

STUDY OF THE REACTIONS OF ALIZARIN GREEN DYES
WITH VANADATES IN THE PRESENCE
OF CETYLTRIMETHYLAMMONIUM
AND $\text{Ag}(1,10\text{-phen})_2^+$ CATIONS

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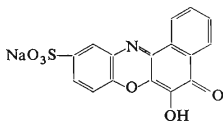
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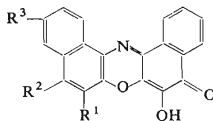
The reactions of five dyes of the alizarin green series with vanadates in the presence of cetyltrimethylammonium (CTA^+ , S) or $\text{Ag}(1,10\text{-phen})_2^+$ cations were studied. At lower concentrations of tenside than the cmc value, defined ternary complexes with composition VL_2S_4 or VL_2S_6 or quaternary complexes $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ are formed in solution. The equilibrium constants of the studied complexation reactions were determined and a method for the photometric and chelometric determination of vanadium were proposed.

Phenoxazone dyes derived from alizarin green (*I*), (*II*), (*III*), (*IV*) and (*V*) with chelating grouping of the carbonyl and phenolic groups have been proposed as metallochromic indicators for the chelometric determination of molybdenum¹, bismuth and copper². It was recently found that sodium 6-hydroxy-5-dibenzo(*a,j*)-phenoxazone-8,11-disulphonate (*V*) reacts with vanadates in weakly acidic media in the presence of CTA^+ to produce the stable ternary VL_2S_4 complex. The reaction was recommended for the photometric determination of vanadium³.

This work was carried out in order to study the coordination equilibria of vanadates with dyes (*I*), (*II*), (*III*), (*IV*) in the presence of CTA^+ or $\text{Ag}(1,10\text{-phen})_2^+$ ions with dye (*V*). Dyes (*II*), (*III*) and (*IV*) were proposed as reagents for the photometric determination of vanadium.



I



- II*, $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{SO}_3\text{Na}$
III, $\text{R}^1 = \text{R}^3 = \text{H}$, $\text{R}^2 = \text{SO}_3\text{Na}$
IV, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{SO}_3\text{Na}$
V, $\text{R}^2 = \text{H}$, $\text{R}^1 = \text{R}^3 = \text{SO}_3\text{Na}$

EXPERIMENTAL

Chemicals and Instruments

The stock solutions of the dyes ($4 \cdot 10^{-4} \text{ M}$ or $8 \cdot 10^{-4} \text{ M}$) were prepared by dissolving the appropriate amount of their sodium salts in water. The purity of the dyes was controlled by elemental analysis, paper chromatography and thin-layer chromatography^{4,5}. A solution of 10^{-2} M -CTA was prepared by dissolving solid cetyltrimethylammonium bromide (*p.a.*, Lachema) in water. The CTA⁺ content was determined by titration of sodium tetraphenylborate by the method of Cross⁶ and Uno⁷. The solution of 10^{-2} M -Ag⁺ ions was prepared by dissolving solid AgNO₃ in 10^{-2} M -HNO₃. The Ag⁺ ion content was determined by titration with a standard NaCl solution using potassium chromate as an indicator⁸. The stock solution of 10^{-2} M vanadate was prepared by dissolving solid NH₄VO₃ in an equimolar amount of NaOH. The vanadium content was determined indirectly by titration of excess Mohr salt with a standard solution of potassium dichromate using diphenylamine^{9,10} as an indicator. An aqueous solution of 1,10-phenanthroline was prepared with a concentration of 10^{-2} M . The concentration of EDTA ($5 \cdot 10^{-2} \text{ M}$) was determined by titration with a standard MgSO₄·7 H₂O solution using eriochrome black T as an indicator¹¹.

The pH was adjusted using formate, chloroacetate, acetate buffers and 0.1M-HCl. The ionic strength *I* was adjusted to a value of 0.01 using 0.1M-KCl solution or a suitable buffer concentration. All the chemicals used were of *p.a.* purity.

The absorbances were measured using Specord UV-Vis (Zeiss, Jena) and Unicam SP 1800 (Cambridge, England) spectrophotometers with 1, 2 and 5 cm cuvettes. The pH was measured with a PHM 4d pH-meter (Radiometer, Copenhagen) (accuracy of measurement, ± 0.02 pH units) with glass and saturated calomel electrodes. The pH-meter was calibrated using a 0.05M solution of potassium hydrogen phthalate (pH 4.01, 25°C) and a 0.05M solution of potassium tetraoxalate (pH 1.68, 25°C).

The complex compositions were determined by the mole ratio method¹², by the Job method of continuous variations¹³ and by the tangent ratio method¹⁴. The stability constants were calculated from the concentration curves (1), (2) or the pH-curves (3):

$$A = f(c_V)_{c_L, c_S, \text{pH}}, \quad c_S > c_L, c_V \quad (1)$$

$$A = f(c_V)_{c_L, c_{1,10\text{-phen}}, c_{\text{Ag}}, \text{pH}} \quad (2)$$

$$A = f(\text{pH})_{c_S, c_V, c_S}, \quad c_S > c_L, c_V \quad (3)$$

where c_L , c_V , c_S , $c_{1,10\text{-phen}}$, c_{Ag} are the overall analytical concentrations of the dye, vanadium, tenside and 1,10-phenanthroline or silver. In study of dependences (1) and (3), vanadium was always added to the solution last.

RESULTS AND DISCUSSION

None of the dyes yields an important reaction with vanadates. In acid medium at $\text{pH} < 4$ the dyes decompose oxidatively in the presence of vanadate; at $\text{pH} > 4$ the reaction appears in equimolar solutions as a small change in colour. In the presence of cationic tensides, blue-green to green coloured ternary complexes are formed

in solutions with pH 2.5–6.5. Absorption curves (*I*) of solutions with constant concentration of dye and tenside ($c_L 8 \cdot 10^{-5}M$, $c_S = (10-100) c_L$) and various concentrations of vanadium at certain pH values exhibit a single isosbestic point λ_{iso} : (*I*) 513 nm (pH 2.73), 483 nm (pH 4.70); (*II*) 564 nm (pH 3.06), 545 nm (pH 4.95); (*III*) 569 nm (pH 2.95), 548 nm (pH 4.69); (*IV*) 556 nm (pH 2.76) 548 nm (pH 4.60).* It was found by the molar ratio method that a complex with ratio V : L = 1 : 2 is formed in every case. The dye concentration c_L in titration (*I*) was $(2.56-8) \cdot 10^{-5}M$. The excess of cationic tenside was equal to $(10-100) c_L$. For each dye, 5–10 titrations (*I*) were carried out in the pH interval 2.73–4.95. Similarly, the tangent ratio method, where excess dye or tenside were present and the vanadate concentration was varied or in excess vanadate and tenside and with varying dye concentration ($c_S 8 \cdot 10^{-5}M$, $c_L 4.8 \cdot 10^{-5}M$ or $c_V 3.2 \cdot 10^{-5}M$, $10^{-4}M$, pH 3.60 (*I*); $c_S 1.6 \cdot 10^{-3}M$, $c_L 8 \cdot 10^{-5}M$, or $c_V 8 \cdot 10^{-5}M$, pH 4.02 (*II*); $c_S 2 \cdot 10^{-2}M$, $c_L 10^{-4}M$ or $c_V 10^{-4}M$, pH 2.95 and 4.69 (*III*); $c_S 4 \cdot 10^{-3}M$, $c_L 8 \cdot 10^{-5}M$ or $c_V 8 \cdot 10^{-5}M$, pH 4.10 (*IV*)) indicated formation of a complex with V : L = 1 : 2. The Job method of continuous variations in solutions with excess tenside and equimolar amounts of dye and vanadium ($c_0 3.2 \cdot 10^{-5}M$, $c_S 2 \cdot 10^{-3}M$, pH 3.98 (*I*); $c_0 8 \cdot 10^{-5}M$, $c_S 1.6 \cdot 10^{-3}M$, pH 4.02 (*II*); $c_0 2 \cdot 10^{-4}M$, $c_S 2 \cdot 10^{-3}M$ pH 2.95 and 4.69 (*III*); $c_0 9.6 \cdot 10^{-5}M$, $c_S 4 \cdot 10^{-3}M$, pH 4.06 (*IV*)) yielded identical results.

In titrations of solutions of dye and vanadium ($c_L 1.6 \cdot 10^{-5}M - 1 \cdot 10^{-4}M$, $c_V < c_L/2$ or $c_V = (1-5) c_L$) with a tenside solution it was found that with dyes (*I*), (*II*) and (*III*) a complex with a ratio of L : S = 1 : 2 and V : S = 1 : 4 (pH 4.34, 4.50, 4.69, 4.76) is formed, whereas with dye (*IV*) (pH 4.60, 5.30), two complexes are formed with ratios of L : S = 1 : 1 and 1 : 3 (Fig. 1). Both complexes are present in equimolar solutions of dye and vanadate and in solutions with five-fold dye excess. There are two isosbestic points λ_{iso} 583 nm ($c_S \leq c_L$) or 548 nm ($c_S \geq c_L$) for the two equilibria on the absorption curves of solutions with constant concentration of the dye and of vanadium ($c_L = c_V = 1.6 \cdot 10^{-5}M$, pH 4.60 and 5.30) and variable tenside concentration. The first complex (L : S = 1 : 1) absorbs very little around 616 nm in the region of the absorption maximum of the ternary complex and the ionic form of the dye. The cationic tenside is probably localized on one of the sulpho groups of the dye.

With dyes (*I*), (*II*), and (*III*), the tangent ratio method ($c_L 8 \cdot 10^{-5}M$, $c_S 2 \cdot 10^{-3}M$ or $c_V 8 \cdot 10^{-5}M$, pH 3.98) yielded a ratio of V : S = 1 : 4. Because the absorption curves $A = f(c_V)_{c_L, c_S, pH}$ and $A = f(c_S)_{c_V, c_L, pH}$ pass through the same isosbestic point and the horizontal branch of the dependences yields the same value of the molar absorption coefficient (Table I–IV), it can be concluded that a single complex is formed in solution with a composition of $V L_2 S_4$ (*I*), (*II*), (*III*). It can be assumed that com-

* The same isosbestic points can be found on the absorption curves of solutions with constant concentrations of dye and vanadate ($c_L = c_V = (1.6-8) \cdot 10^{-5}M$) and variable concentrations of tenside λ_{iso} : 510 nm (pH 4.59) (*I*); 548 nm (pH 4.60) (*IV*).

plex VL_2S_6 is formed with dye (IV) in the presence of a sufficient excess of tenside. A further increase in the tenside concentration results in further small changes in the absorption spectrum of the ternary complex. The formation of submicellar and micellar forms (the critical micellar concentration of CTA^+ is $9.2 \cdot 10^{-4}M$, ref.¹⁵) appears as a slight increase in the molar absorption coefficient (2–3%) (Table I–IV). The wavelength of the absorption maximum practically does not change. In practical applications it is more suitable to use large tenside concentrations to eliminate precipitation of solid ionic associates.

The cationic tenside can be exchanged for another large cation in these reactions. In a weakly acidic medium of formate buffer (pH 3.22–5.0) green quarternary complexes are formed from the dyes and vanadate in the presence of Ag^+ ions and 1,10-phenanthroline. The green colour appears only in the presence of all four components and does not correspond to any of the ternary or binary systems. Phenanthroline complexes of other cations do not have any effect on the vanadate coordination (Cu^+ , Cu^{2+} , Ni^{2+} , Pd^{2+} , Zn^{2+} , Mn^{2+} , Cd^{2+} , Fe^{2+} , Fe^{3+}) or have only a slight effect (Co^{2+}).

The formation of quarternary complexes was studied in more detail with dye (V). To prevent precipitation of the voluminous complex from solution, 0.2% gelatine solutions were used. Under conditions the concentration of Ag^+ ions (at $c_{1,10-phen}/c_{Ag} = 2$) must not be greater than $2 \cdot 10^{-4}M$ at pH > 4.

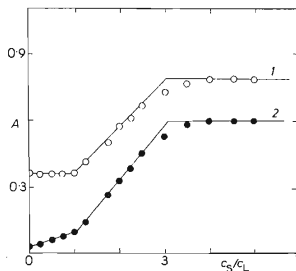


FIG. 1

Molar Ratio Curves c_S/c_L - in the System $V/Dye IV/CTA^+$

$c_L = c_V = 4.0 \cdot 10^{-5}M$, pH 4.60, 2 cm cuvettes; λ 1 583 nm, 2 667 nm.

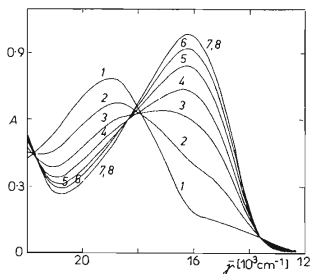


FIG. 2

Absorption Curves for the Quarternary Complex $V/Dye V/Ag/1,10-phen$

$c_L 1.6 \cdot 10^{-5}M$, $c_{Ag} 2 \cdot 10^{-4}M$, $c_{1,10-phen} 4 \cdot 10^{-4}M$, pH 3.66, 5 cm cuvettes; $c_L(M)$: 1 0.0; 2 $1.6 \cdot 10^{-6}$; 3 $3.2 \cdot 10^{-6}$; 4 $4.8 \cdot 10^{-6}$; 5 $8.0 \cdot 10^{-6}$; 6 $1.6 \cdot 10^{-5}$; 7 $4 \cdot 10^{-5}$; 8 $7.8 \cdot 10^{-5}$.

The absorption curves for solutions with constant dye concentration and constant concentration of Ag^+ and 1,10-phenanthroline and with variable concentration of vanadate have two isosbestic points at $\bar{\nu}_{\text{iso}}$ 18350 cm^{-1} (545 nm) and 17985 cm^{-1} (556 nm) (Fig. 2), at pH 3.66. It was found by the molar ratio method ($c_{\text{L}} 1.6 \cdot 10^{-5}\text{M}$, $c_{\text{Ag}} 2 \cdot 10^{-4}\text{M}$, $c_{1,10\text{-phen}} 4 \cdot 10^{-4}\text{M}$, pH 3.22, 3.42, 3.66) that the complex with $\text{V} : \text{L} = 1 : 3$ is formed primarily. At $\text{pH} > 4$ the results are unambiguous. There is one isosbestic point on the absorption curves $\bar{\nu}_{\text{iso}}$ 18350 cm^{-1} (545 nm) (pH 4.15) and a complex with composition $\text{V} : \text{L} = 1 : 3$ was found by the molar ratio method ($c_{\text{L}} 1.6 \cdot 10^{-5}\text{M}$, $c_{\text{Ag}} 2 \cdot 10^{-4}\text{M}$, $c_{1,10\text{-phen}} 4 \cdot 10^{-4}\text{M}$, pH 4.15 and 4.60). This ratio was also found by the method of continuous variations in equimolar solutions of dye and vanadate in an excess of the remaining reaction components ($c_0 1.6 \cdot 10^{-5}\text{M}$, $c_{\text{Ag}} 2 \cdot 10^{-4}\text{M}$, $c_{1,10\text{-phen}} 4 \cdot 10^{-4}\text{M}$, pH 4.16). A mixture of vanadates and the dye in an excess of Ag^+ ions or of 1,10-phenanthroline was titrated with 1,10-phenanthroline or Ag^+ solution respectively. The molar ratio curves were measured for equimolar solutions of the dye and vanadate and also for a three-fold excess of vanadate with respect to the dye and a three-fold excess of the dye with respect to vanadate. Under these conditions the quarternary complex has the ratio $\text{V} : \text{L} = 1 : 3$. It was found in all cases that $\text{L} : \text{Ag} = 1 : 2$ and $1 : 3$ (Fig. 3) ($c_{\text{L}} 3.2 \cdot 10^{-5}\text{M}$, $c_{\text{V}} 1.06 \cdot 10^{-5}\text{M}$, $c_{1,10\text{-phen}} 8 \cdot 10^{-4}\text{M}$, pH 4.53, 4.73); and ratio $\text{L} : 1,10\text{-phen}$ equals $1 : 2$, $1 : 4$ and $1 : 6$ (Fig. 4) ($c_{\text{L}} 3.2 \cdot 10^{-5}\text{M}$, $c_{\text{V}} 1.06 \cdot 10^{-5}\text{M}$, $c_{\text{Ag}} 4 \cdot 10^{-4}\text{M}$, pH 4.53, 4.73). In titration of a solution with a constant concentration of Ag^+ ions or of 1,10-phenanthroline with a solution of 1,10-phenanthroline or Ag^+ ions, respectively, the solution was

TABLE I
Equilibrium Constants of the Ternary System V/dye I/CTA⁺

pH	$\log^* \beta_{1,2,4}$	ϵ_{max} (590 nm)	Medium
1.9–3.0 ^a	14.67 ± 0.01	$2.01 \cdot 10^4$	HCl + KCl
2.73 ^b	14.90	—	acetate buffer
3.35 ^b	14.49	—	
3.58 ^b	14.43	$2.03 \cdot 10^4$	
4.01 ^b	13.99	—	
4.70 ^b	11.96	—	
4.58 ^c	—	$2.01 \cdot 10^4$	

^a Calculated from the pH curves (3) ($c_{\text{L}} = c_{\text{V}} = 4 \cdot 10^{-5}\text{M}$, $c_{\text{S}} 2 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.55$); average of 8 values transferred to logarithmic scale (confidence limits ± 0.01 , 95% probability level); ^b calculated from the concentration curves (I) $c_{\text{L}} 2.56 \cdot 10^{-5}\text{M}$, $c_{\text{S}} 2 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.55$. ^c Calculated from the concentration curves $A = f(c_{\text{S}})_{c_{\text{L}}, c_{\text{V}}}$ pH ($c_{\text{L}} = c_{\text{V}} = 4 \cdot 10^{-5}\text{M}$).

TABLE II
Equilibrium Constants for the Ternary System V/dye II/CTA⁺

pH	$\log^* \beta_{1,2,4}$	ϵ_{\max} (624 nm)	Medium
2.0–3.2 ^a	14.92 ± 0.07	$2.16 \cdot 10^4$	HCl + KCl
3.06 ^b	15.77	—	acetate buffer
3.45 ^b	15.41	—	
4.02 ^b	15.03	$2.17 \cdot 10^4$	
4.59 ^b	13.53	—	
4.95 ^b	12.76	—	
3.43 ^c	15.40	—	
4.02 ^c	15.10	$2.18 \cdot 10^4$	
4.57 ^c	13.54	—	
4.76 ^d	—	2.16	

^a Calculated from pH-curves (3) ($c_L = c_V = 6 \cdot 10^{-5} M$, $c_S 1.6 \cdot 10^{-3} M$, $pK'_a 4.79$); average of 8 values transferred to logarithmic scale (confidence limits ± 0.07 , 95% probability level). ^b Calculated from concentration curves (1) ($c_L 6 \cdot 10^{-5} M$, $c_S 1.6 \cdot 10^{-3} M$, $pK'_a 4.79$). ^c Calculated from the Job curves for equimolar solutions $c_V + c_L$ ($c_0 8 \cdot 10^{-5} M$, $c_S 1.6 \cdot 10^{-3} M$, $pK'_a 4.79$). ^d from concentration curves $A = f(c_S)_{c_L, c_V}$, pH ($c_L = c_V = 4 \cdot 10^{-5} M$).

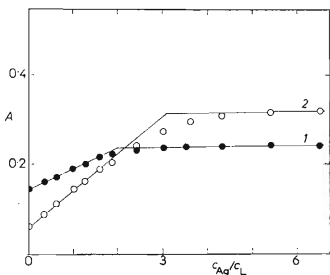


FIG. 3

Molar Ratio Curves c_{Ag}/c_L for the System V/Dye V/Ag/1,10-phen

$c_L 3.2 \cdot 10^{-5} M$, $c_{Ag} 1.06 \cdot 10^{-5} M$,
 $c_{1,10-phen} 8 \cdot 10^{-4} M$, pH 4.73, 1 cm cuvet-
tes; $\lambda 1 568$ nm, 2 625 nm.

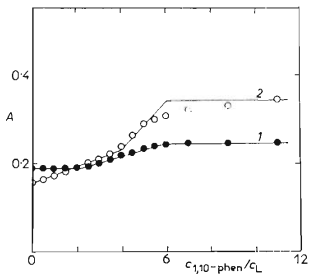


FIG. 4

Molar Ratio Curves $c_{1,10-phen}/c_L$ for the System V/Dye V/Ag/1,10-phen

$c_L 3.2 \cdot 10^{-5} M$, $c_{Ag} 4 \cdot 10^{-4} M$, $c_V 1.06 \cdot 10^{-5} M$, pH 4.53, 1 cm cuvettes; $\lambda 1 558$ nm; 2 625 nm.

found to contain a complex with the ratio $\text{Ag} : 1,10\text{-phen} = 1 : 2$ ($c_L 2.4 \cdot 10^{-5}\text{M}$, $c_V 8 \cdot 10^{-6}\text{M}$, $c_{\text{Ag}} 5.4 \cdot 10^{-5}\text{M}$ or $c_{1,10\text{-phen}} 1.08 \cdot 10^{-4}\text{M}$, pH 4.58, 4.72).

TABLE III

Equilibrium Constants for The Ternary System V/Dye III/CTA⁺ in Formate Buffer Medium

pH	$\log^* \beta_{1,2,4}$	ϵ_{\max} (608 nm)
2.95 ^a	14.82	
3.14 ^a	16.13	
3.76 ^a	15.68	$2.12 \cdot 10^4$
4.15 ^a	13.75	
4.76 ^a	13.08	
4.69 ^b	—	$2.10 \cdot 10^4$

^a Calculated from concentration curves (I) ($c_L 10^{-4}\text{M}$, $c_S 2 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.92$) ^b from concentration curves $A = f(c_S)c_L, c_V, \text{pH}$ ($c_V = c_L = 4 \cdot 10^{-5}\text{M}$).

TABLE IV

Equilibrium Constants for the Ternary System V/Dye IV/CTA⁺

pH	$\log^* \beta_{1,2,6}$	ϵ_{\max} (616 nm)	Medium
2.3–3.3 ^a	18.03 ± 0.10	$2.35 \cdot 10^4$	HCl + KCl
2.76 ^b	18.06	—	
3.28 ^b	18.15	$2.33 \cdot 10^4$	chloroacetate buffer
3.50 ^b	18.12	—	
3.61 ^b	18.08	—	
4.01 ^b	17.62	$2.33 \cdot 10^4$	
4.42 ^b	16.98	—	acetate buffer
4.02 ^c	17.58	$2.32 \cdot 10^4$	
4.60 ^d	—	$2.30 \cdot 10^4$	

^a Calculated from pH-curves (3) ($c_L = c_V = 8 \cdot 10^{-5}\text{M}$, $c_S 4 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.89$); average of 8 values transferred to the logarithmic scale (confidence limits ± 0.10 95%, probability level).

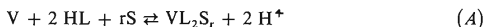
^b Calculated from concentration curves (I) ($c_L 8 \cdot 10^{-5}\text{M}$, $c_S 4 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.89$). ^c Calculated from the Job curves for equimolar solutions $c_V + c_L$ ($c_0 = 9.6 \cdot 10^{-5}\text{M}$, $c_S 4 \cdot 10^{-3}\text{M}$, $\text{p}K'_a 4.89$).

^d from concentration curves $A = f(c_S)c_L, c_V, \text{pH}$ ($c_L = c_V = 1.6 \cdot 10^{-5}\text{M}$).

It can be concluded that, in a sufficient excess of 1,10-phenanthroline, Ag^+ ions and dye, the $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ complex is most probably formed. The presence of large hydrophobic species results in formation of a complex with a maximum number of coordinated dye molecules¹⁶⁻¹⁸.

In all the VL_2S_4 (I), (II), (III), VL_2S_6 (IV) or $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ complexes formed, the number of tensides or particles of $\text{Ag}(1,10\text{-phen})_2^+$ species bound is greater than the number of sulpho groups in the dye complexes. This fact leads to the assumption that the second (I), (II), (III) or third (IV), (V) tenside molecule or of $\text{Ag}(1,10\text{-phen})_2^+$ is bound to a suitable negatively charged or strongly polar part of the dye (chelate grouping of phenolic and carbonyl groups). Differences in composition between the VL_2S_4 (I), (II), (III) and VL_2S_6 (IV) or $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ complexes can be explained by the fact that, compared with the other dyes, dyes (IV) and (V) have one sulpho group more on which the tenside or $\text{Ag}(1,10\text{-phen})_2^+$ species can be bound.

Formation of the VL_2S_r complex can be expressed by equilibrium (A):



where $r = 4, 6$.

The equilibrium constant of reaction (A) is given by expression (4):

$$*\beta_{1,2,r} = [\text{VL}_2\text{S}_r] [\text{H}]^2 [\text{V}]^{-1} [\text{HL}]^{-2} [\text{S}]^{-r}, \quad (4)$$

which can be rearranged to give (5) and (5a)

$$*\beta_{1,2,r} = \frac{(A - A_0)(A_{\max} - A_0)^2 \cdot [\text{H}]^2}{[2 p A_{\max} - A - (p - 1) A_0](A_{\max} - A)^2 \cdot [\text{S}]^r \cdot c_L^2 \cdot \{[\text{H}]/(K'_a + [\text{H}])\}^2} \quad (5)$$

$$\log \frac{(A - A_0)(A_{\max} - A_0)^2}{[2 p A_{\max} - A - (p - 1) A_0](A_{\max} - A)^2} = \log * \beta_{1,2,r} + 2 \text{pH} + 2 \log c_L + r \log [\text{S}] + 2 \log ([\text{H}]/(K'_a + [\text{H}])) , \quad (5a)$$

where $A = \bar{\epsilon}[\text{L}'] + \epsilon[\text{VL}_2\text{S}_r]$, $A_0 = \bar{\epsilon}c_L$, $A_{\max} = \epsilon c_L/2$, $p = c_V/c_L$ and K'_a are the ionization constants of the dye in the presence of CTA^+ : $pK'_a = 4.55$ (I), $pK'_a = 4.79$ (II), $pK'_a = 4.89$ (IV) ($c_L 1.6 \cdot 10^{-5}\text{M}$, $c_S 8 \cdot 10^{-4}\text{M}$, $I 0.01$); $pK'_a 4.92$ (III) ($c_L 10^{-4}\text{M}$, $c_S 2 \cdot 10^{-3}\text{M}$, $I 0.01$) (ref.¹⁹) $[\text{L}']$ is the conditional concentration of the dye ($[\text{HL}] + [\text{L}]$).

In an excess of cationic tenside ($c_S = (50-100) c_L$) dependence (5a) is linear with a slope corresponding to dissociation of two protons (A) for all dyes in the pH range 2-3. The molar absorption coefficient of the VL_2S_r complex was read from

the concentration curve (1) (excess dye and tenside) and pH curves (3) excess vanadate and tenside). The equilibrium constant for reaction (4) and pH 2–3.0 was calculated numerically from equation (5) Tables I, II and IV). At higher pH values, the conditional stability constant (6) was calculated from the differences between the absorbance of the quantitative and actual reaction^{20,21}. Simultaneous absorbance by complexes and by the dye was considered ((7) to (10)):

$$\beta'_{\text{VL}_2\text{S}_r} = [\text{VL}_2\text{S}_r] [\text{V}]^{-1} [\text{L}']^{-2} [\text{S}]^{-r}, \quad (6)$$

$$[\text{VL}_2\text{S}_r] = (Y/Y_{\text{max}}) \cdot c_L/2 \quad (7)$$

where

$$Y = \varepsilon[\text{VL}_2\text{S}_r] + \bar{\varepsilon}([\text{L}'] - c_L), \quad (8)$$

$$Y_{\text{max}} = (\varepsilon/2 - \bar{\varepsilon}) \cdot c_L, \quad (9)$$

$$\beta'_{\text{VL}_2\text{S}_r} = \frac{Y/Y_{\text{max}}}{(1 - Y/Y_{\text{max}})^3 \cdot c_L^2 \cdot [c_S - r(Y/Y_{\text{max}}) \cdot c_L/2]^r}, \quad (10)$$

where $c_V = c_L/2$, $c_S > c_L$ and $[\text{L}']$ is the conditional concentration of the dye ($[\text{HL}] + [\text{L}]$).

The quarternary $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ complex can be characterized by the conditional stability constant (11) in excess 1,10-phenanthroline and Ag^+ ions:

$$\beta'_{\text{VL}_3} = [\text{VL}_3] [\text{V}]^{-1} [\text{L}']^{-3} \quad (11)$$

or by the equilibrium constant for the formalism of the formation of the binary complex (12):

$$*\beta_{\text{VL}_3} = [\text{VL}_3] [\text{H}]^3 [\text{V}]^{-1} [\text{HL}]^{-3}. \quad (12)$$

The conditional stability constants for the quarternary complexes (β'_{VL_3}) were calculated from the differences between the absorbances for the quantitative and actual reaction (13):

$$\beta'_{\text{VL}_3} = (Y/Y_{\text{max}})(1 - Y/Y_{\text{max}})^{-4} \cdot c_L^{-3}, \quad c_V = c_L/3. \quad (13)$$

The conditional constants were recalculated to the equilibrium constants $*\beta$ (Tables I–V).

$$*\beta = \beta'([\text{H}] + K'_a)^n, \quad (14)$$

where $n = 2$ (for the reaction of CTA^+) or 3 (for the reaction of $\text{Ag}(1,10\text{-phen})_2^+$).

TABLE V

Equilibrium Constants of the Quarternary System V/Dye V/Ag/1,10-phen

pH	$\log^* \beta_{VL_3}$	ϵ_{\max} (622 nm)	pH	$\log^* \beta_{VL_3}$	ϵ_{\max} (622 nm)
3.22 ^a	6.94	—	3.90 ^a	6.46	$3.05 \cdot 10^4$
3.42 ^a	6.54	—	4.15 ^a	5.59	—
3.66 ^a	6.50	$3.02 \cdot 10^4$	4.16 ^b	5.88	$3.03 \cdot 10^4$

^a Calculated from concentration curves (2) ($c_L 1.6 \cdot 10^{-5}M$, $c_{Ag} 2 \cdot 10^{-4}M$, $c_{1,10\text{-phen}} 4 \cdot 10^{-4}M$, $pK'_a 4.20$). ^b Calculated from Job plots for equimolar solutions $c_V + c_L$ ($c_0 1.6 \cdot 10^{-5}M$, $c_{Ag} 2 \cdot 10^{-4}M$, $c_{1,10\text{-phen}} 4 \cdot 10^{-4}M$, $pK'_a 4.20$).

TABLE VI

Chelometric Determination of Vanadium

Dye	Added, mg	Found, mg ^a	Relative standard deviation, %
<i>I</i>	1.253	1.260	1.01
<i>II</i>	2.504	2.501	0.66
<i>III</i>	1.626	1.630	0.90
<i>IV</i>	2.504	2.500	0.70

^a Average of seven determinations.

TABLE VII

Photometric Determination of Vanadium

Dye	Range $\mu\text{g/ml}$	λ nm	ϵ	Sensitivity ^b $\mu\text{g V/cm}^2$	Relative standard deviation ^a	
					%	$\mu\text{g V/ml}$
<i>I</i>	0.1 — 1.2	590	18 700	0.0028	0.92	0.74 $\mu\text{g/ml}$
<i>II</i>	0.09 — 1.21	830	20 300	0.0026	0.69	0.81 $\mu\text{g/ml}$
<i>III</i>	0.09 — 1.21	528	17 300	0.0030	0.88	0.813 $\mu\text{g/ml}$
<i>IV</i>	0.09 — 1.21	625	22 800	0.0025	0.86	0.61 $\mu\text{g/ml}$

^a For 7 parallel determinations, ^b for 0.001 A.

The decrease in $*\beta$ at higher pH values can be explained by polymerization and varying degrees of hydrolysis of vanadate. In acid media at pH < 3, VO_2^+ ions can be assumed to exist in solution²².

Determination of Vanadium

The stability of all the complexes is sufficient to allow direct photometric determination of vanadium in excess dye and tenside (or excess Ag^+ ions and 1,10-phenanthroline). In the presence of CTA^+ , the studied dye can be employed as a metallochromic indicator for the chelometric determination of vanadium.

Direct chelometric determination of vanadium was carried out at pH 3.9–4.4 (I) or 4.0–4.7 (II), (III), (IV). During the titration the CTA^+ concentration must be at least twice as large as the vanadium concentration in order for the solution to be transparent at the equivalence point. The colour change is from violet to pure yellow (I), from blue-green to orange-red (II), (IV) and from green to red (III). In a volume of 25–70 ml using 10–20 ml 10^{-2}M-CTA^+ , 0.05–6 mg of vanadium can be reliably determined. The determination is not subject to a systematic error ($t_{\text{exp}} < t_{\text{crit}}$, 95% probability level). The relative standard deviation for 7 parallel determinations has a value smaller than or equal to 1.01% (Table VI). The following ions do not interfere in the determination: NO_3^- , Cl^- , Br^- , I^- , SO_4^{2-} , NH_4^+ , Ba^{2+} , Mg^{2+} , Sr^{2+} , Ag^+ .

Determination procedure: To a 100 ml titration flask containing 20 ml 10^{-2}M-CTA^+ , 1.5 ml of $4 \cdot 10^{-4}\text{M}$ dye and a neutral or slightly basic sample containing 0.05–6 mg of vanadium are added 10 ml of 0.1M acetate buffer of pH 4.3 (I), 4.6 (II), (IV) or formate buffer of pH 4.15 (III). The solution is diluted to 60 ml with water and is titrated to the colour change. (With proper solution mixing the yellow tone corresponding to polymerization of VO_3^- ions in acid solution should not appear).

All the dyes can be used for the direct photometric determination of vanadium in the presence of CTA^+ . In weakly acidic media of acetate buffer (pH 3.7–4.2) and at an ionic strength of 0.01, microamounts of vanadium can be reliably determined (Table VII).

The determination is not disturbed by the alkali and alkaline earth ions, by a 50-fold excess of Al^{3+} , Cr^{3+} , Pb^{2+} , Co^{2+} , Cd^{2+} , Ni^{2+} , Tl^+ ; by a 20-fold excess of Mn^{2+} , Zn^{2+} , La^{3+} , Ce^{3+} , Cu^{2+} , Sc^{3+} , Y^{3+} ions; by a 5 fold excess of Ag^+ , PtCl_6^{2-} or CrO_4^{2-} ions or by equimolar amounts of Zr(IV), Th(IV), Bi(III), Sb(III), Ti(IV). The following ions interfere in the determination: Hg_2^{2+} , Hg^{2+} , Pd^{2+} , Au^{3+} , Ce^{4+} , UO_2^{2+} , Sn^{2+} , Fe^{2+} , Fe^{3+} , In^{3+} , Ga^{3+} , WO_4^{2-} and MoO_4^{2-} .

In the presence of CTA^+ the selectivity of the determination is increased. Hydrolysis of Zr(IV), Th(IV), Bi(III), Sb(III) ions and formation of binary complexes of Cu^{2+} ions are suppressed. The colour development lasts 30 minutes and is stable for

24 hours. It is necessary in sample preparation that the ionic strength of all the solutions be the same. With otherwise constant solution composition and an ionic strength of 0.1, the absorbance is half that at an ionic strength of 0.01. The change in the absorbance is negligible in the ionic strength range 0.005–0.015.

The selectivity of the determination is the same for all the dyes. It is, however, preferable to use dyes *II*, *III* or *IV* because of their greater sensitivity and stability, in view of the precipitation of ion associates of dye *I* with CTA^+ from solution.

The quarternary $\text{VL}_3[\text{Ag}(1,10\text{-phen})_2]_9$ complex is not suitable for analytical use because of the high blank absorbance and because of the tendency to precipitation from the solution.

Determination: A sample containing 4.5–60.5 μg vanadium is added to a 50 ml volumetric flask containing 7.5 ml $8 \cdot 10^{-4}\text{M}$ dye (*II*), (*III*) or (*IV*), 5 ml of acetate or formate buffer of pH 4.0 and 10 ml of 10^{-2}M CTA^+ . The solution is diluted to the mark with water and after 30 minutes the absorbance is measured at λ 625–630 nm (*II*), (*IV*) or λ 528 nm (*III*).

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REFERENCES

1. Šimek J., Lasovský J., Ružička E., Nguyen Truong Son, Sedláčková J., Škvařilová L.: This Journal 42, 2365 (1977).
2. Nguyen Truong Son, Lasovský J., Ružička E., Dohnal A.: Acta Univ. Palacki. Olomuc., Fac. Rerum. Natur., in press.
3. Lasovský J., Ružička E.: This Journal 42, 1941 (1977).
4. Juřina J., Ružička E.: Unpublished results.
5. Sedláčková J.: Thesis, Palacký-University, Olomouc 1975.
6. Cross J. T.: Analyst (London) 90, 315 (1965).
7. Uno T., Miyajima K., Tsukatani H.: Yakugaku Zasshi 80, 153 (1960).
8. Tomiček O.: Kvantitativní analýza, p. 230, Státní zdravotnické nakladatelství, Prague 1954.
9. Suchomelová L., Zýka J.: Analytická chemie méně běžných prvků, p. 239. Published by Státní pedagogické nakladatelství, Prague 1963.
10. Dietrich W. C.: US Atom. Energy Comm., Rep. Y-1294, Mar. 1960, 10; Anal. Abstr. 8, 96 (1061).
11. Přibíl R.: Komplexony v chemické analýze, p. 269. Academia, Prague 1957.
12. Yoe J. A., Jones A. L.: Ind. Eng. Chem., Anal. Ed. 16, 11 (1944).
13. Job. P.: Ann. Chim. (Paris) 9, 113 (1928).
14. Harving A. E., Manning D. L.: J. Amer. Chem. Soc. 72, 4488 (1950).
15. Fendler E., Fendler J.: Advan. Phys. Org. Chem., Vol. 8, p. 271. Academic Press, London, New York, 1970.

16. Noriki Sh.: *Anal. Chim. Acta* **76**, 215 (1975).
17. Kawamoto H., Akaiwa H.: *Japan Analyst* **24**, 127 (1975).
18. Pilipenko A. T., Tananaiko M. M.: *Talanta* **21**, 501 (1974).
19. Nguyen Truong Son, Lasovský J., Ružička E., Šimek J.: Unpublished results.
20. Sommer L., Jin Tsin Jao: *Chem. Listy* **55**, 574 (1961).
21. Nomura T.: *Bull. Chem. Soc. Jap.* **41**, 2803 (1968).
22. Baes Ch. F., jr, Mesmer R. E.: *The Hydrolysis of Cations*, p. 210. Wiley, New York 1976.

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