

THE DISSOCIATION CONSTANTS OF ERIOCHROMCYANINE R  
AND BROMOPYROGALLOL RED IN THE PRESENCE  
OF CARBETHOXPENTADECYLTRIMETHYLAMMONIUM BROMIDE  
(SEPTONEX)

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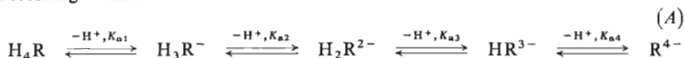
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Dedicated to Professor Dr J. Zýka on the occasion of his 60th birthday.

The values of the mixed dissociation constants  $pK_a$  of triphenylmethane dyes (eriochromcyanine R and bromopyrogallol red) in dependence on the concentration of cation-active tenside (1-carbethoxypentadecyltrimethylammonium bromide — Septonex) were found from spectrophotometric data and the effect of formation of micelle tenside aggregates was evaluated.

On the basis of the observed effect of 1-carbethoxypentadecyltrimethylammonium bromide (Septonex, CPTB), a cation-active tenside, on the absorption spectra of the individual dissociated forms  $H_4R$  of the triphenylmethane dyes eriochromcyanine R (ECR) and bromopyrogallol red<sup>1</sup> (DG), spectrophotometric data were measured as a basis for calculation of the values of the mixed dissociation constants  $K_a$  in dependence on the tenside concentration. In aqueous solutions these dyes dissociate according to the scheme



and the corresponding dissociation constants are affected to varying degrees by the presence of cation-active tensides, as has already been described for some simple triphenylmethane dyes<sup>2</sup>. The literature contains values of  $pK_{a2}$  and  $pK_{a3}$  for chromazurol S in the presence of CPTB (ref.<sup>3</sup>).

Although the  $pK_a$  values have already been found for the dyes in the presence of this cation-active tenside or cetylpyridinium bromide, the measurements have been carried out for only a single concentration value of the tenside without considering the general micelle-forming properties of the tensides<sup>4-7</sup>.

Consequently, this work systematically studies the changes in the corresponding  $pK_a$  values (i.e.  $pK_{a2} - pK_{a4}$ , the  $pK_{a1}$  values were not measured) for both of the given dyes in dependence on the concentration of tenside CPTB below and above the critical micelle concentration ( $c_K$ ), which is known<sup>8</sup>.

## EXPERIMENTAL

### Instruments and Chemicals

The spectrophotometric measurements were carried out on an SP 800 (Pye Unicam, Cambridge, England) recording spectrophotometer with 1.00 cm cuvettes. The pH values of the solutions were measured on a PHM 64 instrument (Radiometer, Copenhagen, Denmark) with a GK 2401 B combined electrode, which was calibrated using standard NBS buffers.

The stock solutions of eriochromcyanine R (ECR) ( $c(\text{ECR}) = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ ) and bromopyrogallol red (DG) ( $c(\text{DG}) = 5 \cdot 10^{-4} \text{ mol l}^{-1}$ ) were prepared from the purified substances (Lachema, Brno, Czechoslovakia)<sup>1</sup>. The stock solutions of 1-carbethoxy-pentadecyltrimethylammonium bromide (CPTB) ( $c(\text{CPTB}) = 5 \cdot 10^{-2}$  or  $5 \cdot 10^{-3} \text{ mol l}^{-1}$ ) were prepared from the Septonex substance (Slovakofarma, Hlohovec, Czechoslovakia), whose purity conformed with Czechoslovak pharmacopoeia 2 (ref.<sup>1</sup>).

The pH of the measured solutions was adjusted using buffers prepared from the following solutions: 0.04M- $\text{H}_3\text{PO}_4$ , 0.04M- $\text{CH}_3\text{COOH}$ , 0.04M- $\text{H}_3\text{BO}_3$  and 0.2M-NaOH; 0.05M- $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10 \text{ H}_2\text{O}$  and 0.1M-NaOH; 0.008M tris(hydroxymethyl)aminomethane, 0.008M Na-EDTA, 0.008M ascorbic acid and 35% NaOH. The ionic strength was maintained constant in the whole pH interval using  $\text{NaNO}_3$  ( $I = 0.2 \text{ mol l}^{-1}$ ).

The dissociation constants were measured using the spectrophotometric method based on determination of the absorbance values of the individual dissociated forms of the dyes<sup>1</sup> in dependence on the pH of the solution; the temperature was  $20 \pm 0.5^\circ\text{C}$ .

In study of the effect of cation-active tenside CPTB in the concentration range  $c(\text{CPTB}) = 5 \cdot 10^{-5}$  to  $5 \cdot 10^{-3} \text{ mol l}^{-1}$  on the dissociation constants of ECR and DG, the absorption spectra of the dyes at  $c(\text{ECR}) = 4 \cdot 10^{-5} \text{ mol l}^{-1}$  and  $c(\text{DG}) = 3 \cdot 10^{-5} \text{ mol l}^{-1}$  were measured at various pH values (0–13) and compared with the spectra of the dyes alone in the absence of tenside.

## RESULTS

The  $\text{p}K_{a2}$  and  $\text{p}K_{a3}$  values for ECR were calculated on the basis of the measured values first for the dye alone in the absence of the tenside and then for six tenside concentrations in the above interval. Because of the low stability of the dye in alkaline medium, the  $\text{p}K_{a4}$  value was not studied in detail. The measured results are given in Table I together with the standard deviation estimates (calculated from range R for number of measurements  $n = 3$ ).

It follows from the given data that the  $\text{p}K_{a2}$  value decreases with increasing tenside concentration up to  $c(\text{CPTB}) = 1 \cdot 10^{-3} \text{ mol l}^{-1}$  and then does not change within experimental error. On the other hand,  $\text{p}K_{a3}$  increases with increasing tenside concentration and remains constant from  $c(\text{CPTB}) = 5 \cdot 10^{-4} \text{ mol l}^{-1}$ .

Distribution diagrams<sup>9</sup> were calculated and constructed from the calculated mixed dissociation constant values for the dye alone and for the dye in the presence of tenside at a concentration of  $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol l}^{-1} > c_K$ , at which the  $\text{p}K_a$  value no longer changes (Fig. 1). The  $\text{p}K_{a4}$  constant values for the dye alone and in the presence of tenside at concentrations  $c(\text{CPTB})$  were taken from the literature: at  $c(\text{CPTB}) = 0$ ,  $\text{p}K_{a4} = 11.85$  (ref.<sup>10</sup>), at  $c(\text{CPTB}) = 8 \cdot 10^{-5} \text{ mol l}^{-1}$ ,

$pK_{a4} = 12.0$  (ref.<sup>7</sup>). Comparison of the diagrams for the distribution of the predominant regions for the existence of the individual dissociated forms of the ECR dye alone and in the presence of tenside above its critical concentration reveals that the presence of tenside micelles in solution suppresses the range of existence of the  $H_3R^-$  form of the dye. On the other hand, the pH region in which the  $H_2R^{2-}$  form of the dye predominates in solution is favourably broadened. The presence of tenside micelles resulted in a shift of the occurrence of the  $HR^{3-}$  and  $R^{4-}$  forms to higher pH values.

The  $pK_{a2}$  to  $pK_{a4}$  values were measured similarly for the DG dye; dissociation constant  $pK_{a1}$ , which is important in strongly acid media, was not measured. The results are given in Table II.

TABLE I

The  $pK_a = f(c_T)$  values for eriochromcyanine R,  $I = 0.2 \text{ mol l}^{-1}$  ( $\text{NaNO}_3$ ),  $20 \pm 0.5^\circ\text{C}$

$c(\text{CPTB})$ $\text{mol l}^{-1}$	$pK_{a2} \pm s^a$	$pK_{a3} \pm s^a$
0	$2.19 \pm 0.317$	$5.67 \pm 0.192$
$5 \cdot 10^{-5}$	$2.15 \pm 0.199$	$5.77 \pm 0.052$
$2 \cdot 10^{-4}$	$1.89 \pm 0.005$	$6.31 \pm 0.031$
$5 \cdot 10^{-4}$	$1.88 \pm 0.220$	$6.41 \pm 0.060$
$1 \cdot 10^{-3}$	$1.67 \pm 0.118$	$6.37 \pm 0.083$
$3 \cdot 10^{-3}$	$1.69 \pm 0.063$	$6.35 \pm 0.075$
$5 \cdot 10^{-3}$	$1.65 \pm 0.234$	$6.38 \pm 0.104$

<sup>a</sup> Standard deviation for  $n = 3$ .

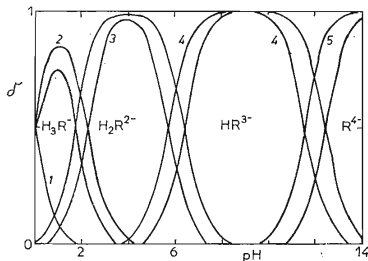


FIG. 1  
Distribution diagram for eriochromcyanine R in dependence on the pH.  $c(\text{ECR}) = 4 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $I = 0.2 \text{ mol l}^{-1}$  ( $\text{NaNO}_3$ ), 1–5:  $c(\text{CPTB}) = 0$ ; the corresponding undesignated curves:  $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol l}^{-1}$

It follows that the  $pK_{a2}$  and  $pK_{a4}$  values decrease with increasing tenside concentration up to  $c(\text{CPTB}) = 1 \cdot 10^{-3} \text{ mol l}^{-1}$  and then do not change within experimental error. In contrast, the  $pK_{a3}$  value increases with increasing tenside concentration and practically does not change above  $c(\text{CPTB}) = 1 \cdot 10^{-3} \text{ mol l}^{-1}$ .

Distribution diagrams were calculated and constructed from the calculated values of the mixed dissociation constants of the dye alone and for the dye in the presence of the tenside at concentrations above the critical concentration, *i.e.*  $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol l}^{-1}$ . It follows from comparison of the diagrams in Fig. 2 that the presence of CPTB micelles in solution practically does not affect the region of predominant existence of the  $\text{H}_3\text{R}^-$  dissociation form, slightly broadens the pH interval in which the  $\text{H}_2\text{R}^{2-}$  form predominates, strongly suppresses the existence of the  $\text{HR}^{3-}$  form and shifts the existence for predominant existence of the  $\text{R}^{4-}$  form to lower pH values.

TABLE II

The  $pK_a = f(c_T)$  values for bromopyrogallol red,  $I = 0.2 \text{ mol l}^{-1}$  ( $\text{NaNO}_3$ ),  $20 \pm 0.5^\circ\text{C}$

$c(\text{CPTB})$ $\text{mol l}^{-1}$	$pK_{a2} \pm s^a$	$pK_{a3} \pm s^a$	$pK_{a4} \pm s^a$
0	$4.39 \pm 0.129$	$9.06 \pm 0.059$	$11.31 \pm 0.306$
$5 \cdot 10^{-5}$	$4.40 \pm 0.066$	$9.10 \pm 0.130$	$11.23 \pm 0.096$
$2 \cdot 10^{-4}$	$4.23 \pm 0.099$	$9.14 \pm 0.085$	$10.63 \pm 0.444$
$5 \cdot 10^{-4}$	$4.19 \pm 0.058$	$9.16 \pm 0.043$	$10.68 \pm 0.551$
$1 \cdot 10^{-3}$	$4.16 \pm 0.066$	$9.22 \pm 0.031$	$10.30 \pm 0.487$
$3 \cdot 10^{-3}$	$4.12 \pm 0.073$	$9.18 \pm 0.106$	$10.31 \pm 0.479$
$5 \cdot 10^{-3}$	$4.16 \pm 0.048$	$9.23 \pm 0.105$	$10.27 \pm 0.552$

<sup>a</sup> Standard deviation for  $n = 3$ .

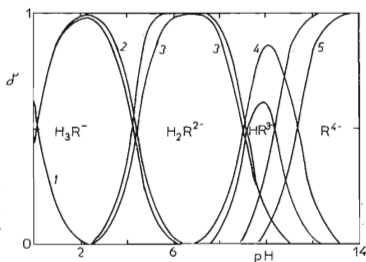


FIG. 2

Distribution diagrams for bromopyrogallol red in dependence on the pH.  $c(\text{DG}) = 3 \cdot 10^{-5} \text{ mol l}^{-1}$ ,  $I = 0.2 \text{ mol l}^{-1}$  ( $\text{NaNO}_3$ ). 1–5:  $c(\text{CPTB}) = 0$ , the corresponding undesignated curves:  $c(\text{CPTB}) = 3 \cdot 10^{-3} \text{ mol l}^{-1}$

## DISCUSSION

It follows from the given dependences of the  $pK_a$  values on  $c(\text{CPTB})$  for the studied ECR and DG dyes that the presence of the cation-active tenside changes all the measured values of the dissociation constants of both dyes and thus all their anionic forms are affected. Similarly as for simple triphenylmethane dyes<sup>2</sup>, the formation of micelle aggregates of the tenside is again decisive; these forms are probably able to attract nucleophilic anion forms of the dyes through electrostatic interactions and thus to affect their dissociability. Consequently, whenever  $c(\text{CPTB}) < c_K$ , the  $pK_a$  values change, probably as a result of formation of dye-tenside ion associates<sup>2</sup>. If, however,  $c(\text{CPTB}) > c_K$ , which occurs at concentrations greater than  $7 \cdot 7 \cdot 10^{-4} \text{ mol l}^{-1}$  (in the absence of a strong electrolyte) to  $1 \cdot 10^{-4} \text{ mol l}^{-1}$  (in the presence of  $\text{NaNO}_3$  electrolyte)<sup>8</sup>, then the dye participates directly through its negatively charged  $-\text{O}^-$ ,  $-\text{COO}^-$  and  $-\text{SO}_3^-$  groups in the formation of micelles aggregates, either through bonding on the surface of the micelles or deeper within the micelles.

In view of the different structures of the dyes and polarities of their individual dissociating groups ( $-\text{COOH}$ ,  $-\text{OH}$  next to  $-\text{SO}_3\text{H}$ ) the structures of the dye-micelle aggregates can, but need not, be different. This then determines the magnitude of the tenside effect. Consequently, as indicated by the distribution diagrams, the existence region of the  $\text{H}_2\text{R}^{2-}$  form of the dye is broadened in the presence of tenside at  $c(\text{CPTB}) > c_K$  as a result of preferred  $\text{H}_2\text{R}^{2-}$ -tenside micelle interaction and the  $\text{H}_3\text{R}^-$  and  $\text{HR}^{3-}$  forms are suppressed; consequently, the pH region which is optimal for formation of complexes of these dyes with metal ions is broader. The results indicate that this effect is more marked for the ECR dye.

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