SPECTROPHOTOMETRIC STUDY OF THE REACTION OF DYES OF THE ALIZARIN GREEN SERIES WITH INDIUM(III) IONS IN THE PRESENCE OF CATIONIC TENSIDES

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The reactions of four dyes of the alizarin green series with indium(III) ions were studied. In weakly acid media of pH 4—6·5, binary InL and InL_2 complexes are formed in solution. In the presence of cationic tensides containing cetyltrimethylammonium and cetyl pyridinium, defined ternary complexes, InL_3S_6, are formed in the solution. The conditional stability constants of the binary In–L complexes and the equilibrium constants of the studied complexing ternary systems were calculated and a procedure for the photometric and chelometric determination of indium was proposed.

In the presence of cationic tensides, dyes of the alizarin green series, (sulpho derivatives of phenoxazone dyes) undergo important analytical reactions, which have been used for the development of methods for the photometric determination of vanadium[1,2], iron[3], uranium and cetyltrimethylammonium[4] and a method for the chelometric determination of vanadium[2].

This work was carried out in order to study the coordination properties of the dyes sodium 6-hydroxy-5-benzo(*a*)phenoxazon-10-sulphanone (*I*), sodium 6-hydroxy-5-dibenzo(*a*,*j*)phenoxazone-8,11-disulphanone (*II*), sodium 6-hydroxy-5-dibenzo-(*a*,*j*)phenoxazone-9,11-disulphanone (*III*) and sodium 6-hydroxy-5-dibenzo(*a*,*j*)-phenoxazone-11,13-disulphenone (*IV*) with indium (*III*) ions in the presence of cationic tensides (S). In the presence of cetyltrimethylammonium (CTA^+) or cetylpyridinium(CPy^+), dye *IV* can be recommended as a reagent for the photometric determination of indium or in the presence of CPy^+ this dye can be used as a metallochromic indicator for the chelometric determination of indium.

EXPERIMENTAL

Chemicals and Instruments

4 . 10^{-4}M and 10^{-3}M dye solutions were prepared by dissolving the required amount of the salt in water. The dye purity was controlled by elemental analysis, paper chromatography and thin-layer chromatography[5,6]. A solution of 10^{-2}M-CTA^+ or CPy^+ was prepared by dissolving solid cetyltrimethylammonium bromide or cetylpyridinium bromide(Lachema, Brno) in water.

The CTA^+ or CPy^+ content was found by titration with sodium tetraphenylborate by the Uno[7] and Cross[8] method. The stock solution of 10^{-2}M-In^{3+} ions was prepared by dissolving $InCl_3$ in 10^{-2}M-HCl. The content of indium(III) ions was found chelometrically using xylenol orange as an indicator[9]. An aqueous solution of EDTA with concentration of 10^{-2}M was employed; its titre was found by titration with a standard $MgSO_4.7\,H_2O$ solution using eriochrome black T as an indicator[10].

The pH of the solutions was adjusted using 0·1M-HCl or acetate buffer (CH_3COOH–NaOH). The ionic strength, I, was adjusted to a value of 0·01 with a 1M-KCl solution or with a suitable amount of buffer. All the chemicals employed were of *p.a.* purity.

The solution absorbances were measured on SPECORD UV VIS (Zeiss, Jena) and Unicam SP 1800 (Cambridge, England) instruments with 1, 2, and 5 cm cuvettes. The pH was measured with a pHM 4d instrument (Radiometer, Copenhagen) (reliability of measurement, ±0·02 pH unit) with glass and saturated calomel electrodes. The pH-meter was calibrated with the NBS solutions (0·05M potassium hydrogen phthalate and 0·05 M potassium tetraoxalate).

Evaluation of Experimental Data

The molar ratio method[11], the Bjerrum method of corresponding solutions[12,13] and the Ketelaar transformation[4,14] were employed for determination of the composition of the binary complexes. The composition of the ternary complexes was found using the molar ratio method[17], the method of continuous variations[15] and the tangent ratio method[16]. The stability constants of the binary complexes or ternary complexes were calculated from concentration curves *1*, *2* or *3*, *4* and from the pH curves *5*.

$$A = f(c_{In})_{c_{Ln},pH} \tag{1}$$

$$A = f(c_L)_{c_{In},pH} \tag{2}$$

$$A = f(c_{In})_{c_L,c_S,pH} \quad c_S \gg c_L,\ c_{In} \tag{3}$$

$$A = f(x)_{c_S,c_0,pH} \quad c_0 = c_L + c_{In},\ c_S \gg c_0 \tag{4}$$

$$A = f(pH)_{c_L,c_{In},c_S} \quad c_S \gg c_L,\ c_{In}\ , \tag{5}$$

where c_{In}, c_L and c_S are the overall analytical concentrations of indium(III) ions, dye and tenside, respectively, and x is the mole fraction of the dye ($x = c_L/c_0$).

RESULTS AND DISCUSSION

In weakly acid medium of pH 3·5–6·5 the studied dyes form coloured binary complexes with indium(III) ions instantaneously after solution mixing. The absorption maxima and molar absorption coefficients of these complexes are given in Table I. In study of dependence *1*, the absorption curves with a constant concentration of dye and a varying concentration of indium(III) ions (c_L 1·6 . 10^{-5}M or 4 . 10^{-5}M,

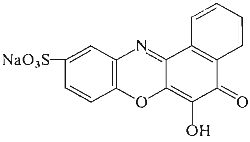
$c_{In} = (0-15) \,.\, c_L$, pH 4–6) exhibit a single isosbestic point for the reactions of dyes *I*, *II* and *IV* (Table I) and two isosbestic points for the reaction of dye *III* λ_{iso} 574 nm ($c_{In} \leqq c_L/2$) and 550 nm ($c_{In} \geqq c_L/2$). It was found by the molar ratio method that complexes are formed in solution with composition In/L = 1 : 2 (dye *I*) or 1 : 1 and 1 : 2 (dye *III*). The 1 : 1 and 1 : 2 composition of the complexes of In with dye was confirmed by the Bjerrum method of corresponding solutions (c_{In} $1{\cdot}4 \,.\, 10^{-5}$M, $2 \,.\, 10^{-5}$M and $2{\cdot}5 \,.\, 10^{-5}$M, $c_L = (0-10)\, c_{In}$, pH 4·5–5·2, 630 and 650 nm). It was found for the reactions of dyes *II* and *IV* by the Ketelaar transformation[4], that

TABLE I

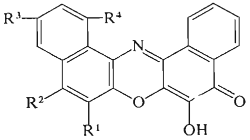
Conditional Stability Constants for the In–L Complexes for Dyes *I*—*IV*

$\log \beta'_1$	$\log \beta'_2$	λ_{max}, nm	ε_{max}	λ_{iso}, nm	pH
		I			
	10·61		7 870	540	4·66
	11·46	530	7 750	539	5·09
	11·75	530	7 750	540	5·51
	9·93			539	5·84
		II			
4·51		570	6 750	548	4·30
4·96			6 700	548	4·69
5·52		569		547	5·06
		III			
	9·83				4·94
5·17	9·78				4·95
	10·09				5·19
		IV			
	8·44	572	20 300	547	4·90
	8·96			547	5·27
	8·46	574	20 100	548	5·80
	7·93		20 200	546	6·40

mononuclear complexes with ratio In : L = 1: 1 (dye *II*) or In : L = 1 : 2 (dye *IV*) are formed.



I



II, $R^2 = R^4 = H$, $R^1 = R^3 = SO_3Na$
III, $R^1 = R^4 = H$, $R^2 = R^3 = SO_3Na$
IV, $R^1 = R^2 = H$, $R^3 = R^4 = SO_3Na$

In the pH region 4 = 5·5, trivalent indium exists as In^{3+}, $In(OH)^{2+}$, $In(OH)_2^+$, $In_3(OH)_4^{5+}$, $In(OH)_3$ (ref.[18]). As the complexes formed are mononuclear, it can be assumed that the In^{3+}, $In(OH)^{2+}$ and $In(OH)_2^+$ forms participate in the complex formation, while the polynuclear form $In(OH)_4^{5+}$ and uncharged form $In(OH)_3$ probably do not take part in the reaction. The formation of a single complex InL_n (n = 1 or 2) can be expressed by the equation (*A*):

$$\mathrm{In(OH)}_q^{(3-q)+} + \mathrm{n\,HL} \rightleftharpoons \mathrm{In(OH)}_{q-w}L_n + (\mathrm{n}-\mathrm{w})\,\mathrm{H}^+ + w\,\mathrm{H_2O} \qquad (A)$$

where q = 0, 1 or 2, $w \leqq q$.

As trivalent indium exists in several forms which complex with the dyes, the equilibrium constant of reaction (*A*) could not be determined, but only the conditional stability constant β'_n (*6*) by the method employing the difference between the absorbance of the quantitative and actual reaction[13] (dye *I*) or by the Ketelaar transformation[4,14] (dyes *II* and *IV*). The simultaneous absorbance of the complexes and of the free dye was considered in all cases. The values obtained are given in Table I

$$\beta'_n = [\mathrm{InL}'_n]\,[\mathrm{In}']^{-1}\,[\mathrm{L}']^{-n}\,, \qquad (6)$$

where

$$[\mathrm{In}'] = [\mathrm{In}^{3+}] + [\mathrm{In(OH)}^{2+}] + [\mathrm{In(OH}_2^+] + [\mathrm{In_3(OH)}_4^{5+}] + [\mathrm{In(OH)}_3]$$

$$[\mathrm{L}'] = [\mathrm{HL}] + [\mathrm{L}]\,; \quad [\mathrm{InL}'_n] = [\mathrm{InL}_n] + [\mathrm{In(OH)L}_n] + [\mathrm{In(OH)}_2\mathrm{L}_n]\,.$$

For the reaction of dye *III*, the stepwise formation of complexes with In : L = 1 : 1 and 1 : 2 can be expressed by equations (*B*) and (*C*)

$$\mathrm{In(OH)}_q^{(3-q)+} + \mathrm{HL} \rightleftharpoons \mathrm{In(OH)}_{q-w}\mathrm{L} + (1-w)\,\mathrm{H}^+ + w\,\mathrm{H_2O} \quad (B)$$

$$\mathrm{In(OH)}_q^{(3-q)+} + 2\,\mathrm{HL} \rightleftharpoons \mathrm{In(OH)}_{q-w}\mathrm{L}_2 + (2-w)\,\mathrm{H}^+ + w\,\mathrm{H_2O} \quad (C)$$

where $q = 0, 1$ or 2 and $w \leqq q$.

These equations are characterized by conditional constants (7)–(9):

$$\beta'_1 = K'_1 = [\mathrm{InL'}]\,[\mathrm{In'}]^{-1}\,[\mathrm{L'}]^{-1} \quad (7)$$

$$K'_2 = [\mathrm{InL'_2}]\,[\mathrm{InL'}]^{-1}\,[\mathrm{L'}]^{-1} \quad (8)$$

$$\beta'_2 = K'_1 \,.\, K'_2 = [\mathrm{InL'_2}]\,[\mathrm{In'}]^{-1}\,[\mathrm{L'_2}]\,, \quad (9)$$

where

$$[\mathrm{InL'}] = [(\mathrm{InL}] + [\mathrm{In(OH)L}] + [\mathrm{In(OH_2L}]\,,$$

$$[\mathrm{InL'_2}] = [\mathrm{InL_2}] + [\mathrm{In(OH)L_2}] + [\mathrm{In(OH)_2L_2}]\,.$$

The Bjerrum method[13] was employed for calculation of both constants β'_1 and β'_2. Constant β'_2 was also calculated from concentration curves *1* by the method involving the difference between the absorbances for the quantitative and actual reactions[13]. The calculation was carried out at λ_{iso} 550 nm. The results obtained by the two methods are given in Table I.

It seems probable that the increasing β'_n value with increasing pH (up to pH 5·5) corresponds to liberation of a proton in reactions (*A*)–(*C*). At higher pH values it can be assumed that the $\mathrm{In(OH)_3}$ form predominates for trivalent indium; this form is less active in complexation equilibria than the positively charged forms of trivalent indium. Thus the β'_n value decreases with increasing pH in this region.

In the presence of cationic tensides ($\mathrm{CTA^+}$, $\mathrm{CPy^+}$), the ternary In–dye–tenside complexes are formed in solution; the formation of these complexes is reflected in increasing values of the molar absorption coefficient for the complexes compared with the corresponding values for the binary complexes (the λ_{max} and $\varepsilon_{\mathrm{max}}$ values for these complexes are given in Table II). In the presence of excess of tenside the colour develops during 5–10 minutes and is constant for several hours. In the presence of excess indium(III) ions the colour formation is instantaneous. In the study of the dependence *3* for the absorption curves with a constant concentration of the dye and tenside and varying concentration of indium(III) ions, a single isosbestic point was observed for a particular pH value (Tables II–V). It was found by the molar ratio method that a complex with ratio In : L = 1 : 3 is formed in the solution. The dye concentration in titration *3* was $c_L = (1\cdot6 - 8) . 10^{-5}$M, the tenside concentration was $c_S = (5 - 50)\, c_L$. The indium(III) ion concentration varied over the range $c_{In} = (0 - 5)\, c_L$. For each system 7–10 titrations were carried out over the pH range 4·3–5·2 (dyes *I–III*) or 4·6–6 (dye *IV*). The method of continuous variations for equimolar solutions of dye and indium ions in the presence of excess tenside yields the same results.

In study of the dependence $A = f(c_S)_{c_L, c_{In}, pH}$, the absorbance curves have also a single isosbestic point (Table II–V). It was found by the molar ratio method that a single complex is formed in the solution with a ratio of L : S = 1 : 2 and In : S = = 1 : 6). The dye concentrations were c_L 1·6 . 10^{-5}M and 4 . 10^{-5}M; the concentration of indium(III) ions was $c_{In} < c_L/3$ or $c_{In} = (1 - 5)\, c_L$. The tenside concentration

TABLE II

Equilibrium Constants for the Ternary In–Dye *I*–Tenside System

log $^*\beta_3$	log $^*\beta_{36}$	ε_{max}, 576mn	λ_{iso} nm	c_S 10^{-4}M	pH
		CTA$^+$			
3·12 ± 0·02	19·42 ± 0·02	23 500	524	20	2·6—3·6^{a,d}
2·95	23·11	23 300	520	5	4·37^{b,e}
2·89	23·06		516	5	4·57^{b,e}
2·45	24·92	23 200	520	2·5	4·75^{b,e}
2·23	24·70		519	2·5	4·97^{b,e}
2·15	24·63		518	2·5	5·20^{b,e}
—	—	23 200	504		5·13^{c,e}
		CPy$^+$			
3·99 ± 0·10	22·21 ± 0·10	23 400	525	10	2·4—3·4^{a,d}
2·89	25·27	23 400	518	2·5	4·39^{b,c}
2·76	22·92		515	5	4·57^{b,e}
2·79	25·19	23 600	517	2·5	4·58^{b,e}
2·71	25·14		516	2·5	4·70^{b,e}
1·10	23·41		502	2·5	5·15^{b,e}
—0·28	27·27	23 200	502		4·72^{c,e}

[a] Calculated from the pH-curves *5*: c_L 3·2 . 10^{-5}M, c_{In} 2 . 10^{-4}M, average of 8 values transferred to the logarithmic scale, confidence limits determined for 95% probability. [b] Calculated from concentration curves *3*: c_L 4 . 10^{-5}M. [c] Calculated from concentration curves $A = f(c_S)_{cL, cIn, pH}$: c_L 4·10^{-5}M, c_{In} 10^{-4}M. [d] KCl + HCl medium, [e] acetate buffer.

varied over the range $c_S = (0-50)\,c_L$. For each system 5 titrations were carried out over the pH range, 4·6–5·2 (dyes *I–III*) or 4·8–6 (dye *IV*). The tangent ratio method yielded the same results for dye *IV* (In : S = 1 : 6) (c_L 8·10^{-5}M, c_S 8 . 10^{-4}M or c_{In} 10^{-4}M, pH 4·78, 5·42, λ 610, 630 and 650 nm).

It follows from the results obtained that a defined ternary complex is formed in solution, InL_3S_6, which is stable even at tenside concentrations below the critical micelle concentration (cmc) (cmc CTA^+ 9·2 . 10^{-4}M, cmc CPy^+ 9 . 10^{-4}M, (ref.[19])). It thus seems that the formation of ion associates through hydrophobic and ion interactions between the binary In–L complexes and the tenside results in the formation of ternary complexes[1,20]. The effect of large hydrophobic grouping of tenside on In–L complex also leads to the formation of ternary complexes with a greater number of coordinated dye molecules than in the binary complexes[21].

The formation of the InL_3S_6 complexes can be expressed by equation (*D*):

$$In^{3+} + 3\,HL + 6\,S \rightleftharpoons InL_3S_6 + 3\,H^+ \qquad (D)$$

TABLE III

Equilibrium Constants for the Ternary In–Dye *II*–Tenside System

log $^*\beta_3$	log $^*\beta_{36}$	ε_{max}, 610 nm (614 nm)	λ_{iso}, nm	c_S 10^{-4}M	pH
		CTA^+			
1·99 ± 0·10	23·39 ± 0·10	24 800	564	3·2	3·5—4·3[a,d]
0·57	22·78	24 800	552	2·5	4·75[b,e]
0·43	22·71	25 100	550	2·5	4·96[b,e]
0·45	20·55		540	5·0	5·13[b,e]
0·34	22·67	25 100	548	2·5	5·14[b,e]
—	—	24 900	556		5·23[c,e]
		CPy^+			
2·32 ± 0·05	22·38 ± 0·05	(23 500)	564	5·0	3·1—4·2[a,d]
0·73	22·91	(23 600)	546	2·5	4·75[b,e]
0·60	22·91	(23 400)	540	2·5	5·12[b,e]
0·44	22·71		536	2·5	5·21[b,e]
—0·67	21·40		522	2·5	5·45[b,e]
—1·12	29·54	(23 400)	560		5·39[c,e]

[a] Calculated from pH-curves *5*: c_L 3·2 . 10^{-5}M, c_{In} 10^{-4}M, average of 9 values transferred to the logarithmic scale, confidence limits found for 95% probability. [b] Calculated from concentration curves *3*: c_L 4 . 10^{-5}M, [c] Calculated from concentration curves $A = f(c_S)_{cL,cIn,pH}$: c_L 4 . 10^{-5}M, c_{In} 10^{-4}M. Medium: [d] KCl + HCl, [e] acetate buffer.

which is characterized by equilibrium constant (*10*) or $^*\beta_3$ for the formalism of formation of the binary complex $\mathrm{LnI_3}$.

$$^*\beta_{36} = [\mathrm{InL_3S_6}]\,[\mathrm{H}]^3\,[\mathrm{In}]^{-1}[\mathrm{HL}]^{-3}\,[\mathrm{S}]^{-6} \tag{10}$$

Using the equations for mass balance of the dye and indium(III)ions and for the solution absorbance, equation (*10*) can be rewritten as equations (*11*) and (*11a*) (ref.[3]).

$$^*\beta_{36} = \\ = \frac{(A - A_\mathrm{L})\,A_\mathrm{max} - A_\mathrm{L})^3 \,.\, [\mathrm{H}]^3 \,.\, \{(K_\mathrm{a} + [\mathrm{H}])/[\mathrm{H}]\}^3}{[3pA_\mathrm{max} - A - (3p - 1)\,A_\mathrm{L}]\,(A_\mathrm{max} - A)^3\,[3sA_\mathrm{max} - 6A - (3s - 6)\,A_\mathrm{L}]^6\,c_\mathrm{L}^3} \tag{11}$$

$$\log \frac{(A - A_\mathrm{L})\,(A_\mathrm{max} - A_\mathrm{L})^3}{[3pA_\mathrm{max} - A - (3p - 1)\,A_\mathrm{L}]\,(A_\mathrm{max} - A)^3\,[3sA_\mathrm{max} - 6A - (3s - 6)\,A_\mathrm{L}]^6} = \\ = \log {}^*\beta_{36} + 3\,\mathrm{pH} + 3\log c_\mathrm{L} + 3\log\{[\mathrm{H}]/(K_\mathrm{a} + [\mathrm{H}]\}\,, \tag{11a}$$

where $A = \bar{\varepsilon}_\mathrm{L}[\mathrm{L'}] + \varepsilon_\mathrm{K}[\mathrm{InL_3S_6}]$, $A_\mathrm{L} = \bar{\varepsilon}_\mathrm{L}c_\mathrm{L}$, $A_\mathrm{max} = \varepsilon_\mathrm{K}c_\mathrm{L}$, $\bar{\varepsilon}_\mathrm{L}$ is the average molar absorption coefficient for the dye forms, ε_K is the molar absorption coefficient for the

TABLE IV

Equilibrium Constants for the Ternary In–Dye *III*–$\mathrm{CTA^+}$ System

pH	log $^*\beta_3$	log $^*\beta_{36}$	ε_max, 618 nm	λ_iso, nm	c_S 10^{-4}M
2·8—3·8[a,e]	2·75 ± 0·07	25·66 ± 0·07	21 400	564	2·0
4·43[b,f]	2·04	24·31	21 300	563	2·5
4·55[b,f]	1·41	19·53		556	10·0
4·58[b,f]	1·99	24·31		562	2·5
4·71[c,f]	2·03	25·40	21 500		2·5
4·75[b,f]	1·99	24·39	21 400	560	2·5
5·13[b,f]	2·03	24·49	21 400	554	2·5
4·68[d,f]	0·37	30·03	21 300	550	

[a] Calculated from pH-curves *5*: c_L 3·2 . 10^{-5}M, c_In 10^{-4}M, average of 8 values transferred to the logarithmic scale, confidence limits found for 95% probability. [b] Calculated from concentration curves *3*: c_L 4 . 10^{-5}M. [c] Calculated from concentration curves R: $c_0 = 6 \,.\, 10^{-d}$. Calculated from concentration curves $A = f(c_\mathrm{S})_{c\mathrm{L},c\mathrm{In},\mathrm{pH}}$: c_L 4 . 10^{-5}M, c_In 10^{-4}M. Medium: [e] KCl + HCl, [f] acetate buffer.

ternary complex, $p = c_{\mathrm{In}}/c_{\mathrm{L}} < 1/3$, $s = c_{\mathrm{S}}/c_{\mathrm{L}} > 2$, K_a is the dissociation constant of the dye in the presence of the tenside[22], $[\mathrm{L}']$ is the conditional dye concentration in the presence of cationic tenside.

In the presence of excess tenside, ($c_{\mathrm{S}} = (15-50)\,c_{\mathrm{L}}$) dependence *11a* for pH 2·5–3·5 (dye *I*), pH 3·5–4·5 (dye *II, III*) or pH 4–5 (dye *IV*, CTA$^+$) or 3–4·2 (dye *IV*, CPy$^+$) is linear with a slope corresponding to dissociation of three protons in reaction (*D*). The molar absorption coefficients for the ternary $\mathrm{InL_3S_6}$ complexes were read from the concentration curves *3* and the pH curves *5* (excess dye or indium(III) ions and excess dye). Equilibrium constants (*10*) were calculated numerically from equation

TABLE V

Equilibrium Constants for the Ternary In–Dye *IV*–Tenside System

log $^*\beta_3$	log $^*\beta_{36}$	$\varepsilon_{\mathrm{max}}$, 614 nm	λ_{iso}, nm	c_{S} 10^{-4}M	pH
		CTA$^+$			
1·98 ± 0·10	20·04 ± 0·10	30 100	555	10	4·2—5·0[a,e]
2·08	20·28		554	10	4·77[b,e]
1·80	20·08		554	10	5·21[b,e]
1·86	20·01	30 100		10	5·39[c,e]
1·83	20·03	30 200	553	10	5·54[b,e]
1·80	22·03		553	5	5·55[b,e]
0·23	18·43		552	10	5·85[b,e]
—	—	30 100	552		5·42[d,e]
		CPy$^+$			
3·74 ± 0·01	23·67 ± 0·01	30 100	556	5	3—4·3[a,f]
2·90	23·11		554	5	4·72[b,e]
2·95	23·17	30 300	552	5	4·99[b,e]
2·80	22·91	30 100		5	5·18[c,e]
2·86	21·06	30 200	551	10	5·23[b,e]
2·88	23·12		552	5	5·24[b,e]
1·34	21·66	30 200	547	5	5·84[b,e]
—	—	30 100	552		4·78[d,e]

[a] Calculated from pH-curves *5*: $c_{\mathrm{L}} = c_{\mathrm{In}} = 1{\cdot}6 \,.\, 10^{-5}$M, average of 9 values transferred to the logarithmic scale, confidence limits found for 95% probability. [b] calculated from concentration curves *3*: c_{L} $4 \,.\, 10^{-5}$M. [c] Calculated from concentration curves *4*: c_0 $4 \,.\, 10^{-5}$M. [d] Calculated from concentration curves $A = f(c_{\mathrm{S}})_{c_{\mathrm{L}},c_{\mathrm{In}},\mathrm{pH}}$: c_{L} $2 \,.\, 10^{-5}$M, c_{In} $4 \,.\, 10^{-5}$M. Medium: [e] acetate buffer, [f] KCl + HCl.

(*11*). At higher pH values the conditional stability constants (*12*) or $^*\beta'_3$ values were calculated by the method of differences in the absorbance for the quantitative and actual reactions[13,32] for concentration curves *3* and *4* for the formalism of the formation of binary complex InL_3:

$$\beta'_{36} = [InL_3S_6]\,[In]^{-1}\,[L']^{-3}\,[S]^{-6}\,. \qquad (12)$$

Constants β'_{36} or β'_{31} were recalculated to the corresponding equilibrium constants $^*\beta_{36}$ or $^*\beta_{31}$ using equation (*13*). Both constants are given in Tables II–V.

$$^*\beta = \beta'(K_a + [H])^3\,, \qquad (13)$$

The different values of $^*\beta_{36}$ at various tenside concentrations or the decrease in constant $^*\beta$ at higher pH values (Tables II–V) can be explained by various degrees of association of the tenside or various degres of hydrolysis of the indium(III) ions[18]. The large differences in the $^*\beta_3$ values found in KCl–HCl and acetate buffer media can be explained by pointing out that in the presence of acetate ions indium(III) ions form the In-acetate complex, which reacts with the studied dye differently than the In^{3+} or $In(Cl)_n^{(3-n)+}$ species. The large differences in the values of $^*\beta_3$ in the presence of CTA^+ and CPy^+ can be explained by the fact that CP_y^+ increases the acidity of the phenol proton of the dye more than CTA^+ (ref.[22]). Thus the In–dye reaction proceeds in a more acid region in the presence of CPy^+ than in the presence of CTA^+, as is reflected in the larger $^*\beta_3$ values for the reaction with CPy^+.

Determination of Indium

At pH ~ 4·8 (dye *I–III*) or 5–6 (dye *IV*) the stability of the ternary InL_3S_6 complexes is sufficient to enable use of these dyes in the presence of cationic tenside as a reagent for the photometric determination of indium. However, only dye *IV* is a useful reagent, as its complexes have larger molar absorption coefficient values (Table II–V); because of the high blank values and the tendency for the L–S ion associates to precipitate from solution (dyes *I*, *II*), dyes *I*, *II* and *III* are not suitable reagents for the photometric determination of indium. When using dye *IV* (c_L 1·6 . 10^{-4}M, c_S 3 . 10^{-3}M), 0·32–4 μg In/ml can be determined (λ 615 nm, ε 30,200). The lower concentration detection limit is the value of which the relative standard deviation value remains less than 10% (6 parallel determinations, 95% probability level). The relative standard deviation for 6 parallel determinations has a value of 0·96% (for 1·76 μg In/ml). The sensitivity of the determination is 0·0048 μg/cm² (for A = 0·001).

The determination is not disturbed by the alkali metal ions, the alkaline earth metals, 50× excess of the following ions: Tl^+, Be^{2+}, Ce^{3+}, La^{3+}, Co^{2+}, Ni^{2+}, Cd^{2+}, 25× excess of Mn^{2+} ions, 5× excess of Zn^{2+}, Pb^{2+}, Ag^{+}, $PtCl_6^{2-}$ and CrO_4^{2-} ions and equimolar amounts of Zr(IV), Th(IV), Bi(III), Sb(III), Ti(IV), Sn(IV) and Y^{3+} ions. The following ions interfere in the determination: Hg^{2+}, Hg_2^{2+}, Fe^{2+}, Fe^{3+}, UO_2^{2+}, Ga^{3+}, Al^{3+}, Sc^{3+}, Pd^{2+}, Cu^{2+} Ti^{3+}, Sn^{2+}, Ce^{4+}, Au^{3+}, VO_3^{-}, MoO_4^{2-}, WO_4^{2-}, PO_4^{3-}, oxalate and hydroxyacids.

The solution colouration develops in 5 minutes and is constant for several hours. The ionic strength was adjusted to a value of 0·005–0·015, where the absorbance was largest and practically did not depend on the ionic strength.

Determination Procedure

A sample amount containing 16—200 µg In is added to a volumetric flask (50 ml) containing 8 ml 10^{-3}M dye *IV*, 5 ml 0·1M acetate buffer pH 5·1—5·3, 15 ml 10^{-2}M tenside. The flask is filled with water to the mark and after 5 minutes standing the absorbance is measured at 610 to 630 nm *vs* a blank.

At pH 4·3—4·7 dye *IV* can also be used in the presence of CPy^{+} as a metallochromic indicator for the chelometric determination of indium. The titration can be carried out at laboratory temperature. At pH 4·7 the titration must be performed at 70—80°C so that the colour change is sufficiently rapid. The colour transition is from blue-green to red. With volumes of 20—30 ml, 0·8—10 mg of indium can be reliably determined and the titration can also be carried out with a 2·5 . 10^{-3}M-EDTA solution. The determination was not accompanied by a systematic error ($t_{exp} < t_{crit}$, 95% probability level). The relative standard deviation for 7 parallel determinations is less than or equal to 1·56%.

The determination is not disturbed by the alkali metal ions, ions of the alkaline earth metals of Ag^{+}, Tl^{+}, Be^{2+}, CrO_4^{2-}, NH_4^{+}, SO_4^{2-}, F^{-}, Cl^{-}, Br^{-}, I^{-}, CN^{-} or NO_3^{-} ions.

Determination Procedure

To a titration flask (50 ml) containing 0·8—10 mg In are added 1·5 ml 4·10^{-4}M dye *IV*, 10 ml of 0·1M acetate buffer of pH 4·5, 5 ml of 10^{-2} CPy^{+}. The mixture is diluted with water to 30 ml and titrated to a change in the solution colour.

Dyes *I*, *II* and *III* in the presence of CTA^{+} or CPy^{+} or dye *IV* in the presence of CTA^{+} are not suitable for the chelometric determination of indium as the colour transition is very slow. The colour transition can be made more rapid by heating the solution.

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