

A Ternary Complex of Vanadium(V) with 4-(2-Pyridylazo)-resorcinol and Thiazolyl Blue and its Application

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Abstract

A new ternary complex of vanadium(V) with 4-(2-pyridylazo)-resorcinol (PAR) and thiazolyl blue (MTT) has been obtained and studied by using an extraction-spectrophotometric method. The complex absorbs light at 560 nm with a molar absorptivity coefficient of $3.84 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at the optimum extraction conditions: pH=5.8±0.7, $C_{\text{PAR}} = 1.2 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{MTT}} = 1.0 \times 10^{-4} \text{ mol L}^{-1}$, extraction time - 2 min. Beer's law is obeyed up to $1.5 \mu\text{g V(V) mL}^{-1}$. The following constants have been calculated: the distribution constant ($\text{Log } K_D = 1.61$), the association constant ($\text{Log } \beta = 15.9$), the extraction constant ($\text{Log } K_{\text{ex}} = 17.5$) and the recovery factor ($R = 97.49\%$). The composition of the complex has been found to be V(V):PAR:MTT=1:2:3. The effect of foreign ions has been studied and a sensitive, selective and precise extraction-spectrophotometric method for the direct determination of vanadium(V) and indirect determination of vanadium(IV) has been proposed.

Key Words: vanadium, speciation, 4-(2-pyridylazo)-resorcinol, tetrazolium salt, extraction, spectrophotometry, catalysts

1. Introduction

Vanadium is an element of industrial, physiological and environmental importance. That is why its chemistry attracts special interest. The role of vanadium in biological systems includes normalization of sugar levels, participation in various enzyme systems as an inhibitor and a cofactor, and catalysis of the oxidation of various amines. Vanadium in trace amounts is reported essential for cell growth, but it can be toxic and genotoxic at higher levels.

Vanadium pollution in the environment comes primarily from combustion of fossil fuels, dyeing and steel manufacturing, but it also enters the environment through its use as a catalyst for a variety of gas-phase oxidation processes. The most frequently used catalyst contains 4-6% vanadium as V_2O_5 immobilised on a silica support. Depending on the production parameters the activity of the catalyst gradually gets worse because of decrease of the vanadium content (due to formation of volatile compounds) and conversion of vanadium(V) to vanadium(IV). These two species have different toxic, catalytic and other properties, hence the methods for vanadium determination must provide information on speciation.¹⁻⁵

In aqueous solution, vanadium reacts with heterocyclic azo reagents to form intensively coloured chelate complexes.^{1,5-8} In contact with heavy organic cations, these chelates may form ternary ion-association complexes with good extraction properties.^{1,2,5,6,7,9} Of

interest to us are the negatively charged complex ions of vanadium(V) with azo derivatives of resorcinol, which interact with tetrazolium cations. Previous investigations¹⁰⁻¹⁵ showed their applicability to extractive-spectrophotometric determination of traces of vanadium, and revealed a relationship between the properties of these complex compounds and the type and number of substituents in the tetrazolium ring.

In the present investigation we report a sensitive and selective extractive-spectrophotometric determination of both vanadium(V) and vanadium(IV) in catalysts for oxidation of SO_2 to SO_3 based on the formation of a new ternary complex of vanadium(V) with 4-(2-pyridylazo)-resorcinol (PAR) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (thiazolyl blue, MTT).

MTT^+ is known to form well extractable ternary ion-associated complexes with polyphenolate anionic species of V(V)¹⁵, Ge(IV)¹⁶, Mo(VI)¹⁷ and W(VI)¹⁸, which are more intensively colored than the corresponding ternary complexes with other tetrazolium cations.

2. Experimental

2.1. Reagents and apparatuses

A standard V(V) solution with a concentration of $2 \times 10^{-4} \text{ mol L}^{-1}$ was prepared by dissolving of NH_4VO_3 (Apolda). PAR disodium salt (Sigma) and MTT (Fluka) aqueous solutions were prepared with concentrations of $2 \times 10^{-3} \text{ mol L}^{-1}$ and $3 \times 10^{-3} \text{ mol L}^{-1}$, respectively. The other

reagents were 1,2-Diamino-cyclohexane-N,N,N',N'-tetraacetic acid (CDTA) (0.125 mol L^{-1}), NH_4F (3.5 mol L^{-1}), NaBrO_3 (0.15 mol L^{-1}), $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ ($5 \times 10^{-2} \text{ mol L}^{-1}$), CH_3COOH (0.1 mol L^{-1}), CH_3COONa (0.1 mol L^{-1}), chloroform, dichloroethane and solutions of diverse ions. All reagents used were of analytical grade. A Specol-11 spectrophotometer (Carl Zeiss, Germany) and a LAMBDA-15 Perkin-Elmer UV-VIS spectrophotometer (USA) equipped with 0.5 and 1.0 cm path-length cells were employed for reading the absorbance.

2.2. General procedure

Aliquots of vanadium(V) solution, buffer solution, PAR solution and MTT solution were introduced into 125-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL (or 20 mL in the presence of foreign ions and masking agents). Then 10 mL of organic solvent were added and the funnels were shaken for 2 min. A portion of the organic layer was filtered through a filter paper into a cell and the absorbance was read against a blank.

2.3. Procedure for determination of vanadium(IV,V) in catalysts

Sample preparation: 50-500 mg of powdered catalyst sample was placed in a 100 mL beaker. 25 mL of H_3PO_4 (1:1) were added and the contents were heated for about 30-40 min in inert atmosphere (N_2 , CO_2). The resulting mixture was diluted to 100 mL and filtered through a filter paper at a medium speed. The precipitate of silicic acid was carefully washed. The filtrate and the liquid fraction obtained after washing were transferred into a 1000 mL volumetric flask and the contents were diluted with distilled water up to the mark.¹⁴

Determination of vanadium(V): An aliquot of the obtained solution corresponding to 2.1-15 μg was transferred to a 125-mL separatory funnel. 2 mL of 0.125 mol L^{-1} CDTA were added and the contents were stirred well. pH was adjusted to 4.5-5.5 by adding dropwise preliminary determined amount of 5% ammonia solution. Then, 5 mL of acetate buffer solution (prepared by mixing of 0.1 mol L^{-1} solutions of CH_3COOH and CH_3COONa in a v/v ratio 8:92), 3 mL of 3.5 mol L^{-1} NH_4F solution, 1 mL of $2 \times 10^{-3} \text{ mol L}^{-1}$ PAR solution, and 3 mL of $3 \times 10^{-3} \text{ mol L}^{-1}$ MTT solution were added. The volume was made up to 20 mL with distilled water, and after that 10 mL of chloroform were added. The contents were shaken well for 2 min and a portion of organic layer was transferred through a filter paper into 1-cm path-length cell. Absorbance was measured at 560 nm against a similarly prepared reagent blank. The content of V(V) was determined from the calibration plot.

Determination of total vanadium and vanadium(IV): For determination of the total vanadium, 1 mL of 0.15 mol L^{-1} NaBrO_3 solution was added to the aliquot of the catalyst sample (for oxidation of V(IV) to V(V))^{11,14,19} and the above procedure was applied. The content of V(IV) was determined from the difference between the total vanadium content and V(V) content.

3. Results and Discussion

3.1. Optimum extraction-spectrophotometric conditions

Preliminary studies showed that the ternary V(V)-PAR-MTT complex could be extracted with chloroform and dichloroethane. We used chloroform for further investigations because of its better extraction ability and instant phase separation. The absorbance in this solvent is stable for a long time (2-3 h) and the blank absorbs insignificantly at $\lambda_{\text{max}} = 560 \text{ nm}$ (Fig. 1). Fig. 2 illustrates the effect of PAR and MTT concentration on the formation and extraction of the ternary complex. It can be concluded that the saturation is easily reached and a large excess of the reagents would not interfere. The optimum extraction-spectrophotometric conditions are shown in table 1.

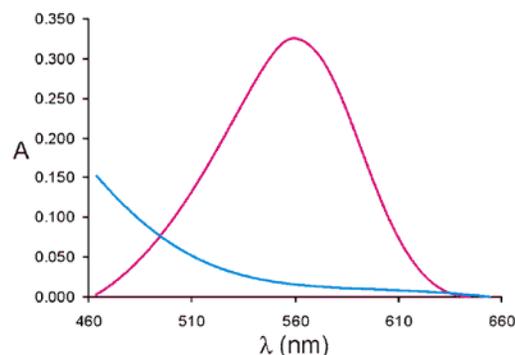


Figure 1. Absorption spectra of the ternary complex (purple) and blank (blue) in chloroform. $C_{\text{V(V)}} = 2 \times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{PAR}} = 1.2 \times 10^{-4} \text{ mol L}^{-1}$, $C_{\text{MTT}} = 1 \times 10^{-4} \text{ mol L}^{-1}$, $\text{pH} = 5.8$, $l = 0.5 \text{ cm}$.

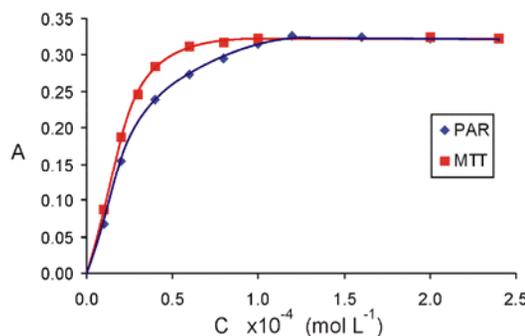


Figure 2. Absorbance vs. concentration of C_{PAR} and C_{MTT} plots. $C_{\text{V(V)}} = 2 \times 10^{-5} \text{ mol L}^{-1}$, $\text{pH} = 5.8$, $l = 0.5 \text{ cm}$.

Table 1. Optimum extraction-spectrophotometric conditions.

Optimum conditions		V(V) – PAR – MTT	V(V) – PAR – MTT – CDTA – NH ₄ F
Absorption maximum (nm)		560	560
Volume of the aqueous phase (mL)		10	20
Volume of the organic phase (mL)		10	10
Extraction time (min)		2	2
pH of the aqueous phase		5.8±0.7	5.8±0.7
Concentration of the reagents in aqueous phase (mol L ⁻¹)	PAR	1.2×10 ⁻⁴	1.0×10 ⁻⁴
	MTT	1.0×10 ⁻⁴	4.5×10 ⁻⁴
	CDTA	-	1.25×10 ⁻²
	NH ₄ F	-	5.25×10 ⁻¹
Validity of Beer's law (µg mL ⁻¹)		up to 1.5	up to 1.5
Molar absorptivity - ε' (L mol ⁻¹ cm ⁻¹)		3.84×10 ⁴	3.30×10 ⁴
Detection limit (ng mL ⁻¹)		2.0	2.3

3.2. Composition of the complex

The molar ratios in the complex of V(V) with PAR and MTT were determined by employing widely used spectrophotometric methods.²⁰ The V(V) to PAR ratio was determined by the equilibrium shift method and the method of saturation. The V(V) to MTT ratio was determined by the equilibrium shift method and the method of Asmus. The results give us grounds to assume that a 1:2:3-complex (V:PAR:MTT) is formed according to equation: $\text{VO}_2^+ + 2\text{HL}^- + 3\text{MTT}^+ \rightleftharpoons (\text{MTT})_3[\text{VO}_2\text{L}_2] + 2\text{H}^+$ (where $\text{H}_2\text{L}=\text{PAR}$).

3.3. Equilibrium constants and molar absorptivity

The association constant β characterizing the equilibrium in the aqueous phase $3\text{MTT}^+ + [\text{VO}_2\text{L}_2]^{3-} \rightleftharpoons (\text{MTT})_3[\text{VO}_2\text{L}_2]$ was determined by using the method of Komar-Tolmatchev²⁰ with a ratio $C_{\text{V(V)}}:C_{\text{MTT}}=1:3$. The equation of the straight line (Fig. 3) allows to calculate both the association constant β and the true molar absorptivity ε of the complex ($\text{Log}\beta=15.9\pm 0.4$; $\varepsilon=(3.96\pm 0.07)\times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$). The apparent molar absorptivity $\varepsilon'=(3.84\pm 0.08)\times 10^4 \text{ L mol}^{-1}\text{cm}^{-1}$ was determined by using Beer's law in the concentration range from 4×10^{-7} to $3\times 10^{-5} \text{ mol L}^{-1}$ V(V).

The distribution constant K_D , characterizing the distribution of the complex between the phases $\{(\text{MTT})_3[\text{VO}_2\text{L}_2]\}_{\text{aq}} \rightleftharpoons \{(\text{MTT})_3[\text{VO}_2\text{L}_2]\}_{\text{org}}$ was evaluated by comparing the absorbance for a single extraction (A_1) to that for triple extraction (A_3) in equal volumes ($K_D=[\text{V}]_{\text{org}}/[\text{V}]_{\text{aq}}=A_1/(A_3-A_1)$; $\text{Log}K_D=1.610\pm 0.005$). Recovery factor $R=(97.49\pm 0.02)\%$ was calculated according to the formula $R\% = K_D \times 100 / (K_D + 1)$.

The extraction constant characterizing the entire process $3\text{MTT}^+ + [\text{VO}_2\text{L}_2]^{3-} \rightleftharpoons \{(\text{MTT})_3[\text{VO}_2\text{L}_2]\}_{\text{org}}$ was determined by the equation $\text{Log}K_{\text{ex}} = \text{Log}K_D + \text{Log}\beta = 17.5\pm 0.4$.

All calculations were carried out for the 95% probability.

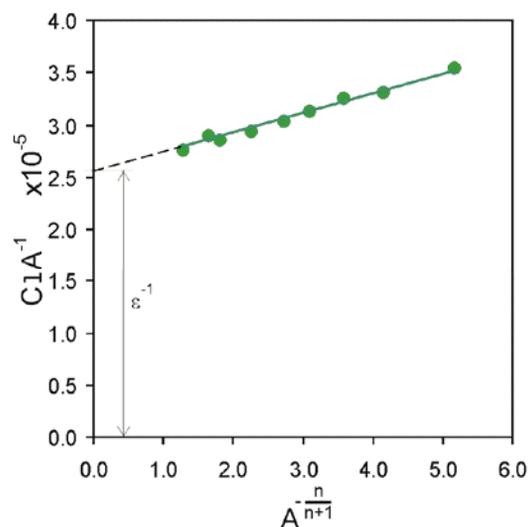


Figure 3. Determination of the association constant β and the molar absorptivity ε of the complex by the method of Komar-Tolmatchev ($C_{\text{V(V)}}$ varies from $8\times 10^{-6} \text{ mol L}^{-1}$ to $4\times 10^{-5} \text{ mol L}^{-1}$, $C_{\text{MTT}}=3\times C_{\text{V(V)}}$, $C_{\text{PAR}}=1.2\times 10^{-4} \text{ mol L}^{-1}$, $\text{pH}=5.8$). The equation of the straight line is $Y=1.937\times 10^6 X + 2.528\times 10^5$.

3.4. The effect of foreign ions

The effect of various ions on the extraction of V(V) with PAR and MTT was studied under the optimum extraction conditions and interferences from Co(II), Fe(III), Cr(III), Al(III), Ni(II), Zn(II), Mn(II), Pb(II), Cu(II) and V(IV) were observed. In order to improve analytical behavior of the system we investigated the effect of foreign ions in the presence of masking agents: CDTA+NH₄F (table 2). It is known that CDTA is an effective masking agent^{21,22} but application of NH₄F as a secondary masking agent offers some advantages, e.g. better selectivity towards several ions (including

V(IV)) and instant colour development.^{11,14} The optimum conditions for extraction of V(V) in presence of CDTA and NH₄F are presented in table 1 (column 3). The sequence of mixing of the reagents was as follows: V(V), CDTA, buffer, NH₄F, PAR and MTT. A change in this sequence may bring about some decrease in the selectivity and repeatability. It is worth to be mentioned that the association process $3\text{MTT}^+ + [\text{VO}_2\text{L}_2]^{3-} \rightleftharpoons (\text{MTT})_3[\text{VO}_2\text{L}_2]$ could be impeded in the presence of moderate amounts of some anions (e.g. NO₃⁻, Br⁻, Cl⁻, ReO₄⁻) which are able to form stable or slightly soluble compounds with MTT⁺. This fact is in accordance with ref.²³ where the inability of application of nitrate as a background electrolyte is reported. If these anions are present in the solution the volume of the aqueous phase or the concentration of tetrazolium salt should be higher.

Table 2. Effect of foreign ions on the determination of 5 µg vanadium(V) per 20 mL in the presence of CDTA and NH₄F as masking agents at the optimum operating conditions (see Table 1, column 3).

Foreign ion	(mg)	Ion to V(V) ratio	Relative error (%)
Al(III)	0.5	100	-3.2
Br ⁻	2.5	500	-2.9
BrO ₃ ⁻	50.0	10000*	0
Ca(II)	0.25	50	-0.9
Cd(II)	10.0	2000	-2.2
Ce(III)	1.0	200	-2.8
Cl ⁻	10.0	2000	0.97
	50.0	10000*	-2.0
Co(II)	1.0	200	-0.96
Cr(III)	0.1	20	0
	0.5	100	-3.2
Cr(VI)	0.5	100	-1.1
Cu(II)	5.0	1000	-1.8
Fe(III)	0.1	20	-3.9
H ₂ PO ₄ ⁻	50.0	10000*	3.2
Mg(II)	50.0	10000*	1.7
Mn(II)	1.5	300	-1.2
Mo(VI)	1.0	200	3.0
Nb(V)	0.05	10	1.3
	0.1	20	-3.2
NH ₄ ⁺	50	10000*	0
Ni(II)	1.0	200	0
	2.5	500	-3.4
NO ₃ ⁻	1.0	200	-1.6
Re(VII)	0.1	20	-2.0
	0.3	60	-4.3
SO ₄ ²⁻	50.0	10000*	0
tartrate ²⁻	10.0	2000	-4.4
Ti(IV)	0.125	25	-3.2
U(VI)	1.0	200	-2.7
V(IV)	0.1	20	2.7
	0.15	30	10.2
W(VI)	0.005	1	0
Zn(II)	2.5	500	-1.2

* - Higher ion to V(V) ratios are not studied.

3.5. Influence of the tetrazolium cation

The extraction of V(V)-PAR anionic chelate with other tetrazolium salts (triphenyltetrazolium chloride, iononitrotetrazolium chloride, tetrazolviolet and neotetrazolium chloride) was investigated under the same conditions (table 1, column 3). The results are shown in table 3. It could be seen that the molar absorptivity in the presence of MTT is the highest.

Table 3. Influence of tetrazolium salt on the apparent molar absorptivity (ε') of the ternary complex in the presence of CDTA and NH₄F.

Tetrazolium salt	ε' (L mol ⁻¹ cm ⁻¹)
Triphenyltetrazolium chloride (TTC)	18 600
Iononitrotetrazolium chloride (INT)	24 000
Tetrazolviolet (TV)	30 500
Neotetrazolium chloride (NTC)	32 500
Thiazolyl blue (MTT)	33 000

4. Analytical Application

The V(V)-PAR-MTT-CDTA-NH₄F-water-chloroform system was applied for the determination of vanadium(V/IV) in catalysts used for oxidation of SO₂ to SO₃. The proposed method gives reliable results (table 4) and could compete successfully with the other methods for determination of vanadium in catalysts in terms of selectivity,^{12,15,25} sensitivity,^{6,11,14,15,25,26} rapidity,^{10,24} reagent consumption^{10,14} and ability for speciation analysis.^{10,12,15,24}

5. Conclusion

A new ternary ion-associated complex was obtained and the systems V(V)-PAR-MTT-water-chloroform and V(V)-PAR-MTT-CDTA-NH₄F-water-chloroform were studied. Having in mind the advantages of the second system a sensitive, selective, precise and inexpensive extractive-spectrophotometric method for the determination of both V(V) and V(IV) was proposed.

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Table 4. Determination of vanadium in used catalysts for conversion of SO₂ to SO₃ during the manufacture of H₂SO₄ (P=95%).

Method		Present method	PAR-INT ¹¹	NC-NTC ²⁴	TAR-TTC ¹²
Sample					
Monsanto LP-110	V _{tot}	2.86±0.02	2.87±0.02	2.87±0.02	2.86±0.02
	V(V)	2.44±0.02	2.45±0.01	-	-
	V(IV)	0.42±0.04	0.42±0.03	-	-
Monsanto LP-120	V _{tot}	2.60±0.02	2.59±0.02	2.59±0.03	2.60±0.02
	V(V)	2.30±0.02	2.31±0.02	-	-
	V(IV)	0.30±0.04	0.28±0.04	-	-
Bitterfeld (sample 1)	V _{tot}	2.50±0.02	2.49±0.02	2.51±0.03	-
	V(V)	1.77±0.01	1.77±0.02	-	-
	V(IV)	0.73±0.03	0.72±0.03	-	-
Bitterfeld (sample 2)	V _{tot}	2.10±0.02	2.09±0.02	2.10±0.02	-
	V(V)	1.27±0.01	1.27±0.02	-	-
	V(IV)	0.83±0.03	0.82±0.03	-	-

Other ingredients (%): SiO₂(43.26-61.30), K(8.72-12.15), Na(0.48-2.78), S(7.61-8.85), Fe(0.27-2.31), Al(0.5-1.24), Ca(0.14-1.37), Mg(0.06-0.10), Cu(0.012-0.96), Zn(0.010-0.015), Pb(0.0075-0.31), Cd(0.0002-0.0034), Co(0.0007-0.0022), Ni(0.0046-0.048), Mn(0.007-0.13), Sb(up to 0.36), As(up to 0.0095), Cr(0.0048-0.028), Hg(up to 0.001), Se(up to 0.001). INT – idonitrotetrazolium chloride, NC – 4-nitrocatechol, NTC – neotetrazolium chloride, TTC – triphenyltetrazolium chloride, TAR – 4-(2-thiazolylazo)-resorcinol.

7. References

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Povzetek

Sintetizirali smo nov kompleks vanadija(V) s 4-(2-piridilazo)-resorcinolom (PAR) in tiazolil modrim (MTT) in ga proučevali z ekstrakcijsko spektrofotometrično metodo. Kompleks z molarnim ekstinkcijskim koeficientom $3.84 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ima absorpcijski maksimum pri valovni dolžini 560 nm. Pri optimalnih ekstrakcijskih pogojih $\text{pH} = 5.8 \pm 0.7$, $C_{\text{PAR}} = 1.2 \times 10^{-4} \text{ mol L}^{-1}$ in $C_{\text{MTT}} = 1.0 \times 10^{-4} \text{ mol L}^{-1}$ je čas ekstrakcije 2 min., Beerov zakon pa velja do koncentracije V(V) $1,5 \mu\text{g mL}^{-1}$. Izračunali smo logaritme porazdelitvene konstante $\log K_D = 1,61$, asociacijske konstante $\log \beta = 15,9$ in ekstrakcijske konstante $\log K_{\text{ex}} = 17,5$ ter faktor izkoristka ekstrakcije $R = 97,49 \pm 0,02\%$. Ugotovljeno je bilo stehiometrijsko razmerje vanadija in ligandov V(V):PAR:MTT=1:2:3. Raziskan je bil vpliv motečih ionov in predlagana občutljiva, selektivna in natančna ekstrakcijsko spektrofotometrična metoda za neposredno določevanje V(V) in posredno določevanje V(IV).