

Extraction-Spectrophotometric Study of Ternary Complexes of Nb^V and Ta^V

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Abstract

29 liquid-liquid extraction-chromogenic systems containing M^V (M=Nb or Ta), thiocatecholic compounds (TCs) and hydrophobic amines (HAs) were studied. The following TCs were used: 2,4-dihydroxythiophenol (DHTP), 2-hydroxythiophenol (HTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HBIP). The HAs were aniline (An), N-methylaniline (MAN), N,N-dimethylaniline (DAn), aminopyridine (APy), dipyridyl (DiPy), guanidine (Gu), diphenylguanidine (DPG), and triphenylguanidine (TPG). The best organic solvent was chloroform. Under the optimum conditions, the molar absorptivities (ϵ_{\max}) and the degrees of M^V extraction (R%) in this solvent were in the ranges $(1.6-3.9) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and (98.1-99.3)%, respectively. The molar ratio of the reacting species was 1:2:2 (M^V:TC:HA). Relationships were studied between the acid-base properties of the sulfhydryl group of TCs (pK_{SH}) and some characteristics of the ternary complexes (ϵ_{\max} and ΔpH_{50}).

Keywords

Liquid-Liquid Extraction, Niobium, Tantalum, Complex Formation, Ion-Associate, Constants of Dissociation, Relationship, Spectrophotometric Investigation

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1. Introduction

The chemical similarity of the transition metals Nb and Ta caused by their belonging to the same group of the Periodic Table and the phenomenon of the lanthanide contraction, leading to equalization of the ionic radii, requires a joint study of their compounds.¹ Many reagents and techniques have been applied for simultaneous^{1c, 2} or separate³ determination of these elements. However, the developed procedures are most often characterized by drawbacks, such as low selectivity, high running costs, need of expensive equipment, preliminary separation, well-trained personnel, etc.

In the present work we use conventional spectrophotometry to investigate the formation and liquid-liquid extraction (LLE) of series of Nb^V and Ta^V ternary complexes which seems to be prospective for the spectrophotometric

determination of these elements. The following reagents were used: i) thiocatechols (TCs): 2,4-dihydroxythiophenol (DHTP), 2-hydroxythiophenol (HTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP), and 2-hydroxy-5-iodothiophenol (HBIP); and (ii) hydrophobic amines (HAs): aniline (An), N-methylaniline (MAN), N,N-dimethylaniline (DAn), aminopyridine (APy), dipyridyl (DiPy), guanidine (Gu), diphenylguanidine (DPG), and triphenylguanidine (TPG).

Some of the mentioned reagents have been recently applied for LLE-spectrophotometric determination of various elements in real samples.⁴ For the determination of Nb^V one of us used the couples HBTP-Gu, HBTP-DPG, and HBTP-TPG.^{3m} To best of our knowledge, investigations on the Ta^V-TC-HA complexes have not been performed so far.

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2. Experimental

2.1. Reagents and Instruments

Stock solutions of Nb^V and Ta^V were prepared according to known procedures.⁵ They were standardized gravimetrically with phenylarsonic acid and N-benzoil-N-phenylhydroxylamine, respectively.^{3a} Working solutions (0.1 mg mL⁻¹) were prepared by appropriate dilution of the stock solutions. Chloroform solutions (1.3×10⁻² mol L⁻¹) of the reagents TCs and HAs were used. HAs (97-99% purity) were purchased from Sigma-Aldrich. TCs were synthesized according to the procedure of Kuliev et al.⁶ Their purity was verified by melting point determination and paper chromatography. The acidity was adjusted by adding HCl or NaOH solutions (0.1 mol L⁻¹). pH was measured using an I-120.2 potentiometer with a glass electrode. The absorbance was recorded with a KFK-2 photocolormeter and a Camspec M508 spectrophotometer, equipped with 5 and 10 mm path-length cells.

2.2. Optimization Procedure

An aliquot containing M^V solution (M=Nb or Ta) was placed

in a calibrated tube. Chloroform solutions of TC and HA were added and the organic phase was diluted to 5 mL with organic solvent. The volume of the aqueous phase was increased to 25 mL. The tube was closed and shaken for a fixed time. After separation of the layers, a portion of the organic extract was transferred into a cell and the absorbance was read against simultaneously prepared blank sample.

3. Results and Discussion

The binary complexes, Nb^V-TC and Ta^V-TC, cannot be extracted in chloroform or other slightly polar organic solvents. Experiments with KU-2 and AV-17 ion-exchangers showed that these yellow species are charged negatively. Electroneutral ternary complexes can be formed in the presence of HAs. The following organic solvents were tested for the extraction of these complexes: chloroform, 1,2-dichloroethane, carbon tetrachloride, benzene, toluene, xylene, iso-butanol, and iso-pentanol. Chloroform was found to be the most effective. At the optimum conditions this solvent provides degrees of extraction R>98.1% (Tables 1 and 2).

Table 1. Characteristics of the Nb^V-TC-HA-water-chloroform extraction-chromogenic systems

Reagents	pH _{opt}	λ _{max} (nm)	ε _{max} ×10 ⁻⁴ (L mol ⁻¹ cm ⁻¹)	R (%)	Linear range (μg mL ⁻¹)
DHTP+An	4.5-6.3	420	3.5	98.3	2.2-100
DHTP+MAn	4.8-6.8	425	3.8	98.5	2.2-100
DHTP + DAn	5.0-6.8	430	3.9	98.6	2.2-100
HTP+AmPy	6.2-7.8	445	2.1	98.3	1.5-115
HTP+DiPy	5.0-6.1	458	2.5	98.6	1.8-90
HTP+An	4.2-6.5	435	3.3	98.5	2.0-90
HCTP+An	4.1-6.4	438	2.8	98.3	1.0-95
HCTP+Gu	4.2-6.6	418	3.6	98.2	3.2-80
HCTP+DPG	4.1-6.4	425	3.4	98.1	3.1-75
HCTP+TPG	4.0-6.2	430	3.2	99.3	3.2-70
HBTP+An	4.0-6.3	442	2.7	99.1	1.0-105
HIITP+AmPy	5.8-6.5	452	1.8	98.3	2.6-110
HIITP+DiPy	4.9-5.7	475	1.9	98.4	3.4-100
HIITP+An	3.9-6.1	447	2.6	98.6	2.0-120

Table 2. Characteristics of the Ta^V-TC-HA-water-chloroform extraction-chromogenic systems

Reagents	pH _{opt}	λ _{max} (nm)	ε _{max} ×10 ⁻⁴ (L mol ⁻¹ cm ⁻¹)	R (%)	Linear range (μg mL ⁻¹)
DHTP+An	3.6-5.7	418	3.3	98.5	1.0-80
DHTP+MAn	4.2-6.7	423	3.6	98.3	1.0-80
DHTP+DAn	4.3-6.8	428	3.9	98.2	1.0-80
HTP+AmPy	5.0-6.0	453	2.0	98.1	2.4-100
HTP+DiPy	5.1-6.0	465	2.2	98.2	1.8-90
HTP+An	4.1-6.4	440	3.0	98.3	1.0-100
HCTP+Gu	4.1-6.5	436	3.0	98.4	4.2-90
HCTP+DPG	4.0-6.3	440	3.3	98.6	3.6-95
HCTP+TPG	4.1-6.0	447	3.3	98.5	3.8-100
HBTP+Gu	3.1-5.7	435	3.2	98.3	1.6-100
HBTP+DPG	2.5-5.7	442	3.1	98.3	2.0-80
HBTP+TPG	2.4-5.3	451	3.0	98.6	3.0-90
HIITP+AmPy	4.6-5.4	460	1.6	98.6	3.0-100
HIITP+DiPy	4.8-5.6	470	1.7	98.5	2.6-100
HIITP+An	3.8-6.0	450	2.5	98.3	2.8-90

3.1. Effect of pH

Extractable ternary complexes are formed in acidic and neutral media. The optimum pH intervals (Tables 1 and 2) are wide enough to ensure stable and reproducible results without using buffer solutions. The course of all pH-curves supports the assumption that only one complex is formed in each of the extraction-chromogenic systems (Fig. 1). At pH values higher than pH_{opt}, the extraction efficiency reduces most likely due to a decrease of the degree of HA protonation. At pH values lower than pH_{opt}, the concentration of the anionic TC species is insufficient for quantitative complex formation.

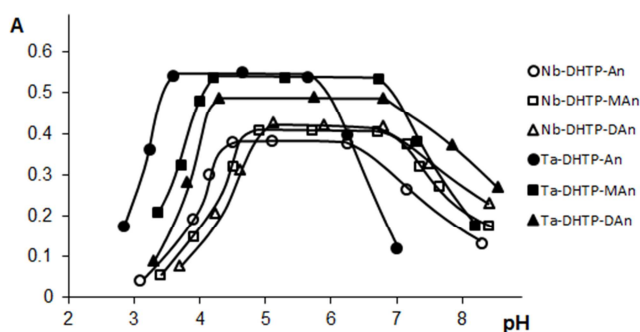


Figure 1. Absorbance of the ternary M^V-TC-HA complexes vs. pH of the aqueous phase. C_{Nb}=2.15×10⁻⁵ mol L⁻¹, C_{Ta}=3.3×10⁻⁵ mol L⁻¹, C_{TC}=1.3×10⁻³ mol L⁻¹, C_{HA}=1.0×10⁻³ mol L⁻¹, ℓ=0.5 cm

3.2. Absorption Spectra

The absorption bands in the visible range of the ternary M^V-TC-HA complexes are symmetrical and relatively narrow (Fig. 2). They are situated in the range of 418-475 nm (M=Nb) and 418-470 nm (M=Ta) (Tables 1 and 2, respectively). The color reactions are very contrast. The bathochromic shifts Δλ calculated towards λ_{maxTC} are in the range of 135-185 nm (Δλ_{Nb}) or 140-187 nm (Δλ_{Ta}).

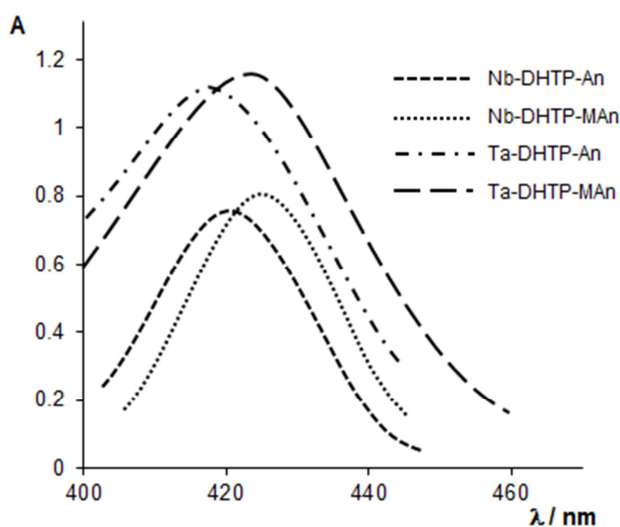


Figure 2. Absorption spectra of extracted ternary complexes of Nb^V and Ta^V. C_{Nb}=2.15×10⁻⁵ mol L⁻¹, C_{Ta}=3.3×10⁻⁵ mol L⁻¹, C_{TC}=1.3×10⁻³ mol L⁻¹, C_{HA}=1.0×10⁻³ mol L⁻¹, ℓ=1.0 cm

3.3. Reagents Concentrations, Molar Absorptivities and Effect of Time

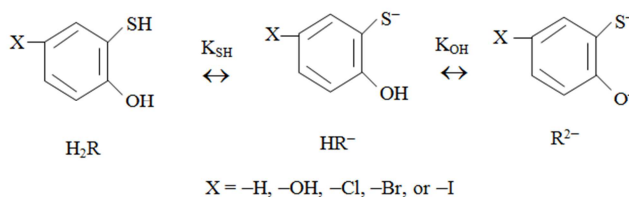
Maximum and constant M^V extraction can be achieved at TC and HA concentrations not lower than (0.95-1.28)×10⁻³ mol L⁻¹ and (5.2-9.4)×10⁻⁴ mol L⁻¹, respectively. M^V concentration ranges in which the Beer's law is obeyed are listed in Tables 1 and 2. The molar absorptivities (ε_{max}) belong to the interval (1.6-3.9)×10⁴ L mol⁻¹ cm⁻¹ and (1.8-3.9)×10⁴ L mol⁻¹ cm⁻¹ for the complexes of Nb^V and Ta^V, respectively. The couples DHTP-DAn and HTP-AmPy ensure the highest and the lowest ε_{max} values, respectively. The extraction equilibria establish within 5-10 minutes. The absorbance of the extracts is stable for at least 72 hours.

3.4. Stoichiometry of the Ternary Complexes and General Formula

The molar ratios TC:M^V and HA:M^V in the ternary complexes were determined by the mobile equilibrium method,⁷ straight line method of Asmus,⁸ and relative yield method.⁹ The results show a complex composition of 1:2:2 (M^V:TC:HA). Using the Nazarenko's method,¹⁰ we found that the coordinating ion is [M(OH)₃]²⁻. Hence, the complexes can be regarded as ion-associates between doubly charged anionic chelates [M^V(OH)₃(TC²⁻)₂]²⁻ and two protonated HA species: (HHA⁺)₂[M^V(OH)₃(TC²⁻)₂].

3.5. Dissociation Constants of TCs

TCs contain -OH and -SH groups in their molecules. Depending on the acidity of the medium TCs can exist in molecular (H₂R) or anionic (HR⁻ and R²⁻) forms. The process of dissociation can be presented by the following scheme:



Scheme 1. Dissociation of TCs (H₂R) in aqueous solutions

To determine the corresponding constants of dissociation, K_{SH} and K_{OH}, we used pH-titration with NaOH.¹¹ The results are presented in Table 3.

Table 3. Calculated pK values for the studied ligands at μ=0.1 (NaClO₄) and 25±0.5°C

TC	pK _{SH}	pK _{OH}
DHTP	6.33	11.2
HTP	5.8	10.9
HCTP	5.1	10.6
HBTP	5.05	10.4
HITP	5.0	10.2

3.6. Correlation Between Properties of the Reagents and Complexes

To establish relationships between the acid-base properties of the sulfhydryl group (pK_{SH}) and some properties of the ternary complexes (ΔpH_{50} and ϵ_{max}) we constructed Fig. 3 and Fig. 4. The pH_{50} values were determined graphically from the dependence $A=f(pH)$ (see Fig. 1) for absorbance of 50%. ΔpK_{SH} values in Fig. 3 and Fig. 4 are the differences between pK_{SH} of the unsubstituted reagent (HTP; X=H) and pK_{SH} of its substituted analogues (X=OH, Cl, B, and I). ΔpH_{50} in Fig. 3 is the corresponding difference between the pH_{50} values for HTP and DHTP, HCTP, HBTP or HITP.

The relationship between ΔpK_{SH} and ΔpH_{50} (Fig. 3) can be adequately described by a straight-line equation ($R^2=0.9998$). The relationship between ΔpK_{SH} and ϵ_{max} can be better described by a non-linear regression type equation (Fig. 4). The linear model applied to this set of data gave R-squared value of 0.9728. All calculations were made using MS Excell software.

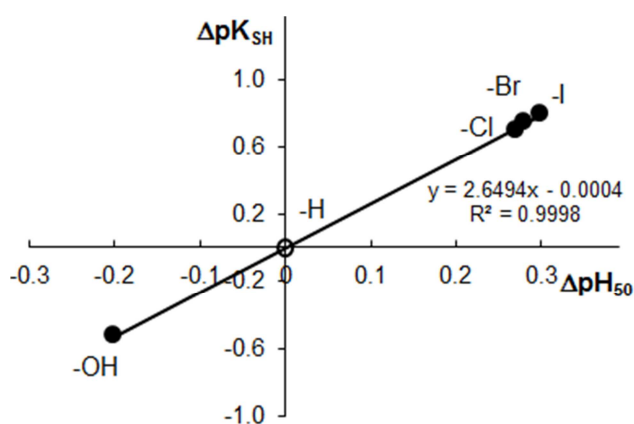


Figure 3. Correlation between the acidic properties of TCs (ΔpK_{SH}) and ΔpH_{50} for the Nb^V -TC-An complexes

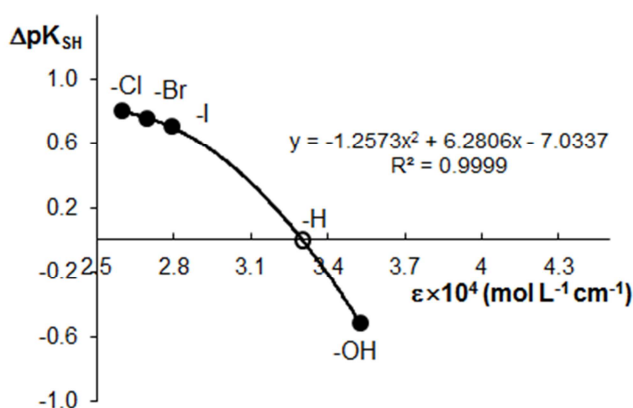


Figure 4. Correlation between the acidic properties of TCs (ΔpK_{SH}) and molar absorptivity of the Nb^V -TC-An complexes

4. Summary and Conclusions

1. Nb^V and Ta^V form well chloroform-extractable ternary complexes with thiocatechols (TCs) and hydrophobic amines (HAs).

2. The molar ratio of the reacting M^V , TC and HA species is 1:2:2. The general formula of the ternary complexes is $(HHA^+)_2[M^V(OH)_3(TC^{2-})_2]$. They can be regarded as ion-associates between doubly charged anionic chelates $[M^V(OH)_3(TC)_2]^{2-}$ and protonated HA species.

3. The molar absorptivities (ϵ_{max}) belong to the interval $(1.6-3.9) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $(1.8-3.9) \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ for the complexes of Nb^V and Ta^V , respectively. The highest molar absorptivity can be achieved with the couple DHTP-DAN.

4. Relationships exist between the acid-base properties of the sulfhydryl group of TCs (pK_{SH}) and some characteristics of the ternary complexes. The relationship between ΔpK_{SH} and ΔpH_{50} for the Nb^V complexes can be adequately described by a straight-line equation ($y=2.6494x-0.0004$). The relationship between ΔpK_{SH} and ϵ_{max} for the same complexes can be described by a non-linear regression equation ($y=-1.2573x^2+6.2806x-7.0337$).

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