ELSEVIER

Dyes and Pigments 44 (2000) 181–193

DYES and PIGMENTS

Aggregation of *o,o′*- Dihydroxy azo Dyes III. Effect of cationic, anionic and non-ionic surfactants on the electronic spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4″-sulfophenyl)-5-pyrazolone]

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Received 22 June 1999; accepted 7 September 1999

Abstract

The effect of Septonex, TX-100 and SDS surface-active agents on the aggregation, the acid-base, and the optical properties of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4″-sulfophenyl)-5-pyrazolone] was studied by the spectrophotometric method. The study was performed in submicelle and micelle surfactant concentration, and at different dye/surfactant concentrations in a buffered system. Both the aqueous and micellar dissociation constants of the dye under investigation were evaluated at 22 ± 1°C. The changes in the absorption pattern resulted from the addition of surfactants at different pHs, where different species exist, and is explained on the basis of electrostatic interactions between the different existing dye species (azo/hydrazo/dimer/monomer) and the surfactant micelles and pre-micellar aggregates. Different tautomeric forms of the dye are suggested based on the different spectral changes. A model for the interaction between surfactants and the different dye species is proposed. This model explains both the observed spectral changes in micellar solution and the obtained micellar dissociation constants of the dye.

Keywords: Aggregation; Tautomerism; Surfactants; Dissociation; Spectroscopy; Azodyes

1. Introduction

Azo dyes are a versatile class of coloured organic compounds that have been extensively used in both industry and analytical chemistry. In particular *o,o′*-dihydroxy azodyes, which have been used as metal-chelates for dyeing protein fibres, find important applications in analytical chemistry as chromogenic indicators [1–5]. Complexation reactions with metal ions under specific conditions have been utilised for the spectrophotometric determination of metal ions. Recent work has made use of the favourable effects of surfactants on the spectrophotometric characteristics of metal complexes with various dyes. This effect has found many analytical applications, particularly in the development of new methods for metal-ions determination by chromogenic indicators in the presence of various surfactants [6–11]. The addition of cationic surfactants to a negatively-charged coloured binary complex may result in the formation of new analytical systems; it may lead to lowering of the pH at which the complex is formed, red-shifts in the absorption

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0143-7208/00/$ - see front matter
PII: S0143-7208(99)00086-8

bands, better solubilisation, more selectivity and increase in molar absorptivity [12]. The metal–dye complexes formed in the presence of surfactant are usually more stable than those formed in the absence of micelles. Azo dyes [6–8] and triphenylmethane dyes [9–11] are some of the more common chromogenic reagents that have been used in metal determination by the ternary system (metal–dye–surfactant).

The interactions between the dyes and surfactants alone represent the cornerstone in understanding and explaining the spectral changes observed in such complexation reactions. Investigations have however focused on the quantitative determination of the changes in both the acid-base and the optical properties [13–26]. Less attention have been paid to the nature and mechanism of these types of interactions which are still not clearly understood. It is clear that dye–surfactant interaction is of great value in understanding the chemical equilibria, mechanisms and kinetics of surfactant sensitised colour reactions [27–29]. In this paper the effect of Septonex as cationic, (TX-100) as nonionic and SDS as anionic surfactants on the electronic absorption spectra of 2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4″-sulfophenyl)-5-pyrazolone] is studied in aqueous medium. The spectral changes are explained on the basis of selective solubilisation, hydrophobic interactions and the concentration effect in the micellar pseudo phase. Several mechanisms have been given to explain the enhancement of solubility of the organic compounds in general, and azo dyes in particular, in surfactants [17,27–29]. Comparing these mechanisms, a model of the interaction between the dye under investigation and the different surfactants is suggested. This model explains the observed changes resulting from the dye incorporation into the micelle, where the different dye species experience an altered micro-environment.

2. Experimental

2.1. Chemicals

The azo dye was prepared and its purity was checked by TLC, elemental analysis, IR and NMR spectra [30]. Septonex, 1-ethoxycarbonylpentadecyl trimethylammonium bromide, M_w 422.57 and CMC $= 7.0\times10^{-4}$ mol l^{-1} was supplied by Spofa Praha. TX-100, octyl phenolpoly ethylene glycol ether, $M_w = 624.9$ and CMC $= 9.0\times10^{-4}$ mol l^{-1} was obtained from Koch Light, UK. The purity and structures of the surfactants were checked by elemental analysis and ^{1}H-NMR. The structure of the dye and surfactants used are shown in Scheme 1. Universal buffer solution (borate–acetate–phosphate) 0.4 mol l^{-1} was used with different volumes of 0.2 mol l^{-1} NaOH to give the required pH values. A stock solution of 1.0 mol l^{-1} KCl was used to stabilise the ionic strength.

2.2. Instruments

A pH 64 Radiometer (Copenhagen, Denmark) combined with a GK 2401 B electrode was used for the pH measurements after calibration with standard phthalate, phosphate and borate buffer solutions. All the samples were weighed on the Sartorius A 200 S. A Perkin–Elmer 684 SP combined with a P.E. data station was used for the IR spectra measurement of the azo dye used in KBr discs and also in Nujol. ^{1}H NMR and H,H-cosy spectra of the azo dye was measured in DMSO-d_6 at 400.13 MHz using a Burker AM400 (Belgium). UV–vis measurements were performed using the PU 8800 SP (Pye Unicam, Cambridge, UK) combined with a cell temperature controller.

2.3. Measurements

10^{-3} mol l^{-1} stock solution of the azo dye was prepared by dissolving the appropriate weight of the solid in double distilled water. This solution was monitored spectrophotometrically and found to be stable for months. More dilute solutions were prepared by further dilution of the stock.

7.0×10^{-2}, 9.0×10^{-2} and 2.0×10^{-1} mol l^{-1} Septonex, TX-100 and SDS, respectively, were prepared by dissolving the calculated weight in double distilled water. Different lower concentrations were obtained by further dilution of the stocks. The equivalent number of ml for a desired concentration of the dye and surfactants were taken from the stocks and mixed in a 10 ml flask

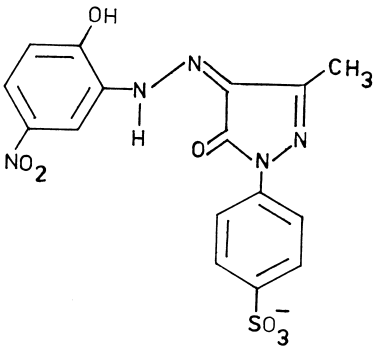
with 1 ml KCl of the stock. The volumes were completed with double- distilled water or buffer and were measured immediately at 22 ± 1.0°C. The p*K*a and apparent p*K*a values were determined by graphical and graphical–logarithmic analysis of the correlation $A = f(\mathrm{pH})$ at analytical wavelength in the region of maximum absorbance of both acid-base forms and in their immediate vicinity.

3. Results and discussions

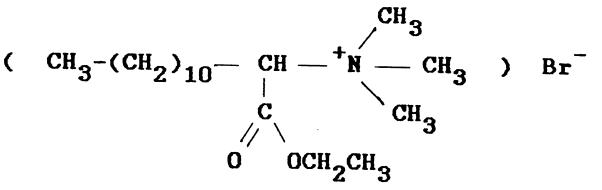
3.1. Effect of pH on the electronic absorption spectra

The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} of the dye solution in universal buffer with different pH ranging from 1.65 to 12.83 was measured in the presence of 0.1 molar KCl. The dye

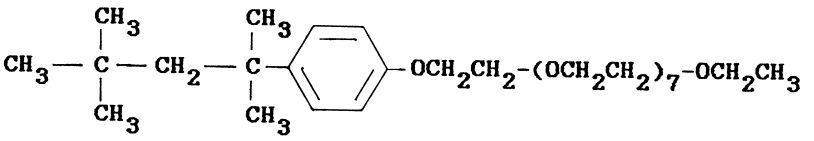
2-hydroxy-5-nitrophenylazo-4-[3-methyl-1-(4"-sulfophenyl)-5-pyrazolone]



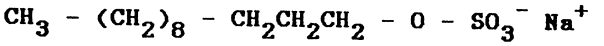
Septonex



Triton X-100



Sodium Dodecyl Sulfate



Scheme 1. The structure of the Dye, Septonex, TX-100 and SDS.

under investigation contains three ionizable protons and could be symbolised as H_3Ar in the molecular form. The first proton, (in the sulfonate group) is very acidic and was non-detectable in the pH range of determination [31]. Hence, the existing species in the acidic range up to pH 4.0 is H_2Ar^- and is shown by the absorption band with a maximum at $\lambda = 400$ nm (Fig. 1). At higher pH values, a new absorption band appears at $\lambda = 480$ nm. The propagation of this band is accompanied by a hypochromic shift of the 400 nm band and an appearance of another new band at 328 nm. The 480 nm band is most probably due to the second ionised form HAr^{2-}. The absorption curves of H_2Ar^- and HAr^{2-} forms give a distorted isosbestic point which is gradually red shifted (425–440 nm) on going to higher pH values. The absorption of the third ionised form Ar^{3-} appears at pH over 9.00 and is hypsochromic shifted compared to the HAr^{2-}. It exists in equilibrium with the azo form and gives a broad absorption band with a maximum between 400 and 460 nm. The HAr^{2-} species in the 1.0×10^{-4} mol l^{-1} solution exists in the hydrazo-dimer form $(HAr^{2-})_2$ at the pH range below 5.0 [30]. At pH 5.6, the more acidic proton (from the *p*-nitrophenol portion) ionises where the hydrazo-dimer form dissociates into two hydrazo-monomers in the ionic form $[(H_2Ar^{1-})_2 \leftrightarrow 2(HAr^{2-}) + 2H^+]$. The latter form is partially in equilibrium with its azo tautomer. At pH 10.05, the imino group proton ionises, but the hydrazo-monomer tautomeric form Ar^{3-} is probably shifted to its azo form to separate the two negative charges as shown in the ionisation mechanism in Scheme 2. It can be concluded that the ionisation step from $(H_2Ar^{1-})_2$ to the HAr^{2-} passes through the formation of the hydrazo-monomer form H_2Ar^{1-}, as in the Eq. (1).

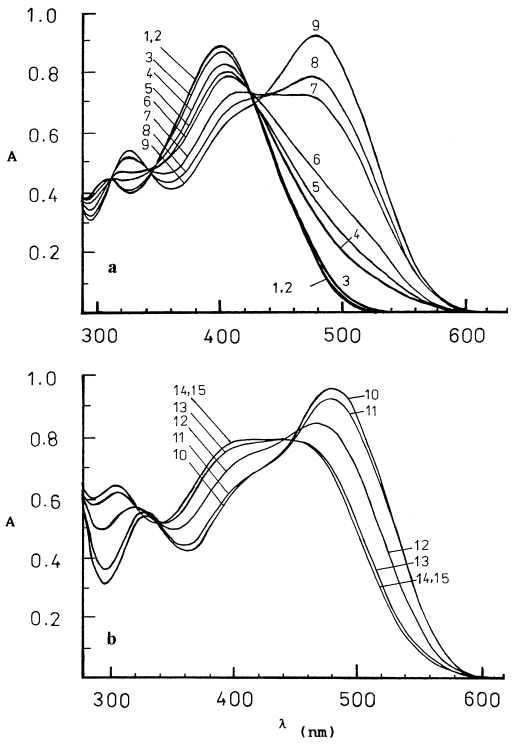


Fig. 1. The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer solutions ($\mu = 0.1$ mol l^{-1} KCl). Curves 1–15 represent the pH values: 1.65, 2.73, 3.73, 4.86, 5.03, 5.27, 5.85, 6.10, 7.05, 7.95, 9.01, 10.02, 11.24, 12.54 and 12.83, respectively.

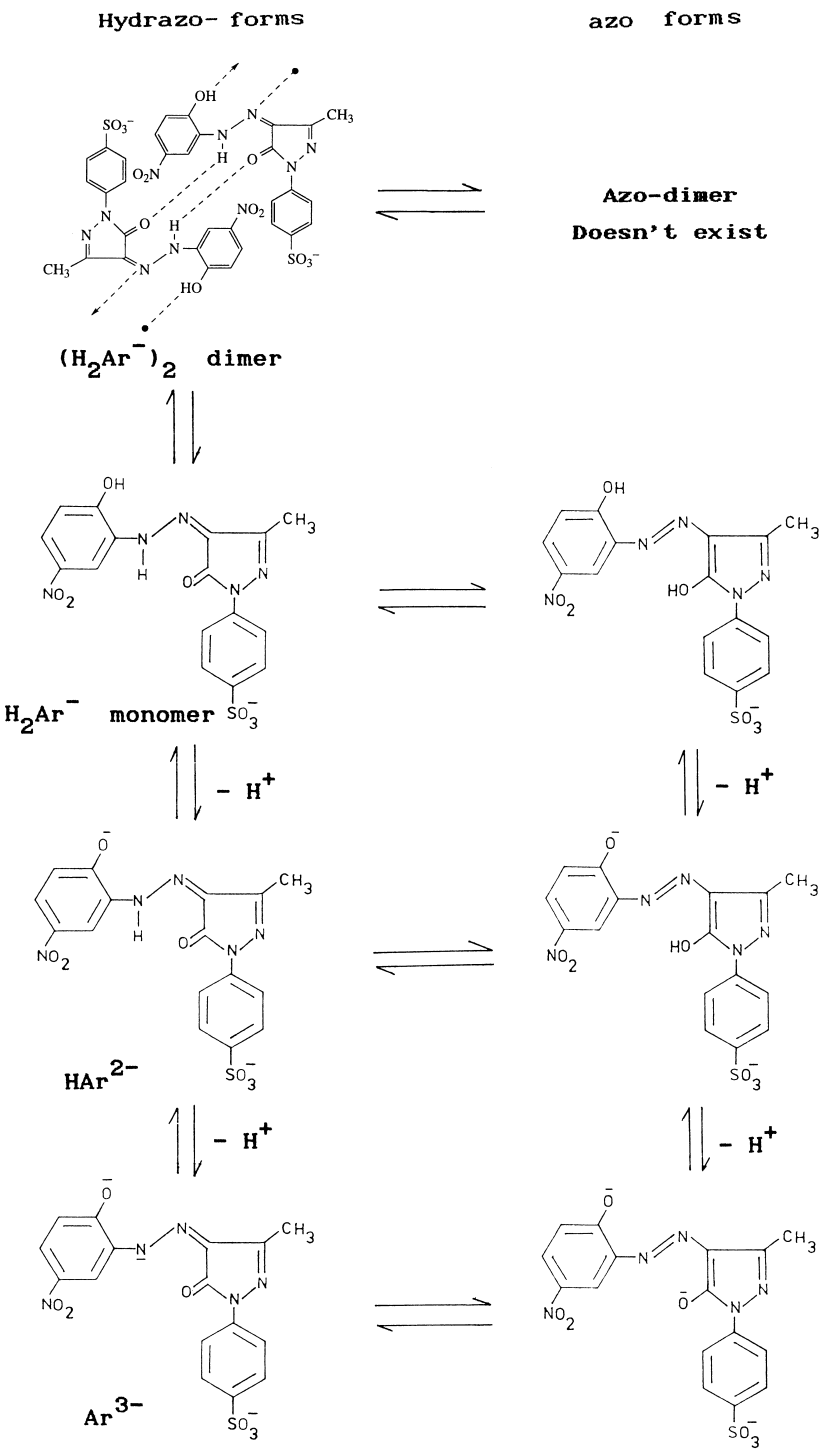
$$(H_2Ar^{1-})_2 \overset{pH<5.4}{\leftrightarrow} \underset{\lambda=400\,nm}{2H_2Ar^{1-}} \overset{pH5.49}{\leftrightarrow} \underset{\lambda=480\,nm}{2HAr^{2-}} + 2H^+ \quad \underset{\lambda=480nm\pm\Delta\lambda}{} \quad (1)$$

This non-simple ionisation step gives rise to the appearance of the distorted isosbestic point between 425 and 440 nm, where $\Delta\lambda$ in the previous equation is <15 nm. Both the pK_2 and the pK_3 values of the dye were evaluated from the pH-absorbance correlation at different analytical wavelengths ($\lambda = 400$ and 480 nm) and data are given in Table 1.

3.2. Effect of Septonex

3.2.1. Effect of Septonex on the spectral absorption pattern

In a strong acidic medium, 0.02 mol l^{-1} HCl, the dye exists in the $(H_2Ar^{1-})_2$ form shown by the absorption band at $\lambda = 400$ nm. Addition of various concentrations of Septonex causes only a gradual slight bathochromic shift to 416 nm (at Septonex concentration 3.5×10^{-2} mol l^{-1}). The shift is accompanied by a very small hyperchromic shift around the wavelength position assigned to the hydrazo-monomer H_2Ar^{1-}, $\lambda = 480$ nm. Hence it is concluded that either Septonex is unable to micellise at such pH range and only acts as salt, or



Scheme 2. The mechanism of ionisation for the DYE in buffered aqueous solution.

its micelles are not able to affect the stable $(H_2Ar^{1-})_2$ form with its strong intermolecular hydrogen bonding in this strong acidic medium. At pH 3.6, where mainly the $(H_2Ar^{1-})_2$ dimeric form exists, increase of Septonex from 0.7 to 2.8×10^{-3} mol l^{-1} (Fig. 2), causes a gradual appearance of an absorption band at 508 nm. This new band is due to either the monomeric form (H_2Ar^{1-}–Septonex) or the ionised form (HAr^{2-}–Septonex), or a mixture of both. The addition of Septonex to the 1.0×10^{-4} mol l^{-1} dye solution in water, pH 4.94, causes significant changes and clearly affects the absorption spectra of the dye solution (Fig 3). At this pH the free dye mainly gives an absorption band at 400 nm representing the hydrazo-dimer form $(H_2Ar^{1-})_2$. Two other residual absorbencies are observed at 338 and 500 nm. The former is due to the azo monomer form and the latter belongs to either the hydrazo-monomer form H_2Ar^{1-} or the partially ionised form HAr^{2-}, or both together. In presence of Septonex far below the cmc ($\cong$7.0-4$\times$10 mol l^{-1}), slight turbidity occurs, which might be argued be due to the formation of partially insoluble dye-Septonex ion associates or aggregates. At 2.8×10^{-4} mol l^{-1} of Septonex and above, increasing Septonex concentration causes a hypochromic shift of the dimer form (H_2Ar^{-}) 2 band at $\lambda=400$ nm. The hydrazo-monomer (or the ionised form HAr^{2-}) band at $\lambda=500$ nm and its coexisting azo

Table 1
Aqueous and micellar pK_a values of the azo dye[a]

Surfactant type	Surfactant concentration	pK_2	pK_3	Analytical wavelength
No surfactant	–	5.49	10.16	400, 480 nm
Septonex	3.5×10^{-4}	4.92	10.61	420, 500 nm
Septonex	7.0×10^{-4}	4.56	10.28	420, 500 nm
Septonex	1.4×10^{-3}	4.32	10.24	420, 500 nm
Septonex	3.5×10^{-3}	4.30	10.22	420, 500 nm
TX-100	5.0×10^{-4}	5.80	10.14	420, 480 nm
TX-100	8.0×10^{-4}	5.82	10.25	420, 480 nm
TX-100	1.0×10^{-3}	5.88	10.41	420, 480 nm
TX-100	2.0×10^{-3}	5.93	10.63	420, 480 nm

[a] $\mu=0.1$ mol l^{-1} Kcl, $t=22\pm1.0$°C.

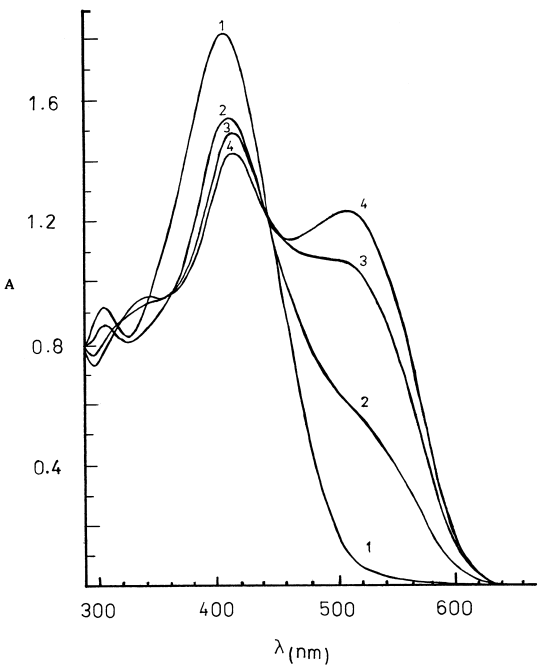


Fig. 2. Effect of Septonex on the electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer with pH 3.6. Curves 1–4: 0.0, 7.0×10^{-4}, 1.4×10^{-3} and 2.8×10^{-4} mol l^{-1} Septonex.

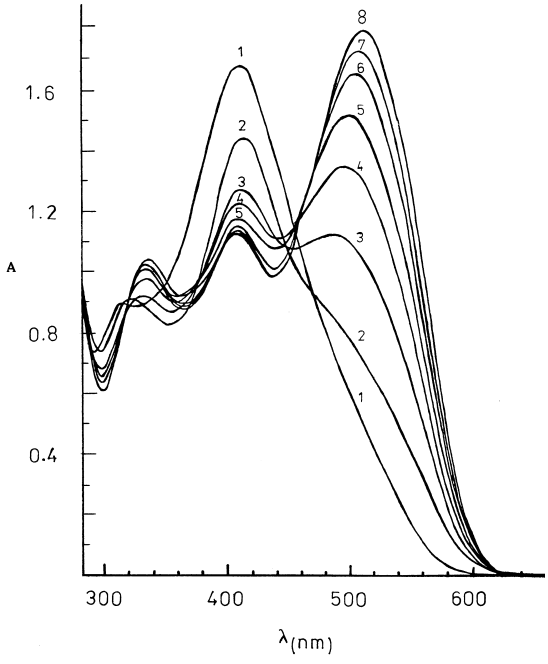


Fig. 3. Effect of Septonex on the electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in water (pH = 4.9). Curves 1–8: 0.0, 2.8, 3.5, 4.9, 7.0 ($\times10^{-4}$), 1.06, 1.42 and 4.25 ($\times10^{-3}$) mol l^{-1} Septonex, respectively.

band at $\lambda = 328$ nm both undergo strong hyperchromic shift. At the same pH, Septonex affects the 1.0×10^{-5} mol l^{-1} dye solution in the same above mentioned way with only one difference. The 1.0×10^{-5} mol l^{-1} dye solution displays two overlapped electronic absorption bands at 400 and 500 nm due to the dimer and monomer forms (Fig. 4). Addition of 3.5×10^{-4} mol l^{-1} Septonex gradually suppresses the 500 nm band (monomer band) (Fig. 4). This may be attributed to the formation of preliminary ion associates or aggregates in which a small volume the dye is concentrated. Increasing Septonex concentration, exceeding the limit to dissolve the aggregates or to form micelles, results in normal shift from the dimer to the monomer form and dissociation of the dye. At pH 7.9, the ionised form HAr^{2-} exists predominantly, and gives a shouldered absorption band at 480 and 420 nm (Fig. 5). Addition of Septonex only affects the spectral band resolution where this shouldered electronic absorption band is successfully separated into two maxima at 520 and 410 nm, respectively. This is probably due to the stabilisation of the ionised form HAr^{2-} by forming the more stable HAr^{2-} –Septonex, which absorbs at longer wavelength.

3.2.2. *Effect of Septonex on the dissociation constant values*

The effect of pH on the electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer solution at the pH range 1.72–12.81 was studied in the presence of 0.1 KC mol l^{-1} and different Septonex concentrations below and above the cmc. Septonex concentrations were 3.5, 7.0×10^{-4}, 1.40 and 3.52×10^{-3} mol l^{-1}. Fig. 6 shows the effect of pH on the absorption spectra of the dye solution in the presence of 1.4×10^{-3} mol l^{-1} Septonex. The isosbestic points at $\lambda = 316$, 358 and 452 nm indicate equilibrium between the H_2Ar^{1-} and the HAr_{2-} species and those at $\lambda = 340$ and 480 nm indicate the HAr^{2-} and Ar^{3-} equilibrium. The equilibrium between the different species is simpler in the presence (Fig. 6) than in the absence of Septonex (Fig. 1). Increasing Septonex concentration causes better spectral band resolution, and more ordered spectral patterns are obtained. The

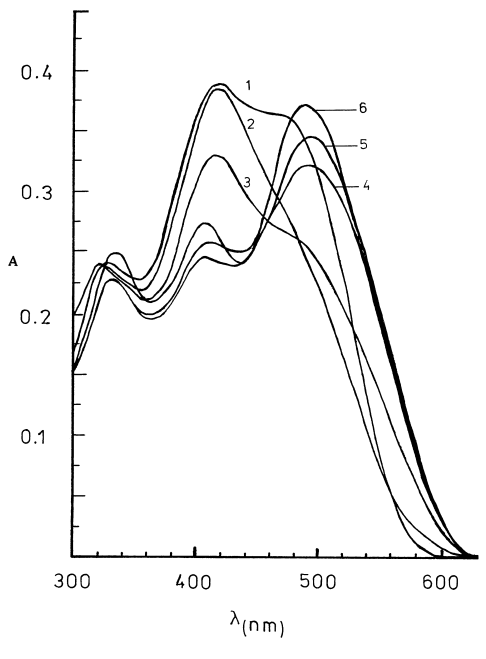


Fig. 4. Effect of Septonex on the electronic absorption spectra of 1.0×10^{-5} mol l^{-1} dye in water (pH = 4.9). Curves 1–6: 0.0, 3.5×10^{-6}, 1.4×10^{-5}, 7.0×10^{-5}, 1.4×10^{-4} mol l^{-1} Septonex, respectively.

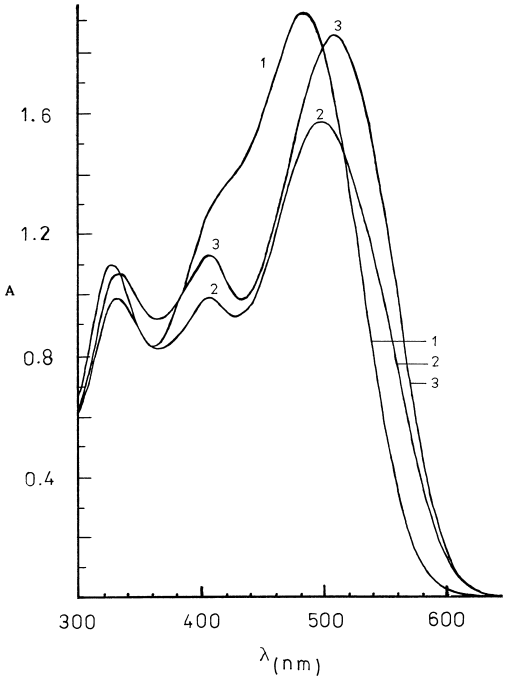


Fig. 5. The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer solution with pH 7.5 in presence of Septonex. Curves 1–3: 0.0, 2.8×10^{-4} and 2.8×10^{-4} mol l^{-1} Septonex.

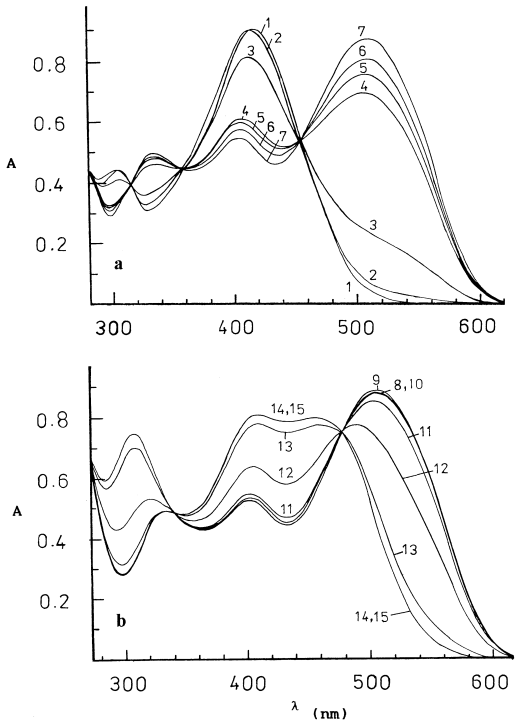


Fig. 6. The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer solutions and 1.4×10^{-3} mol l^{-1} Septonex ($\mu=0.1$ mol l^{-1} KCl). Curves 1–15 represent the pH values: 1.62, 2.70, 3.72, 4.85, 5.00, 5.26, 5.82, 6.00, 7.10, 7.98, 9.00, 10.04, 11.23, 12.50 and 12.81, respectively.

apparent pK_a values were evaluated in the presence of the above-mentioned Septonex concentrations and the obtained apparent pK_2 and pK_3 values are given in Table 1. It is apparent from the pK_a values that increasing Septonex concentration lowers the pK_2 values. This effect is maximum near the cmc value. The pK_3 value is also affected, but in a different way. The first addition of Septonex raises the pK_3 to a value (10.61) higher than that of the dye (10.16), and then further increases of Septonex concentration gradually lower the pK_3 values.

3.2.3. Mechanism of dye–Septonex interaction

In order to propose a mechanism for the dye–Septonex interaction, two main factors should be taken into consideration: The dye molecule is mainly hydrophobic with one strong hydrophilic (solubilising) $-SO_3^-$ group and other hydrophiles such as the hydroxyl groups. Septonex molecules are also long hydrophobic chains with small hydrophilic head groups. In order to minimise contact with water and reduce the interfacial free energy of the system, the dye molecule dimerizes at relatively high concentration [32] and Septonex micellize at critical concentration (cmc) [33]. Now let us consider the interaction between the predominant hydrazo-dimer form and the micelles of Septonex. The organic hydrophobic part of the dye is solubilised into the micellar core while the ionic $-SO_3^-$ group, the hydroxyl and hydrazo groups lie in the Stern-layer oriented near the micelle surface. This interaction prefers the existence of hydroxyl groups which are not participating in intermolecular hydrogen bonding (which only exists in the monomeric form). The vacancies inside the micelle core may not be able to accommodate the bulky and rigid dimer molecule but only the flexible monomer form (rotation around the single bond of the hydrazo group). In the reverse way, the dimer may not be able to penetrate the micelle except after monomerisation. This leads to the most stable form of interaction, which is the micelle monomer. The residual amount of dimer which exists in all cases comes from that amount of the dye in the bulk solution and outside the micelles. The equilibrium between the different dye species and the micelles of Septonex can be indicated by Eq. (2).

$$\begin{aligned}&\text{Dye molecules in the bulk solution}\\&\qquad\text{monomer}+\text{dimer}\\&\leftrightarrow\ \text{dye molecules in micelles}\\&\qquad\text{monomer}\end{aligned}\qquad(2)$$

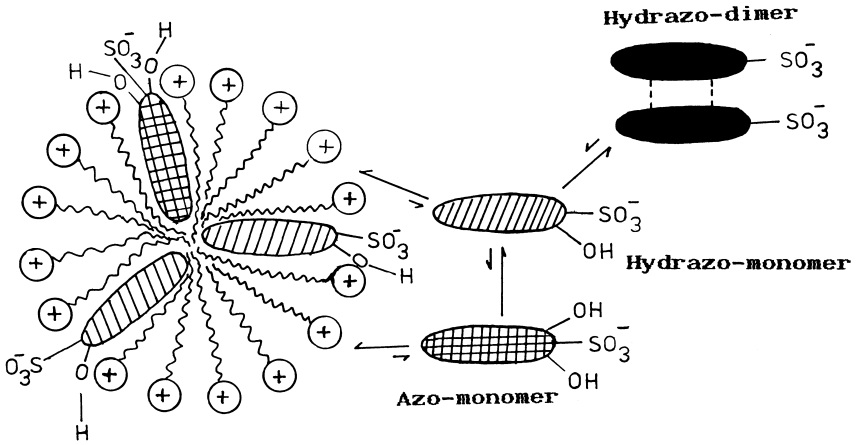
As an alternative explanation, the surfactant (Septonex) micelle cavities act as a porous catalyst, so that the dye molecules exist mostly in the monomeric form. This assumed micellar solublization has a character similar to the hydrophilic effect that plays a role in the formation of inclusion complexes with cyclodextrin [34,35]. Scheme 3 shows a simplified two dimensional model for the dye–Septonex interaction. A change in the polarity of the medium also takes place due to the incorporation of the dye into the surfactant micelles. This leads to a shift in the absorption maxima of all forms of the dye compared to their positions in the aqueous phase. This change is a consequence of the energy change of the ground and excited states of the dye. Septonex affects the

pK_a values of the dye as follows: The organic hydrophobic part of the dye is dissolved into the micelles while the ionic or polar groups lie in the Gouy–Chapman layer the near Stern layer (short penetration) [34]. The ionisable protons are oriented and organised at the micelle surface, which gives rise to the lowering of the pK values as a consequence of the pH difference (ΔpH) between the bulk solution and that near the micelle surface [27]. This ΔpH is negative, due to the attraction of the OH^- or the repulsion of the H^+ ions at the micelle surface by the cationic head groups, which plays an important role in increasing the dissociation constant values. The deprotonation step was sharp and selective where all the ionisable protons exist in the same environment near the micelle surface, and the micelle acts as a solid support in solution which facilitates easier ionisation at a narrow pH range (Scheme 4).

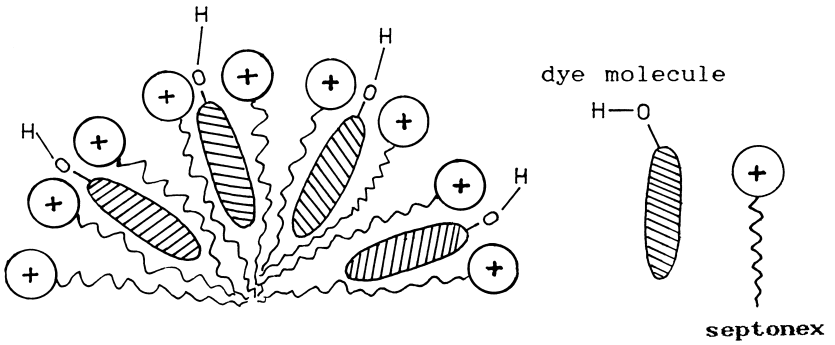
On the other hand, the pK_3 values were higher than that of the free dye, which is probably due to stabilisation of the HAr^{2-} form of the dye by ion pair formation with the surfactant cation before the micelle or pre-micelle formation at C < CMC and/or the excessive negative charge on the Ar^{3-} species. Further increase of Septonex concentration and the formation of micelles slightly lowers the pK_3, due to enlargement of the micellar size to better accommodate and separate the Ar^{3-} forms.

3.2.4. *Effect of TX-100 concentration on the EAS of the dye*

TX-100 as non-ionic surfactant affects the absorption spectra of 1.0×10^{-4} mol l^{-1} dye aqueous



Scheme 3. Two-dimensional representation for the mechanism of penetrating the dye molecule into Septonex micelle.



Scheme 4. Two-dimensional representation for the mechanism of proton ionisation from the dye bounded to the Septonex micelle.

solution at pH values higher than 4.0. At lower pH, the absorption pattern shows no changes at all TX-100 concentrations. However, at pH 5.3 (Fig. 7) increasing TX-100 concentration from 4.28×10 to 6.42×10^{-4} mol l^{-1} (i.e. below, at and above the cmc) causes a gradual hypochromic shift at $\lambda=500$ nm accompanied with simultaneous hyperchromic shift of the absorption band at $\lambda=400$ nm. The former belongs to the hydrazo-monomer form (H_2Ar^{1-}) and to small amount of the ionised form (HAr^{2-}), while the latter corresponds to the hydrazo-dimer form $(H_2Ar^{1-})_2$. Two isosbestic points are apparent at $\lambda=440$ and 370 nm, indicating equilibrium between the dimer and monomer forms. The equilibrium is shifted towards the dimer formation by increasing TX-100 concentration. Fig. 8 shows the effect of TX-100 on 1.0×10^{-5} mol l^{-1} dye solution, at pH 5.3 where the free dye displays three electronic absorption bands at 328, 400 and 480 nm corresponding to the azo, dimer and hydrazo-monomer forms [30], respectively. Addition of TX-100 gradually damp the hydrazo-monomer and the HAr^{2-} band at $\lambda=480$ nm and its coexisting azo band at $\lambda=328$ nm. This is accompanied by a hyperchromic shift at the band position corresponding to the hydrazo-dimer as the $(H_2Ar^{1-})_2$ forms. Two isosbestic points are observed at $\lambda=420$ and 355 nm, indicating equilibrium between the different species. At pH 7.5 (Fig. 9) the free dye in 1.0×10^{-4} mol l^{-1} solution displays a shouldered absorption band between 400 and 480 nm with a maxima at 480 and shoulder at 425 nm, representing the HAr^{2-} and H_2Ar^{1-} species, respectively. Addition of Triton X-100 results in gradual successive band resolution, shifting the HAr^{2-} band bathochromically to $\lambda=502$ nm and hypochromically, while the H_2Ar^{1-} band is shifted hypsochromically to $\lambda=410$ nm.

3.2.5. *Effect of TX-100 on the dissociation constant values*

The effect of pH on the electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye in buffer solution at the pH range 1.61–12.80 was studied in the presence of different TX-100 concentrations below and above the cmc, 5.0×10, 1.0×10 and 2.0×10 mol l^{-1} in the presence of 0.1 mol l^{-1} KCl. Fig. 10

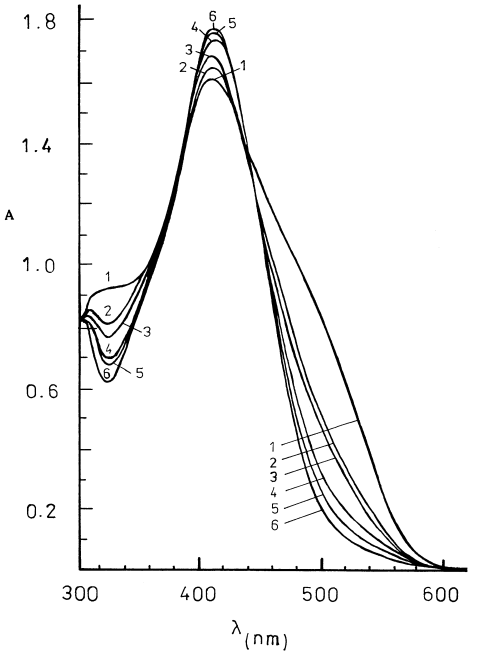


Fig. 7. The electronic absorption spectra of 1.0×10^{-4} mol l^{-1} dye at pH 5.3 and in the presence of TX-100. Curves 1–6 represent: 0.0, 4.28×10^{-4}, 8.56×10^{-4}, 1.07×10^{-3}, 2.14×10^{-3} and 6.42×10^{-3} mol l^{-1} TX-100.

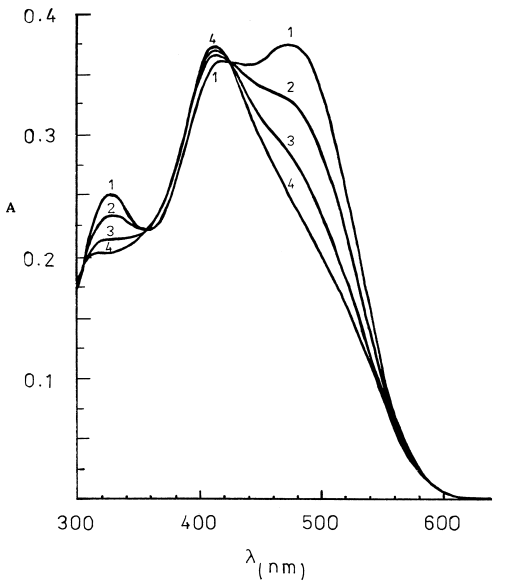


Fig. 8. The electronic absorption spectra of 1.0×10^{-5} mol l^{-1} dye at pH 5.3 and in the presence of TX-100. Curves 1–4 represent: 0.0, 4.28×10^{-4}, 8.56×10^{-4} and 5.35×10^{-3} mol l^{-1} TX-100.

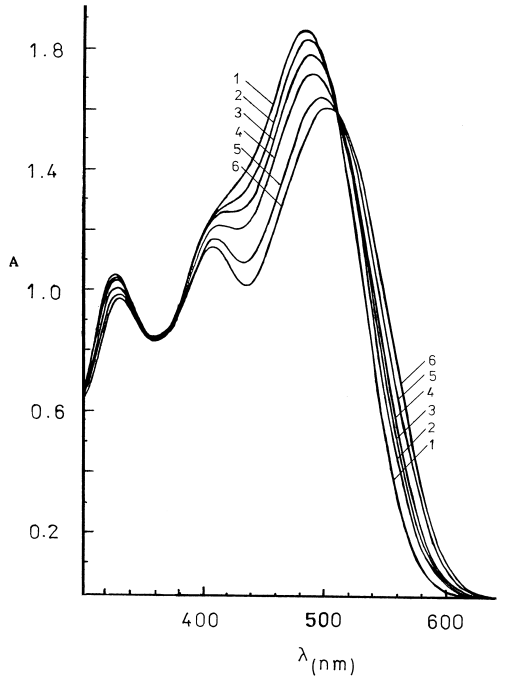


Fig. 9. The electronic absorption spectra of 7.5 1.0×10^{-4} mol l^{-1} dye at pH 7.5 and in the presence of TX-100. Curves 1–5 represent: 0.0, the free dye in 1.0×10^{-4} mol 6.42×10^{-4}, 1.07×10^{-3}, 2.14×10^{-3} and mol $litre^{-1}$ TX-100.

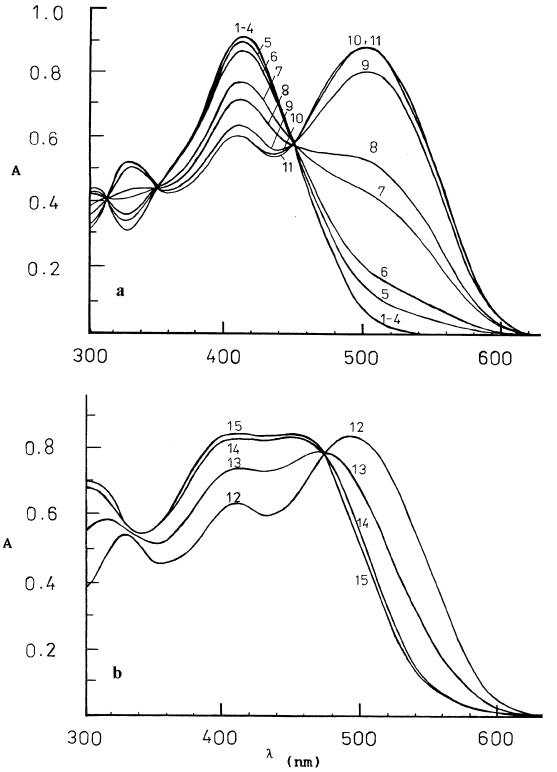
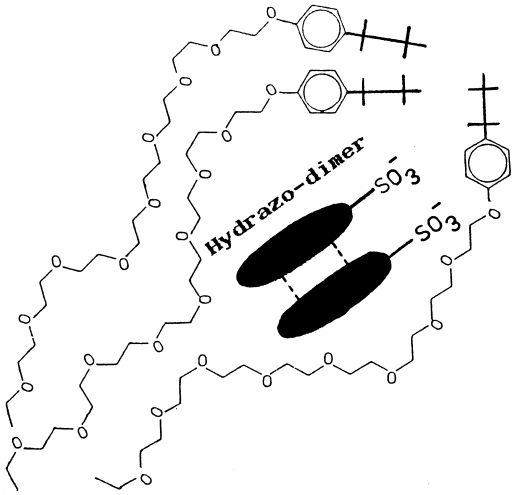


Fig. 10. The electronic absorption spectra of 1.0×10^{-4} mol $litre^{-1}$ dye in buffer solutions and 2.0×10^{-3} mol l^{-1} TX-100 1($\mu=0.1$ mol l^{-1} KCl). Curves 1–15 represent the pH values: 1.61, 2.70, 3.68, 4.80, 5.00, 5.20, 5.80, 6.00, 7.00, 7.90, 9.00, 10.02, 11.20, 12.49 and 12.80, respectively.

shows the effect of pH on the absorption spectra of the 1.0×10^{-4} mol l^{-1} dye solution in presence of 2.0×10^{-3} mol l^{-1} TX-100. Comparing the absorption pattern with that of the free dye, TX-100 was found to organise and uniform the different species to be in simple equilibrium. This is indicated from the fine resulting absorption pattern with different isosbestic points throughout the whole absorption range at $\lambda=315$, 350 and 450 nm at the pH range 1.61–7.80, and at $\lambda=475$ nm at the pH range 9.06–12.80. On the other hand, in contrast to Septonex, TX-100 depresses the monomer formation and hence retardes ionisation of the H_2Ar^{1-} form, which absorbs at $\lambda=412$ nm, to the form HAr^{2-} given by the electronic absorption band at 500 nm. This is probably because it stabilises the hydrazo-dimer form which absorbs at $\lambda=412$ nm, and is bathochromically shifted compared with that of the free dye or dye in presence of Septonex ($\lambda=400$ nm). Both the pK_2 and pK_3 values (Table 1) in presence of TX-100 were found to be higher than that of the free dye without TX-100.

3.2.6. The mechanism of the Dye–TX-100 interaction

TX-100 as non-ionic surfactant was found to have a reverse effect on both the absorption spectra and p*K*a values compared with Septonex. TX-100 preferentially stabilises the hydrazo dimer form of the dye via a deep penetration mechanism in which the OH groups are not free due to their participation in intermolecular hydrogen bonding. The hydrazo monomer and its coexisting azo monomer were retarded by the addition of TX-100. Its addition causes either partial or complete damping of the electronic absorption band corresponding to the monomer form with a consequent hyperchromic shift at the absorption position of the dimer form. For instance, on the addition of TX-100, the absorption band of the dye at $\lambda=500$ nm



Scheme 5. Two-dimensional representation for the mechanism of penetrating the dye molecule into TX-100 micelle.

(due to the monomer form) was hypochromic shifted with a simultaneous hyperchromic shift of the band at $\lambda = 400$ nm (due to the dimer form). Both the pK_2 and pK_3 values of the studied dye were affected in the same direction by the addition of TX-100. The pK_a values were higher in the presence rather than in the absence of TX-100. The most pronounced effect was around the cmc. The effect of TX-100 to increase the pK_a values was accompanied with a selective ionisation step in the narrow pH range due to the arrangement of the dye molecules into the surfactant micelles in the same environment. In contrast to Septonex, the Δ pH between the bulk solution and the TX-100 micelle surface is positive due to the repulsion with the OH^- or the attraction of the H^+ ions in this case. This retards the proton ionisation and higher the pK_a values. Increasing the TX-100 concentration gives larger micelles and more stabilises the dimeric form and hence, retards the breakage of the intermolecular hydrogen bonding in the dimer to the monomer form with its free OH groups (Scheme 5). Consequently, it retards the creation of the HAr^{2-} and Ar^{3-} ions by proton attraction to the micelle surface.

3.3. *Effect of sodium dodecyl sulfate*

The presence of various concentrations of SDS—5.68×10^{-3}–5.7×10^{-2} mol litre^{-1} — showed negligible effect on the absorption pattern of 1.0×10^{-4} mol l^{-1} dye solution at all pH values. No changes on the band position or shape were evident. Accordingly, it is concluded that SDS, as a common ion to that of the dye, does not affect the absorption spectra and the dissociation constant values for the azo dye studied.

4. Conclusion

The aggregation of *o,o′*-dihydroxy azo dyes in solution is highly affected by the concentration of the dye [30], the temperature and the solvent at which the measurements are performed [36]. Surfactants were found to cause pronounced changes on the absorption spectra of this class of dye in general, and specifically the dye under investigation. The observed changes of the electronic absorption spectra are concluded to be the following:

- A change in the aggregation of the dye molecule. Formation of aggregates, usually dimers of the dye, which appear as changes in the absorption spectra and affected by incorporation of the individual forms of the dye into the micelles of the surfactant.
- The shift of the dimer monomer equilibrium (by surfactant addition) influences the keto-enol tautomerism that is reflected in a change in the intensity of the absorption

bands corresponding to these tautomeric forms (azo/hydrazo).

- The effects on the dye dissociation where the dissociation constant is increased or suppressed depending on the type of surfactant. This change is due to the bonding of the dye molecules in the surfactant micelles and the attraction or repulsion of H^+ and/or OH^- ions to the surface of the micelles. Before cmc, the formation of ion pairs between the dye and the surfactant pre-micellar aggregates is the most probable [28].
- During the incorporation of the dye into the surfactant micelles, a change in the polarity of the medium leads to a shift in the absorption maxima of all forms of the dye compared to their positions in the aqueous phase. This change is a consequence of the energy change of the ground and excited states of the dye molecule.

In Septonex the dye is most preferably solubilised into the micellar core exposing its solubilising groups in the vicinity of the Stern Layer of the cationic surfactant (short penetration mechanism). This leads to selective, sharp deprotonation, and lower apparent ionisation constant. The micelle here acts as a sieve, where only the monomer form penetrates the micelle; hence a shift from the dimer to the monomer occurs by addition of Septonex. In TX-100, the dye is totally solubilised inside the micelle core with its solubilising groups partially de-shielded from the aqueous medium (deep penetration mechanism). This leads to an increase in the apparent ionisation constant values, and stabilisation of the dimeric form.

Acknowledgements

The authors thank the UNALCO program and the Anal. Chem. Dept., Charles University for the financial support given during part of this study.

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