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 (cTAO = 1.6×10−3 mol dm−3, cA336 = 1.3×10−2 mol dm−3 and pH 5.0), vanadium(V) is extracted as a ternary complex which can be represented by the formula (R4N+) [VO2(TAO2−)]. The key extraction-spectrophotometric characteristics were determined. The interfering effect of foreign ions was studied as well. The wavelength of maximum absorption (λmax), molar absorptivity (εmax), constant of extraction (Kex) and fraction extracted (E) were found to be λ = 547 nm, ε = 3.1 × 10 4 dm3 mol–1 cm–1, Log Kex = 2.8 and E = 90.2%, respectively. Beer’s law was obeyed in the range of 0.084–2.0 µg 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 make ILs of fundamental interest to specialists in various areas of chemistry and physics.1,2 The IL Aliquat 336 (A336; R4N+Cl−) finds applications as a surfactant, phase-transfer catalyst and ion-association reagent.3 The methyltrialkyl(C8-C10)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,6 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 at to study the LLE of VV in a chromogenic system containing 5-methyl-4-(2-thiazolylazo)resorcinol (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 VV-TAO ternary complexes with tetrazolium cations were recently investigated in our laboratory.20,21 It was found that their structures differs from the structures of the ternary complexes of VV with similar ligands, such as 4-(2-thiazolylazo)resorcinol (TAR) and 4-(2-pyridylazo)resorcinol (PAR), due to the influence of the -CH3 group of TAO, which is capable to form a H-bond with an oxygen atom of the -VO2 group.21
The list of related studies can be extended by the chloroform extraction of VV as a ternary complex with PAR and methyltrioctylammonium chloride, which is one of the main components of A336. Ligandless LLE of VV with A336 in acidic and alkaline 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.

2. Experimental

2.1. Reagents and Apparatus

Vanadium(V) solution (2 × 10⁻⁴ mol dm⁻³) was prepared by dissolving NH₄VO₃ (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. 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 CH₃COOH 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 VV, 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, dried with a pinch of anhydrous Na₂SO₄ 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 VV were also run.

2.3. Determination of the Coefficient of Distribution

The coefficient of distribution D was calculated by the formula \( D = A_j / (A_3 - A_j) \), where \( A_j \) is the absorbance obtained after a single extraction (under the optimal extraction conditions, Table 1), and \( A_j \) is the absorbance obtained after a triple extraction under the same conditions. The final volume of the solutions in both cases was 25 cm³.

2.4. Investigation of the Influence of Foreign Ions

Solutions of VV (1 cm³, 2 × 10⁻⁴ mol dm⁻³), foreign ion, TAO (3 cm³, 5.3 × 10⁻³ mol dm⁻³) and buffer (1 cm³, 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 cm³, 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 Na₂SO₄ 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 VV were also run.

3. Results and Discussion

3.1. LLE-Spectrophotometric Optimization

It is known that VV forms a red complex with TAO in aqueous ethanolic medium. It has a composition of 1:1 and cannot be extracted in chloroform, due to its anionic nature. Our preliminary studies on the VV-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.
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). 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. 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 $\left[\text{V(O)}_x\text{TAO}_y\right]^{n-}$ (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.

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, it is clear that the TAO concentration in the present system should be higher $[1.6 \times 10^{-3} \text{ mol dm}^{-3}]$ vs. $(3.0–4.5) \times 10^{-4} \text{ mol dm}^{-3}]$. The same is valid for the concentration of the cationic ion-association reagent $[1.3 \times 10^{-2} \text{ mol dm}^{-3}]$ vs. $(3.9–9.4) \times 10^{-4} \text{ mol dm}^{-3}]$. 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.

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.

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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$^{-3}$ | $(0.08–2) \times 10^{-3}$ | $1.6 \times 10^{-3}$ |
| Concentration of Aliquat 336, mol dm$^{-3}$ | $(0–1.56) \times 10^{-2}$ | $1.3 \times 10^{-2}$ |
| Extraction time, seconds    | 5–240                  | 30            |
as reported in the literature\textsuperscript{34} on the extraction of \( V^V \) with \( \text{PAR} \) 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)\textsuperscript{20,21} and much shorter than the times for \( V^V \) extraction by Aliquat 336 in the absence of chelate reagents.\textsuperscript{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 Asmus\textsuperscript{35} (Fig. 4a) and the mobile equilibrium method\textsuperscript{36} (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-methyltrioctylammonium complex.\textsuperscript{22} There are no signs of dimerization in the organic phase, as in the extraction of the \( V^V \)-TAO anionic complex \([\text{VO}_2(\text{TAO})]^-\) with tetrazolium salts.\textsuperscript{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 \( V^V \)\textsuperscript{37} and TAO\textsuperscript{38} at the reaction conditions.

\[
\text{VO}_3^- (aq) + H\text{TAO}^- (aq) \rightleftharpoons [\text{VO}_2(\text{TAO})]^- (aq) + OH^- (aq)
\]  

(1)

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

\[
[\text{VO}_2(\text{TAO})]^- (aq) + R_4N\text{Cl} (org) \rightleftharpoons (R_4N^+)[\text{VO}_2(\text{TAO})^-] (org) + Cl^- (aq)
\]  

(2)

In it, A\textsubscript{336} and its cation are denoted as \( R_4\text{NCl} \) and \( R_4\text{N}^+ \), respectively. The conditional equilibrium constant characterizing equation 2 was calculated by the mobile equilibrium method\textsuperscript{36} (Fig. 5, straight line 2). The obtained value was \( \log K_{ex} = 2.8 \pm 0.1 \). The coefficient of distribution \( D \) was found by comparison of the absorbance values obtained after single and triple extractions as described above: \( \log D = 0.97 \pm 0.04 \) (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 cm\(^3\), respectively. A good linearity was obtained in the range of 0.084–2.0 \( \mu g \) 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 \( \gamma \) is the concentration of \( \text{VV} \) (\( \mu g \text{ cm}^{-3} \)). 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 LOD = 25 ng cm\(^{-3}\) and LOQ = 84 ng cm\(^{-3}\). The molar absorptivity (\( \varepsilon \)) and Sandell's sensitivity (S) at \( \lambda_{\text{max}} = 547 \text{ nm} \) were \( \varepsilon = 3.1 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1} \) and \( S = 1.6 \times 10^{-3} \mu g \text{ cm}^{-2} \), 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 \( \text{VV} \). 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. \( \text{VV} \) causes an increase in absorption as if it were \( \text{VV} \). Most likely, it is oxidized to \( \text{VV} \) 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 \( \text{VV}-\text{TAO}-\text{Aliquat 336} \) 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 \( \text{R}_4\text{N}^+ \) is responsible for the easy extraction of the target metal ion (\( \text{VV} \)) 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.

5. References

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### Table 2. Effect of foreign ions in determination of 10.2 µg of \( \text{VV} \).

| Foreign ion (FI) added | Added salt          | FI : VV mass ratio | Amount of VV found (µg) | Amount of VV found (%) |
|------------------------|---------------------|--------------------|-------------------------|------------------------|
| Al\( ^{III} \)        | Al\(_2\)(SO\(_4\))\(_3\) \cdot 18H\(_2\)O | 10                 | 9.8                     | 96.2                   |
| Br\( ^{-} \)           | NaBr                | 100                | 10.2                    | 100                    |
| Co\( ^{II} \)          | CdCl\(_2\)          | 5                  | 10.7                    | 105                    |
| Cl\( ^{-} \)           | NH\(_4\)Cl          | 200                | 10.0                    | 98.3                   |
| Co\( ^{II} \)          | Co\(_2\)(SO\(_4\))\(_3\) | 1                  | 17.5                    | 172                    |
| Fe\( ^{III} \)         | Cr\(_2\)(SO\(_4\))\(_3\) | 2                  | 9.8                     | 96.1                   |
| Fe\( ^{II} \)          | Cr\(_2\)(SO\(_4\))\(_3\) | 1                  | 11.2                    | 110                    |
| Cu\( ^{II} \)          | Cu\(_2\)(SO\(_4\))\(_3\) | 2                  | 19.9                    | 195                    |
| F\( ^{-} \)            | NH\(_4\)F            | 300                | 10.2                    | 100                    |
| Fe\( ^{III} \)         | Fe\(_2\)(SO\(_4\))\(_3\) | 1                  | 14.8                    | 145                    |
| HPO\(_4\)^{2-}         | Na\(_2\)HPO\(_4\)   | 200                | 10.4                    | 102                    |
| I\( ^{-} \)            | KI                   | 100                | 9.69                    | 95.0                   |
| Mg\( ^{II} \)          | MgSO\(_4\)          | 300                | 10.2                    | 100                    |
| Mn\( ^{II} \)          | MnSO\(_4\) \cdot 5H\(_2\)O | 2                  | 10.6                    | 104                    |
| Mo\( ^{VI} \)          | (NH\(_4\))\(_6\)Mo\(_2\)(SO\(_4\))\(_4\) \cdot 4H\(_2\)O | 100                  | 10.2                    | 100                    |
| Ni\( ^{II} \)          | NiSO\(_4\) \cdot 7H\(_2\)O | 1                  | 14.9                    | 146                    |
| NO\(_3\)^{-}           | NH\(_4\)NO\(_3\)    | 200                | 10.2                    | 100                    |
| Re\( ^{VII} \)         | NH\(_4\)ReO\(_4\)   | 20                  | 10.0                    | 98.0                   |
| Tartrate               | KNaC\(_4\)H\(_4\)O\(_6\) \cdot 4H\(_2\)O | 100                  | 9.75                    | 95.9                   |
| U\( ^{VI} \)           | UO\(_2\)(CH\(_3\)COO\(_2\)) \cdot H\(_2\)O | 2                  | 10.6                    | 104                    |
| V\( ^{IV} \)           | VOSO\(_4\) \cdot 5H\(_2\)O | 1                  | 20.3                    | 199                    |
| W\( ^{VI} \)           | Na\(_2\)WO\(_4\) \cdot 2H\(_2\)O | 5                  | 10.2                    | 100                    |
| Zn\( ^{II} \)          | ZnSO\(_4\) \cdot 7H\(_2\)O | 30                  | 10.2                    | 100                    |
Povzetek
Proučevali smo možnost uporabe kvarterne amonijeve soli Aliquat 336 (A336; R4N+Cl−) in delež ekstrakcije (Kex) in delež ekstrakcije (E) so λ = 547 nm, ε = 3.1 × 104 dm3 mol−1 cm−1, log Kex = 2.8 in E = 90.2 %. Beerov zakon velja v območju 0.084–2.0 µg cm−3, meja detekcije za vanadij(V) je 25 ng cm−3.

Toncheva et al.: Liquid-Liquid Extraction-Chromogenic System ...