

## Liquid-Liquid Extraction-Spectrophotometric Investigations of Three Ternary Complexes of Vanadium(V)

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**Abstract.** Complex formation and liquid-liquid extraction (LLE) were studied in systems containing vanadium(V), 5-methyl-4-(2-thiazolylazo)resorcinol (TAO), tetrazolium salt (TZS), water and chloroform. The following three TZSs were used: 3-(4,5-dimethyl-2-thiazol)-2,5-diphenyl-2*H*-tetrazolium bromide (MTT), 3-(2-naphthyl)-2,5-diphenyl-2*H*-tetrazolium chloride (Tetrazolium violet, TV), and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride (INT). Concentration of the reagents (TAO and TZS), pH of the aqueous medium, and shaking time were subjects of optimization experiments. Formation of ternary complexes with a composition of 2:2:2 was demonstrated by a set of different methods. Some key characteristics concerning the analytical application of the studied LLE-chromogenic systems were established as well.

**Keywords:** solvent extraction, 4-(2-thiazolylazo)resorcinol, tetrazolium salt, ion-association, 2:2:2 complex

### INTRODUCTION

The azo compound 4-(2-thiazolylazo)resorcinol {TAO; 5-methyl-4-(2-thiazolylazo)resorcinol} was synthesized in 1960 by Jensen.<sup>1</sup> He showed its applicability for complexometric titration of metal ions {*e.g.* Cu(II), Co(III), Ni(II), Mg(II), Ca(II), Mn(II), and Cd(II)} and noted the formation of colored species with Th(IV), La(III), U(VI), Hg(II), Pb(II), Zn(II) and Zr(IV). In the 1970–1980s the list of metal ions which form colored complexes with TAO was enriched with V(V),<sup>2</sup> Co(II)<sup>3</sup> and Fe(II).<sup>4</sup> Since many azo dyes were examined in the mentioned works<sup>1–4</sup> and TAO turned out to be less sensitive colorimetric reagent than other of the suggested compounds,<sup>1–7</sup> its analytical potential remained unexploited for 2–3 decades. It was not until the beginning of the new millennium, that some analytical applications of TAO appeared, namely determination of cobalt,<sup>8</sup> cadmium,<sup>9</sup> titanium,<sup>9,10</sup> gold, palladium and lead,<sup>11</sup> copper and nickel,<sup>12</sup> and cadmium and lead.<sup>13</sup> The separation/preconcentration techniques used in these applications were chromatography,<sup>8,9</sup> sorption onto activated carbon,<sup>9,10</sup> coprecipitation,<sup>11</sup> solid phase extraction,<sup>12</sup> and cloud-point extraction.<sup>13</sup>

TAO was characterized in Ref. 13 as “a very stable and fairly selective complexing reagent”. One can expect that this reagent is better for liquid-liquid extraction (LLE) separation/preconcentration based on ion-

association systems<sup>14</sup> than the well-known 4-(2-thiazolylazo)resorcinol (TAR)<sup>5,7</sup> and 4-(2-pyridylazo)resorcinol (PAR)<sup>15,16</sup> by virtue of the additional CH<sub>3</sub> group in its molecule (Table 1). However, the LLE behavior of TAO has never been studied. The only work which has touched the problems related to LLE (*i.e.* determination of the LLE distribution ratio of TAO in acetonitrile-water/*n*-octane extraction system) was devoted to the retention behavior in reversed phase liquid chromatography.<sup>17</sup>

The objectives of this work were to investigate three LLE systems containing vanadium(V), TAO, tetrazolium salt (TZS; see Table 1), water and chloroform. TZSs are cationic ion-association reagents<sup>18</sup> with recent applications for LLE separation<sup>19</sup> and spectrophotometric determination of metal and nonmetal ions.<sup>20–23</sup> LLE systems involving PAR-TZS or TAR-TZS were systematically investigated in our laboratory and some of these systems were applied for V(V) determination<sup>24</sup> and V(IV)/V(V) speciation.<sup>25–27</sup>

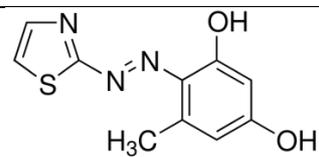
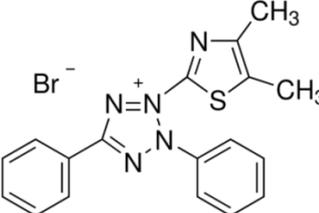
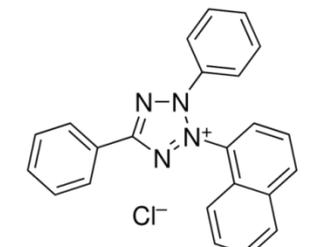
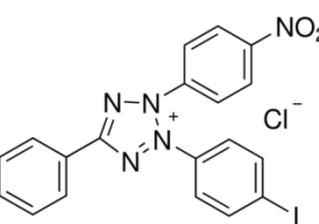
### EXPERIMENTAL

#### Reagents and Apparatus

- NH<sub>4</sub>VO<sub>3</sub> (puriss. p.a., VEB Laborchemie Apolda) dissolved in doubly distilled water, 2 × 10<sup>-4</sup> mol L<sup>-1</sup>.

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**Table 1.** Reagents used in the present study

Formula	Name	Abbreviation
	4-(2-Thiazolylazo)resorcinol (5-Methyl-4-(2-thiazolylazo)resorcinol)	TAO
	3-(4,5-Dimethyl-2-thiazol)-2,5-diphenyl-2H-tetrazolium bromide	MTT
	3-(2-Naphtyl)-2,5-diphenyl-2H-tetrazolium chloride (Tetrazolium violet)	TV
	2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H- tetrazolium chloride	INT

- TAO (95 %, Sigma-Aldrich Chemie GmbH) dissolved in slightly alkalized (KOH) distilled water,  $3 \times 10^{-3}$  mol L<sup>-1</sup>.
- TZSs: MTT (p.a., Loba Feinchemie), TV (p.a., Loba Feinchemie) and INT (p.a., Fluka AG),  $3 \times 10^{-3}$  mol L<sup>-1</sup> aqueous solutions.
- Chloroform (p.a.), additionally distilled.
- Acetate buffer solution prepared from 2 mol L<sup>-1</sup> aqueous solutions of CH<sub>3</sub>COOH and NH<sub>4</sub>OH. The resulting pH was checked by HI-83140 pH meter.
- A CamSpec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells.

### General Procedure

Aliquots of V(V) solution, TAO solution (up to 2.7 mL), buffer solution (1–3 mL; pH ranging from 3.2 to 7.3) and TZS solution (up to 1.7 mL) were pipetted into 100 mL separatory funnels. The volumes were made up to 10 mL with distilled water. Then 10 mL of chloroform were added. The funnels were closed with stoppers and shaken for a fixed time (up to 6.0 min). After separation of the layers, portions of the chloroform extracts were transferred through filter papers into cells. The

absorbance was read against simultaneously prepared blank sample (TAO-buffer-TZS) or chloroform.

### Procedure for Determining the Distribution Coefficients

The distribution coefficients  $D = \frac{\sum c(V)_{\text{org}}}{\sum c(V)_{\text{aq}}}$  were found from the ratio  $D = A_1 / (A_3 - A_1)$ , where  $A_1$  and  $A_3$  are the absorbances (measured against blanks), obtained after a single and triple extraction, respectively. The single extraction and the first stage of the triple extraction were performed with 10 mL chloroform under the optimum extraction-spectrophotometric conditions (Table 2). The organic layers were transferred into 25-mL calibrated flasks and the flask for the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding a 7-mL portion of chloroform to the aqueous phase, which remained after the first stage. The third stage was performed in the same manner. The two successive organic layers were transferred to the flask containing the organic layer obtained after the first stage. The volume was brought to the mark with chloroform and shaken for homogenization.

**Table 2.** Optimum operating conditions

System	$\lambda_{\max}$ / nm	pH	$c(\text{TAO})$ / mol L <sup>-1</sup>	$c(\text{TZS})$ / mol L <sup>-1</sup>	Extraction time / min
V(V)-TAO-H <sub>2</sub> O-ethanol <sup>(a)</sup>	540	5.0–5.5	No data	–	–
V(V)-TAO-MTT-H <sub>2</sub> O-chloroform <sup>(b)</sup>	545	4.9–5.6	$4.5 \times 10^{-4}$	$3.9 \times 10^{-4}$	3–4
V(V)-TAO-TV-H <sub>2</sub> O-chloroform <sup>(b)</sup>	545	4.9–5.6	$3.0 \times 10^{-4}$	$3.9 \times 10^{-4}$	3–4
V(V)-TAO-INT-H <sub>2</sub> O-chloroform <sup>(b)</sup>	544	5.1–5.6	$3.0 \times 10^{-4}$	$4.0\text{--}5.0 \times 10^{-4}$	1.5–2.5

<sup>(a)</sup> According to Ref. 2.

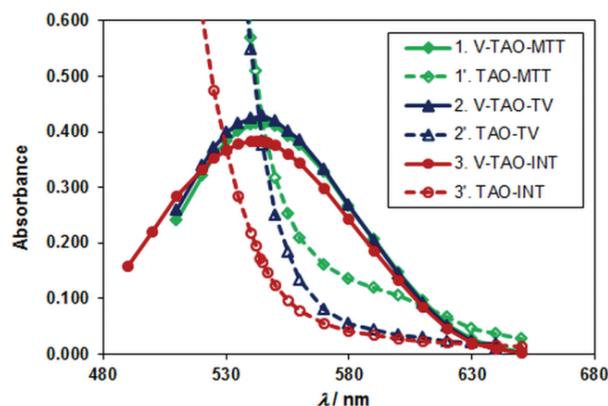
<sup>(b)</sup> The optimization experiments were carried out at room temperature of  $\approx 22^\circ\text{C}$ .

## RESULTS AND DISCUSSION

### Optimum Conditions and Spectral Characteristics

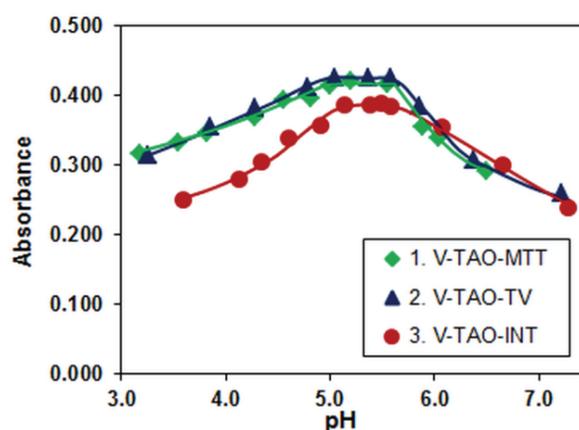
It is known that TAO reacts with V(V) in a slightly acidic medium ( $\text{pH}_{\text{opt}} 5.0\text{--}5.5$ ) to form a red-colored complex with  $\lambda_{\max} = 540$  nm and  $\varepsilon = 1.3 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>.<sup>2</sup> This information, along with our experience with the extraction systems V(V)-PAR-TZS-H<sub>2</sub>O-chloroform<sup>27</sup> and V<sup>V</sup>-TAR-TZS-H<sub>2</sub>O-chloroform,<sup>24</sup> gave us a hint that well chloroform-extractable ternary ion-association complexes can be formed at mixing V(V), TAO and TZS. The preliminary investigations and subsequent optimization experiments confirmed our expectations. They also showed that the molar absorptivity of the ternary complexes in chloroform can be 45–65 % higher than that of the binary V(V)-TAO complex,<sup>2</sup> depending on the nature of the TZS used.

Recorded spectra of the extracted at the optimum conditions (Table 2) ternary complexes are shown in Figure 1. One can judge that TV (curve 2;  $\varepsilon_{\max} = 2.14 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) and MTT (curve 1;  $\varepsilon_{\max} =$

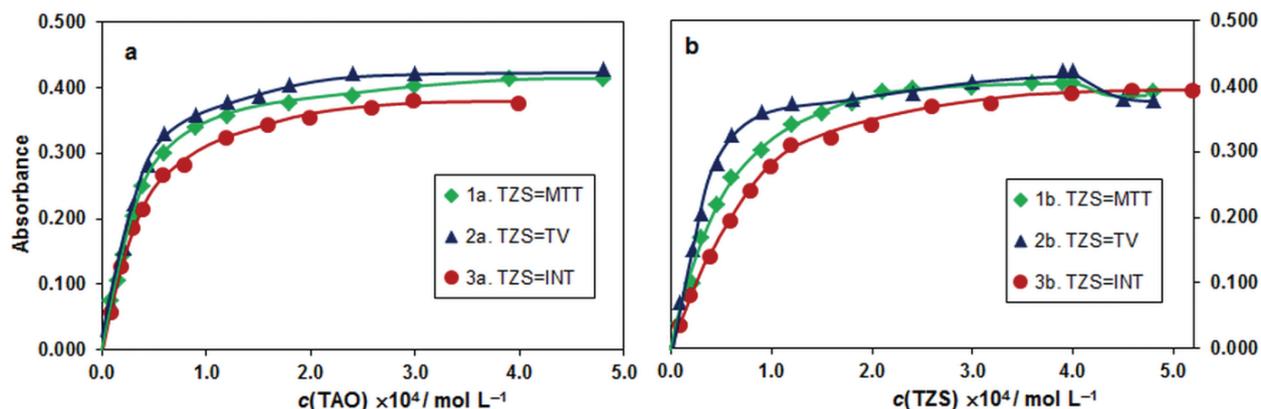


**Figure 1.** Absorption spectra of the ternary complexes (curves 1–3;  $c(\text{V(V)}) = 2 \times 10^{-5}$  mol L<sup>-1</sup>) and blank samples (curves 1'–3') in chloroform at the optimum conditions. (1,1')  $c(\text{TAO}) = 4.5 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{MTT}) = 3.9 \times 10^{-4}$  mol L<sup>-1</sup>, pH = 5.2; (2,2')  $c(\text{TAO}) = 3.0 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{TV}) = 3.9 \times 10^{-4}$  mol L<sup>-1</sup>, pH = 5.2; (3,3')  $c(\text{TAO}) = 3.0 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{INT}) = 4.0 \times 10^{-4}$  mol L<sup>-1</sup>, pH = 5.5.

$2.09 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) ensure higher molar absorptivity than INT (curve 3;  $\varepsilon_{\max} = 1.92 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>). The maximum of V(V)-TAO-INT was recorded at 544 nm; it is shifted to 4 nm as compared to the maximum of the binary V(V)-TAO complex.<sup>2</sup> The maxima of the V(V)-TAO-MTT and V(V)-TAO-TV were located at  $\lambda = 545$  nm. The small difference (1 nm) between the absorption maxima of V(V)-TAO-INT and the other two complexes can be attributed to the more significant influence of the blank samples with MTT and TV (curves 1' and 2') on the resulting absorbance ( $\Delta A = A_{\text{V(V)-TAO-TZS}} - A_{\text{TAO-TZS}}$ ). Our observations and the literature concerning the ion-pair formation in the systems TAR-TZS-H<sub>2</sub>O-chloroform and PAR-TZS-H<sub>2</sub>O-chloroform<sup>28</sup> indicate that the TAO-TZS blank samples (spectral curves 1'–3') most probably contain species which could be represented with the general formula  $(\text{TZ}^+)(\text{HTAO}^-)$ , where  $\text{HTAO}^-$  is the monoprotonated form of  $\text{TAO} = \text{H}_2\text{TAO}$ . The expected<sup>18,28</sup> higher stability of  $(\text{MTT}^+)(\text{HTAO}^-)$  ( $\lambda_{\max} = 410$  nm) and  $(\text{TV}^+)(\text{HTAO}^-)$  ( $\lambda_{\max} = 415$  nm) in comparison to the stability of  $(\text{INT}^+)(\text{HTAO}^-)$  ( $\lambda_{\max} = 412$  nm) was in



**Figure 2.** Absorbance of V(V)-TAO-TZS complexes vs. pH. (1–3)  $c(\text{V(V)}) = 2.0 \times 10^{-5}$  mol L<sup>-1</sup>; (1)  $c(\text{TAO}) = 4.5 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{MTT}) = 3.9 \times 10^{-4}$  mol L<sup>-1</sup>; (2)  $c(\text{TAO}) = 4.5 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{TV}) = 3.9 \times 10^{-4}$  mol L<sup>-1</sup>; (3)  $c(\text{TAO}) = 3.0 \times 10^{-4}$  mol L<sup>-1</sup>,  $c(\text{INT}) = 4.0 \times 10^{-4}$  mol L<sup>-1</sup>.



**Figure 3.** Effect of TAO and TZS concentration on the absorbance of the extracted ternary complexes ( $c(V(V)) = 2.0 \times 10^{-5} \text{ mol L}^{-1}$ ): a) absorbance vs. concentration of TAO; b) absorbance vs. concentration of TZS. (1a,1b) pH = 4.9; (1a)  $c(\text{MTT}) = 6.0 \times 10^{-4} \text{ mol L}^{-1}$ , (1b)  $c(\text{TAO}) = 4.5 \times 10^{-4} \text{ mol L}^{-1}$ ; (2a,2b) pH = 5.2; (2a)  $c(\text{TV}) = 3.9 \times 10^{-4} \text{ mol L}^{-1}$ , (2b)  $c(\text{TAO}) = 3.0 \times 10^{-4} \text{ mol L}^{-1}$ ; (3a,3b) pH = 5.4; (3a)  $c(\text{INT}) = 4.0 \times 10^{-4} \text{ mol L}^{-1}$ , (3b)  $c(\text{TAO}) = 3.0 \times 10^{-4} \text{ mol L}^{-1}$ .

accordance with the observed asymmetric trend of the resulting spectral curves 1 and 2 with left slopes steeper than the right ones and maxima located at slightly higher wavelengths ( $545 \text{ nm} > 544 \text{ nm}$ ).

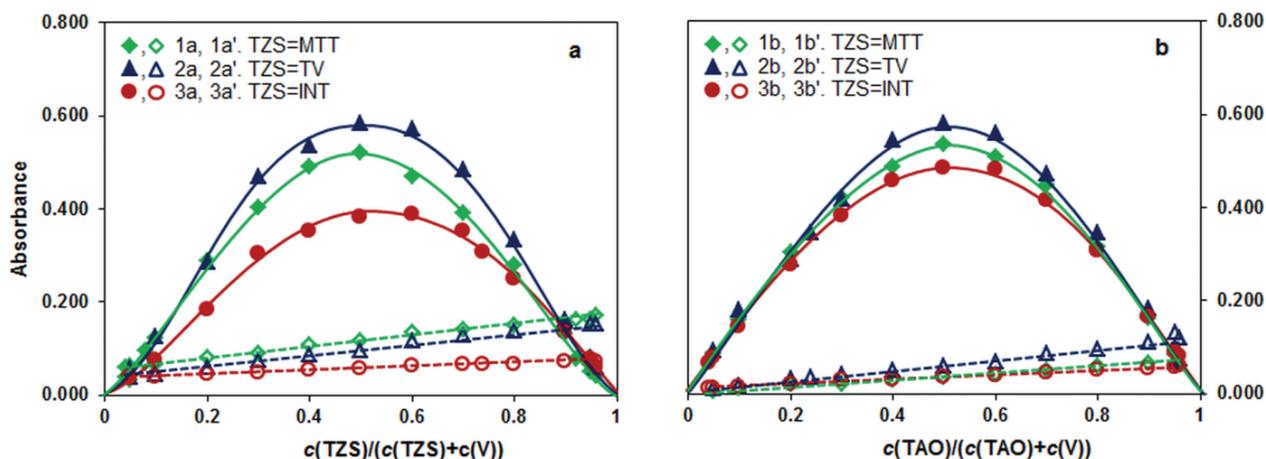
The effect of pH of the aqueous phase on the absorbance of the extracted ternary complexes is shown in Figure 2. A buffer solution with a concentration of  $2 \text{ mol L}^{-1}$  was applied to control pH. The use of different volumes of the buffer in the range of 1–3 mL (per 10 mL total volume of the aqueous phase) did not exert noticeable influence on the absorbance value. All further experiments were carried out with 2 mL buffer solutions with pH in the intervals of 4.9–5.2 (when TZS = MTT and TV) or 5.4–5.5 (when TZS = INT).

The extraction time, the concentration of the reagents TAO and TZS (Figure 3) were other variables

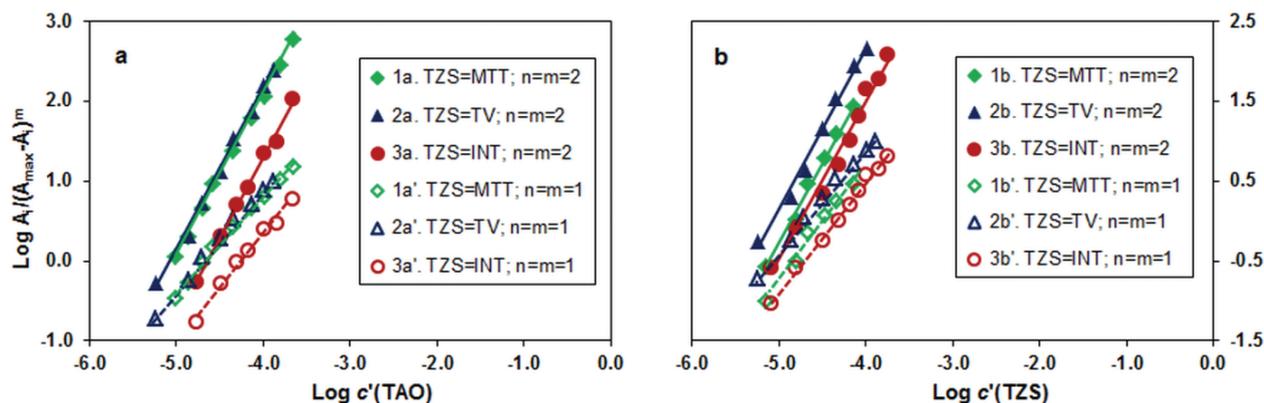
optimized in our study. The established optimum conditions are listed in Table 2.

#### Composition and General Formula

The method of continuous variations,<sup>29</sup> whose applications have been extended to LLE systems<sup>30</sup> and complexes of the type  $A_nB_n$  (where  $n > 1$ ),<sup>31</sup> was applied to determine the V(V)-to-TZS and V(V)-to-TAO molar ratios in the ternary complexes. The results are presented in Figure 4. One can assume that the absorption maxima are located at a mole fraction of 0.5. However, the trend of the isomolar curves in both cases is not identical when we discuss the possibility of formation of 1:1:1 or higher ternary species (2:2:2, 3:3:3, etc.). The concavities, which are visible at the ends of the curves in Figure 4a, are indicative for the formation of com-



**Figure 4.** Determination of TZS/V(V) and TAO/V(V) ratios: a) isomolar TZS-V(V) curves (1a,2a,3a;  $k = c(\text{TZS}) + c(\text{V(V)}) = 1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) and blank samples (1a', 2a', 3a'); b) isomolar TAO-V(V) curves (1b,2b,3b;  $k = c(\text{TAO}) + c(\text{V(V)}) = 1.0 \times 10^{-4} \text{ mol L}^{-1}$ ) and blank samples (1b', 2b', 3b'). (1a,b) pH = 4.9, (2a,b) pH = 5.2, (3a,b) pH = 5.4; (1a)  $c(\text{TAO}) = 4.5 \times 10^{-4} \text{ mol L}^{-1}$ , (2a,3a)  $c(\text{TAO}) = 3.0 \times 10^{-4} \text{ mol L}^{-1}$ ; (1b,2b)  $c(\text{TZS}) = 3.9 \times 10^{-4} \text{ mol L}^{-1}$ ; (3b)  $c(\text{INT}) = 5.0 \times 10^{-4} \text{ mol L}^{-1}$ .



**Figure 5.** Straight lines obtained by the mobile equilibrium method<sup>36</sup> for molar ratios of a) TAO to V(V); b) TZS to V(V). Straight lines equations: (1a)  $y = 2.004x + 10.065$ ;  $R^2 = 0.999$ ; (1a')  $y = 1.199x + 5.586$ ;  $R^2 = 0.994$ ; (2a)  $y = 2.009x + 10.19$ ;  $R^2 = 0.996$ ; (2a')  $y = 1.2662x + 5.953$ ;  $R^2 = 0.993$ ; (3a)  $y = 2.010x + 9.297$ ;  $R^2 = 0.995$ ; (3a')  $y = 1.337x + 5.661$ ;  $R^2 = 0.991$ ; (1b)  $y = 2.014x + 9.761$ ;  $R^2 = 0.992$ ; (1b')  $y = 1.4658x + 6.5669$ ;  $R^2 = 0.984$ ; (2b)  $y = 2.033x + 10.295$ ;  $R^2 = 0.989$ ; (2b')  $y = 1.309x + 6.148$ ;  $R^2 = 0.993$ ; (3b)  $y = 2.004x + 9.461$ ;  $R^2 = 0.983$ ; (3b')  $y = 1.376x + 5.950$ ;  $R^2 = 0.995$ .

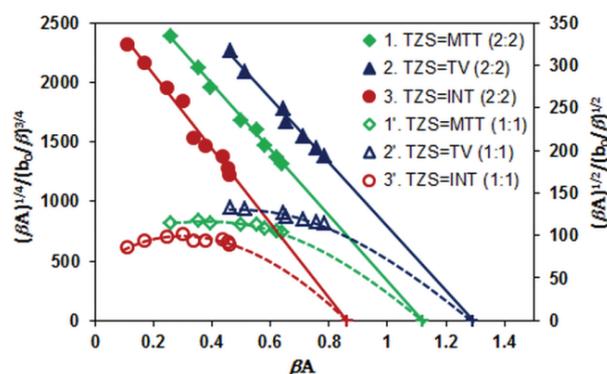
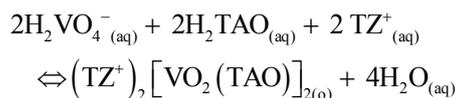
plexes with 2:2 or higher [V(V)-TAO]-to-TZS ratio.<sup>31</sup> On the other hand, the curves presented in Figure 4b suggest the formation of simple ternary complexes with a 1:1 V(V)-to-TAO ratio.

The literature survey has shown that the differentiation between 1:1 and 2:2 species by the method of continuous variations<sup>31</sup> is not always an easy and feasible task.<sup>31–35</sup> In fact, the concavities are only evident on the curves for complexes of low and medium stability<sup>31,33,34</sup> at small isomolar concentrations.<sup>33</sup> Having in mind the ion-association nature of the tetrazolium ternary complexes<sup>18</sup> we expected higher stability of the V<sup>V</sup>-TAO bonds than the bonds between the tetrazolium

cation (TZ<sup>+</sup>) and the anionic V(V)-TAO chelate. From this point of view, the conventional shape (without inflections) of the isomolar curves in Figure 4b (suggesting 1:1 complex formation) was considered misleading.

In order to clear up the composition of the ternary complexes (1:1:1 or 2:2:2) we used two other methods: the mobile equilibrium method<sup>36</sup> (Figure 5) and the dilution method<sup>37</sup> (Figure 6). The obtained results are in accordance with the concept that 2:2:2 ternary ion-association complexes are formed in all three LLE systems.

Having in mind that in most cases V(V) (in the form of VO<sub>2</sub><sup>+</sup>) produces 1:1:1 complexes with azoderivatives of resorcinol (PAR, TAR) and heavy organic cations<sup>38–48</sup> (tetrazolium complexes with different molar ratios are described in the review<sup>18</sup> – e.g. V(V):PAR:TZS = 1:2:3 or 1:2:1 and V(V):TAR:TZS = 1:2:3), we assume that the investigated in our study ternary complexes can be regarded as dimers and expressed with the general formula (TZ<sup>+</sup>)<sub>2</sub>[VO<sub>2</sub>(TAO<sup>2-</sup>)<sub>2</sub>]. The suggested equation of complex formation and extraction, based on information concerning the state of V(V)<sup>49</sup> and TAO<sup>50</sup> at pH<sub>opt</sub>, is as follows:



**Figure 6.** Straight lines (1–3; left ordinate) and curves (1'–3'; right ordinate) obtained by the dilution method<sup>37</sup> for molar ratios of TZS to V(V). (1, 1')  $c(\text{V(V)}) = c(\text{MTT})$ ,  $c(\text{TAO}) = 4.5 \times 10^{-4} \text{ mol L}^{-1}$ , pH = 5.1; (2, 2')  $c(\text{V(V)}) = c(\text{TV})$ ,  $c(\text{TAO}) = 3.0 \times 10^{-4} \text{ mol L}^{-1}$ , pH = 5.4; (3, 3')  $c(\text{V(V)}) = c(\text{INT})$ ,  $c(\text{TAO}) = 4.5 \times 10^{-4} \text{ mol L}^{-1}$ , pH = 5.4. Straight lines equations: (1)  $y = -2753.4x + 3077.5$ ;  $R^2 = 0.996$ ; (2)  $y = -2710.9x + 3491.7$ ;  $R^2 = 0.998$ ; (3)  $y = -3123.2x + 2688$ ;  $R^2 = 0.993$ .

### Constants of Extraction and Other Characteristics Concerning the Application of the Complexes

The dilution method<sup>37</sup> (Figure 6) also allows calculating the conditional extraction constants of the ternary complexes. The results are shown in Table 3 along with

**Table 3.** Calculated values ( $P = 95\%$ ) of the extraction constants ( $K_{\text{ex}}$ ), distribution coefficients ( $D$ ) and recovery factors ( $R\%$ ) at the optimum conditions

Extraction system	Log $K_{\text{ex}}$	Log $D$ <sup>(e)</sup>	$R\%$ <sup>(f)</sup>
V(V)-TAO-MTT-H <sub>2</sub> O-chloroform	13.60±0.02 ( $N = 8$ ) <sup>(a)</sup>	1.33±0.01 ( $N = 3$ )	95.5±0.09 ( $N = 3$ )
	13.54±0.08 ( $N = 4$ ) <sup>(b)</sup>		
	13.60±0.07 ( $N = 3$ ) <sup>(c)</sup>		
V(V)-TAO-TV-H <sub>2</sub> O-chloroform	13.76±0.02 ( $N = 7$ ) <sup>(a)</sup>	1.67±0.01 ( $N = 4$ )	97.9±0.03 ( $N = 4$ )
	13.76±0.06 ( $N = 4$ ) <sup>(b)</sup>		
	13.8±0.1 ( $N = 3$ ) <sup>(c)</sup>		
V(V)-TAO-INT-H <sub>2</sub> O-chloroform	13.48±0.02 ( $N = 9$ ) <sup>(a)</sup>	1.55±0.01 ( $N = 4$ )	97.3±0.06 ( $N = 4$ )
	13.12±0.03 ( $N = 4$ ) <sup>(b,d)</sup>		
	13.52±0.07 ( $N = 3$ ) <sup>(c)</sup>		

<sup>(a)</sup> Calculated by the dilution method<sup>37</sup> (Figure 6).

<sup>(b)</sup> Calculated by the Likussar-Boltz method<sup>51</sup> based on the V(V)-TZS isomolar series (Figure 4a).

<sup>(c)</sup> Calculated by the Likussar-Boltz method<sup>51</sup> based on the V(V)-TAO isomolar series (Figure 4b).

<sup>(d)</sup> Unreliable value.

<sup>(e)</sup> Determined at the optimum extraction-spectrophotometric conditions (Table 2) by comparing the absorbances for single extraction and triple extraction in equal volumes (25 mL).

<sup>(f)</sup> Calculated by the equation  $R\% = D \times 100 / (D + 1)$ .

results obtained by the Likussar-Boltz method<sup>51</sup> based on the isomolar curves shown in Figure 4 and additional experiments for determining the values of  $y_{\text{max}}$ . Since the Likussar-Boltz method uses the “normalized absorbance” concept, the validity of Beer’s law had to be checked first<sup>14</sup> for vanadium concentrations up to at least  $5 \times 10^{-5}$  mol L<sup>-1</sup> (2.55 µg mL<sup>-1</sup>). The data included in Table 4 show that there are no obstructions to use the method, connected to the linearity of the  $A = f(c(V(V)))$  plots. However, Likussar and Boltz did not consider in their work<sup>51</sup> the case for 2:2 complexes formation in detail. That is why, we performed our calculations by an equation,  $K_{\text{ex}} = 0.0625 \times (4/k)^3 \times y_{\text{max}} \times (1 - y_{\text{max}})^{-4}$ , which was additionally derived from the mentioned source<sup>51</sup>.

It could be seen from Table 3 that the results for Log  $K_{\text{ex}}$  are statistically indistinguishable when TZS is MTT or TV in all three cases of calculation (dilution method, Likussar-Boltz method based on Figure 4a, and Likussar-Boltz method based on Figure 4b). However, the obtained value of the extraction constant for the V-TAO-INT system was lower (Log  $K_{\text{ex}} = 13.12 \pm 0.03$ ) when the isomolar curve 3a (Figure 4) was used. An explanation can be the influence of the side reaction, which is responsible for the distortion of straight line 3b in Figure 5 and straight line 3 in Figure 6. In fact,  $(\text{INT}^+)_2[\text{VO}_2(\text{TAO}^{2-})]_2$  is more unstable than  $(\text{MTT}^+)_2[\text{VO}_2(\text{TAO}^{2-})]_2$  and  $(\text{TV}^+)_2[\text{VO}_2(\text{TAO}^{2-})]_2$ . The lowest values of the  $y$ -intercepts for the 2:2 straight

**Table 4.** Characteristics concerning the application of the ternary complexes for LLE-spectrophotometric determination of vanadium

Analytical characteristics	V(V)-TAO-MTT-H <sub>2</sub> O- CHCl <sub>3</sub>	V(V)-TAO-TV-H <sub>2</sub> O- CHCl <sub>3</sub>	V(V)-TAO-INT-H <sub>2</sub> O- CHCl <sub>3</sub>
Molar absorptivity ( $\epsilon$ ) / L mol <sup>-1</sup> cm <sup>-1</sup>	$(2.09 \pm 0.05) \times 10^4$	$(2.14 \pm 0.08) \times 10^4$	$(1.92 \pm 0.03) \times 10^4$
Sandell’s sensitivity / ng cm <sup>-2</sup>	2.44	2.38	2.65
Adherence to Beer’s law / µg mL <sup>-1</sup>	up to 3.6	up to 4.1	up to 4.6
Linear regression equation $y = ax + b$	$y = 0.4202x - 0.0076$ ( $R^2 = 0.9991$ ; $N = 15$ )	$y = 0.4413x - 0.0096$ ( $R^2 = 0.9992$ ; $N = 14$ )	$y = 0.3791x + 0.0003$ ( $R^2 = 0.9996$ ; $N = 13$ )
Standard deviations of the slope ( $a$ ) and $y$ -intercept ( $b$ )	0.0034; 0.0058	0.0035; 0.0060	0.0021; 0.0046
Limit of detection (LOD) / µg mL <sup>-1</sup>	0.11 <sup>(a)</sup>	0.12 <sup>(a)</sup>	0.09 <sup>(a)</sup>
Limit of quantitation (LOQ) / µg mL <sup>-1</sup>	0.36 <sup>(b)</sup>	0.39 <sup>(b)</sup>	0.30 <sup>(b)</sup>
Standard deviation of the blank	0.0062	0.0080	0.0013
Relative standard deviation (RSD) / %	1.6 <sup>(c)</sup>	2.3 <sup>(c)</sup>	1.0 <sup>(c)</sup>

<sup>(a)</sup> Calculated by  $3\sigma$  criterion.<sup>55</sup>

<sup>(b)</sup> Calculated by  $10\sigma$  criterion.<sup>55</sup>

<sup>(c)</sup> Calculated ( $P = 95\%$ ) from the results of five replicate measurements of samples containing 1.0 µg mL<sup>-1</sup> V(V).

lines in Figure 5 are evidence for the correctness of this statement. It is more reasonable to expect<sup>34</sup> that other complex species are also present in the solution, along with the principle 2:2:2 complex, when the complexation interaction is weak. In this case, the continuous variation curve loses its symmetric character (see curve 3a, Figure 4); and this inevitably will reflect on the reliability of the results<sup>14,52,53</sup> obtained by the Likussar-Boltz method.

Table 4 shows that the influence of side reactions on the complex formation with INT can be neglected when the extraction is performed at the optimum conditions. The linear regression equations and the attendant parameters listed in this table (standard deviation of the slopes and *y*-intercepts, standard deviation of the blank samples, LODs, LOQs, and RSDs) show that INT can be recognized as the best TZS for LLE-spectrophotometric determination of vanadium. An additional reason to make such a conclusion is the literature,<sup>18,25,54</sup> which suggests that INT can ensure better selectivity than many other cationic ion-association reagents, including MTT and TV.

## CONCLUSION

The present paper is the first one, which deals with the LLE-spectrophotometric behaviour of TAO. It was found that V(V) forms colored and well chloroform-extractable ternary complexes with this reagent and TZS (INT, TV and INT). Generally speaking, the extraction efficiency of these complexes is higher than those for the V(V)-TAR-TZS complexes<sup>24</sup> and their composition is different – 2:2:2. They can be regarded as dimers {2×(1:1:1)} with a general formula expressing their ion-association character: (TZ<sup>+</sup>)<sub>2</sub>[VO<sub>2</sub>(TAO<sup>2-</sup>)]<sub>2</sub>. TV<sup>+</sup>, as a component of the ternary complex, can ensure the highest extractability (Log *K*<sub>ex</sub> = 13.76; *R* = 97.9 %) and molar absorptivity ( $\epsilon_{545} = 2.14 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). However, INT can be recognized as the best reagent for extraction-spectrophotometric determination of V(V) due to the lowest limits of detection and quantitation, the lowest absorption of the blank, the widest dynamic range, and the highest reproducibility of the results achieved with this reagent.

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