SPECTROPHOTOMETRIC STUDY OF THE INTERACTION OF BROMOPYROGALLOL RED WITH TENSIDES AND THE EFFECT OF $NaNO_3$

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A study was carried out of the effect of a strong electrolyte ($NaNO_3$) on the change in the electron spectra (in the visible region) of bromopyrogallol red in the presence of Septonex, sodium dodecyl sulfate and Triton X-100. It was confirmed that $NaNO_3$ has a marked effect on the solubilization of the dissociated forms of the dye in Septonex, in contrast to solubilization by Triton X-100.

Study of the interaction of organic spectrophotometric reagents with the group of surface-active substances denoted as tensides has become a subject of continuing interest because it has been demonstrated that these interactions are decisive for explanation of the favourable effect of tensides on the spectrophotometric determination of metal ions. The information obtained is also equally interesting for industrial applications.

The effect of cationogenic tensides of the quaternary ammonium salt type on the absorption spectra and dissociation constants of bromopyrogallol red have been studied[1 – 3]. However, it has already been shown in a study of the use of bromopyrogallol red in spectrophotometry[4,5] that the absorption spectra and dissociation constants in the presence of a tenside are affected by the ionic strength of the solution. Consequently, this effect was studied in greater detail in this work. The study was carried out not only with the cationogenic tenside Septonex (CPTB) but also with the anionogenic tenside sodium dodecyl sulfate (SDS) and the nonionogenic tenside Triton X-100 (TX), as they can also be expected to have an effect by analogy with other dyes.

EXPERIMENTAL

Instruments and Chemicals

The spectrophotometric measurements were carried out on the PU 8800 UV/VIS instrument (Pye Unicam, Cambridge, England) with 1 cm quartz cuvettes. The pH was measured on a Radiometer PHM 64 acidimeter (Radiometer, Copenhagen, Denmark) using a GK 2401 B combined glass electrode.

The stock solution of $5 \cdot 10^{-4}$ mol l^{-1} bromopyrogallol red (5,5'-dibromosulfogallein, DG, $M_r = 576.203$) was prepared by dissolving 0.0288 g of purified[4] and dried substance, whose purity was controlled by elemental analysis, in 20 ml of pure ethanol and diluting with distilled water to 100 ml. This solution is stable for only 48 h.

The stock solution of 1 . 10^{-1} mol l^{-1} 1-carbethoxypentadecyl trimethyl ammonium bromide (CPTB) was prepared from the substance Septonex (Slovakofarma, Hlohovec, Czechoslovakia), whose purity corresponds to Czechoslovak Pharmacopoeia (ref.[1]). The stock solution of 1 . 10^{-1} mol l^{-1} sodium dodecyl sulfate (SDS) was prepared from the recrystallized substance[6] (Zdravotnické zásobování, Prague, Czechoslovakia) whose purity was controlled by two-phase titration[7]. The stock solution of 1 . 10^{-1} mol l^{-1} Triton X-100 (TX) was prepared from the pure substance (Serva, Heidelberg, F.R.G.).

The ionic strength of the test solutions was adjusted using a 5 mol l^{-1} $NaNO_3$ solution.

The pH of the solutions was adjusted using universal Britton–Robinson buffer. Solutions with pH > 7 were treated by the addition of 0.2 ml (per 25 ml of final solution) of freshly prepared 1% solution of ascorbic acid to prevent oxidation of DG.

RESULTS AND DISCUSSION

As a tetrabasic acid, bromopyrogallol red can dissociate in aqueous solution according to the scheme

$$H_4R \xrightleftharpoons{-H^+,\,K_{a1}} H_3R^- \xrightleftharpoons{-H^+,\,K_{a2}} H_2R^{2-} \xrightleftharpoons{-H^+,\,K_{a3}} HR^{3-} \xrightleftharpoons{-H^+,\,K_{a4}} R^{4-}$$

The values of the dissociation constants are given in the literature[1 – 3] ($pK_{a1} \approx 0.1$, $pK_{a2} \approx 4$, $pK_{a3} \approx 9$, $pK_{a4} \approx 11$). The regions of predominant existence of the individual dissociated forms of the dye are depicted in Fig. 1.

The absorption spectra of the individual dissociated forms H_3R^-, H_2R^{2-}, HR^{3-} and R^{4-} were measured at the pH values where only the given dye species is present in solution. The magnitude of the ionic strength, adjusted by the addition of $NaNO_3$ in the range $I = 0.1$ to 1.0 mol l^{-1} in bromopyrogallol red solutions in the absence of tensides, does not affect the positions of the absorption bands of any of the dye forms, but only slightly decreases the absorbance values (Fig. 2).

The Effect of the Tenside in the Absence of Strong Electrolyte

The effect of the individual tensides in sub- and supercritical concentrations[8,9] on the absorption spectra of bromopyrogallol red are depicted in Figs 3 – 7.

The presence of cationogenic tenside Septonex produces a bathochromic shift in the original bands of the absorption spectra of the individual dissociated forms of DG and also sometimes leads to the formation of new bands. A new band appears for the H_3R^- form with λ_{max} = 575 nm (Fig. 3, curves 3 – 7); the band of the H_2R^{2-} species is also shifted to this wavelength in the presence of Septonex (Fig. 4, curves 3 – 6). As the presence of Septonex increases the dissociation of DG in solutions in the absence of a strong electrolyte or at very low ionic strength values (adjusted with a strong electrolyte[3,4,10]), it is apparent that the absorption spectra in Fig. 3 at high tenside concentrations contain both residual bands of the H_3R^- form as well as primarily the band of the H_2R^{2-} form, whose position is affected by the presence of Septonex. At $c_{CPTB} > 1 \,.\, 10^{-3}$ mol l^{-1}, the absorption maximum of the H_2R^{2-} form at $\lambda = 575$ nm again decreases and the maximum of the H_3R^- form at $\lambda = 430$ nm increases. The dissociation of the H_3R^- form is again suppressed; this effect can be explained as a consequence of a decrease in the effective concentration of the dye and OH^- ions in the increasing volume of the micellar pseudophase[10] or a decrease in the surface potential of the micelles with an increase in the tenside concentration[11].

The positions of the absorption maxima of the H_2R^{2-} and HR^{3-} forms are identical (at 558 nm in the absence of tenside, at 575 nm in the presence of the tenside (Figs 4, 5)), so that the presence of the HR^{3-} form cannot be determined in the spectrum of the H_2R^{2-} form (Fig. 4). A slight maximum is formed at a wavelength of about 650 nm at low Septonex concentrations on the curves of both forms. This increase in the absorbance can be a consequence of the formation of ion associates of the dye anions

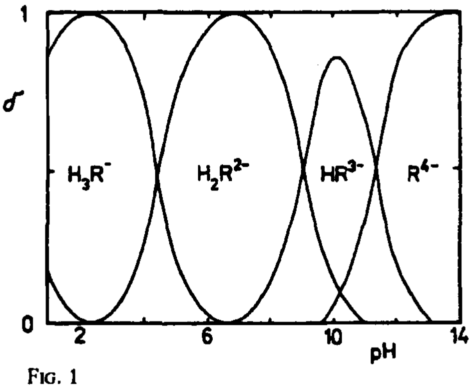

Fig. 1

The distribution diagram[2] of DG in dependence on the pH. $c_{DG} = 3 \,.\, 10^{-5}$ mol l^{-1}, $I = 0.2$ mol l^{-1} ($NaNO_3$), $pK_{a2} = 4.39$, $pK_{a3} = 9.06$, $pK_{a4} = 11.31$

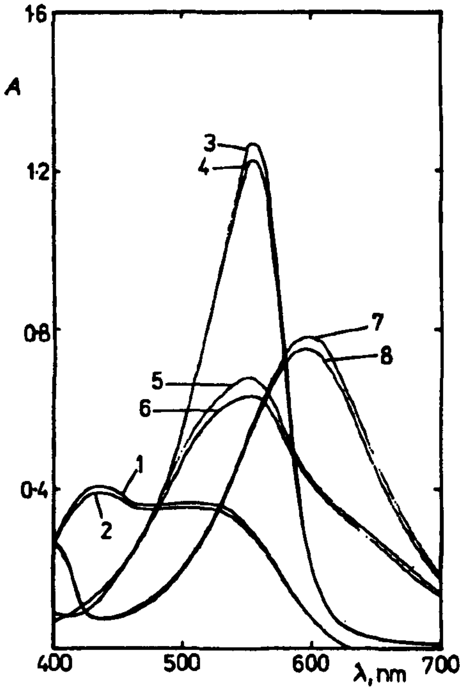

Fig. 2

The effect of $NaNO_3$ on the absorption spectra of the individual dissociated forms of DG. $c_{DG} = 3 \,.\, 10^{-5}$ mol l^{-1}; I_{NaNO_3} (mol l^{-1}) for curves 1, 3, 5, 7 $1 \,.\, 10^{-1}$, 2, 4, 6, 8 1.0; pH for curves 1, 2 2.4 (H_3R^-), 3, 4 6.6 (H_2R^{2-}), 5, 6 10.0 (HR^{3-}), 7, 8 13.0 (R^{4-})

with the cationogenic tenside[12]. This is apparently true especially of the H_2R^{2-} form. The formation of micelles in solution at c_{CPTB} > cmc leads to a decrease in the absorbance in this region accompanied by an increase in the maximum at 575 nm, corresponding to incorporation of the H_2R^{2-} form into the tenside micelle. The increase in the absorbance at about 650 nm for the HR^{3-} form at high Septonex concentrations is retained; as the absorption maximum of the R^{4-} form in the presence of Septonex also lies in this region (Fig. 6), the increase in the absorbance at 650 nm in Fig. 5 can be a consequence of the presence of R^{4-} form in solution. The dissociation of the HR^{3-} form is thus favoured by the presence of Septonex.

The anionogenic tenside SDS does not change the wavelength of the maxima of the absorption bands of any of the DG forms,

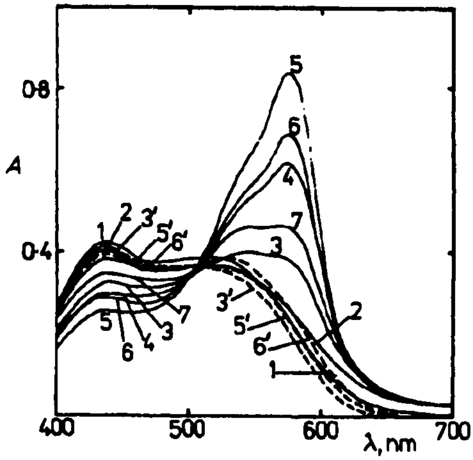

FIG. 3

The effect of Septonex and $NaNO_3$ on the absorption spectrum of the H_3R^- form. $c_{DG} = 3 . 10^{-5}$ mol l^{-1}; pH 2.4; I unadjusted for curves 1 to 7, I = 0.1 mol l^{-1} for curves 3', 5', 6'; c_{CPTB} (mol l^{-1}) for curves 1 0, 2 3 . 10^{-5}, 3, 3' 8 . 10^{-5}, 4 2 . 10^{-4}, 5, 5' 1 . 10^{-3}, 6, 6' 1 . 10^{-2}, 7 3 . 10^{-2}

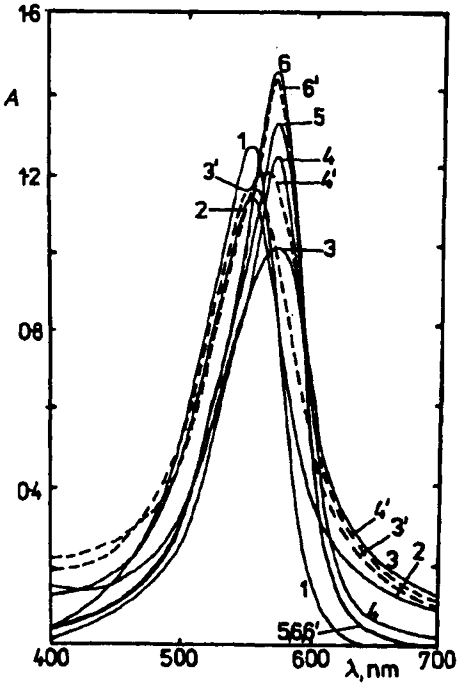

FIG. 4

The effect of Septonex and $NaNO_3$ on the absorption spectrum of the H_2R^{2-} form. $c_{DG} = 3 . 10^{-5}$ mol l^{-1}; pH 6.6; I unadjusted for curves 1 to 6, I = 0.1 mol l^{-1} for curves 3', 4', 6'; c_{CPTB} (mol l^{-1}) for curves: 1 0, 2 3 . 10^{-5}, 3, 3' 8 . 10^{-5}, 4, 4' 2 . 10^{-4}, 5 1 . 10^{-3}, 6, 6' 1 . 10^{-2}

but does, however, decrease the absorbance at all the maxima (only slightly for the H_3R^- and H_2R^{2-} forms, more for the HR^{3-} and R^{4-} forms), analogous to the effect of an increase in the ionic strength (Fig. 2).

The nonionogenic tenside Triton X-100 has only a slight effect (Fig. 7). For the H_3R^- form (Fig. 7, curves 1 – 3), increasing tenside concentration in the range $3 \,.\, 10^{-5} \leq c_{TX} \leq 1 \,.\, 10^{-2}$ mol l^{-1} does not change the wavelength of the absorption maxima and behaves similarly to the cationogenic tenside at very low concentrations (Fig. 3, curves 1, 2); an isosbestic point again appears at $\lambda \approx 550$ nm. Simultaneously, the absorbance increases slightly in the wavelength interval 550 to 650 nm. Even in the presence of the micelle form of the tenside, however, an absorption band does not appear at 575 nm; apparently, the dissociation equilibrium is not sharply shifted in favour of the formation of the micelle-solubilized form of H_2R^{2-}. The absorption maximum of the H_2R^{2-} form (curves 4 – 6) shifts to 570 nm for $c_{TX} \geq 1 \,.\, 10^{-2}$ mol l^{-1}, i.e. for tenside micellar solutions. The position of the absorption maximum at 558 nm for the HR^{3-} form does not change (curves 7 and 8) for solutions with tenside concentrations below the critical value; however, in contrast to the cationogenic tenside, a hyperchromic effect appears. At tenside concentrations above the critical value, the band maximum shifts to 570 nm.

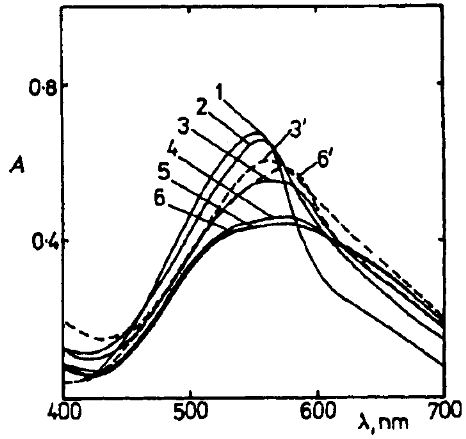

FIG. 5

The effect of Septonex and $NaNO_3$ on the absorption spectrum of the HR^{3-} form. $c_{DG} = 3 \,.\, 10^{-5}$ mol l^{-1}; pH 10.0; I unadjusted for curves 1 to 6, $I = 0.1$ mol l^{-1} for curves 3', 6'; c_{CPTB} (mol l^{-1}) for curves 1 0, 2 3 . 10^{-5}, 3, 3' 8 . 10^{-5}, 4 2 .10^{-4}, 5 1 . 10^{-3}, 6, 6' 1.10^{-2}

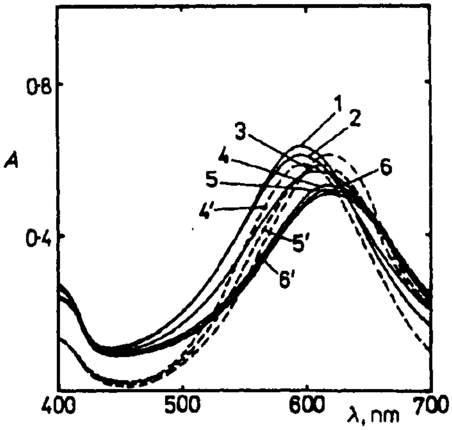

FIG. 6

The effect of Septonex and $NaNO_3$ on the absorption spectrum of the R^{4-} form. $c_{DG} = 3 \,.\, 10^{-5}$ mol l^{-1}; pH 12.9; I unadjusted for curves 1 to 6, $I = 0.1$ mol l^{-1} for curves 4', 5', 6'; c_{CPTB} (mol l^{-1}) for curves 1 0; 2 3 . 10^{-5}, 3 8 . 10^{-5}, 4, 4' 2 . 10^{-4}, 5, 5' 1 . 10^{-3}, 6, 6' 1 . 10^{-2}

This bathochromic shift is apparently a consequence of bonding of the HR^{3-} form to the micellar pseudophase, whose micropolarity produces a change in the position of the absorption maximum. Simultaneously, the absorbance decreases at wavelengths greater than 600 nm. In contrast to the effect of Septonex, the maximum of the band of the R^{4-} form remains at 600 nm in the presence of TX and a slight hypochromic effect occurs on an increase in the tenside concentration.

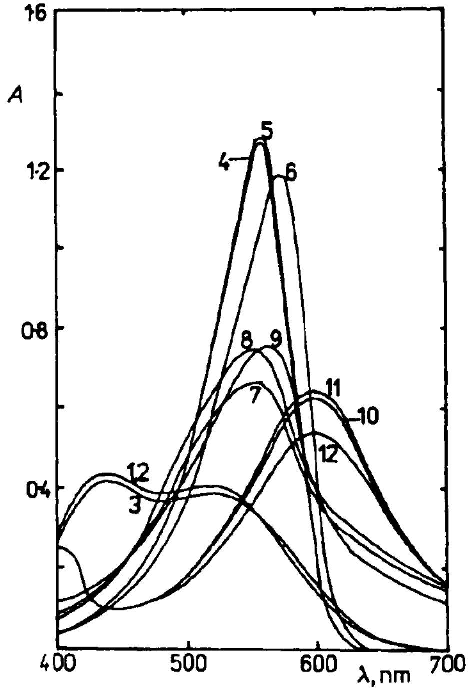

FIG. 7

The effect of Triton X-100 on the absorption spectra of the individual dissociated forms of DG. c_{DG} = 3 . 10^{-5} mol l^{-1}; I unadjusted; c_{TX} (mol l^{-1}) for curves 1, 4, 7, 10 0, 2, 5, 8, 11 3 . 10^{-5}, 3, 6, 9, 12 1 . 10^{-2}; pH for curves 1, 2, 3 2.4 (H_3R^-), 4, 5, 6 6.6 (H_2R^{2-}), 7, 8, 9 10.0 (HR^{3-}), 10, 11, 12 13.0 (R^{4-})

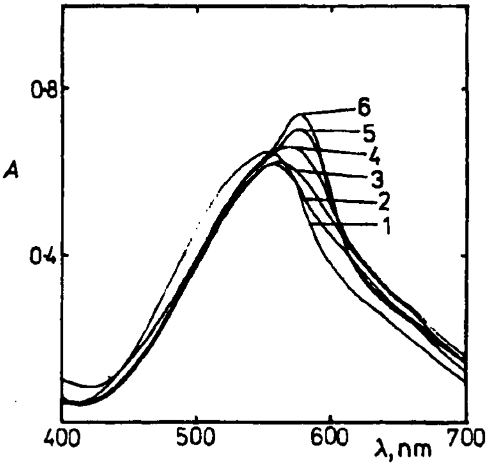

FIG. 8

The effect of Septonex on the absorption spectrum of the HR^{3-} form at high I values. c_{DG} = 3 . 10^{-3} mol l^{-1}; pH = 10.0; I = 0.5 mol l^{-1}; c_{CPTB} (mol l^{-1}) for curves 1 0, 2 3 . 10^{-5}, 3 8 . 10^{-5}, 4 2 . 10^{-4}, 5 1 . 10^{-3}, 6 1 . 10^{-2}

The Effect of the Tenside in the Presence of a Strong Electrolyte

It was found in a previous study[1] that the changes in the absorption spectra produced in the presence of Septonex are relatively small in solutions with $I = 0.2$ mol l^{-1}, while the changes described above (i.e. in the absence of a strong electrolyte) are very strong. Consequently, the effect of the ionic strength was studied in greater detail with maintenance of the other conditions constant.

It is apparent from the comparison in Fig. 3 that the effect of Septonex on the H_3R^- is greatly suppressed at $I = 0.1$ mol l^{-1} (curves 3, 5, 6 and 3′, 5′ and 6′). Similar results were found for $I = 0.5$ mol l^{-1} where the changes in the spectra with increasing tenside concentration are only slight. The character of the changes in the absorption spectra for the H_2R^{2-} form (Fig. 4) at both $I = 0.1$ (curves 3′, 4′, 6′) and also 0.5 mol l^{-1} is analogous to the effect in solutions in the absence of a salt; however, the absorption maximum is shifted in the presence of the salt at higher Septonex concentrations. However, the increase in the absorbance at supercritical tenside concentrations is less at higher ionic strength of the solution.

The effect of the ionic strength is very strong for the HR^{3-} form. In solutions in the absence of salt and at $I = 0.1$ mol l^{-1} (Fig. 5), an increase in the Septonex concentration leads to a continuous decrease in the absorption maximum at 558 nm with simultaneous increase in the absorbance at about 575 and 650 nm. The maximum at 575 nm for the same tenside concentration is greater at $I = 0.1$ mol l^{-1} (evident from comparison of curves 3, 3′ and 6, 6′). At $I = 0.5$ mol l^{-1} (Fig. 8) the effect of the tenside on the absorption spectrum of this form is different – the absorbance at 558 nm decreases at low tenside concentrations and that at about 650 nm increases slightly; at a higher tenside concentrations, the absorption maximum at 575 nm increases markedly with increasing Septonex concentration. This maximum apparently corresponds to the solubilized form of HR^{3-} in the tenside micelles. It thus follows from Figs 5 and 8 that an increase in the strong electrolyte concentration suppresses dissociation of the HR^{3-} form.

For the R^{4-} form, an increase in the ionic strength at low tenside concentrations decreases the effect of the latter (Fig. 6, curves 4, 4′ and 5, 5′); at high tenside concentrations, an increase in the ionic strength leads to an increase in the absorbance, i.e. it favours solubilization of the dye in the tenside micelles.

The anionogenic tenside SDS at $I = 0.1$ and 0.5 mol l^{-1}, similarly as in the absence of $NaNO_3$ has no effect on the position of the absorption maxima of any of the DG forms. The decrease in the absorption maxima of the bands of the individual dissociated forms of the dye with increasing tenside concentration is less here than in the absence of the salt.

Nonionogenic tenside Triton X-100 has an analogous effect as in the presence as in the absence of the strong electrolyte, i.e. primarily on the positions of the maxima of the H_2R^{2-} and HR^{3-} forms (shift to 575 nm) and slightly also on the R^{4-} form. The changes in the spectra are thus not affected by the electrolyte and correspond to the effect of the cationogenic tenside in the presence of high electrolyte concentrations.

In conclusion, the presence of the cationogenic and nonionogenic tenside both affect the dissociation of bromopyrogallol red and also affect the positions of their bands. At low tenside concentrations, the formation of ion associates seems probable[12]. However, the combination of a strong electrolyte with a particular type of tenside is important. When a cationogenic tenside is employed, whose micelles have the opposite charge to the individual negatively charged anions of various dissociation forms of the dye, it has been found that the concentration of the strong electrolyte has an important effect, which can be explained by competing equilibria in the framework of the ion-exchange model of the micellar effect for dyes[13]. In the presence of a nonionogenic tenside, whose interactions with the dye anions are far weaker, the changes in the band positions are practically not affected by the presence of the strong electrolyte, indicating that hydrophobic interactions between the dye and tenside have a predominant effect.

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