Bhattacharyya, J. Mol. Liq. 77 (1998) 121.
[40] A.P. Abbott, C.L. Miaw, J.F. Rusling, J. Electroanal. Chem. 327 (1992) 31.
[41] S.K. Saha, P.K. Tiwari, S.K. Dogra, J. Phys. Chem. 98 (1994) 5953.
[42] M.S. Tute, Adv. Drug. Res. (1979) 6.