

SPECTROPHOTOMETRIC INVESTIGATION OF INTERACTIONS OF SULFOPHTHALEIN DYES WITH SURFACTANTS

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The effect of cationic (hexadecylpyridinium bromide, hexadecyltrimethylammonium bromide, Septonex), anionic (sodium dodecyl sulfate) and nonionic (Brij 35, Triton X-100) surfactants on the deprotonation of the phenolic oxygen in bromophenol red, bromophenol blue and bromocresol green is studied. The conditional dissociation constants K_{ai}^* depend on the surfactant concentration and, in the alkylpyridinium surfactant series, on the alkyl chain length at a constant concentration of inert electrolyte, and on the concentration of the inert electrolyte (Cl^- , Br^- , NO_3^- , SO_4^{2-} , H_2PO_4^- , CH_3COO^- , HCOO^- , ClO_4^-) or of the sulfophthalein dye at a constant concentration of a cationic surfactant. In acid and alkaline solutions, cationic surfactants (tensides, T) and the dyes (H_2L) form ionic associates with the stoichiometric composition $\{\text{T}^+, \text{LH}^-\}$ and $\{\text{T}_2^+, \text{L}^{2-}\}$, respectively, exhibiting absorption maxima at 400–430 nm ($\epsilon = 1.3\text{--}2.0 \text{ m}^2 \text{ mmol}^{-1}$) and at 570–630 nm ($\epsilon = 3.5\text{--}4.5 \text{ m}^2 \text{ mmol}^{-1}$), respectively; formation of these associates was confirmed for chloroform extracts by the continuous variations and molar ratios methods.

Interactions of surfactants with organic analytical reagents have been attracting interest over the past three decades^{1–12}. In the presence of low concentrations of ionic surfactants (tensides, T), low soluble ionic associates with the stoichiometric composition $\{\text{L}^+, \text{T}^-\}$, $\{\text{T}^+, \text{L}^-\}$, etc. (L stands for ligand), are formed in aqueous solutions. Extracted into organic solvents, such electroneutral species can be employed for the quantitation of some of the components involved, e.g. by extraction photometric or two-phase titrimetric methods^{13,14}.

In the region of submicellar and micellar surfactant concentrations (typically $c(\text{T}) \geq 80 \mu\text{mol l}^{-1}$), the ionic associates are subject to solubilization. This is accompanied by changes in both the optical and acid-base properties^{3–12}, the absorption bands being shifted ($\Delta\lambda \leq 30 \text{ nm}$) and the $\text{p}K_{ai}^*$ values altered ($\Delta\text{p}K_{ai}^* \leq 2$). These changes are explained qualitatively or quantitatively using various hydration, solvation, electrostatic or ionic models of mutual interactions^{1–12}.

In the present work, the validity of the quantitative relations for changes in the conditional dissociation constants, suggested previously¹², is verified on the case of the $\text{LH}^-/\text{L}^{2-}$ acid-base transition, i.e. deprotonation of the phenolic oxygen, of bromophenol red (henceforth BR), bromophenol blue (BB) and bromocresol

green (BG) in various experimental conditions. The stoichiometry of the ionic associates of the sulfophthalein dyes with Septonex, extracted into chloroform, is verified by means of the continuous variations and molar ratios methods.

EXPERIMENTAL

Chemicals and Apparatus

Bromophenol red (Chemapol, Prague), bromophenol blue (E. Merck, Darmstadt, F.R.G.) and bromocresol green (Lachema, Brno) were purified by repeated precipitation in the form of the free acids (H_2L). Stock solutions at concentrations $c(L) = 10$ to $200 \mu\text{mol l}^{-1}$ were prepared by dissolution of the chromatographically pure preparations¹⁵ in $0.1M$ -KOH and dilution and acidification to pH 2.

Septonex (SPX) (Slovakofarma, Hlohovec), hexadecylpyridinium bromide (CPB) and hexadecyltrimethylammonium bromide (CTMAB) (both Lachema, Brno) were purified by repeated precipitation with diethyl ether from hot (50°C) saturated ethanolic solutions. Dodecylpyridinium chloride (DPC), tetradecylpyridinium bromide (TPB), pentadecylpyridinium bromide (PPB) and octadecylpyridinium bromide (OPB) were synthesized by reacting the corresponding 1-alkyl halides with pyridinium¹⁵, and purified by repeated crystallization from methanol. Sodium dodecyl sulfate (SDS) (BDH, Poole, U.K.) was used as received. Stock solutions of the ionic surfactants at concentrations from 1 to 10 mmol l^{-1} were prepared by dissolving the chemicals in water (SDS) or in 20% (v/v) ethanol.

Stock solutions of Brij 35 (E. Merck, Darmstadt, F.R.G.) at a concentration of $\rho = 10 \text{ g l}^{-1}$ and Triton X-100 (TX-100) (Koch Light, Poole, U.K.) at a volumetric concentration of $\varphi = 5\%$ were prepared from commercial preparations of reagent grade purity. The other chemicals and solvents used, also of reagent grade purity, were commercial preparations supplied by Lachema, Brno. Ethanol containing water and methanol in concentrations of 4.5 and 5% (v/v), respectively, was purified by distillation.

Acidity of solutions was measured with a PHM 84 pH-meter equipped with a G 202B glass electrode and a K 401 saturated calomel electrode (Radiometer, Copenhagen, Denmark), calibrated periodically with NBS buffers at pH 1.68, 4.01, 7.00, and 9.18. Spectrophotometric measurements were carried out at room temperature (25°C) on a Superscan 3 double-beam digital spectrophotometer (Varian, Zug, Switzerland) on-line controlled by a HP 9815A desk-top computer (Hewlett-Packard, U.S.A.), using quartz cells of 1 to 50 mm optical pathlength. Spekol 10 and Spekol 21 single-beam photometers were used for extraction studies; glass cells of 10 and 20 mm optical pathlength were employed. Ionic associates were extracted by 2 min hand agitation in 40 ml ground-in test tubes. After phase separation, the pH of the aqueous phase was measured and the organic phase was centrifuged at 3 000 rpm. for 5 min. The phase volumes were 5 ml/5 ml or 5 ml/10 ml.

Methodology

The effect of the individual factors on the conditional dissociation constant ($pK_{a_i}^*$ value) of the LH^-/L^{2-} acid-base equilibrium associated with the deprotonation of the phenolic oxygen of the dyes was examined by measuring the $A = f(\text{pH})$ dependences (absorbance-pH curves). The dye concentrations were held constant at $c(\text{BR}) = 20 \mu\text{mol l}^{-1}$, $c(\text{BB}) = 12.5 \mu\text{mol l}^{-1}$ or $c(\text{BG}) = 17.5 \mu\text{mol l}^{-1}$ in the presence of $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$ and $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$. Measurements were performed at 6 to 10 wavelengths in the regions of the maximum absorption

by the acid-base species of the dyes, the pH step was 0.1 to 0.3 pH units. The average $pK_{a_i}^*$ values were determined from the curves by graphical and numerical treatment¹⁶; the standard deviation of the mean did not exceed 0.03 pK units.

The effect of the kind and concentration of surfactant was studied over the concentration regions of $c(T) = 0.08$ to 10 mmol l^{-1} for cationic surfactants, 0.01 to 1 mmol l^{-1} for SDS, $\varphi = 0.01$ to 10 g l^{-1} for Brij 35 and $\varphi = 0.01$ to 1% for TX-100. Concentration of inert electrolyte (chloride) was held constant at 0.01 , 0.05 or 0.10 mol l^{-1} (HCl + NaOH or KOH).

The effect of the alkyl chain length (C_{10} to C_{18}) in the alkyipyridinium surfactants on the $pK_{a_i}^*$ value of BG at $c(L) = 17.5 \text{ } \mu\text{mol l}^{-1}$ was investigated at a constant concentration $c(T) = 0.5 \text{ mmol l}^{-1}$ and a constant concentration of inert electrolyte, $c(\text{HCl} + \text{KOH}) = 0.01 \text{ mol l}^{-1}$, using solutions with $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$ and $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$. In the case of DPC, $\varphi(\text{C}_2\text{H}_5\text{OH})$ had to be increased to 50% in view of the lower solubility of this surfactant and its ionic associate with the dye in water.

The effect of the kind and concentration of inert electrolyte (chloride, nitrate, sulfate, perchlorate, acetate, formate, dihydrogenphosphate) was studied over the region of $c(\text{X}^-) = 0.01$ to 1 mol l^{-1} at a constant concentration of cationic surfactant $c(T) = 0.5 \text{ mmol l}^{-1}$ and dye concentrations as given above. The effect of the chloride-to-bromide and chloride-to-nitrate concentration ratios was studied in the same conditions, the total concentration of the two anions was 0.1 and 0.01 mol l^{-1} , respectively.

The effect of the total concentration of the dye on its $pK_{a_i}^*$ value was studied at concentrations $c(L) = 7$ to $20 \text{ } \mu\text{mol l}^{-1}$ and an ionic strength $I = 0.01 \text{ mol l}^{-1}$ (HCl + NaOH or KOH) in the above conditions.

Absorption spectra of the ionic associates of the dyes and SPX in the organic phase were measured over the region of 320 to 720 nm under conditions given in Table I; for this, 5 ml of

TABLE I

Optical characteristics of ionic associates of BR, BB and BG with SPX extracted into chloroform. $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $I = 0.1 \text{ mol l}^{-1}$ (HCl + KOH), $V_{\text{aq}}/V_{\text{org}} < 1$

| Dye | $c(L)$ $\mu\text{mol l}^{-1}$ | $c(T)$ $\mu\text{mol l}^{-1}$ | $\{T^+, LH^-\}$ | | $\{T_2^+, L^{2-}\}$ | | λ_{ip}^a nm |
|-----|----------------------------------|----------------------------------|------------------------------|---|------------------------------|---|------------------------|
| | | | λ_{max} nm | ϵ_{max} $\text{m}^2 \text{ mmol}^{-1}$ | λ_{max} nm | ϵ_{max} $\text{m}^2 \text{ mmol}^{-1}$ | |
| BR | 40 | 100 | 422 | 1.70 | 577 | 4.37 | 475 |
| | 200 | 50 | 422 | 1.70 | — | — | — |
| BB | 50 | 250 | 414 | 1.87 | 604 | 4.28 | 429 |
| | 250 | 25 | 414 | 1.82 | 604 | 4.54 | 500 |
| BG | 20 | 500 | 414 | 1.35 | 628 | 3.49 | 497 |
| | 35 | 100 | 404 | 1.35 | 628 | 3.50 | 497 |

^a Isosbestic point.

aqueous solution of the dye with the surfactant was extracted at pH 2 to 11, using 7 or 10 ml of chloroform. This organic solvent was also used as the reference system.

The stoichiometric composition of the ionic associates at a concentration of 0.1 mol l^{-1} in formate (pH 3.0), acetate (pH 4.75 and 6.0), phosphate (pH 10.0) or the universal Davies (pH 3.0, 4.5, 6.0, and 10.0) buffers was investigated by the continuous variations method using $c_0 = c_L + c_T = 50 \text{ } \mu\text{mol l}^{-1}$ and $V_{\text{aq/org}} = 1.5$, and by the molar ratios method using $c(L)$ or $c(T) = 50 \text{ } \mu\text{mol l}^{-1}$, by measuring the $\Delta A = f(x_L)$, $\Delta A = f(c_L)$ and $\Delta A = f(c_T)$ dependences at wavelengths of the maximum absorption by the three dyes and SPX as the surfactant.

RESULTS AND DISCUSSION

The ionic associates of the LH^- and L^{2-} species of the dyes with SPX display absorption maxima at 400–430 nm ($\epsilon = 1.3\text{--}2.0 \text{ m}^2 \text{ mmol}^{-1}$) and 570–630 nm ($\epsilon = 3.5\text{--}4.5 \text{ m}^2 \text{ mmol}^{-1}$), respectively (Table I); their mutual transformations in dependence on acidity give rise to sharp isosbestic points at 475 (BR), 497 (BG) and 500 nm (BB).

Only the ionic associates of the LH^- species are easily extracted into chloroform from acid or neutral aqueous solutions of SPX ($c = 25\text{--}50 \text{ } \mu\text{mol l}^{-1}$) with a concentration excess of the dye; the ionic associates of the L^{2-} species are extracted to a negligible extent.

The absorbance–pH curves of the chloroform extracts of aqueous solution of the dyes with a concentration excess of SPX give evidence of a quantitative formation of the two ionic associates of the acid-base species of the dyes with SPX at $\text{pH} < 3$ and $\text{pH} > 8$, respectively.

The continuous variations method confirms the existence of the ionic associate with the composition $\{\text{T}^+, \text{LH}^-\}$ in acid to neutral solutions. In alkaline solutions the ionic associate $\{\text{T}_2^+, \text{L}^{2-}\}$ occurs, the $\{\text{T}^+, \text{LH}^-\}$ associate, however, is also present to some extent, as indicated by the distortion of the $\Delta A = f(x_L)$ curves at $x_L < 0.5$ and the maximum of the curves at $x_L = 0.35$.

The molar ratios method, $\Delta A = f(c_T)$ and $\Delta A = f(c_L)$ over the concentration regions of $c(T)$ or $c(L) \leq 5 \text{ mmol l}^{-1}$ at $c(L)$ or $c(T) = 50 \text{ } \mu\text{mol l}^{-1}$, respectively ($T = \text{SPX}$), also confirm the occurrence of the ionic associates $\{\text{T}^+, \text{LH}^-\}$ at $\text{pH} \leq 6$ for the three dyes. In alkaline solutions, the results obtained by this method are not unique.

If the cationic surfactants CPB, CTMAB or SPX are present in total concentrations higher than 0.08 mmol l^{-1} , solubilization of the ionic associates takes place and the optical properties¹⁵ are altered, as are the acid-base properties: when the concentration of cationic surfactant is increased from 0.08 to 0.5 mmol l^{-1} , the $\text{p}K_{\text{ai}}^*$ values for the $\text{LH}^-/\text{L}^{2-}$ acid-base transition of the three dyes decrease about one pK unit or even more (Table II), over the region of $c(T)$ from 0.5 to 1 mmol l^{-1} the change in $\text{p}K_{\text{ai}}^*$ lowers or becomes nil within the experimental error, and at $c(T) > 1 \text{ mmol l}^{-1}$ the $\text{p}K_{\text{ai}}^*$ values increase by tenths of a pK unit. The two $c(T)$ concentration regions

correspond roughly to the region of critical micellar concentrations (CMC) of the majority of cationic surfactants at the ionic strengths used¹⁷.

TABLE II

pK_{ai}^* values of BR, BB and BG in dependence on the concentration of cationic surfactant. $c(\text{BR}) = 20 \mu\text{mol l}^{-1}$, $c(\text{BB}) = 12.5 \mu\text{mol l}^{-1}$, $c(\text{BG}) = 17.5 \mu\text{mol l}^{-1}$, $c(\text{EDTA}) = 0.1 \text{ mmol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $I = 0.05$ and 0.10 mol l^{-1} (HCl + KOH) for BR and BB, $I = 0.01 \text{ mol l}^{-1}$ (HCl + NaOH) for BG, respectively

| $c(\text{T})$ $\mu\text{mol l}^{-1}$ | BR | | | | BB | | | BG | |
|---|------|------|-------|------|-------------------|------|------|------|------|
| | SPX | SPB | CTMAB | SDS | SPX | CPB | SDS | SPX | CPB |
| 0.00 ^{ab} | 8.00 | 8.00 | 8.00 | 8.00 | 4.02 | 4.10 | 4.22 | 5.03 | 4.85 |
| 0.01 | — | — | — | 8.00 | — | — | 4.03 | — | — |
| 0.08 | 7.78 | 7.25 | 7.37 | — | 3.15 | 3.02 | — | 4.25 | — |
| 0.10 | — | 7.05 | 7.12 | — | — | — | — | 4.00 | 3.82 |
| 0.20 | 7.06 | 6.60 | 6.66 | 7.97 | 2.98 | 2.86 | 3.99 | — | — |
| 0.30 | — | — | 6.64 | — | — | — | — | 3.35 | 3.15 |
| 0.50 | 6.85 | 6.55 | 6.62 | 7.95 | 2.68 ^b | — | — | 3.20 | 3.10 |
| 1.00 | 6.83 | — | — | — | 2.95 | 2.81 | 4.02 | 3.23 | 3.15 |
| 2.00 | 7.08 | 6.80 | 6.82 | — | 2.90 | 2.80 | — | — | — |
| 5.00 | 7.08 | — | — | — | 2.85 | 2.80 | — | — | — |
| 10.00 | 7.68 | 7.45 | 7.54 | — | 2.95 | 2.89 | — | 3.35 | 3.60 |

^a Ref. 7; ^b Zephiramin.

TABLE III

pK_{ai}^* values of BR and BB in dependence on the concentration of nonionic surfactant. $c(\text{BR}) = 20 \mu\text{mol l}^{-1}$, $c(\text{BB}) = 12.5 \mu\text{mol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $I = 0.1 \text{ mol l}^{-1}$ (HCl + KOH)

| $c(\text{Brij 35})$ g l^{-1} | pK_{ai}^* | | $\varphi(\text{TX-100})$ % | pK_{ai}^* BB |
|--|-------------|------|-------------------------------|-------------------|
| | BR | BB | | |
| 0.01 | 8.00 | — | 0.05 | 4.55 |
| 0.05 | — | 4.55 | 0.20 | 4.75 |
| 0.10 | 8.05 | 4.90 | 0.50 | 4.95 |
| 0.20 | — | 5.00 | 1.00 | 4.97 |
| 0.50 | — | 5.05 | — | — |
| 1.00 | 8.15 | — | — | — |
| 10.00 | 8.28 | 5.17 | — | — |

TABLE IV

Effect of concentration of inert electrolyte on the pK_{ai}^* values of BR, BB and BG. Conditions as in Table II

| Anion X^- | pK_{ai}^* at $c(X^-)$, mol l ⁻¹ | | | | | | | |
|---|---|-------|-------|-------|-------|-------------------|-------|-------|
| | 0.000 | 0.003 | 0.010 | 0.050 | 0.100 | 0.200 | 0.500 | 1.000 |
| BR | | | | | | | | |
| Cl ⁻ | 8.00 | — | 7.96 | 7.81 | 7.73 | — | 7.54 | 7.41 |
| BR + SDS | | | | | | | | |
| Cl ⁻ | 8.06 | 8.05 | 7.90 | — | 7.73 | — | 7.55 | — |
| BR + SPX | | | | | | | | |
| Cl ⁻ | 7.08 | — | 7.13 | 7.28 | 7.42 | — | 7.63 | 7.70 |
| NO ₃ ⁻ | — | — | 7.44 | 7.50 | 7.51 | 7.64 | — | — |
| SO ₄ ²⁻ | — | — | 7.34 | 7.36 | 7.45 | 7.50 | 7.58 | 7.60 |
| BR + CPB | | | | | | | | |
| Cl ⁻ | 6.42 | — | 6.65 | 7.25 | 7.50 | — | 7.85 | 7.95 |
| NO ₃ ⁻ | — | — | 7.10 | 7.75 | 7.85 | 7.90 | — | — |
| SO ₄ ²⁻ | — | — | — | — | 7.48 | 7.55 | 7.60 | 7.65 |
| BB + CPB | | | | | | | | |
| Cl ⁻ | 4.02 | — | — | — | 2.65 | 2.98 | 3.30 | 3.70 |
| NO ₃ ⁻ | — | — | — | — | 3.20 | 3.42 | 3.70 | — |
| SO ₄ ²⁻ | — | — | — | — | 2.72 | 2.92 ^a | 2.95 | — |
| H ₂ PO ₄ ⁻ | — | — | — | — | 2.23 | 2.45 | 2.65 | — |
| Br ⁻ | — | — | — | — | — | 3.55 | — | 2.77 |
| HCOO ⁻ | — | — | — | — | — | 2.57 | — | — |
| Ac ⁻ | — | — | — | — | — | 2.50 | — | — |
| BG + SPX | | | | | | | | |
| Cl ⁻ | — | — | 3.20 | — | 3.80 | 4.05 | 4.30 | 4.40 |
| NO ₃ ⁻ | — | — | 3.35 | 3.90 | 4.25 | 4.35 | — | — |
| Br ⁻ | — | — | 3.52 | — | 4.33 | — | 4.84 | 5.00 |
| SO ₄ ²⁻ | — | — | 3.35 | 3.50 | 3.55 | 3.60 | 3.70 | — |
| BG + CPB | | | | | | | | |
| Cl ⁻ | — | — | 3.10 | — | 3.85 | 4.00 | 4.30 | 4.40 |
| NO ₃ ⁻ | — | — | 3.45 | 3.97 | 4.25 | — | 4.65 | — |
| Br ⁻ | — | — | 3.55 | — | 4.30 | — | 4.85 | 4.95 |
| SO ₄ ²⁻ | — | — | 3.50 | 3.70 | 3.77 | — | 3.90 | — |

^a $c(X^-) = 0.300 \text{ mol l}^{-1}$.

In the series of alkylpyridinium surfactants, the formation parts of the absorbance–pH curves of BG at a constant concentration of the surfactant are shifted to the acid region with increasing alkyl chain length in the alkylpyridinium moiety (C_{10} through C_{18} , Fig. 1). The pK_{ai}^* values decrease in the series $pK_{ai}^* (\pm 0.02) = 5.00, 3.40, 3.25, 3.10,$ and 3.05 for DPC (for which $\varphi(C_2H_5OH) = 50\%$), TPB, PPB, CPB ($=C_{16}$) and OPB, respectively; for SPX the value is 3.20 . The decrease from 3.40 to 3.05 when passing from TPB (C_{14}) to OPB (C_{18}) indicates that the stability of the ionic associates of the dyes with the alkylpyridinium increases in this series. The marked change in pK_{ai}^* when passing from DPC to TPB is primarily due to the pronounced difference in the micellation properties of the two surfactants, and also to the easier dissociation of alkylpyridinium chlorides as compared to the corresponding bromides; of importance is also the fact that the measurements with DPC were performed in a solvent with a high ethanolic fraction ($\varphi(C_2H_5OH) = 50\%$).

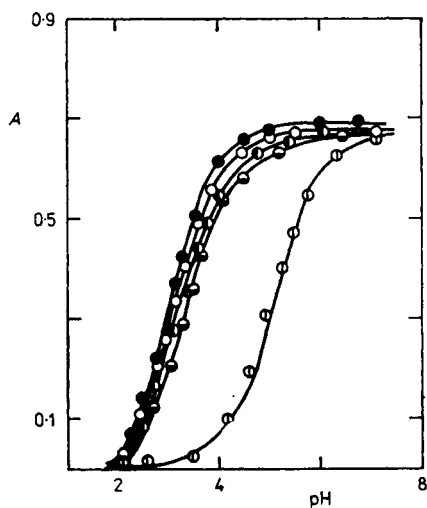


FIG. 1

Absorbance–pH curves of BG in the presence of alkylpyridinium surfactants. $c(L) = 17.5 \mu\text{mol l}^{-1}$, $c(T) = 0.5 \text{ mmol l}^{-1}$, $\varphi(C_2H_5OH) = 5\%$, $I = 0.01 \text{ mol l}^{-1}$ (HCl + NaOH). Surfactant, wavelength (nm): ● OPB, 624; ○ CPB, 628; ● PPB, 624; ● TPB, 624; ⊕ DPC ($\varphi(C_2H_5OH) = 50\%$), 615

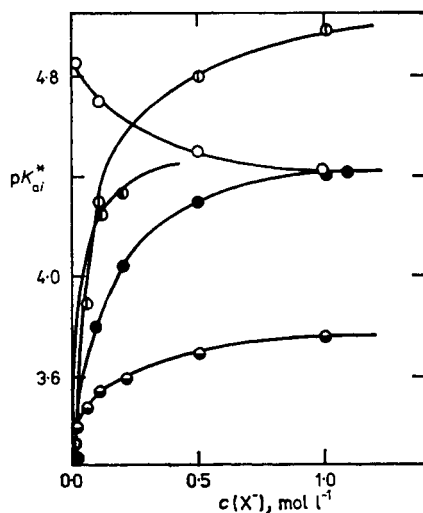


FIG. 2

Effect of ionic strength on the pK_{ai}^* value of BG in the presence of SPX. $c(L) = 17.5 \mu\text{mol l}^{-1}$, $c(T) = 0.5 \text{ mmol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $\varphi(C_2H_5OH) = 5\%$, $\lambda 614 \text{ nm}$ (○), 628 nm (●, ⊙, ⊖, ⊕). Anion: ○ Cl^- (in the absence of SPX), ● Cl^- , ● NO_3^- , ⊖ SO_4^{2-} , ⊕ Br^-

In the presence of SDS, Brij 35 or TX-100 in concentrations of $0.01 - 0.1 \text{ mmol l}^{-1}$, $0.01 - 10 \text{ g l}^{-1}$ and $0.001 - 1\%$ (v/v), respectively, the changes in the pK_{ai}^* values of BR and BB make tenths of a pK unit (Tables II and III).

Increase in the concentration of inert electrolyte (chloride) from 0.01 to 1 mol l^{-1} is accompanied by a change in pK_{ai}^* of about half a pK unit for aqueous solutions of the three dyes in the absence of surfactants (Fig. 2); in the presence of cationic surfactants ($c(T) = 0.5 \text{ mmol l}^{-1}$) the pK_{ai}^* values can increase as much as 1.5 pK units (Table IV).

At higher concentrations of nitrate and bromide ($c > 0.15 \text{ mol l}^{-1}$) or sulfate ($c > 0.5 \text{ mol l}^{-1}$) or roughly equimolar concentrations of perchlorate, precipitation of highly stable ionic associates of these anions with the cationic surfactant, $\{T^+, X^-\}$, takes place.

The effect of the anion of the inert electrolyte on the pK_{ai}^* value increases in order dihydrogenphosphate, formate, acetate, sulfate, chloride, bromide, nitrate, perchlorate.

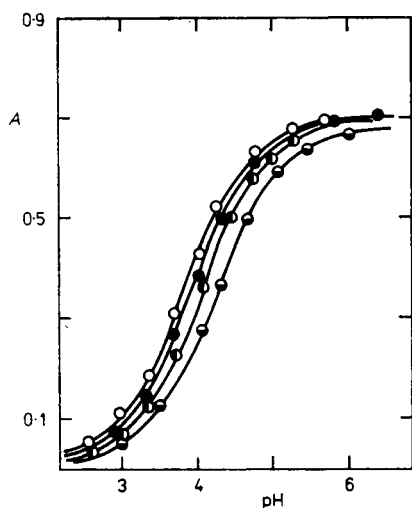


FIG. 3

Absorbance-pH curves of BG in the presence of SPX in dependence on the chloride-to-nitrate concentration ratio. $c(L) = 17.5 \mu\text{mol l}^{-1}$, $c(T) = 0.5 \text{ mmol l}^{-1}$, $c(\text{Cl}^-) + c(\text{NO}_3^-) = 100 \text{ mmol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $\lambda = 628 \text{ nm}$. $c(\text{Cl}^-): c(\text{NO}_3^-)$: \circ 2:1, \bullet 1:1, \bullet 1:2, \circ 0:1

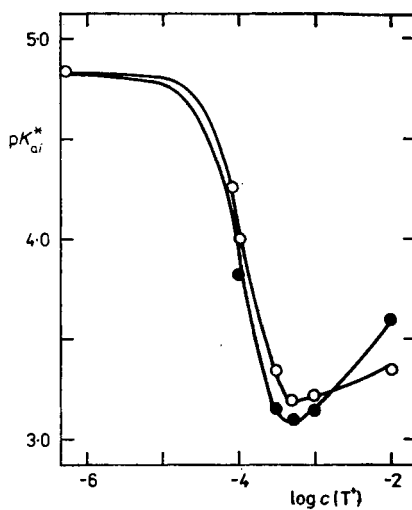


FIG. 4

Dependence of the pK_{ai}^* values of BG on the concentration of surfactant. $c(L) = 17.5 \mu\text{mol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $I = 0.01 \text{ mol l}^{-1}$ (HCl + NaOH), $\lambda = 628 \text{ nm}$. Surfactant: \circ SPX, \bullet CPB

te. The stability of the ionic associates $\{T^+, X^-\}$ increases with increasing lipophilic nature of anion X^- , whereupon competitive equilibria between the ionic associates of the two kinds, $\{T^+, LH^-\}$ and $\{T^+, X^-\}$, play an increasingly important role,

TABLE V

Effect of the chloride-to-nitrate concentration ratio on the pK_{ai}^* values of BR, BB and BG in the presence of cationic surfactants. $c(BR) = 20 \mu\text{mol l}^{-1}$, $c(BB) = 12.5 \mu\text{mol l}^{-1}$, $c(BG) = 17.5 \mu\text{mol l}^{-1}$, $c(T) = 0.5 \text{ mmol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $c(\text{HI}^-) + c(\text{NO}_3^-) = 0.10 \text{ mol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$.

| $c(\text{HI}^-) : c(\text{NO}_3^-)$ | pK_{ai}^* | | | | |
|-------------------------------------|-------------|----------|----------|----------|----------|
| | BR + CPB | BR + SPX | BB + SPX | BG + SPX | BG + CPB |
| 1 : 0 | 7.40 | 6.80 | 2.65 | 3.80 | 3.85 |
| 2 : 1 | 7.40 | — | 2.98 | 3.80 | 4.00 |
| 1 : 1 | 7.65 | 6.90 | 3.05 | 3.90 | 4.05 |
| 1 : 2 | 7.70 | — | 3.10 | 4.03 | 4.15 |
| 0 : 1 | 7.80 | 7.20 | 3.20 | 4.25 | 4.25 |

TABLE VI

Effect of concentrations of BR, BB, and BG on their pK_{ai}^* values in the presence of cationic surfactants. $c(T) = 0.5 \text{ mmol l}^{-1}$, $c(\text{EDTA}) = 0.5 \text{ mmol l}^{-1}$, $\varphi(\text{C}_2\text{H}_5\text{OH}) = 5\%$, $I = 0.1 \text{ mol l}^{-1}$ (for BR and BB), 0.01 (for BG) (HCl + NaOH or KOH)

| System | $c(L)$ $\mu\text{mol l}^{-1}$ | pK_{ai}^* | $c(L)$ $\mu\text{mol l}^{-1}$ | pK_{ai}^* |
|----------|----------------------------------|-------------|----------------------------------|-------------|
| BR + SPX | 4.0 | 6.80 | 20.0 | 6.87 |
| | 8.0 | 6.85 | 100.0 | 7.05 |
| | 10.0 | 6.87 | 200.0 | 7.03 |
| BR + CPB | 3.0 | 6.80 | 100.0 | 6.95 |
| | 8.0 | 6.80 | 200.0 | 6.90 |
| | 20.0 | 6.83 | | |
| BB + SPX | 3.1 | 2.75 | 62.5 | 3.05 |
| | 6.2 | 2.78 | 125.0 | 3.10 |
| | 12.5 | 2.82 | | |
| BG + SPX | 7.0 | 2.90 | 17.5 | 3.13 |
| BG + CPB | 7.0 | 3.08 | 17.5 | 3.12 |

and this results in a suppression of the effect of the cationic surfactant on the pK_{ai}^* values of the sulfophthalein dyes.

In the case of perchlorate, which forms the most stable ionic associates with the surfactants, the latter are quantitatively bonded in these associates $\{T^+, ClO_4^-\}$ and the sulfophthalein dyes behave as if the surfactants were absent.

When keeping the total anion concentration constant, the pK_{ai}^* values decrease with increasing chloride-to-nitrate concentration ratio for the three dyes, and with increasing chloride-to-bromide concentration ratio for BR and BB (Fig. 3, Table V). The pK_{ai}^* changes are more pronounced in the former case than in the latter case, due to the higher difference in the stability of the ionic associates of the surfactants with nitrate as compared to bromide.

Keeping the remaining concentrations constant, the pK_{ai}^* values increase 0.2 to 0.5 pK units with dye concentrations increasing over the $1-200 \mu\text{mol l}^{-1}$ region (Table VI); molar absorptivities of the two ionic associates decrease less than 5%, which indicates that the mutual associating ability of the dyes is low.

Assuming that the ionic associates of the surfactants with the dyes and with the anions X^- are very stable, the dependence of pK_{ai}^* of sulfophthalein dyes on the concentrations and kind of cationic surfactant and inert electrolyte can be described by the equation¹²

$$pK_{ai}^* = pK_{ai} - \log [1 + (\beta_{TL}c_T/n)/(1 + \beta_{TX}c_X)], \quad (1)$$

where β_{TL} and β_{TX} are the stability constants of the ionic associates $\{T^+, HL^-\}$ and $\{T^+, X^-\}$, respectively, c_T and c_X are the total concentrations of surfactant and inert electrolyte, respectively, and n is the number of surfactant molecules in a micelle. This equation describes well the behaviour of the sulfophthalein dyes treated, as evidenced by the plots of pK_{ai}^* vs $\log c_T$ for BG, shown in Fig. 4.

The formation of the ionic associates $\{T^+, LH^-\}$ and $\{T_2^+, L^{2-}\}$ of cationic surfactants and anionic acid-base species of the three dyes, or their solubilized products in the region of micellar and submicellar concentrations of the surfactants, and the formation of the highly stable ionic associates of cationic and anionic surfactants $\{T^+, T^-\}$, can be employed in titrimetric methods for the determination of ionic surfactants using photometric end-point indication with sulfophthalein dyes. Methods of two-phase titration and titration of a cationic surfactant with a titrant solution of an anionic surfactant (or vice versa) in aqueous solution at a suitable pH give comparable results particularly for samples with a simple matrix¹⁸.

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