Research Article

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Complex formation in a liquid-liquid extraction-chromogenic system for vanadium(IV)

<https://doi.org/10.1515/chem-2019-0071>

received June 25, 2018; accepted March 30, 2019.

Abstract: The azo dye 4-(2-thiazolylazo)orcinol (TAO) and the cationic ion-pair reagent 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) were examined as constituents of a water-chloroform extraction-chromogenic system for vanadium(IV). The effects of TAO concentration, TTC concentration, pH and extraction time were examined. Under the optimum conditions the extracted complex has a composition of 1:2:1 (V:TAO:TTC). The absorption maximum, molar absorptivity and constant of extraction were determined to be $\lambda_{\max}=544$ nm, $\varepsilon_{544}=1.75 \times 10^4$ dm³ mol⁻¹ cm⁻¹ and $\text{Log } K_{\text{ex}}=4.1$. The ground state equilibrium geometries of the possible monoanionic V^{IV}-TAO 1:2 species were optimized by the HF method using 3-21G* basis functions. Their theoretical time dependent electronic spectra were simulated and compared with the experimental spectrum. The best fit was obtained for the structure in which one of the TAO ligands is tridentate, but the other is monodentate (bound to V^{IV} through the oxygen which is in the ortho-position to the azo group) and forms a hydrogen bond N–H...O=V through its protonated heterocyclic nitrogen. Based on this unusual structure, which can explain some peculiarities of the complex formation between V^{IV} and commonly used azo dyes, the ground state equilibrium geometry of the whole ternary 1:2:1 complex was computed at the HF and BLYP levels.

Keywords: azo dye; tridentate/monodentate coordination; ternary complex; hydrogen bond; HF and DFT calculations.

1 Introduction

Vanadium occupies position 23 in the periodic table. It is the fifth most abundant transition element in the Earth's crust and has applications in many industries. Apart from natural processes, such as volcanic activity, wild forest fires, continental dust and marine aerosols formation, vanadium compounds can enter the biosphere as a result of burning crude petroleum and coal, mining, processing of ores, steel refining, production of dyes, glasses, ceramics and alloys, and its use as a catalyst in large-scale processes [1, 2]. Various hazards are associated with elevated concentrations of vanadium in the environment [3]. On the other hand, health disorders can arise from vanadium deficiency [2, 4]. The window between beneficial and toxic action of this element is not well defined and depends on many factors, including the oxidation state. For example V^V can be almost as toxic as lead, cadmium, and mercury [5], while vanadyl(IV) sulfate is a common supplement (Vana Trace) used to enhance weight training in athletes [6, 7]. Uncertainties in the correlation between toxicity–oxidation state and toxicity–ligand system [8-10], along with vanadium's stereochemical flexibility [11, 12] define the necessity for thorough investigations on its coordination chemistry. In addition, it is important to develop reliable methods for determining V^{IV} and V^V in their joint presence [13-15].

In a previous paper [16] we characterized the coordination compound formed in a liquid-liquid extraction-chromogenic system containing V^V, 4-(2-thiazolylazo)orcinol (TAO) and 2,3,5-triphenyl-2H-tetrazolium chloride (TTC). We discussed the special features of the extracted 2:2:2 complex and highlighted the differences between it and other complexes with related azo dyes (AD) [17-20]. Here we describe a similar water-chloroform extraction system containing V^{IV} instead of V^V.

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The structural formulae of the reagents TAO and TTC are shown in Figure 1.

It should be noted that ternary complexes of V^{IV} with ADs have been less studied. Moreover, the conclusions drawn are not always convincing enough due to the possibility of oxidation of V^{IV} by the oxygen in air [21, 22]; lower stability of the complexes [23, 24]; inconsistencies associated with the opinion that ADs, such as 4-(2-thiazolylazo)resorcinol (TAR) and 4-(2-pyridylazo)resorcinol (PAR), act as tridentate ligands [25-28]; the experimentally determined molar V^{IV} :AD ratios (e.g. 1:2) [21, 24, 29]; the stability of the V=O bond, which is likely to remain unaffected in the process of complex formation [30] and the common coordination numbers of V^{IV} (5 and 6) [31].

In the interpretation of the obtained experimental results, we used information for the complex formation between V^{IV} and ADs in the presence [32-35] or absence [23, 35-38] of auxiliary reagents. We suggested several structures of the chromogenic anionic part of the extracted species. To evaluate them, we compared the theoretically simulated spectra and the experimentally obtained spectrum. This approach is known to give good results [39] and can be especially useful for complexes that are easily altered in attempts to be isolated in solid state.

For stabilization of V^{IV} reducing reagents, such as ascorbic acid (AA), are often added [14, 33]. However, AA can enter the coordination entity and form ternary complexes in similar systems [33]. On the other hand, the reducing reagent can convert the tetrazolium salt to formazan [40]. In order to avoid the possibility of such side processes, no additional stabilizing reagents of V^{IV} were used in the present work.

2 Methods

2.1 Reagents and Apparatus

Stock V^{IV} aqueous solution (5×10^{-2} mol dm $^{-3}$) was prepared from $VOSO_4 \cdot 5H_2O$ (Fluka, purum) and standardized by potassium permanganate titration. Working 2×10^{-4} mol dm $^{-3}$ solutions with pH 2-3 were prepared every day by an appropriate dissolution of standard solution in the presence of H_2SO_4 . TAO (95%, Sigma-Aldrich Chemie GmbH) was dissolved in dilute KOH; the obtained neutral aqueous solution was at concentration of 3×10^{-3} mol dm $^{-3}$. TTC (p.a. Loba Feinchemie GMBH) was dissolved in water ($c_{TTC} = 4.7 \times 10^{-3}$ mol dm $^{-3}$) and stored in a dark place. The acidity of the aqueous medium was set by the addition

Figure 1: Structural formulae of the reagents TAO (a) and TTC (b).

of buffer solution, prepared by mixing 2.0 mol dm $^{-3}$ aqueous solutions of CH_3COOH and NH_4OH . The pH was checked using a Hanna HI-83141 (Romania) and a WTW InoLab 7110 (Germany) instruments. Distilled water and additionally distilled commercial chloroform (p. a.) were used throughout the work. Absorbance measurements were performed using a Camspec M508 or a Ultrospec3300 pro UV-Vis spectrophotometers (UK), equipped with 1 cm path-length glass cells. All experiments were performed in an air conditioned laboratory at $22 \pm 1^\circ C$.

2.2 Procedure

Solutions of V^{IV} , TAO, buffer (2 cm 3 ; pH 3.5 – 6.4) and TTC were placed into a separatory funnel. The resulting mixture was diluted with water to a total volume of 10 cm 3 ; the corresponding concentrations of V^{IV} , TAO and TTC in the aqueous phase were 2×10^{-5} mol dm $^{-3}$, $(0.60 - 14.3) \times 10^{-4}$ mol dm $^{-3}$ and $(0.24 - 14.1) \times 10^{-4}$ mol dm $^{-3}$ respectively. Then 10 cm 3 of chloroform was added and the funnel was shaken for a fixed time period. After a short wait for phase separation (ca. 10 – 15 seconds), a portion of the organic extract was transferred (through a filter paper impregnated with chloroform) into the spectrophotometer cell. The absorbance was measured against a simultaneously prepared blank solution.

2.3 Theoretical calculations

The ground-state equilibrium geometries of the anionic complexes were optimized at the Hartree-Fock (HF) level of theory using 3-21G* basis functions. The charge and the spin multiplicity were set as -1 and doublet, respectively. Subsequently, at the same level, the vertical excitation energies of the anions were calculated. The structure of the 2,3,5-triphenyl-2*H*-tetrazolium cation (TT^+) was also optimized. Then the whole ternary complex was constructed and optimized at the same level (HF) and by means of BLYP functional based on DFT theory. All calculations were performed with the GAUSSIAN 03 program package (Gaussian, Inc., Wallingford CT, 2004). The output files were visualized by means of the ChemCraft program (v. 1.8, b. 523a, <http://www.chemcraftprog.com>).

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and discussion

3.1 Absorption spectra

V^{V} forms an anionic 1:1-chelate with TAO in a water-ethanol medium [16]. In the presence of tetrazolium salt, a neutral chloroform-extractable ion-associate is formed. During its extraction dimerization occurs, the final product being a 2:2:2 complex [16, 41]. When the tetrazolium salt is TTC, the optimum pH interval for complex formation is 4.8–5.2. The absorption maximum in chloroform lies at 545 nm and its position is slightly affected by changes in pH and reagent concentrations [16].

Absorption spectra of V^{IV} –TAO–TTC extracts in the same solvent are shown in Figure 2, curves 1–3. In contrast to the system with V^{V} (curve 4), spectral differences are observed with changing experimental conditions. Except for competitive TAO–TTC ion-pair formation [42, 43], several other reasons can cause spectral differences: isomerism, hydrolysis and changes in the composition and/or oxidation state [44, 45]. In order to clarify the running processes, we collected additional information for the effects of pH and reagent concentrations.

3.2 The effect of pH and reagents concentrations

The effect of pH is shown in Figure 3 for two different TAO concentrations. At $c_{\text{TAO}} = 3.4 \times 10^{-4} \text{ mol dm}^{-3}$ and c_{TTC}

Figure 2: Absorption spectra of V^{IV} (1–3) and V^{V} (4) extracts against blank; $c_{\text{V}} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, extraction time $t = 2 \text{ min}$.

(1) $c_{\text{TAO}} = 5.4 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 1.4 \times 10^{-3} \text{ mol dm}^{-3}$, pH 4.9;
 (2) $c_{\text{TAO}} = 1.1 \times 10^{-3} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 1.4 \times 10^{-3} \text{ mol dm}^{-3}$, pH 5.2;
 (3) $c_{\text{TAO}} = 4.5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 9.4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 5.0;
 (4) $c_{\text{TAO}} = 4.5 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 9.4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 5.2.

Figure 3: Absorbance of the complex (1, 2) and blank (1') in chloroform vs pH of aqueous phase; $c_{\text{V}} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, extraction time $t = 2 \text{ min}$, $\lambda = 544 \text{ nm}$.

(1, 1') $c_{\text{TAO}} = 5.4 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 7.1 \times 10^{-4} \text{ mol dm}^{-3}$;
 (2) $c_{\text{TAO}} = 3.4 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{TTC}} = 9.4 \times 10^{-4} \text{ mol dm}^{-3}$.

$= 9.4 \times 10^{-4} \text{ mol dm}^{-3}$ (the optimum concentrations for V^{V} extraction [16]) the absorbance of the V^{IV} –TAO–TTC complex is maximal for pH-values between 5.0 and 5.9 (series 2). This interval is different and wider than those for the V^{V} complex mentioned above. At higher TAO concentrations, the optimum pH-interval is expanded even more (series 1). These observations are consistent with the literature [35] (devoted to V^{IV} / V^{V} –PAR complexes) and indicate that different complexes are formed with V^{V} and V^{IV} . In addition, it can be concluded from Figure 3 that the complexes of V^{IV} are at least two.

a

b

Figure 4: Absorbance of extracted species vs concentration of TAO (a) and TTC (b); $c_v = 2 \times 10^{-5} \text{ mol dm}^{-3}$, extraction time $t = 2 \text{ min}$, $\lambda = 544 \text{ nm}$.

a) $c_{\text{TTC}} = 9.4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 5.2 (1) or 4.9 (2);

b) $c_{\text{TAO}} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ (1) or $5.4 \times 10^{-4} \text{ mol dm}^{-3}$ (2), pH 5.2 (1) or 4.9 (2).

The fact that both pH and c_{TAO} play an important role in the complex formation mechanism can also be seen in Figure 4a. The saturation series 1 (for pH 5.2) is atypical; a well-defined fall of the absorbance is visible for c_{TAO} ca. $(6 - 8) \times 10^{-4} \text{ mol dm}^{-3}$. However, the series 2 (for pH 4.9) is simpler. It is characterized by a maximum at $c_{\text{TAO}} = 5.4 \times 10^{-4} \text{ mol dm}^{-3}$. This concentration is about 2.5 times smaller than the concentration needed to obtain the same absorbance at pH 5.2.

Figure 4b shows the effect of c_{TTC} on the absorbance. The series for both pH values are almost identical. They allow for a reliable determination of the molar $\text{TTC} : \text{V}^{\text{IV}}$ ratio by different methods.

Figure 5: Determination of the R-to- V^{IV} molar ratio by the mobile equilibrium method. The experimental conditions are given in Fig. 3.

(1) $\text{R} = \text{TAO}$, pH 4.9;

(1') $\text{R} = \text{TAO}$, pH 5.2;

(2) $\text{R} = \text{TTC}$, pH 4.9;

(2') $\text{R} = \text{TTC}$, pH 5.2.

Straight line equations: (1) $y = 1.94x + 7.35$; (1') $y = 1.03x + 3.51$; (2) $y = 1.07x + 4.32$; and (2') $y = 1.07x + 4.22$.

3.3 Complex stoichiometry

The mobile equilibrium method [46] (Figure 5, lines 2 and 2') and the straight-line method of Asmus [47] showed that $n_{\text{TTC}} : n_v = 1:1$ irrespective of pH. The same two methods were used to determine the $\text{TAO-to-V}^{\text{IV}}$ molar ratio at pH 4.9. They demonstrate that $n_{\text{TAO}} : n_v = 2:1$ (Figure 5, line 1). However, the determination of $n_{\text{TAO}} : n_v$ for pH 5.2 was impeded by the above-mentioned absorbance fall. The results for the low TAO concentrations, $(1.4 - 4.3) \times 10^{-4} \text{ mol dm}^{-3}$, indicate that $n_{\text{TAO}} : n_v = 1:1$ (Figure 4, line 1').

The application of the Bent-French limited logarithm method [48] (Figure 6, straight line 1) for the same concentration interval led to a slope of 0.65. This slope is significantly smaller than the integer value of 1. On the other hand, it is known that the method gives best results (integer values) when (i) the complex is unstable, (ii) the metal concentration is low and (iii) the reagent excess is small [44, 45]. If these conditions are not met, the obtained slope is smaller. Consequently, the molar $n_{\text{TAO}} : n_v$ ratio is 1:1, a result consistent with the mobile equilibrium method (Figure 5, line 1'). For the concentration interval $(4.3 - 5.7) \times 10^{-4} \text{ mol dm}^{-3}$ (or $-\text{Log } c_{\text{TAO}}$ between 3.37 and 3.24) the slope is different (1.6; straight line 2). This value shows that most probably $n_{\text{TAO}} : n_v = 2:1$. To the best of our knowledge, there are no reports for coordination compounds of $\text{V}^{\text{IV/V}}$ and ADs with $n_{\text{AD}} : n_v > 2 : 1$ and such

Figure 6: Application of the Bent-French limited logarithm method for determination of the TAO-to- V^{IV} molar ratio at pH 5.2. $c_V = 2 \times 10^{-5}$ mol dm $^{-3}$, $c_{TTC} = 9.4 \times 10^{-4}$ mol dm $^{-3}$, extraction time $t = 2$ min, $\lambda = 544$ nm.

ratios are characteristic for heavier elements e. g. Eu^{III} , Ho^{III} , Hf^{IV} and Th^{IV} [27].

From the experimental results, it is not possible to determine the complex composition in the region of the absorbance fall, i.e. c_{TAO} ca. $(6 - 8) \times 10^{-4}$ mol dm $^{-3}$, nor to draw explicit conclusions about its origin. Assuming that there is no change in the composition with further increase in c_{TAO} ($n_{TAO} : n_V = 2:1$), two explanations seem possible: (i) change in the chromophore system (isomerism, hydrolysis, protonation, etc.) or (ii) decrease in the extraction rate due to formation of non-extractable charged complexes. The second explanation is not very likely because the 2,3,5-triphenyl-2*H*-tetrazolium cation (TT^+) is known to form neutral chloroform-extractable complexes with high-charge anions of the type $[VO_2(PAR)_2]^{3-}$ [20] and $[VO_2(TAR)_2]^{3-}$ [19].

3.4 State of the reactants and possible formulae of the extracted species

In order to determine the most likely formulas of the extracted complexes, it is necessary to know the state of the reactants in the reaction mixture.

TAO is a triprotic acid (H_3TAO^+) giving up its first proton (that at the heterocyclic nitrogen) in an acidic medium. Under the experimental pH it probably exists mainly as H_2TAO with two protonated oxygen atoms. According to Menek et al. [49], the pK_2 and pK_3 values of TAO for aqueous medium are 5.7 and 11.8, respectively (pK_2

refers to the p-OH and pK_3 refers to the o-OH). However, in the presence of a cationic surfactant these pK_a values get lower due to ion-pair formation [49].

TTC dissociates to TT^+ in aqueous solutions and shown in our previous work [50], this salt also decreases the pK_a values of reagents involved in the complexation processes.

$[VO(H_2O)_5]^{2+}$ is the most common V^{IV} form in acidic aqueous solution. With increasing pH, hydrolyzed species, such as $[VO(OH)(H_2O)_4]^+$ and $[(VOOH)_2(H_2O)_n]^{2+}$, can be stable [30]. At pH 5.0, water-insoluble $VO(OH)_2$ starts to form, which turns into soluble $[(VO)_2(OH)_5]^-$ and $[VO(OH)_3]^-$ species with further increase in alkalinity [51].

The experimentally determined TTC-to- V^{IV} molar ratio (1:1), means that the extracted ternary complexes are ion-associates between TT^+ and monoanions. The following anionic species seem possible taking into consideration the experimental conditions: $[V^{IV}(OH)(TAO)_2]^-$, $[V^{IV}O(HTAO)(TAO)]^-$ or $[V^{IV}O(OH)(HTAO)_2]^-$ (when $n_{TAO} : n_V = 2 : 1$), and $[V^{IV}O(OH)TAO]^-$ (when $n_{TAO} : n_V = 1 : 1$). Since the molar absorptivity under the optimal extraction-spectrophotometric conditions is relatively high (see Table 1), the existence of $[V^{IV}O(OH)(HTAO)_2]^-$, in which both the TAO ligand are protonated, is not very likely. The same applies to the complex $[V^{IV}O(OH)TAO]^-$, which dominates only at low TAO concentrations and pH values higher than ca. 5.

3.5 Possible structures and HF optimization

When discussing the possible structures and their optical properties, it should be taken into account that: (i) the $V=O$ bond is strong and difficult to break [30]; (ii) square pyramidal complexation is a favored coordination mode, with the VO bond projecting vertical to the plane of the remaining coordinating atoms [30]; (iii) V^{IV} -TAR complex in water-ethanol medium most probably contains a coordinated -OH group instead of bare oxygen [23]; (iv) ligands, similar to TAO are considered tridentate [25-28] and (v) the spectral characteristics in the visible range of the ion-association complexes of TT^+ are governed primarily by the anionic moiety [40].

Keeping the above in mind, we optimized the ground state equilibrium geometry of the monoanionic chelates which match to the 2 : 1 (TAO : V^{IV}) composition requirement. We started the optimization process with two different mutual arrangements of the TAO ligands – coplanar and perpendicular. In the course of optimization, we found that some of the structures with perpendicular ligands (TAO^{2-} or $HTAO^-$) are unstable; the oxygen atom of

Table 1: Extraction-spectrophotometric optimization of the V^{IV} – TAO – TTC – water – chloroform system.

Parameter	Optimization range	Optimal value/range	Figure
Wavelength, nm	Visible range	545	Fig. 1
pH of the aqueous phase	3.6 – 6.4	4.9	Fig. 2
Concentration of TAO, mol dm ⁻³	$(0.60 - 14.3) \times 10^{-4}$	5.4×10^{-4}	Fig. 3a
Concentration of TTC, mol dm ⁻³	$(0.24 - 14.1) \times 10^{-4}$	9.4×10^{-4}	Fig. 3b
Extraction time, sec.	5 – 240	120	-

the VO group releases, which in turn changes the charge requirement.

The ground state equilibrium geometries of the remaining structures are shown in Figure 7 where one of the TAO ligands is tridentate and the second is monodentate. In all three structures, V^{IV} occupies the center of a square pyramid with oxygen O_{18} at the apex and nitrogen and oxygen atoms (N_{12} , N_9 , O_7 and O_{32}) in the distorted basal plane. N_{12} , N_9 and O_7 belong to the tridentate ligand. The monodentate TAO is bound to V^{IV} through O_{32} , the oxygen atom in ortho position to the azo group.

In structure **I**, the oxygen in the para position to the azo group of the monodentate TAO is protonated ($O_{33}-H_{44}$). In this structure, the two TAO ligands are almost coplanar and the coordination polyhedron is the least distorted.

In structure **II**, the oxygen of the VO group is protonated ($O_{18}-H_{21}$) and the hydrogen atom forms a weak H-bond ($H_{21} \cdots N_{37} = 2.227 \text{ \AA}$) with the heterocyclic nitrogen of the monodentate ligand.

Structure **III** appears to be the most stable. A stronger hydrogen bond $N_{37}-H_{44} \cdots O_{18}-V_{17}$ ($1.688 \text{ \AA}$) is visible in it. This bond is part of a 10-membered ring (consisting of V_{17} , O_{18} , H_{44} , N_{37} , C_{36} , N_{35} , N_{34} , C_{29} , C_{30} and O_{32}), which additionally stabilizes the coordination entity. It is important to note that the existence of a hydrogen atom (H_{44}) attached to the heterocyclic nitrogen is unusual since it should be the first hydrogen that separates [27, 49, 52] from the isolated ligand (H_3TAO^+) by increasing the pH of the solution. As mentioned above, under the optimum acidity (pH 4.9), the reagent is predominantly in its neutral form (H_2TAO) with hydrogen atoms at the two oxygens.

3.6 Comparison between theoretical and experimental spectra

The next step in elucidating the structure of the extracted complex was the comparison between the normalized experimental spectrum (Figure 8, full red line) and

theoretical spectra of structures **I**, **II** and **III**. The theoretical HF/3-21G* spectra were modeled by calculated TD electron transition lines and a Lorentzian broadening of the bands. A scale factor of 1.1 was applied. This relatively small factor provides good correlation between the experimental spectrum and that of the structure **III** (dotted green line). The spectra of structures **I** and **II** are rather different. The corresponding maxima are blue shifted by almost 170-180 nm. Most probably they are not formed in noticeable amounts at the optimum extraction conditions. However, we consider that structure **II**, which has some similarities to structure **III** (10-membered ring involving a H-bond), is responsible for the abnormal course of series 1 in Figure 4a due to complications induced by the presence of vanadium as $VO(OH)_2$ at pH > 5.

3.7 Ground state equilibrium geometry of the ternary complex

The results obtained allowed the modelling of the structure of the entire ion-association complex. For this purpose, we combined structure **III** with the pre-optimized structure of the tetrazolium cation [16, 53]. In addition to the HF calculations, we carried out calculations based on DFT. The ground state equilibrium geometry of the ion-associate optimized by the BLYP/3-21G* method is shown in Figure 9. Selected bond lengths and angles obtained by both methods are listed in Table 2. The results obtained by DFT are considered to be more reliable and are consistent with the expected length of the $V=O$ bond ($1.6 \text{ \AA}$) [30]. The distortion of the basal plane (N_{12} , N_9 , O_7 , O_{32}) obtained by this method is smaller and the closest interaction contacts between the complex anion $[VO(H^+TAO)(TAO)]^-$ and TT^+ are shorter: $O_{26} \cdots H_{82}$ ($2.109 \text{ \AA}$) and $N_{10} \cdots H_{84}$ ($2.657 \text{ \AA}$). It should be mentioned that these distances are shorter than the closest contacts reported for TT^+ -containing ion-associates involving anions, such as $[PCl_6]^-$, $[PO_2Cl_2]^-$, $[NbCl_6]^-$, $[NbOCl_4(CH_3CN)]^-$, $[SbCl_6]^-$ and $[CuCl_4]^-$ [54-57].

I

II

III

Figure 7: Ground state equilibrium geometries of the monoanionic chelates.

Figure 8: Comparison of the normalized experimental spectrum (full line) and theoretical HF/3-21G* spectra of Structures I, II and III (dotted lines) scaled by a factor of 1.1.

Figure 9: The optimized ground state geometry of the ion-associate.

3.8 Extraction-spectrophotometric characteristics

On the basis of the studies carried out, it can be concluded that the formation and extraction of the ternary complex under the optimal conditions can be expressed by the following equation:

The equilibrium constant characterizing this equation was calculated by two methods: mobile equilibrium method [46, 58] ($\text{Log } K_{\text{ex}} = 4.0 \pm 0.4$; $N = 4$) and Holme-Langmyhr method [59] ($\text{Log } K_{\text{ex}} = 4.1 \pm 0.2$; $N = 7$). As can be seen, the results are statistically identical.

The apparent molar absorptivity calculated by the saturation method was $\varepsilon_{\text{max}} = 1.75 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ (Figure 4). It is about 11% lower than that of the V^{V} complex

Table 2: Selected bond lengths (Å) and angles (°) calculated by HF and DFT methods using 3-21G* basis set.

Bonds	Å		Angles	°	
	DFT	HF		DFT	HF
V ₁₇ -O ₇	1.865	1.922	C ₄ -N ₉ -N ₁₀	121.954	122.663
V ₁₇ -O ₂₅	1.770	1.823	N ₉ -N ₁₀ -C ₁₁	105.660	110.520
V ₁₇ -N ₉	2.120	2.144	C ₂₂ -N ₂₇ -N ₂₈	117.829	115.905
V ₁₇ -N ₁₂	2.024	2.260	N ₂₇ -N ₂₈ -C ₂₉	110.076	114.837
V ₁₇ -O ₁₈	1.633	1.863	O ₇ -N ₉ -N ₁₂ -O ₂₅	19.960	36.160
O ₁₈ ...H ₄₄	1.695	1.745	N ₉ -N ₁₂ -O ₂₅ -O ₇	-17.565	-29.540
H ₄₄ -N ₃₀	1.055	1.017	N ₁₂ -O ₂₅ -O ₇ -N ₉	17.691	29.934
N ₉ -N ₁₀	1.416	1.366	O ₂₅ -O ₇ -N ₉ -N ₁₂	-19.768	-35.890
N ₂₇ -N ₂₈	1.423	1.404			
C ₂₃ -O ₂₅	1.370	1.338			
C ₅ -O ₇	1.382	1.336			
N ₅₀ -N ₅₄	1.434	1.424	N ₅₄ -N ₅₀ -C ₅₃	105.434	105.999
N ₅₀ -N ₅₁	1.516	1.463	N ₅₄ -N ₅₀ -N ₅₁	104.992	105.187
N ₅₁ -N ₅₂	1.400	1.393	N ₅₀ -N ₅₁ -N ₅₂	108.241	108.077
N ₅₂ -C ₅₃	1.383	1.357	N ₅₀ -N ₅₁ -C ₅₃	104.393	105.318
C ₅₃ -N ₅₄	1.360	1.348	N ₅₂ -C ₅₃ -N ₅₄	116.432	114.687
			N ₅₄ -C ₅₃ -C ₅₆ -C ₇₂	-2.377	0.929
			N ₅₁ -N ₅₀ -C ₅₅ -C ₆₇	-41.916	-32.946
			N ₅₂ -N ₅₁ -C ₅₇ -C ₆₂	-12.443	-42.184
O ₂₆ ... H ₈₂	2.109	2.438			
N ₁₀ ... H ₈₄	2.657	3.336			

with the same reagents, $\epsilon_{\text{max}} = 1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ [16]. A similar decrease can be noted when comparing the ϵ_{max} values of V^{IV} and V^V complexes with other ADs and monotetrazolium salts [29, 34].

4 Conclusions

The principal complex formed in the liquid-liquid extraction-chromogenic system V^{IV}-TAO-TTC has a composition of 1:2:1 and can be represented by the formula (TT⁺)[VO(H^NTAO)(TAO)]. The complex anion [VO(HTAO)(TAO)]⁻ has a relatively intense red coloration, while the tetrazolium cation TT⁺ is bulky and determines the ease of extraction into chloroform. With the help of theoretical

calculations and simulated spectra, it was shown that one of the TAO ligands is monodentate. It is protonated at the heterocyclic nitrogen and the hydrogen forms a H-bond (1.695 Å) with the oxygen that is in the apex of the distorted square pyramid containing V^{IV} in its center. The closest interaction contacts between the complex anion [VO(HTAO)(TAO)]⁻ and TT⁺ are two weak H-bonds formed between hydrogen atoms of the phenyl substituents in the tetrazolium ring and (i) the oxygen in para-position relative to the azo group of the monodentate TAO (2.109 Å) and (ii) the noncoordinating nitrogen of the azo group of the tridentate ligand (2.657 Å).

The present investigations can assist in clarifying some ambiguities and apparent inconsistencies related to chemistry of V^{IV}. They are a good basis for explaining experimental facts with the formation of a hydrogen bond

of the type N-H...O, where N is an azo dye heterocyclic nitrogen.

Acknowledgements: Published with a grant under Project N° BG05M2OP001-2.009-0025, “Doctoral training at MU-Plovdiv for Competence, Creativity, Originality, Realization and Academism in Science and Technology - 2 (DOCTORANT - 2)”, funded under the Operational Programme “Science and Education for Smart Growth”, co-funded by the Structural and Investment Funds of the EU.

Conflict of interest: Authors declare no conflict of interest.

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