# Ternary complexes of vanadium(IV) with 4-(2-thiazolylazo)resorcinol and tetrazolium chlorides

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Dedicated to Professor George Andreev on his 70-year birthday

Complex formation and liquid-liquid extraction (LLE) have been studied for ternary complexes of vanadium(IV) with 4-(2-thiazolylazo)resorcinol (TAR) and tetrazolium salts (TS). The following parameters have been optimized: TS, organic solvent, pH, extraction time, amount of TAR, amount of TS. The specific TSs used in the present study were: i) 2,3,5-triphenyl-2H-tetrazolium chloride (TTC); ii) 3-(1-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium Violet, TV); iii) 3-(4-iodophenyl)-2-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT); iv) 3,3'-(4,4'-biphenylene)-bis-(2,5-diphenyl-2H-tetrazolium) chloride (Neotetrazolium chloride, NTC); and v) 3,3'-(3,3'-dimetoxy-4,4'-biphenylene)-bis-[2-(4-nitrophenyl)-5-phenyl-2H-tetrazolium] chloride (Nitro Blue Tetrazolium chloride, NBT). NBT appears to be the best TS for the LLE-spectrophotometric determination of vanadium(IV) due to the following reasons: a) only one complex with composition V(IV):TAR:NBT=1:2:2 and suggested formula (NBT)<sub>2</sub>[VO(OH)<sub>2</sub>(TAR)<sub>2</sub>] is extracted into organic phase (no stepwise complexation); b) the molar absorptivity is the highest ( $\epsilon$ '=2.83×10<sup>4</sup> L mol<sup>-1</sup>cm<sup>-1</sup> at  $\lambda_{max}$ =550 nm); c) the pH-range for maximum extraction of V(IV) is the broadest (4.6-5.3) and allows work in the most acidic media. Some equilibrium constants for the V(IV)–TAR–NBT–water–chloroform system have been determined. Comparison with similar systems which involve vanadium(V) or 4-(2-pyridylazo)resorcinol has been made. © Anita Publications. All rights reserved.

#### **1** Introduction

Vanadium is a transition element with essential and toxic nature [1-14], which may enter the biosphere from various natural and anthropogenic sources, e.g. volcanic activity, burning of crude petroleum and coal, dyeing, steel and catalysts production, petrochemical industries. A number of hazards are associated with the extensive industrial use of vanadium [3,4,7-13], however its beneficial effects are the topic of many present day researches [1,2]. Vanadium is a prospective antidiabetic agent, but its application is problematic due to the high toxicity observed after prolonged administration [6]. Vanadium toxicity is dependent on the oxidation state and usually increases as the oxidation state increases [4,10,11]. Vanadium(V) can be almost as toxic as lead, cadmium, and mercury [10], whereas vanadium(IV) (VOSO<sub>4</sub>) is a common supplement used to enhance weight training in athletes (at doses up to 60 mg/d) [4]. Under common conditions vanadium can easily switch [1,5] between these two most important oxidation states what imposes additional requirements on the analytical procedures.

Instrumental techniques such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF) are extensively used for vanadium determination. However, speciation analysis with these techniques is possible only after preliminarily separation of the vanadium species. In addition, when the levels are low, an enrichment step is necessary to improve the precision and accuracy. Neutron activation analysis (NAA) is a very sensitive technique, but its use for vanadium determination is complicated by the short half-life of <sup>52</sup>V and by the masking of <sup>52</sup>V activity by <sup>24</sup>Na present in the matrix [11]. <sup>51</sup>V nuclear magnetic resonance (NMR) spectrometry and electron paramagnetic resonance (EPR) spectrometry have been used to determine vanadium(V) and vanadiumV(IV), respectively, but are impeded by non-routine instrumental requirements [11]. Spectrophotometry is the most common technique used for vanadium determination and valence speciation [5,11].

Spectrophotometric methods are low-cost, simple, and fast. When they are combined with liquid-liquid extraction (LLE) the mentioned advantages are little affected, but some characteristics of the determination, including selectivity and sensitivity can significantly improve [15-18].

N-heterocyclic o-hydroxy-substituted azo compounds are well-known class of highly sensitive complexing reagents [18-22] which play an important role in LLE-spectrophotometry [17-20]. They react with metal ions at different oxidation states [19] and can enter into the composition of multicomponent systems [15-19]. A variety of complexes formed with these reagents make them interesting in speciation analysis [19]. Vanadium(V) is known to form ternary ion-associate complexes with 4-(2-thiazolylazo)resorcinol (TAR) in the presence of high molecular weight amines [23], tetraphenylarsonium [24], tetraphenylphosphonium [24] and tetrazolium salts (TS) [25-27]; these complexes are suitable for LLE-spectrophotometric determination of vanadium(V). However, no attention has been paid to the complexation between V(IV), TAR and auxiliary reagents. Here, we report the complex formation and LLE in the vanadium(IV)-TAR-TS-water-organic solvent system. The following TSs have been selected for the present investigations:

i) 2,3,5-triphenyl-2H-tetrazolium chloride (TTC);

ii) 3-(1-naphthyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium Violet, TV);

iii) 3-(4-iodophenyl)-2-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT);

iv) 3,3'-(4,4'-biphenylene)-bis-(2,5-diphenyl-2H-tetrazolium) chloride (Neotetrazolium chloride, NTC);

v) 3,3'-(3,3'-dimetoxy-4,4'-biphenylene)-bis-[2-(4-nitrophenyl)-5-phenyl-2H-tetrazolium] chloride (Nitro Blue Tetrazolium chloride, NBT).

TSs are well-known compounds [28] possessing a positively charged five-membered ring(s) of one carbon and four nitrogen atoms (Fig. 1). They are able to form slightly water-soluble ion-associated complexes with various anions and could potentially be used for LLE-spectrophotometric or potentiometric determinations of metal and non-metal species involved in the anionic part of the complex [28]. Unlike amines, tetrazolium halides can be used without preliminary protonation. They are thermally stable, and less toxic than arsoniumand phosphonium salts.



Figure 1. Structure of mono- and ditetrazolium salts deriving from 2H-tetrazole. Three locations for substitutes in the tetrazolium ring are possible, ensuring the diversity of properties for this class of compounds

## 2 Experimental

# 2.1 Reagents and apparatus

VOSO<sub>4</sub>.5H<sub>2</sub>O from Fluka AG, *purum*, as a  $5 \times 10^{-2}$  mol L<sup>-1</sup> stock aqueous solution. The concentration was checked by titration with a standard solution of potassium permanganate. The working  $2 \times 10^{-4}$  mol L<sup>-1</sup> aqueous solutions acidified with sulphuric acid to pH=2-3 were prepared every day. TAR from Aldrich Chem. Co, *pro analysis*, as a  $2 \times 10^{-3}$  mol L<sup>-1</sup> aqueous solution. TSs as  $2 \times 10^{-3}$  mol L<sup>-1</sup> aqueous solutions: TTC and TV from Loba Feinchemie; INT and NTC from Fluka AG; and NBT from Merck. Redistilled chloroform was used. The acidity of aqueous medium was set by the addition of buffer solution, prepared by mixing 0.1 mol L<sup>-1</sup> aqueous solutions of CH<sub>3</sub>COOH and CH<sub>3</sub>COONa.3H<sub>2</sub>O. The resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells, was employed for reading the absorbance.

### 2.2 Procedure

Aliquots of V(IV) solution, buffer solution, TAR solution and TS 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 were added and the funnels were shaken for 0.5-3.0 min. A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.



Figure 2. Absorbance spectra of the V(IV)-TAR-TS complexes against blank samples obtained at pH=4.95 and  $C_{V(IV)}$ =  $2 \times 10^{-5}$  mol L<sup>-1</sup>. Curve 1:  $C_{TAR}$ =3.2×10<sup>-4</sup> mol L<sup>-1</sup> and  $C_{TTC}$ =2.4×10<sup>-4</sup> mol L<sup>-1</sup>; Curves 2-5:  $C_{TAR}$ = $C_{TV}$ = $C_{INT}$ = $C_{NBT}$ = $C_{NBT}$ =2.0×10<sup>-4</sup> mol L<sup>-1</sup>



Figure 3. Absorbance of V(IV)-TAR-TS extracts against blank vs. pH of the aqueous phase plots.  $C_{V(IV)}=2\times10^{-5} \text{ mol } L^{-1} \text{ (curves 1-5); } C_{TAR}=C_{TV}=C_{INT}=C_{NTC}=C_{NBT}=2.0\times10^{-4} \text{ mol } L^{-1} \text{ (curves 2-5); } C_{TAR}=3.2\times10^{-4} \text{ mol } L^{-1}, C_{TTC}=2.4\times10^{-4} \text{ mol } L^{-1} \text{ (curve 1)}$ 

#### **3 Results and Discussion**

Complex equilibria of vanadium(IV) with TAR were studied by Langova at al [29] in 30% v/v ethanol. The formation of a 1:1-chelate from pH>2.2 with  $\lambda_{max}$ = 545-550 and a molar absorptivity coefficient of 2.43×10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> was established. On the base of absorbance-pH curves analysis and the colour properties of the chelete (which are typical for unprotonated complexes) the authors rejected the existence of VOL and VO(LH)<sup>+</sup> (TAR=LH<sub>2</sub>). They demonstrated that the complex formation is considerably affected

by hydrolysis of the vanadium(IV) and concluded that  $V(OH)L^+$  is the most probable species at pH 4.5-5.5 [29]. Our investigations on the vanadium(IV) – TAR system were performed in the presence of TS, acetate buffer and slightly polar organic solvent (chloroform or dichloroethane). Ternary complexes, which are sparingly soluble in water, are formed and extracted into the organic phase after shaking for a short time. Chloroform was chosen for our further LLE-experiments, because of the instant phase separation and the possibility for making comparison with similar systems, which involve vanadium(V) [25-27] or 4-(2-pyridylazo)resorcinol (PAR) [30,31]. Having in mind that TSs participate in such complexes as cations (TT<sup>+</sup>, TV<sup>+</sup>, INT<sup>+</sup>, NBT<sup>2+</sup>) [25-28,30,31], one can conclude that the above mentioned cationic chelate V(OH)L<sup>+</sup> [29] is transformed to anionic before the formation of easily extracted ion-associate.

## 3.1 Absorption spectra, optimum conditions and molar absorptivitiy coefficients

Absorption spectra of V(IV)-TAR-TS ternary complexes at pH=4.95 are shown in Fig. 2. This relatively low pH-value (Fig. 3) was chosen in order to avoid a possible V(IV) $\rightarrow$ V(V) transformation caused by air oxygen; such oxidation is suspected for similar systems involving PAR at pH>5.05-5.1 [30,31]. The spectral maxima positions are relatively constant; they are situated at different wavelength (Table 1, Fig. 2) what is an indication that different TSs may stabilize different vanadium-containing anionic species, or/and some of the substituents on the tetrazolium ring(s) (e.g.  $-NO_2$ ) are capable of influencing the colour properties of the chromophore (anionic chelate). No evidence for V(IV) $\rightarrow$ V(V) oxidation has been noticed in the pH-absorbance curves (Fig. 3), in contrast to the systems with PAR [30,31]. However, one resemblance between the spectra of the two series (V(IV)-PAR-TS [30,31] and V(IV)-TAR-TS) should be pointed out: the absorption bands of the complexes which involve nitro-group containing TSs (NBT and INT) are wider (see Fig. 2 and Ref. 31).

Fig. 3 shows different pH regions for maximum and constant absorbance for the different complexes:  $5.35\pm0.05$ ,  $5.35\pm0.25$ ,  $4.9\pm0.2$ ,  $5.2\pm0.1$  and  $4.95\pm0.35$  for complexes involving TTC, TV, INT, NTC and NBT, respectively. The conclusion is that the most suitable TS for the LLE-spectrophotometric determination of V(IV) is NBT: i) The optimum pH-interval is the broadest; ii) The optimum pH-interval covers the most acidic media, hence, better selectivity is expected, the blank is lower, and there is no trouble with V(IV) aerial oxidation; iii) The sensitivity is the highest.

The last point is better elucidated in Table 1, where apparent molar absorptivity coefficients for the complexes of vanadium(IV) and vanadium(V) with TAR and TSs are included. It can be seen that NBT is the most sensitive auxiliary reagent for vanadium(IV), but the least sensitive for vanadium(V).

TS	V(IV)-TAR-TS			V(V)-TAR-TS [25-27]					
	pН	C <sub>TAR</sub> C <sub>TS</sub>	$\lambda_{max}$	ε"·10 <sup>-4</sup>	pН	C <sub>TAR</sub>	C <sub>TS</sub>	$\lambda_{max}$	ε'·10 <sup>-4</sup>
		$[mol L^{-1}] [mol L^{-1}]$	[nm]	[L mol <sup>-1</sup>		$[mol L^{-1}]$	$[mol L^{-1}]$	[nm]	[L mol <sup>-1</sup>
				cm <sup>-1</sup> ]					cm <sup>-1</sup> ]
TTC	5.3-5.4	3.2×10 <sup>-4</sup> 2.4×10 <sup>-4</sup>	550	1.70	4.3-5.3	2×10 <sup>-4</sup>	3×10 <sup>-4</sup>	550	2.37
TV	5.1-5.6	$2 \times 10^{-4}$ $2 \times 10^{-4}$	560	2.25	4.3-5.1	$2 \times 10^{-4}$	$2 \times 10^{-4}$	550	2.60
INT	4.7-5.1	$2 \times 10^{-4}$ $1.6 \times 10^{-4}$	550	2.35	4.3-5.1	$2 \times 10^{-4}$	$2 \times 10^{-4}$	550	2.56
NTC	5.1-5.3	1.6×10 <sup>-4</sup> 1.6×10 <sup>-4</sup>	555	2.60	4.5-5.0	$2 \times 10^{-4}$	3×10 <sup>-4</sup>	555	2.39
NBT	4.6-5.3	$2 \times 10^{-4}$ $2 \times 10^{-4}$	550	2.83	5.1-5.65	$2 \times 10^{-4}$	$2 \times 10^{-4}$	550	2.36

Table 1. Optimum operating conditions<sup>a</sup> and molar absorptivity coefficients for ternary complexes of vanadium(IV) and vanadium(V) [25-27] with TAR and TSs

a - optimum extraction time in all cases is 2 min

### 3.2 Composition of the complexes and reaction schemes

The molar PAR-to-V(IV) and TS-to-V(IV) ratios were determined by the methods of Asmus (Table 2) [32] and equilibrium shift [32] (Figures 4 and 5). The results show that TAR-to-V(IV) and TS-to-V(IV) ratios could be 1:1 or 2:1. Both of the ratios are constant and equal to 2 (straight lines 5 in Fig. 4 and Fig. 5) only when TS = NBT. In all the other cases stepwise complexation takes place.

Relatively simple are the complex formation schemes for the systems V(IV)-TAR-INT and V(IV)-TAR-TV. In the first case TAR-to-V(IV) ratio is constant and equal to 2 independently from the TAR concentration (Fig. 4, straight line 3; Table 2). In the second case TV-to-V(IV) ratio is constant and equal to 1 independently from the TV concentration (Fig. 5, straight line 2; Table 2).

In the rest systems V(IV)-TAR-TTC and V(IV)-TAR-NTC the complex formation takes place in two steps: TAR-to-V(IV) and TS-to-V(IV) ratios can be 1:1 or 2:1, depending on the reagent concentrations and pH. At low reagent concentrations ternary complexes with 1:1-ratios are extracted, while at high concentrations and pH ternary complexes with 2:1-ratios prevail (Fig. 4, dashed curves 1 and 4; Fig. 5, dashed curves 1 and 4; Table 2).



Figure 4. Determination of the TAR to V(IV) molar ratios by the equilibrium shift method.  $C_{V(IV)}=2\times10^{-5}$  mol L<sup>-1</sup>, pH=4.95 (curves 1-5);  $C_{TTC}=2.4\times10^{-4}$  mol L<sup>-1</sup> (curve 1),  $C_{TV}=C_{INT}=C_{NTC}=C_{NBT}=2.0\times10^{-4}$  mol L<sup>-1</sup> (curves 2-5)



Figure 5. Determination of the TS to V(IV) molar ratios by the equilibrium shift method.  $C_{V(IV)}=2\times10^{-5}$  mol L<sup>-1</sup>, pH=4.95 (curves 1-5);  $C_{TAR}=3.2\times10^{-4}$  mol L<sup>-1</sup> (curve 1),  $C_{TAR}=2.0\times10^{-4}$  mol L<sup>-1</sup> (curves 2-5)

Table 2. Determination of the TAR-to-V(IV) and TS-to-V(IV) molar ratios (n and m, respectively) by the Asmus method.  $C_{V(IV)}=2\times10^{-5}$  mol L<sup>-1</sup>, pH=4.95; obtained molar ratios are given in bold.

System	Correlation coefficient squired values (CC <sup>2</sup> ) corresponding to molar ratios 1, 2 and 3					
	TAR	:V(IV)	TS:V(IV)			
	Low TAR conc.	High TAR conc.	Low TS conc.	High TS conc.		
V(IV)-TAR-TTC	CC <sup>2</sup> =0.9971 <sup>a</sup> ( <b>n=1</b> )	$CC^2=0.9899^{b} (n=1)$	CC <sup>2</sup> =0.9990 <sup>c</sup> ( <b>m</b> =1)	$CC^2 = 0.9851^d (m=1)$		
	CC <sup>2</sup> =0.9824 <sup>a</sup> (n=2)	CC <sup>2</sup> =0.9999 <sup>b</sup> ( <b>n=2</b> )	CC <sup>2</sup> =0.9661 <sup>c</sup> (m=2)	$CC^2 = 0.9971^d (m=2)$		
	$CC^2 = 0.9470^a (n=3)$	$CC^2 = 0.9905^b (n=3)$	$CC^2 = 0.9275^c (m=3)$	$CC^2 = 0.9723^d (m=3)$		
V(IV)-TAR-TV	CC <sup>2</sup> =0.9996 <sup>e</sup> ( <b>n=1</b> )	$CC^2=0.9812^a$ (n=1)	$CC^2 = 0.9912^g (m=1)$			
	$CC^2 = 0.9667^e (n=2)$	CC <sup>2</sup> =0.9965 <sup>a</sup> ( <b>n=2</b> )	$CC^2 = 0.8940^g (m=2)$			
	$CC^2 = 0.9290^e (n=3)$	CC <sup>2</sup> =0.9794 <sup>a</sup> (n=3)	CC <sup>2</sup> =0.8303 <sup>g</sup> (m=3)			
V(IV)-TAR-INT	$CC^{2}=0.9$	$533^{h} (n=1)$	$CC^2 = 0.9985^i (m=1)$	$CC^2 = 0.9786^{j} (m=1)$		
	$CC^{2}=0.9$	$CC^2 = 0.9945^{h}$ (n=2)		$CC^2 = 0.9834^{j}$ (m=2)		
	$CC^{2}=0.9$	$467^{h}$ (n=3)	$CC^2 = 0.8651^i (m=3)$	$CC^2 = 0.9601^{j} (m=3)$		
V(IV)-TAR-NTC	$CC^2 = 0.9994^k (n=1)$	$CC^2 = 0.9595^1 (n=1)$	$CC=0.9965^{m} (m=1)$	$CC^2 = 0.9961^n (m=1)$		
	$CC^2 = 0.9713^k (n=2)$	$CC^2 = 0.9749^1$ ( <b>n=2</b> )	$CC=0.9725^{m}$ (m=2)	$CC^2 = 0.9997^n (m=2)$		
	$CC^2 = 0.9382^k (n=3)$	$CC^2 = 0.9544^1 (n=3)$	$CC=0.9228^{m}$ (m=3)	$CC^2 = 0.9993^n (m=3)$		
V(IV)-TAR-NBT	V(IV)-TAR-NBT $CC^2=0.9863^{\circ}$ (m=1)			$CC^2 = 0.9275^p (m=1)$		
	$CC^{2}=0.99$	$992^{\circ}$ (m=2)	$CC^2 = 0.9998^p (m=2)$			
	CC <sup>2</sup> =0.9888°(m=3)			$CC^2 = 0.9836^p (m=3)$		
a – TAR varies from $1.0 \times 10^{-5}$ mol L <sup>-1</sup> to $6.0 \times 10^{-5}$ mol L <sup>-1</sup> ; C <sub>TTC</sub> = $2.4 \times 10^{-4}$ mol L <sup>-1</sup>						
b - TAR varies from	b – TAR varies from $1.2 \times 10^{-4}$ mol L <sup>-1</sup> to $3.2 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>TTC</sub> = $2.4 \times 10^{-4}$ mol L <sup>-1</sup>					
c – TTC varies from 1	1.0×10 <sup>-5</sup> mol L <sup>-1</sup> to 6.0×1	0 <sup>-5</sup> mol L <sup>-1</sup> ; C <sub>TAR</sub> =3.2×1	$0^{-4} \text{ mol } L^{-1}$			
d – TTC varies from $6.0 \times 10^{-5}$ mol L <sup>-1</sup> to $2.4 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>TAR</sub> = $3.2 \times 10^{-4}$ mol L <sup>-1</sup>						
e – TAR varies from $4.0 \times 10^{-6}$ mol L <sup>-1</sup> to $6.0 \times 10^{-5}$ mol L <sup>-1</sup> ; C <sub>TV</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
f – TAR varies from 6	5.0×10⁻⁵ mol L⁻¹ to 2.0×1	$0^{-4} \text{ mol } L^{-1}; C_{TV} = 2.0 \times 10^{-1}$	$1^{-4} \text{ mol } L^{-1}$			
g – TV varies from 4.	$0 \times 10^{-6}$ mol L <sup>-1</sup> to 2.0×10	<sup>-4</sup> mol L <sup>-1</sup> ; C <sub>TAR</sub> =2.0×10	$^{-4}$ mol L <sup>-1</sup>			
$\tilde{h}$ – TAR varies from 1.0×10 <sup>-5</sup> mol L <sup>-1</sup> to 2.0×10 <sup>-4</sup> mol L <sup>-1</sup> ; C <sub>INT</sub> =2.0×10 <sup>-4</sup> mol L <sup>-1</sup>						
i – INT varies from $6.0 \times 10^{-6}$ mol L <sup>-1</sup> to $6.0 \times 10^{-5}$ mol L <sup>-1</sup> ; C <sub>TAR</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
j – INT varies from $6.0 \times 10^{-5}$ mol L <sup>-1</sup> to $1.6 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>TAR</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
k – TAR varies from $4.0 \times 10^{-6}$ mol L <sup>-1</sup> to $4.0 \times 10^{-5}$ mol L <sup>-1</sup> ; C <sub>NTC</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
$l - TAR$ varies from $4.0 \times 10^{-5}$ mol L <sup>-1</sup> to $1.2 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>NTC</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
m – NTC varies from $1.0 \times 10^{-5}$ mol L <sup>-1</sup> to $1.4 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>TAR</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
n – NTC varies from $1.0 \times 10^{-4}$ mol L <sup>-1</sup> to $1.4 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>TAR</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
o – TAR varies from $1.0 \times 10^{-5}$ mol L <sup>-1</sup> to $2.0 \times 10^{-4}$ mol L <sup>-1</sup> ; C <sub>NBT</sub> = $2.0 \times 10^{-4}$ mol L <sup>-1</sup>						
p – NBT varies from	1.0×10 <sup>-5</sup> mol L <sup>-1</sup> to 2.0×1	$10^{-4} \text{ mol } L^{-1}; C_{TAR} = 2.0 \times 10^{-1}$	$10^{-4} \text{ mol } \text{L}^{-1}$			
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It is known that  $VO^{2+}$  ( $[VO(H_2O)_5]^{2+}$ ) is the most common vanadium(IV)-form in acidic aqueous solutions [5,6,10,33]. The other reported cationic species are  $VOOH^+$ , ( $VO_2$ )( $OH_2^{2+}$  [33] and  $V(OH_2^{2+}$  [29]. At pH values higher than 3.2-3.5 (if  $C_{V(IV)}$  is in the interval from 10<sup>-5</sup> mol L<sup>-1</sup> to 10<sup>-4</sup> mol L<sup>-1</sup>) a neutral V(IV)-form  $VO(OH_2)$  prevails [33]. This form can be stable up to pH 6.3-6.4 [33], provided that precautions are taken to avoid aerial oxidation of V(IV) [34,35].

TAR can exist in several forms depending on pH [20,36]. In the pH-interval from 1.5 to 6.0 the most important TAR species are  $H_2L$  (absorbance maximum at 415-435 nm in chloroform) [20].

TSs dissociate in aqueous solution to form bulky organic cations having one or two positive charges for mono- and ditetrazolium salts respectively; complex formation schemes, in which ditetrazolium salts act as monotetrazolium salts have not been reported so far [28,31].

The molar ratios obtained (Fig. 4, Fig. 5, Table 2) and the known properties of V(IV), TAR and TSs, as outlined above, suggest the following scheme for complex formation in the most simple case (when TS=NBT):

$VO(OH)_2 + 2H_2L \leftrightarrow [VO(OH)_2L_2]^{4-} + 4H^+$	(1)
$[VO(OH)_2L_2]^{4+} + 2NBT^{2+} \leftrightarrow (NBT)_2[VO(OH)_2L_2]$	(2)
Probable formulae of the extracted ternary complexes in all the other cases are included in	Table 3.

LLE system	Molar ratios (V(IV):TAR:TS) and suggested formulae				
	1:1:1	1:2:1	1:2:2		
V(IV)-TAR-TTC-water-chloroform	(TT <sup>+</sup> )[VO(OH)L] <sup>b</sup>	-	$(TT^+)_2[V(OH)_2L_2]^a$ or/and		
			$(TT^+)_2[VOL_2]^a$		
V(IV)-TAR-TV-water-chloroform	(TV <sup>+</sup> )[VO(OH)L] <sup>b</sup>	$(TV^{+})[V(OH)L_2]^{a}$	not exists		
V(IV)-TAR-INT-water-chloroform	not exists	$(INT^{+})[V(OH)L_{2}]^{b}$	(INT <sup>+</sup> ) <sub>2</sub> [VOL <sub>2</sub> ] <sup>a</sup> or/and		
			$(INT^{+})_2[V(OH)_2L_2]^a$		
V(IV)-TAR-NTC-water-chloroform	_	$(NT^{2+})[VOL_2]^{b,c}$	$(NT^{2+})_2[VO(OH)_2L_2]^a$		
V(IV)-TAR-NBT-water-chloroform	not exists	not exists	$(NBT^{2+})_2[VO(OH)_2L_2]$		
, ,• <b>1•</b> .•					

Table 3. Probable formulae of the extracted ternary complexes

a – at optimum conditions

b – with low reagent excess

c - at lower pH

### 3.3 Other LLE-spectrophotometric characteristics for the V(IV)-PAR-NBT-water-chloroform system

NBT appears to be the best TS for the LLE-spectrophotometric determination of vanadium(IV). That is why some additional investigations on the V(IV)-PAR-NBT-water-chloroform system were performed. The constant of association characterizing equation 2 was calculated by the Komar-Tolmachev method [32]. For this purpose various volumes of  $2 \times 10^{-4}$  mol L<sup>-1</sup> aqueous solutions of vanadium(IV) and NBT were mixed in 1:2 ratio and the extraction procedure was performed in the presence of buffer solution (pH=4.75) and constant TAR concentration (C<sub>TAR</sub>= $2 \times 10^{-4}$  mol L<sup>-1</sup>). The following straight line equation (Y=aX+b) was obtained: Y= $5.94 \times 10^{-6}$ X +  $3.345 \times 10^{-5}$ . It allows the calculation both of the association constant  $\beta$  and of the true molar absorptivity of the complex ( $\epsilon$ =1/b). The value of  $\epsilon$  thus obtained:  $\epsilon$ = ( $3.0\pm0.1$ )×10<sup>4</sup> L mol<sup>-1</sup> cm<sup>-1</sup> is close to that calculated using Beer's law at the optimum reagent concentrations and pH (see Table 1). This is an indication of the correctness of the suggested equations and of the absence of serious side-reactions [32].

The constant of distribution expressed as  $K_D = [(NBT)_2[VO(OH)_2L_2]]_{org} / [(NBT)_2[VO(OH)_2L_2]]_{aq}$  was determined by comparison of the absorbance values obtained after single extraction (A<sub>1</sub>) and triple extraction (A<sub>3</sub>) in equal volume (25 mL) [27]:  $K_D = A_1/(A_3 - A_1)$ . The recovery factor R% was calculated by the formula R=100×K<sub>D</sub>/(K<sub>D</sub>+1). The constant of extraction expressed as  $K_{ex} = [(NBT)_2[VO(OH)_2L_2]]_{org} / [[VO(OH)_2L_2]^{4-}]_{aq} \times [NBT^{2+}]_{aq}^2$  was calculated by the equation  $LogK_{ex} = Log\beta + LogK_D$ .

The values of the mentioned equilibrium constants are shown in Table 4; they are juxtaposed with those for similar systems, which involve PAR [30,31] or vanadium(V) [25-27].

Equilibrium	Extraction system					
constant	V(IV)-TAR-NBT-water-	V(IV)-PAR-NBT-water-	V(V)-TAR-NBT-water-			
	chloroform	chloroform <sup>a</sup>	chloroform <sup>b</sup>			
LogK <sub>ex</sub>	11.7±0.8	10.8±0.9	8.4±0.4			
Logβ	10.6±0.8	9.5±0.9	7.7±0.4			
LogK <sub>D</sub>	$1.05\pm0.01$	$1.27\pm0.01$	$0.691 \pm 0.001$			

94.47±0.07

83.09±0.01

 Table 4. Equilibrium constants for V(IV)-TAR-NBT-water-chloroform and V(IV)-PAR-NBT-water-chloroform [31]

 and V(V)-TAR-NBT-water-chloroform [27] ( 95% probability).

a – suggested formula of the extracted complex is  $(NBT)_2[VO(OH)_2(PAR)_2]$  [31]

b – suggested formula of the extracted complex is  $(NBT)_3[VO_2(TAR)_2]_2$  [27]

91.87±0.06

#### 4 Conclusions

R%

1. V(IV) forms ternary ion-associated complexes with TAR and TSs which are efficiently extractable into chloroform.

2. V(IV) and TAR can form several anionic species in the presence of TSs. Ternary ion-association complexes with different composition could be obtained, varying TS, concentration of the reagents and pH.

3. NBT is the best auxiliary reagent for V(IV): a) only one complex with suggested formula  $(NBT)_2[VO(OH)_2(TAR)_2]$  is extracted into organic phase; b) the molar absorptivity of this complex is the highest:  $\epsilon'_{550}=2.83 \times 10^4$  L mol<sup>-1</sup>cm<sup>-1</sup>; c) the pH-range for its maximum extraction is the broadest (from pH=4.6 to 5.3) and allows work in the most acidic media.

4.  $(NBT)_2[VO(OH)_2(TAR)_2]$  is more stable (Log  $\beta$ =10.6) and extractable (K<sub>ex</sub>=11.7) than the similar complexes with participation of PAR or vanadium(V) and could be recommended for LLE-spectrophotometric determination of vanadium (after preliminary investigations on the interfering effect of the matrix components).

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