

TERNARY COMPLEXES OF VANADIUM(V) WITH 4-NITROCATÉCHOL AND NEOTETRAZOLIUM CHLORIDE. EXTRACTION-SPECTROPHOTOMETRIC STUDY

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Abstract

The system V(V) – 4-nitrocatechol (NC) – neotetrazolium chloride (NTC) – water – chloroform - n-butanol has been studied. Optimum conditions (reagent concentration in aqueous phase: $C_{NC}=2.4 \times 10^{-3} \text{ mol l}^{-1}$ and $C_{NTC}=1 \times 10^{-4} \text{ mol l}^{-1}$, pH=4.7, chloroform to butanol ratio = 7:3 (v/v), extraction time – 20 min) have been established providing most favorable spectral characteristics of vanadium extracts: $\epsilon_{\text{max}}=2.20 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ ($\lambda=420 \text{ nm}$). Two ternary complexes have been formed: $\text{NT}[\text{VO}_2\text{NC}]_2$ ($\lambda_{\text{max}}=400 \text{ nm}$) and $(\text{NT})_3[\text{VO}_2(\text{NC})_2]_2$ (absorbs light in a wide spectral range, $\epsilon_{660}=7 \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$). In both complexes vanadium keeps its initial oxidation state +5. The recovery factor ($R=96.1\%$), the association constant of the second complex ($\beta=8.7 \times 10^8$) and the detection limit ($C_{DL}=0.13 \mu\text{g V ml}^{-1}$) have been determined. Beer's law is obeyed up to $3.56 \mu\text{mg V(V) ml}^{-1}$. The effect of foreign ions has been studied as well.

Introduction

Vanadium (IV,V) is known to form ternary complexes with 4-nitrocatechol (NC) and tetrazolium salts [1-6]. Intense color of the complexes and big differences in their solubility in water and in organic solvents favors their practical applications [2,3,6]. On the other hand, the complexity of regarded systems provided by a number of factors, strongly affecting the complex formation and further extraction (e.g. interaction between the reagents, formation of binary complexes, effect of organic solvent on the composition of extracted species, equilibrium shift and redistribution of species in the organic layer,

redox processes, tautomeric equilibria), stimulate further investigations in the field. Our previous paper [5] reported data about the system: V(IV)–4-nitrocatechol–neotetrazolium chloride–chloroform–water–n-butanol. The present paper aims at studying a similar system with participation of V(V).

Experimental

Reagents and apparatus:

- Ammonium vanadate, puriss., from Apolda, 2×10^{-4} mol l⁻¹ aqueous solution;
- 4-Nitrocatechol (NC), GR, from Fluka, 2.5×10^{-2} mol l⁻¹ aqueous solution;
- 2,2',5,5'-Tetraphenyl-3,3'-(p-biphenyl)-ditetrazolium chloride (neotetrazolium chloride, NTC) from Fluka, 2.0×10^{-3} mol l⁻¹ aqueous solution;
- buffer solution prepared by mixing 1×10^{-1} mol l⁻¹ aqueous solutions of CH₃COONa·3H₂O (GR, from Valerus) and CH₃COOH (GR, from Teokom) in a proper ratio;
- Chloroform (GR, Khimnab) + 1-butanol (GR, Reakhim) mixture in a 7:3 v/v ratio;
- Spectrophotometer Specol, Carl Zeiss (Germany) supplied with 0.2, 0.5 cm and 1.0 cm cells;
- Shaking machine Thys 2 (Germany).

Procedure

In 125-ml separatory funnels are successively introduced portions of V(V), buffer, NTC and NC solutions. The resulting solutions are diluted to 10 ml (15 ml in studying interference of foreign ions) with distilled water. 10 ml portion of organic solvent is then added and the mixture shaken for 20 min. A portion of the organic layer is transferred through a paper filter into a cell and the absorbance measured at 420 nm (or at 660 nm) against a blank run in parallel.

The distribution coefficient (under optimum conditions) is found from the ratio $D_{V(V)} = A_1 / (A_2 - A_1)$, where A_1 and A_2 are the light absorbances measured after single and double extraction, respectively. Prior to absorbance measurements, the volume of the extracts is brought to 25 ml.

Results and discussion

Absorption spectra. Extraction time. Fig.1 shows the absorption spectra of the extracts of V(V) with NC and NTC in chloroform, butanol and in chloroform+butanol, respectively. As seen from the spectra absorbance of the mixed chloroform+butanol extract surpasses that of pure solvent extracts. The 7:3 chloroform to butanol ratio was established to be the optimum one with a view to achieving higher molar absorptivity for a relatively shorter extraction time (20 min). With increase of the butanol share in the solvent mixture the time for maximum extraction is reduced, but the molar absorptivity is lower.

Pure chloroform preferably extracts the salt-like compound formed between the reagents: NTNC [5] ($\lambda_{max} = 350$ nm). This fact explains the observed course of curve 3 on

Fig.1 – absorbance of the complex is lower than that of the blank.

Sequence of reagent introduction. It is known that o-phenols reduce V(V) to V(IV) [7,8]. On the other hand tetrazolium salts are known to stabilize V(V) in its ternary complexes with participation of o-polyphenols [3,4,9]. One can judge from Fig.2 how the order in which NC and NTC are added to the V(V) solution influence the final results. When NC is introduced prior to NTC, V(V) is partially reduced. In order to avoid reduction of V(V) and to achieve better repeatability of results, in further studies NTC was introduced prior to NC.

Effect of pH and reagent concentration. Fig 3 demonstrates spectra taken at varying pH of the aqueous phase (curves 1-6). At lower pH (curves 1-3) the basic absorbance maximum lies at about 420 nm. With increase in pH a minimum appears, which is attributed to the high absorbance of the blank in the range of 435 nm. It has been reported that the compound between NC and NTC in chloroform+butanol absorbs light at this wavelength [5]. The impact of this compound on absorbance at $\lambda=420$ can be reduced if extraction is performed at higher acidity and with lower concentrations of the reagents (Figs.4,5). NTNC compound shows no absorbance at $\lambda=660$ nm and hence concentration and pH intervals providing maximum absorption are wider. The following operating conditions are considered to be the optimum ones: $\lambda=420$ nm, pH=4.9, $C_{NC}=2.4 \times 10^{-3}$ mol l⁻¹, $C_{NTC}=1 \times 10^{-4}$ mol l⁻¹.

Composition of the complexes. The molar V(V) to NC and V(V) to NTC ratios (Figs.6-8) have been determined using known methods [11]. The formation of two ternary complexes was established. At lower concentrations of the reagents the dominating extracted species is NT[VO₂NC]₂ (see Fig.6, lines 1 and 3; Fig.7, curve 1; Fig.8, curve 3) with $\lambda_{max}=400$ nm (Fig.3, curve 7). At higher reagent concentrations the dominating species is (NT)₃[VO₂(NC)₂]₂ (see Fig.6, line 2; Fig.7, line 2; Fig.8, curves 1 and 2). It absorbs light in a wide spectral range. It is very likely that both complexes attribute to the basic absorption maximum at 420 nm under optimum operating conditions, while the maximum at $\lambda=660$ nm is attributed to the second complex.

Beer's law. Molar absorptivity. Limit of detection. Association constant. Recovery factor.

Beer's law is obeyed up to 7×10^{-5} mol l⁻¹ V(V) at $\lambda=420$ and 660 nm, e.g. up to 35.6 $\mu\text{g} / 10$ ml. Molar absorptivity was calculated from the expression $\epsilon = A / Cl$ ($C_V = 4 \times 10^{-6} - 7 \times 10^{-5}$ mol l⁻¹, $n=10$) and is $\epsilon_{420} = (2.20 \pm 0.04) \times 10^4$ l mol⁻¹ cm⁻¹, $\epsilon_{660} = (7.0 \pm 0.2) \times 10^3$ l mol⁻¹ cm⁻¹. C_{DL} was estimated based on data about dispersion of the blank [12] at $\lambda=420$ nm {SD=0.0048, $n=9$ ($A_{blank}=0.374$)}: $C_{DL} = 2.6 \times 10^{-6}$ mol l⁻¹ or 1.3 $\mu\text{g} V(V) / 10$ ml.

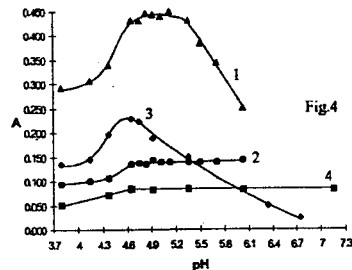
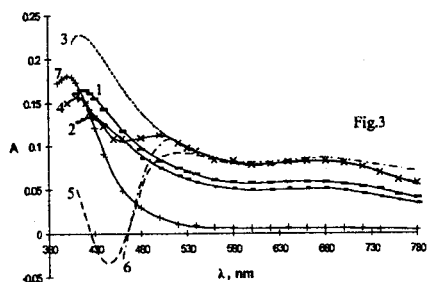
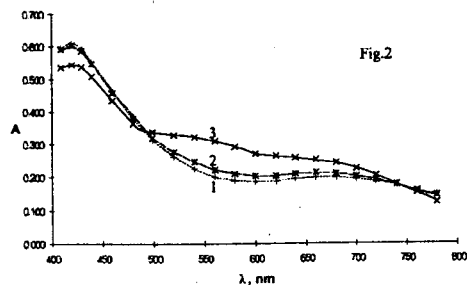
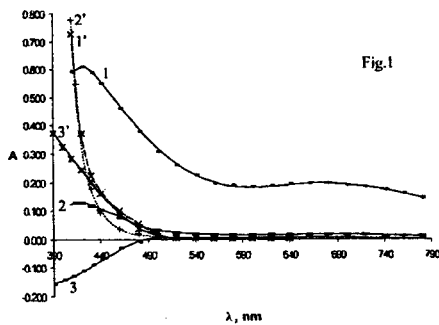


Fig. 1. Absorption spectra of extracts of V+NTC+NC (curves 1-3) against blank (NTC+NC, curves 1'-3') in different solvents: curves 1 and 1' – chloroform+butanol (7:3, v/v); curves 2 and 2' – butanol; curves 3 and 3' - chloroform. $C_{V(V)}=6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NC}=2.5 \times 10^{-3} \text{ mol l}^{-1}$, $\text{pH}=4.9$, $l=0.5 \text{ cm}$.

Fig. 2. Effect of the order of introduction of NTC and NC; comparison between V(V) and V(IV) spectra: 1 – V(V)+NTC+NC; 2 – V(V)+NC+NTC; 3 – V(IV)+NC+NTC or V(IV)+NTC+NC. $C_{V(V)} = C_{V(IV)} = 5.5 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NC}=2.5 \times 10^{-3} \text{ mol l}^{-1}$, $\text{pH}=4.9$, $l=0.5 \text{ cm}$.

Fig. 3. Spectra against blank recorded under different conditions: 1-6 - $C_{V(V)}=6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=2 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NC}=2.5 \times 10^{-3} \text{ mol l}^{-1}$, $l=0.2 \text{ cm}$, $\text{pH} = 2.5$ (1), 3.8 (2), 4.7 (3), 5.4 (4), 6.0 (5) and 7.2 (6); 7 - $C_{V(V)} = C_{NC} = 1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NTC}=2 \times 10^{-4} \text{ mol l}^{-1}$, $\text{pH}=4.7$, $l=0.5 \text{ cm}$.

Fig. 4. Effect of pH at $\lambda=420 \text{ nm}$ (curves 1 and 3) and $\lambda=660 \text{ nm}$ (curves 2 and 4). 1, 2 - $C_{V(V)}=4 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=1 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NC}=2.5 \times 10^{-3} \text{ mol l}^{-1}$, $l=0.5 \text{ cm}$; 3, 4 - $C_{V(V)}=6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=2 \times 10^{-4} \text{ mol l}^{-1}$, $C_{NC}=5 \times 10^{-3} \text{ mol l}^{-1}$, $l=0.2 \text{ cm}$.

Association constant β characterizing the equilibrium $3\text{NT}^{2+} + 2[\text{VO}_2(\text{NC})_2]^{3-} \rightleftharpoons (\text{NT})_3[\text{VO}_2(\text{NC})_2]_2$ was determined using the Komar's method [11] at concentrations of V(V) of 6×10^{-5} and $7 \times 10^{-5} \text{ mol l}^{-1}$: $\lg \beta = 8.7 \pm 0.4$ ($n=4$, $\lambda=660 \text{ nm}$). Molar absorptivity, calculated according to the same method - $\epsilon_{660} = (7.0 \pm 0.3) \times 10^3 \text{ l mol}^{-1} \text{ cm}^{-1}$ - is in good agreement with the above cited value.

Recovery factor is $R\% = D \times 100 / (D+1) = (96.1 \pm 0.8)\%$.

All calculations are carried out at probability of 95%.

Effect of foreign ions. It was established that equal amounts of Al(III), Cu(II), Ti(IV),

Nb(V), Zr(IV), Mo(VI) and W(VI) interfered with complex formation and extraction of $20 \mu\text{g V(V)}$. The majority of these elements can be masked with different masking agents (see Table). The attempts to mask Ti(IV) and Mo(VI) failed. The interference of Mo(VI) can be prevented by measuring absorbance at 660 nm .

The selectivity towards many ions is lower as compared to the similar system with V(IV) [5] except for Zn(II) , H_2PO_4^- and thiourea. This fact is very likely connected with limited concentration ranges and/or higher stability of the V(IV)-NC-bond. Similar tendency (higher selectivity with V(IV) complexes) has been observed as well in the systems V(IV or V)-NC-INT- $\text{H}_2\text{O}-\text{CHCl}_3$ [2,4]. High tolerable foreign ion to V(V) ratios can be achieved if necessary after extraction of V(V) with 8-hydroxiquinoline [2].

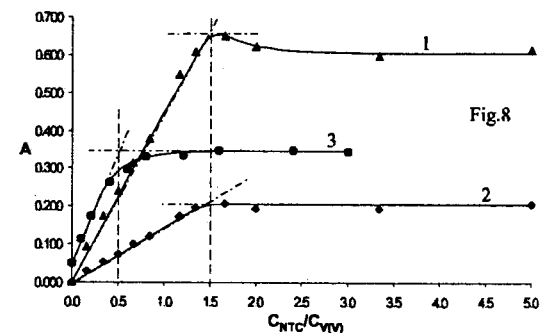
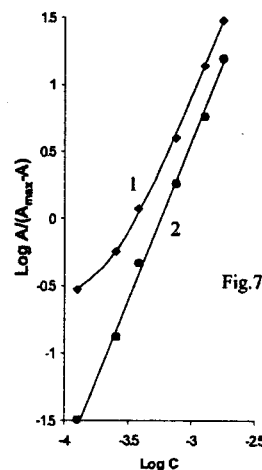
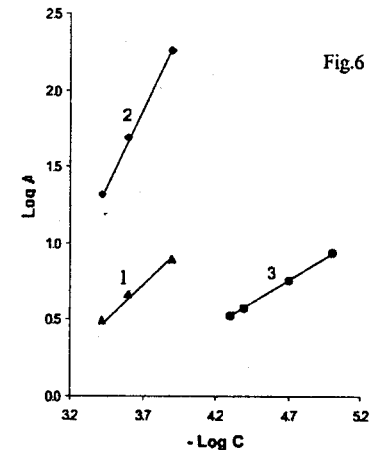
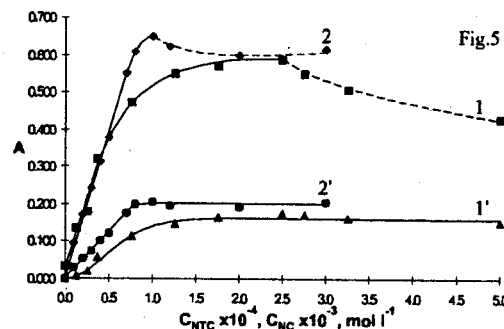


Fig. 5. Effect of reagent concentration: NC {curves 1 ($\lambda=420 \text{ nm}$) and 1' ($\lambda=660 \text{ nm}$)} and NTC {curves 2 ($\lambda=420 \text{ nm}$) and 2' ($\lambda=660 \text{ nm}$)}. 1, 1' - $C_{V(V)} = 6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=2 \times 10^{-4} \text{ mol l}^{-1}$, $\text{pH}=4.7$, $l=0.5 \text{ cm}$; 2, 2' - $C_{V(V)} = 4 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NC}=2.5 \times 10^{-3} \text{ mol l}^{-1}$, $\text{pH}=4.7$, $l=0.5 \text{ cm}$.

Fig. 6. Determination of V(V) to NC ratio (method of Bent and French) (line 1: $\lambda=420 \text{ nm}$, $\text{tg} \alpha \approx 1$; line 2: $\lambda=660 \text{ nm}$, $\text{tg} \alpha \approx 2$) and of V(V) to NTC ratio at low concentration of NC (line 3, $\text{tg} \alpha \approx 0.5$). 1, 2 - $C_{V(V)} = 6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC}=2 \times 10^{-4} \text{ mol l}^{-1}$, $\text{pH}=4.7$; 3 - $C_{V(V)} = C_{NC} = 1 \times 10^{-4} \text{ mol l}^{-1}$, $\text{pH}=4.7$, $\lambda=400 \text{ nm}$.

Fig.7. Determination of the V(V) to NC ratio according to the equilibrium shift method. $C_{V(V)} = 6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NTC} = 2 \times 10^{-4} \text{ mol l}^{-1}$, $pH=4.7$. 1 - $\lambda=420 \text{ nm}$; 2 - $\lambda=660 \text{ nm}$.

Fig.8. Determination of the V(V) to NTC ration according to the molar ratio method: 1 - $C_{V(V)} = 6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NC} = 2.5 \times 10^{-3} \text{ mol l}^{-1}$, $pH=4.7$, $\lambda=420 \text{ nm}$; 2 - $C_{V(V)} = 6 \times 10^{-5} \text{ mol l}^{-1}$, $C_{NC} = 2.5 \times 10^{-4} \text{ mol l}^{-1}$, $pH=4.7$, $\lambda=660 \text{ nm}$; 3 - $C_{V(V)} = C_{NC} = 1 \times 10^{-4} \text{ mol l}^{-1}$, $pH=4.7$, $\lambda=400 \text{ nm}$.

Conclusion

The present paper is a continuation of the studies on ion-associate complexes of V(V) with o-polyphenols and tetrazolium salts and confirms the conclusions made earlier [3,9,10] that the initial oxidation state of vanadium (+5) is preserved in the resulting ternary complexes. The comparison of the studied system V(V)-NC-NTC-H₂O-CHCl₃-BuOH with analogous systems allows the formulation of the following advantages and disadvantages, respectively: *Advantages*: i) high molecular absorptivity ($\epsilon_{420} = 2.20 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$); ii) high recovery factor of vanadium ($R=96.1\%$). The cited values are higher than those reported in [1-3,5,7,9,10,13-15]. *Disadvantages*: i) intense absorbance of the blank at the basic absorption maximum; ii) strong limitations in reagent concentrations. These drawbacks are due the simultaneous formation of NT²⁺NC²⁻ compound ($\lambda=435 \text{ nm}$) at operating conditions.

Table. Effect of diverse ions

Diverse ion,	mg	Ion to V ratio	E _r , %	Diverse ion,	mg	Ion to V ratio	E _r , %
Ag(I)	0.02	1	-0.8	Mn(II)	5	250	-2.8
Al(III)	0.02	1	5.4 ^a	Mo(VI)	0.02	1	2.3 ^c
Cd(II)	8	400	-2.6	Nb(V)	0.02	1	7.7 ^d
Ca(II)	0.6	30	2.5	Ni(II)	5	250	0
CDTA	0.5	25	-2.7	NO ₃ ⁻	0.2	10	-3
Ce(III)	5	250	-2.8	Re(VII)	0.04	2	-0.5
Cl ⁻	1	50	-2.4	SO ₄ ²⁻	100	5000	0
Co(II)	5	250	2.8	sulfosalicylate ⁻	0.2	10	interferes
Cr(III)	0.4	20	1.8	tartrate ²⁻	10	500	-2.5
CrO ₄ ²⁻	0.02	1	0.2	Ti(IV)	0.02	1	interferes
Cu(II)	0.2	10	0.5 ^b	thiourea	60	3000	3.6
F ⁻	1	50	2.9	U(VI)	0.02	1	1.3
Fe(III)	0.02	1	2.2	W(VI)	0.02	1	-3 ^b , 3.8 ^e
HPO ₄ ²⁻	1	50	1.4	Zn(II)	60	3000	-1
H ₂ PO ₄ ⁻	60	3000	1.2	Zr(IV)	0.02	1	0 ^d
Mg(II)	1	50	-0.2				

a - in the presence of 10 mg tartrate²⁻; b - in the presence of 60 mg thiourea; c - measured at $\lambda=660 \text{ nm}$;

d - in the presence of 1 mg F⁻; e - in the presence of 60 mg H₂PO₄²⁻

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