SPECTROPHOTOMETRIC STUDY OF THE INTERACTION
OF FERRIC IONS WITH CHROMAZUROL S IN THE PRESENCE
OF CETYLPYRIDINIUM BROMIDE

Vlastimil KUBÁŇ[a], Dagmar GOTZMANNOVÁ[b] and Siegfried KOCH[c]

[a] Department of Analytical Chemistry, Purkyně University, 611 37 Brno,
[b] Department of Clinical Biochemistry,
District Hospital and Health Centre, 703 00 Ostrava - Zábřeh and
[c] Department of Analytical Chemistry,
Chemical Section, Bergakademie, 92 Freiberg, GDR

The properties of the Fe(III)–Chromazurol S–cetylpyridinium bromide system were found by graphical and numerical interpretation of the absorbance curves using a desk-top calculator controlled Superscan TM 3 spectrophotometer and programs for the direct recording and treatment of experimental data. The composition and probable structure of the ternary species FeL.2 T and Fe(LH)₂.n T under various experimental conditions and the probable reaction mechanism of its formation are discussed.

Hydroxytriphenylmethane dyes with the salicylic acid functional group — Chromazurol S, Eriochromazurol B, Eriochromcyanine R, etc. — are very sensitive spectrophotometric reagents for the determination of Fe(III) ions in aqueous or mixed aqueous-ethanol media[1-11], where the values of the molar absorption coefficients vary in the interval $6—8 . 10^4 \text{ mmol}^{-1} \text{ cm}^2$. The sensitivity of these reactions is much higher in the presence of surface active substances — tensides[11-20] with cationic character. The molar absorption coefficients of these systems attain values of $1·2—1·7 . 10^5 \text{ mmol}^{-1} \text{ cm}^2$. The precision of the determination and its accuracy when using the metal ion–chromogenic agent–tenside ternary system are affected by many factors (concentration of the components, method and procedure of component mixing, solution temperature, etc.). The mechanism of the interaction of the tenside with the reagent and with its metal ion chelates is very complicated and can be explained in a number of ways.

This work deals with the spectrophotometric study of the interaction between Fe(III) ions and Chromazurol S in the presence of cetylpyridinium bromide. The composition of the ternary Fe(III)–CAS–CPB species, the reaction mechanism of its formation, the molar absorption coefficients and further parameters were determined from the absorbance curves of solutions with a concentration excess of Fe(III) ions or of Chromazurol S for several tenside concentrations by graphical and numerical interpretation[21].

EXPERIMENTAL

Chemicals and Instruments

The stock solution of 0.1008M-Fe(III) was prepared by dissolving *p.a.* Fe(NO$_3$)$_3$.6 H$_2$O (Lachema, Czechoslovakia), recrystallized from 1M-HNO$_3$. The Fe(III) concentration was determined gravimetrically. Chromazurol S (3″-sulpho-2″,6″-dichloro-3,3′-dimethyl-4-hydroxyfuchson-5,5′--dicarboxylic acid, C$_{23}$H$_{16}$Cl$_2$O$_4$.2 H$_2$O, $M_r = 575·382$ designated CAS) was purified by a combination of precipitation and extraction methods[22] using the commercial substance from the firm Geigy (Basle, Switzerland). The $2 . 10^{-5}$—$1 . 10^{-3}$M stock solutions were prepared by dissolving the solid free acid LH$_5^0$ in a small amount of 1M-KOH; after complete dissolution the solution was diluted to the mark with redistilled water. The solution was stable for at least a week.

Cetylpyridinium bromide (C$_{21}$H$_{38}$NBr, $M_r = 383·44$, designated CPB) was the product of Lachema (Czechoslovakia) recrystallized from ethanol. The $2 . 10^{-2}$M stock solution in 20% v/v ethanol was prepared fresh daily. The remaining chemicals were commercial substances of *p.a.* purity (EDTA, KOH, NaOH) or *p.p.* purity (NH$_4$OH, HNO$_3$, HCl) from Lachema (Czechoslovakia). The ethanol contained 5% v/v methanol. The KOH solution was purified by coprecipitation of the metallic impurities on BaCO$_3$.

The acidity was measured on a PHM 64 pH meter with a G 202 B glass and K 401 saturated calomel electrode (Radiometer, Denmark). The instrument was standardized by a set of buffers[11]. All the spectrophotometric measurements were carried out on a Superscan ^{TM} 3 double--beam digital recording spectrophotometer (Varian, Switzerland) controlled by an HP 9815A desk-top calculator (Hewlett–Packard, USA) at a constant temperature of 25°C. The recording and direct treatment of the results was carried out using data recording and treatment programs[11].

The complex equilibria in the Fe(III)–Chromazurol S–cetylpyridinium bromide system were studied by classical graphical interpretation of the absorbance-pH curves of solutions with a concentration excess of Fe(III) ions or reagent for various tenside concentrations. The results were supplemented by data obtained by numerical interpretation of selected absorbance-pH curves using the adjusted PRCEK program. The stoichiometry was also verified by the molar ratio method and method of continuous variations at the optimum acidity and concentration ratios.

RESULTS AND DISCUSSION

The absorbance of solutions in the ternary Fe(III)–CAS–CPB system depends, among other things, on the order in which the components of the reaction mixture are mixed. In practice, the order tenside, ethanol, HNO$_3$, reagent, Fe(III) solution and final pH adjustment by gradual addition of KOH, NaOH or NH$_4$OH was found most suitable. When this procedure was maintained, the maximum absorbance in the pH interval $2-5$ was attained during $2-3$ min and the absorbance was then independent of time. In the pH interval, $6-5$, the measurement has to be carried out within 15 min after pH adjustment, as after a longer time the absorbance decreased with a simultaneous increase in the pH to higher values.

The absorption spectra of the Fe(III)–CAS–CPB ternary system in solutions with a concentration excess of Fe(III) ions ($c_L = 7·5 . 10^{-6}$M, $c_M = 7·5 . 10^{-5}$M and $c_{CPB} = 2·0 . 10^{-3}$M) indicate that several species are formed in solution de-

pending on the acidity, with absorption maxima at 650 nm (pH ~ 3), 650 and 680 nm (pH $\sim 3{\cdot}7$) and 500 nm (pH ~ 5).

The absorption spectra were measured in dependence on the tenside concentration, $A = f(\lambda, c_{CPB})$ at the maximum for the formation of the ternary species with absorption maxima in the long wavelength region (pH 3 or 3·6). At pH 3, $c_L = 1{\cdot}125$ . . 10^{-5}M, $c_M = 7{\cdot}5 . 10^{-5}$M and $c_{CPB} = 2 . 10^{-5}$–$2 . 10^{-3}$M, the absorption maximum at 650 nm increases with increasing CPB concentration up to a concentration of 1 . . 10^{-4}M and at CPB concentrations $c_{CPB} > 4 . 10^{-4}$M the absorption maximum decreases with increasing CPB concentration up to a concentration of $c_{CPB} = 2 . 10^{-2}$M. In the narrow concentration interval $c_{CPB} = 1-4 . 10^{-4}$M, the absorbance is independent of the tenside concentration. Under these conditions the absorption maxima lie at 653 and 672 nm and do not correspond to the shape of the absorption maxima of solutions with concentration excess of ligand, where the characteristic double maximum is formed by two clearly split absorption bands (see below). At low tenside concentrations ($c_{CPB} = 2-8 . 10^{-5}$M), a turbidity is formed as a result of the formation of the poorly soluble ion associate of the reagent with the tenside with composition $LH_2^{2-}.2 T^+$ (ref.[23]).

micelle
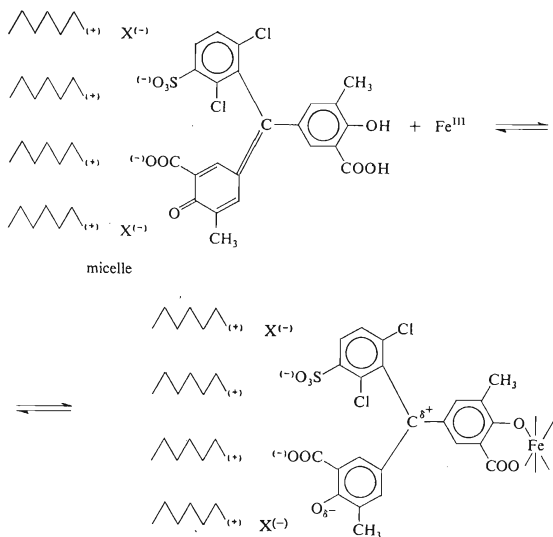
At pH 3·6 under the above experimental conditions, the absorbance continuously increases with increasing tenside concentration up to $c_{CPB} = 4 . 10^{-4}$M, in the concentration interval $c_{CPB} = 4 . 10^{-4} - 3 . 10^{-3}$M is independent of the tenside concentration and at $c_{CPB} > 3 . 10^{-3}$M continuously decreases. The absorption spectra exhibit a characteristic double maximum at 652 and 675 nm with the dominant absorption maximum at 652 nm.

For the two above optimal concentrations of tenside, $c_{CPB} = 2 . 10^{-4}$M and $c_{CPB} = 2 . 10^{-3}$M (Fig. 1) the absorption spectra were measured in dependence on the acidity of the solution for several concentration excesses of Fe(III) ions (for experimental conditions, see Table I); the absorption spectra were also measured in dependence on the Fe(III) ion concentration at pH 3·0, 3·5 and 3·75. A survey of the optical characteristics of the ternary Fe(III)–CAS–CPB system is given in Table I.

It follows from the results that, in solutions with high concentration excesses of Fe(III) ions three optically different species are formed with absorption maxima at 620, 665 and 615 nm. The values of the molar absorption coefficients are much lower than for the corresponding curves with concentration excess of the ligand. For concentration excess $c_M/c_L = 33$, the characteristic maximum is at 665 nm; in equimolar solutions and solutions with small concentration excess of reagent, the characteristic double maximum at 650 and 675 nm is most marked.

The absorbance-pH curves of solutions with $c_L = 1·125 . 10^{-5}$M and $c_M = 1·125 . 10^{-5} - 1·25 . 10^{-3}$M were measured for $c_{CPB} = 2 . 10^{-4}$M and $2 . 10^{-3}$M and wave-
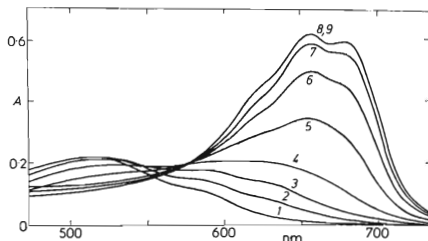

FIG. 1

The absorption Spectra of the Fe(III)–CAS–CPB Ternary System in Dependence on the Solution Acidity in a Concentration Excess of Fe(III) Ions

$c_M = 3·75 . 10^{-4}$M, $c_L = 1·125 . 10^{-5}$M, $c_{CPB} = 2 . 10^{-3}$M, 8% v/v ethanol, $I = 0·01$ (HNO$_3$ + KOH), 25°C, $l = 10$ mm.

Curve pH: 1 1·90, 2 2·18, 3 2·36, 4 2·50, 5 2·64, 6 2·90, 7 3·01, 8 3·21, 9 3·34.

lengths of 620, 625, 630, 645, 655 and 680 nm. (Fig. 2). With increasing concentration excess of Fe(III) ions the absorbance-pH curves are shifted to the acid region and simultaneously the absorbance at the maximum of the $A = f(\text{pH})$ curve decreases with simultaneous narrowing of the optimum pH interval for absorbance independent of the pH.

The absorbance spectra of solutions with $c_L = 2 \cdot 25 . 10^{-5}\text{M}$ and $c_M = 7 \cdot 5 . 10^{-6}\text{M}$ were measured for both CPB concentrations in dependence on the acidity. In both cases $\left(c_{CPB} = 2 . 10^{-4}\text{M} \text{ or } 2 . 10^{-3}\text{M}\right)$ absorption maxima gradually appear at 625 nm

TABLE I

The Optical Characteristics of the Ternary Fe(III)–CAS–CPB System

c_M/c_L	$c_M{}^a$	pH	λ^b	ε^c	λ^d	pH	λ^b	ε^c	λ^d
			$2 . 10^{-3}$ M-CPB				$2 . 10^{-4}$ M-CPB		
111·1	125·0	1·6—2·2	620	0·16	547	1·5—1·9	620	0·30	—
		2·2—2·8	650	0·31	—	2·2—2·7	625	0·36	565
			680	0·27	—		660	0·38	
		3	620	0·48	—	3	615	0·41	637
33·3	37·5	1·9—2·6	635	0·26	—	1·6—2 0	620	0·27	—
							650	0·31	
		2·8—3·2	655	0·54	578	2·1—2·9	665	0·57	592
			682	0·53	—	3	665	0·55	
1·0	1·125	2·9	650	0·22	—	1·9—2·4	620	0·22	
		3·3—3·8	655	0·56	590	2·6—3·1	655	0·54	
		3·9—4·6	650	0·67	—	3·1—4·0	650	0·68	605
			680	0·60	—		678	0·69	—
1/3	0·75	2·0	625	0·08	—	1·8—2·5	625	0·76	—
		2·6—4·2	655	1·22	—	2·6—4·2	655	1·30	—
		4·2—4·9	678	1·20	630	5·0	655	1·28	610
			655	1·30	—				
3·0^e	7·5—500		655	0·58	592	3·0^f	655	0·58	
							680	0·54	
							620	0·35	
	7·5—500					3·6^f	655	0·63	
							680	0·58	
							620	0·35	
	7·5—500					3·7^f	655	0·67	

^{a} $10^5 . c_M(\text{M})$, ^{b} λ_{max} (nm), ^{c} $10^{-5} . \varepsilon$ (mmol^{-1} cm^2), ^{d} λ_{ip} (nm), ^{e} pH 3·00, $c_L = 1 \cdot 125 . 10^{-5}\text{M}$, ^{f} values for pH 3·0, 3·6 and 3·75, $c_L = 1 \cdot 125 . 10^{-5}\text{M}$.
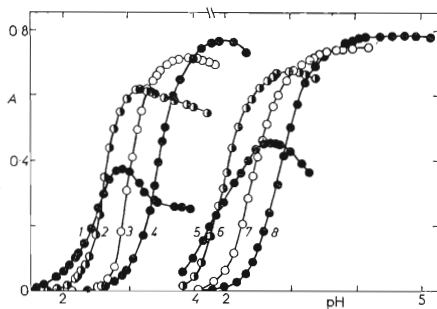
Fig. 2

The Absorbance-pH Curve for Fe(III)–CAS–CPB Solutions with Various Concentration Excesses of Fe(III) Ions and for Equimolar Solutions

$c_L = 1.125 . 10^{-5}$M, $c_{CPB} = 2 . 10^{-3}$M for curves 1—4, $c_{CPB} = 2 . 10^{-4}$M for curves 5—8, 680 nm, for other data see Fig. 1. Curve $10^5 . c_M$(M): 1 112·5, 2 37·5, 3 7·5, 4 1·125, 5 112·5, 6 37·5, 7 7·5, 8 1·125.
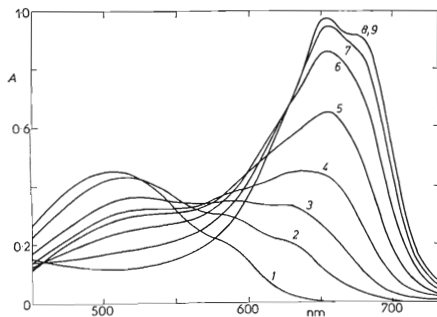

Fig. 3

The Absorption Spectra of the Fe(III)–CAS–CPB System in Dependence on the Acidity of Solutions with a Concentration Excess of Reagent

$c_M = 7.50 . 10^{-6}$M, $c_{CPB} = 2 . 10^{-3}$M, $c_L = 2.25 . 10^{-5}$M, for other data, see Fig. 1. Curve pH: 1 1·98, 2 2·86, 3 3·08, 4 3·25, 5 3·49, 6 3·87, 7 4·22, 8 5·00, 9 5·21.

(pH 2 or 1·8−2·5), 655 nm (pH 2·6−4·9 or 2·6−4·2) and at pH > 5·8 and pH > 5·0, respectively, the absorbance decreases. In solutions with $c_{CPB} = 2 . 10^{-3}$M in the pH interval 4·2−4·9 a further maximum appears at 678 nm and at pH ~ 5 the characteristic double maximum is formed with the predominant absorption band at 650 nm, which, however, does not appear in solutions with $c_{CPB} = 2 . 10^{-4}$M (Figs 3 and 4).

The absorbance-pH curves for solutions with concentration excess of reagent $\left(c_M = 7·5 . 10^{-6}\text{M}, c_L = 2·25−7·50 . 10^{-5}\text{M}, c_L/c_M = 3, 5, 8, 10 \text{ and } 15\right)$ measured for $c_{CPB} = 2 . 10^{-4}$M and $2 . 10^{-3}$M and wavelengths of 620, 625, 630, 644, 655 and 680 nm (Fig. 5) indicate that, for concentration $c_{CPB} = 2 . 10^{-4}$M, lower concentration excesses of the reagent and a wavelength of about 625 nm are more suitable for quantitative formation of the ternary species.

The results of graphical interpretation of absorbance-pH curves for solutions with concentration excesses of Fe(III) ions, $c_M/c_L = 7$, indicate formation of a ternary species by direct interaction of the Fe(III) ions with Chromazurol S and cetylpyridinium ions. This ternary species with a molar ratio of M : L = 1 : 1 is formed according to equation (A) with simultaneous dissociation of two protons:

$$\text{Fe} + \text{LH}_2 + n\,\text{T} \rightleftharpoons \text{FeL}.n\text{T} + 2\,\text{H} \tag{A}$$
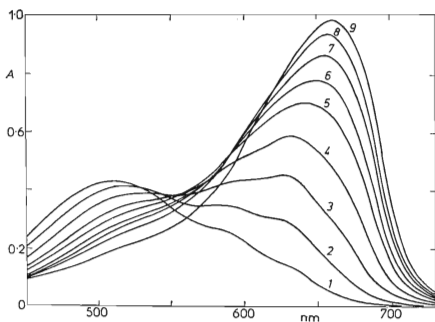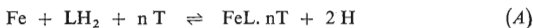

Fig. 4

The Absorption Spectra of the Fe(III)–CAS–CPB System in Dependence on the Acidity of Solutions with a Concentration Excess of Reagent

$c_{CPB} = 2 . 10^{-4}$M, for other data, see Fig. 3. Curve pH: *1* 1·81, *2* 2·14, *3* 2·32, *4* 2·52, *5* 2·70, *6* 2·83, *7* 3·05, *8* 3·48, *9* 4·92.

The dissociation of two protons during the reaction is also confirmed by the value of the slope of the graphical logarithmic analysis equal to two. The molar ratio $M : L = 1 : 1$ was confirmed by the results of the method of continuous variations at pH 2·5 and 3·0, where the value of the maximum absorbance for both tenside concentrations $c_{CPB} = 2 . 10^{-4}M$ and $2 . 10^{-3}M$ and $c_0 = c_M + c_L = 2·25 . 10^{-5}M$ lies in the region $x_L = c_L/c_0 = 0·51 - 0·55$.

The results of the interpretation of the absorbance-pH curves with larger concentration excesses of Fe(III) ions, $c_M/c_L = 33$ and $c_M/c_L = 111$ are nonlinear in the whole pH interval for all the tested reaction mechanisms. The decreasing values of the molar absorption coefficients (Table II) indicate the presence of simultaneous competing equilibria for formation of the binary chelates of Fe(III) ions with Chromazurol S with compositions FeLH and Fe_2L with absorption maxima in the region 575 to 590 nm and molar absorption coefficient $\varepsilon = 6 . 10^4$ mmol^{-1} cm^2, whose existence was unambiguously demonstrated in a study of the interaction of Fe(III) ions with Chromazurol S and Eriochromcyanine R in aqueous media[1,2]. The values of the molar absorption coefficient for individual concentration excesses of Fe(III) ions and wavelengths of 625, 655 and 680 nm are given in Table II together with the values from the direct calculation according to the equation $\varepsilon = A_{0i}/c_L$ or $\varepsilon = A_{0i}/c_M$,

TABLE II
Molar Absorption Coefficient Values for the Fe(III)–CAS–CPB System

c_M/c_L, $10^5 c_M$	680 nm		655 nm		625 nm	
111·1, 125[a]	28 720,	13 700[b]	35 400,	22 500	44 900	
111·1, 125[c]	33 500		40 360		45 900	
33, 37·5[d]	53 720		54 960		41 200	
33, 37·5[c]	56 100		60 200		43 000	
7, 7·5[a]	63 500		62 100		40 000	
6·7, 7·5[c]	66 300		62 700		42 700	
1·0, 1·125[a]	59 240		67 920		42 940	
1·0, 1·125[c]	54 900		57 200		42 700	
1/3, 0·75[a,d]	121 700		130 120[e]		120 600	
1/5, 0·75[c,d]	58 700, 107 600[e]		128 960[e],	83 790	119 740	
1/10, 0·75[a,d]	59 600, 108 620[e]		130 760[e],	83 160	124 200,	96 000[e]
1/3, 0·75[c,d]	57 740, 106 900[e]		128 740[e],	101 300	128 750,	96 000[e]
1/5, 0·75[c,d]	62 400, 108 400[e]		130 000[e],	96 420	132 610,	105 620[e]
1/10, 0·75[c,d]	62 700, 107 960[e]		77 400		48 720	

[a] $c_{CPB} = 2 . 10^{-3}M$, [b] values calculated from the horizontal plateau of the curve at pH 4, [c] $c_{CPB} = 2 . 10^{-4}M$, [d] solutions with concentration excess of reagent, [e] values calculated from the horizontal portion of the second formation region of the curve.

where A_{0i} is the absorbance in the horizontal portion of the curve $\Delta A = f(\text{pH})$.

Treatment of the first formation region of the absorbance-pH curves for solutions with concentration excesses of reagent $c_L/c_M \geqq 8$ using slope-intercept transformations indicates that, in the interval pH 2—4 in solutions with larger tenside concentrations $c_{CPB} = 2 . 10^{-3}$M, the ternary species $FeL_nH_q . x T^+$ is formed by direct interaction of the components of the reaction mixture with simultaneous dissociation of two protons according to the equilibrium:

$$Fe + n LH_2 + x T^+ \rightleftharpoons FeL_nH_q . x T^+ + 2 H . \qquad (B)$$

The shape of the plot of the corresponding transformations is linear in the whole pH interval for molar coefficients $m = 1$ and $n = 1$ or 2. The graphical logarithmic analysis is also linear with slope $q = 2$ corresponding to dissociation of two protons.
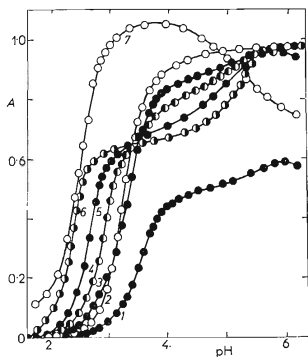

Fig. 5

The Absorbance-pH Curves for Fe(III)–CAS–CPB Solutions with a Concentration Excess of Reagent

$c_M = 7.50 . 10^{-6}$M, $c_{CPB} = 2 . 10^{-3}$M, for other data, see Fig. 1. Curve $10^5 . c_L$(M) λ (nm): *1* 3·75 680, *2* 2·25 655 pH 3, *3* 3·75 655 pH 5, *4* 6·00 655, *5* 7·50 655, *6* 11·25 655, *7* 7·50 625.

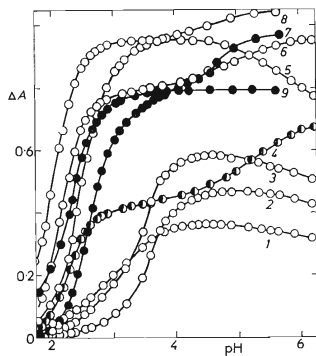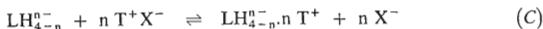Fig. 6

The Absorbance-pH Curves of Fe(III)–CAS–CPB Systems with a Concentration Excess of Reagent

$c_M = 7.50 . 10^{-6}$M, $c_{CPB} = 2 . 10^{-4}$M, for other data, see Fig. 1. Curve $10^5 . c_L$(M) λ (nm): *1* 7·50 650, *k* 7·50 655, *3* 7·50 625, *4* 3·75 680, *5* 3·75 655, *6* 3·75 625, *7* 2·25 680, *8* 2·25 655, *9* 2·25 625.
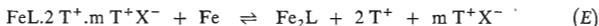
The plot of the corresponding slope-intercept transformations of the absorbance-pH curves with lower concentration excesses of reagent $c_L/c_M < 8$, for which the second formation branch is poorly developed or missing, is not linear in practically the whole studied pH interval and thus does not yield unambiguous conclusions on the course of the reaction mechanism. Interpretation of the second formation region of the absorbance-pH curves for solutions with $c_L/c_M \geqq 8$ does not allow conclusions to be made on whether the process involves mutual transition of two species with bonding of further reagent or tenside molecules. Both processes probably involve formation of the ternary species $FeL_nH_q.xT$ by direct reaction of the components according to equilibrium (B) with transition of the ternary species with molar ratio of $M : L = 1 : 1$ to the above mentioned ternary species $FeL_nH_q . xT$, as indicated by some of the results of the method of continuous variations. At pH values of 4·0 and 5·0 the maximum of the $\Delta A = f(x_L)$ curves lies at $x_L = 0.55-0.60$, corresponding to a mixture of species with mole ratios $M : L = 1 : 1$ and $1 : 2$. At pH values of 6·0, 6·5 and 7·0 the ternary species with ratio $M : L = 1 : 2$ predominates in solution and is bonded with several tenside molecules.

The mechanism of the interaction in the ternary Fe(III)–CAS–CPB system is very complicated, as even the interaction in the binary tenside-chromogenic agent system proceeds differently in dependence on the acidity of the medium and on the tenside concentration. In solutions of cationic tensides at submicelle concentrations $(c \leqq 1 . 10^{-4}M)$, interaction of the ion pairs of the tenside and then mineral acid anions T^+X^- $(X^- = Br^-, Cl^-, NO_3^-, ClO_4^-, etc.)$ with the individual acid–base forms of Chromazurol S leads to formation of binary species with defined composition $LH_3^-.T^+$, $LH_2^{2-}.2 T^+$, $LH_3^{3-}.3 T^+$. Species with lower charge are poorly soluble in aqueous solutions and are precipitated. These species are readily extracted into chloroform. With increasing tenside concentration their solubility rapidly increases[23]. This phenomenon is associated with incorporation of the hydrophobic part of the tenside molecule, bonded to the reagent molecule, into the structure of the micelles formed, with simultaneous formation of the complex species $LH_{4-n}^{n-}.n T^+.m T^+X^-$ according to the equilibria:

$$LH_{4-n}^{n-} + n T^+X^- \rightleftharpoons LH_{4-n}^{n-}.n T^+ + n X^- \qquad (C)$$

$$LH_{4-n}^{n-}.n T^+ + m T^+X^- \rightleftharpoons LH_{4-n}^{n-}.n T^+.m T^+X^- . \qquad (D)$$

In the region of formation of binary and ternary species of Fe(III) ions with Chromazurol S and cetylpyridinium ions, the binary species $LH_2^{2-}.2 T^+$ or LH_2^{2-}. $.2 T^+.m T^+X^-$ with salicylic acid functional group oriented out of the micelle layer predominates in solution. In solutions with concentration excesses of Fe(III) ions, this group reacts with the metal ions to form the ternary species $FeL.2 T^+.m T^+X^-$ with simultaneous dissociation of two protons from the carboxylic group and phenolic

oxygen of Chromazurol S according to equilibrium (A). With increasing Fe(III) ion concentration the binary chelates of Fe(III) ions with Chromazurol S with compositions Fe_2L and FeHL are formed with simultaneous dissociation of the Chromazurol S molecule from the tenside micelle:

$$FeL.2\,T^+.m\,T^+X^- \;+\; Fe \;\rightleftharpoons\; Fe_2L \;+\; 2\,T^+ \;+\; m\,T^+X^- \qquad (E)$$

$$FeL.2T^+.m\,T^+X^- \;+\; H \;\rightleftharpoons\; FeLH \;+\; 2\,T^+ \;+\; m\,T^+X^- \qquad (F)$$

In solutions with concentration excesses of the reagent in the presence of cetylpyridinium ions, the ternary species with molar ratio M : L = 1 : 1 is gradually formed, with the same structure as the $FeL.2\,T^+$ species which is converted into a species with ratio M : L = 1 : 2. In the presence of high concentrations of tenside $(c_{CPB} > 3 . 10^{-2}M)$ both species decompose.

The ternary species have much higher molar absorption coefficient values than the corresponding binary chelates, which was used in the development of very sensitive spectrophotometric methods for the determination of Fe(III) ions at pH 4·8 or 6·2 in the presence of $2 . 10^{-4}$M-CPB and pyridine buffer or $2 . 10^{-3}$M-CPB and hexamethylenetetramine buffer[11]. The high values of the molar absorption coefficient are connected with dissociation of a proton from the phenolic oxygen, enabling more complete delocalization of the electron pair of the oxygen into the π-electron system of the reagent molecule. This increase in the value of the molar absorption coefficient is similar to the marked increase in the ε value for the completely deprotonated acid–base form of the reagent L^{4-} $(\varepsilon = 7.79 . 10^4\ mmol^{-1}\ cm^2)$ compared with the values for the other acid–base forms $(\varepsilon = 2.04-2.17 . 10^4\ mmol^{-1} . cm^2)$, involving complete delocalization of the electron pair of the phenolic oxygen with formation of the completely symmetrical reagent molecule L^{4-} (ref.[23]). The marked colour contrast of the reaction $(\Delta\lambda_{max} \sim 140\ or\ 170\ nm)$ can be explained similarly by the higher degree of delocalization of the electron pair of the oxygen into the π-electron system of the ternary complex Fe(III)–Chromazurol S–cetylpyridinium bromide compared with the delocalization in the reagent molecule L^{4-}.

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