SPECTROPHOTOMETRIC STUDY OF REACTION OF SODIUM 6-HYDROXY-5-DIBENZO(*a,j*)PHENOXAZONE-11,13-DISULFONATE WITH ALUMINIUM IONS IN THE PRESENCE OF CATIONOID TENSIDES

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In weakly acidic medium, pH 3·5—6·5, the title dye forms with aluminium ions a complex with the Al : L ratio 1 : 1. In the presence of cetylpyridinium or carbethoxypentadecyltrimethylammonium, ternary complexes AlL_3S_r ($r = 6$ or 9, respectively) are formed. The equilibrium constants of the complexing equilibria in the binary and ternary systems concerned were calculated, and a method of photometric determination of aluminium has been suggested.

Sodium 6-hydroxy-5-dibenzo(*a,j*)phenoxazone-11,13-disulfonate is among phenoxazone sulfo derivatives and benzo homologues that have been employed in the presence of cationoid tensides as reagents for photometric determination of uranium, cetyltrimethylammonium[1], vanadium[2–4], iron[5,6], and indium[7], or as metalochromic indicators for chelatometric determination of vanadium[3] and indium[7].

   The aim of this work was to study the coordination properties of this dye with aluminium ions in the presence of cetylpyridinium(CPy^+, S) or carbethoxypentadecyltrimethylammonium (Sep^+, S) cations. The dye has been proposed as a reagent for photometric determination of aluminium.

EXPERIMENTAL

Chemicals and Apparatus

The dye stock solutions ($4 . 10^{-4}$M and 10^{-3}M) were prepared by dissolving the corresponding amount of the sodium salt in water. The purity of the dye way checked by elemental analysis and paper chromatography[8]. 10^{-2}M solutions of the cationoid tensides were prepared by dissolving solid cetylpyridinium bromide (Lachema, Brno) or Septonex (carbethoxypentadecyltrimethylammonium bromide) (Spofa) in water. The content of the tensides was determined by titration with sodium tetraphenylborate[9,10]. The 10^{-2}M stock solution of Al^{3+} ions was prepared by dissolving $Al_2(SO_4)_3.18 H_2O$ in water. The content of Al^{3+} ions was determined by indirect chelatometric titration[11].

   The pH of the solutions was maintained by using acetate buffers, the ionic strength was adjusted to 0·01 with appropriate amounts of the buffer. All chemicals used were *p.a.* purity.

The absorbances were measured on a spectrophotometer Unicam SP 1800 (Pye Unicam, Cambridge) in 1 cm and 2 cm cells. The pH was measured on a pH-meter PHM 4d (Radiometer, Copenhagen) (precision ± 0.02 pH units) with a system of glass and saturated calomel electrodes. The pH-meter was calibrated by means of NBS solutions (0·05M potassium hydrogenphthalate and phosphate buffer).

Data Evaluation

The composition of the ternary complexes was found by subjecting the concentration curves $(1)-(3)$ to analysis by the molar ratios method[12] or continual variations method[13]. The stability constants of the ternary complexes were evaluated from the concentration curves (1) and (2) and from the pH-curve[5] (4). The composition and stability constants of the Al–L binary complexes were determined from the Ketelaar's transformation[1,14] of the dependence (5), or by analysis of the pH-curves[15] (6)

$$A = f(c_{Al})_{c_L, c_S, pH} \qquad c_S > c_L; \; c_{Al} \qquad (1)$$

$$A = f(x)_{c_S, pH(c_L + c_{Al}) = c_0} \qquad c_S > c_0 \qquad (2)$$

$$A = f(c_S)_{c_{Al}, c_L, pH} \qquad (3)$$

$$A = f(pH)_{c_{Al}, c_L, c_S} \qquad c_S > c_L; \; c_{Al} \qquad (4)$$

$$A = f(c_{Al})_{c_L, pH} \qquad (5)$$

$$A = f(pH)_{c_{Al}, c_L}, \qquad (6)$$

where c_L, c_{Al}, and c_S are the total concentrations of the dye, aluminium ions, and the tenside, respectively, and x is the mole fraction of the dye (c_L/c_0).

RESULTS AND DISCUSSION

In weakly acidic medium, pH $3.5-6.5$, aluminium ions form with the dye studied coloured binary complexes exhibiting absorption maximum at 586 nm. The absorption curves (5) for constant concentration of the dye and variable concentration of aluminium ions ($c_L = 1.6 \cdot 10^{-5}$M or $4 \cdot 10^{-5}$M, $c_{Al} = (0-8) c_L$) show a single isosbestic point at 546 nm (pH $5.14-5.95$), the same isosbestic point was found from the absorption curves (6). The complex composition (the Al : L ratio) was found by analysis of the pH-curves[15] and by the Ketelaar's transformation[1,14]. In the region pH $3.5-4.5$, the Al^{3+} form predominates in the solution ($\sim 100\%$, 93%, and 73% at pH 3·5, 4·0, and 4·5, respectively),* so the Al–L complex formation can be written as

$$m \, Al^{3+} + n \, HL \rightleftharpoons Al_m L_n + n \, H^+ \qquad (A)$$

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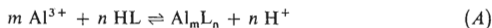
* The values of $\log Q_{11} = -5.15$ and $\log Q_{12} = -9.90$ were used, where Q_{11} and Q_{12} are the hydrolytic constants[16] of Al^{3+} to the species $AlOH^{2+}$ and $Al(OH)_2^+$, respectively.

with the corresponding equilibrium constant

$$*\beta_{mn} = [Al_mL_n][H]^n[Al]^{-m}[HL]^{-n}. \tag{7}$$

In this pH region, the HL form also predominates ($[HL] \approx [L']$, pK_a 7·50). Using the mass balance equations for the aluminium ions ($c_{Al} = [Al^{3+}] + [Al(OH)^{2+}] + [Al(OH)_2^+] + m[Al_mL_n]$) and the dye ($c_L = [HL] + n[Al_mL_n]$) and the equation for the absorbance of the solution ($A = \varepsilon_{HL}[HL] + \varepsilon_C[Al_mL_n]$), we can transform Eq. (7) to the relations

$$\log \frac{(A - A_{HL})(A_{max} - A_{HL})^{m+n-1} \cdot (1 + Q_{11}[H]^{-1} + Q_{12}[H]^{-2})^m \cdot n^{m-1}}{[npA_{max} - mA - (np - m)A_{HL}]^m[A_{max} - nA]^n} =$$
$$= \log *\beta_{nm} + npH + (m + n - 1)\log c_L \tag{8}$$

for $c_{Al}/c_1 = p > m/n$, $A_{max} = \varepsilon_C c_L/n$,

and

$$\log \frac{(A - A_{HL})(mqA_{max} - nA_{HL})^{m+n-1} \cdot (1 + Q_{11}[H]^{-1} + Q_{12}[H]^{-2})^m}{[mA_{max} - mA + (m - n/q)A_{HL}]^m(mqA_{max} - nA)^n} =$$
$$= \log *\beta_{nm} + np\,H + (m + n - 1)\log(qc_L) \tag{9}$$

for $c_L/c_{Al} = q > n/m$, $A_{max} = \varepsilon_C c_{Al}/m$,
where $A_{HL} = \varepsilon_{HL}c_{HL}$, and ε_{HL} and ε_C are the molar absorptivities of the HL^{2-} form and of the complex, respectively.

At pH 3·5–4·7, the dependences (8) ($c_L = 1·6 . 10^{-5}M$, $c_{Al} = 8 . 10^{-5}M$) and (9) ($c_L = 8 . 10^{-5}M$, $c_{Al} = 1·6 . 10^{-5}M$) are linear and their slopes correspond to one detached proton (A) ($m = n = 1$). The Ketelaar's transformation

$$c_L/\Delta A = n/\Delta\varepsilon + 1/[\beta'_{nm}\Delta\varepsilon(c_{Al} - m\,\Delta A/\Delta\varepsilon)^m\Delta A^{n-1}]^{1/n} \tag{10}$$

is also linear only for $m = n = 1$ ($c_L = 1·6 . 10^{-5}M$ or $4 . 10^{-5}M$, $c_{Al} = (0-50)c_L$, pH 5–6). The molar absorptivity of the complex is ε_{max} (586 nm) = 9670 (Table I).

It can be thus claimed that at pH 3·5–6·5, a single complex with the aluminium-to-dye ratio 1 : 1 is formed. For pH 3·5–4·7, the equilibrium constant (7) was calculated from Eqs (8) and (9) (Table I). For pH 5–6·5, the conditional stability constant

$$\beta'_{11} = [Al_mL'_n][Al']^{-m}[L']^{-n} \tag{11}$$

was calculated from the concentration curve (5) by applying the transformation (10) (Table I). The decrease of β'_{11} with increasing pH can be explained by the fact that at pH > 5 the $Al(OH)^{2+}$ and $Al(OH)_2^+$ species can take part in the reaction

$$Al(OH)_q^{(3-q)+} + HL \rightleftharpoons Al(OH)_{q-w}L + (1-w)H^+ \qquad (B)$$
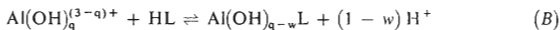
($q = 1$ or 2, $w \leqq 1$).

In the presence of cationoid tensides (CPy^+, Sep^+), ternary complexes aluminium–dye–tenside are formed in the solution, absorbing at 606 nm. The stability of these complexes depends on the ionic strength, particularly at $I \geqq 0.03$. At lower concentrations of the electrolytes this dependence is negligible, and in the region of I $0-0.015$ the absorbance is constant. For this reason, all measurements were performed with ionic strength I 0.01. Organic solvents exert a negative effect upon the ternary complex formation: ethanol present in 10% (vol.) concentration brings about a 25% decrease in absorbance, and in 50% (vol.) concentration it prevents the formation of the ternary complexes altogether.

The absorption curves (1) for constant concentrations of the dye and the tenside ($c_L = 1.6 . 10^{-5}M$, $4 . 10^{-5}M$, or $8 . 10^{-5}M$, $c_S = (5-50) c_L$) and variable concentration of aluminium ions ($c_{Al} = (0-5) c_L$) exhibit a single isosbestic point for a given pH (λ_{iso} 552 nm, pH 5.15; λ_{iso} 545 nm, pH 5.94). The pH-curves display a single isosbestic point too, λ_{iso} 552 nm (pH $4-6.5$), and a horizontal branch in the region pH $5.4-6.5$. The application of the molar ratios method (1) (λ 490, 606, and 650 nm) revealed the occurrence of a single complex in the solution, Al : L ratio 1 : 3. Eight

TABLE I

Equilibrium Constants, Conditional Stability Constants and Molar Absorbtivity of the Complex AlL

pH	log β'_{11}	log $^*\beta_{11}$	ε_{max}, 586 nm
$3.5-4.7^a$		-0.37 ± 0.05	9 680
$3.5-4.6^b$		-0.41 ± 0.05	
5.16^c	4.76 ± 0.07		9 670
5.40^c	4.78 ± 0.10		9 670
6.01^d	4.42 ± 0.04		

Calculation from the pH-curves (6): ^{a} $c_L = 8 . 10^{-5}M$, $c_{Al} = 1.6 . 10^{-5}M$; ^{b} $c_L = 1.6 . 10^{-5}M$, $c_{Al} = 8 . 10^{-5}M$. Calculation from the concentration curves (5): ^{c} $c_L = 4 . 10^{-5}M$; ^{d} $c_L = 1.6 .$ $. 10^{-5}M$. The confidence interval determined for 95% probability (for $8-10$ values).

to ten titrations (1) were carried out for each tenside in the region pH $5-6.5$. The same conclusion was obtained from the results of the continual variations method for equimolar solutions of the dye and aluminium ions containing excess tenside ($c_0 = 4 . 10^5$M or $8 . 10^{-5}$M, $c_S = 4 . 10^{-4}$M or $8 . 10^{-4}$M, pH 5·39 or 5·94, λ 490, 606, and 650 nm).

The absorption curves obtained from the titration (3) also show one isosbestic point, λ_{iso} 544 nm, pH 6·51. Complexes L : S = 1 : 2 and 1 : 3 were found for S = = CPy$^+$ and Sep$^+$, respectively, by using the molar ratios method (λ 606 and 650 nm). The concentration of the dye for the titration (3) was $c_L = 1.6 . 10^{-5}$M or $4 . 10^{-5}$M,

TABLE II

Equilibrium Constants of the Ternary Systems Aluminium–Dye–Tenside

log *β_3	log *β_{3r}	ε_{max}, 610 nm $. 10^4$	x_S 10^{-4} M	pH
		Sep$^+$, $r = 9$		
1·31 ± 0·10	34·25 ± 0·10	3·16	2·5	3·8 − 5[a]
0·15 ± 0·10	28·23 ± 0·10	3·15	8·0	4·3 − 5·3[a]
−1·55	22·88		20·0	5·36[b]
0·64	29·04	3·14	8·0	5·38[b]
0·27	34·42		2·5	5·39[b]
0·61	32·32	3·15	4·0	5·39[b]
−1·30	30·50		4·0	6·51[b]
—	—	3·13	—	6·15[c]
		CPy$^+$, $r = 6$		
1·20 ± 0·01	23·26 ± 0·01	3·13	2·5	4 − 5·1[a]
−1·08	15·18	3·14	20·0	5·35[b]
0·64	20·82		5·0	5·37[b]
0·02	18·19	3·14	10·0	5·40[b]
0·11	22·69		2·5	5·41[b]
−0·22	19·92		5·0	5·96[b]
−4·33	15·83		5·0	6·72[b]
—	—	3·13	—	6·51[d]

[a] Calculation from the pH-curves (4); $c_{Al} = c_L = 1.6 . 10^{-5}$M, average from $8-10$ values transformed into the logarithmic scale, confidence interval determined for 95% probability; [b] calculation from the concentration curves (1), $c_L = 4 . 10^{-5}$M; [c−d] calculation from the concentration curves (3): [c] $c_L = 1.6 . 10^{-5}$M, $c_{Al} = 8 . 10^{-5}$M; [d] $c_L = 1.6 . 10^{-5}$M, $c_{Al} = 4 . 10^{-5}$M.

the concentration of the aluminium ions was $c_{Al} = (3-10)\,c_L$, and the concentration of the tenside varied within the range of $c_S = (0-20)\,c_L$. Four titrations were accomplished for each tenside in the region pH 5·7—6·6. The tangent ratios method[17], where in the one case the tenside concentration varies in excess dye and aluminium ions and in the other case the aluminium ion concentration is variable in excess dye and tenside, was used to find complexes Al : S = 1 : 6 and 1 : 9 for S = CPy$^+$ and Sep$^+$, respectively ($c_L = 8 \cdot 10^{-5}$M, $c_{Al} = 2 \cdot 10^{-4}$M or $c_S = 8 \cdot 10^{-4}$M, pH 5·91 or 6·23, λ 606 and 650 nm).

As the two titrations (1) and (3) yielded the same molar absorptivity value (Table II), it can be claimed that ternary complexes AlL$_3$S$_6$ (with CPy$^+$) and AlL$_3$S$_9$ (with Sep$^+$) are formed in the solution. The presence of the hydrophobic group of the cationoid tenside affects the dye hydration and prevents hydrolysis of the aluminium ions[18,19]; this makes possible the formation of ternary complexes with the highest number of coordinated dye molecules.

The formation of the ternary complexes AlL$_3$S$_r$ (r = 6 or 9) can be written as

$$Al^{3+} + 3\,HL^{2-} + r\,S^+ \rightleftharpoons AlL_3S_r^{(r-6)+} + 3\,H^+ , \qquad (C)$$
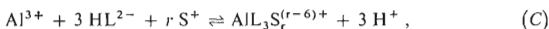
which is characterized by the equilibrium constant

$$*\beta_{3r} = [AlL_3S_r][H]^3[Al]^{-1}[HL]^{-3}[S]^{-r} \qquad (12)$$

or the $*\beta_3$ constant for the formalism of the AlL$_3$ binary complex formation.

Using the equation for the mass balance of aluminium ions, the dye, and the tenside, and the equation for the absorbance of the solution, we can transform Eq. (12) to

$$\log \frac{(A - A_L)(A_{max} - A_L)^{3+r}}{[3pA_{max} - A - (3p-1)\,A_L](A_{max} - A)^3[3sA_{max} - rA - (3s-r)\,A_L]^r} =$$
$$= \log *\beta_{3r} + 3p\,H + (r+3)\log c_L + 3\log\{[H]/(K_a + [H])\} , \qquad (13)$$

where $A = \bar\varepsilon_L[L'] + \varepsilon_C[AlL_3S_r]$, $A_L = \bar\varepsilon_L c_L$, $A_{max} = \varepsilon_C c_L/3$, $p = c_{Al}/c_L > 1/3$, ε_C is the molar absorptivity of the ternary complex and $\bar\varepsilon_L$ the average molar absorptivity of all dye species (HLS$_2$, LS$_3$) in the presence of the cationoid tenside, K_a is the dissociation constant of the phenolic proton of the dye in the presence of the tenside[20], and $[L']$ is the conditional concentration of the dye ($[LS_3] + [HLS_2]$).

In the presence of excess cationoid tenside ($c_S = (10-50)\,c_L$), the dependence (13) s linear with slope corresponding to three detached protons in accordance with reaction (C). The molar absorptivity of the ternary complexes AlL$_3$S$_r$ was determined from the concentration curves (1) or the pH-curves (4) (excess tenside and dye or aluminium ions). The $*\beta_{3r}$ (12) and $*\beta_3$ constants were calculated numerically for pH

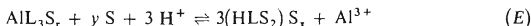4 − 5 (Table II). The conditional stability constants β'_{3r}

$$\beta'_{3r} = [\text{AlL}_3\text{S}_r][\text{Al}]^{-1}[\text{L}']^{-3}[\text{S}]^{-r} \qquad (14)$$

(where $[\text{L}'] = [\text{HLS}_2] + [\text{LS}_3]$) or β'_3 (for the formalism of the AlL$_3$ binary complex formation) were calculated for higher pH from the difference of absorbance of the concentration curves (1) and (3) for the quantitative and the actual reactions[21,22]. These constants were then recalculated to the corresponding equilibrium constants $*\beta_{3r}$ or $*\beta_3$ by using the relation

$$*\beta = \beta'([\text{H}] + K_a)^3 , \qquad (15)$$

where K_a is the dissociation constant of the phenolic proton of the dye in the presence of the cationoid tenside[20].

The decrease in the $*\beta$ value at higher pH (pH > 5·3) can be explained in terms of different degree of hydrolysis and polymerization of the aluminium ions[16]. The differences in the $*\beta_{3r}$ values for different concentrations of the tenside are accounted for by the different degree of association of the latter. Furthermore, the decrease of $*\beta_3$ at higher tenside concentrations ($c_S > 10c_L$) can be interpreted taking into account the competitive mechanisms (D) and (E),

$$\text{HLS}_2 + x\,\text{S} \rightleftharpoons (\text{HLS}_2)\,\text{S}_x \qquad (D)$$

$$\text{AlL}_3\text{S}_r + y\,\text{S} + 3\,\text{H}^+ \rightleftharpoons 3(\text{HLS}_2)\,\text{S}_x + \text{Al}^{3+} \qquad (E)$$

due to the high tenside[23] concentration.

Photometric Determination of Aluminium

The stability of the ternary complexes formed at pH 5−6 is sufficient to allow the dye studied to be employed in the presence of cationoid tenside (CPy$^+$, Sep$^+$) for photometric determination of aluminium. With $1.6 \cdot 10^{-4}$M dye, $1.6 \cdot 10^{-3}$M tenside, and ionic strength 0·01, the Lambert–Beer law is obeyed in the region of $0−0.77\mu$g Al/ml (λ 610 nm, ε 30200). The relative standard deviation for 6 parallel determinations was 0·98% (for 0·38 μg Al/ml). The limit of determination, $c_{min} = ts(dA/dc)$ (where c_{min} expresses the lowest determinable quantity of aluminium in μg/ml, s is the standard deviation of determination in absorbance units, and t is the value of the Student's coefficient for 95% probability)[24], was 0·0016 μg/ml.

Determination with relative error not exceeding 4% can be accomplished in the presence of alkali metal ions, alkaline earth ions, 50-fold excess of Tl$^+$, Be^{2+}, Ce^{3+},

La^{3+}, Ni^{2+}, Co^{2+}, and Cd^{2+} ions, 5-fold excess of Mn^{2+}, Zn^{2+}, Pb^{2+}, Ag^+, Cr^{3+}, CrO_4^{2-}, and $PtCl_6^{2-}$ ions, and equimolar quantities of Hg^{2+}, Bi(III), Ti(IV), Sb(III), Sn(IV), Th(IV), and Zr(IV) ions. Ga^{3+}, In^{3+}, Fe^{2+}, Fe^{3+}, MoO_4^{2-}, Wo_4^{2-}, VO_3^{-}, UO_2^{2+}, Pd^{2+}, Cu^{2+}, Sc^{3+}, Y^{3+}, Sn^{2+}, Ti^{3+}, Au^{3+}, Ce^{4+}, F^-, and PO_4^{3-} ions interfere.

The interfering effect of the In^{3+}, Ga^{3+}, Pd^{2+}, Cu^{2+}, and Sc^{3+} ions can be masked with cadmium chelatonate IV; the ions may be then present in tenfold excess, the sensitivity of determination, however, is approximately 10% lower.

The colouration of the solutions develops for 45 min (2 hours in the presence of cadmium chelatonate) and is steady for 24 h. The absorbance is affected by the ionic strength of the solution, the latter was therefore adjusted to $0.005 - 0.015$; in this range the absorbance variation is negligible.

Determination Procedure

The sample containing $4.5 - 38.5$ µg Al is placed in a 50 ml volumetric flask, and 5 ml of cadmium chelatonate IV (0.346 g of Chelaton IV $+$ 0.370 g of $CdCl_2$ is 100 ml), 5 ml of $0.1M$ acetate buffer pH 5.3, 10 ml of $10^{-2}M$ tenside, and 8 ml of $10^{-3}M$ dye solution are added. The system is diluted to volume with water, and after 45 min or 2 h (if cadmium chelatonate is present) the absorbance is measured at 610 nm against a blank.

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