STUDY OF REACTION OF 5-HYDROXY-6-(2-HYDROXY-5-SULFOPHENYLAZO)BENZO(*a*)-PHENAZINE WITH VANADATES IN THE PRESENCE OF SEPTONEX

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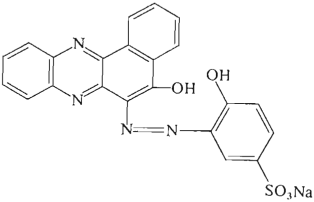
Reaction of 5-hydroxy-6-(2-hydroxy-5-sulfophenylazo)benzo(*a*)phenazine with vanadates in aqueous medium was studied in the presence and in the absence of the tenside Septonex. In acidic medium (pH 2—6), the complex VO_2L is formed in both cases. The equilibrium constants for the equilibria studied were calculated and a procedure was suggested for spectrophotometric determination of vanadium.

Azo dyes are among important organic reagents employed in various methods of determination of many elements[1,2]. One of such dyes is 5-hydroxy-6-(2-hydroxy-5-sulfophenylazo)benzo(*a*)-phenazine, which has been recently prepared. With this dye, only the acid-base properties have been so far studied and the pK_{a2} (8·34 ± 0·03) and pK_{a3} (13·05 ± 0·05) values for the phenolic protons have been determined[3].



The aim of the present work was to study the complex formation of this dye with vanadates in the presence of Septonex (carbethoxypentadecyltrimethylammonium bromide) and to find conditions for analytical application.

EXPERIMENTAL

Chemicals and Apparatus

The dye was prepared by coupling of 5-hydroxybenzo(*a*)phenazine with 2-hydroxy-5-sulfophenyldiazonium sodium salt[3]. The substance was recrystallized from alkaline medium, and its purity was tested by paper chromatography (Whatman No 4; water–ethanol–ammonia 10 : 8 : 2), thin layer chromatography (silica gel L 40/100 μ, Lachema, Brno; acetone–ammonia 17 : 3), and elemental analysis (C, H, N). Aqueous solutions, concentrations $4 . 10^{-4}$M and $8 . 10^{-4}$M, served for the spectrophotometric investigations. 10^{-2}M vanadate stock solution was prepared by dissolving solid NH_4VO_3 *p.a.* (Lachema, Brno) in 10^{-2}M-NaOH. The vanadate content was determined indirectly ferrometrically[4].

Aqueous solutions of Septonex (S) (Spofa, Hlohovec) were used in 10^{-2}M and 10^{-1}M concentrations.

The pH of the solutions was adjusted with 1M-HCl and with acetate buffers (CH_3COOH–NaOH), the ionic strength with 1M-KCl or appropriate amounts of the buffer. All chemicals were *p.a.* purity.

The absorbances were measured on a spectrophotometer Unicam SP 1800 (Pye, Cambridge) in 1 cm and 2 cm cells. The pH was measured on a pH-meter PHM 4d with the system of a glass electrode G 200B and a saturated calomel electrode K 100 (all Radiometer, Copenhagen), calibrated by means of NBS standards.

RESULTS AND DISCUSSION

At pH 2·5 – 7, the dye forms with vanadates coloured solutions with the absorption maximum at 520 nm. The colouration develops for 1 hour and is then steady for 24 hours. The vanadium–dye complexes are poorly extracted into conventional organic solvents. The complex formation depends on the ionic strength of the solution: the dependence of absorbance on the ionic strength (for constant concentrations and pH) is of maximum value at $I < 0{\cdot}03$; up to this value the absorbance is practically constant. For this reason, all subsequent measurements were carried out at ionic strength I 0·02. The effect of ionic strength on the vanadium–dye complex formation can be explained in terms of the salting-out effect of the indifferent electrolyte on the dye, which manifests itself by separation of the dye from the solution at ionic strength I 0·1 and decrease of absorbance of the solution over the entire spectral region examined (400 – 650 nm).

Absorption curves for constant dye concentration ($c_L = 1{\cdot}6 . 10^{-5}$M or $4 . 10^{-5}$M) and variable vanadate concentration ($c_V = (0-5)\, c_L$) display a single isosbestic point at 488 nm in the range of pH 4 – 6. The same isosbestic point was found from the pH-curves $A = f(\text{pH})_{c_L, c_V}$ (for pH 2·5 – 6), whose horizontal branches indicate that the most stable complex forms in the region of pH 4 – 6. Applying the molar ratios method[5] $A = f(c_V)$ for constant concentrations of the dye and protons ($c_L = 1{\cdot}6 . 10^{-5}$M or $4 . 10^{-5}$M, $c_V = (0-5)\, c_L$, pH 4·08, 4·87, and 5·34) and $A = f(c_L)_{c_V, \text{pH}}$ ($c_V = 1{\cdot}6 . 10^{-5}$M or $3{\cdot}2 . 10^{-5}$M, $c_L = (0-5)\, c_V$, pH 4·58 and 4·87) at the wavelengths 460, 530, and 550 nm, a single complex, ratio V : L = 1 : 1, was found to form in the solution. The same result was obtained from the continual variations method[6] ($c_0 = 4 . 10^{-5}$M, pH 4·09 and 4·87, λ 460, 530, and 550 nm).

The presence of the carbethoxypentadecyltrimethylammonium cation prevents separation of the protonized dye at pH < 2, which enables the formation of the vanadium–dye complex at pH > 1·5. The sensitivity of the vanadium–dye reaction is ten times increased by the presence of Septonex (pH 4–5, p*D* 6). In these circumstances, the complex formation is also faster – 30 min is sufficient for the colouration to completely develop; it is then steady for 48 h. The dependence of absorbance on the Septonex concentration was studied and found to attain maximum at $c_S \geqq 50c_L$. In case that Septonex is present in too low concentrations ($c_S < 10c_L$), precipitate separates. The absorbance of the solution is highest at the lowest possible ionic strength, analogously as in the case of the reaction without Septonex. At $I < 0{\cdot}05$, the change in absorbance is negligible. The subsequent study was therefore conducted at I 0·02 and $c_S \geqq 50c_L$.

The complexes formed in the presence of Septonex are easily extracted into organic solvents such as cyclohexanol or ethyl acetate, less easily into chloroform.

The absorption curves for constant concentrations of the dye ($c_L = 1{\cdot}6 \,.\, 10^{-5}$M, $3{\cdot}2 \,.\, 10^{-5}$M, or $4 \,.\, 10^{-5}$M) and Septonex ($c_S = 50c_L$) and variable concentration of vanadates ($c_V = (0-5)\,c_L$) also exhibit one isosbestic point, λ_{iso} 494 nm, for pH 3·5–5·5. The same isosbestic point is found from the pH-curves $A = f(\text{pH})_{c_L, c_V, c_S}$ ($c_L = c_V = 1{\cdot}6 \,.\, 10^{-5}$M, $c_S = 8 \,.\, 10^{-4}$M, pH 1·5–6), which also demonstrate that the most stable complexes form at pH 3·3–6.

The molar ratios method[7] $A = f(c_V)_{c_L, c_S, \text{pH}}$ (for pH 3·8–5·3, λ 460, 530, and 550 nm) revealed the formation of a single complex possessing the V : L ratio 1 : 1. The same result was derived from the results of the continual variations method[8] for equimolar solutions of the dye and vanadates ($c_0 = 4 \,.\, 10^{-5}$M, $c_S = 2 \,.\, 10^{-3}$M, pH 4·04, 4·84, λ 460, 530, and 550 nm).

The complex formed in the absence as well as in the presence of Septonex absorbs at λ_{max} near 520 nm, where lies also λ_{max} of the L^{3-} form of the dye ($\lambda_{max}(L^{3-})$ 520 nm, $\lambda_{max}(HL^{2-})$ 574 nm (in the presence of Septonex)). Both phenolic protons of the dye are likely to be released during the formation of the complex V : L = 1 : 1. With the vanadate concentration applied, the VO_2^+ form can be assumed to prevail in the solution at pH < 3·2, whereas at pH > 4 the $VO_2(OH)_2^-$ species predominates[9]. The V : L = 1 : 1 complex formation can be then written as

$$VO_2 + H_2L^- \rightleftarrows VO_2L^{2-} + 2\,H^+ \quad \text{for} \quad \text{pH} < 3{\cdot}2\,, \qquad (A)$$

$$^*\beta_{11} = [VO_2L]\,[H]^2\,[VO_2]^{-1}\,[H_2L]^{-1} \qquad (1)$$

and

$$VO_2(OH)_2^- + H_2L^- \rightleftarrows VO_2L^{2-} + 2\,H_2O \quad \text{for} \quad \text{pH} > 4\,, \qquad (B)$$

$$\beta_{11} = [VO_2L]\,[VO_2(OH)_2]^{-1}\,[H_2L]^{-1}\,. \qquad (2)$$

In the region pH 3·3–4, the $VO(OH)_3$ form predominates in the solution. In the presence of cationoid tensides, the reaction $VO(OH)_3 \rightleftharpoons VO_2(OH)_2^- + H^+$ is assumed to be promoted owing to the formation of the tenside–$VO_2(OH)_2^-$ associate (white precipitate appears at $pH > 3{\cdot}8$, $c_V < 5 \,.\, 10^{-4}$M, $c_S < 5c_V$). The effect of the $VO(OH)_3$ form can be disregarded in these conditions.

At $pH < 4$, which is more than 2·5 orders of magnitude lower than the pK_{a2} value of the dye, a single ligand species – H_2L^- – exists in the solution. Using the relations for mass balance of the dye and of the V(V) ions and the equation for the solution absorbance, Eq. (*1*) can be transformed to

$$\log \frac{(A - A_L)(pA_{max} - A_L)(1 + Q_{11}H^{-1})}{[A_{max} - A - (1 - 1/p)A_L](pA_{max} - A)} = \log {}^*\beta_{11} + 2\,pH + \log(pc_V)\,, \tag{3}$$

where $A = \varepsilon_C[VO_2L] + \varepsilon_{H_2L}[H_2L)$, $A_{max} = \varepsilon_C\varepsilon_M$, $A_L = \varepsilon_{H_2L}c_L$, Q_{11} is the hydrolytic constant of the equilibrium $VO_2^+ + 2\,H_2O \rightleftharpoons VO(OH)_3 + H^+$ ($\log Q_{11} = -3{\cdot}20$, ref.[9]), and $p = c_L/c_V \geqq 1$.

In the range pH 2·5–3·3 (in the absence of Septonex) or pH 1·7–2·5 (in the presence of Septonex, $c_S = 50c_L$), the relation (*3*) is linear and its slope corresponds to two detached protons (*A*). The molar absorptivities of the VO_2L complex were read from the pH-curve $A = f(pH)_{c_L,c_V}$ and from the concentration curves $A = f(c_V)_{c_L,pH}$ (for excess dye and Septonex, if present). The equilibrium constants of the reaction (*A*), ${}^*\beta_{11}$, were calculated from Eq. (*3*) and are given in Table I.

In the region pH 3·7–5·5, various species involving pentavalent vanadium coexist, the conditional free concentration of the latter can be thus written as

$$[V'] = [VO_2^+] + [VO(OH)_3] + [VO_2(OH)_2^-]\,, \tag{4}$$

the concentration of the $VO_2(OH)_2^-$ form being

$$[VO_2(OH)_2^-] = (1 + [H]^2/Q_{12} + Q_{11}[H]/Q_{12})^{-1}\,[V']\,, \tag{5}$$

where Q_{11} and Q_{12} are the hydrolytic constants of the VO_2^+ form for the formation of the $VO(OH)_3$ or $VO_2(OH)_2^-$ species, respectively ($\log Q_{12} = -6{\cdot}98$, ref.[9]).

The equilibrium constant β_{11} cannot be obtained directly from the concentration curves $A = f(c_V)_{c_L,pH}$, only the conditional stability constant β'_{11},

$$\beta'_{11} = [VO_2L]\,[V']^{-1}\,[L']^{-1}\,, \tag{6}$$

can be calculated, *e.g.* by using the absorbance difference of the quantitative and the actual reactions[10]. The constant β'_{11} was recalculated to β_{11} according to the relation

$$\beta_{11} = \beta'_{11}(1 + [H]^2/Q_{12} + Q_{11}[H]/Q_{12})(K_{a2} + [H])[H]^{-1}\,, \qquad (7)$$

where K_{a2} is the dissociation constant of the phenolic proton bonded in the benzo(*a*)-phenazine ring system (pK_{a2} 8·34 in water, 6·47 in the presence of Septonex).

The β_{11} values obtained (Table I) virtually do not vary with pH (pH 3·8–5·5), which bears out the occurrence of the reaction (*B*). A small deviation of the β_{11} value in the presence of Septonex is due to the fact that [V′] has been equated with $[VO_2(OH)_2^-]$ for the calculation.

TABLE I

Equilibrium Constants of the System Vanadium(V) Dye

pH	log $^*\beta_{11}$	log β_{11}	λ_{max} nm	ε_{max} l mol^{-1} cm^{-1}	Medium
		In the absence of tenside			
2·6—3·3[a]	—1·29 ± 0·07	—	518	16 300	KCl + HCl
4·08[b]	—	5·26			acetate
4·51[b]	—	5·43	520	16 400	buffer
4·87[b]	—	5·51			
5·32[b]	—	5·46	520	16 400	
		In the presence of Septonex			
1·7—2·7[c]	0·43 ± 0·06	—	522	18 900	KCl + HCl
1·7—2·7[d]	0·48 ± 0·06	—			
3·81[e]	—	6·40	524	18 900	acetate
4·04[e]	—	6·66			buffer
4·57[e]	—	6·98			
4·84[e]	—	6·88	524	18 900	
5·31[e]	—	6·91			

Calculation from the pH-curve $A = f(\mathrm{pH})_{c_V, c_L}$: [a] $c_L = c_V = 1{\cdot}6\,.\,10^{-5}$M; [c] $c_L = 5{\cdot}6\,.\,10^{-5}$M, $c_V = 1{\cdot}44\,.\,10^{-5}$M, $c_S = 2{\cdot}8\,.\,10^{-3}$M; [d] $c_L = c_V = 1{\cdot}6\,.\,10^{-5}$M, $c_S = 8\,.\,10^{-4}$M; average from 8—10 values converted to the logarithmic value, the confidence interval determined for 95% probability. Calculation from the concentration curves $A = f(c_V)_{c_L,\mathrm{pH}}$: [b] $c_L = 4\,.\,10^{-5}$M; [e] $c_L = 4\,.\,10^{-5}$M, $c_S = 2\,.\,10^{-3}$M, $[V'] \equiv [VO_2(OH)_2^-]$.

The results given in Table I indicate that a more stable complex forms in the presence of Septonex. Since the VO_2L and $(VO_2L)\,S_x$ complexes differ only little in colour and the latter complexes separate from the solution if Septonex is present in low concentration, their composition was not determined. The dye involves a sulpho group, it can be therefore supposed that an ionic associate is formed according to the scheme

$$VO_2L^{2-} + x\,S \rightleftharpoons (VO_2L)\,S_x^{(x-2)+}\,, \qquad (C)$$

which promotes the formation of the vanadium(V)–dye complex.

Determination of Vanadium

The stability of the VO_2L complex at pH 3·5–5 and in the presence of Septonex is high enough to allow the dye studied to be employed for photometric determination of vanadium. The analysis was conducted at 545 nm, where the difference $\varepsilon_C - \varepsilon_{H_2L}$ is highest. For $c_L = 1{\cdot}5 \,.\, 10^{-4}$M, $c_S = 50c_L$, and ionic strength 0·01–0·05, the Lambert–Beer law holds true for $c_V < 3$ μg/ml ($\varepsilon_C = 16500$, $\varepsilon_{H_2L} = 4100$ l mol^{-1} cm^{-1}). The relative standard deviation for six replicates was 0·4% (for $c_V = 1{\cdot}6$ μg/ml). The *Q*-test[11] demonstrated that no gross error resulted from the determinations. The limit of determination, calculated according to the relation[11] $c_{min} = ts(dA/dc)$ (where c_{min} is the lowest determinable quantity of vanadium 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), was 0·018 μg V/ml.

A determination of vanadium with relative error of ±4% can be accomplished in the presence of alkali metals, alkaline earth ions, 100-fold excess of Tl^+, Be^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, 50-fold excess of La^{3+}, Ce^{3+}, Sc^{3+}, Y^{3+}, Al^{3+}, Cr^{3+}, 10-fold excess of In^{3+}, Ga^{3+}, Pb^{2+}, Ni^{2+}, 5-fold excess of MoO_4^{2-}, WO_4^{2-}, $PtCl_6^{2-}$, Ag^+, Pd^{2+} ions, and equimolar quantities of Zr(IV), Th(IV), Bi(III), Sb(III), Ti(IV), Hg^{2+}, Au^{3+} ions. Trace quantities of Fe^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}, UO_2^{2+} interfere.

At pH 3·5–4, the interfering effect of Fe^{3+}, Co^{2+}, and Cu^{2+} can be suppressed to an extent by adding cadmium chelatonate (3·72 g of Chelaton 3 and 3·0 g of $CdCl_2$ in 1 litre); the interfering ions are bonded in complex with Chelaton, and the Cd^{2+} ions released do not interfere with the determination. Under these conditions, Fe^{3+} and Co^{2+} may be present in 10-fold excess, Cu^{2+} ions in 5-fold excess.

Determination Procedure

a) The sample containing 5—15 μg of vanadium is added to a mixture of 9·5 ml of 8 . 10^{-4}M dye solution, 10 ml of 0·1M acetate buffer pH 3·5—4, and 7·5 ml of 0·1M Septonex in 50 ml volumetric flask. The system is diluted to volume with water, and after 45 minutes' standing the absorbance is measured at 545 nm against a blank.

b) The sample containing 5—15 µg of vanadium is placed in a 50 ml volumetric flask, and 2 ml of 10^{-2}M cadmium chelatonate, 10 ml of 0·1M acetate buffer pH 3·5—4, 7·5 ml of 0·1M Septonex, and 9·5 ml of 8 . 10^{-4}M dye solution are added. The system is brought to volume with water and allowed to stand for 45 min, then the absorbance is measured at 545 nm against a blank.

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