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Liquid-Liquid Extraction-Chromogenic System for Vanadium(V) Based on 4-(2-thiazolylazo)orcinol (TAO) and Aliquat 336

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Abstract

The quaternary ammonium salt Aliquat 336 (A336; $R_4N^+Cl^-$) and the azo dye 4-(2-thiazolylazo)orcinol (TAO) were examined as constituents of a water-isobutanol extraction-chromogenic system for vanadium(V). Under the optimum conditions ($c_{TAO} = 1.6 \times 10^{-3} \text{ mol dm}^{-3}$, $c_{A336} = 1.3 \times 10^{-2} \text{ mol dm}^{-3}$ and pH 5.0), vanadium(V) is extracted as a ternary complex which can be represented by the formula $(R_4N^+)[VO_2(TAO_2^-)]$. The key extraction-spectrophotometric characteristics were determined. The interfering effect of foreign ions was studied as well. The wavelength of maximum absorption (λ_{max}), molar absorptivity (ϵ_{max}), constant of extraction (K_{ex}) and fraction extracted (E) were found to be $\lambda = 547 \text{ nm}$, $\epsilon = 3.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\text{Log } K_{ex} = 2.8$ and $E = 90.2\%$, respectively. Beer's law was obeyed in the range of $0.084\text{--}2.0 \text{ }\mu\text{g cm}^{-3}$ and the limit of detection was 25 ng cm^{-3} of vanadium(V).

Keywords: Vanadium(V); 5-methyl-4-(2-thiazolylazo)resorcinol; ternary complex; solvent extraction; spectrophotometric determination; room temperature ionic liquid

1. Introduction

Ionic liquids (ILs) possess fascinating properties that are rather different from those of conventional molecular solvents. This makes ILs of fundamental interest to specialists in various areas of chemistry and physics.^{1,2} The IL Aliquat 336 (A336; $R_4N^+Cl^-$) finds applications as a surfactant, phase-transfer catalyst and ion-association reagent.³ The methyltrialkyl($C_8\text{--}C_{10}$)ammonium cations it contains can form hydrophobic ion-associates with various anions and the obtained compounds can be separated by extraction methods, such as liquid-liquid extraction (LLE) and cloud-point extraction. In LLE procedures, A336 is dissolved in organic solvents, which improve its physical properties, such as viscosity and surface tension. The following solvents have been used: carbon tetrachloride,^{4,5} benzene,^{6,7} toluene,⁸ xylene,⁹ chloroform,⁵ cyclohexane,⁵ 1-octanol¹⁰ and kerosene + higher alcohols.^{11–15} Unfortunately, many of them are highly toxic which limits the application of the developed methods.

The present paper aims to study the LLE of V^V in a chromogenic system containing 5-methyl-4-(2-thiazolylazo)resorcinol {4-(2-thiazolylazo)orcinol, TAO} and A336, dissolved in isobutanol (2-methylpropan-1-ol). This solvent is among the least toxic butanols.¹⁶ It is not as volatile or corrosive as lower alcohols,¹⁶ can be produced from renewable resources¹⁷ and is either added as a flavoring agent or present naturally in food and drink systems, such as cognac, whiskey, wine, brandy, arrack, Chinese quince fruit, nectarine, hog plum, etc.¹⁸

It should be mentioned that the LLE of TAO-containing complexes is an almost unexplored area.^{19,20} Chloroform-extracted V^V -TAO ternary complexes with tetrazolium cations were recently investigated in our laboratory.^{20,21} It was found that their structures differ from the structures of the ternary complexes of V^V with similar ligands, such as 4-(2-thiazolylazo)resorcinol (TAR) and 4-(2-pyridylazo)resorcinol (PAR), due to the influence of the $-CH_3$ group of TAO, which is capable to form a H-bond with an oxygen atom of the $-VO_2$ group.²¹

The list of related studies can be extended by the chloroform extraction of V^V as a ternary complex with PAR and methyltriethylammonium chloride,²² which is one of the main components of A336.²³ Ligandless LLE of V^V with A336 in acidic^{11,12,14} and alkaline¹² medium was studied as well. However, in the absence of a chelating reagent, the extraction equilibrium is established slowly and there are practical problems with the formation of a third phase.²⁴

2. Experimental

2.1. Reagents and Apparatus

Vanadium(V) solution (2×10^{-4} mol dm⁻³) was prepared by dissolving NH_4VO_3 (puriss. p.a., VEB Laborchemie Apolda, Germany) in water. TAO (95%, Sigma-Aldrich Chemie GmbH) was dissolved in the presence of KOH (1–2 pellets per 100 cm³); the obtained slightly alkaline aqueous solution (pH 8–9) was at concentration of 5.3×10^{-3} mol dm⁻³. Aliquat 336 was purchased from Sigma-Aldrich Chemie and dissolved in isobutanol (p. a. Merck). Solutions with concentrations of 1.6×10^{-2} and 1.3×10^{-2} mol dm⁻³ were used; the calculations were based on the average molar mass of A336, 432 g mol⁻¹.³ 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 checked by a Hanna HI-83141 (Romania) and a WTW InoLab 7110 (Germany) instruments. Absorbance measurements were performed by using a Camspec M508 and a Ultrospec3300 pro UV-Vis spectrophotometers (UK), equipped with 1 cm path-length glass cells. Distilled water was used throughout the work.

2.2. Determination of the Optimum LLE-Spectrophotometric Conditions

Solutions of V^V , TAO and buffer were placed into separatory funnels. The aqueous phase volume was made up to 10 cm³ with water. Then A336 solution was added and the organic phase was made up to 5 cm³ or 10 cm³ with isobutanol. The funnel was shaken for a fixed time interval. After separation of the phases, the aqueous phase was discarded, the organic phase was transferred into a beaker and dried with a pinch of anhydrous Na_2SO_4 . Finally, the dried extract was poured into the spectrophotometer cell and the absorbance was measured against isobutanol or simultaneously prepared blank solution.

2.3. Determination of the Coefficient of Distribution

The coefficient of distribution D was calculated by the formula $D = A_1/(A_3 - A_1)$, where A_1 is the absorbance obtained after a single extraction (under the optimal ex-

traction conditions, Table 1), and A_3 is the absorbance obtained after a triple extraction under the same conditions. The final volume of the solutions in both cases was 25 cm³.^{21,25,26}

2.4. Investigation of the Influence of Foreign Ions

Solutions of V^V (1 cm^3 , 2×10^{-4} mol dm⁻³), foreign ion, TAO (3 cm^3 , 5.3×10^{-3} mol dm⁻³) and buffer (1 cm^3 , pH 5) were successively placed into a separatory funnel. The aqueous phase volume was made up to 10 cm³ with water. Then A336 solution (5 cm^3 , 1.3×10^{-2} mol dm⁻³) was added and the funnel was shaken for 30 sec. After separation of the phases, the organic phase was transferred into a beaker, dried with a pinch of anhydrous Na_2SO_4 and poured into the spectrophotometer cell. The absorbance was measured at 547 nm against isobutanol. For control, samples prepared in the absence of the foreign ion or V^V were also run.

3. Results and Discussion

3.1. LLE-Spectrophotometric Optimization

It is known that V^V forms a red complex with TAO in aqueous ethanolic medium.^{21,27} It has a composition of 1:1 and cannot be extracted in chloroform, due to its anionic nature.²¹ Our preliminary studies on the V^V -TAO-water-isobutanol system showed that the red complex can partially pass into the organic phase (Fig. 1, spectrum 1). This can be explained by the existing equilibrium between anionic and neutral (protonated) complex species.^{28,29}

Figure 1. Absorption spectra in isobutanol of complexes against blanks (1–3; $c_V = 2 \times 10^{-5}$ mol dm⁻³) and blanks against isobutanol (1'–3'). (1, 1') $c_{TAO} = 1.6 \times 10^{-3}$ mol dm⁻³, pH 5.0, extraction time $t = 120$ sec; (2, 2') $c_{TAO} = 2.0 \times 10^{-4}$ mol dm⁻³, pH 5.0, $c_{A336} = 1.3 \times 10^{-2}$ mol dm⁻³, extraction time $t = 30$ sec; (3, 3') $c_{TAO} = 1.6 \times 10^{-3}$ mol dm⁻³, pH 5.0, $c_{A336} = 1.3 \times 10^{-2}$ mol dm⁻³, extraction time $t = 30$ sec.

Upon addition of A336, the rate of extraction increases sharply due to the formation of a ternary complex (Fig. 1, spectra 2 and 3). At that, the absorption maximum shifts hipsochromically by several nanometers. The profile of the absorption band of the ternary complex and the exact position of the maximum depend on the concentration of the reagents. At high concentrations, ensuring V^V fraction extracted close to 90%, the profile of the absorption band is asymmetric (Fig. 1, spectrum 3) and the absorption maximum lies at 547 nm.

The effect of pH on the absorbance of the extract is shown in Fig. 2. The results were obtained in the presence of ammonia-acetate solutions (1 cm^3), which provide buffering around pH 4.75 (the pK_a of acetic acid) and pH 9.25 (the pK_a of ammonium).³⁰ In the absence of the buffer, a stable emulsion is formed and the phase separation is slow.

Fig. 2 shows that the absorbance of the complex is maximal in the pH range of 4.9–5.2. This range is close to the pK_a value of acetic acid, indicating that the buffer used is suitable. The decrease in absorbance at pH-values less than *ca.* 4.9 can be attributed to incomplete complex formation due to the prevalence of protonated TAO species in the solution.³¹ The decrease in absorbance at pH-values higher than *ca.* 5.2 can be explained by the formation of non-extractable negatively charged vanadium-containing species of the type $[V(O)_x(TAO)_y]^{n-}$ (where $n > 1$ and vanadium oxidation state is +5). Another reason can be the simultaneous extraction of the TAO-A336 ion-pair, which reduces the effective reagents concentrations with increasing pH (see Fig. 2, series 2). A change in the oxidation state of vanadium under the reaction conditions is not expected.^{20,21}

Further optimization experiments were directed to the selection of working concentrations of the reagents, TAO and A336 (Fig. 3), and the time of extraction. The optimization ranges and the set of optimal values are summarized in Table 1.

When comparing the optimal TAO concentrations in this work and in our previous studies with tetrazolium salts,^{20,21} it is clear that the TAO concentration in the present system should be higher $\{1.6 \times 10^{-3}\text{ mol dm}^{-3}\text{ vs. } (3.0\text{--}4.5) \times 10^{-4}\text{ mol dm}^{-3}\}$. The same is valid for the concentration of the cationic ion-association reagent $\{1.3 \times 10^{-2}\text{ mol dm}^{-3}\text{ vs. } (3.9\text{--}9.4) \times 10^{-4}\text{ mol dm}^{-3}\}$. This disadvantage can be attributed to the lower stability of the ternary

complex, provoked by the shape of the cation used and localized charge in it.^{32,33}

It is important to be mentioned that the extraction time in the present work does not affect the absorbance in the entire investigated range (5–240 sec). No decrease in absorption was observed by increasing the extraction time

Figure 2. Absorbance of the V^V – TAO – A336 complex (1) and the blank (2) vs. pH of the aqueous phase. $c_V = 2 \times 10^{-5}\text{ mol dm}^{-3}$, $c_{TAO} = 1.6 \times 10^{-3}\text{ mol dm}^{-3}$, pH 5.0, $c_{A336} = 1.3 \times 10^{-2}\text{ mol dm}^{-3}$, extraction time $t = 120\text{ sec}$.

Figure 3. Effect of TAO (1) and A336 (2) concentration on the absorbance. (1) $c_V = 2 \times 10^{-5}\text{ mol dm}^{-3}$, pH 5.0, $c_{A336} = 1.3 \times 10^{-2}\text{ mol dm}^{-3}$, extraction time $t = 120\text{ sec}$; (2) $c_V = 2 \times 10^{-5}\text{ mol dm}^{-3}$, $c_{TAO} = 1.6 \times 10^{-3}\text{ mol dm}^{-3}$, pH 5.0, extraction time $t = 120\text{ sec}$.

Table 1. LLE-spectrophotometric optimization of the V^V – TAO – Aliquat 336 – water – isobutanol system.

Parameter	Optimization range	Optimal value
Wavelength, nm	Visible range	547
pH	4.0–7.0	5.0
Concentration of TAO, mol dm^{-3}	$(0.08\text{--}2) \times 10^{-3}$	1.6×10^{-3}
Concentration of Aliquat 336, mol dm^{-3}	$(0\text{--}1.56) \times 10^{-2}$	1.3×10^{-2}
Extraction time, seconds	5–240	30

as reported in the literature³⁴ on the extraction of V^V with PAR into similar solvents, such as n-pentanol and n-butanol. We extracted for 30 seconds in our further investigations. This contact time is slightly shorter than the times for V^V extraction by TAO and tetrazolium salts (several minutes)^{20,21} and much shorter than the times for V^V extraction by Aliquat 336 in the absence of chelate reagents.^{11,12,14}

3. 2. Molar Ratios, Complex Composition and Extraction Characteristics

The molar TAO-to-V^V ratio was determined by the method of Asmus³⁵ (Fig. 4a) and the mobile equilibrium method³⁶ (Fig. 5, line 1). The molar Aliquat 336-to-V^V ratio was determined by the same methods (Fig. 4b and Fig. 5, line 2). The results show that the composition of the ternary complex is 1:1:1. Such a composition was reported for the chloroform extracted V^V-PAR-methyltriocetylammmonium complex.²² There are no signs of dimerization in the

Figure 4. Determination of the TAO/V^V (a) and A336/V^V (b) molar ratios by the straight-line method of Asmus. The experimental conditions are given in Fig. 3.

Figure 5. Determination of the TAO/V^V (1) and A336/V^V (2) molar ratios by the mobile equilibrium method. The experimental conditions are given in Fig. 3.

organic phase, as in the extraction of the V^V-TAO anionic complex $[\text{VO}_2(\text{TAO})]^-$ with tetrazolium salts.^{20,21}

The formation of the binary complex in the aqueous phase can be represented by equation 1. It is based on information concerning the state of V^V³⁷ and TAO²⁹ at the reaction conditions.

The next steps, ion-association and extraction, are represented by equation 2.

In it, A336 and its cation are denoted as R_4NCl and R_4N^+ , respectively. The conditional equilibrium constant characterizing equation 2 was calculated by the mobile equilibrium method³⁶ (Fig. 5, straight line 2). The obtained value was $\text{Log } K_{\text{ex}} = 2.8 \pm 0.1$. The coefficient of distribution D was found by comparison of the absorbance values obtained after single and triple extractions as described above: $\text{Log } D = 0.97 \pm 0.04$ (three replicate measurements). The fraction extracted, $E = (90.2 \pm 0.8)\%$, was calculated by the formula $E\% = 100 \times D / (D + 1)$.

3. 3. Beer's Law and Analytical Characteristics

The dependence between the concentration of V^V in the aqueous phase and the absorbance of the extracted complex was studied under the optimum conditions (Table 1). The volumes of the aqueous and organic phase were set to 10 and 5 cm³, respectively. A good linearity was obtained in the range of $0.084\text{--}2.0 \mu\text{g cm}^{-3}$ ($r^2 = 0.9994$, $N =$

9). The linear regression equation was $A = 0.615\gamma - 0.0067$, where A is the absorbance and γ is the concentration of V^V ($\mu\text{g cm}^{-3}$). The standard deviations of the slope and intercept were both equal to 0.005. The limits of detection (LOD) and quantitation (LOQ), calculated as 3 and 10 times standard deviation of the intercept divided by the slope, were $\text{LOD} = 25 \text{ ng cm}^{-3}$ and $\text{LOQ} = 84 \text{ ng cm}^{-3}$. The molar absorptivity (ϵ) and Sandell's sensitivity (S) at $\lambda_{\text{max}} = 547 \text{ nm}$ were $\epsilon = 3.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $S = 1.6 \times 10^{-3} \mu\text{g cm}^{-2}$, respectively.

3. 4. Effect of Foreign Ions

Various ions which are often found together with vanadium in environmental and industrial samples were used to test the selectivity of the developed procedure. Their effect at $\lambda = 547 \text{ nm}$ is presented in Table 2. Co^{II} , Cu^{II} , Ni^{II} and Fe^{III} form intensively colored extractable complexes with TAO. They cause serious positive errors in the spectrophotometric determination of V^V . Mo^{VI} , Al^{III} , Cr^{III} , Re^{VII} and W^{VI} can cause negative errors, however their interfering effect is smaller. When present in moderate amounts, alkaline and alkaline earth cations and the most of the anions studied do not significantly affect the absorbance. V^{IV} causes an increase in absorption as if it were V^V . Most likely, it is oxidized to V^V by the air oxygen^{38,39} in the initial step of the procedure when the slightly alkaline TAO solution is added to the vanadium.

4. Conclusions

The ternary complex formed in the liquid-liquid extraction-chromogenic system V^V -TAO-A336 has a composition of 1:1:1 and can be represented by the formula $(\text{R}_4\text{N}^+)[\text{VO}_2(\text{TAO})]$. Its anionic part $[\text{VO}_2(\text{TAO})]^-$ has an intense red coloration, while the bulky cationic part R_4N^+ is responsible for the easy extraction of the target metal ion (V^V) into organic phase. The organic solvent, isobutanol, is less toxic than the solvents commonly applied in methods involving Aliquat 336. Additional advantages of the proposed procedure are its simplicity and rapidity. Disadvantages in comparison to similar extraction systems, containing tetrazolium salts (instead of Aliquat 336), are the need for higher concentration of the reagents and smaller fraction extracted. These disadvantages can be attributed to the lower stability of the ion-associate, provoked by the shape of the cation and localized charge in it.

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Table 2. Effect of foreign ions in determination of $10.2 \mu\text{g}$ of V^V .

Foreign ion (FI) added	Added salt	FI : V^V mass ratio	Amount of V^V found (μg)	(%)
Al^{III}	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	10	9.8	96.2
Br^-	NaBr	100	10.2	100
Cd^{II}	CdCl_2	5	10.7	105
Cl^-	NH_4Cl	200	10.0	98.3
Co^{II}	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	1	17.5	172
Cr^{III}	$\text{Cr}_2(\text{SO}_4)_3$	2	9.8	96.1
Cr^{VI}	K_2CrO_4	1	11.2	110
Cu^{II}	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	2	19.9	195
F^-	NH_4F	300	10.2	100
Fe^{III}	$\text{Fe}_2(\text{SO}_4)_3$	1	14.8	145
HPO_4^{2-}	Na_2HPO_4	200	10.4	102
I^-	KI	100	9.69	95.0
Mg^{II}	MgSO_4	300	10.2	100
Mn^{II}	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	2	10.6	104
Mo^{VI}	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	100	10.2	100
Ni^{II}	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	1	14.9	146
NO_3^-	NH_4NO_3	200	10.2	100
Re^{VII}	NH_4ReO_4	20	10.0	98.0
Tartrate	$\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	100	9.75	95.9
U^{VI}	$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	2	10.6	104
V^{IV}	$\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$	1	20.3	199
		0.5	15.3	150
W^{VI}	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$	5	10.2	100
Zn^{II}	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	30	10.2	100

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Povzetek

Proučevali smo možnost uporabe kvarterne amonijeve soli Aliquat 336 (A_{336} ; $R_4N^+Cl^-$) in azo barvila 4-(2-tiazolilazo) orcinol (TAO) kot komponenti ekstrakcijsko-kromogenega sistema za vanadij(V) v zmesi voda-izobutanol. Pod optimalnimi pogoji ($c_{TAO} = 1,6 \times 10^{-3} \text{ mol dm}^{-3}$, $c_{A_{336}} = 1,3 \times 10^{-2} \text{ mol dm}^{-3}$ in pH 5,0) smo ekstrahirali vanadij(V) kot ternarni kompleks s formulo $(R_4N^+)[VO_2(TAO^{2-})]$. Določili smo ključne ekstrakcijsko-spektrofotometrične karakteristike. Proučili smo tudi interferenco nekaterih ionov. Valovna dolžina maksimalne absorpcije (λ_{max}), molska absorptivnost (ϵ_{max}), konstanta ekstrakcije (K_{ex}) in delež ekstrakcije (E) so $\lambda = 547 \text{ nm}$, $\epsilon = 3,1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, $\log K_{ex} = 2,8$ in $E = 90,2 \%$. Beerov zakon velja v območju $0,084\text{--}2,0 \mu\text{g cm}^{-3}$, meja detekcije za vanadij(V) je 25 ng cm^{-3} .