SPECTROPHOTOMETRIC STUDY OF THE EFFECT OF TENSIDES ON TRIPHENYLMETHANE DYES

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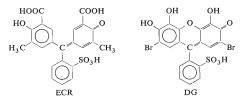
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Dedicated to Professor V. Suk on the occasion of his 60th birthday.

The effect of cation-active tenside 1-carbethoxypentadecyltrimethylammonium bromide (Septonex) on the absorption spectra of selected triphenylmethane dyes, eriochromcyanine R and bromopyrogallol red, was studied. The effect of the micelle aggregates of the tenside on the spectrophotometric characteristics of the individual dissociated forms of the dyes was demonstrated and the influence of strong electrolytes (NaCl, NaNO₃) was studied. The interaction of both dyes with the micelle form of the nonionic tenside Triton X-100 was studied under similar experimental conditions.

In the spectrophotometric determination of metal ions with some dyes, especially of the triphenylmethane series, the presence of tensides is used even more frequently as further components with favourable effects on the determination conditions and increasing the sensitivity. Consequently, systematic attention has also recently been paid to the interactions of the dyes alone with these tensides considering their properties, which are dependent on their concentrations. The behaviour of the triphenylmethane dyes (phenol red, bromophenol blue and bromocresol green) with the cation-active tenside 1-carbethoxypentadecyltrimethylammonium bromide (Septonex)¹ has already been discussed in the literature.

This work described the behaviour of complexing triphenylmethane dyes eriochromcyanine R (ECR), and bromopyrogallol red (DG) in the pH region 0-14, as representatives of dyes used very frequently for direct and indirect photometric determination of elements²⁻⁴ in the presence of tensides. Both dyes belong to the sulphophthalein group and differ somewhat in structure and various substituents, of which four can dissociate a proton:



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In dependence on the acidity of the medium, the dye usually acts in aqueous solution through one of its dissociated forms, characterized by a maximum of one or more absorption bands and the corresponding values of the molar decadic absorption coefficients^{5,6}.

The cation-active tenside 1-carbethoxypentadecyltrimethylammonium bromide (Septonex, CPTB) and the nonionogenic tenside, *p*-octylphenolpoly(oxyethylene) (n = 9) (Triton X-100) were chosen for study of the effect of tensides on these dyes. They have a common basic property in their ability to form micelles in aqueous solutions; the values of their critical micelle concentrations $c_{\rm K}$ are known^{7,8}.

EXPERIMENTAL

Instruments and Chemicals

The spectra in the visible region were measured on an SP 800 (Pye Unicam, Cambridge, England) recording spectrophotometer with cuvettes with an internal path length of 1-00 cm. The pH values of the solutions were measured on a Mera-Elmat typs N-512 instrument (Polymetron, Wroclaw, Poland) with a combined SAgP-210 W electrode. The electrode was calibrated using NBS standard buffers.

The stock solution of eriochromcyanine R (ECR) $(c(\text{ECR}) = 1 \cdot 10^{-3} \text{ mol } 1^{-1})$ was prepared from the substance (Lachema, Czechoslovakia), purified by precipitation as the acid⁹, the composition was verified by elemental analysis. The stock bromopyrogallol red (DG) solution (c(DG)= $5 \cdot 10^{-4} \text{ mol } 1^{-1})$ was prepared⁵ from the substance (Lachema, Brno, Czechoslovakia) purified by chromatography on a polyamide column (Miramid, GDR) (ref.¹⁰), the content was verified by elemental analysis. The stock 1-carbethoxypentadecyltrimethylammonium bromide (CPTB) solution $(c(\text{CPTB}) = 5 \cdot 10^{-2} \text{ or } 5 \cdot 10^{-3} \text{ mol } 1^{-1})$ was prepared using the substance Septonex (Slovakofarma, Hlohovec, Czechoslovakia), whose purity corresponded to Czechoslovak pharmacopoeia No 2 (ref.¹). The stock solution of *p*-octylphenoloploy(oxyethylene) $(c(\text{TX}) = 5 \cdot 10^{-3} \text{ or } 5 \cdot 10^{-2} \text{ mol } 1^{-1})$ was prepared by suitable dilution of a pure solution of Triton X-100 (Rohm and Haas, USA, $M_r = 624\cdot9$) with distilled water.

The pH was adjusted using buffers prepared from the solutions: $0.04M-H_3PO_4$, $0.04M-CH_3$. COOH, $0.04M-H_3BO_3$ and 0.2M-NaOH; 0.05M Na₂B₄O₇.10 H₂O and 0.1M-NaOH. The ionic strength of the solutions was adjusted by addition of suitable amounts of 2M or $4M-NaNO_3$ or 4M-NaCl.

Because of the possible low stability of some forms of the dyes, especially at certain pH values, the measurement was carried out immediately after mixing the solution and finished after 2 min at the latest.

RESULTS AND DISCUSSION

Interaction of Eriochromcyanine R and Bromopyrogallol Red with Septonex

Study of the absorption spectra of the individual dyes ECR and DG in the visible region, whose dissociation can be depicted according to the scheme

$$H_4R \stackrel{-H^+}{\longleftrightarrow} H_3R^- \stackrel{-H^+}{\longleftrightarrow} H_2R^2 \stackrel{-H^+}{\longleftrightarrow} HR^3 \stackrel{-H^+}{\longleftrightarrow} R^4 \stackrel{(A)}{\longleftrightarrow}$$

and whose comparison with the analogous absorption spectra of solutions containing a dye tenside mixture demonstrated the effect of the tenside, whose presence at various concentrations affects to varying degree all the studied dye anions, *i.e.* H_3R^- , H_2R^{2-} , HR^{3-} and R^{4-} . This effect appears as a change in the character of the spectra and in hypsochromic or bathochromic shifts of the maxima of the absorption bands, generally accompanied by hyperchromic or hypochromic changes in the absorbance. The H_4R form (or H_5R^+), which predominates in strongly acid medium, was not studied. An interesting finding in preliminary experiments, similarly as for simple dyes¹, was that these spectral changes, which are dependent on the interactions with tensides, increase at constant dye concentration with increasing tenside concentration c(CPTB) up to a concentration close to the critical micelle concentration c_x and then no longer change.

Consequently, the effect of the tenside was studied in dye solutions at pH values where a single dissociated from of the dye markedly predominates and the concentration of tenside CPTB was varied in the range $5 \cdot 10^{-5} \text{ mol } l^{-1} \leq c(\text{CPTB}) \leq 5 \cdot 10^{-3} \text{ mol } l^{-1}$.

The results obtained in evaluation of changes in the spectra of the ECR dye are given in Table I. It follows that the effect of increasing the tenside concentration is analogous for all the individual forms, H_3R^- , H_2R^{2-} and HR^{3-} : the maximum for each form in the tenside concentration interval 5.10⁻⁵ mol l⁻¹ $\leq c(CPTB) \leq$

TABLE I

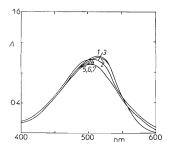
	ł	I ₃ R ⁻	н	$_{2}R^{2}$ -	H	-1R ³		R ⁴⁻
c(CPTB) mol l ⁻¹	λ _{max} nm	$\varepsilon \cdot 10^{-4}$ $l \text{ mol}^{-1}$ $\cdot \text{ cm}^{-1}$	λ _{max} nm	$\varepsilon . 10^{-4}$ l mol ⁻¹ . . cm ⁻¹	λ _{max} nm	$\varepsilon . 10^{-4}$ l mol ⁻¹ . . cm ⁻¹	λ _{max} nm	$\varepsilon \cdot 10^{-4}$ l mol ⁻¹ . cm ⁻¹
0	474	2.80	516	2.66	434	2.00	586	6.52
5.10-5	474	2.48	515	2.62	433	1.93	586	6.46
2.10-4	470	1.95	507	2.46	430	1.85	586	6.44
5.10-4	466	1.95	505	2.32	429	1.70	586	5.25
1.10-3	466	1.95	504	2.32	426	1.68	586	4.29
3.10^{-3}	466	1.95	504	2.32	426	1.68	586	2.74
5.10^{-3}	466	1.95	504	2.32	426	1.68	586	2.31

The λ_{\max} values and corresponding ε values for eriochrom yanine R at various Septonex concentrations

 $\leq 5 \cdot 10^{-4} \text{ mol } l^{-1}$ shifts to shorter wavelengths and simultaneously the value of the corresponding coefficient ε decreases. This effect does not increase above $c(\text{CPTB}) \geq 5 \cdot 10^{-4} \text{ mol } l^{-1}$: the maximum of the absorption band and the value of ε are constant to at least $c(\text{CPTB}) = 5 \cdot 10^{-3} \text{ mol } l^{-1}$. The absorption spectrum of the $H_2 R^{2-}$ form of dye ECR is given as an example in Fig. 1.

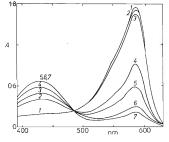
The dissociated form \mathbb{R}^{4^-} of ECR exhibits different behaviour in study of these spectral dependences on c(CPTB). Fig. 2 indicates that the wavelength of the maximum corresponding to \mathbb{R}^{4^-} does not change; however, a marked decrease in the height of the absorbance maximum occurs in the whole concentration range of c(CPTB), together with the appearance of an absorption maximum corresponding to the HR^{3^-} -tenside aggregate (as given in Table I) *i.e.* at $\lambda = 426$ nm. The absorbance value at $\lambda = 426$ nm increases only to $c(\text{CPTB}) = 1 \cdot 10^{-3}$ mol I^{-1} and then remains constant. A marked isosbestic point at $\lambda = 483$ nm is also apparent.

It was found from study of the time stability of the individual dissociated forms of eriochromcyanine R, H_3R^- , H_2R^{2-} and HR^{3-} , as well as of their dye-tenside associates, whose existence can be assumed at $c(CPTB) < c_K$, and the micelle aggregates of the dye, whose existence can be assumed at $c(CPTB) > c_K$, that the presence of the micelle in solution at $c(CPTB) > c_K$ leads to increased thermodynamic

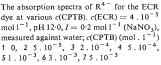




The absorption spectra for H_2R^{2-} of the ECR dye at various c(CPTB). $c(ECR) = 4 \cdot 10^{-5} \text{ mol} 1^{-1}$, pH 3.5, $I = 0.2 \text{ mol} 1^{-1}$ (NaNO₃), measured against water; c(CPTB) (mol 1^{-1}): 1 0, 2 5.10⁻⁵, 3 2.10⁻⁴, 4 5.10⁻⁴, 5 1.10⁻³, 6 3.10⁻³, 7 5.10⁻³



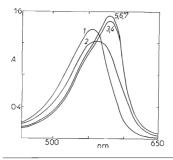




stability of dye anions with larger negative charges. Experiments were carried out at $c(\text{ECR}) = 4 \cdot 10^{-5} \text{ mol } 1^{-1}$ for two tenside concentrations, $c(\text{CPTB}) = 5 \cdot 10^{-5} \text{ mol } 1^{-1}$, which is less than the critical concentration, and $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol } 1^{-1}$. 1^{-1} , which is larger than $c_{\rm K}$ for the tenside. In the presence of the H_3R^- and H_2R^{2-1} forms at $c(\text{CPTB}) = 5 \cdot 10^{-5} \text{ mol } 1^{-1}$, the ion associate is precipitated from the solution within several minutes; under the same conditions, the HR^{3-1} form remains as a dissolved associate. At $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol } 1^{-1}$, where the micelle aggregates of all forms of the dye remain dissolved, the values of their absorbance maxima may decrease after a longer period of time (*e.g.* for the H_3R^- form, the decrease in $A(\lambda_{max})$ at 474 nm after 10 min is about 2.8% of the original value, for H_2R^{2-1} after 2 h at $\lambda_{max} = 516 \text{ nm}$, the decrease is about 6% and for HR³⁻¹ at λ_{max} the absorbance value remains constant for 8 h).

In contrast to ECR dye DG, behaves somewhat differently under analogous conditions. The H_3R^- form, which exhibits two absorption maxima in the absence of the tenside, a strong one at $\lambda = 440$ nm and a weak one at about 558 nm, is practically not affected by the presence of the CPTB tenside in the given concentration range. A similar trend as for ECR can be discerned, *i.e.* a slight decrease in the maximum of the absorption band at 440 nm, a shift to shorter wavelengths and stabilization at $c(CPTB) > c_K$, as given in Table II; this effect is, however, very weak. The effect of the presence of tenside on the H_2R^{2-} form is basically opposite to that for ECR. It is apparent from Fig. 3 and Table II that increasing c(CPTB) leads first to a decrease in the maximum of the absorption band and then to a shift to longer λ , together with a hyperchromic shift, which is stabilized for $c(CPTB) > c_K$.

The HR³⁻ form, again characterized in the absence of tenside by quite a broad absorption band with strong maxima at $\lambda = 558$ nm and 598 nm, is affected less





The absorption spectra of H_2R^{2-} for the DG dye at various c(CPTB). c(DG) = 3 . 10⁻⁵ mol 1⁻¹, pH 6.5, $I = 0.2 \text{ mol } 1^{-1} (\text{NaNO}_3)$, measured against water; c(CPTB) (mol 1⁻¹): 1 0, 2 5. 10⁻⁵, 3 2. 10⁻⁴, 4 5. 10⁻⁴, 5 1. 10⁻³, 6 3. 10⁻³, 7 5. 10⁻³

		H ₃ R ⁻		H_2R^2 -		HR ^{3 –}		R⁴	\mathbb{R}^{4-}	
c(CPTB) mol l ⁻¹	λ_{\max} nm	$\varepsilon \cdot 10^{-4}$ 1 mol ⁻¹ cm ⁻¹	λ _{max} nm	ε .10 ⁻⁴ l mol ⁻¹ cm ⁻¹	λ _{max} nm	$\lim_{n \to \infty} \frac{\varepsilon \cdot 10^{-4}}{1 \text{ mol}^{-1} \text{ cm}^{-1}}$	λ _{max} nm	$\frac{\epsilon}{10^{-4}} \cdot \frac{10^{-4}}{10^{-1}}$	λ _{max} nm	£.10 ⁻⁴ mol ⁻¹ cm ⁻¹
0	440	1.45	558	5-35	558	2.57	598	2-97	394	1.81
5.10 ⁻⁵	440	1-21	562	4-84	562	2-60	909	2.71	394	2-83
2.10^{-4}	436	1.36	580	5-45	580	2.78	620	2-58	394	3-26
5.10 ⁻⁴	436	1.36	580	5-45	580	2.86	624	2-57	394	3-44
1.10^{-3}	436	1-36	580	5-62	580	3.23	624	2.57	394	3-74
3.10 ⁻³	436	1.36	580	5.62	580	3.23	624	2.57	394	3-97
5.10^{-3}	436	1.36	580	5.62	580	3-23	624	2.57	394	4.80

÷ 4 TABLE II

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by the presence of the tenside. The absorption band at 558 nm decreases with increasing c(CPTB) and merges with the band at $\lambda = 598$ nm, which appears as a bathochromic shift to 580 nm (Table II).

In strongly alkaline media, the \mathbb{R}^{4-} form predominates, reflected in two maxima at $\lambda = 598$ nm and in the short wavelength region of the spectrum at 394 nm. The long wavelength maximum shifts to 624 nm with increasing tenside concentration and no longer changes at $c(\text{CPTB}) > c_{\kappa}$; this is accompanied by a hypochromic effect. The wavelength of the maximum at $\lambda = 394$ nm does not change in the prepresence of the tenside, but the absorbance value increases steadily with increasing tenside concentration; the results are given in Table II and Fig. 4.

The stability of the individual forms of the DG dye in the absence of the tenside is unlimited for at least 8 h. The stabilities of the H_3R^- and H_2R^{2-} forms are not affected by the presence of tenside in concentrations of $c(CPTB) < c_k$ as well as c(CPTB) > $> c_k$. In solutions where the HR^{3-} form predominates, the absorbance of the dye alone decreases, as does that of the dye in the presence of the tenside, immediately after pH adjustment and the solution becomes almost colourless after several hours. This is a result of rapid oxidation of the dye in alkaline medium⁵ and can be prevented by adding a small amount of freshly prepared 1% aqueous solution of ascorbic acid. Only a small absorbance change occurs in this dye solution (about 4% over 8 h.). At tenside concentrations of $5 \cdot 10^{-5}$ mol 1⁻¹, the absorbance decreases even in the presence of ascorbic acid, but micelle formation at $c(CPTB) = 3 \cdot 10^{-3}$ mol 1⁻¹ ensures the stability of the absorbance value for at least 8 h.

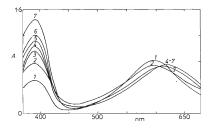


Fig. 4

The absorption spectra of R^{4-} for the DG dye at various c(CPTB) c(DG) = 3 . 10⁻⁵ mol 1⁻¹, pH 12·9, $I = 0.2 \text{ mol } 1^{-1}$ (NaNO₃), measured against water; c(CPTB) (mol 1⁻¹): 1 0, 2 5 . 10⁻⁵, 3 2 . 10⁻⁴, 4 5 . 10⁻⁴, 5 1 . 10⁻³, 6 3 . 10⁻³, 7 5 . 10⁻³

Effect of the Electrolyte

It was found in study of the optimal conditions for the determination of metals with triphenylmethane dyes in the presence of tenside that the absorbance value of the ternary metal-dye-tenside complex and thus the sensitivity of the method are sometimes very dependent on the ionic strength of the solution and on the nature of the electrolyte present. The $c_{\rm K}$ value of the tenside is also affected by strong electrolytes⁷. Consequently, the effects of NaCl and NaNO₃, on the absorption spectra of the given predominating forms of the dye were studied both in the presence and in the absence of tenside. The measurements were carried out immediately after mixing the solutions with strong electrolyte concentrations of 0-1 to 1-0 moll⁻¹. The tenside CPTB concentrations were again 5 . 10^{-5} moll⁻¹ and 3 . 10^{-3} moll⁻¹.

The magnitude of the ionic strength has very little effect on the individual studied forms of the dyes alone. However, the presence of very low tenside concentrations leads to a marked effect of the ionic strength and primarily of the character of the electrolyte used. The absorbance value then does not change with increasing electrolyte concentrations, NaCl or NaNO₃, except for the H_2R^{2-} form of DG, where the presence of electrolytes leads to a shift in the wavelength maxima. It is thus probable that the electrolyte alone does not have a marked effect on the individual dye forms, but that the principal role in changes in the spectral quantities is played by tenside–electrolyte interactions.

At concentrations $c(CPTB) > c_{\kappa}$, the presence of NaNO₃ and NaCl leads to a shift in the absorption maxima of the H₃R⁻ and HR³⁻ forms of ECR and these two types of electrolyte have opposite effects on the magnitude of the absorbance of HR³⁻. The wavelength maxima of the individual dissociated forms of the DG dye are not shifted, but there is a strong individual increase or decrease in the absorbance value at low electrolyte concentrations compared to the absorbances of solutions of the dye alone with an ionic strength given by the buffer used.

Generally, the effect of $NaNO_3$ on both dyes is stronger than that of NaCl and the size of the anions of the electrolyte used is also important.

Interaction of Eriochromcyanine R and Bromopyrogallol Red with Triton X-100

It was found in study of the effect of the nonionogenic tenside TritonX-100(TX) on the individual dye forms, carried out under analogous conditions as those used for the CPTB tenside, that TX affects all forms of the dye to various degree in a somewhat different manner than CPTB. Because of the very different $c_{\rm K}$ values for TX given by various authors⁸, the measurement was carried out at two c(TX) values, $c_1(TX) = 1 \cdot 10^{-4} \text{ mol } 1^{-1}$ and $c_2(TX) = 5 \cdot 10^{-2} \text{ mol } 1^{-1}$, for which it holds that $c_1 \leqslant c_{\rm K} \leqslant c_2$.

It was found that, at $c(TX) = 1 \cdot 10^{-4} \text{ mol } 1^{-1}$, the absorption spectra of the dye remain practically unchanged and that the tenside has almost no effect. If c(TX) =

= 5. 10^{-2} mol l⁻¹ and the presence of micelles can be assumed in solution, then an effect of the tenside on all forms of the dye is apparent, but is somewhat different than for CPTB: the wavelength and absorbance values for the H₃R⁻ form of the ECR dye are decreased; in contrast, the effect on the DG is negligible. The λ_{max} value for the H₂R²⁻ form of ECR decreases, for DG increases and the absorbance value decreases for both dyes. There is a bathochromic shift of the λ_{max} value for the HR³⁻ forms of both dyes, the absorbance of ECR decreases and that of DG increases to almost twice the original value.

The results show the marked effect of tensides, and especially of their micelle forms, on the given triphenylmethane dyes and their spectrophotometric characteristics. These effects are individual and depend on the dye structure and also on the different properties of the micelles of the cation-active and nonionogenic tensides.

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