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**EXTRACTION-SPECTROPHOTOMETRIC STUDY OF THE
SYSTEM VANADIUM(V) – 4-(2-THIAZOLYLAZO) -
RESORCINOL (TAR) – TRIPHENYLTETRAZOLIUM CHLORIDE
(TTC) – WATER – CHLOROFORM**

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ABSTRACT

The system vanadium(V) - 4-(2-thiazolylazo)-resorcinol (TAR) - triphenyltetrazolium chloride (TTC) - water - chloroform is studied using an extraction-spectrophotometric method. The optimum conditions for extraction of vanadium are found: $\text{pH}=4.75$, reagent concentration in aqueous phase - $C_{\text{TAR}}=2.0 \times 10^{-4} \text{ mol l}^{-1}$, $C_{\text{TTC}}=3.0 \times 10^{-4} \text{ mol l}^{-1}$, extraction time - 2 min. Beer's law is obeyed in the concentration interval 1 - 40 $\mu\text{g V(V)} / 10 \text{ ml}$. Molar absorptivity calculated using the Beer's law is $\epsilon_{550} = (2.37 \pm 0.07) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. Under the optimum extraction conditions the dominating vanadium species is established to be $(\text{TT})_3[\text{VO}_2(\text{TAR})_2]$. The following constants are calculated: distribution constant ($\text{Log}K_D=1.130 \pm 0.001$), association constant ($\text{Log}\beta=14 \pm 1$), extraction constant ($\text{Log}K_{\text{ex}}=15 \pm 1$), recovery factor $\{R=(93.03 \pm 0.01)\%$. The effect of foreign ions on the extraction of vanadium is studied as well.

Keywords: Vanadium, TAR, Triphenyltetrazolium chloride, Ternary complex, Extraction-spectrophotometry

INTRODUCTION

Vanadium(V) forms intensively coloured, easily extracted into organic solvents ternary complexes with azo-derivatives of resorcinol and organic bases [1-10]. In our previous works we investigated complexes of V(V) with 4-(2-pyridilazo)-resorcinol and tetrazolium salts [5-8], 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) - triphenyltetrazolium chloride (TTC) - water - organic solvent. Such a system with par-

icipation of tetrazolium salts has not been studied so far. Preliminary investigations indicate that a ternary complex is formed and vanadium is extracted for about a minute into chloroform with recovery factor $R > 90\%$. In contrast to some vanadium(V) - 4-(2-pyridilazo)-resorcinol - organic base systems [5,7,9,10] no waiting is necessary for colour development.

EXPERIMENTAL

Reagents and Apparatus

- Ammonium vanadate (*Apolda*, analytical grade), 2.0×10^{-4} mol l^{-1} aqueous solution.
- 4-(2-Thiazolylo)-resorcinol (*Aldrich Chem. Co*), 2.0×10^{-3} mol l^{-1} aqueous solution prepared by addition of KOH.
- 2,3,5-Triphenyltetrazolium chloride (*Loba Feinchemie*, analytical grade), 2.0×10^{-3} mol l^{-1} aqueous solution.
- Acetate buffer solution prepared by mixing of 1.0×10^{-1} mol l^{-1} solutions of CH_3COOH and CH_3COONa (freshly prepared).
- Chloroform (*Valerus*, analytical grade).
- Specol spectrophotometer (*Carl Zeiss*, Germany) supplied with 0.5 cm cells.

Procedure

Aliquots of vanadium(V) solution, buffer solution, TAR solution and TTC solution were introduced into 150 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.

The distribution constant K_D was found from the ratio $K_D = A_1/(A_3 - A_1)$ where A_1 is the light absorbance for single extraction at the optimum extraction conditions and A_3 is the absorbance for a triple extraction (under the same conditions). In both cases the organic layers were collected in 25-ml calibrated flasks and brought to volume with chloroform. Absorbances were read against a blank.

The association constant β and the true molar absorptivity of the complex ϵ were determined by the method of Komar-Tolmatchev [11] at a ratio $C_{V(V)}:C_{TTC}=1:3$, $C_{TAR}=2 \times 10^{-4}$ mol l^{-1} , $pH=4.75$.

RESULTS AND DISCUSSION

Optimal extraction-spectrophotometric conditions

The absorption maximum of the ternary complex of vanadium(V) with TAR and TTC in chloroform lies at $\lambda=550-555$ nm where the ternary V(V)-TAR-complexes with other organic bases [2,3] absorb. A well defined maximum at $\lambda=550$ nm is observed at optimal extraction conditions. The blank absorbs insignificantly at this wavelength. The light absorbance is stable for several hours.

The effect of TAR and TTC concentrations on the extraction of V(V) is shown in Fig. 1. It can be concluded that a small excess of the reagents towards V(V) ensures its maximum extraction.

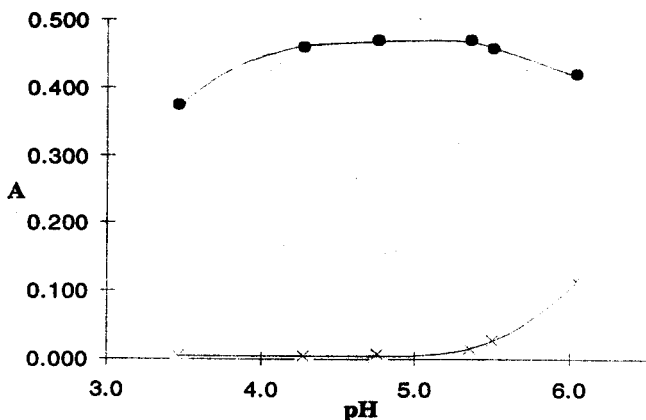


Figure 2. Absorbance of the complex (●) and the blank (×) vs. pH of the aqueous phase plot. $C_{V(V)}=4.0 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR}=2.0 \times 10^{-4} \text{ mol l}^{-1}$, $C_{TTC}=3.0 \times 10^{-4} \text{ mol l}^{-1}$

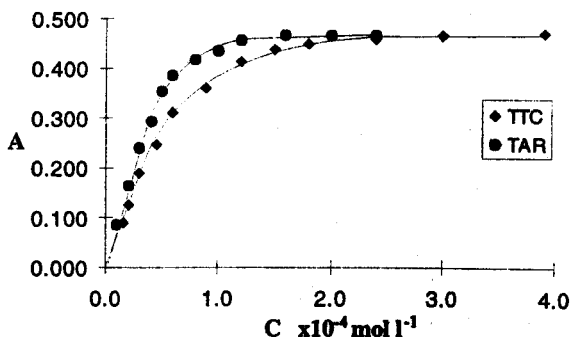


Figure 1. Absorbance of V(V) extracts vs. C_{TTC} and C_{TAR} plots.

$C_{V(V)}=4.0 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR}=2.0 \times 10^{-4} \text{ mol l}^{-1}$, $C_{TTC}=3.0 \times 10^{-4} \text{ mol l}^{-1}$, $\text{pH}=4.75$

The pH interval for maximum absorption is assumed to be from 4.3 to 5.3 (Fig. 2). Beer's law is obeyed in the concentration range from 1 to 25 $\mu\text{g V(V)}$ per 10 ml (Experiments were carried out at $\text{pH}=4.75$, $C_{TAR}=2 \times 10^{-4} \text{ mol l}^{-1}$, $C_{TTC}=3 \times 10^{-4} \text{ mol l}^{-1}$).

Effect of foreign ions

The effect of foreign ions on the extraction of 20 $\mu\text{g V(V)}$ is summarized in a table. It can be assumed that large amounts of alkaline and alkaline-earth ions, NH_4^+ , Ce(III) , Zn(II) , Mn(II) , SO_4^{2-} , H_2PO_4^- , BrO_3^- , Br^- , NO_3^- and moderate amounts of

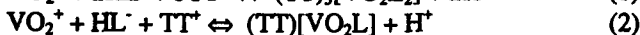
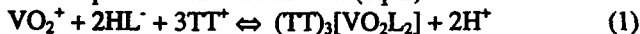
Al(III), Cr(VI), Cd(II), Cl⁻, F⁻, HPO₄²⁻, tartrate²⁻, CDTA and Mo(VI) are tolerable. Co(II), Fe(III), Cr(III), Zr(IV), W(VI) and Re(VII) interfere seriously. The interference of Fe(III), Co(II) and Cr(III) can be decreased in a small extent by masking with CDTA.

Table. Effect of foreign ions

Foreign ion, mg	Ion to V ratio	E _r , %	Foreign ion, mg	Ion to V ratio	E _r , %		
Al(III)	4	200	-2.8	H ₂ PO ₄ ⁻	40	2000	0.9
Br ⁻	40	2000	-2.8	Mg(II)	200	10000	3.2
BrO ₃ ⁻	200	10000	1.1	Mn(II)	20	1000	2.1
Cd(II)	2	100	2.2	Mo(VI)	0.4	20	-1.1
CDTA	1	50	-5.0	Ni(II)	0.04	2	-1.1
	4	200	-30				
Ce(III)	60	3000	-2.1	NO ₃ ⁻	20	1000	2.0
					40	2000	-5.5
Cl ⁻	20	1000	3.4	Pb(II)	0.04	2	-2.1
	200	10000	7.5				
Co(II)	0.02	1	60	Re(VII)	0.02	1	6.3
Cr(III)	0.02	1	-13.5	SO ₄ ²⁻	200	10000	0
Cr(VI)	0.04	2	5.1	tartrate ²⁻	2	100	-1.9
	5	250	-2.3				
Cu(II)	0.04	2	2.2	U(VI)	0.04	2	1.9
	0.1	5	4.3				
F ⁻	20	1000	-4.9	W(VI)	0.02	1	-11.0
Fe(III)	0.02	1	36	Zn(II)	40	2000	0
HPO ₄ ²⁻	10	500	2.1	Zr(IV)	0.02	1	-11.6

Composition of the complexes

The molar V(V) to TAR and V(V) to TTC ratios were determined by using a set of known methods (equilibrium shift method, method of Bent & French and method of Asmus) [11]. The results give us grounds to assume that a 1:2:3-complex is formed (see eq. 1) at a relatively small excess of the reagents. At deficiency of the reagents a 1:1:1-complex is extracted as well (eq. 2).



Determination of the equilibrium constants and the molar absorptivity

The association constant β characterizing the equilibrium in the aqueous phase $3\text{TT}^+ + [\text{VO}_2\text{L}_2]^{3-} \rightleftharpoons (\text{TT})_3[\text{VO}_2\text{L}_2]$ was determined by using the method of Komar-Tolmachev [11] (Fig. 3): $\text{Log}\beta = 14 \pm 1$. This method allows also to calculate the real molar absorptivity ε of the complex: $\varepsilon = (2.6 \pm 0.2) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$.

The apparent molar absorptivity $\epsilon'=(2.37\pm 0.07)\times 10^4 \text{ l mol}^{-1}\text{cm}^{-1}$ was determined by using Beer's law in the concentration range from 2×10^{-6} to $8\times 10^{-5} \text{ mol l}^{-1}$ V(V).

The distribution constant K_D characterizing the distribution of the complex between the phases $\{(TT)_3[VO_2L_2]\}_w \rightleftharpoons \{(TT)_3[VO_2L_2]\}_o$ was evaluated by comparing absorbance values measured with single extraction and with triple extraction: $\text{Log}K_D=1.130\pm 0.001$. Recovery factor $R=(93.03\pm 0.01) \%$ was calculated according to the formula $R\% = K_D 100/(K_D+1) \%$.

The extraction constant $\text{Log}K_{ex}=15\pm 1$ was determined by the equation $\text{Log}K_{ex}=\text{Log}K_D+\text{Log}\beta$.

All calculations were carried out at probability of 95 %.

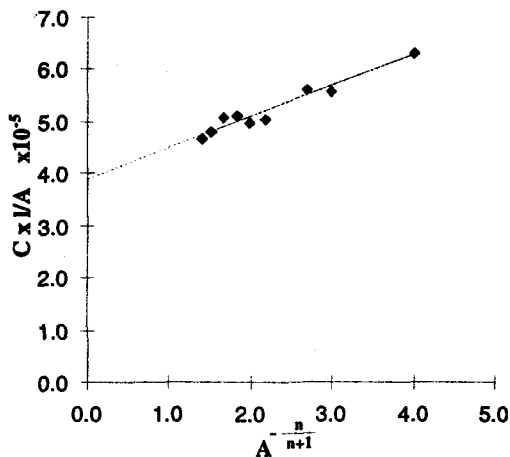


Figure 3. Determination of the association constant β by the method of Komar-Tolmachev. The equation of the line is $Y=5.96\times 10^{-6} X + 3.89\times 10^{-5}$

CONCLUSION

The present investigation shows that TTC as a component of a ternary complex is able to stabilize V(V) - TAR molar ratio equal to 1:2 in contrast to other previously studied reagents {tetraphenylarsonium and tetraphenylphosphonium salts [2], amines, quinine and diphenylguanidine [3]} forming ternary V(V) - TAR complexes with composition 1:1:1. TTC forms two ternary ion-association complexes with V(V) and TAR: $(TT)[VO_2L]$ and $(TT)_3[VO_2L_2]$. The second one is of analytical importance and can be used as a basis for development of competitive hybrid methods for determination of vanadium.

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