# SPECTROPHOTOMETRIC STUDY OF THE INTERACTION OF CHROMAZUROL S AND ERIOCHROMAZUROL B WITH SURFACE ACTIVE SUBSTANCES – TENSIDES

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The acid–base and optical properties of Chromazurol S and Eriochromazurol B in the presence of $1 \,.\, 10^{-6}$—$2 \,.\, 10^{-2}$M solutions of cetylpyridinium bromide, cetyltrimethylammonium bromide and 1-ethoxycarbonylpentadecyltrimethylammonium bromide (Septonex) and 0·001—1·0% w/v solutions of octylphenolpolyethylene glycol ether (Triton X-100), polyoxyethylenemonolauryl ether (Brij 35) and lauryl sulphate sodium salt were determined by graphical and numerical interpretation of absorbance curves. The poorly soluble ion associates, which can be extracted into chloroform and which have the defined composition $[LH_{4-n}^{n-}.n\,T^+]$ or $[LH_{3-n}^{n-}.n\,T^+]$ are formed at submicellar concentration of the tenside. In regions close to the critical micellar concentration of the tenside, soluble binary complexes of the acid–base forms of the reagent are formed with tenside micelles. The conditional stability constants of the reagent acid–base equilibrium depend on the type and concentration of the tenside, on the reagent concentration, on the concentration and type of inorganic acid anions and on the ionic strength of the solution. The mechanism of interaction of the reagent with the tenside and the probable structure of the binary species are discussed.

In the last ten years, the metal ion–organic chelating dye–surface active substance ternary systems have been studied extensively in an attempt to increase the selectivity, the colour contrast and the sensitivity of spectrophotometric methods. The molar absorption coefficients of the ternary species, in systems containing hydroxytriphenylmethane dyes with a greater number of donor atoms in the presence of cationic and non-ionic tensides, attain values of 1·0—1·7 . . $10^5$ $\text{mmol}^{-1}$ $\text{cm}^{-2}$ and the colour contrast of the reaction varies around $\Delta\lambda_{\text{max}}$ (complex–reagent) ~80—200 nm (ref.[1–9]), while the selectivity is unchanged.

In spite of the large number of papers that have been published on the practical use of ternary systems for the determination of trace concentrations of metal ions, there is a lack of detailed information on the actual reaction mechanism of the action of the tenside on the binary metal ion–reagent system. The actual reaction course is complicated[1–7], as metal ion–reagent, reagent—tenside, tenside–mineral acid anion and other binary species are formed in the systems in addition to the ternary species with defined composition $[M_aL_bH_c.n\,T]$, in dependence on the experimental conditions and type of tenside. In addition to the formation of these species with stoichiometric composition, the solubilizing effect of the tenside micelles, interaction of the binary and ternary species with the micelles and a number of other factors[5–8] became important at higher tenside concentrations. Thus, in order to clarify the reaction mechanism of the formation of the ternary species it is first necessary to clarify the mechanism of the interaction of the reagent alone with the tenside molecules under various experimental conditions.

This work deals with the effect of cationic (cetylpyridinium, Septonex, cetyltrimethylammonium), non-ionic (Triton X-100, Brij 35) and anionic (lauryl sulphate) tensides on the acid–base and optical properties of Chromazurol S and Eriochromazurol B, as typical representatives of the hydroxytriphenylmethane dyes with salicylic acid functional analytical groups.

## EXPERIMENTAL

### Chemicals and Instruments

Chromazurol S (3″-sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid, $C_{23}H_{16}SO_9Cl_2.2\,H_2O$, $M_r$ 575·382, CAS) and Eriochromazurol B (2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchsone-5,5′-dicarboxylic acid, $C_{23}H_{16}Cl_2O_6$, $M_r$ 459·942, CAB) were purified by a combination of precipitation and extraction methods[10] using the commercial substance from the firm Geigy (Basle, Switzerland) or from ICN Pharmaceuticals Inc. (New York, USA) as the free acid $LH_4^0.2\,H_2O$ or $LH_3^0$. The content of the active component 86·89% or 97·86% was found by elemental analysis (CHN) and spectrophotometrically[11]. The stock solutions of Chromazurol S and Eriochromazurol B with concentrations of 1·00—3·75 . $10^{-4}$M were prepared by dissolving weighed amounts of the chromatographically pure substance, which had been equilibrated with the air, in several ml of 1M-KOH; after complete dissolution the solution was diluted to the required volume with water.

The working solution of CAS was prepared by adding stepwise 20 ml water, 10 ml of 3·75 . . $10^{-4}$M-CAS, the required volume of ethanolic or aqueous tenside solution, 1 ml of 0·05M-EDTA to 10 ml of 1M-$HNO_3$ (HCl, $H_2SO_4$, $HClO_4$) and diluting to 100 ml with water. The working CAB solution was prepared by adding 20 ml water, 10 ml of 1M-$HNO_3$ (HCl, $HClO_4$, $H_2SO_4$), 10 ml of an alkaline solution of CAB and 1 ml of 0·05M-EDTA to the required volume of ethanolic or aqueous tenside solution; use of the above procedure for CAB in strongly acid media lead to precipitation of the molecular form of CAB.

Brij 35 (polyoxyethylenemonolauryl ether, $n \sim 20$, $M_r \sim 900$) was the product of the firm Merck (Darmstadt, GFR); the stock solution was 10% w/v in water. Triton X-100 (octylphenol polyethylene glycol ether, analytical grade) was the product of Koch-Light Lab. Ltd. Great Britain; the stock solution contained 2% w/v of the substance in water. Sodium lauryl sulphate ($C_{12}H_{25}O—SO_3Na$, $M_r$ 288·35, designated SDS) was the product of BDH, Ltd., (Poole, Great Britain); the stock solution was 2% w/v in water.

Cetylpyridinium bromide ($C_{21}H_{38}BrN$, $M_r$ 384·44, CPB) was the product of Lachema (Brno, ČSSR) and was recrystallized from ethanol. Septonex (1-ethoxycarbonylpentadecyltrimethylammonium bromide, $C_{21}H_{44}BrNO_2$, $M_r$ 422·5, SPX) was the product of Slovakofarma (Hlohovec, Czechoslovakia). Cetyltrimethylammonium bromide ($C_{19}H_{42}BrN$, $M_r$ 354·45, CTMA) was recrystallized from ethanol. The cationic tenside solutions were added in the form of ethanolic solutions prepared immediately before the measurement by dissolving the required weighed amount of the solid substance in 5 ml of ethanol. Use of older solutions led to a marked decrease in the reproducibility of the measuring results, a colloidal or crystalline precipitate is formed and the solutions exhibit a marked Tyndall effect in the presence and absence of reagent.

The other chemicals were of for semiconductors (Suprapure) purity ($HNO_3$, HCl, $NH_4OH$), or *p.a.* purity ($H_2SO_4$, KOH, EDTA, $CHCl_3$, $C_2H_4Cl_2$, $HClO_4$). The organic solvents were purified by distillation; ethanol contained 5 v/v% methanol. The ionic strength of the solutions was maintained at a constant value of $I$ 0·10 or 1·00 by mixing with the required volume of mineral acid ($HNO_3$, HCl, $HClO_4$, $H_2SO_4$) and KOH. Water was doubly distilled using a Bi 18 Destamat$^R$ quartz appařatus (Heraus Quarzschmelze, GFR).

The absorbance curves were measured using a titration technique at 25°C in 10—40 mm quartz cuvettes on a digital double-beam Superscan$^{TM}$ 3 spectrophotometer (Varian, Switzerland) controlled by a HP 9815A desk-top calculator (Hewlett–Packard, USA) using a program for direct measurement and treatment of experimental data[12]. Extraction photometric measurements were carried out on a manual single-beam SF-D2 spectrophotometer (LOMO, USSR). The solution acidity was measured on a digital PHM 64 pH meter (Radiometer, Denmark) with a G 202 B glass and K 401 saturated calomel electrode. The instrument was calibrated regularly with a set of standard NBS buffers.

### Methods

The extraction of ion associates of the reagents with the tensides was carried out using 10 ml of tenside–reagent reaction mixture with the required pH value and with an identical volume of chloroform or dichloroethane for a period of 60 min. After separation of the phases, the optical parameters of the binary species were measured in the organic phase and the final acidity of the solution after the extraction was measured in the aqueous phase. Graphical methods were employed for interpretation of the absorbance spectra in dependence on the acidity and of the continuous variation curves.

Absorption spectra in graphical and digital forms were measured in dependence on the acidity of the medium for both reagents and for the individual types of tenside in the critical micelle concentration (CMC) region, $c_T \sim 10^{-3}$M, in the pH interval 0—14 and at wavelengths of 350 to 750 nm in steps of ΔpH ~0·1—0·3. In the region of existence of the individual binary species of the reagent with the tenside, the absorption spectra were measured under similar experimental conditions in dependence on the tenside concentration in the interval $c_T = 10^{-6}$—$10^{-2}$M or 0·001—1·00%. The positions of the absorption maxima of the individual species, the positions of the isosbestic points and selected wavelengths for recording of the absorbance-pH curves were found from the graphs.

The stability of the individual binary species was checked by measuring the absorbance at time intervals of 5, 10, 15, 30, 60, 120, 300 and 720 min.

The absorbance-pH curves for the individual types and concentrations of tenside at a constant reagent concentration, for various reagent concentrations and tenside CMC and for various types and concentrations of inorganic acid anions were measured by a titration technique for 6—10 wavelength values in the region of maximum absorbance of the individual binary species in steps of ΔpH ~0·1—0·2. The values of the conditional equilibrium constants of the interconversion of the individual binary species under various experimental conditions were found by graphical[13] and numerical interpretation of the absorbance-pH curves.

Numerical interpretation was carried out using a modified version of the PRCEK program, in which the iterative procedure for finding the optimal parameters of the absorbing species was replaced by a procedure for finding the minimum of the function $U = f(A_{01}, A_{02}, \beta^*)$ by the interval halving method. The program was modified for direct treatment of the experimental data by a Superscan$^{TM}$ 3 spectrophotometer controlled by an HP 9815A desk-top calculator. The program function was checked using data published previously and the results agreed very well.

## RESULTS AND DISCUSSION

Poorly soluble yellow to red-purple coloured ion associates are formed as a result of the interaction of CAS or CAB with all the tested cationic and non-ionic tensides at low concentration excesses ($c_T/c_L < 10$) and at low overall tenside concentrations ($c_T < 5 . 10^{-4}$M); these associates are readily extracted into chloroform and less readily extracted into $C_2H_4Cl_2$ and other organic solvents.

The absorption spectra of the chloroform extract of CAS with Septonex ($c_L = 3{\cdot}00 . 10^{-5}$M, $c_T = 4{\cdot}5 . 10^{-5}$M) and the continuous variation method ($c_0 = c_L + c_T = 7{\cdot}5 . 10^{-5}$M) confirm stepwise formation of two absorbing species in dependence on the acidity of the medium. In strongly acidic medium with pH 1·5, only the yellow binary species of the reagent with the tenside is extracted; this species has an absorption maximum at 458 nm ($\varepsilon = 2{\cdot}07 . 10^4$ mmol$^{-1}$ cm$^2$) and a molar ratio of L : T = 1 : 1. In weakly acid media with pH > 3, a red-purple species with a double absorption band with absorbance maxima at 555 and 596 nm ($\varepsilon = 1{\cdot}75$ and $5{\cdot}15 . 10^4$ mmol$^{-1}$ cm$^2$) is extracted. A binary species with molar ratio L : T = 1 : 2 is extracted from 0·1M acetate buffer and from unbuffered solutions with pH 4·5.

In the pH region 1·75–2·5, a mixture of both these species is extracted, with absorption maxima at 596, 555 and 458 nm; in the alkaline region the organic phase is colourless and all the reagent remains in the aqueous phase (Fig. 1). The absorbance maximum of the continuous variation curves $\Delta A = f(x_L = c_L/c_0)$ of the chloroform extract of the solution with pH 3·0 and for all the wavelengths lies in the region $x_L = c_L/(c_L + c_T) = 0{\cdot}55-0{\cdot}60$.

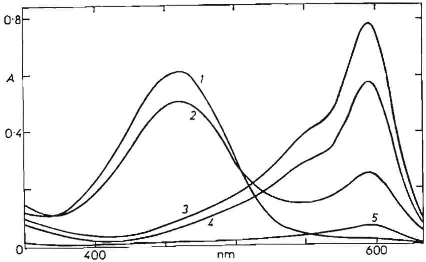


FIG. 1

Absorption Spectra of the Chloroform Extract of CAS with SPX in Dependence on the Acidity of the Aqueous Phase

$c_L = 3 . 10^{-5}$M, $c_T = 4{\cdot}5 . 10^{-5}$M, $v_{aq} = v_{org} = 10$ ml, $I = 0{\cdot}10$ ($HNO_3$ + KOH), 60 min. Curve pH: *1* 1·5, *2* 2·0, *3* 3·0, *4* 3·5, *5* 7·0.

Aqueous solutions of CAS and CAB in the presence of $10^{-3}$M or 0·1% concentration of tenside are stable for at least 5 hours.

The absorption spectra of a 3·75 . $10^{-5}$M aqueous solution of CAS or CAB in the presence of the above concentrations of cationic, non-ionic or anionic tensides (Fig. 2, 3) confirm the existence of four optically different species in dependence on the acidity of the medium. Sharp isosbestic points correspond to the interconversions (Table I).

The absorption maxima of all species in the presence of anionic sodium lauryl sulphate differ only slightly from the absorption maxima of the individual acid–base forms of both reagents in aqueous or aqueous ethanolic medium[10]. The regions of existence of the individual species are in agreement with those corresponding to the acid–base forms of the reagents in solutions without tensides.

In the presence of cationic (CPB, CTMA and SPX) and non-ionic (Brij 35, Triton X-100) tensides, the absorption maxima of the species in strongly acid media with pH < 1 and in neutral and alkaline media with pH > 7 are only slightly shifted compared with the absorption maxima of the corresponding acid–base forms of CAS ($LH_4^0$, $LH_3^-$, $LH^{3-}$ and $L^{4-}$) and CAB ($LH_3$, $LH^{2-}$ and $L^{3-}$). In acid media with pH 1–7, the shape of the absorption spectra changes sharply and a double ab-

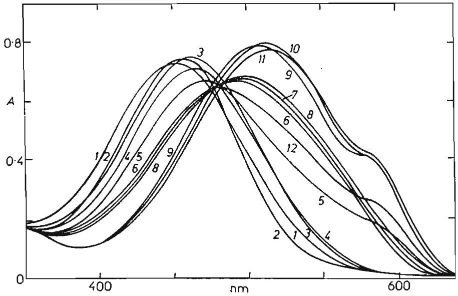


FIG. 2

Absorption Spectra of Aqueous Solutions of Chromazurol S in the Presence of $10^{-3}$M or 0·1% Tenside Solution

$c_L = 3{\cdot}75 \,.\, 10^{-5}$M, $c_{EDTA} = 5 \,.\, 10^{-4}$M, $I = 0{\cdot}10$ ($HNO_3$ + KOH), $t = 25$°C,Curve pH tenside: *1* 1·19 Brij 35, *2* 1·12 Triton X-100, *3* 1·21 SDS, *4* 0·98 SPX, *5* 1·10 CPB, *6* 3·73 without tenside, *7* 3·87 SDS, *8* 3·75 Brij 35, *9* 3·77 SPX, *10* 3·75 CPB, *11* 3·74 CTMA, *12* 1·43 CTMA.

sorption band with dominant absorption maximum at 490–510 nm ($\varepsilon = 2 . 10^4$ . . $\text{mmol}^{-1}\,\text{cm}^2$) and less marked absorption maximum at 580–590 nm ($\varepsilon = 1 . 10^4$ . . $\text{mmol}^{-1}\,\text{cm}^2$) appears in all cases. The long wave absorption band is characteristic for formation of a binary species of the reagent with the tenside (see the absorption band of a chloroform extract of CAS with SPX), while the short wave band corresponds to the $LH_2^{2-}$ or $LH_2^-$ acid–base form of Chromazurol S and Eriochromazurol B.

The character of the absorption spectra of CAS and CAB at constant reagent concentration, constant pH value and variable tenside concentration in the region of the existence of the individual binary species varies in dependence on the concentration excess of tenside. In acid medium with pH 1–7 and with increasing tenside concentrations, the concentration of species with a double absorption maximum at 490–510 and 580–590 nm increases and, at the same time, the absorbance and concentration of species with absorption maxima at 460–470 nm (pH $< 3$) and 420–430 nm (pH $> 3$) decreases. In strongly alkaline media at pH 10–14, the concentration of species with absorption maxima at 420–430 nm increases and the concentration of species with maxima at 594–615 nm decreases (Fig. 4 and 5). A similar shift of the concentrations of the individual species was observed in solu-

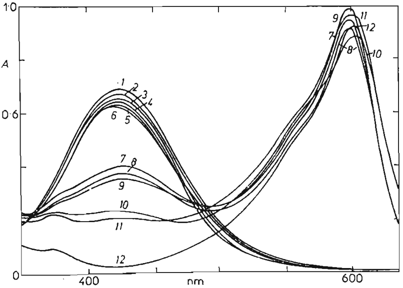


FIG. 3

Absorption Curves of Aqueous Solutions of CAS in the Presence of $10^{-3}$M or 0·1% Tenside Solution, Experimental Conditions as in Fig. 2

Curve pH tenside: *1* 7·24 SDS, *2* 7·33 Brij 35, *3* 7·33 without tenside, *4* 7·37 SPX, *5* 6·44 CPB, *6* 7·47 CTMA, *7* 12·04 SDS, *8* 12·09 Brij 35, *9* 11·62 without tenside, *10* 13·38 CTMA, *11* 13·50CPB, *12* 13·45SPX.

TABLE I

The Optical Characteristics of Chromazurol S and Eriochromazurol B in the Presence of Tenside
$c_L = 3{\cdot}75 \,.\, 10^{-5}$M, $c_T = 1{\cdot}0 \,.\, 10^{-3}$M, $c_{EDTA} = 5 \,.\, 10^{-4}$M, 5% v/v ethanol, $I = 0{\cdot}10$ ($HNO_3$ + KOH), $t = 25$°C.

| Tenside | Acid–base form, $\lambda_{max}$, nm | | | | Equilibrium $\lambda_{IP}$, nm | | |
|---|---|---|---|---|---|---|---|
| | L | LH | $LH_2$ | $LH_3$ | $LH_3/LH_2$ | $LH_2/LH$ | LH/L |
| | | | Chromazurol S | | | | |
| — | 599 (5·73) | 427 (2·09) | 492 (2·04) | 468 (2·17) | | | |
| SPX | 598 (5·28) | 419 (1·76) | 510 (2·12), 588 (1·02) | 457 (1·73) | 349, 476 | 350, 454 | 356, 481 |
| CPB | 604 (5·87) | 420 (1·81) | 510 (2·21), 585 (0·94) | 468 (—) | 360, 478 | 342, 456 | 357, 487 |
| CTMA[c,d] | 603 (5·56) | 420 (2·00) | 515 (1·98), 583 (0·97) | 470 (2·10) | 362, 481 | 350, 454 | 353, 487 |
| Brij[a,f] | 600 (5·39) | 425 (1·95) | 510 (1·92), 582 (1·00) | 468 (1·97) | 362, 476 | 348, 460 | 354, 486 |
| Triton[a] | 600 (5·30) | 426 (1·98) | 510 (1·96), 581 (1·03) | 467 (1·96) | 362, 477 | 348, 459 | 355, 487 |
| SDS | 600 (5·74) | 426 (1·99) | 495 (2·01) | 468 (2·17) | 350, 476 | 350, 455 | 355, 480 |
| $CHCl_3$[b] | — | — | 555 (1·76), 596 (5·15) | 400 (2·07) | | | |
| | | | Eriochromazurol B | | | | |
| — | 599 (6·15) | 428 (2·10) | 508 (2·19) | 460 (2·19) | | | |
| SPX | 608 (5·60) | 428 (2·11) | 510 (2·40), 588 (1·10) | 466 (—) | 360, 478 | 357, 461 | 363, 494 |
| CPB | 614 (5·89) | 428 (2·03) | 510 (2·48), 586 (1·13) | 468 (—) | 361, 478 | 357, 461 | 364, 498 |
| Brij[a] | 600 (5·92) | 428 (2·12) | 510 (2·37), 582 (1·16) | 465 (1·71) | | | |
| CTMA | 610 (5·79) | 426 (2·01) | 510 (2·20), 582 (1·17) | 470 (1·99) | 350, 480 | 350, 460 | 366, 498 |
| SDS | 599 (5·96) | 427 (2·00) | 509 (2·01) | 462 (2·01) | 365, 481 | 350, 459 | 355, 491 |

[a] $c_T = 0{\cdot}1\%$ w/v, [b] absorption maximum of the chloroform extract, $c_L = 3{\cdot}00 \,.\, 10^{-5}$M CAS, $c_T = 4{\cdot}50 \,.\, 10^{-5}$M SPX, $v_{aq} = v_{org} = 10$ ml, [c] absorption maxima for 1M-$HNO_3$, HCl and $H_2SO_4$: 457 (1·75), 458 (1·73), 457 (1·76), [d] absorption maxima for 1M-HCl, $HNO_3$ and $H_2SO_4$: 510 (2·12), 588 (1·03), 5·10 (1·64), 587 (1·00), 510 (2·10) 588 (1·01), [e] ref.[17] gives absorption maxima 466 (1·94) in 10M-$H_2SO_4$, 510 (1·92) and 420 (1·57) at pH 3 and 9, 600 (2·12) in 2M-NaOH, [f] absorption maxima[18] 430—435 and 680 nm or 440, 530 and 590 nm for the species LT and $LT_2$ with non-ionic tensides OP-10, OP-7 and DS-10 at pH 6·8.

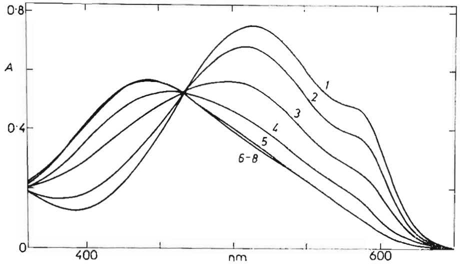


FIG. 4

Absorption Spectra of CAS Solutions in Dependence on the Concentration of Brij 35 at Constant pH Value of 4·50

$c_L = 3{\cdot}05 \,.\, 10^{-5}$M, $c_{EDTA} = 5 \,.\, 10^{-5}$M, $c_T = 0{\cdot}00001 - 1\%$, *I* 0·10 ($HNO_3 + KOH$) 25°C. Curve $c_T$ (%): *1* 1, *2* 0·1, *3* 0·03, *4* 0·01, *5* 0·001, *6* 0·0001, *7* 0·00001, *8* without tenside.

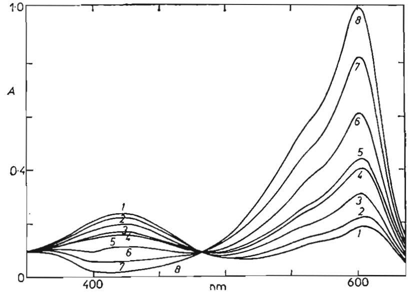


FIG. 5

Absorption Spectra of Alkaline CAS Solutions in Dependence on the Septonex Concentration

$c_L = 3{\cdot}75 \,.\, 10^{-5}$M, $c_{EDTA} = 5 \,.\, 10^{-4}$M, or otfher conditions see Fig. 4, pH 13·0; Curve $c_T$ M: *1* $10^{-2}$, *2* $5 \,.\, 10^{-3}$, *3* $2 \,.\, 10^{-3}$, *4* $1 \,.\, 10^{-3}$, *5* $5 \,.\, 10^{-4}$, *6* $2 \,.\, 10^{-4}$, *7* $1 \,.\, 10^{-4}$, *8* without tenside.

tions with varying concentrations of inorganic acid anions ($HCl$, $HNO_3$, $HClO_4$, $H_2SO_4$) and thus with changing ionic strength of the solution. A change in the kind of anion also changes the concentration ratios among the individual species, but has slight effect on the character of the spectra.

The formation regions in the absorbance curves for the individual types and concentrations of cationic tensides in the region of the $LH_3/LH_2$ acid–base equilibria is shifted into the acid region, while in the region of the $LH_2/LH$ and $LH/L$ acid–base equilibria it is shifted to more alkaline values in dependence on the character and overall concentration of the tenside (Fig. 6 and 7).

In the acid region at $pH < 3$, the shift of the formation region of the absorbance-pH curve of CAS and CAB is most marked in the presence of submicellar concentrations of cationic and nonionic tensides ($c_T < 10^{-3}$M). Higher concentrations of both tensides, as well as of anionic sodium lauryl sulphate do not change the formation regions on the curves.The shape and thus also the position of the curves for CAS in the presence of Triton X-100 and SDS are affected by the formation of a colloidal precipitate and an increase in the absorbance of the solution in the acid region at $pH < 2$.

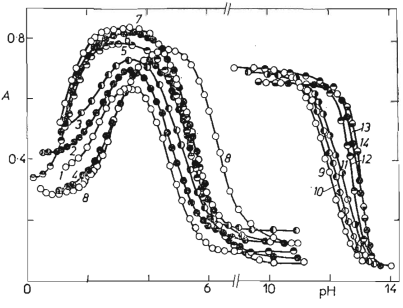


FIG. 6

Absorbance pH Curves of CAS in the Presence of $10^{-3}$M or 0·1% Tenside Solution

Experimental conditions as in Fig. 4; Curve tenside $c_T$(M, %): *1* without tenside, *2* Brij 35 0·01, *3* SDS $10^{-3}$, *4* Brij 35 0·1, *5* CTMA $10^{-3}$, *6* SPX $10^{-3}$, *7* CPB $10^{-3}$, *8* Brij 35 1·0, *9* without tenside, *10* SPX $1 . 10^{-4}$, *11* CPB $1 . 10^{-4}$, *12* CPB $5 . 10^{-4}$, *13* SPX $1 . 10^{-3}$, *14* SPX $1 . 10^{-2}$.

The second formation region of the absorbance-pH curves in the region, pH $> 3$, is shifted to a more alkaline region in dependence on the type and concentration of cationic and nonionic tenside; this is also true for the acid region. In the presence of Brij 35, the shift increases with increasing tenside concentration, even in the region above the CMC value (Fig. 6, curve *8*). In the alkaline region at pH 10–14, the formation region of the $A = f(\mathrm{pH})$ curve is shifted to higher pH values and at pH $> 13$ the curves are deformed as a result of decomposition of CPB and SPX.

At a constant tenside concentration of $c_\mathrm{T} \sim 10^{-3}$ and at constant ionic strength of the solution, the formation region of the absorbance-pH curves is shifted to more acid regions with increasing concentration excess of tenside, $c_\mathrm{T}/c_\mathrm{L} > 5$.

Depending on the type of inorganic acid anion, the first formation region of the absorbance curves is shifted to more acid regions, in the order $\mathrm{HCl} \sim \mathrm{H_2SO_4} > > \mathrm{HNO_3} > \mathrm{HClO_4}$, according to the magnitude of shift of the curves. At low $\mathrm{HClO_4}$ concentrations, a white crystalline precipitate of the ion associate of the tenside with $\mathrm{ClO_4^-}$ ions is formed. The absorption spectra and absorbance-pH curves of the reagent correspond to the curves of the reagent alone without tenside. The magnitude of the shift decreased with increasing concentration of the anion of the inorganic acid ($c = 0{\cdot}1 - 3\,\mathrm{M}$). In a mixture of HCl and $\mathrm{HNO_3}$ at various concentration ratios ($1\,\mathrm{M}$-HCl, $1\,\mathrm{M}$-$\mathrm{HNO_3}$, $0{\cdot}67\,\mathrm{M}$-HCl + $0{\cdot}33\,\mathrm{M}$-$\mathrm{HNO_3}$, $0{\cdot}50\,\mathrm{M}$-HCl + $0{\cdot}50\,\mathrm{M}$-$\mathrm{HNO_3}$, $0{\cdot}33\,\mathrm{M}$-HCl + $0{\cdot}67\,\mathrm{M}$-$\mathrm{HNO_3}$) and at constant ionic strength of the solution, $I = 1{\cdot}00$

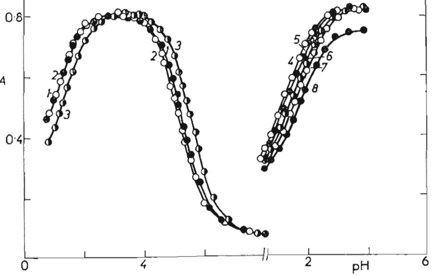


FIG. 7

Absorbance pH Curves for CAS in the Presence of $1 \,.\, 10^{-3}\,\mathrm{M}$ Septonex for Various Kinds and Concentrations of Inorganic Acid Anions

Experimental conditions, see Fig. 4; Curve anion $c_\mathrm{X}$: *1* $\mathrm{Cl^-}$ 0·1, *2* $\mathrm{SO_4^{2-}}$ 0·1, *3* $\mathrm{NO_3^-}$ 0·1, *4* $\mathrm{Cl^-}$ 1·0, *5* $\mathrm{Cl^-/NO_3^-}$ 0·67/0·33, *6* $\mathrm{Cl^-/NO_3^-}$ 0·50/0·50, *7* $\mathrm{Cl^-/NO_3^-}$ 0·33/0·67, *8* $\mathrm{NO_3^-}$ 1·0.

the formation region is shifted to a more acid region with increasing concentration ratio $HCl/HNO_3$ (Fig. 7). This fact reflects the important effect of the type of anion of the inorganic acid and negligible effect of the ionic strength of the solution.

The equilibrium constants corresponding to the formation of the individual absorbing species under the given experimental conditions, found by graphical and numerical interpretation of the absorbance-pH curves, are given in Table II together with some data from the literature. The equilibrium constant values and the corresponding shift of the formation regions of the absorbance-pH curves depend

TABLE II

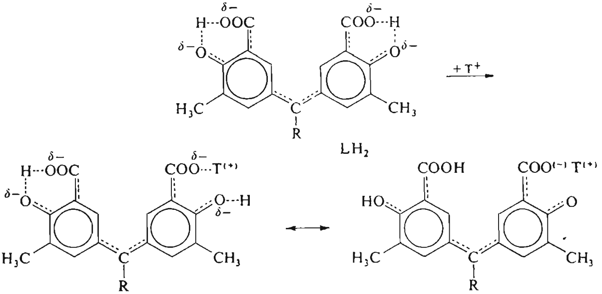
Equilibrium Constant Values for Various Tenside Types and Concentrations for Reactions of the Type $LH_{4-n}^{n-} + n[T^+X^-] + m\,X_2 \rightleftarrows [LH_{4-n}^{n-}.n\,T^+] + n\,X_1^- + m\,X_2^-$
$c_L = 3{\cdot}75 \,.\, 10^{-5}$M, $c_{EDTA} = 5 \,.\, 10^{-4}$M, 5% v/v ethanol, $t = 25$°C.

| Tenside | $c_T$, mol . l$^{-1}$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ |
| | | | | | Chromazurol S | | | | |
| CPB | 1·00[a] | 1·06 | — | — | 5·44 | 5·41 | 12·40 | 12·70[a] | 12·95 |
| CTMA[e] | 1·52[a] | 1·12 | — | 5·22[a] | 5·62 | 5·65 | — | — | — |
| SPX | — | 1·18 | 0·99 | — | 5·57 | 5·48 | 12·00 | 12·90 | 12·95 |
| Brij[b,f] | 2·35 | 2·85 | 2·95 | 4·90 | 5·50 | 6·25 | 11·90 | 11·95 | 12·15 |
| Triton[b] | 2·34 | 2·74 | 2·90 | — | 5·40 | — | — | — | — |
| SDS | — | 2·29 | — | — | 4·90 | — | — | — | — |
| —[c] | — | 2·27 | — | — | 4·87 | — | — | 11·79 | — |
| | | | | | Eriochromazurol B | | | | |
| CPB | — | 0·86 | 0·63 | — | 5·16 | 5·21 | 12·50[a] | 12·65 | 12·80 |
| CTMA | — | 1·09 | 0·98 | — | 5·13 | 5·18 | — | — | — |
| SPX | — | 1·22 | 1·24 | — | 5·26 | 5·32 | 12·70[a] | 12·76 | — |
| Brij[b] | — | 2·80 | 2·90 | — | 6·27 | 6·83 | 12·00 | 12·16 | 12·70 |
| Triton[b] | — | 2·70 | — | — | 5·98 | — | — | — | — |
| SDS | — | 2·36 | — | — | 4·92 | — | — | — | — |
| —[d] | — | 2·68 | — | — | 6·07 | — | — | 11·95 | — |

[a] $c_T = 5 \,.\, 10^4$M, [b] $c_T = 0{\cdot}01$; 0·1 and 1·0% w/v, [b] dissociation constant of CAS in aqueous medium (ref.[10]), [d] dissociation constant of CAB in 50% v/v ethanol medium (ref.[10]), [e] dissociation constants[17] 0·88, 0·81 (0·7), 0·73 and 0·85; 4·94, 4·79 (4·87), 4·76 and 4·86; 12·71, 12·78 (12·76), 12·78 and 12·81 for CAS : CTMA ratios of 1 : 5, 1 : 10, 1 : 50 and 1 : 100, [f] dissociation constants[19] 3·10, 7·20 and 12·4 in the presence of non-ionic tenside OP-10.

primarily on the overall tenside concentration; the greatest effect is evident at submicellar concentrations, $c_T < 10^{-3}$M. At higher tenside concentrations the equilibrium constants change only slightly. The equilibrium constants also change in dependence on the overall concentration of the reagent at constant tenside concentration of $c_T \sim 10^{-3}$M, in dependence on the overall concentration and type of inorganic acid anion.

It follows from these results of the study of the effect of the kind and concentration of tenside, reagent concentration and type and concentration of inorganic acid anion on the acid–base and optical properties of CAS and CAB that ion associates with a defined stoichiometric composition $[LH_3^-.T^+]$, $[LH_2^{2-}.2\,T^+]$ or $[LH_2^-.T^+]$ are formed at submicellar concentrations of cationic tensides. At submicellar concentrations of the tensides, these ion associates are poorly soluble in water. With increasing tenside concentrations near the CMC value, the solubilizing effect of the micelles begins to be important and the ion associates are fixed on their surfaces. The reagent molecules are probably oriented perpendicularly to the micelle surface with a free salicylic acid functional analytical group, forming one of the limiting structures *I* or *II* (see below). The spectra of the chloroform extracts and of the ion associate



LH₂

LH₂ . nT (*I*)

LH₂ . nT (*II*)

of the reagent with the tenside fixed on the micelles differ in the relative intensity of both the absorption bands and in a shift of the short-wave band of the reagent to longer wavelengths. In strongly acid medium the tenside is bonded to the dissociated sulpho group of the $LH_3^-$ acid–base form of Chromazurol S, whose π-electron system is strongly localized, so that this bond does not produce a marked change in the spectrum.

Bonding of the tenside to the $LH_2^{2-}$ or $LH_2^-$ forms produces a marked change in the spectrum of the ion associate. A completely new absorption band appears near the absorption maximum of the completely deprotonated acid–base form of the reagent, $L^{4-}$ or $L^{3-}$, and the absorption maximum of the metal chelates (580 to 590 nm). This radical change indicates a significant change in the structure of the whole $\pi$-electron system of the molecule or in the dye structure.

Bonding of the tenside molecule to the completely symmetrical $LH_2$ acid–base form of the reagent probably proceeds through bonding of a carboxyl group with a partial negative charge. The electrostatic effect of the positive charge on the tertiary nitrogen and the steric conditions in the tenside molecule lead to strong polarization of the intramolecular hydrogen bond and to its dissociation. This leads to a loss of symmetry in the $LH_2$ species with emphasis on the quinoid and phenolic character of the oxygen atoms on both benzene rings. The ion associate can then be depicted by two limiting structures with quinoid or phenolic oxygens in the *o*-position relative to the carboxyl group bonded through an ionic bond to the tenside molecule.

Steric and electrostatic conditions in structure *I* indicate strong polarization of the bond of the phenolic proton and partial strengthening of the hydrogen bond, leading to more complete delocalization of the electron pair on the phenolic oxygen to the $\pi$-electron system of the molecule and shift of the absorption maximum of the $LH_2$ form to longer wavelengths and splitting into two absorption bands. Structure *II* with the quinoid oxygen in the *o*-position relative to the carboxylic group bonded to the tenside and with carboxylic and phenolic groups on the second benzene ring appears to be more probable for steric reasons. This structure also seems probable from the point of view of the number of protons dissociated in the complexation equilibrium of Fe(III) with CAS in the presence of cetylpyridinium and $UO_2^{2+}$ ions with CAS or CAB in the presence of Septonex[14–16]. The formation of the ion associate $[ML.2\,T^+]$ with dissociation of two protons from the $LH_2$ acid–base form of the reagent has been demonstrated[5,14–16] in solutions with concentration excess of metal ions. This structural change can also produce the splitting of the absorption band of the reagent.

Unambiguous experimental demonstration of the existence of the individual structures is lacking; however, the equilibrium between the two structures may also depend on the polarity of the medium. In polar solvents structure *I* will probably predominate, whereas structure *II* will probably be present in media with low polarity. Interaction of the ion associate of the reagent with the tenside can also lead to preference of one of the structures.

It follows from comparison of the conditional equilibrium constants under various experimental conditions that the change in the acid–base characteristics of both reagents in the presence of the tensides depends on the formation of various stable ion associates of the tenside with the reagent ($[LH_3.T]$ and $[LH_2.2\,T]$ for CAS and $[LH_2.T]$ for CAB, bonded to the tenside micelle) and with a suitable counter ion or inorganic acid anion $[T^+X^-]$. The formation of the ion associates with the reagent can then be considered as an equilibrium competing with the formation of ion associates of the tensides with the inorganic acid anions ($Br^-$, $Cl^-$, $NO_3^-$, $ClO_4^-$, $SO_4^{2-}$, *etc.*) according to the equilibria:

$$LH_2^{n-} + n[T^+X^-] \xrightleftharpoons{{}^*\beta_{LT2}} [LH_2^{n-}.n\,T^+] + n\,X^- \qquad (A)$$

$$LH_3^{(n-1)-} + n - 1[T^+X^-] \xrightleftharpoons{{}^*\beta_{LT3}} [LH_3^{(n-1)-}.(n-1)\,T^+] + \\ + (n-1)\,X^- \qquad (B)$$

with simultaneous acid–base equilibrium

$$LH_3 \xrightleftharpoons{K_{a1}} LH_2 + H\,, \qquad (C)$$

where $n = 1$ or 2 for CAS and $n = 1$ for CAB.

The change in the conditional equilibrium constants of reactions (*A*) and (*B*) then depends on a shift in the reaction equilibrium of both reactions towards formation of the ion associate $[LH_2^{n-}.n\,T]$ with increasing reagent or tenside concentration. The shift in the reaction equilibria of reactions (*A*) and (*B*) affects the equilibrium between the acid–base forms of the reagent $LH_3/LH_2$ and thus also the acid–base behaviour of both reagents.

The stability of the ion associates of the reagent with the individual cationic tensides depends very little on the type of tenside (Table II) and on its structure. The stability of the associates with CAS and CAB decreases in the order CPB > CTMA > SPX. The different stability of the ion associates of the tensides with the inorganic acid anions and their concentration have a much greater effect on the reaction equilibrium (Tables II and III). The formation of the ion associates of the tensides with the reagents is suppressed with increasing stability of the $[T^+X^-]$ associate, as is reflected in the decreasing value of the conditional equilibrium constant of reaction (*A*) with increasing stability of the $[T^+X^-]$ associate in the order $Cl^- \sim SO_4^{2-} < NO_3^- < < ClO_4^-$. In the presence of the very stable associate of the tenside with $ClO_4^-$ ions, the reagent behaves the same as in the absence of the tenside and acid–base equilibrium (*C*) is practically unaffected. The different stabilities of the ion associates of the tensides with the inorganic acid anions affect not only the acid–base and optical characteristics of the hydroxytriphenylmethane dyes but also the complexation equilibria of these dyes with metal ions. Consequently, when studying the complexation equilibria and developing spectrophotometric methods for determining the individual elements, it is better to employ chloride or sulphate medium and perchlorate or nitrate ions must be excluded from the sample preparation procedure.

The changes in the conditional equilibrium constants of reactions (*A*)–(*C*) for different concentrations of inorganic acid anions are a result of a shift in the reaction equilibria towards formation of the ion associates $[T^+X^-]$ with increasing $X^-$ concentration according to the equilibrium

$$T^+ + X^- \overset{*\beta_{TX}}{\rightleftarrows} [T^+X^-] . \qquad (D)$$

The dependence of the equilibrium constant on the concentration ratio $HCl/HNO_3$ is also connected with the different stabilities of the ion associates of the tenside with $Cl^-$ and $NO_3^-$ ions. With increasing concentration ratio $HCl/HNO_3$, the concentration of the more stable associate $[T^+NO_3^-]$ decreases and the concentrations of ion associates $[T^+Cl^-]$ and $[LH_2^{n-}.n\,T^+]$ increase. Then the conditional equilibrium constant of reaction (*A*) is proportional to the ratio of the stability constants

TABLE III

Equilibrium Constant Values in the Region of the Tenside CMC for Various Experimental Conditions

| Tenside | $10^3 . c_L$ | $X^-$ | $c_X$ | Chromazurol S | | Eriochromazurol B | |
|---|---|---|---|---|---|---|---|
| CBP | 0·93 | $NO_3^-$ | 0·1 | 1·00 | 5·40 | 0·81 | 5·08 |
| | 3·75 | $NO_3^-$ | 0·1 | 1·06 | 5·44 | 0·86 | 5·16 |
| | 7·50 | $NO_3^-$ | 0·1 | — | — | 1·05 | 5·14 |
| Brij[3] | 0·03 | $NO_3^-$ | 0·1 | | | 2·85 | — |
| | 3·75 | $NO_3^-$ | 0·1 | 2·85 | 5·50 | 2·90 | 6·83 |
| | 7·50 | $NO_3^-$ | 0·1 | | | 2·90 | 6·81 |
| SPX | 0·93 | $NO_3^-$ | 0·1 | 1·04[b] | 5·52[b] | 1·18[f] | 5·25[f] |
| | 3·75 | $NO_3^-$ | 0·1 | 1·18 | 5·57 | 1·22 | 5·26 |
| | 7·50 | $NO_3^-$ | 0·1 | 1·24 | 5·62 | 1·28 | 5·38 |
| | 3·75 | $ClO_4^-$ | 0·1 | 2·27 | 4·89 | — | — |
| | 3·75 | $SO_4^{2-}$ | 0·1 | 0·75 | | | |
| | 3·75 | $Cl^-$ | 0·1 | 0·73 | | | |
| | 3·75 | $Cl^-$ | 1·0 | 0·97 | | | |
| | 3·75 | $NO_3^-$ | 1·0 | 1·53 | | | |
| | 3·75 | $Cl^-/NO_3^-$ | 1·0[c] | 1·09 | | | |
| | 3·75 | $Cl^-/NO_3^-$ | 1·0[d] | 1·19 | | | |
| | 3·75 | $Cl^-/NO_3^-$ | 1·0[e] | 1·35 | | | |

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[a] 0·1% w/v, [b] for 8 . $10^{-6}$M CAS and 1·6 . $10^4$M, 1·6 . $10^{-3}$M, 8·0 . $10^{-3}$M and 8·0 . $10^{-2}$M SPX, ref.[15] gives values 1·39—1·53, 1·12—1·42, 1·23—1·25, 1·24—1·41 or 5·48—5·49, 5·60—5·59, 5·63, 5·67—5·68, [c] 0·67M-HCl + 0·33M-$HNO_3$, [d] 0·50M-HCl + 0·50M-$HNO_3$, [e] 0·33M-HCl + + 0·67M-$HNO_3$, [e] for $c_T = 10^{-3}$M-SPX and 5·2 . $10^{-6}$M-CAB or 6 . $10^{-5}$M-CAB in 0·1M-$HNO_3$ medium, ref.[16] gives values 1·32—1·34 or 1·28—1·21 and 5·17—5·18 or 5·21—5·27 and for $c_L$ = 6 . $10^{-5}$M and 0·1M-$Cl^-$ medium values 0·81—0·82 or 4·78—4·80.

of the ion associates of the tensides with $Cl^-$ and $NO_3^-$ ions and is inversely proportional to the ratio of the equilibrium concentrations of $Cl^-$ and $NO_3^-$ ions.

The conditional equilibrium constant for the formation of the ion associate of the reagent with the tensile

$$LH_2^{n-} + n\,T^+ \xrightleftharpoons{\beta_{LT2}} [LH_2^{n-}.n\,T^+] \qquad (E)$$

depends on the equilibrium concentration of the $LH_2$ acid–base form of the reagent or of the corresponding ion associate $[LH_3^-.T^+]$ with Chromazurol S and the equilibrium concentration of the cationic tenside $T^+$, which depend on the equilibrium constants of reactions (*C*), (*D*), (*F*) and (*G*):

$$LH_3^- + T^+ \xrightleftharpoons{\beta_{LT3}} [LH_3^-.T^+] \qquad (F)$$

$$LH_3^-.T^+ + T^+ \xrightleftharpoons{\beta_{LT2H}} [LH_2^{2-}.2\,T^+] + H\,. \qquad (G)$$

The shift in the conditional constant for the formation of a species with an absorption maximum at 420–430 nm in neutral and weakly acid media can also be explained by the existence of the stable ion associate $[LH_2^{n-}.n\,T^+]$. The acid–base transition $LH_2/LH$ depends on the stability of the ion associate of the reagent with the tenside and on the relative stabilities of the ion associates of the tenside with the reagent and with the inorganic acid anion.

In strongly alkaline media at pH > 10, changes in the acid–base properties of the reagent are connected with preferential protonation of the LH species, as a result of changes in the character of the solvation sphere and possible fixation of the charged species on the surface of the tenside micelles.

In the presence of non-ionic tenside, the shift of the acid–base characteristics in acid media is opposite that for cationic tensides. The increase in the value of the equilibrium constants with increasing concentration of non-ionic tenside (Brij 35, Triton X-100), which also occurs beyond the CMC value, suggests a different interaction mechanism. This is most probably a result of a change in the character of the medium connected with the possibility of formation of intermolecular hydrogen bonds between the reagent protons and the tenside oxygen atoms, as indicated by the results of extraction photometric measurements[18,19]. Intermolecular hydrogen bonds increase the ionic character of the oxygen–hydrogen bonds in the reagent and thus allow more complete delocalization of the electron pairs on the oxygen atoms over the whole $\pi$-electron system of the reagent. This leads to a shift in the absorption maximum of the $LH_2$ species to higher wavelengths and to splitting of the absorption band, similar to the splitting of the band in the presence of cationic tensides.

The corresponding changes in the acid–base characteristics in the presence of non-ionic tensides are probably also the result of changes in the dielectric constant of the solvent, which markedly changes the character of the proton bonds. The changes in the acid–base characteristics are then similar to the changes in the $pK_{ai}$ values in mixed water-organic solvent media.

Changes in the acid–base characteristics of the individual organic chelating agents in the presence of surface active substances can strongly affect the usefulness of these reagents for determination of a number of metal ions. The shift in the acid–base equilibrium LH/L in strongly alkaline media, with the corresponding suppression of the absorption maximum of the completely deprotonated species L($\lambda_{max}$ ~600 nm, $\varepsilon = 5{\cdot}2 - 5{\cdot}8 \,.\, 10^4$ mmol$^{-1}$ cm$^2$ at the expense of the absorption maximum of the LH form ($\lambda_{max}$ ~420–430 nm, $\varepsilon = 1{\cdot}7 - 2{\cdot}1 \,.\, 10^4$ mmol$^{-1}$ cm$^2$) permits use of CAS and CAB for determination of the alkaline earth metals (Ca, Sr, Ba, Mg), whose reactions with these reagents in the absence of cationic tensides are disturbed by the large absorption maximum of the reagent. This possibility has been demonstrated for the chelometric titration and spectrophotometric determination of the alkaline earth metals with xylenol orange[20–22].

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