EXTRACTION STUDIES ON THE SYSTEM VANADIUM(V) – 4-(2-THIAZOLYLAZO)-RESORCINOL – NEOTETRAZOLIUM CHLORIDE – WATER – CHLOROFORM

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ABSTRACT

The system vanadium(V)– 4-(2-thiazolylazo)-resorcinol (TAR) – neotetrazolium chloride (NTC) – water – chloroform has been studied by using an extraction-spectrophotometric method. The optimum conditions for extraction of vanadium have been found: pH, concentration of reagents, extraction time. Molar absorptivity calculated using the Beer's law is $\varepsilon_{555} = 2.39 \times 10^4$ l mol^{-1} cm^{-1}. Under the optimum extraction conditions the dominating vanadium species is established to be $(NT)_3[VO_2(TAR)_2]_2$. The following constants have been calculated: distribution constant ($LogK_D = 1.21$), association constant ($Log\beta = 7.0$), extraction constant ($LogK_{ex} = 8.2$), recovery factor ($R = 93.78$ %). The effect of foreign ions on the extraction has been studied as well.

Keywords: vanadium(V), 4-(2-thiazolylazo)-resorcinol, neotetrazolium chloride, extraction-spectrophotometry.

INTRODUCTION

Vanadium(V) forms intensively coloured, easily extracted into organic solvents ternary complexes with azoderivatives of resorcinol and organic bases [1-16]. Of interest are the ion-association complexes between vanadium(V)-azoderivative of resorcinol anionic chelates and tetrazolium cations [9-14] which are appropriate for extraction-spectrophotometric determination of vanadium in complex matrices. The present paper aims at studying the system V(V) - 4-(2-thiazolylazo)-resorcinol (TAR) - 2,2';5,5'-tetraphentyl-3,3'-(p-biphenyl) - ditetrazolium chloride (neotetrazolium chloride, NTC) - water - organic solvent. Preliminary investigations indicate that a stable ternary complex is formed and vanadium is extracted for a short time into chloroform with recovery factor R > 90%.

EXPERIMENTAL

Reagents and Apparatus

A standard V(V) solution with a concentration of 2×10^{-4} mol l^{-1} was prepared by dissolving of NH_4VO_3 (Apolda). TAR (Aldrich Chem. Co) and NTC (Fluka) aqueous solutions were prepared with concentrations of 2×10^{-3} mol l^{-1}. The other reagents were CH_3COOH (0.1 mol l^{-1}), CH_3COONa (0.1 mol l^{-1}), chloroform and solutions of diverse ions and reagents. All reagents used were of analytical grade.

A Specol – 11 spectrophotometer (Carl Zeiss, Germany) supplied with 0.5 cm cells was employed for reading the absorbance.

Procedure

Aliquots of vanadium(V) solution, buffer solution, TAR solution and NTC solution were introduced into 125 ml separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 ml. Then 10 ml of organic solvent was 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.

RESULTS AND DISCUSSION

Optimum extraction-spectrophotometric conditions

Fig. 1 shows the absorbance spectra of the ternary complex and of the blank at different pH values in chloro-

form. At higher pH values a salt-like compound between the reagents TAR and NTC (similar to that described in [17]) is extracted in greater extent. Thus the spectral curve of the ternary complex (obtained like a difference between the curves in presence and in absence of vanadium) is found to be deformed at his left part and the absorption maximum shifts to longer wavelength. At pH = 4.75 (optimum pH – see Fig. 2) λ_{max} = 555 nm. The light absorbance is stable for a long time (2-3 hours) and the blank absorbs insignificantly at this wavelength. In contrast to some vanadium(V) - 4-(2-pyridilazo)-resorcinol – organic base systems [10,12,15,16] no waiting is necessary for colour development.

The effect of TAR and NTC concentrations on the extraction of V(V) is shown in Fig. 3. It can be concluded that a small excess of the reagents towards V(V) ensures its maximum extraction. Beer's law is obeyed in the concentration range from 0.5 to 40 μ g V(V) per 10 mL (The experiments were carried out at pH = 4.75, C_{TAR} = 2x10⁻⁴ mol l⁻¹, C_{NTC} = 3x10⁻⁴ mol l⁻¹).

Table 1. Effect of foreign ions.

Foreign ion, mg		Ion to V ratio	E$_r$, %	Foreign ion, mg		Ion to V ratio	E$_r$, %
Al³⁺	1	50	-0.7	H₂PO₄⁻	100	5000	0.4
Br⁻	0.2	10	-2.2	Mg²⁺	100	5000	0.7
BrO₃⁻	1	50	-2.8	Mn²⁺	40	2000	-1.1
Cd²⁺	2	100	3.7	Mo(VI)	0.2	10	-4.3
CDTA	1	50	-2.0	Ni²⁺	0.04	2	-1.1
	4	200	-19.0		0.2	10	-2.3*
Ce(III)	20	1000	-2.1	NO₃⁻	0.2	10	-4.1
Cl⁻	2	100	-3.8	Pb²⁺	0.02	1	-0.2
Co²⁺	0.02	1	153	Re(VII)	0.02	1	0
	0.15	7.5	2.2*				
Cr³⁺	0.02	1	-9.9	SO₄²⁻	100	5000	0
	0.1	5	-2.0*				
Cr(VI)	0.2	10	3.6	tartrate²⁻	20	1000	-2.1
Cu²⁺	0.02	1	22.8	U(VI)	0.02	1	0.9
	0.4	20	1.4*				
F⁻	13.3	666	-2.1	W(VI)	0.02	1	-20.7
Fe³⁺	0.02	1	18.8	Zn²⁺	100	5000	0
	0.02	1	2.1*				
HPO₄²⁻	2	100	4.5	Zr(IV)	0.02	1	-16.9

* - in presence of 4 mg CDTA

Fig. 1. Absorbance spectra at different pH values. $C_{V(V)}$ = 4.0x10⁻⁵ mol l⁻¹, C_{TAR} = 2,0x10⁻⁴ mol l⁻¹, C_{NTC} = 4.0x10⁻⁴ mol l⁻¹.

Composition of the complex

The molar V(V) to TAR and V(V) to NTC ratios were determined by using a set of known methods (Figs. 4-6) [18]. On the basis of the results it is possible to assume that a 3:2:4-complex is formed at optimum operating conditions according to equation:

$$2VO_2^+ + 4HL^- + 3NT^{2+} \Leftrightarrow (NT)_3[VO_2L_2]_2 + 4H^+, \text{ (where } H_2L = TAR).$$
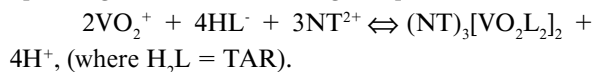
Determination of the equilibrium constants and the molar absorptivity

The association constant characterizing the equilibrium in aqueous phase:

$$3NT^{2+} + 2[VO_2L_2]^{3-} \Leftrightarrow (NT)_3[VO_2L_2]_2$$

was determined by using the method of Komar-Tolmatchev [18] with a ratio $C_{V(V)}$:C_{NTC} = 2:3. The equation of the straight line (Fig. 7) allows to calculate both the association constant β and the true molar absorp-

Fig. 2. Absorbance of the complex (curve 1) and the blank (curve 2) vs. pH of the aqueous phase plot. $C_{V(V)} = 4.0 \times 10^{-5}$ mol l^{-1}, $C_{TAR} = 2.0 \times 10^{-4}$ mol l^{-1}, $C_{NTC} = 4.0 \times 10^{-4}$ mol l^{-1}.
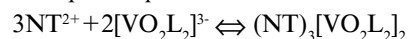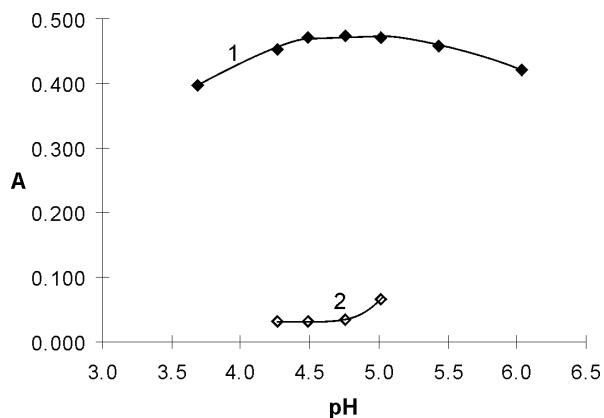

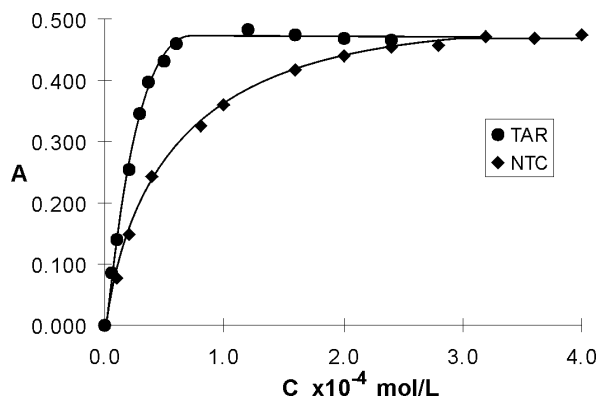
Fig. 3. Absorbance of V(V) extracts vs. C_{NTC} and C_{TAR} plots. $C_{V(V)} = 4.0 \times 10^{-5}$ mol l^{-1}, pH = 4.75.
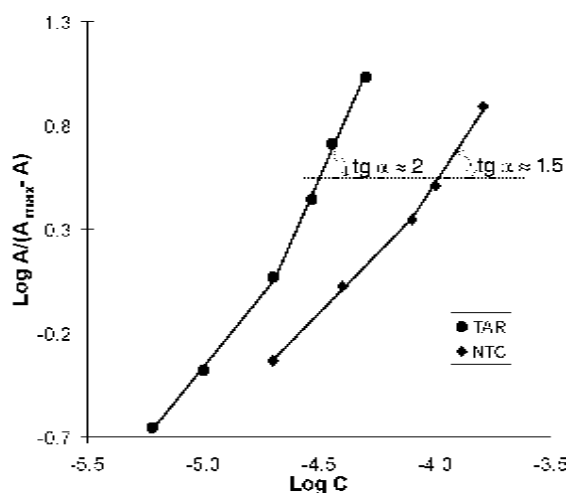

Fig. 4. Determination of the TAR to V(V) ($C_{V(V)} = 4 \times 10^{-5}$ mol l^{-1}, $C_{NTC} = 4 \times 10^{-4}$ mol l^{-1}) and NTC to V(V) ($C_{V(V)} = 4 \times 10^{-5}$ mol l^{-1}, $C_{TAR} = 2 \times 10^{-4}$ mol l^{-1}) molar ratios according to the equilibrium shift method.
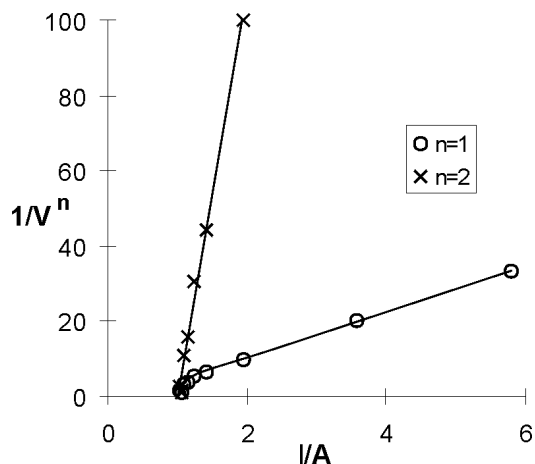

Fig. 5. Determination of the TAR to V(V) molar ratio according to the method of Asmus.
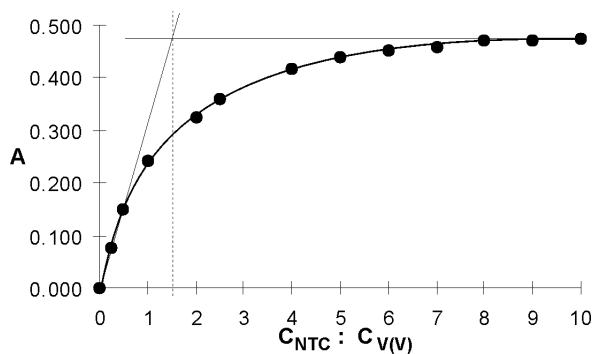

Fig. 6. Determination of the NTC to V(V) molar ratio according to the method of saturation.
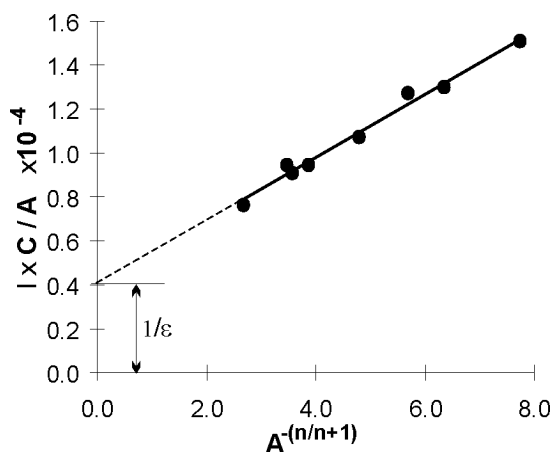

Fig. 7. Determination of the association constant β and the molar absorptivity ε of the $(NT)_3[VO_2(TAR)_2]_2$ by the method of Komar-Tolmatchev ($C_{TAR} = 2 \times 10^{-4}$ mol l^{-1}, pH = 4.75). The equation of the straight line is: $Y = 1,43 \times 10^{-5}X + 4,08 \times 10^{-5}$.

tivity ε of the complex. The apparent molar absorbtivity ε' was determined by using Beer's law in the concentration range from $1x10^{-6}$ to $8x10^{-5}$ mol l^{-1} V(V).

The distribution constant K_D characterizing the distribution of the complex between the phases $\{(NT)_3[VO_2L_2]_2\}_{aq} \Leftrightarrow \{(NT)_3[VO_2L_2]_2\}_o$ was evaluated by comparing the absorbance for a single extraction (A_1) to that for triple extraction (A_3) in the equal volumes – 25 ml $\{K_D=[V]_o/[V]_{aq}=A_1/(A_3-A_1)\}$. Recovery factor R = (93.78 ± 0.07) % was calculated according to the formula R % = $K_D 100/(K_D+1)$ %.

The extraction constant characterizing the entire process:

$$3NT^{2+}+2[VO_2L_2]^{3-} \Leftrightarrow \{(NT)_3[VO_2L_2]_2\}_o$$
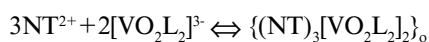
was determined by the equation $K_{ex}=K_D x \beta$. The values obtained are given bellow:

Log β = $7,0\pm0,7$; $LogK_D$ = 1.21 ± 0.01; $LogK_{ex}$ = $8,2\pm0,7$; R = (93.78 ± 0.07) %; $\varepsilon=(2.5\pm0.4)x10^4$ l $mol^{-1}cm^{-1}$; $\varepsilon'=(2.39\pm0.07)x10^4$ l $mol^{-1}cm^{-1}$

All calculations were carried out at probability of 95 %.

Effect of foreign ions

The effect of foreign ions on the extraction of 20 μg V(V) is summarized in Table 1. It can be assumed that large amounts of alkaline ions, NH_4^+, Mg^{2+}, Zn^{2+}, Ce(III), Mn^{2+}, SO_4^{2-}, $H_2PO_4^-$ and tartrate^{2-}, moderate amounts of Al^{3+}, Cd^{2+}, Cl^-, F^-, HPO_4^{2-}, BrO_3^- and CDTA, and small amounts of Mo(VI), Cr(VI), NO_3^-, Br^-, Ni^{2+}, Pb^{2+}, Re(VII) and U(VI) are tolerable. Co^{2+}, Cu^{2+}, Fe^{3+}, Cr^{3+}, Zr(IV) and W(VI) interfere seriously at a ratio 1:1 with respect to vanadium. Co^{2+}, Cu^{2+}, Cr^{3+}, Ni^{2+} and Fe^{3+} can be masked successfully with CDTA.

CONCLUSIONS

The present study shows that NTC as a component of a ternary complex is able to stabilize V(V) to TAR molar ratio equal to 1:2 in contrast to other reagents (R) previously used by Maric et al. [6] and by Grzegrzolka [7] which form ternary 1:1:1 V(V)-TAR-R complexes. Similar peculiarity is also observed in the ternary V(V)-PAR complex with NTC [12] and V(V)-TAR complex with triphenyltetrazolium chloride [14]. The ion-associate $(NT)_3[VO_2(TAR)_2]_2$ is relatively stable and can be applied for extraction and spectrophotometric determination of traces of vanadium. Because of the limited selectivity the accompanying ions should be masked (or separated) prior analysis of some samples.

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