Scientific paper

Study on the Chelate Formation and the Ion-association of Anionic Chelate of Molybdenum(VI) with 3,5-Dinitrocatechol and Monotetrazolium Cation

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> > Received: 21-09-2017

Abstract

The equilibria of the chelate formation and ion-association in the liquid-liquid extraction system Mo(VI)–3,5-DNC-INT-H₂O-CHCl₃ were studied by spectrophotometry. The optimum conditions for the chelate formation and extraction of the ion-associated complex formed between the anionic chelate of Mo(VI)–3,5-dinitrocatechol (3,5-DNC) and the cation of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2*H*-tetrazolium chloride (INT) were established. The validity of Beer's law was checked and some analytical characteristics were calculated. The effect of various co-existing ions and reagents on the process of complex formation was investigated. The molar ratio of the components in the ternary ion-associated complex Mo(VI)–3,5-DNC–INT was determined by independent methods. The association process in aqueous phase and the extraction equilibria were investigated and quantitatively characterized. The following key constants of the processes were calculated: association constant, distribution constant, extraction constant and recovery factor. Based on this, a reaction scheme, a general formula and a structure of the complex were suggested.

Keywords: molybdenum(VI); chelate formation, ion-associate; extraction equilibria

1. Introduction

The molybdenum and its compounds are widely used in various important areas of technology, science, and medicine. Molybdenum is present in all living plant and animal matter in micro-trace quantities and it is essential from a biochemical point of view. It stimulates the synthesis of nucleic acids and proteins. In the biological systems, the molybdenum forms complexes with the carboxylic or hydroxide groups of tyrosine and serine. The most important utilization of the molybdenum atom in the living organisms is as a metal hetero-atom at the active site in certain enzymes, e.g. xanthine oxidase, aldehyde oxidase, sulfite oxidase, nitrate reductase and dimethyl sulfoxide reductase.¹⁻⁴

The molybdenum has a rich chemistry, it occurs in various oxidation states, coordination numbers and geometries. 1,5,6 Molybdenum(VI) forms complexes with various natural organic ligands, such as polyphenols and their functional derivatives, polyhydroxycarboxylic acids, aminopolycarboxylic acids, hydroxamic acids, amines (primary, secondary and tertiaty), 8-hydroxyquinoline and its derivatives, aldehyde hydrazones, oximes, β -diketones, fluorones, hydroxyazodyes, biomolecules (chitosan, chitin, D-glucosamine, L-alanine, L-phenylalanine). $^{7-20}$ Molybdenum(VI) gives colored chelates with aromatic compounds, containing two or more hydroxyl groups in *ortho* position relative to each other. The colored anionic chelates of molybdenum(VI) form ion-associated complexes

with bulky organic cations, like methyltrioctylammonium, cetylpyridinium, cetyltrimethylammonium, tetraphenylammonium tetraphenylphosphonium.^{7,21-23}

The preparation and application of ion-associated complexes of anionic chelates of metals with various natural organic and inorganic ligands with N- and O-containing donor atoms and with the participation of mono and ditetrazolium cations is a special scientific research field of the chemistry of the coordination compounds. It is up-todate 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. The structure and properties of tetrazolium salts determine their ability to form ion-associated complexes. The bulky hydrophobic organic substituents in the molecules of the tetrazolium salts increase the extractability of the ion associated complexes. 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.²⁴⁻²⁶ 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).26-31

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. 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 aim of this research was to study spectrophotometrically the extraction equilibria of the complex formation between the anionic chelate of Mo(VI)-3,5-dinitrocatechol (3,5-DNC) and the cation of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) in the liquid-liquid system Mo(VI)-3,5-DNC-INT-H₂O-CHCl₃ as well as to evaluate the possible applications of the system for determination of traces of molybdenum(VI) in alloys, biological, medical and pharmaceutical samples.

2. Experimental

2. 1. Reagents and Apparatus

 $\rm Na_2MoO_4\cdot 2H_2O$ (Fluka AG, p.a.): an aqueous 1.04 \times 10^{-2} M solution was prepared. 3,5-Dinitrocatechol (3,5-DNC) (Sigma-Aldrich, p.a.): 3,5-DNC was dissolved in CHCl $_3$ to give a 1.0×10^{-3} M solution. 2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) (Sigma-Aldrich, p.a.): an aqueous 2.0×10^{-3} M solution was prepared. $\rm H_2SO_4$ (95–97 % for analysis, Merck): a 2 M solution was prepared. The concentration of $\rm H_2SO_4$ 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 CHCl₂ was additionally distilled.

2. 2. Procedure for Establishment of the Optimum Conditions for Complex Formation

The required aliquots of the solutions of Mo(VI), INT and $\rm H_2SO_4$ 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 240 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.

2. 3. Procedure for Determination of the Distribution Constant

The distribution constant (K_D) was determined by Eq. (1), where A_1 and A_3 are the absorbance (measured against blanks) obtained after a single and triple extraction, respectively.

$$K_{\rm D} = A_1 / (A_3 - A_1) \tag{1}$$

The single extraction and the first stage of the triple extraction were performed under the optimum conditions for complex formation (Table 1, column 1). The organic layers were transferred into 25 mL calibrated flasks and the flask from the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding 7 mL of chloroform to the aqueous phase that remained after the first stage. After extraction, the obtained extract was added to this first stage of the triple extraction was performed in the same manner as for the second stage and the extract was added to those of the first two stages. The volume of the flask was brought to the mark with chloroform. The calibrated flasks were shaken before the spectrophotometric measurements.³⁹

3. Results and Discussion

3. 1. Optimum Extraction-Spectrophotometric Conditions

The absorption spectrum of the extract of the ion-associated complex formed between the anionic chelate of Mo(VI)-3,5-DNC and the cation of monotetrazolium salt

INT in CHCl₃ was characterized by an absorption maximum in the visible range ($\lambda_{\rm max}$ = 395 nm) (Figure 1.). The acidity of the aqueous phase influences on the extraction of the anionic chelate Mo(VI)-3,5-DNC into the organic phase in the form of ion-associate with the monotetrazolium cation of INT. The maximum and constant extraction of the ion-associated complex is achieved in strongly acidic solution of $(1.6-6.0)\times 10^{-1}$ M H₂SO₄. The results from the experiments showed that the extraction equilibrium cannot be achieved within less than 30 s. The prolonged shaking does not have an impact on the absorbance. The next experiments were performed for 1 min. The chelate formation of Mo(VI)-3,5-DNC requires 3.6-fold excess of 3,5-DNC ($\geq 1.0\times 10^{-4}$ M) and 7.1-fold excess of INT ($\geq 2.0\times 10^{-4}$ M) for maximum association and extraction.

The optimum experimental conditions for the extraction of the ion-associated complex are summarized in Table 1, column 1.

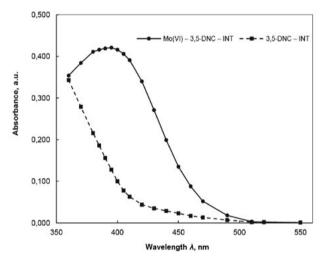


Figure 1. Absorption spectra of the complex Mo(VI)-3,5-DNC-INT and of the blank sample 3,5-DNC-INT in CHCl₃ $C_{\text{Mo(VI)}} = 2.08 \times 10^{-5}$ M; $C_{3.5\text{-DNC}} = 2.0 \times 10^{-4}$ M, $C_{\text{INT}} = 2.0 \times 10^{-4}$ M; $C_{\text{H2SO4}} = 4.0 \times 10^{-1}$ M; λ = 395 nm; τ = 1 min

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

The range of obedience to Beer's law, i.e. the linear relationship between the molybdenum concentration in the aqueous phase ($C_{\text{Mo(VI)}}$, µg 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 = 0.2081X + 0.0098 with a correlation coefficient squared 0.9968. Under the optimum conditions for complex formation, the linearity is observed for concentrations up to 4.99 µg 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.

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 complex formation between the anionic chelate Mo(VI)-3,5-DNC and monotetrazolium cation 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 the extraction of Mo(VI) as an associated complex with 3,5-DNC and INT. The extraction equilibrium is hindered by Fe(III), V(V) and W(VI). 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 investiga-

Table 1. Optimum extraction-spectrophotometric conditions and analytical characteristics of the system Mo(VI)–3,5-DNC-INT-H,0-CHCl₃

Optimum conditions	Analytical characteristic	
Absorption maximum (λ_{max}) 395 nm	Apparent molar absorptivity (ε')	
Absorption maximum (n_{max}) 373 mm	$(2.05 \pm 0.06) \times 10^{4} \mathrm{L}\mathrm{mol}^{-1}\mathrm{cm}^{-1}$	
Volume of the aqueous phase 10 mL	True molar absorptivity (ε)	
volume of the aqueous phase to mil.	$(1.92 \pm 0.07) \times 10^{4} L \text{ mol}^{-1} \text{ cm}^{-1}$	
Volume of the organic phase 10 mL	Sandell's sensitivity (SS) 4.68 ng cm ⁻²	
Concentration of H ₂ SO ₄ in the aqueous phase	Adherence to Beer's law	
$(1.6-6.0) \times 10^{-1} \mathrm{M}$	up to 4.99 μg cm ⁻³	
Shaking time (τ) 1 min	Relative standard deviation (RSD) 1.92%	
Concentration of 3,5-DNC	Limit of detection (LOD) 0.31 $\mu g \text{ cm}^{-3}$	
$C_{3.5\text{-DNC}} \ge 1.0 \times 10^{-4} \mathrm{M}$		
Concentration of INT	Limit of quantification (LOQ) 1.03 $\mu g \ cm^{-3}$	
$C_{\text{INT}} \ge 2.0 \times 10^{-4} \text{ M}$		

tions as well as the studies published in the literature show that the same co-existing ions, like Al(III), Fe(II) and Fe(III) can be removed by their pre-precipitation with OH at pH = $11.^{40}$ 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. Vanadium(V) can be co-precipitated with Fe(III) in alkali medium.⁴¹

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

Co-existing ion and reagent	Co-existing ion and reagent, µg/10 cm³ aqueous phase	Mo(VI) found, μg	R, %
Na ⁺	10000	20.45	102.25
K^{+}	10000	20.21	101.05
Mg^{2+}	10000	20.55	102.75
Ca ²⁺	10000	20.07	100.35
Cu^{2+}	10000	19.54	97.68
Zn^{2+}	10000	19.98	99.92
Cd^{2+}	10000	20.39	101.95
Ni^{2+}	10000	19.77	98.86
Co^{2+}	10000	20.39	101.95
Al^{3+}	2000	20.09	100.45
Cr^{3+}	10000	19.94	99.68
Fe^{2+}	750	19.61	98.05
Fe^{3+}	100	16.21	81.03
V(V)	100	21.83	109.14
Cr(VI)	100	20.39	101.96
W(VI)	50	25.95	129.75
F-	10000	20.53	102.65
Br-	10000	20.55	102.77
PO ₄ 3-	10000	20.19	100.97
P ₂ O ₇ ⁴⁻	10000	19.84	99.18
$C_{2}O_{4}^{2-}$	10000	13.98	69.89
CH ₃ COO-	10000	20.55	102.74
$C_4 H_4 O_6^{2-}$	10000	20.22	101.11
$C_6H_5O_7^{3-}$	10000	20.24	100.21
Complexone III	10000	20.07	100.35
Complexone IV	10000	20.41	102.03
L- Ascorbic acid	1000	20.04	100.18

3. 4. Molar Ratios of the Complex, Reaction Scheme and Suggested General Formula

The molar ratios of the complex were determined by three independent methods: the mobile equilibrium method, the straight-line method of Asmus and the method of continuous variations.⁴² Results from the application of these independent methods are shown in Figures 2–5, respectively. On the basis of the results it can be concluded that Mo(VI), 3,5-DNC and INT interact in molar ratio 1:2:2.

The carried out experiments showed that the complex formation and the extraction of the ion-associated

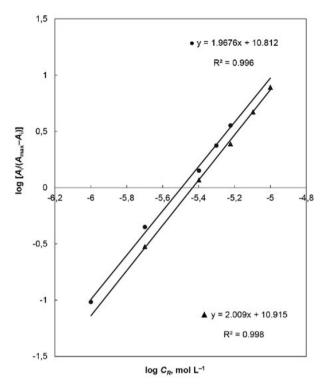


Figure 2. Straight lines by the mobile equilibrium method for determination of the molar ratios Mo(VI):3,5-DTC and Mo(VI):INT $C_{\text{Mo(VI)}} = 2.08 \times 10^{-5} \text{ M}; C_{\text{H2SO4}} = 4.0 \times 10^{-1} \text{ M}; \lambda = 395 \text{ nm}; \tau = 1 \text{ min}$

- Mo(VI): 3,5-DNC, $C_{INT} = 2.0 \times 10^{-4} \text{ M}$;
- ▲ Mo(VI): INT, $C_{3,5-DNC} = 2.0 \times 10^{-4} \text{ M}$

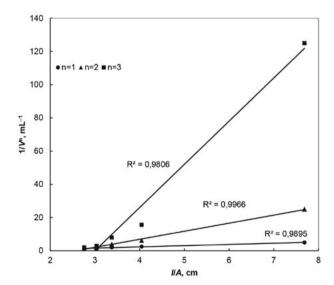


Figure 3. Determination of molar ratio (n) Mo(VI):3,5-DNC by the method of Asmus

 $C_{_{
m Mo(VI)}} = 2.08 \times 10^{-5} \text{ M}; C_{_{
m INT}} = 2.0 \times 10^{-4} \text{ M};$ $C_{_{
m H2SO4}} = 4.0 \times 10^{-1} \text{ M}; \lambda = 395 \text{ nm}; \tau = 1 \text{ min}$

complex occurred in strongly acidic solution. Under these conditions, the complex formation of anionic chelate Mo(VI)-3,5-DNC is given by the equation (2):

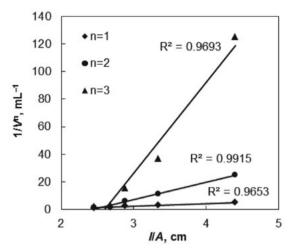


Figure 4. Determination of the molar ratio (*n*) Mo(VI):INT by the method of Asmus

$$C_{ ext{Mo(VI)}} = 2.08 \times 10^{-5} \text{ M}; C_{3,5\text{-DNC}} = 2.0 \times 10^{-4} \text{ M};$$

 $C_{ ext{H2SO4}} = 4.0 \times 10^{-1} \text{ M}; \lambda = 395 \text{ nm}; \tau = 1 \text{ min}$

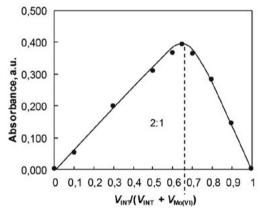


Figure 5. Determination of the molar ratio (n) Mo(VI):INT by the method of continuous variations

$$C_{ ext{Mo(VI)}} + C_{ ext{INT}} = 8.0 \times 10^{-5} \text{ M}; C_{3,5\text{-DNC}} = 2.0 \times 10^{-4} \text{ M}; C_{ ext{H2SO4}} = 4.0 \times 10^{-1} \text{ M}; \lambda = 395 \text{ nm}; \tau = 1 \text{ min})$$

$$MoO_4^{2^-} + 2 (HO)_2C_6H_2(NO_2)_2 = \{MoO_2[O_2C_6H_2(NO_2)]_2\}^{2^-} + 2 H_2O$$
(2)

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 (3–5).

$$2(INT)^{+}_{(aq)} + \{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}^{2^{-}}_{(aq)}$$

$$(INT)_{2}\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}_{(aq)}$$

$$(3)$$

$$2(INT)^{+}_{(aq)} + \{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}^{2^{-}}_{(aq)} \iff (5)$$

$$(INT)_{2}\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}_{(org)}$$

Therefore, the ion-associated chelate of Mo(VI)-3,5-DNC with INT can be represented by the general formula (INT), $\{MoO_2[O_2C_6H_2(NO_2)_2],\}$.

3. 5. Extraction Equilibria, True Molar Absorptivity

Recovery Factor and Structure of the 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, distribution constant, extraction constant and recovery factor.

The association constant β and the true molar absorptivity ε were determined by the method of Komar-Tolmachev from equation (6):⁴²

$$\beta = (1/n)^{n} / \left[\varepsilon \left(\operatorname{tg} \alpha \right)^{n+1} \right]$$
 (6)

where l is the cuvette thickness (l = 1 cm); n is 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 is the true molar absorptivity.

The true molar absorptivity ε was determined by the method of Komar-Tolmachev from the equation of a straight line (Figure 6) and its value is given in Table 1, column 2.

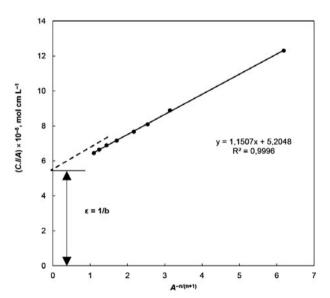


Figure 6. Dependency of (*C.l/A*) on $A^{\text{-n/(n+1)}}$ (method of Komar–Tolmachev)

$$C = C_{\text{Mo(VI)}}$$
; $C_{\text{INT}} = 2$ $C_{\text{Mo(VI)}}$; $C_{3,5\text{-DNC}} = 2.0 \times 10^{-4}$ M; A – absorbance; l – cell thickness, l = 1 cm; n = 2

The distribution constant (K_D) was determined by the equation (7), where A_1 and A_3 are the absorbance (measured against blanks) obtained after a single and triple extraction, respectively.

$$K_{D} = \{ (INT)_{2} \{ MoO_{2} [O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2} \} \}$$

$$(org)/\{ (INT)_{2} \{ MoO_{2} [O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2} \} \} (aq)$$

$$= A_{1}/(A_{2}-A_{1})$$
(7)

The recovery factor was determined from the equation (8):

$$R\% = 100 K_D / (K_D + 1) \tag{8}$$

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

(i)
$$\log K_{\rm av} = \log K_{\rm D} + \log \beta$$
 (9)

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

(ii) the method of Likussar-Boltz:43

The method uses the data from the method of continuous variations (Figure 5.). The extraction constant K_{ex} was calculated by the equation of Likussar-Boltz for molar ratio 1:2 (equation 10):

$$\log K_{\text{ex}} = 0.3522 - 2 \log K + \log Y_{\text{max}} - 3 \log (1 - Y_{\text{max}})$$
 (10)

where *K* is the total concentration of reagents $-(K = C_{\text{Mo(VI)}} + C_{\text{INT}} = 8.0 \times 10^{-5} \,\text{M})$; Y_{max} and $(1 - Y_{\text{max}})$ are determined by additionally plotted normalized absorption curve ($Y_{\text{max}} = 0.849$; $(1 - Y_{\text{max}}) = 0.151$) (Figure 5).

The values of the equilibrium constants and the recovery factor 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-pair in the aqueous phase, its distribution between the aqueous and the organic phases and its extraction in chloroform. Based on this, the proposed structure of the ion-associated complex is represented in Figure 7.

4. Conclusion

The equilibria of the chelate formation and extraction of the ion-associated complex formed between the anionic chelate of Mo(IV)-3,5-dinitrocatechol (3,5-DNC) and the cation of 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) was studied by spectrophotometry. The optimum conditions for the association in aqueous phase and extraction of the ion-associated complex into chloroform were established. The validity of Beer's law was checked and the effect of co-existing ions and reagents on the process of complex formation was studied. The equilibrium constants and analytical characteristics needed for the quantitative assessment of the extraction equilibrium were calculated, i.e. the association constant (β) , the distribution constant (K_D) , the extraction constant (K_{∞}) , the recovery factor (R), 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-INT-H₂O-CHCl₂, it can be concluded that the ion-associate formed between

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

Equilibrium constant and recovery factor	Value
Equilibrium (equation 3) – Association constant β	
$\beta = (INT)_{2}\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}(aq) / \{[(INT)^{+}]^{2}(aq) \beta \{\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}^{2-}\}(aq)\}$	$\log \beta = (9.93 \pm 1.38)^{a}$
Equilibrium (equation 4) - Distribution constant K_D	$\log K_{\rm p} = (1.23 \pm 0.01)^{\rm b}$
$K_{D} = \{(INT)_{2}\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}\} (org) / \{(INT)_{2}\{MoO_{2}[O_{2}C_{6}H_{2}(NO_{2})_{2}]_{2}\}\} (aq)$	$\log K_{\rm p} = (1.23 \pm 0.01)$ $\log K_{\rm ex} = (11.16 \pm 1.39)^{\rm c}$
Equilibrium (equation 5) – Extraction constant K_{ex}	$\log R_{\rm ex} = (11.10 \pm 1.55)$
$K_{\text{ex}} = \{(\text{INT})_2 \{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\} \} \text{ (org)} / \{\{[\text{INT}]^+\}^2(\text{aq}) \beta \{\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]_2\}^{2-}\} \text{ (aq)}\}$	$\log K_{\rm ex} = (10.95 \pm 0.15)^{\rm d}$
Recovery factor R%	$R = (94.39 \pm 0.05)\%^{e}$

^a Calculated by Komar–Tolmachev method (equation 6); ^b Calculated by equation (7); ^c Calculated by equation (9), where β is determined by the Komar–Tolmachev method; ^d Calculated by Likussar–Boltz method (equation (10)); ^c Calculated by equation (8).

Figure 7. Structure of the ion-associated complex Mo(VI)-3,5-DNC-INT

the anionic chelate of Mo(VI)-3,5-DNC and the monotetrazolium cation allows determinations of Mo(VI) with a high sensitivity. The presence of hydrophobic substituents, phenyl groups in the molecule of the monotetrazolium cation, increased the solubility of the ion-associated complex in the organic solvent. The molar ratio of the components, determined by independent methods, shows that the ion-associated complex could be represented with the general formula (INT) $_2$ {MoO $_2$ [O $_2$ C $_6$ H $_2$ (NO $_2$) $_2$] $_2$ }. A corresponding reaction scheme and a structure of the complex were also suggested.

5. 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 proučili ravnotežja tvorbe kelata in ionskega asociata v tekočina–tekočina ekstrakcijskem sistemu Mo(VI)–3,5-DNC-INT-H₂O-CHCl₃. Določili smo optimalne pogoje za tvorbo kelata in ekstrakcijo ionskega asociata nastalega med anionskim kelatom Mo(VI)–3,5-dinitrokatehol (3,5-DNC) in kationom iz spojine 2-(4-jodofenil)-3-(4-nitrofenil)-5-fenil-2*H*-tetrazolijevega klorida (INT). Preverili smo veljavnost Beerovega zakona in izračunali nekatere analizne karakteristike. Preverili smo vpliv različnih ionov in reagentov na proces tvorbe kompleksa. Molsko razmerje komponent v ternarnem kompleksu ionskega asociata Mo(VI)–3,5-DNC–INT smo določili z neodvisnimi metodami. Proučili smo asociacijski proces v vodni fazi in ekstrakcijsko ravnotežje, ki smo ga tudi kvantitativno okarakterizirali. Izračunali smo sledeče najpomembnejše konstante procesov: asociacijska konstanta, distribucijska konstanta, ekstrakcijska konstanta in izkoristek ekstrakcije. Na podlagi dobljenih podatkov je predlagana reakcijska shema, splošna formula in struktura kompleksa.