

Scientific paper

Study on the Complex Formation and the Ion-Association of Anionic Chelate of Molybdenum(VI) with Bidentate Ligand and the Cation of 2,3,5-Triphenyl-2*H*-tetrazolium Chloride

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Received: 10-01-2019

Abstract

The complex formation between the anionic chelate of molybdenum(VI) with the bidentate ligand of 3,5-dinitrocatechol (3,5-DNC) and its ion-association with the cation of 2,3,5-triphenyl-2*H*-tetrazolium chloride (TTC) in the liquid-liquid extraction system Mo(VI)-3,5-DNC-TTC-H₂O-CHCl₃ were studied by spectrophotometry. The validity of Beer's law was checked and some analytical characteristics of the system were calculated under the optimum conditions for the chelate formation and extraction. The effect of various co-existing ions and reagents on the process of chelate formation and ion-association was investigated. The molar ratio of the components in the ion-associated complex Mo(VI)-3,5-DNC-TTC was determined by independent methods. The association process in aqueous phase and the extraction equilibria were investigated and quantitatively characterized by the following equilibrium constants: association constant, distribution constant, extraction constant and recovery factor. Based on this, a reaction scheme, a general formula and a structural formula of the complex were suggested.

Keywords: Molybdenum(VI); bidentate ligand; chelate formation; extraction equilibria

1. Introduction

The molybdenum is a transition metal with rich coordination chemistry, it occurs in various oxidation states, coordination numbers and geometries.¹⁻³ Molybdenum(VI) forms complexes with various organic ligands, such as polyphenols and their functional derivatives, polyhydroxycarboxylic acids, aminopolycarboxylic acids, hydroxamic acids, amines (primary, secondary and tertiary), 8-hydroxyquinoline and its derivatives, aldehyde hydrazones, oximes, β -diketones, fluorones, hydroxyazodyes, biomolecules (chitosan, chitin, D-glucosamine, L-alanine, L-phenylalanine).⁴⁻¹⁷ Molybdenum(VI) complexes with bidentate ligands, containing [S,S], [S,O], [S,N] donor atoms, like toluene-3,4-dithiol, 2-mercaptophenol, 2-amino-

thiophenol, ethane-1,2-dithiol, dithiooxamide, 2-thiopheno-carboxamide, were obtained and structurally characterized.¹⁸ Molybdenum(VI) gives colored anionic chelates with bidentate ligands of aromatic compounds, containing two or more hydroxyl groups in *o*-position relative to each other. 1,2-Dihydroxybenzene, 1,2,3-trihydroxybenzene and 3,4,5-trihydroxybenzoic acid form colored bidentate chelates, while phenol, 1,3-dihydroxybenzene and 1,4-dihydroxybenzene do not form colored chelates in the pH range 1.1–10.9.⁴ The colored anionic chelates of molybdenum(VI) form ion-associated complexes with bulky organic cations, like methyltriethylammonium, cetylpyridinium, cetyltrimethylammonium, tetraphenylphosphonium.^{4,19-21}

The ion-associated complexes of anionic chelates of metals with various natural organic and inorganic ligands

with N-, S- and O-containing donor atoms and with the participation of mono- and ditetrazolium cations are a special scientific research field of the chemistry of the coordination compounds. It is up-to-date topic, not only as a theoretical background for the preparation of novel ion-associated complexes, but mainly due to the possibility for their application in the Analytical Chemistry for determination of various metals in natural, industrial, pharmaceutical and biological samples, addressing in such a way a number of ecological issues. Tetrazolium salts are used as reagents for the preparation of various ion-associated complexes of metals, e.g. W(VI), Ge(IV), Tl(III), Nb(V), V(V), Ga(III), Co(II), Ge(IV).^{22–31} The structure and properties of mono- and ditetrazolium salts, the bulky hydrophobic organic substituents in their molecules, determine their ability to form ion-associated complexes, increasing the extractability in non-polar solvents. The presence of a quaternary nitrogen atom in the molecules of the tetrazolium salts determines the ability to form ionic associates in the aqueous phase without protonation, as opposed to the amines.^{22,32,33}

The liquid-liquid extraction is a part of the chemistry of the solutions and the coordination compounds. It is applied to study the processes of complex formation and the extraction equilibria. The extraction spectrophotometry is a relatively simple, convenient, rapid to perform and inexpensive method for preparation and characterization of new complex compounds as well as for their application in the chemical analysis.^{34–40}

The aim of our current investigation was to synthesize molybdenum(VI) ion-associated complex in liquid-liquid extraction system and estimate its feasibility in analytical chemistry of Mo(VI), in order to evaluate the possible applications of the system for determination of traces of molybdenum(VI) in alloys, biological, medical and pharmaceutical samples. The extraction equilibria of the chelate formation between molybdenum(VI) with the bidentate ligand of 3,5-dinitrocatechol (3,5-DNC) and the cation of 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) in the liquid-liquid system Mo(VI)–3,5-DNC–TTC–H₂O–CHCl₃ was studied spectrophotometrically.

2. Experimental

2.1. Reagents and Apparatus

Na₂MoO₄ · 2H₂O (Fluka AG, p.a.): an aqueous 1.6 × 10⁻² mol L⁻¹ solution was prepared.

3,5-Dinitrocatechol (3,5-DNC) (Sigma-Aldrich, p.a.): 3,5-DNC was dissolved in CHCl₃ to give a 1.0 × 10⁻² mol L⁻¹ solution. 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) (Loba Feinchemie, p.a.): an aqueous 3.0 × 10⁻³ mol L⁻¹ solution was prepared. H₂SO₄ (95–97% for analysis, Merck): 9 mol L⁻¹ solution was prepared. The concentration of H₂SO₄ was determined titrimetrically. A Camspec M508 spectrophotometer (UK), equipped with 10 mm path length cells,

was employed for measurement of the absorbance. The organic solvent CHCl₃ was additionally distilled.

2.2. Procedure for Establishment of the Optimum Conditions for Chelate Formation and Ion-Association

The required aliquots of the solutions of Mo(VI), TTC and H₂SO₄ were introduced into 250 mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. A required aliquot of a chloroform solution of 3,5-DNC was added and then the organic phase was adjusted to a volume of 10 mL with chloroform. The funnels were shaken for a fixed time (up to 300 s). A portion of the organic extract was filtered through a filter paper into a 1 cm cell and the absorbance was measured against a blank. The blank extraction was performed in the same manner in the absence of molybdenum.²⁹

2.3. Procedure for Determination of the Distribution Constant

The distribution constant (K_D) can be calculated according to the ratio $K_D = A_1/(A_3 - A_1)$, where A_1 and A_3 are respectively the light absorbance after a single extraction in chloroform under optimum operating conditions and after a triple extraction performed under the same conditions. Single extraction: the single extraction was performed under the optimum conditions for chelate formation (Table 1, column 1). The organic layer was transferred into 25 mL calibrated flask and the flask was brought to volume with chloroform. The measurement of the light absorbance A_1 is done against a blank sample, prepared under the same conditions. Triple extraction: the first stage of the triple extraction is performed with 10 mL of chloroform and the extract is transferred into a 25 mL calibrated flask. During the second stage of the extraction, 8 mL of chloroform are added to the aqueous phase remaining after the first stage. The organic layer is added to that from the first stage. For the third stage of extraction, 7 mL of chloroform are added to the aqueous phase remaining after the second stage and for the third time an extraction is performed. The organic layer is transferred to the previous two. The calibrated flask is brought to volume with chloroform. The measurement of A_3 is performed against a blank sample prepared in the same way.⁴¹

3. Results and Discussion

3.1. Optimum Extraction-Spectrophotometric Conditions for Chelate Formation and Ion-Association

The colored anionic chelate of molybdenum(VI) with the bidentate ligand of 3,5-dinitrocatechol (3,5-

DNC) was extracted in chloroform in the presence of the bulky hydrophobic monotetrazolium cation of 2,3,5-triphenyl-2H-tetrazolium chloride (TTC). The absorption spectrum of the extract of the studied ion-associated complex Mo(VI)-3,5-DNC-TTC in CHCl_3 was characterized by an absorption maximum in the visible range ($\lambda_{\text{max}} = 410 \text{ nm}$) (Figure 1). The acidity of the aqueous phase influences the extraction of the anionic chelate Mo(VI)-3,5-DNC into the organic phase in the form of ion-associate with the tetrazolium cation of TTC. The maximum and constant extraction of the ion-associated complex is achieved in strongly acidic solution of H_2SO_4 ($(0.9\text{--}7.2) \times 10^{-1} \text{ mol L}^{-1}$) (Figure 2). The results from the experiments showed that the extraction equilibrium cannot be achieved within less than 120 s. The prolonged shaking does not have an impact on the absorbance. The next experiments were performed for 3 min. The concentrations of the reagents are the most important factor, influencing the extraction equilibrium. The chelate formation of Mo(VI)-3,5-DNC requires 6.25-fold excess of 3,5-DNC ($\geq 1.0 \times 10^{-3} \text{ mol L}^{-1}$) and 1.13-fold excess of TTC ($\geq 1.8 \times 10^{-4} \text{ mol L}^{-1}$) for maximum association and extraction.

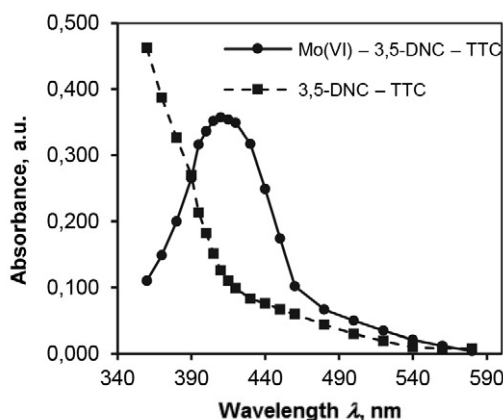


Figure 1. Absorption spectra of the complex Mo(VI)-3,5-DNC-TTC and of the blank sample 3,5-DNC-TTC in CHCl_3 . $C_{\text{Mo(VI)}} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$; $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$; $C_{\text{TTC}} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$; $C_{\text{H}_2\text{SO}_4} = 4.5 \times 10^{-1} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$

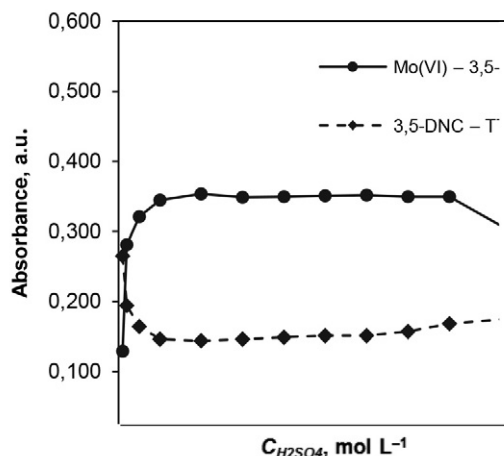


Figure 2. Absorption spectra of the complex Mo(VI)-3,5-DNC-TTC in CHCl_3 against 3,5-DNC-TTC extract vs. acidity of the aqueous phase: $C_{\text{Mo(VI)}} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$; $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$; $C_{\text{TTC}} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$

The optimum experimental conditions for the extraction of the ion-associated complex Mo(VI)-3,5-DNC-TTC are summarized in Table 1, column 1.

3. 2. Beer's Law, Apparent Molar Absorptivity and other Analytical Characteristics

The range of agreement with Beer's law, i.e. the linear relationship between the molybdenum concentration in the aqueous phase ($C_{\text{Mo(VI)}}$, $\mu\text{g mL}^{-1}$) and the absorbance of the ion-association complex in the organic phase after extraction regression analysis under the optimum conditions for complex formation was used. The equation of a straight line was found to be $Y = 0.1806 X + 0.0022$ with a correlation coefficient squared 0.9994. Under the optimum conditions for complex formation, the linearity is observed for concentrations up to $6.72 \mu\text{g mL}^{-1}$ Mo(VI). Further analytical characteristics, e.g. apparent molar absorptivity ϵ' , Sandell's sensitivity, limit of detection and limit of quantification, are shown in Table 1, column 2.

From the analytical characteristics of the extraction system Mo(VI)-3,5-DNC-TTC- H_2O - CHCl_3 , it can be

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system Mo(VI)-3,5-DNC-TTC- H_2O - CHCl_3

| Optimum conditions | Analytical characteristic |
|--|---|
| Absorption maximum (λ_{max}) 410 nm | Apparent molar absorptivity (ϵ') (2.16 ± 0.03) $\times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ |
| Volume of the aqueous phase 10 mL | True molar absorptivity (ϵ) (2.01 ± 0.04) $\times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ |
| Volume of the organic phase 10 mL | Sandell's sensitivity (SS) 4.45 ng cm^{-2} |
| Concentration of H_2SO_4 in the aqueous phase ($0.9\text{--}7.2$) $\times 10^{-1} \text{ mol L}^{-1}$ | Adherence to Beer's law up to $6.72 \mu\text{g cm}^{-3}$ |
| Shaking time (τ) 3 min | Relative standard deviation (RSD) 1.17% |
| Concentration of 3,5-DNC $\geq 1.0 \times 10^{-3} \text{ mol L}^{-1}$ | Limit of detection (LOD) 0.19 $\mu\text{g mL}^{-1}$ |
| Concentration of TTC $\geq 1.8 \times 10^{-4} \text{ mol L}^{-1}$ | Limit of quantification (LOQ) 0.62 $\mu\text{g mL}^{-1}$ |

concluded that the ion-associate formed between the anionic chelate of Mo(VI) with the bidentate ligand of 3,5-DNC and the monotetrazolium cation allows determination of Mo(VI) with a high sensitivity.

3. 3. Effect of Co-Existing Ions and Reagents on the Complex Formation

The effect of various co-existing ions and reagents on the process of the association in aqueous phase and the extraction equilibria was studied under optimum extraction conditions (Table 1, column 1). The concentration of Mo(VI) in the presence of the co-existing ions and reagents was determined from the sequence of Beer's law. A deviation of $\pm 3\%$ from the absorbance of the complex in the absence of co-existing ions was accepted as an interfering effect. The results are presented in Table 2. From them, it can be concluded that most of the ions studied do not interfere, but some of them, like Al(III), Fe(II) and Cr(VI) in concentrations higher than the indicated ones, hinder

Table 2. Effect of co-existing ions and reagents on the complex formation of the ion-associate Mo(VI)-3,5-DNC-TTC for extraction in the presence of 20 μg Mo(VI)

| Co-existing ion and reagent | Co-existing ion and reagent, $\mu\text{g}/10\text{ cm}^3$ aqueous phase | Mo(VI) found, μg | R, % |
|--|---|-----------------------------|--------|
| Na ⁺ | 10000 | 20.19 | 100.95 |
| K ⁺ | 10000 | 20.24 | 101.20 |
| Mg ²⁺ | 10000 | 19.87 | 99.35 |
| Ca ²⁺ | 10000 | 19.77 | 98.85 |
| Cu ²⁺ | 10000 | 19.95 | 99.75 |
| Zn ²⁺ | 10000 | 19.63 | 98.15 |
| Cd ²⁺ | 10000 | 20.46 | 102.30 |
| Ni ²⁺ | 10000 | 20.29 | 101.45 |
| Mn ²⁺ | 10000 | 20.01 | 100.05 |
| Co ²⁺ | 10000 | 19.92 | 99.60 |
| Al ³⁺ | 4000 | 20.32 | 101.61 |
| Cr ³⁺ | 10000 | 19.97 | 99.83 |
| Fe ²⁺ | 750 | 20.20 | 101.02 |
| Fe ³⁺ | 100 | 17.59 | 87.95 |
| V(V) | 100 | 21.17 | 105.87 |
| Nb(V) | 50 | 15.94 | 79.68 |
| Cr(VI) | 100 | 19.91 | 99.56 |
| W(VI) | 50 | 25.06 | 125.32 |
| F ⁻ | 10000 | 19.96 | 99.79 |
| Br ⁻ | 10000 | 20.22 | 101.08 |
| NO ₃ ⁻ | 2500 | 20.82 | 104.09 |
| PO ₄ ³⁻ | 10000 | 20.42 | 102.10 |
| P ₂ O ₇ ⁴⁻ | 10000 | 20.37 | 101.83 |
| CH ₃ COO ⁻ | 10000 | 20.43 | 102.16 |
| C ₄ H ₄ O ₆ ²⁻ | 10000 | 19.94 | 99.69 |
| C ₆ H ₅ O ₇ ³⁻ | 10000 | 20.20 | 101.02 |
| Complexone III | 10000 | 20.03 | 100.15 |
| Complexone IV | 10000 | 20.10 | 100.52 |
| L-Ascorbic acid | 1000 | 20.21 | 101.05 |

the extraction of Mo(VI) as an associated complex with 3,5-DNC and TTC. The extraction equilibrium is severely interfered by Fe(III), V(V) and W(VI) ions at very low concentrations. The interfering ions can be masked or removed from the extraction system to avoid this. Our investigations as well as the studies published in the literature show that some of the co-existing ions, like Al(III), Fe(II) and Fe(III) can be removed by their pre-precipitation with OH⁻ at pH = 11.⁴² Vanadium(V) can be co-precipitated with Fe(III) in alkali medium.⁴³ The co-existing ions, like Fe(II), Fe(III) and Al(III) can be masked with added Complexone III, Complexone IV or L-ascorbic acid in concentrations lower than the indicated.

3. 4. Molar Ratios of the Ion-Associated Complex

The molar ratios of the ion-associated complex were determined by three independent methods: the mobile equilibrium method, the straight-line method of Asmus and the method of continuous variations.⁴⁴

The mobile equilibrium method and the straight-line method of Asmus were applied to prove the molar ratios Mo(VI):3,5-DNC and Mo(VI):TTC. The results from the application of these methods are shown in Figures 3-5, respectively.

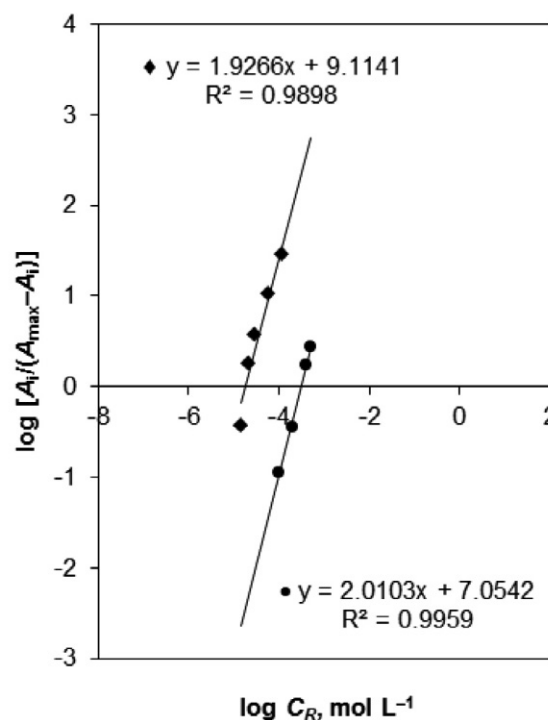


Figure 3. Straight lines by the mobile equilibrium method for determination of the molar ratios Mo(VI):3,5-DNC and Mo(VI):TTC $C_{\text{Mo(VI)}} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$; $C_{\text{H}_2\text{SO}_4} = 4.5 \times 10^{-1} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$
 • Mo(VI) : 3,5-DNC, $C_{\text{TTC}} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$;
 ♦ Mo(VI) : TTC, $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$

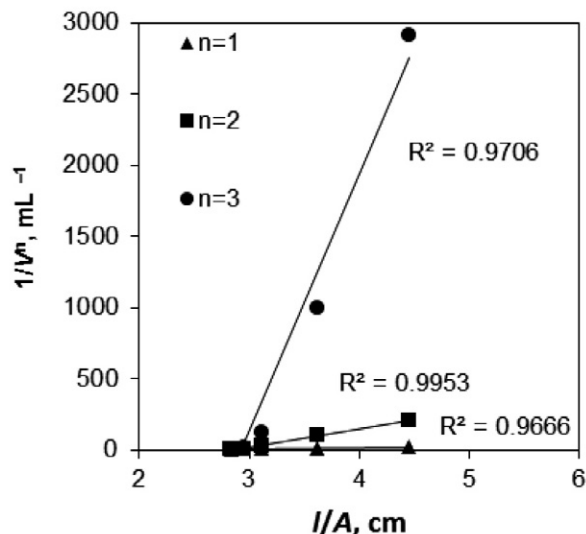


Figure 4. Determination of the molar ratio (n) Mo(VI):TTC by the method of Asmus $C_{\text{Mo(VI)}} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$; $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$; $C_{\text{H}_2\text{SO}_4} = 4.5 \times 10^{-1} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$

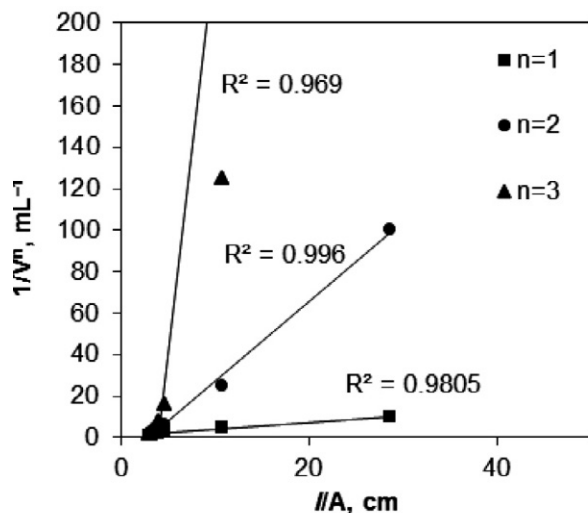


Figure 5. Determination of the molar ratio (n) Mo(VI):3,5-DNC by the method of Asmus $C_{\text{Mo(VI)}} = 1.6 \times 10^{-5} \text{ mol L}^{-1}$; $C_{\text{TTC}} = 2.4 \times 10^{-4} \text{ mol L}^{-1}$; $C_{\text{H}_2\text{SO}_4} = 4.5 \times 10^{-1} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$

On the basis of the results it can be concluded that Mo(VI), 3,5-DNC and TTC interact in molar ratio 1:2:2. The application of the method of continuous variations confirmed the molar ratio Mo(VI):TTC = 1:2 (Figure 6).

3. 5. Reaction Scheme and Suggested General Formula

The carried out experiments showed that the chelate formation and the extraction of the ion-associated complex occurred in strongly acidic solution. Under these conditions, the chelate formation between molybdenum(VI) and the bidentate ligand 3,5-dinitrocatechol (3,5-DNC) is given by the equation (1):

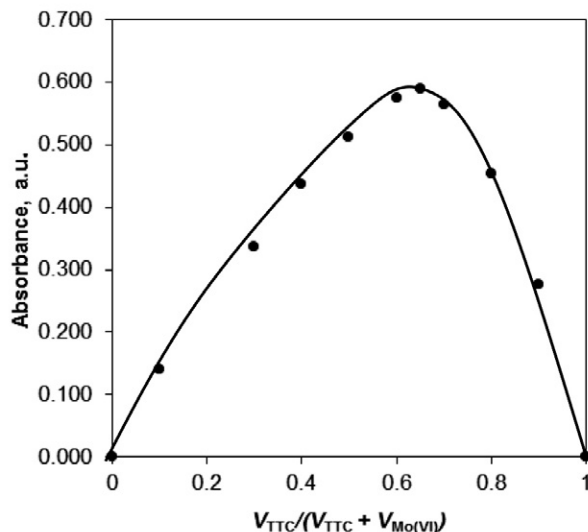
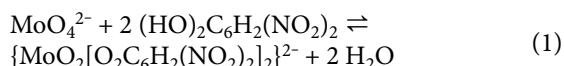
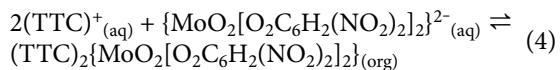
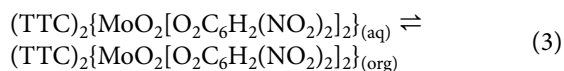
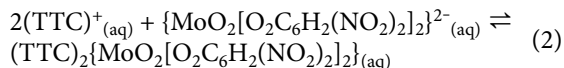


Figure 6. Determination of the molar ratio (n) Mo(VI):TTC by the method of continuous variations $C_{\text{Mo(VI)}} + C_{\text{TTC}} = 8.0 \times 10^{-5} \text{ mol L}^{-1}$; $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$; $C_{\text{H}_2\text{SO}_4} = 4.5 \times 10^{-1} \text{ mol L}^{-1}$; $\lambda = 410 \text{ nm}$; $\tau = 3 \text{ min}$



Having in mind the reaction of chelate formation of Mo(VI)-3,5-DNC and the molar ratio indicated above, it can be suggested that the formation of the ion-associate in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction in chloroform can be given by the following equations (2-4).



Therefore, the ion-associated chelate of Mo(VI)-3,5-DNC with the cation of the monotetrazolium salt 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) can be represented by the general formula $(\text{TTC})_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}$.

3. 6. Extraction Equilibria, True Molar Absorptivity, Recovery Factor and Structural Formula of the Ion-Associated Complex

The association process in aqueous phase and the extraction equilibria were investigated and quantitatively characterized with respect to the following key constants: association constant β , distribution constant K_D , extraction constant K_{ex} and recovery factor $R\%$.

The association constant β and the true molar absorptivity ε were determined by the method of Komar-Tolmachev from equation (5):⁴⁴

$$\beta = (l/n)^n / [\varepsilon (\text{tg } \alpha)^{n+1}] \quad (5)$$

where l is the cuvette thickness ($l = 1$ cm); n - the molar ratio between the components independently determined (e.g. by the mobile equilibrium method, the straight-line method of Asmus or the method of continuous variations) ($n = 2$), ε - the true molar absorptivity.

The true molar absorptivity ε was determined by the method of Komar-Tolmachev (Figure 7) from the equation of a straight line $Y = 1.6762 X + 4.9692$ ($(\varepsilon = 1 / (4.9692 \times 10^{-5}, \text{L mol}^{-1} \text{cm}^{-1}))$) and its value is given in Table 1, column 2.

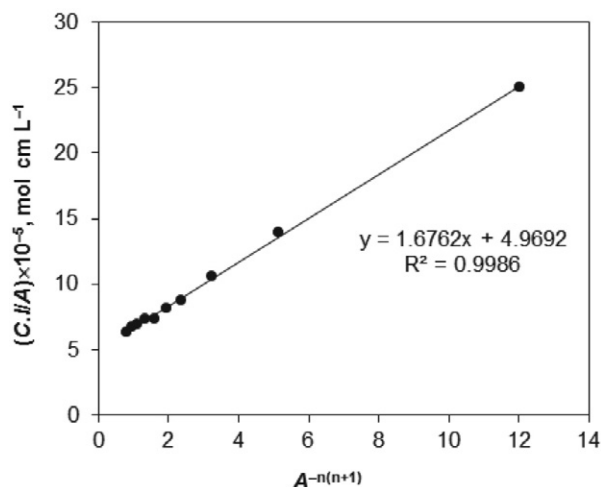


Figure 7. Dependency of $(C//A)$ on $A^{-n/(n+1)}$ (method of Komar-Tolmachev) $C = C_{\text{Mo(VI)}} \text{ mol L}^{-1}$; $C_{\text{TTC}} = 2 C_{\text{Mo(VI)}} \text{ mol L}^{-1}$; $C_{3,5\text{-DNC}} = 1.2 \times 10^{-3} \text{ mol L}^{-1}$; A - absorbance; l - cell thickness, $l = 1$ cm; $n = 2$

The distribution constant (K_D) was determined by the equation (6), where A_1 and A_3 are the absorbance (measured against blanks) obtained after a single and triple extraction, respectively.

$$K_D = \frac{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{org})}\}}{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{aq})}\}} \cdot \frac{A_1}{(A_3 - A_1)} \quad (6)$$

The recovery factor was determined from the equation (7):

$$R\% = 100 K_D / (K_D + 1) \quad (7)$$

The extraction constant K_{ex} was calculated by two independent methods:

$$(i) \log K_{\text{ex}} = \log K_D + \log \beta \quad (8)$$

where β was determined by the method of Komar-Tolmachev.

(ii) the method of Likussar-Boltz:⁴⁵

The method uses the data from the method of continuous variations (Figure 6). The extraction constant K_{ex} was calculated by the equation of Likussar-Boltz for molar ratio 1:2 (equation 9):

$$\log K_{\text{ex}} = 0.3522 - 2 \log K + \log Y_{\text{max}} - 3 \log (1 - Y_{\text{max}}) \quad (9)$$

where K is the total concentration of reagents ($K = C_{\text{Mo(VI)}} + C_{\text{TTC}} = 8.0 \times 10^{-5} \text{ mol L}^{-1}$); Y_{max} and $(1 - Y_{\text{max}})$ are determined by additionally plotted normalized absorption curve ($Y_{\text{max}} = 0.689$; $(1 - Y_{\text{max}}) = 0.311$) (Figure 6).

The values of the equilibrium constants and the recovery factor, describing quantitatively the equilibrium in the aqueous phase and the extraction of the ion-associated complex in the organic phase are presented in Table 3.

The results obtained by independent methods are statistically similar and confirm the proposed scheme of the process of complex formation of the ion-associated complex in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction in chloroform. Based on this, the proposed structural formula of the ion-associated complex is represented in Figure 8.

Table 3. Values of the equilibrium constants and the recovery factor

| Equilibrium constant and recovery factor | Value |
|---|---|
| Equilibrium (Eq. 2) – Association constant b $b = \frac{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{aq})}\}}{\{[(TTC)^+]^2_{(\text{aq})}\} \{[\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}^2_{(\text{aq})}\}}$ | $\log b = (9.42 \pm 1.08)^a$ |
| Equilibrium (Eq. 3) – Distribution constant K_D $K_D = \frac{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{org})}\}}{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{aq})}\}}$ | $\log K_D = (1.15 \pm 0.01)^b$ |
| Equilibrium (Eq. 4) – Extraction constant K_{ex} $K_{\text{ex}} = \frac{\{(TTC)_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}_{(\text{org})}\}}{\{[(TTC)^+]^2_{(\text{aq})}\} \{[\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}^2_{(\text{aq})}\}}$ $\log K_{\text{ex}} = (9.86 \pm 0.06)^d$ | $\log K_{\text{ex}} = (10.57 \pm 1.09)^c$ |
| Recovery factor $R\%$ | $R = (93.39 \pm 0.05)\%^e$ |

^a Calculated by Komar-Tolmachev method (equation 5); ^b Calculated by equation (6); ^c Calculated by equation (8), where β is determined by the Komar-Tolmachev method; ^d Calculated by Likussar-Boltz method (equation (9)); ^e Calculated by equation (7).

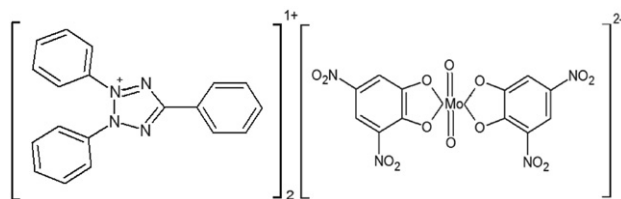


Figure 8. Structural formula of the ion-associated complex Mo(VI)-3,5-DNC-TTC

4. Conclusion

The equilibria of the complex formation of the anionic chelate of molybdenum(VI) with the bidentate ligand of 3,5-dinitrocatechol (3,5-DNC) and its extraction with the cation of 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) in the form of an ion-associated complex in the liquid-liquid extraction system Mo(VI)-3,5-DNC-TTC-H₂O-CHCl₃ was studied by spectrophotometry. In the presence of the monotetrazolium cation, the yellow-colored anionic chelate of Mo(VI)-3,5-DNC forms an ion-associated complex well soluble in chloroform. The bulky organic molecule of the tetrazolium salt determined the extractability of the ion-associate in the organic phase. The optimum conditions for the association in aqueous phase and for extraction of the ion-associated complex Mo(VI)-3,5-DNC-TTC into chloroform were established. The effect of co-existing ions and reagents on the process of chelate formation and ion-association was studied. The validity of Beer's law was checked and the following analytical characteristics were calculated: the apparent molar absorptivity (ϵ'), the true molar absorptivity (ϵ), the limit of detection (LOD), the limit of quantification (LOQ) and the Sandell's sensitivity (SS). From the analytical characteristics of the extraction system Mo(VI)-3,5-DNC-TTC-H₂O-CHCl₃, it can be concluded that the ion-associate formed between the anionic chelate of Mo(VI)-3,5-DNC and the monotetrazolium cation allows determinations of Mo(VI) with a high sensitivity. The equilibrium constants needed for the quantitative assessment of the extraction equilibrium were also calculated, i.e. the association constant (β), the distribution constant (K_D), the extraction constant (K_{ex}) and the recovery factor ($R\%$). The molar ratio of the components, determined by independent methods, shows that the ion-associated complex could be represented with the general formula $(TTC)_2[MoO_2(O_2C_6H_2(NO_2)_2)_2]$. A corresponding reaction scheme and a structural formula of the ion-associated complex were also suggested.

Acknowledgements

The authors would like to thank the Research Fund of the University of Plovdiv for the financial support of the current research.

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Povzetek

S spektrofotometričnimi metodami smo raziskali tvorbo kompleksa med anionskim kelatom molibdena(VI) z dvo-veznim ligandom 3,5-dinitrokateholom (3,5-DNC) in ionski asociat s kationom 2,3,5-trifenil-2*H*-tetrazolijevim kloridom (TTC) v tekoče-tekoče ekstrakcijskem sistemu Mo(VI)-3,5-DNC-TTC-H₂O-CHCl₃. Preverili smo veljavnost Beerovega zakona ter izračunali nekatere analizne karakteristike pri optimalnih pogojih za tvorbo kelata in ekstrakcijo. Raziskali smo vpliv različnih prisotnih ionov in reagentov na proces tvorbe kelata in ionskega asociata. Molsko razmerje komponent v ionsko asociiranem kompleksu Mo(VI)-3,5-DNC-TTC smo določili na podlagi neodvisnih metod. Asociacijski proces v vodni fazi in ekstrakcijsko ravnotežje smo proučili ter kvantitativno karakterizirali sledeče ključne konstante: konstanto asociacije, porazdelitveno in ekstrakcijsko konstanto ter izkoristek ekstrakcije. Na podlagi dobljenih podatkov je predlagana reakcijska shema, splošna formula in struktura kompleksa.



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