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TERNARY ION-ASSOCIATED COMPLEXES OF VANADIUM(IV) WITH 4-(2-PYRIDYLAZO)-RESORCINOL AND TETRAZOLIUM SALTS. LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC INVESTIGATIONS

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Abstract

The complex formation and liquid-liquid extraction in the vanadium(IV) – 4-(2-pyridylazo)-resorcinol (PAR) – tetrazolium salt {TS: 2,3,5-triphenyl-2H-tetrazolium chloride, 3-(1-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride} – water – chloroform system have been studied. The optimum extraction-spectrophotometric conditions (pH, concentration of the reagents, extraction time, wavelength), composition of the complexes (V:PAR:TS=1:2:2), molar absorptivities (ε) and constants of association (β) between the vanadium(IV) – PAR anionic chelate {$VO(PAR)_2^{2-}$} and the tetrazolium cation (TS^+) have been determined. The results have been compared with those for similar complexes of vanadium(V).

Introduction

Vanadium(V) is known to form ternary complexes with 4-(2-pyridylazo)-resorcinol (PAR) and tetrazolium salts (TS) [1-3]. Intense color of the complexes and big differences in their solubility in water and organic solvents favors their practical applications. Several extraction-spectrophotometric procedures for vanadium(V) determination and vanadium(IV,V) valence speciation have been reported [3]. However, vanadium(IV) has been determined indirectly from the difference in the absorbance of V(V)-PAR-TS complex measured in the presence and absence of the oxidizing agent, which oxidised V(IV) to V(V). In order to find a better way for V(IV) determination we decided to investigate the complex formation and liquid-liquid extraction in the V(IV) – PAR – TS system. There is no information in the literature about characteristics of such complexes and optimum conditions of their existence.

Experimental

Reagents and apparatuses: $VOSO_4.5H_2O$ from Fluka, *purum*, as a 5×10^{-2} mol/dm^3 stock aqueous solution. The working 2×10^{-4} mol/dm^3 aqueous solutions acidified with sulphuric acid to pH=2-3 were prepared every day; PAR from Fluka, *pro analysis*, as a 2×10^{-3} mol/dm^3 aqueous solution; TS: 2,3,5-triphenyl-2H-tetrazolium chloride (TTC), 3-(1-naphtyl)-2,5-diphenyl-2H-tetrazolium chloride (TV) and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) from Loba Feinchemie AG, *pro analysis*, as 3×10^{-3} mol/dm^3 aqueous solutions; and chloroform, redistilled. The acidity of aqueous medium was set by the addition of buffer solution, prepared by mixing 0.1 mol/dm^3 aqueous solutions of CH_3COOH and CH_3COONa. The resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 UV/Vis spectrophotometer, equipped with 5 mm path-length cells, was employed for reading the absorbance.

Procedure: Aliquots of V(IV) solution, buffer solution, PAR solution and TS solution were introduced into 125-cm^3 separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 cm^3. Then 10 cm^3 of organic solvent were added and the funnels were shaken for 1.5 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

It is known that in aqueous medium V(IV) forms two binary 1:1-complexes with PAR (H_2L): $[VO(HL)]^+$ and $[VO(L)]^0$ [4]. The first complex is formed in pH region 1.0- 4.8 and has a molar absorptivity coefficient of $\varepsilon'=1.65\times10^4$ dm^3/mol.cm at $\lambda_{max}=520$ nm. At higher pH values the second complex ($\lambda_{max}=540$ nm, $\varepsilon'=3.3\times10^4$ dm^3/mol.cm) is formed. At similar conditions (pH 4.5-8.0) V(V) forms anionic complex $[VO_2(L)]^-$ with slightly higher molar absorptivity: $\varepsilon'=(3.6\text{-}3.7)\times10^4$ dm^3/mol.cm at $\lambda_{max}=545$ nm [4,5]. Since V(IV) is oxidized by air oxygen in slightly acidic and neutral media [2,4-6] a conclusion has been drawn for V(V)-complex formation at pH 5.2 [6] or 6.0 [4] independently from the original vanadium oxidation state.

Absorption spectra of V(IV)-PAR-TS ternary complexes in chloroform are shown in Fig. 1. At pH values from 3.5 to 5.2 the maximum is at $\lambda=557$ nm for all investigated TS. This maximum is shifted with 17 nm as compared to the maximum of $[VO(L)]^0$ in aqueous medium. The observed bathochromic effect is similar to that noticed in [7,8] for V(V)-PAR-TS-water-chloroform systems (equation 1):

$$\underset{545\text{ nm}}{\{[VO_2L_2]^{3-} + 3TS^+\}_{aq}} \rightarrow \underset{560}{\{(TS)_3[VO_2L_2]\}_o} \qquad (1)$$

and gives us grounds to assume that it is provided by the formation of a similar ternary ion-associated complexes of V(IV).

At pH >5.1 the absorption maximum of V(IV)-PAR-TS is gradually shifted to 560 nm (Fig. 1) what is an indication for V(IV)→V(V) conversion [2,4-6]. Another proof for V(V)-complex existence at pH >5.1 could be seen in Fig. 2. All pH-curves visibly change their trends: the absorbance values at pH>5.1 increase in some extent what can be attributed to the higher molar absorptivity of V(V)-PAR-TS complexes.

The molar PAR-to-V(IV) and TS-to-V(IV) ratios were determined at pH=4.8 by the method of Asmus [9] (Fig. 3) and equilibrium shift method [9] (Fig. 4). The results showed that 1:2:2-complexes {V(IV):PAR:TS} are formed at the optimum reagent concentrations: $C_{PAR}=1\times10^{-4}$ mol/dm^3 and $C_{TS}=2\times10^{-4}$ mol/dm^3 (5-fold and 10-fold excess respectively). Therefore, the following equations for complex formation could be suggested:

$$VO^{2+} + 2L^{2-} \Leftrightarrow [VOL_2]^{2-} \qquad (2)$$

$$[VOL_2]^{2-} + 2TS^+ \Leftrightarrow (TS)_2[VOL_2] \qquad (3)$$

The constants of formation (β) characterising the association process (eq. 3) and the true molar absorptivities of the complexes (ε) were determined by the method of Komar-Tolmachev [9] (Fig. 5). The apparent molar absorptivities (ε') were determined by using Beer's law in the concentration range from 2.0×10^{-6} to 3×10^{-5} mol/dm^3 V(IV). Obtained information, along with information for V(V)-complexes taken from Ref. [3,8] is presented in Table 1. All calculations were carried out for the 95% probability.

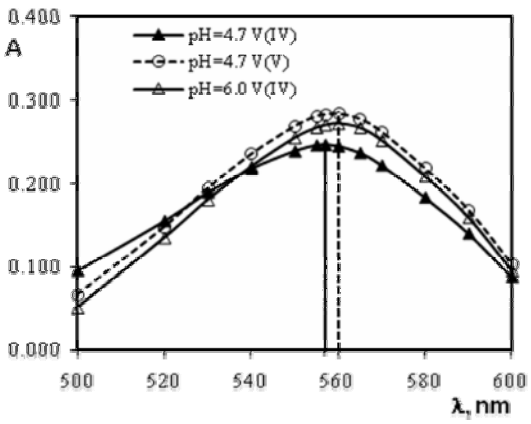


Figure 1. Absorption spectra of V(IV)-PAR-INT and V(V)-PAR-INT complexes in chloroform. $C_V=1.4\times10^{-5}$ mol/dm^3, $C_{PAR}=C_{TS}=2\times10^{-4}$ mol/dm^3, l=0.5 cm.

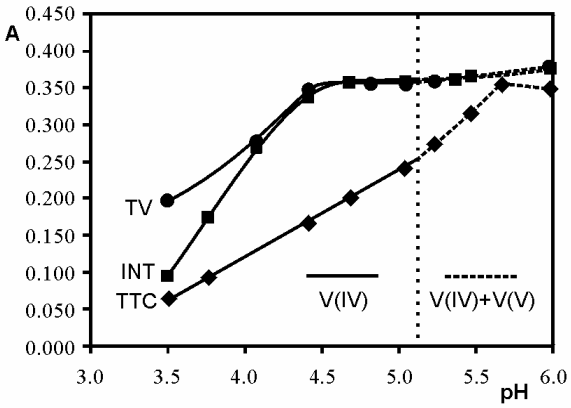
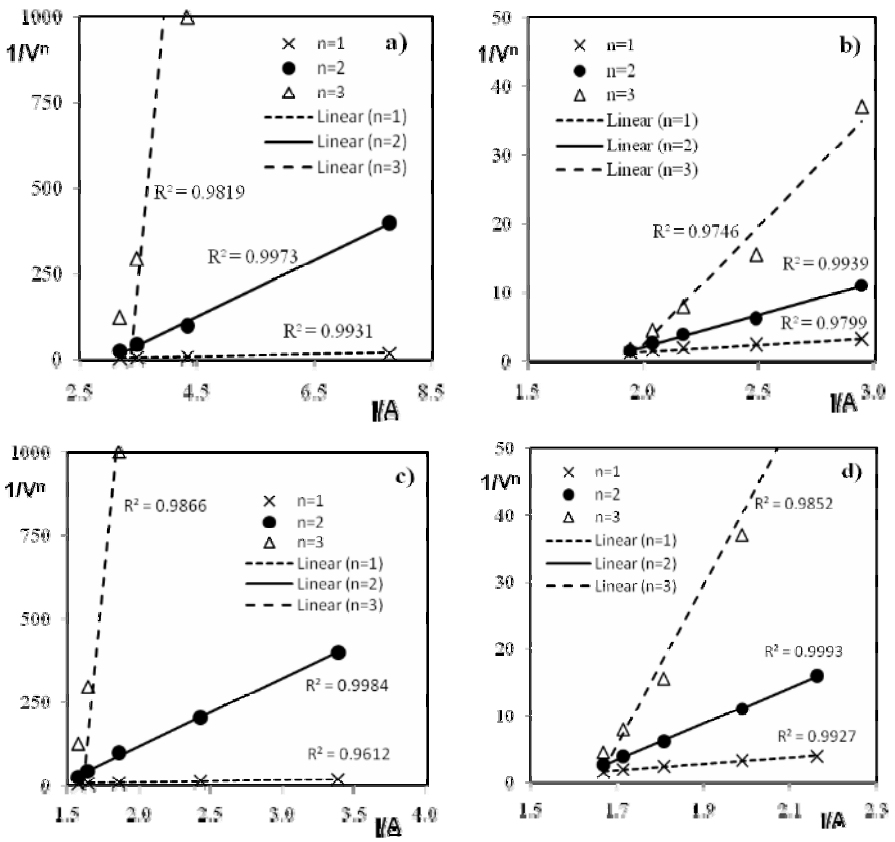


Figure 2. Absorbance of V(IV)-PAR-TS complexes in chloroform vs. pH of the aqueous phase plots. $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{PAR}=C_{TS}=2\times10^{-4}$ mol/dm^3, l=0.5 cm.



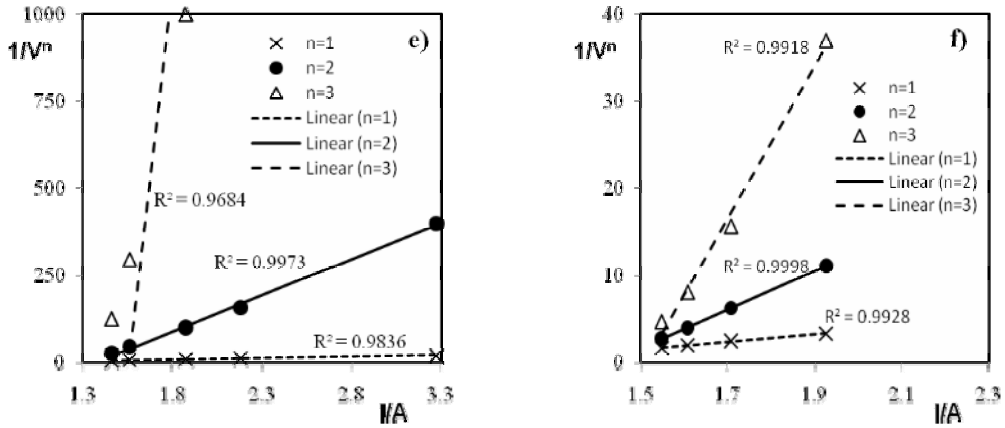


Figure 3. Determination of the reagent(R)-to-V(IV) molar ratio by the Asmus' method.
a) R=PAR, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{TTC}=2\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm;
b) R=TTC, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{PAR}=2\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm;
c) R=PAR, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{INT}=2\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm;
d) R=INT, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{PAR}=2\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm;
e) R=PAR, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{TV}=3\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm;
f) R=TV, $C_{V(IV)}=2\times10^{-5}$ mol/dm^3; $C_{PAR}=2\times10^{-4}$ mol/dm^3, pH=4.8, l=0.5 cm

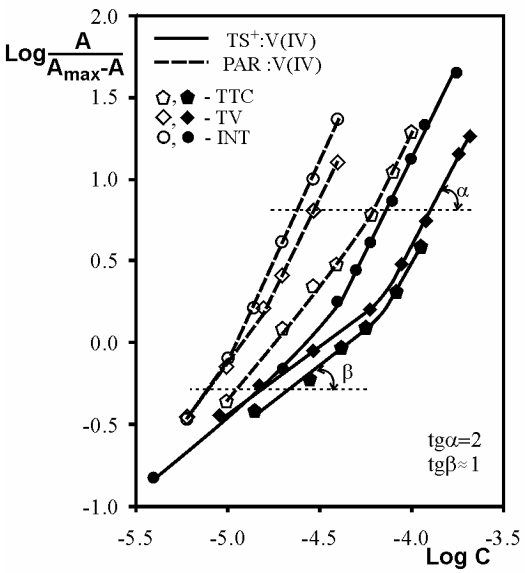


Figure 4. Determination of the TS-to-V(IV) and PAR-to-V(IV) molar ratios by the Equilibrium shift method. $C_{V(IV)}=2\times10^{-5}$ mol/dm^3, pH=4.8, l=0.5 cm

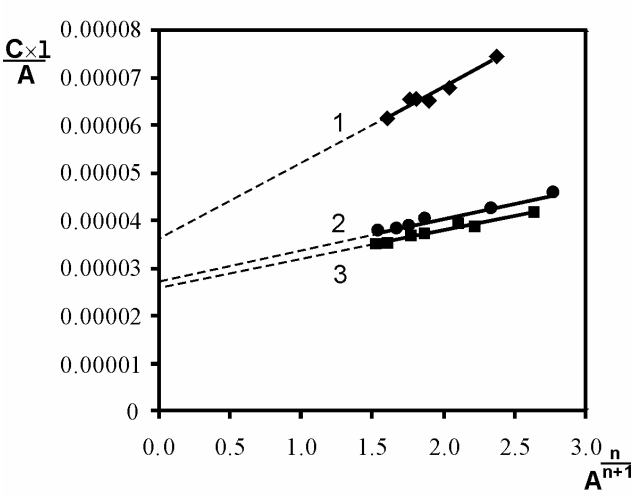


Figure 5. Determination of the constants of association (β) and true molar absorptivities (ε) by the method of Komar-Tolmatchev. $C_{PAR}=2\times10^{-4}$ mol/dm^3, $C_{TS}=2\times C_{V(IV)}$. The following straight lines equations were obtained: $Y=1.46\times10^{-6}X + 3.751\times10^{-5}$ (line 1: TTC), $Y=6.241\times10^{-6}X + 2.81\times10^{-5}$ (line 2: TV) and $Y=6.085\times10^{-6}X + 2.61\times10^{-5}$ (line 3: INT)

Table 1. Molar absorptivity coefficients, constants of association (β) and optimum pH for ternary complexes of V(IV) and V(V) with PAR and TS

Ternary complexes		pH	Molar Absorptivity [dm^3/mol cm]		Log β
			Apparent (ε')	True (ε)	
V(IV)	$(TT)_2[VO(PAR)_2]$	5.1	$(2.6\pm0.1)\times10^4$	$(2.7\pm0.2)\times10^4$	8.9±0.8
	$(TV)_2[VO(PAR)_2]$	4.5-5.1	[a]$(3.6\pm0.1)\times10^4$	$(3.5\pm0.1)\times10^4$	9.9±1.0
	$(INT)_2[VO(PAR)_2]$	4.5-5.1	[a]$(3.6\pm0.1)\times10^4$	$(3.8\pm0.2)\times10^4$	9.8±1.0
V(V) [3,8]	$(TT)_3[VO_2(PAR)_2]$	4.8-6.2	$(3.44\pm0.05)\times10^4$	$(3.22\pm0.05)\times10^4$	14.7±0.4
	[b]$(TV)_3[VO_2(PAR)_2]$	5.2-6.3	$(4.0\pm0.1)\times10^4$	$(4.14\pm0.02)\times10^4$	16.4±1.8
	$(INT)_3[VO_2(PAR)_2]$	5.5-7.5	$(3.9\pm0.1)\times10^4$	$(3.66\pm0.05)\times10^4$	14.8±0.4

a-Beer's law is valid from 0.2 to 1.5 μg/cm^3 vanadium(IV), Limit of detection $(LOD)_{3\sigma}$ = 0.06 μg/cm^3
b-extracted in dichloroethane

Conclusion

1. V(IV) forms well extractable in chloroform ternary ion-associated 1:2:2 complexes with PAR and TS^+ (TT^+, INT^+, TV^+) with λ_{max}=557 nm which tend to be oxidised to V(V)-complexes at pH>5.1 by air oxigen.

2. The ion-associates with TV^+ and INT^+ have similar characteristics and stability. They have higher molar absorptivity than the V(IV)-PAR [4], V(IV)-TAR [11] and V(IV)-TAC-ascorbic acid [12] complexes and could be used for direct V(IV) determination.

3. The V(IV)-PAR-TT complex is rather unstable. The big difference in the stability of this complex and the V(V)-PAR-TT complex make perspective special investigations on development of a procedure for V(IV)/V(V) speciation based on the model [7,10].

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