Scientific paper

Complex Formation in a Liquid-Liquid Extraction System Containing Vanadium(IV/V), 2,3-Dihydroxynaphtahlene and Thiazolyl Blue

Galya K. Toncheva,[1] Zlatimir T. Zhelev,[1] Vassil B. Delchev[1] and Kiril B. Gavazov[2,*]

[1] *Faculty of Chemistry, University of Plovdiv "Paisii Hilendarski", Plovdiv 4000, Bulgaria*

[2] *Faculty of Pharmacy, Medical University of Plovdiv, Plovdiv 4002, Bulgaria*

* *Corresponding author: E-mail: kgavazov@abv.bg*

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Abstract

Liquid-liquid extraction systems for $V^{IV/V}$ containing 2,3-dihydroxynaphtahlene (DN) and 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide (thiazolyl blue, MTT) were studied. The optimum conditions for V^{IV} and V^{V} extraction were found. V^{IV} is extracted in chloroform as a 1:2:2 complex (V:DN:MTT) with λ_{max} = 570 nm and $\varepsilon_{570} = 2.9 \times 10^4$ dm^3 mol^{-1} cm^{-1}. However, this wavelength was found unsuitable for precise spectrophotometric measurements due to time dependent absorbance changes. V^{V} forms predominantly a 1:1:1 complex with λ_{max} = 335 nm. The calibration graph for this oxidation state is linear in the range of 0.06–1.5 μg cm^{-3}. The molar absorptivity, Sandell's sensitivity and limit of detection were calculated to be 1.6×10^4 dm^3 mol^{-1} cm^{-1}, 3.2 ng cm^{-2} and 0.02 μg cm^{-3}, respectively. The ground-state equilibrium geometries of the anionic parts of the extracted ion-associates, $[V^{IV}O(DN^{2-})_2]^{2-}$ and $[V^{V}O_2(DN^{2-})]^{-}$, were optimized at the BLYP/6-31++G* level of theory.

Keywords: Vanadium(IV/V); 2,3-dihydroxynaphtahlene; ternary complex; liquid-liquid extraction; spectrophotometry; DFT calculations

1. Introduction

Vanadium is an essential trace element for living organisms[1] and a pillar of modern technology[2] with a potentially significant environmental impact due to human activity, such as the burning of fossil fuels, manufacturing of steel alloys, dyes, glass and ceramics, and application as a catalyst in various processes.[2,3] Vanadium is the fifth most abundant transition element in the Earth's crust with an average content of 0.014%.[3] Natural sources of airborne vanadium include continental dust, volcanic activity, marine aerosols and wild forest fires.[2]

It is known that prolong exposure to vanadium increases the risk of lung cancer and can damage the integumentary, respiratory, central nervous and digestive systems.[4] The amount of vanadium resorbed in the gastrointestinal tract is a function of the oxidation state and coordination environment.[5] The most important oxidation states of vanadium are IV and V. The ability to switch easily between them, along with the stereochemical flexibility of this element[6] are key factors that determine its role in biological systems.[1,7]

Vanadium deficiency in animal species is related to stunted growth, impaired reproduction, altered red blood cell formation, disturbed iron metabolism and abnormalities in blood lipid levels.[2,8] There is an opinion among health specialists that vanadium deficiency can affect humans in a similar way.[2] Insufficiently studied issues concerning the balance between its toxicity and essentiality[8,9] define the necessity for vanadium determination in various samples and call for investigations of coordination compounds, which have the potential to be used for V^{IV}/V^{V} speciation.

Many methods have been proposed for vanadium determination and speciation.[10–13] Very sensitive and cost effective are the spectrophotometric methods based on ternary complexes with catechol type ligands.[14–19] However, the mechanism of colour development in some of these methods[14,15] is debatable because it is not clear whether the main spectral bands are due to the formation of coordination compounds or are products of reagent(s) oxidation and polymerization.[20,21] On the other hand, it is difficult to find conditions for speciation analysis with such reagents as they are capable of reducing V^V to V^{IV}.[19–26] In fact, little is known about the stabilizing effects of additional reagents on the initial oxidation state of vanadium in ternary complexes of this kind.

Several papers[27–30] describe liquid-liquid extraction (LLE) of V^V with 2,3-dihydroxynaphthalene (DN), a ligand incorporating a catechol moiety, the interest in which has been revived thanks to Tarafder et al.[31–33] In a previous paper,[21] we compared the behaviour of V^{IV} and V^V in a LLE-chromogenic system involving DN and 2,3,5-triphenyl-2*H*-tetrazolium chloride (TTC). We found evidence for aggregation of the ternary complexes in the organic phase and shed light on the differences in the extraction mechanism for V^{IV} and V^V.

Here, we report results for LLE-chromogenic systems containing V^{IV} or V^V, DN and an alternative ion-association reagent: 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-2*H*-tetrazolium bromide (thiazolyl blue, MTT). MTT is a commercially available tetrazolium salt with many applications as a redox[34] and ion-association reagent.[35] MTT is known to have advantages over similar compounds in terms of stability and molar absorptivity of the obtained complexes[35–38] and their applicability for V^{IV}/V^V speciation analysis.[26]

2. Experimental Procedure and Theoretical Details

2. 1. Reagents and Apparatus

Stock V^{IV} aqueous solution (*ca.* 5×10^{-2} mol dm^{-3}) was prepared from $VOSO_4 \cdot 5H_2O$ (purum, Fluka AG, Switzerland) and standardized by potassium permanganate titration. Working solutions at a concentration of 2×10^{-4} mol dm^{-3} and pH *ca.* 3.0 were prepared daily by suitable dilution. V^V solution (2×10^{-4} mol dm^{-3}) was prepared by dissolving NH_4VO_3 (puriss. p.a., VEB Laborchemie Apolda, Germany) in water. Fresh DN chloroform solutions (2×10^{-3} mol dm^{-3}) were prepared daily from the solid reagent (purum, Fluka AG, Switzerland). The concentration of MTT (p.a., LOBA Feinchemie GmbH, Austria) was 3×10^{-3} mol dm^{-3} (aqueous solution). The chloroform (p.a., Valerus, Bulgaria) was additionally distilled. The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2.0 mol dm^{-3} aqueous solutions of CH_3COOH and ammonia. pH was measured by a Hanna HI-83141 pH meter (Romania). Absorbance measurements were performed by using a Camspec M508 spectrophotometer (United Kingdom), equipped with 1 cm path-length glass cells. Distilled water was used throughout the work.

2. 2. Procedure

Aliquots of V^{IV} or V^V solution, buffer solution (1 cm^3) and MTT solution were placed into 125 cm^3 separatory funnels. The volume was made to 10 cm^3 with water. An aliquot of DN chloroform solution was added and the organic phase was made up to 10 cm^3 with chloroform. The funnel was shaken for a fixed time period (10–240 s). After the separation of the phases, a portion of the organic extract was transferred through filter paper into the spectrophotometer cell. The absorbance was measured against chloroform or simultaneously prepared blank solution (containing all of the reagents with the exception of vanadium).

2. 3. Theoretical Details

The structures of the anionic coordination compounds were optimized at the BLYP/6-31++G* level of theory as described in the literature.[21] The charge and multiplicity for $[V^{IV}O(DN^{2-})_2]^{2-}$ were set to –2 and doublet, respectively. The theoretical calculations were performed with the GAUSSIAN 03 program package. The results were visualized with the ChemCraft program.

3. Results and Discussion

The following variables were considered for the performed LLE-spectrophotometric optimisation experiments: organic solvent, wavelength for spectrophotometric measurements, pH, extraction time and concentration of the reagents.

3. 1. Choice of Organic Solvent and Spectral Characteristics

Chloroform,[21] dichloroethane,[39] ethyl acetate[29] and methyl isobutyl ketone[30] were used in previous studies as extraction solvents for DN-containing complexes. Preliminary investigations showed that chloroform is the best solvent for the $V^{IV/V}$–DN–MTT species. Absorption spectra of these species are shown in Fig 1. Fig. 1a includes spectra obtained with a low DN concentration (8.0×10^{-5} mol dm^{-3}). Significant differences can be observed for the two oxidation states. The V^{IV} complex (spectrum 1) has two intensive maxima (at 330 and 560 nm), while the V^V complex (spectrum 2) is characterized by an intense maximum (at 335 nm). Another maximum for this oxidation state is at 680 nm; the corresponding band is broad and low intensive.

Spectra with a high DN concentration (1.6×10^{-3} mol dm^{-3}) are depicted in Fig. 1b. The spectral changes accompanying the increase of the DN concentration can be attributed to reduction of V^V to V^{IV}. However, this reduction is only partial: there is no complete matching of the two spectra as observed under similar conditions in our previous studies[21] for the couple V^{V}-DN-TTC and V^{IV}-DN-TTC.

It should be mentioned that the absorbance of the blank is not stable in time (Fig. 1c). The increase of the absorbance at 580 nm fits well to a second order polynomial equation: $y = -0.0001x^2 + 0.0138x + 0.1477$, $R^2 = 0.9996$. The observed instability can be attributed to aggregation of the DN–MTT species in the organic phase. To eliminate this factor, in our further studies, we measured the absorbance at wavelengths outside the range of instability.

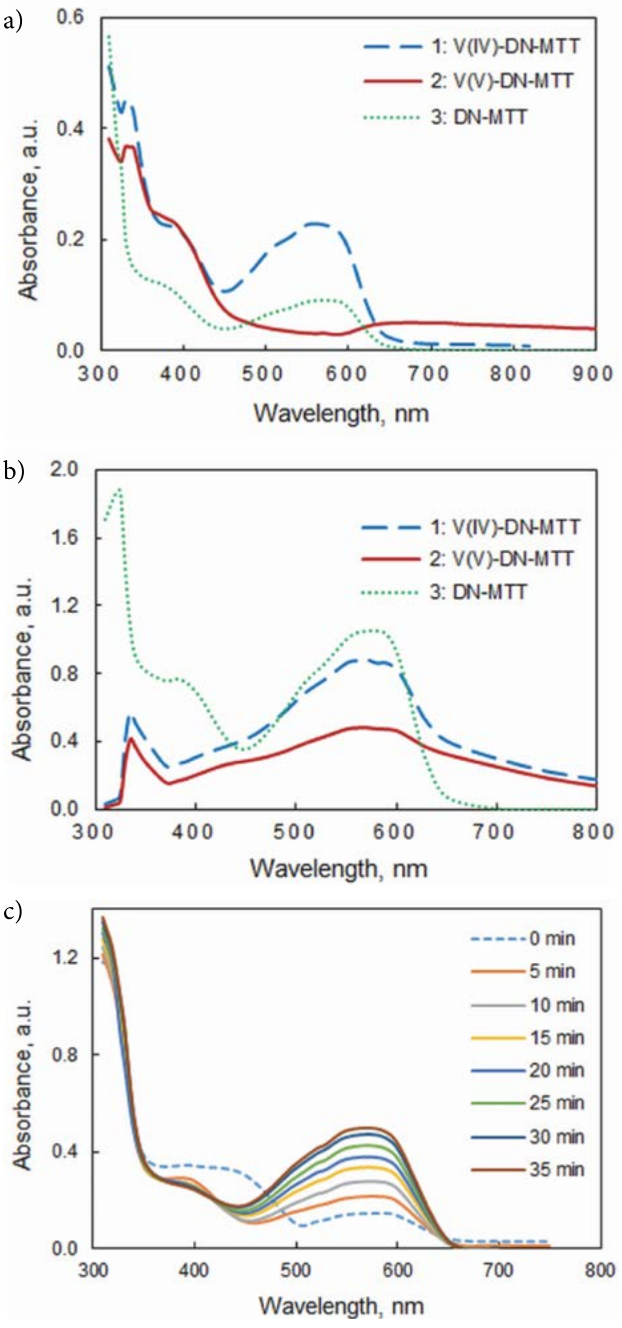

Figure 1. Absorption spectra in chloroform. **a**) At a low DN concentration, 8×10^{-5} mol dm^{-3}: 1 – V^{IV}-DN-MTT against blank; 2 – V^{V}-DN-MTT against blank; 3 – blank (DN-MTT) against chloroform. $c_{V(IV)} = c_{V(V)} = 3 \times 10^{-5}$ mol dm^{-3}, $c_{MTT} = 1.5 \times 10^{-4}$ mol dm^{-3}, pH 5, extraction time 2 min. **b**) At a high DN concentration, 1.6×10^{-3} mol dm^{-3}: 1 – V^{IV}-DN-MTT against blank; 2 – V^{V}-DN-MTT against blank; 3 – blank (DN-MTT) against chloroform. $c_{V(IV)} = c_{V(V)} = 3 \times 10^{-5}$ mol dm^{-3}, $c_{MTT} = 2.4 \times 10^{-4}$ mol dm^{-3}, pH 5, extraction time 2 min. **c**) Influence of time on the spectrum of the blank: $c_{DN} = 4 \times 10^{-4}$ mol dm^{-3}, $c_{MTT} = 1.0 \times 10^{-4}$ mol dm^{-3}, pH 5, extraction time 2 min.

3. 2. Effect of pH

The effect of pH on the extraction is shown in Fig. 2. The absorbance of the V^{IV} complex was measured at 335 (series 1) and 700 nm (series 1'). There are no significant differences in the pH profile for these wavelengths. This indicates that only one complex is extracted under the mentioned conditions (high DN concentration). Our further experiments were carried out at pH 5.0.

Series 2 represents the results for the complex obtained with V^{V}. The course of the obtained curve is different, especially for the pH region above 5.5. This is in agreement with the concept that different complexes are formed with V^{IV} and V^{V} under the experimental conditions.

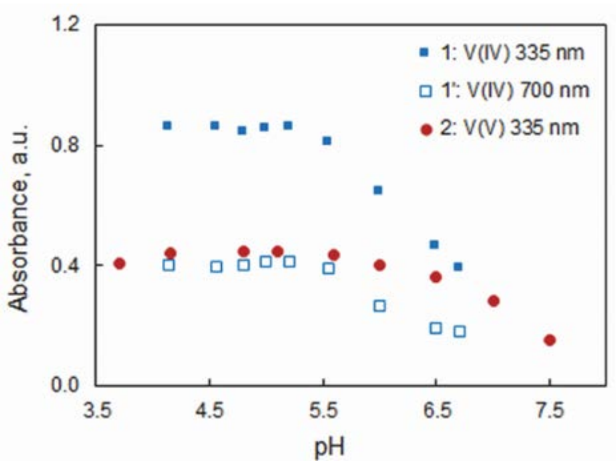

Figure 2. Absorbance of the V^{IV} complex (1 and 1') and V^{V} complex (2) vs pH of aqueous phase. 1,1' – $c_{V(IV)} = 4 \times 10^{-5}$ mol dm^{-3}, $c_{DN} = 1.6 \times 10^{-3}$ mol dm^{-3}, $c_{MTT} = 1.0 \times 10^{-4}$ mol dm^{-3}, $\lambda = 335$ nm (1) or 700 nm (1'); 2 – $c_{V(V)} = 3 \times 10^{-5}$ mol dm^{-3}, $c_{DN} = 6.0 \times 10^{-4}$ mol dm^{-3}, $c_{MTT} = 1.0 \times 10^{-4}$ mol dm^{-3}, $\lambda = 335$ nm, extraction time 2 min.

3. 3. Effect of Extraction Time

The influence of extraction time on the absorbance was followed in the interval from 10 seconds to 4 minutes. The results show that the time of 1.5 min is sufficient for quantitative extraction. Extraction times longer than 2.5 min can lead to a slight decrease of the absorbance. Hence, we extracted for 2 min in the further experiments.

3. 4. Effect of DN Concentration

The effect of DN concentration is shown in Fig. 3. Fig. 3a represents the results for V^{V}. The absorbance at 335 nm is maximal when $c_{DN} \geq 6 \times 10^{-4}$ mol dm^{-3}. Fur-

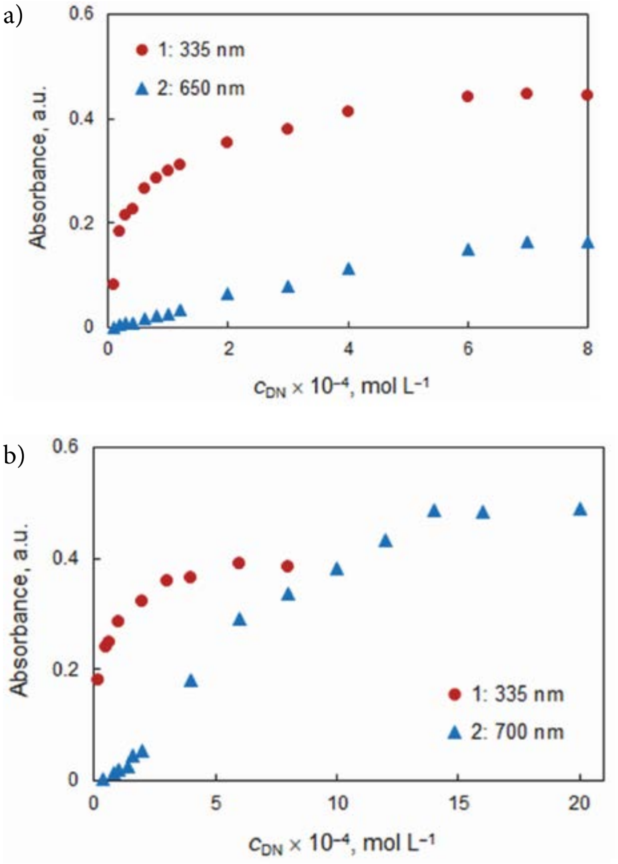

Figure 3. Absorbance of extracted complexes of V^V (a) and V^{IV} (b) vs DN concentration. **a)** $c_{V(V)} = 2 \times 10^{-5}$ mol dm^{-3}, $c_{MTT} = 1.5 \times 10^{-4}$ mol dm^{-3}, pH 5.5, λ = 335 nm (1) and 650 nm (2). **b)** $c_{V(IV)} = 2 \times 10^{-5}$ mol dm^{-3} (1) or 4×10^{-5} mol dm^{-3} (2); $c_{MTT} = 3.5 \times 10^{-4}$ mol dm^{-3} (1) or 1.0×10^{-4} mol dm^{-3} (2); pH 5.5 (1) or 5.0 (2); λ = 335 nm (1) and 700 nm (2).

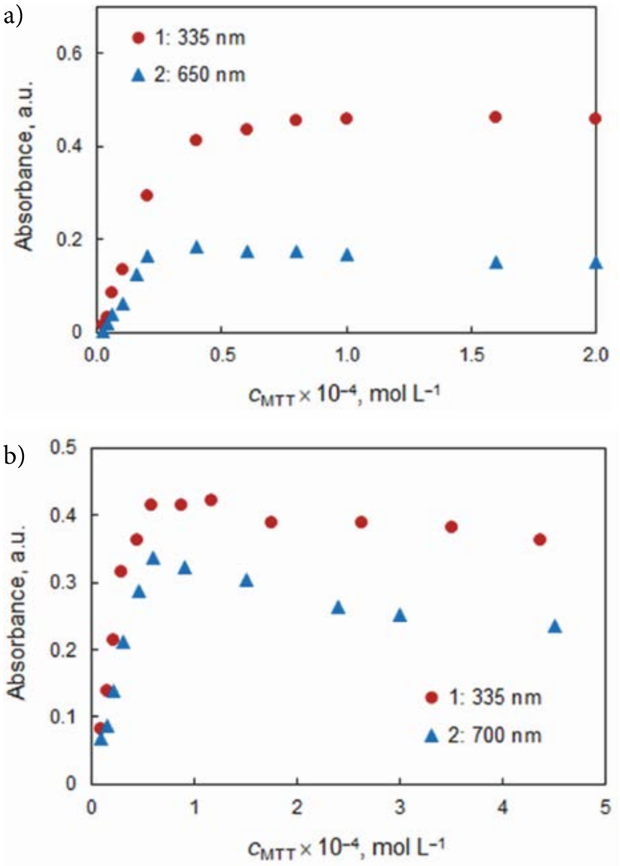

Figure 4. Absorbance of extracted complexes of V^V (a) and V^{IV} (b) vs MTT concentration. **a)** $c_{V(V)} = 3 \times 10^{-5}$ mol dm^{-3}, $c_{DN} = 6.0 \times 10^{-4}$ mol dm^{-3}, pH 5.5, λ = 335 nm (1) and 650 nm (2). **b)** $c_{V(IV)} = 2 \times 10^{-5}$ mol dm^{-3} (1) or 3×10^{-5} mol dm^{-3} (2); $c_{DN} = 4.0 \times 10^{-4}$ mol dm^{-3} (1) or 1.6×10^{-3} mol dm^{-3} (2); pH 5.0; λ = 335 nm (1) and 700 nm (2).

ther studies were performed at this DN concentration. Fig. 3b shows the results for V^{IV}. It is noteworthy that the saturation at the two wavelengths (335 and 700 nm) is achieved at different DN concentrations: 6×10^{-4} mol dm^{-3} (for 335 nm) and 1.4×10^{-3} mol dm^{-3} (for 700 nm). This can be explained with the formation of different ternary complexes (see below): a 1:1 (V^{IV}:DN) complex with λ_{max} close to 335 nm and a 1:2 (V^{IV}:DN) complex with absorbance bands at higher wavelengths (λ_{max} = 570 nm). Similar behaviour has been noticed in the V^{IV}-DN-TTC system.[21]

3. 5. Effect of MTT Concentration

The effect of MTT concentration is shown in Fig. 4. Fig. 4a gives the results for V^V at the optimum DN concentration (6×10^{-4} mol dm^{-3}). The absorbance at 335 nm reach its maximal value for $c_{MTT} \geq 8 \times 10^{-5}$ mol dm^{-3}. Our further studies were performed at $c_{MTT} = 1 \times 10^{-4}$ mol dm^{-3}. The saturation curves for V^{IV} are more complex (Fig. 4b). The absorbance steeply increases to about $c_{MTT} = 6 \times 10^{-5}$ mol dm^{-3} and then decreases. A narrow plateau is observed in the concentration range from 6×10^{-5} to 1.2×10^{-4} mol dm^{-3} for λ = 335 nm.

3.6. Molar Ratios, Formulae and Equations

To determine the DN : V molar ratios in the ternary complexes, we used two methods: the straight line method of Asmus[40] and the mobile equilibrium method[41] (Fig. 5). These methods give reliable results for relatively weak chemical bonds.[42,43] The MTT : V molar ratios were determined by the Yoe & Jones method[44] (Fig. 6). The method is applicable for strong bonds,[42,43] for which the two above-mentioned methods are usually inappropriate.

The results given in Fig. 5 (full markers; lines 1 and 1') show that there is a difference in the molar ratio for 335 nm (DN:V^{IV} = 1:1) and 700 nm (DN:V^{IV} = 2:1). Fig. 6a, in its turn, shows that the molar MTT:V^{IV} ratio is 2:1 independently of the wavelength. Therefore, the composition of the two ternary complexes is 1:1:2 (V^{IV}:DN:MTT; low DN concentration) and 1:2:2 (optimum conditions).

The following equation can be proposed for V^{IV} extraction under the optimum conditions (Table 1):

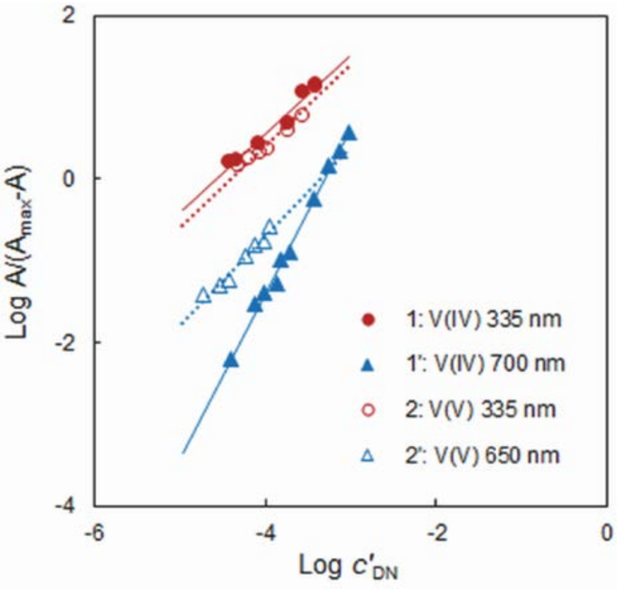

Figure 5. Determination of the DN:V^{IV} (1,1') and DN:V^{V} (2,2') molar ratios by the mobile equilibrium method at different wavelengths. Straight line equations: 1) $y = 0.97x + 4.45$; 1') $y = 2.01x + 6.66$; 2) $y = 1.00x + 4.41$; and 2') $y = 1.09x + 3.64$.

$$VO^{2+}(aq) + 2H_2DN(org) + 2MTT^+(aq) \rightleftharpoons (MTT^+)_2[V^{IV}O(DN^{2-})_2](org) + 4H^+(aq) \qquad (1)$$

The optimised ground-state geometry of the anionic chelate, $[V^{IV}O(DN^{2-})_2]^{2-}$, is shown in Fig. 7, structure I. In contrast to the V^{IV} complex with DN and TTC[21] for which a 1:2:1 composition has been determined (the anionic chelate in it contains one doubly deprotonated and one singly deprotonated ligand, structure II), the two DN ligands in the present research are doubly deprotonated. As a result, the four V–O bonds (with the oxygen atoms of DN) have equal length (2.020 Å) and the structure is more stable. The dihedral angle between the two planar DN ligands is higher than that described in the literature.[21] (Fig. 7, structure II) and the structure is not twisted: $C_{19}O_{24}V_{25}O_{22} = C_5O_{21}V_{25}O_{23} = 152.7°$ and $C_4O_{22}V_{25}O_{24} = C_{18}O_{23}V_{25}O_{21} = -152.7°$. The corresponding angles for structure II are 144.0°, 158.7°, −134.3° and −129.5°.

The composition of the ternary complex of V^V is 1:1:1 (see Fig. 5, lines 2 and 2', and Fig. 6b). Its extraction can be expressed by equation 2.

$$H_2VO_4^-(aq) + H_2DN(org) + MTT^+(aq) \rightleftharpoons (MTT^+)[V^VO_2(DN)](org) + 2H_2O(aq) \qquad (2)$$

Similar equation was proposed for the V^V–DN–TTC system.[21] However, it was considered only as a first stage of a series of processes leading ultimately to the formation of a V^{IV} complex. In contrast to $(TT^+)[V^VO_2(DN)]$,[21] $(MTT^+)[V^VO_2(DN)]$ is a stable ion-pair, less susceptible to oxidation-reduction events. Hence, MTT plays a stabilizing role on V^V in a higher degree than TTC.

The optimised ground-state geometry of $[VO_2(DN)]^{2-}$ is shown in Fig. 7, structure III. The complex is tetrahedral with distances $V_{14}–O_{11} = V_{14}–O_{12} = 1.927$, $V_{14}–O_{13} = 1.636$ and $V_{14}–O_{15} = 1.641$.

Table 1. Optimum conditions for extraction of the ternary complexes

Parameter	Optimal value/range V^{IV}	V^{V}	Figure
pH	5.0–5.2	4.8–5.5	Fig. 2
Concentration of DN, mol L^{-1}	1.6×10^{-3}	6×10^{-4}	Fig. 3
Concentration of MTT, mol L^{-1}	1.2×10^{-4}	1×10^{-4}	Fig. 4
Extraction time, s	120	120	–

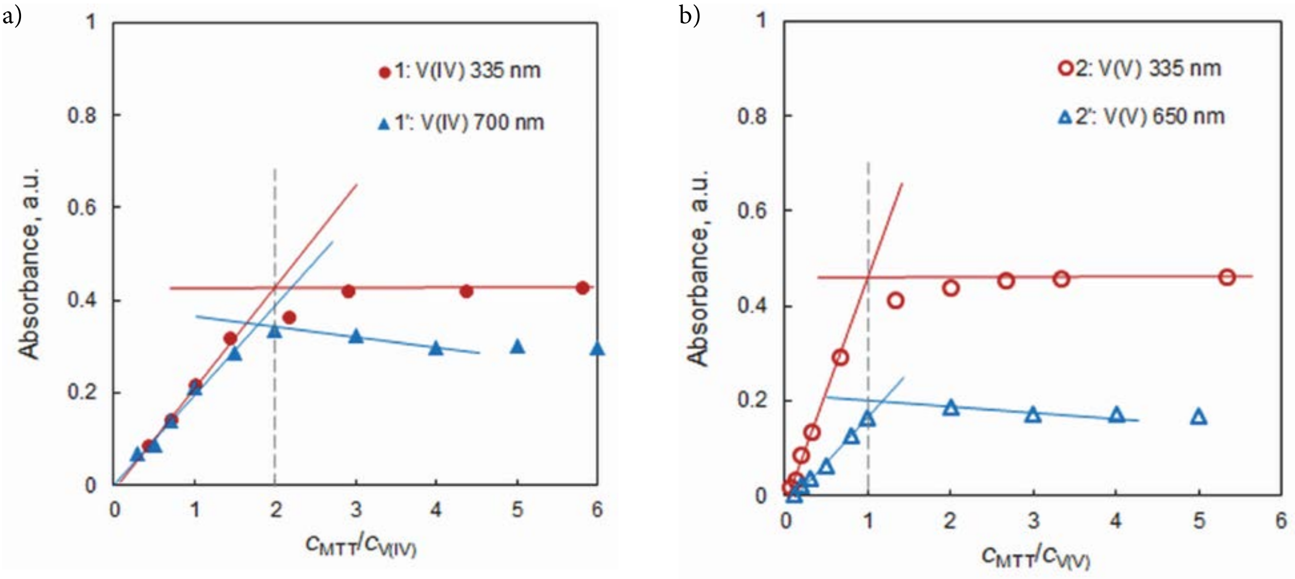

Figure 6. Determination of the MTT:V^{IV} (**a**) and MTT:V^{V} (**b**) molar ratios by the Yoe & Jones method.

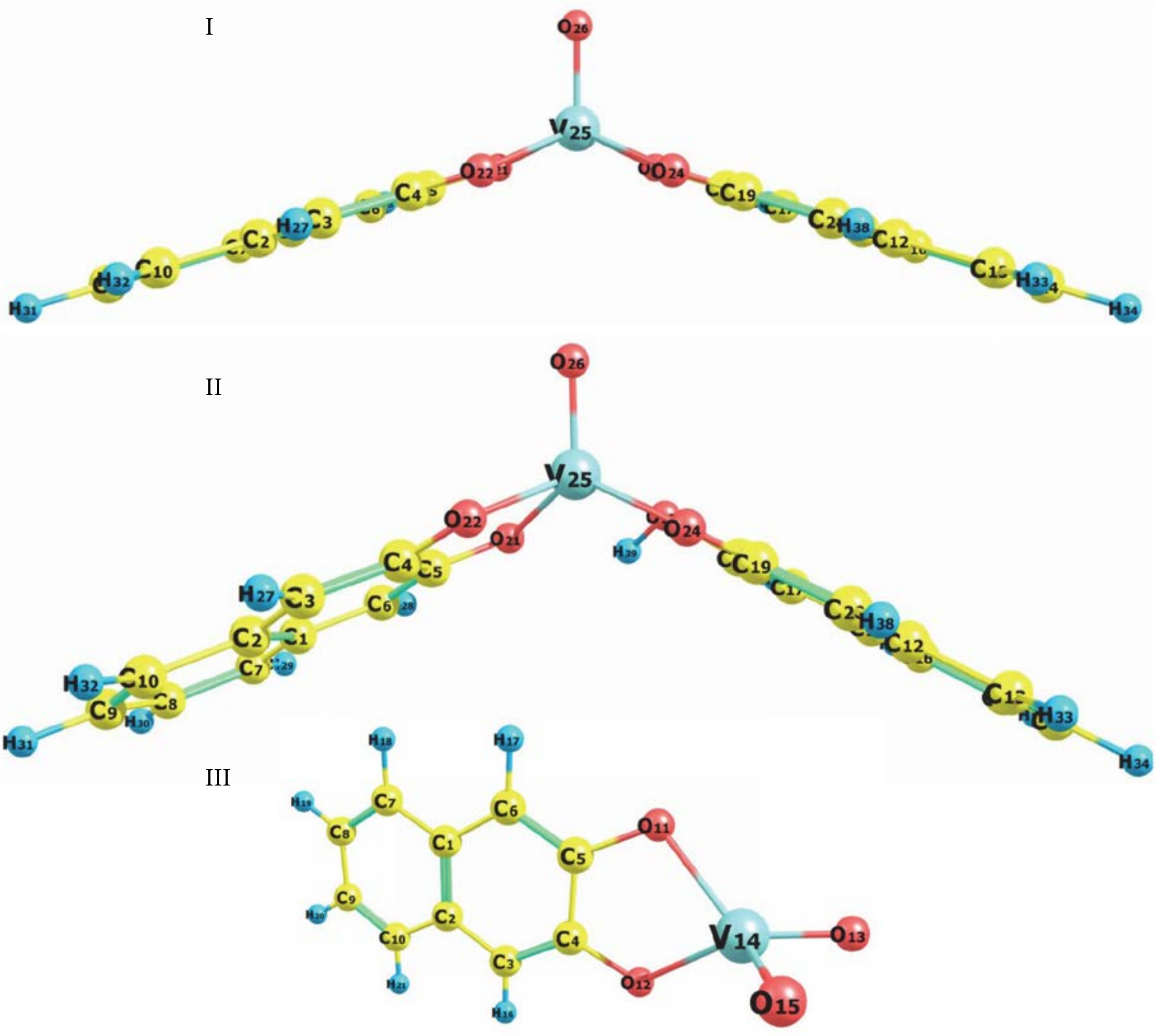

Figure 7. The optimized ground-state geometry of $[V^{IV}O(DN^{2-})_2]^{2-}$ (**I**), $[V^{IV}O(DN^{2-})(DNH)^-]^-$ (**II**)[21] and $[V^VO_2(DN^{2-})]^-$ (**III**).[21]

3. 7. Analytical Characteristics

Under the optimum conditions (Table 1), V^{IV} is extracted as an ion-association complex, $(MTT^+)_2[VO(DN^{2-})_2]$. Its molar absorptivity at λ_{max} (ε_{570} = 2.9 × 10^4 dm^3 mol^{-1} cm^{-1}; Fig. 1b), calculated from the absorbance measured immediately after the extraction, is higher than the molar absorptivities of similar complexes (Table 2). However, this wavelength was found unsuitable for precise spectrophotometric measurements due to the above-mentioned instability of the absorbance (Fig. 1c). Because of the relatively high DN concentration, the results for the second maximum (λ = 335 nm; ε_{335} = 1.9 × 10^4 dm^3 mol^{-1} cm^{-1}) were also not satisfactory (high absorbance of the blank; insufficient repeatability).

By comparing the conditions for V^{IV} and V^V (Table 1), it is noticeable that lower reagents concentrations are needed for quantitative extraction of V^V. It was found that the results are repeatable and the dependence between the absorbance at λ_{max} = 335 nm and concentration of V^V is linear (R^2 = 0.9994, *N* = 10) in a wide range (0.06–1.5 µg cm^{-3}). The regression equation was *A* = 0.316γ – 0.0002. The standard deviations of the slope and intercept were 0.003 and 0.002, respectively. The limits of detection (LOD) and quantitation (LOQ) calculated as 3 and 10 times SD of the intercept divided by the slope were 0.02 µg cm^{-3} and 0.06 µg cm^{-3}. The molar absorptivity and Sandell's sensitivity were 1.6 × 10^4 dm^3 mol^{-1} cm^{-1} and 3.2 ng cm^{-2}.

4. Conclusions

Vanadium(IV) and vanadium(V) form different chloroform-extractable ternary complexes with DN and MTT. Under the optimum conditions, V^{IV} is extracted as a 1:2:2 complex (V:DN:MTT) with λ_{max} = 570 nm. V^V, in its turn, forms a 1:1:1 complex with λ_{max} = 335 nm. This com-

Table 2. Influence of the cationic ion-association reagent on the complex's characteristics

Complex*	Composition	Organic solvent	λ_{max}, nm	ε_{max}, dm^3 mol^{-1} cm^{-1}	Ref.
V^V-DN	1:2	MIBK	530	1.5×10^4	[30]
V^V-DN-CTAB	Not studied	ethylacetate	530	1.5×10^4	[29]
V^V-DN-TV	1:2:1	chloroform	342	1.5×10^4	[28]
V^V-DN-INT	1:2:1	chloroform	340	2.5×10^4	[27]
V^{IV}-DN-TTC	1:2:1	chloroform	333	2.1×10^4	[21]
V^V-DN-MTT	1:1:1	chloroform	335	1.6×10^4	This work
V^{IV}-DN-MTT	1:2:2	chloroform	570	2.9×10^4	This work

* – The initial oxidation state of vanadium is given

Abbreviations: CTAB, cetyltrimethylammonium bromide; TV, tetrazolium violet; INT, iodonitrotetrazolim chloride; TTC, triphenyltetrazolium chloride

plex is obtained under mild conditions (low concentration of the reagents and wide pH range) and can be used for spectrophotometric determination of vanadium. When the DN concentration is not very high, the well-documented in the literature $V^V \rightarrow V^{IV}$ reduction by DN (a catecholic type ligand) is not observed. This fact can be a starting point for future research on the development of a method for spectrophotometric determination of V^V and V^{IV} in their co-presence.

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Povzetek

Proučili smo ekstrakcijski sistem tekočina–tekočina za $V^{IV/V}$, ki vsebuje 2,3-dihidroksinaftalen (DN) in 3-(4,5-dimetiltiazol-2-il)-2,5-difenil-2*H*-tetrazolijev bromid (tiazolil modro, MTT). Določili smo optimalne pogoje za ekstrakcijo V^{IV} in V^{V}. V^{IV} smo ekstrahirali v kloroformu kot 1:2:2 kompleks (V:DN:MTT) z $\lambda_{max} = 570$ nm in $\varepsilon_{570} = 2.9 \times 10^4$ dm^3 mol^{-1} cm^{-1}, vendar ta valovna dolžina ni primerna za natančne spektrofotometrične meritve zaradi časovno odvisne spremembe absorbance. V^{V} tvori predvsem 1:1:1 kompleks z $\lambda_{max} = 335$ nm. Za to oksidacijsko stanje je umeritvena krivulja linearna v območju 0.06–1.5 μg cm^{-3}. Vrednosti za molsko absorptivnost, Sandellovo občutljivost in mejo detekcije so 1.6×10^4 dm^3 mol^{-1} cm^{-1}, 3.2 ng cm^{-2} in 0.02 μg cm^{-3}. Osnovno stanje struktur anionov prisotnih v ravnotežju, $[V^{IV}O(DN^{2-})_2]^{2-}$ in $[V^{V}O_2(DN^{2-})]^{-}$, smo optimizirali na BLYP/6-31++G* nivoju teorije.