Spectrophotometric study of the reaction between dyes of the alizarin green series and vanadates in the presence of cetylpyridinium cation

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The reaction between six dyes of the alizarin green series (L) and vanadates (V) in the presence of cetylpyridinium ion (CPy^+, S) was studied. Provided the concentration of surfactant was lower than the critical micellar concentration, defined ternary complexes of the type VL_2S_4 or VL_2S_6 arose in the solution. The values of equilibrium constants of the investigated complex-forming equilibria were determined and a method of photometric and chelatometric determination of vanadium in the interval 4.5—60 µg and 0.05—6 mg was proposed. The mechanism of ternary complex formation was also explained.

Была исследована реакция шести красителей ряда ализариновой зелени (L) с ванадатами (V) в присутствии иона цетилпиридиния (CPy^+, S). При концентрации ПАВ (CPy^+) низшей, чем является критическая мицеллярная концентрация, возникают в растворе определенные тройные комплексы типа VL_2S_4 или VL_2S_6. Были найдены величины констант равновесия изучаемых комплексообразующих равновесий и был предложен метод фотометрического и хелатометрического определения ванадия в интервале 4,5—60 µг и 0,05—6 мг. Был объяснен механизм образования тройных комплексов.

The sulfonated derivatives of phenoxazone dyes of the alizarin green type exhibit important analytical reactions in the presence of cationic surfactants. These dyes were used as metallochromic indicators for chelatometric determination of vanadium [1] in the presence of cetyltrimethylammonium bromide and as reagents for direct photometric determination of vanadium [1, 2], iron [3], uranium and cetyltrimethylammonium [4]. These dyes were also used for photometric determination of iron [5] in the presence of cetylpyridinium.

The aim of this study is to elucidate the coordination equilibria of six dyes of the alizarin green series (*I—VI*) in the presence of cetylpyridinium (CPy^+, S). Dyestuffs *II—IV* were proposed as reagents for photometric determination of

vanadium. All investigated dyes are suited as metallochromic indicators to chelatometric determination of vanadium.
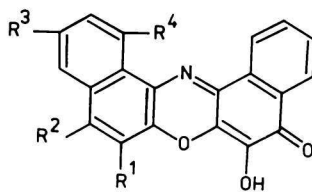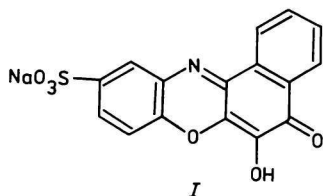
II $R^1 = R^3 = R^4 = H,$ $R^2 = SO_3Na$
III $R^1 = R^2 = R^4 = H,$ $R^3 = SO_3Na$
IV $R^2 = R^4 = H,$ $R^1 = R^3 = SO_3Na$
V $R^1 = R^4 = H,$ $R^2 = R^3 = SO_3Na$
VI $R^1 = R^2 = H,$ $R^3 = R^4 = SO_3Na$

Experimental

Chemicals and instruments

The stock solutions of dyes in concentration $c = 4 \times 10^{-4}$ mol dm^{-3} or $c = 1 \times 10^{-3}$ mol dm^{-3} were prepared by dissolving corresponding amounts of their sodium salts in water. The purity of dyes was checked by elemental analysis, paper chromatography, and thin-layer chromatography [6, 7].

The stock solutions of cetylpyridinium in concentration $c = 1 \times 10^{-2}$ mol dm^{-3} or $c = 2.5 \times 10^{-3}$ mol dm^{-3} were prepared by dissolving corresponding quantities of the solid preparation (Lachema, Brno) in water. The content of CPy$^+$ was determined volumetrically by the method according to *Uno* [8] and *Cross* [9].

The stock solution of vanadates $c(V) = 1 \times 10^{-2}$ mol dm^{-3} was obtained by dissolving convenient quantity of NH$_4$VO$_3$ in equimolar quantity of NaOH. The content of vanadates was determined indirectly by titrating the excess Mohr salt with a standard solution of potassium dichromate and using diphenylamine as an indicator [10, 11]. The solution of Chelaton 3 in concentration $c = 1 \times 10^{-2}$ mol dm^{-3} was prepared by dissolving corresponding amount of the solid preparation (Normanal 1031175) in water. The content of this chemical was determined volumetrically by titrating with a standard solution of MgSO$_4 \cdot$ 7H$_2$O and using Eriochrome Black T as a metallochromic indicator [12].

For adjusting the pH value of solutions, 0.1 M-HCl and acetate buffer solutions (CH$_3$COOH—NaOH system) were used. The ionic strength I was adjusted to the constant value $I = 0.01$ mol dm^{-3} by a solution of KCl or convenient concentration of the used buffer solution. All chemicals used were anal. grade reagents.

The spectrophotometric measurements were performed with instruments Specord UV VIS (Zeiss, Jena) and SP 1800 (Pye Unicam, Cambridge) in 10 mm, 20 mm, and

50 mm cells. The pH values were measured with a pH-meter PHM 4d (Radiometer, Copenhagen) which was equipped with a glass and calomel electrode (reliability of measurement ± 0.02 pH unit). The instrument was calibrated with the 0.05 M solution of potassium hydrogen phthalate and 0.05 M solution of potassium tetraoxalate.

Evaluation of experimental data

The composition of ternary complexes was determined by the analysis of concentration curves (1—4) using the method of molar ratios [13], the Job method of continual variations [14], and the method of tangent ratios [15]. The stability constants of the formed complexes were determined from the concentration curves (1), (3) or from the pH curves (5).

$$A = f\big(c(V)\big)_{c(L),c(S),pH} \qquad c(S) > c(L) \text{ or } c(V) \qquad (1)$$

$$A = f\big(c(S)\big)_{c(V),c(L),pH} \qquad (2)$$

$$A = f(x)_{c(O),c(S),pH} \qquad c(S) > c(O) \qquad (3)$$

where

$$c(O) = c(L) + c(V) \text{ and } x = c(V)/(c(V) + c(L))$$

$$A = f\big(c(L)\big)_{c(V),c(S),pH} \qquad c(S) > c(L) \text{ or } c(V) \qquad (4)$$

$$A = f(pH)_{c(V),c(L),c(S)} \qquad c(S) > c(L) \text{ or } c(V) \qquad (5)$$

The symbols $c(V)$, $c(L)$, and $c(S)$ stand for total analytical concentration of vanadates, dyestuff, and surfactant, respectively.

In investigations of relationships (1), (3—5) the solutions were mixed in the order dye—surfactant—vanadates. As for relationship (2) (pH > 4), the reaction components were mixed in the order: dye—vanadates—surfactant. The reason for doing it was to restrict the formation of associates of the L—S type.

Results and discussion

None of the investigated dyes gives a significant analytical reaction with vanadates. Provided the solutions of the investigated dyes have pH < 4, these dyes undergo oxidation in the presence of vanadates and are destroyed. Provided pH > 4, a positive reaction manifests itself at equimolar concentrations of components by an insignificant change in colour shade. In the presence of a cationic surfactant, blue (I) or green (II—VI) ternary complexes arise in the pH interval

2.0—6.5 (dyes *I, II, IV*, and *VI*) or in the pH interval 2.0—5.0 (dyes *III* and *V*).

The absorption curves (*1*) of solutions with constant concentration of dye and surfactant and varying concentration of vanadates exhibit single isosbestic point at constant pH and $c(S)$ (Tables 1—6). It was determined by the method of mole ratios that only one complex with the ratio of reacting components $n(V):n(L) = 1:2$ arose in solution in all investigated cases. Eight to ten titrations of type (*1*) were carried out with each dye in the pH interval 3.5—5.0. We used the concentration of ligand $c(L) = (1.6—8.0) \times 10^{-5}$ mol dm^{-3}, excess cationic surfactant $c(S) = (10—100)c(L)$, and concentrations of vanadates $c(V) = (0—5)c(L)$. The method of tangent ratios as well as the Job method of equimolar solutions of dye and vanadates (*3*) gave identical results.

If the solutions of vanadates and dye are titrated with a solution of surfactant, the absorption curves (*2*) give single isosbestic point for the reactions of dyes *I—IV* and *VI* (Tables 1 and 2) but two isosbestic points for the reaction of dye $V(\lambda(\text{iso}; 1) = 625$ nm; $c(S) \leqslant 2c(L)$; $\lambda(\text{iso}; 2) = 532$ nm; $c(S) > 2c(L)$; $c(L)$ or $c(V) = 1.6 \times 10^{-5}$ mol dm^{-3}; pH = 4.37). It has been ascertained by the method of mole ratios that complexes with the following ratios of reacting components $n(L):n(S) = 1:2$, $n(V):n(S) = 1:4$ (dyes *I—IV*; $n(L):n(S) = 1:3$, $n(V):n(S) = 1:6$ (dye *VI*) arise in the solution. As for dye *V*, two complexes with the ratio of reacting components $n(L):n(S) = 1:2$ or $1:3$ and $n(V):n(S) = 1:6$ are gradually formed. In titrations (*2*), we used the concentration of ligand $c(L) = (1.6—4.0) \times 10^{-5}$ mol dm^{-3}, the concentration of vanadates $c(V) < c(L)/2$ and $c(V) = (1—2.5)c(L)$, while the concentration of surfactant varied in the range $c(S) = (0—50)c(L)$. Six titrations in the pH interval 4.2—5.0 were carried out with each dye.

As titrations (*1*) and (*2*) evidence complexes with equal values of molar absorption coefficients, we may assume that defined ternary complexes of the type VL$_2$S$_4$ (dyes *I—IV*) and VL$_2$S$_6$ (dye *VI*) arise in the solutions. As for dye *V*, we may suppose that the complex VL$_2$S$_6$ comes into existence provided the excess concentration of surfactant is sufficient. The first complex with the ratio of reacting components $n(L):n(S) = 1:2$ may be a binary complex LS$_2$ in which the surfactant is localized on the sulfo groups of the dye. The reason for this assumption is the fact that this complex exhibits small absorbance at the wavelength $\lambda = 625$ nm where the absorption maximum of ternary complex occurs and its absorption maximum is analogous to the spectrum of the binary complex LS$_2$ arising in the mixture of dye *V* and surfactant. An increase in concentration of surfactant ($c(S) > 3c(L)$) results in small change in the absorption spectrum of ternary complexes. The origination of premicellar and micellar formations ($c(\text{mc})$ for CPy$^+$ is 9×10^{-4} mol dm^{-3} [16]) manifests itself by a slight increase in molar absorption coefficients (Tables 1 and 2), while the wavelengths of absorption maxima do not exhibit any significant change.

Table 1. Equilibrium and conditioned stability constants of ternary complexes in the systems vanadates—dye $(I—IV)$—CPy^+

Dye	pH	$\log {}^*\beta_{1,2}$	$\log \{{}^*\beta_{1,2,4}\}$	$\dfrac{\varepsilon_{max}(\lambda = 573 \text{ nm})}{dm^3\ mol^{-1}\ cm^{-1}}$	$\lambda(iso)/nm$
	$1.9—2.9^a$	4.91 ± 0.07	17.55 ± 0.06	21 100	515
		$\log \{\beta'_{1,2}\}$	$\log \{\beta'_{1,2,4}\}$		
I	3.78^b	4.16	15.22		513
	3.98^b	3.93	16.77	20 800	513
	4.19^c	3.61	19.01	20 800	513
	4.73^b	3.00	16.57	20 700	512
	5.12^b	2.69	16.55	20 700	512
		$\log {}^*\beta_{1,2}$	$\log \{{}^*\beta_{1,2,4}\}$	$\dfrac{\varepsilon_{max}(\lambda = 619 \text{ nm})}{dm^3\ mol^{-1}\ cm^{-1}}$	
	$2.3—3.2^a$	4.88 ± 0.09	17.01 ± 0.10	22 500	574
		$\log \{\beta'_{1,2}\}$	$\log \{\beta'_{1,2,4}\}$		
II	3.80^b	11.99	24.03		
	4.18^b	12.39	24.81	22 500	573
	4.38^b	12.20	24.33	22 400	573
	4.38^c	11.89	29.17	22 400	572
		$\log {}^*\beta_{1,2}$	$\log \{{}^*\beta_{1,2,4}\}$	$\dfrac{\varepsilon_{max}(\lambda = 630 \text{ nm})}{dm^3\ mol^{-1}\ cm^{-1}}$	
	$2.0—3.2^a$	4.81 ± 0.07	17.13 ± 0.07	23 000	571
		$\log \{\beta'_{1,2}\}$	$\log \{\beta'_{1,2,4}\}$		
III	3.80^b	12.04	24.49	22 900	564
	4.19^b	12.51	24.96		557
	4.38^b	12.14	24.59	22 900	546
	4.36^c	11.39	34.72	22 800	562
		$\log {}^*\beta_{1,2}$	$\log \{{}^*\beta_{1,2,4}\}$	$\dfrac{\varepsilon_{max}(\lambda = 616 \text{ nm})}{dm^3\ mol^{-1}\ cm^{-1}}$	
	$2.0—3.1^a$	4.64 ± 0.10	16.94 ± 0.10	22 300	560
		$\log \{\beta'_{1,2}\}$	$\log \{\beta'_{1,2,4}\}$		
IV	3.78^b	4.48	16.80		552
	3.98^c	4.39	16.71	22 500	
	4.18^b	4.01	16.32	22 200	547
	4.60^b	3.41	15.73		532
	4.16^d			22 000	546

a) Calculated from pH curve (*5*), average of 6—8 values, transformed in logarithmic scale, pH adjusted with a KCl + HCl mixture ($*\beta = *\bar{\beta} + ts/\sqrt{n}$, $\alpha = 0.05$); *b*) calculated from concentration curves (*1*), pH adjusted with a HOAc—NaOAc mixture; *c*) calculated from Job curves of equimolar solutions (*3*) $c(O) = c(V) + c(L)$, pH adjusted with HOAc—NaOAc buffer solution; *d*) calculated from concentration curves (*2*), pH adjusted with HOAc—NaOAc buffer solution.

Table 2

Equilibrium and conditioned stability constants of ternary complexes in the systems vanadates—dye (*V, VI*)—CPy$^+$

Dye	pH	log $*\beta_{1,2}$	log $\{*\beta_{1,2,6}\}$	$\dfrac{\varepsilon_{max}(\lambda = 625 \text{ nm})}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	$\lambda(\text{iso})/\text{nm}$
	2.3—3.0^a	4.63 ± 0.11	23.29 ± 0.11	23 500	561
		log $\{\beta'_{1,2}\}$	log $\{\beta'_{1,2,6}\}$		
V	3.62^b	12.08	31.40		561
	3.81^b	12.47	31.79	23 400	560
	4.16^b	12.38	31.58		546
	4.38^b	11.27	30.29		510
	4.60^b	10.96	29.80		500
	4.38^c	—	—	23 000	
		log $*\beta_{1,2}$	log $\{*\beta_{1,2,6}\}$	$\dfrac{\varepsilon_{max}(\lambda = 590 \text{ nm})}{\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}}$	
	2.1—3.4^a	4.20 ± 0.08	24.18 ± 0.08	23 000	543
		log $\{\beta'_{1,2}\}$	log $\{\beta'_{1,2,6}\}$		
VI	3.79^b	3.84	23.94		544
	4.36^b	3.25	23.47	22 900	544
	4.60^b	2.70	22.92		542
	4.57^c	1.59	33.66	22 800	545

For *a*)—*c*) see Table 1.

The number of the molecules of surfactant associated with arising ternary complexes VL_2S_4 (dyes *I—III*) and VL_2S_6 (dyes *V* and *VI*) is higher than the number of sulfo groups in the complex. This fact leads to the assumption that the second (*I—III*) or third (*V, VI*) molecule of surfactant is bound to places with the highest electron density in a molecule of dye [17] (*i.e.* to chelate-forming grouping of the hydroxyl and carbonyl group). This linking is an impulse to the origination of ternary complex because it has been ascertained that a linkage of two molecules of surfactant to the sulfo groups of dye does not give rise to a ternary complex (see

dye V). The difference in composition between the complex VL_2S_4 (dyes I—III) and VL_2S_6 (dyes V and VI) may be explained by the number of the sulfo groups in a molecule of dye to which the surfactant may be linked [1, 3]. On the basis of the suggested mechanism, the formation of the complex VL_2S_4 in the presence of dye IV may be explained by the bond of one molecule of surfactant to the chelate-forming grouping and of the second molecule to the sulfo group. The bonding of the third molecule of surfactant to the second sulfo group must be sterically hindered by the bonded two molecules of surfactant. The rightness of this assumption is confirmed by the fact that dye IV forms in basic medium the complex LS_2 with surfactant, while dyes V and VI form in equal medium the complex LS_3 [2, 18].

The formation of the ternary complexes VL_2S_r ($r = 4$ or 6) may be described by the following equation

$$V + 2HL + rS \rightleftharpoons VL_2S_r + 2H^+ \tag{A}$$

which is characterized by equilibrium constant (6) or (7) for the formalism of formation of the binary complex VL_2

$$*\beta_{1,2,r} = [VL_2S_r] [H]^2 [V]^{-1} [HL]^{-2} [S]^{-r} \tag{6}$$

$$*\beta_{1,2} = [VL_2] [H]^2 [V]^{-1} [HL]^{-2} \tag{7}$$

In the presence of excess amount of surfactant the constant in eqn (6) may be expressed by eqn (8) or in logarithmic form by eqn (9)

$$*\beta_{1,2,r} = \frac{(A - A_0) (A_{max} - A_0)^2 [H]^2}{[2pA_{max} - A - (2p - 1)A_0] (A_{max} - A_0)^2 [S]^r (c(L))^2 \{[H]/(K_a' + [H])\}^2} \tag{8}$$

resp.

$$\log \frac{(A - A_0) (A_{max} - A_0)^2}{[2pA_{max} - A - (2p - 1) A_0] (A_{max} - A_0)^2} = \log Z$$

$$\log Z = \log (*\beta_{1,2,r} [S]^r) + \log \frac{([H]/K_a' + [H])^2 (c(L))^2}{[H]^2} \tag{9}$$

where $A = \bar{\varepsilon}_L [L'] + \varepsilon [VL_2S_r]$, $A_{max} = \varepsilon c(L)/2$, $A_0 - \bar{\varepsilon}_L c(L)$, $p = c(V)/c(L) > 1/2$, K_a' is the dissociation constant of dye in the presence of the surfactant (CPy^+) in solution [18], and $[L']$ is the conditioned concentration of free dye $[L'] = ([HL] + [L])$.

Provided the cationic surfactant is present in excess $c(S) = (50$—$100)c(L)$, relationship (9) exhibits linear course for all investigated dyes in the pH range 2—3. It has the slope corresponding to two abstracted protons, which is in agreement with eqn (A) expressing the formation of ternary complex. The molar absorption coefficient of the complex VL_2S_r was obtained from concentration

curves (1) and pH curves (5). The equilibrium constants of eqn (A) were numerically calculated from eqn (8) and are listed in Tables 1 and 2. At higher values of pH the difference between the absorbances of concentration curves (1—3) of the theoretical and real reaction [19, 20] was used for calculating the value of the conditioned stability constant according to eqn (10), while the equlibrium constant for the formalism of formation of the binary complex VL$_2$ was calculated according to eqn (11). The simultaneous absorbance of the complex and free ligand is respected in both relationships.

$$\beta'_{1,2,r} = [VL_2S_r]\,[V]^{-1}[L']^{-2}[S]^{-r} \tag{10}$$

$$\beta'_{1,2} = [VL_2]\,[V]^{-1}\,[L']^{-2} \tag{11}$$

The transformation of the conditioned constants $\beta'_{1,2,r}$ or $\beta'_{1,2}$ to the corresponding equilibrium stability constants $*\beta_{1,2,r}$ and $*\beta_{1,2}$ was performed according to eqn (12)

$$*\beta = \beta'([H] + K'_a)^2 \tag{12}$$

The decrease in the values of equilibrium constants at higher pH values may be explained by polymerization and different degree of hydrolysis of vanadates. In acid medium (pH < 3), we may assume the existence of the VO_2^+ ions [21]. The different values of equilibrium constants $*\beta_{1,2,r}$ at different concentrations of surfactant may be also explained by different degree of association of CPy^+

Determination of vanadium

The stability of all ternary complexes is sufficient and permits a direct photometric determination of vanadium provided the dye and surfactant are present in excess. We may use the investigated dyes in the presence of surfactant as a metallochromic indicator for direct chelatometric determination of vanadium.

The direct chelatometric determination of vanadium was carried out at pH = 3.9—4.4 (dyes I—IV) or pH = 4.0—4.7 (dyes V, VI). In the course of titration, the concentration of surfactant must be at least two times higher than the concentration of vanadates in order that the solution may be clear before the point of equivalence. The colour transition is from violet to yellow (I), from green to red (II) or from blue-green to orange-red (III—VI). The amount of 0.05—6 mg of vanadium can be reliably determined in the volume 25—50 cm^3 by using 10—20 cm^3 of CPy^+ The determination is not loaded by a systematic error ($t_{exp} < t_{crit}$, $\alpha = 0.05$). The relative standard deviation for 7 parallel determinations does not exceed 1.1 % (Table 3).

The ions NO_3^-, Cl^-, I^-, Br^-, SO_4^{2-}, NH_4^+, Ba^{2+}, Mg^{2+}, Sr^{2+}, Ag^+, Tl^+, and CrO_4^{2-} do not interfere with the determination.

Table 3

Chelatometric determination of vanadium

Dye	Given m/mg	Found m/mg	$s_r/\%^a$	pH
I	1.253	1.260	1.01	4.0
II	1.016	1.011	0.98	4.1
IV	1.626	1.635	1.10	4.2
VI	0.504	0.503	0.86	4.6

a) $s_r/\% = (s/\bar{x}) \cdot 100$, $s = [\Sigma(x_i - \bar{x})^2/(n-1)]^{1/2}$, $n = 7$—10.

Working procedure A

0.1 M-acetate buffer solution (10 cm³) with pH = 4.1 (dyes *I—IV*) or pH = 4.3 (dyes *V*, *VI*) is added into a titration flask (100 cm³) which contains 10^{-2} M-CPy⁺ (20 cm³), 4×10^{-4} M-dye (1.5 cm³) and neutral or weakly alkaline solution of a sample with 0.05—6 mg of vanadium. The solution is filled up to 40 cm³ and titrated with a volumetric solution of Chelaton 3 to the colour change of indicator. (If the solutions for titration are correctly mixed, the sample is without any yellow shade due to polymerization of vanadates in acid medium.)

All investigated dyes may be used for photometric determination of vanadium in the presence of surfactant. The determination may be reliably accomplished at pH = 3.5—4.0 (dyes *I—V*) or pH = 3.7—5.0 (dye *VI*) (Table 4).

The determination is not hindered by the presence of the ions of alkaline and alkali earth metals, 50-fold excess of the Al^{3+}, Cr^{3+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, and Tl^+

Table 4

Photometric determination of vanadium

Dye	Concentration range [μg cm⁻³]	λ/nm	Sensitivity^a μg cm⁻³	$s_r/\%(\varrho/\mu g\ cm^{-3})$	pH
I	0.1—1.6	590	0.0028	0.92 (0.74)	3.85
II	0.1—1.6	524	0.0026	0.97 (0.74)	3.80
III	0.1—1.6	630	0.0026	0.70 (0.81)	3.80
IV	0.1—1.6	630	0.0026	0.90 (0.98)	3.80
V	0.1—1.6	625	0.0025	0.88 (0.81)	3.80
VI	0.1—1.6	610	0.0025	0.75 (1.24)	3.80

a) For $A = 0.001$.
$s_r/\% = (s/\bar{x}) \cdot 100$, $s = K_n R$, $n = 6$, $\alpha = 0.05$.

ions, 25-fold excess of the Mn^{2+}, La^{3+}, Ce^{3+}, Zn^{2+}, Cu^{2+}, Ln^{3+}, Sc^{3+}, Y^{3+} ions, 5-fold excess of the Ag^+, $PtCl_6^{2-}$, CrO_4^{2-} ions, and equimolar amount of the Zr^{4+}, Th^{4+}, Ti^{4+}, Bi^{3+}, Sb^{3+}, Sn^{4+} ions. The ions Hg_2^{2+}, Hg^{2+}, Pd^{2+}, Fe^{2+}, Fe^{3+}, In^{3+}, Ga^{3+}, UO_2^{2+}, MoO_4^{2-}, WO_4^{2-}, Sn^{2+}, Ti^{3+}, Au^{3+}, Ce^{4+} and polyhydroxy acids interfere with the determination.

The selectivity of determination increases in the presence of the surfactant (CPy^+). The hydrolysis of the Zr^{4+}, Th^{4+}, Sn^{4+}, Bi^{3+}, Sb^{3+}, Ti^{4+} ions and the formation of coloured products from the Cu^{2+} ions and dyes are suppressed. The preparation of samples necessitates equal ionic strength of all measured samples (the samples of equal composition in a solution of ionic strength $I = 0.1$ mol dm^{-3} exhibit only half absorbance when compared with a solution of ionic strength $I = 0.01$ mol dm^{-3}). However, the change in absorbance due to the change in ionic strength is negligible in the range of ionic strength $I = 0.005—0.015$ mol dm^{-3}.

The selectivity of determination is equal for all investigated dyes. The use of dyes *II—VI* is more convenient because of higher sensitivity and stability with respect to exclusion of ionic associates L—S (dye *I*).

Working procedure B

A sample with 4.5—60 µg of vanadium is added into a volumetric flask (50 cm^3) containing 1×10^{-3} M-dye *II—VI* (6 cm^3), acetate buffer solution of pH = 3.8 (5 cm^3), and 1×10^{-2} M-CPy$^+$ (10 cm^3). It is filled up to the mark and after 30 min the absorbance is measured at the wavelength $\lambda = 625$ nm—630 nm (*II—V*) or $\lambda = 610$ nm (*VI*) with respect to the blank test.

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