EFFECT OF TENSIDES ON THE OPTICAL PROPERTIES OF SULFOPHTHALEIN DYES

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Dedicated to Prof. Lumír Sommer on the occasion of his 60th birthday.

The optical properties of bromocresol red, bromophenol blue and bromocresol green were studied spectrophotometrically in aqueous systems in the absence and in the presence of submicellar and micellar concentrations of cationic (Septonex, hexadecylpyridinium and hexadecyltrimethylammonium bromides), nonionic (Brij 35, Triton X-100) and anionic (sodium dodecylsulfate) tensides. The positions of the absorption maxima and molar absorptivities of the LH^- and L^{2-} acid-base species of the dyes depend on the kind and concentration of tenside, alkylpyridinium chain length, and kind and concentration of inert electrolyte.

The acid-base and optical properties of organic analytical reagents and their chelates with metal ions are affected by micellar systems. In view of this, the effect of ionic and nonionic tensides on the colour contrast, sensitivity and selectivity of reactions used for the spectrophotometric determination of metals or the extraction photometric determination of ionic tensides has been studied[1-5].

The changes in the mechanisms and rates of reactions of organic analytical reagents brought about by the presence of tensides, as well as the shifts of the reaction equilibria due to the reaction components being concentrated in the vicinity of the electrically charged surface of the micelles, are included in the general concept of micellar catalysis[6]. All these effects stimulate interest particularly from the point of view of the possibility of predicting the behaviour of organic analytical reagents and their chelates with metal ions in the range of submicellar and micellar concentrations of tensides. Various hypotheses, semiquantitative considerations and quantitative relations have been suggested[7-10] to account for the changes in the optical and, particularly, acid-base properties of organic analytical reagents and their chelates.

In this work, the effects of ionic and nonionic tensides on the optical properties of three sulfophthalein dyes, viz. bromophenol red, bromophenol blue and bromocresol green, are studied with a view to gaining a better insight into the effect of the kind and concentration of the tenside, length of the alkyl chain and kind and con-

centration of inert electrolyte on the optical characteristics of the anionic acid-base species of the dyes.

EXPERIMENTAL

Chemicals and Apparatus

Bromocresol red (3,3′-dibromosulfophthalein, henceforth BR) (Chemapol, Prague), bromophenol blue (3,3′,5,5′-tetrabromosulfophthalein, henceforth BB) (Merck, Darmstadt, F.R.G.) and bromocresol green (3,3′,5,5′-tetrabromo-*m*-cresol-sulfophthalein, henceforth BG) (Lachema, Brno) were used after double purification. Their alkaline solutions (pH $\approx$ 10) were filtered through an S3 frit and precipitated with dilute (1 + 4) HCl to a final concentration of $c(HCl) = 2 \text{ mol l}^{-1}$. The dyes precipitated in the form of the free acids LH_2 were rinsed multiply with $1M$-HCl and redistilled water and collected on a frit. The preparations were dried in a vacuum over KOH for 5 days and over P_2O_5 for 10 days. The active content was determined by elemental analysis (C, H, S) and photometric titration. The purification recovery was about 50%.

Chromatographic purity of the chemicals was checked on strips of Silufol 150 × 25 mm (Kavalier, Votice), impregnated by development in the ascending mode with $0.01M$ to $0.05M$-EDTA after removing impurities by development in the ascending mode with chloroform to overflow. Prior to use, the foils were activated for 30 min at 110°C in a drying oven and deactivated in air for 4 h. The chemicals were applied to the start in the form of ethanolic solutions at a concentration of $\varrho_L = 5 \text{ g l}^{-1}$. The chromatograms were developed in a 40 ml ground-in extraction test tube using 5 ml of the 1-butanol–glacial acetic acid–ammonia (4 : 3 : 9) mixture. All the chemicals tested gave a single colour spot.

Stock solutions of BR, BB and BG at concentrations of 10 to 200 μmol l^{-1} were prepared by diluting precisely weighed amounts of the chromatographically pure chemicals in 1 ml of $0.1M$-KOH, diluting to c. 50% of a total volume with water, acidifying the solution with 1·5 ml of $1M$-HCl and diluting to volume. By making the solutions acidic to pH 1—2, their stability was increased to 3—4 days for BB and 5—7 days for BR and BG, whereas in alkaline solutions, absorbance changes were observed in 2 and 3—4 days, respectively.

Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide, henceforth SPX) (Slovakofarma, Hlohovec), hexadecylpyridinium bromide (henceforth CPB) (Lachema, Brno), hexadecyltrimethylammonium bromide (henceforth CTMAB) (Lachema, Brno) and Zephiramin (benzyldimethyltetradecylammonium bromide, henceforth ZPA) (Dojindo, Japan) were purified by precipitation of their warm (50°C) ethanolic solutions ($\varphi = 30\%$) with ethyl ether. Stock solutions of 1 to 10 mmol l^{-1} in 20% (v/v) ethanol were prepared immediately prior to measurement, with aged solutions the repeatability of measurement was poorer.

Dodecylpyridinium chloride (DPC), tetradecylpyridinium bromide (TPB), pentadecylpyridinium bromide (PPB) and octadecylpyridinium bromide (OPB) were synthesized by reacting the n-alkyl bromide (chloride) with pyridinium. The chemicals were purified by repeated crystallization from methanol; their purity was checked by titrimetric determination of chloride or bromide.

Sodium dodecyl sulfate (SDS) (BDH, Poole, U.K.) was used without purification in the form of its aqueous solution at concentrations of 0·1 to 10 mmol l^{-1}. Brij 35 (polyoxyethylene dodecyl ether) (Merck, Darmstadt, F.R.G.) and Triton X-100 (octylphenol polyethylene glycol ether, henceforth TX 100) (Koch Light, U.K.) were used in the form of aqueous solutions at $\varrho_T = 100 \text{ g l}^{-1}$ or $\varphi_T = 2\%$, respectively.

The other chemicals and organic reagents used were of reagent grade purity (Lachema, Brno). Ethanol was purified by distillation and its water and methanol contents were 4·5% and 5% (v/v),

respectively. Water was redistilled in a Bi 18 Destamat quartz still (Heraeus Quarzschmelze, Hanau, F.R.G.).

Acidity was measured with a PHM 84 digital pH-meter equipped with a G 202 B glass electrode and a K 401 saturated calomel electrode (Radiometer, Copenhagen, Denmark), which was checked periodically using standard NBS buffers at pH 1·68, 4·01, 7·00 and 9·18 at 25°C.

Spectrophotometric measurements were performed on a Superscan 3 double-beam recording spectrophotometer (Varian, Zug, Switzerland) on-line controlled with an HP 9815A desk-top computer (Hewlett–Packard, U.S.A.). Quartz cells with optical pathlengths 10 to 40 mm were used at ambient temperature (25°C).

RESULTS AND DISCUSSION

Absorption spectra of aqueous or aqueous-ethanolic $(\varphi(C_2H_5OH) = 0.5$ or $5\%)$ solutions of the three dyes in a concentration of 20 µmol l^{-1} (BR, BG) or 12·5 µmol . . l^{-1} (BB) were measured in the presence of EDTA $(0.1$ or 0.5 mmol $l^{-1})$ over the region of $320-730$ nm. The pH was varied over the region of pH $1-12$, ionic strength was held constant at $I = 0.1, 0.01$ and 0.15 mol . l^{-1} (HCl + KOH) for BR, BG and BB, respectively; for BR and BB, measurements were also performed in 1M to 17M-H_2SO_4 without ionic strength adjustment.

In dependence on the acidity of medium, the three dyes release consecutively protons from the quinoid oxygen, the sulfo group and the phenolic oxygen, and four acid-base species, viz. LH_3^+, LH_2, LH^- and L^{2-}, emerge. These are characterized by absorption bands in the regions of $480-520$, $400-440$, $400-440$ and 560 to 630 nm, respectively. The LH_2 and LH^- species, whose interconversion is associated with the deprotonation of the sulfo group, do not differ in this respect (Table I). The acid-base transformations are indicated by sharp isosbestic points (Fig. 1, Table I).

Within the limit of experimental error, the positions of the absorption maxima and isosbestic points as well as the molar absorptivities calculated from the absorbances of the solutions in the regions of existence of each species solely are inde-
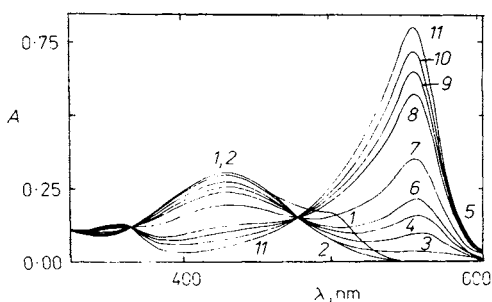

FIG. 1

Absorption spectra of BR; $c(BR) = 20$ µmol . . l^{-1}, $c(EDTA) = 0.1$ mol l^{-1}, $\varphi(C_2H_5OH)$ $= 0.5\%$, I 0·01 (HCl + KOH). pH: 1 1·17, 2 2·27, 3 3·27, 4 7·09, 5 7·65, 6 7·89, 7 8·32, 8 8·66, 9 9·26, 10 10·29, 11 10·90

pendent of ionic strength over the region of $I = 0.01$ to 0.1 mol l^{-1} (HCl + KOH) and minor changes in the optical characteristics are observed at higher ionic strengths.

TABLE I

Optical characteristics of the dyes in the presence of tensides. $c(BR) = c(BG) = 20$ µmol l^{-1}, $c(BB) = 12.5$ µmol l^{-1}, $c(EDTA) = 0.01$ and 0.05 mmol l^{-1}, respectively, $\varphi(C_2H_5OH) = 0.5\%$ and 5%, respectively, $c(T^+) = c(T^-) = 0.5$ mmol l^{-1} for BR and BG, $c(T^+) = c(T^-) = 0.25$ mmol l^{-1} for BB (see text)

Tenside	λ_{max}, nm (ε_{max}, m^2 mmol^{-1})			λ_{IP}, nm
		BR		
—	430[a](1·50)	560[b](4·00),	357 (0·90)	361, 480
—	504 (6·25)[c]	571 (393)		
SPX	422[d](1·45)	571 (3·93)		364, 479
CPB	423 (1·95)	573 (5·15)		365, 479
TX 100[e]	428 (1·49)	567 (4·20)		365, 480
Brij 35[f]	427 (1·51)	566 (4·15)		364, 478
SDS	430 (1·50)	560 (4·07)		361, 480
SPX[g]	402 (1·75)	577 (4·38)		475
		BB		
—	435[h](2·12)	590[i](6·14)		326, 495
—	542 (6·91)[c]			
SPX	425[j](1·88)	604[k](6·60)		326, 494
CPB	424 (1·95)	605 (6·57)		330, 493
Brij 35[f]	433 (2·08)	592 (6·20)		327, 495
SPX[g]	414 (1·87)	604 (4·14)		341, 492
		BG		
—	440[l](1·77)	614[m](4·32),	400 (0·90)	510
SPX	424[n](1·80)	628[o](5·00),	392 (0·90)	502
CPB	424 (2·10)	628 (4·50),	390 (0·80)	502
OPB	422 (2·60)	624 (4·23),	389 (0·77)	499
PPB	424 (2·30)	624 (4·26),	390 (0·80)	501
TPB	423 (2·20)	624 (4·25),	390 (0·81)	502
DPC	441 (1·68)	615 (4·23),	397 (0·88)	510
Brij 35	443 (1·77)	615 (4·43),	394 (1·00)	498
TX 100	435 (1·82)	620 (4·40),	395 (0·91)	499
SDS	443 (2·14)	614 (4·30),	398 (0·80)	510
SPX[g]	414 (1·35)	628 (3·49)		497

Ref.[11]: [a] 433; [b] 558; [d] 424; [h] 438; [i] 590; [j] 428; [k] 603; [l] 444; [m] 615; [n] 425; [o] 627; [c] in 17M, 0·2M or 2M-H$_2$SO$_4$; [e] φ(TX 100) = 0·1%; [f] ϱ(Brij 35) = 10 g l^{-1}; [g] value for ionic associate after extraction into chloroform.

The optical characteristics of the three dyes in various experimental conditions and in the presence of tensides at different concentrations are given in Table I.

In the presence of a 20-fold excess of the cationic tensides SPX and CPB $(c_T = 0·5,$ 0·25 and 0·5 mmol l^{-1} for BR, BB and BG, respectively), the absorption maxima of the LH^- and L^{2-} species exhibit shifts to shorter (LH^-) and longer (L^{2-}) wavelengths up to 20 nm (Table I). The isosbestic points are shifted as well, up to 15 nm, and molar absorptivities in the maxima of the two species change approximately 10%. CPB affects the optical characteristics more than CPX or CTMAB.

The positions of the maxima of the two acid-base species of BG at $c_T = 0·5$ mmol . . l^{-1} exhibit shifts to shorter (LH^-) and longer (L^{2-}) wavelength with increasing alkyl chain length $(C_{10}$ to $C_{18})$ in the alkylpyridinium salt series DPC, TPB, PPB, OPB; for the DPC–OPB limiting pair the shifts are from 441 to 422 nm and from 615 to 624 nm, respectively. For the LH^- species the molar absorptivity increases appreciably, from 1·68 m^2 $mmol^{-1}$ (DPC) to 2·60 m^2 $mmol^{-1}$ (OPB). For the L^{2-} species the ε value decreases from 0·88 to 0·77 m^2 $mmol^{-1}$ in the short-wavelength absorption maximum and increases over the $4·23 - 5·00$ m^2 $mmol^{-1}$ range for the long-wavelength absorption maximum.

In the presence of nonionic tensides $(\varrho(\text{Brij } 35) = 10$ g l^{-1} or $\varphi(\text{TX } 100) = 0·1\%)$ the absorption maxima of the L^{2-} species of BG are shifted slightly; the shift is more marked for the absorption maximum of the LH^- species (from 441 to 424 nm). The molar absorptivity increases slightly.

In the presence of anionic tensides $(c(\text{SDS}) = 0·5$ mmol $l^{-1})$ the spectral patterns of the three dyes are identical with those of the pure aqueous or aqueous-ethanolic solutions; the changes in the absorption maxima positions never exceed 3 nm, which is within the limits of experimental error.

The changes in the optical characteristics of the dyes in dependence on the concentration of cationic tenside were studied over the regions of $c(\text{SPX}) = 0·1$ to 10 mmol l^{-1} and $c(\text{CPB}) = 0·1$ to 1 mmol l^{-1} (Table II). The absorption spectra were measured at pH 9·1, 10·5 and 11·4 and $I = 0·1$, 0·05 and 0·15 (HCl + KOH). Ethanol in the solvent $(\varphi = 5\%)$ was used for a perfect solubilitation of the tenside and ionic associates even at relatively high tenside concentrations at which the Tyndall effect is observed in pure aqueous solutions. Alkaline medium was chosen because the absorption bands of the dyes then are sharper and absorption intensity is higher, which makes for a better reading of the positions of the absorption maxima and determination of the molar absorptivities.

With increasing concentration of cationic tenside, the absorption maxima of the L^{2-} species of the dyes shift $10 - 20$ nm with respect to the positions in aqueous solutions (560, 590 and 614 nm for BR, BB and BG, respectively). The dependence of the molar absorptivities on the concentration of tenside has a roughly parabolic shape with a minimum within the region of $c_T = 0·1$ to 0·3 mmol l^{-1}.

In the presence of cationic tenside at $c_T \approx 0.1$ mmol l^{-1} the spectra form clear-cut isosbestic points at $560-575$ nm; at higher tenside concentrations the isosbestic points are somewhat disperse (see Fig. 2), presumably because of the complex chemical

TABLE II

Optical characteristics of dyes in dependence on the concentration of cationic tensides. $c(BR) = 20$ μmol l^{-1}, $c(BB) = 12.5$ μmol l^{-1}, pH 10·50 or 9·12 for BR with SPX and CPB, respectively, I 0·10 and 0·05, respectively (HCl + KOH), $\varphi(C_2H_5OH) = 5\%$

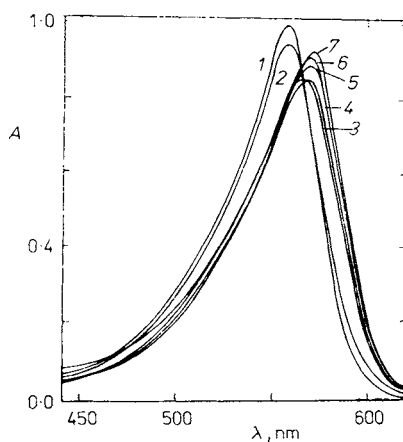| c_T mmol l^{-1} | λ_{max}, nm (ε_{max}, m^2 mmol^{-1}) | | |
| | BR | | BB |
	SPX	CPB	SPX
0	558 (5·00)	558 (4·78)	592 (5·36)
0·001	—	—	592 (5·32)
0·01	—	—	592 (5·12)
0·05	—	—	592 (5·00)
0·1	559 (4·75)	560 (4·45)	604 (4·64)
0·2	565 (4·30)	—	—
0·3	567 (4·30)	569 (4·50)	—
0·5	569 (4·30)	571 (4·65)	—
0·7	570 (4·45)	—	—
1·0	570 (4·58)	573 (4·83)	604 (5·32)
5·0	—	—	604 (5·52)
10·0	572 (4·65)	573 (4·88)	604 (5·60)

FIG. 2

Absorption spectra of the L^{2-} acid-base species of BR in the presence of SPX. $c(BR) = 20$ μmol l^{-1}, $c(EDTA) = 0.1$ mol . l^{-1}, $\varphi(C_2H_5OH) = 0.5\%$, pH 10·0, I 0·05 (HCl + KOH). $c(SPX)$ (mmol l^{-1}): *1* 0·0, *2* 0·1, *3* 0·2, *4* 0·3, *5* 0·5, *6* 0·7, *7* 1·0 and 10

processes occurring in the systems at submicellar and micellar concentrations of the cationic tenside (critical micellar concentration is about 0.1 mmol l^{-1}).

The effect of the concentration and kind of inert electrolyte was investigated by measuring the absorption spectra of BR in the presence of different concentrations of chloride, nitrate or sulphate at $c(BR) = 20$ μmol l^{-1}, $\varphi(C_2H_5OH) = 0.5\%$, pH 10.0 and $c(SPX$ or $CPB) = 0.5$ mmol l^{-1}. The data are given in Table III.

Over the region of $c(NO_3^-) = 1$ to 300 mmol l^{-1} (SPX) or $c(NO_3^-) = 20$ to 300 mmol l^{-1} (CPB) the absorption maximum of the L^{2-} species shifts from 571 nm at $c(NO_3^-) \leq 20$ mmol l^{-1} to 559 nm at $c(NO_3^-) \geq 300$ mmol l^{-1}; the latter value corresponds to that for aqueous solutions in the absence of cationic tenside (Table I). The dependence of molar absorptivity on the concentration of nitrate for BR in the presence of SPX or CPB has a roughly parabolic shape with a minimum of $\varepsilon_{565} = 4.7$ m^2 mmol^{-1} at $c(NO_3^-) \approx 50$ mmol l^{-1}. The value of $\lambda_{min} = 565$ nm corresponds to the position of the isosbestic point for absorption spectra of BR in the presence of SPX or CPB (Fig. 3b).

Increasing concentration of chloride over the region of 0.05 to 1 mol l^{-1} has a less marked effect on the optical properties of BR in the presence of SPX or CPB. The absorption curves form no isosbestic point. The absorption band intensity

TABLE III

Optical characteristics of BR in the presence of CPB or SPX in dependence on the concentration of inert electrolyte. $c(BR) = 20$ μmol l^{-1}, $c(SPX) = c(CPB) = 0.5$ mmol l^{-1}, pH 10.00, $\varphi(C_2H_5OH) = 0.5\%$

c_X mmol l^{-1}	λ_{max}, nm (ε_{max}, m^2 mmol^{-1})			
	SPX	CPB		
	$X = NO_3^-$ [a]	$X = NO_3^-$ [b]	$X = Cl^-$	$X = SO_4^{2-}$
10	571 (4.90)	—	—	—
20	—	572 (4.95)	—	—
30	568 (4.73)	—	—	—
50	564 (4.70)	570 (4.65)	571 (5.00)	566 (5.15)
100	560 (4.88)	566 (4.63)	571 (4.95)	566 (5.24)
150	559 (4.95)	—	—	—
200	559 (5.03)	560 (4.75)	571 (4.85)	566 (4.93)
250	—	559 (4.80)	—	—
300	558 (5.08)	559 (4.88)	570 (4.80)	566 (5.05)
500	—	—	566 (4.50)	566 (4.89)
1 000	—	—	563 (4.02)	—

[a] $\lambda_{IP} = 565$ nm; [b] $\lambda_{IP} = 566$ nm.

decreases monotonically while the band position shifts to shorter wavelengths, from 571 nm to 563 nm for the two chloride concentration extremes (Fig. 3a).

In the presence of sulfate at concentrations $c(SO_4^{2-}) = 0.05$ to 0.5 mol l^{-1}, the changes in the absorption band position in dependence on the sulfate concentration lie within the limits of experimental error (566 ± 2 nm). Molar absorptivities do not correlate with the sulphate concentrations and vary over the region of 4.8 to 5.2 m^2 . . mmol^{-1}.

The two other sulfophthalein dyes exhibit more complex dependences of absorption spectral patterns on the concentration of inert electrolyte. Isosbestic points are disperse or do not exist. The $\varepsilon = f(c_X)$ dependence correlates in no case. The spectral patterns resemble those of BR in the presence of chloride or sulfate (Fig. 3).

At higher concentrations of inert electrolyte (above 0.3, 1.0 or 0.5 mol l^{-1} for NO_3^-, Cl^- and SO_4^{2-}, respectively), ionic associates of the tensides with the inorganic anions precipitate. The dyes then behave as in the absence of tenside, similarly as in the presence of comparable concentrations of perchlorate.
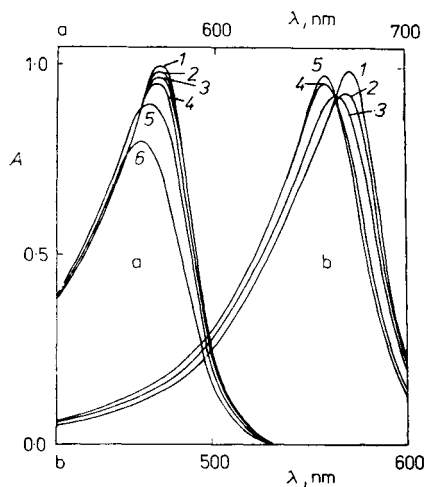

FIG. 3

Absorption spectra of the L^{2-} acid-base species of BR in the presence of CPB and chloride (a) or nitrate (b) ions. c (BR) = = 20 μmol l^{-1}, $c(EDTA) = 0.1$ mol l^{-1}, $c(CPB) = 0.5$ mmol l^{-1}, $\varphi(C_2H_5OH) = 0.5\%$, pH 10.00, I 0.05. a $c(Cl^-)$ (mol l^{-1}): 1 0.05, 2 0.10, 3 0.20, 4 0.30, 5 0.50, 6 1.00. b $c(NO_3^-)$ (mol l^{-1}): 1 0.02, 2 0.05, 3 0.10, 4 0.20, 5 0.30
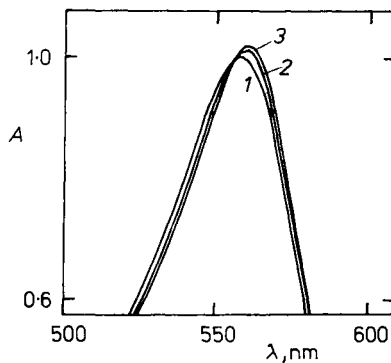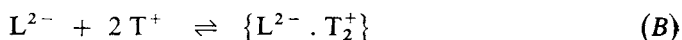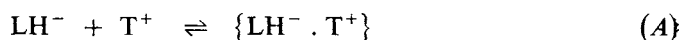
FIG. 4

Absorption spectra of the L^{2-} acid-base species of BR in the presence of CPB and chloride and nitrate ions. $c(BR) = 20$ μmol . .l^{-1}, $c(EDTA) = 0.1$ mol l^{-1}, $c(CPB) =$ $= 0.5$ mmol l^{-1}, $\varphi(C_2H_5OH) = 0.5\%$, pH 10.0, I 0.1 (HCl + HNO$_3$ + KOH); $c(Cl^- + NO_3^-) = 0.1$ mol l^{-1}. Chloride-to- -nitrate molar ratio: 1 0.5, 2 1, 3 2
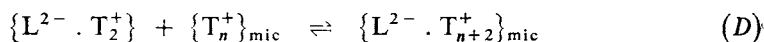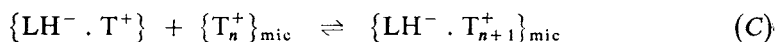
At a constant total concentration of inert electrolyte, $c(\text{Cl}^- + \text{NO}_3^-) = 0.10 \text{ mol}$.
. l^{-1} and at variable chloride-to-nitrate ratios, the position of the band of the L^{2-}
species of BR or BB varies over the wavelength region whose limits correspond to
the positions of the band in the presence of chloride or nitrate solely at $c(\text{Cl}^-)$ or
$c(\text{NO}_3^-) = 0.10 \text{ mol l}^{-1}$ in the presence of cationic tenside (Fig. 4). The curves
form an isosbestic point at 556 nm.

All the above changes in the optical properties of the sulfophthalein dyes are
related with the formation of stable ionic associates of their anionic species with the
cationic (or also nonionic) tenside present,

$$\text{LH}^- + \text{T}^+ \rightleftharpoons \{\text{LH}^- . \text{T}^+\} \qquad (A)$$

$$\text{L}^{2-} + 2\text{T}^+ \rightleftharpoons \{\text{L}^{2-} . \text{T}_2^+\} \qquad (B)$$

The formation of these ionic associates, with a stoichiometric composition, gives rise
to a haze or precipitate in solutions with a low concentration excess of tenside.
The associates are extractable into organic solvents, where the absorption maxima
exhibit marked bathochromic or hypsochromic shifts.

Solubilization of ionic associates in solutions with a higher concentration excess
of tenside is largely accompanied by minor changes in the optical characteristics.
This solubilization is explained by the formation of ionic associates (pairs) with
simple tenside molecules or micelles, by electrostatic bonding of the dyes and their
ionic associates at the micelle surface, or extraction of the dyes and their ionic as-
sociates into the internal structure of the micelles in the sense of the equilibria

$$\{\text{LH}^- . \text{T}^+\} + \{\text{T}_n^+\}_{\text{mic}} \rightleftharpoons \{\text{LH}^- . \text{T}_{n+1}^+\}_{\text{mic}} \qquad (C)$$

$$\{\text{L}^{2-} . \text{T}_2^+\} + \{\text{T}_n^+\}_{\text{mic}} \rightleftharpoons \{\text{L}^{2-} . \text{T}_{n+2}^+\}_{\text{mic}} \qquad (D)$$
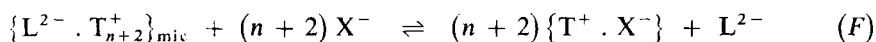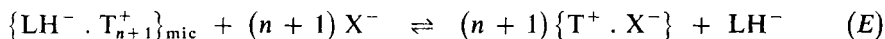
Changes in the absorption spectra of the dyes in the presence of tenside then are
due to changes in the electronic systems. Changes in their optical properties are also
directly related with the formation of micelles, as indicated by the dependence of the
absorption band position on the alkylpyridinium chain length. Whereas for DPC,
with 10 carbon atoms in the alkyl chain, its characteristic micellar properties are
minimal and this tenside exerts no major effect on the optical properties of BG, in the
TPB to OPB series, with clear-cut micellar properties, the absorption maxima are
shifted as much as 20 nm.

Anionic tensides do not alter the character of the optical properties; nonionic
tensides do, but to a lesser extent than cationic tensides.

The limiting positions of the absorption maxima mostly coincide with those for
aqueous and organic solutions respectively.

As the concentration of tenside in the presence of inert electrolyte is increased, the equilibria of formation of ionic associates shift in favour of the $\{LH^- . T^+\}$ and $\{L^{2-} . T_2^+\}$ associates, and the absorption maximum shifts within the region mentioned. At tenside concentrations approaching or exceeding the critical micellar concentration, polymeric tenside species are formed, and because of these more complex equilibria no isosbestic point is formed.

If the concentration of inert electrolyte is increased at a constant concentration of cationic tenside, the equilibria

$$\{LH^- . T_{n+1}^+\}_{mic} + (n + 1) X^- \rightleftharpoons (n + 1)\{T^+ . X^-\} + LH^- \qquad (E)$$

$$\{L^{2-} . T_{n+2}^+\}_{mic} + (n + 2) X^- \rightleftharpoons (n + 2)\{T^+ . X^-\} + L^{2-} \qquad (F)$$

shift in the forward direction. The formation of the $\{T^+ . X^-\}$ associates competes markedly with the formation of the coloured ionic associates of the tenside with the dye and at the limiting concentrations of the inert electrolyte, or in the case of anions forming very stable ionic associates (such as perchlorate), the absorption spectra are identical with those of the respective acid-base species in aqueous solutions. Ionic associates $\{T^+ . X^-\}$ precipitate.

The changes in the optical characteristics depend not only on the concentration of the inert electrolyte but also on the anion involved, this anion determining the stability of the ionic associate $\{T^+ . X^-\}$ and thereby, the state of the equilibria (E) and (F).

Whereas the concentration and kind of the tenside and inert electrolyte affect the optical characteristics rather appreciably, the kind of the sulfophthalein dye itself has a minor effect; the positions of the absorption maxima of the three dyes are identical to within ±5 to 7 nm. Some hydroxytriphenylmethane dyes (Chromazurol S, Eriochromazurol B, etc.) are exceptions, their interaction with cationic tensides giving rise to new absorption bands[12].

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