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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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-2H-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 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 tertiary), 8-hydroxyquinoline and its derivatives, aldehyde hydrazones, oximes, β-diketones, fluorones, hydroxyazoxydes, biomolecules (chitosan, chitin, D-glucosamine, L-alanine, L-phenylalanine).⁷⁻¹⁰ 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 methyltriocylammonium, cetylpyridinium, cetyltrimethylammonium, tetraphenylammonium tetraphenylphosphonium.

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-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. 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. Tetrazolium salts are used as reagents for the preparation of various ion-associated complexes of metals, e.g. W(VI), Ge(IV), Ti(III), Nb(V), V(V), Ga(III), Co(II).

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 concept 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. Tetrazolium salts are used as reagents for the preparation of various ion-associated complexes of metals, e.g. W(VI), Ge(IV), Ti(III), Nb(V), V(V), Ga(III), Co(II).

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

Na2MoO4·2H2O (Fluka AG, p.a.): an aqueous 1.04 × 10−2 M 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 × 10−3 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. H2SO4 (95–97% for analysis, Merck): a 2 M solution was prepared. H2SO4 (95–97% for analysis, Merck): a 2 M 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 Complex Formation

The required aliquots of the solutions of Mo(VI), INT 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 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 (Kn) was determined by Eq. (1), where Ai and A3 are the absorbance (measured against blanks) obtained after a single and triple extraction, respectively.

Kn = A3/(A1 − A3) (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. The third 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.

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 mono-tetrazolium salt...
INT in CHCl₃ was characterized by an absorption maximum in the visible range (λ_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) × 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 (≥1.0 × 10⁻⁴ M) and 7.1-fold excess of INT (≥2.0 × 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.

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_{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 \( \varepsilon' \), 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 ±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–H₂O–CHCl₃

<table>
<thead>
<tr>
<th>Optimum conditions</th>
<th>Analytical characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption maximum (λ_max) 395 nm</td>
<td>Apparent molar absorptivity (( \varepsilon' )) (2.05 ± 0.06) × 10⁴ L mol⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>Volume of the aqueous phase 10 mL</td>
<td>True molar absorptivity (( \varepsilon )) (1.92 ± 0.07) × 10⁴ L mol⁻¹ cm⁻¹</td>
</tr>
<tr>
<td>Volume of the organic phase 10 mL</td>
<td>Sandell’s sensitivity (SS) 4.68 ng cm⁻²</td>
</tr>
<tr>
<td>Concentration of H₂SO₄ in the aqueous phase (1.6–6.0) × 10⁻¹ M</td>
<td>Adherence to Beer’s law up to 4.99 μg cm⁻³</td>
</tr>
<tr>
<td>Shaking time (( \tau )) 1 min</td>
<td>Relative standard deviation (RSD) 1.92%</td>
</tr>
<tr>
<td>Concentration of 3,5-DNC C₃,5-DNC ≥ 1.0 × 10⁻⁴ M</td>
<td>Limit of detection (LOD) 0.31 μg cm⁻³</td>
</tr>
<tr>
<td>Concentration of INT C₅NT ≥ 2.0 × 10⁻⁴ M</td>
<td>Limit of quantification (LOQ) 1.03 μg cm⁻³</td>
</tr>
</tbody>
</table>

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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)

<table>
<thead>
<tr>
<th>Co-existing ion and reagent</th>
<th>Co-existing ion and reagent, μg/10 cm³</th>
<th>Mo(VI) found, μg</th>
<th>R, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na+</td>
<td>10000</td>
<td>20.45</td>
<td>102.25</td>
</tr>
<tr>
<td>K+</td>
<td>10000</td>
<td>20.21</td>
<td>101.05</td>
</tr>
<tr>
<td>Mg2+</td>
<td>10000</td>
<td>20.55</td>
<td>102.75</td>
</tr>
<tr>
<td>Ca2+</td>
<td>10000</td>
<td>20.07</td>
<td>100.35</td>
</tr>
<tr>
<td>Cu2+</td>
<td>10000</td>
<td>19.54</td>
<td>97.68</td>
</tr>
<tr>
<td>Zn2+</td>
<td>10000</td>
<td>19.98</td>
<td>99.92</td>
</tr>
<tr>
<td>Cd2+</td>
<td>10000</td>
<td>20.39</td>
<td>101.95</td>
</tr>
<tr>
<td>Ni2+</td>
<td>10000</td>
<td>19.77</td>
<td>98.86</td>
</tr>
<tr>
<td>Co2+</td>
<td>10000</td>
<td>20.39</td>
<td>101.95</td>
</tr>
<tr>
<td>Al3+</td>
<td>2000</td>
<td>20.09</td>
<td>100.45</td>
</tr>
<tr>
<td>Cr3+</td>
<td>10000</td>
<td>19.94</td>
<td>99.68</td>
</tr>
<tr>
<td>Fe2+</td>
<td>750</td>
<td>19.61</td>
<td>98.05</td>
</tr>
<tr>
<td>Fe3+</td>
<td>100</td>
<td>16.21</td>
<td>81.03</td>
</tr>
<tr>
<td>V(V)</td>
<td>100</td>
<td>21.83</td>
<td>109.14</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>100</td>
<td>20.39</td>
<td>101.96</td>
</tr>
<tr>
<td>W(VI)</td>
<td>50</td>
<td>25.95</td>
<td>129.75</td>
</tr>
<tr>
<td>F–</td>
<td>10000</td>
<td>20.53</td>
<td>102.65</td>
</tr>
<tr>
<td>Br–</td>
<td>10000</td>
<td>20.55</td>
<td>102.77</td>
</tr>
<tr>
<td>PO4 3–</td>
<td>10000</td>
<td>20.19</td>
<td>100.97</td>
</tr>
<tr>
<td>P2O7 4–</td>
<td>10000</td>
<td>19.84</td>
<td>99.18</td>
</tr>
<tr>
<td>C2O4 2–</td>
<td>10000</td>
<td>13.98</td>
<td>69.89</td>
</tr>
<tr>
<td>CH3COO–</td>
<td>10000</td>
<td>20.55</td>
<td>102.74</td>
</tr>
<tr>
<td>C4H4O6 2–</td>
<td>10000</td>
<td>20.22</td>
<td>101.11</td>
</tr>
<tr>
<td>C6H5O7 3–</td>
<td>10000</td>
<td>20.24</td>
<td>100.21</td>
</tr>
<tr>
<td>Complexone III</td>
<td>10000</td>
<td>20.07</td>
<td>100.35</td>
</tr>
<tr>
<td>Complexone IV</td>
<td>10000</td>
<td>20.41</td>
<td>102.03</td>
</tr>
<tr>
<td>L- Ascorbic acid</td>
<td>10000</td>
<td>20.04</td>
<td>100.18</td>
</tr>
</tbody>
</table>

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 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):
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).

\[
\begin{align*}
2(\text{INT})^{2+ \text{(aq)}} + \text{MoO}_2[O_2C_6H_2(NO_2)_2]^{2-} & \rightleftharpoons (\text{INT})_2\text{MoO}_2[O_2C_6H_2(NO_2)_2]^{2-} + 2\text{H}_2\text{O} \\
(\text{INT})_2\text{MoO}_2[O_2C_6H_2(NO_2)_2]^{2-} & \text{org} \\
\end{align*}
\]

Therefore, the ion-associated chelate of Mo(VI)–3,5-DNC with INT can be represented by the general formula \((\text{INT})_2\text{[MoO}_2[O_2C_6H_2(NO_2)_2]]_1\).

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 \(\beta\) and the true molar absorptivity \(\varepsilon\) were determined by the method of Komar-Tolmachev from equation (6):\(^{42}\)

\[
\beta = \frac{l}{[\varepsilon \cdot \text{tg} \alpha]^{n+1}}
\]

where \(l\) is the cuvette thickness \((l = 1\ \text{cm})\); \(n\) 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) \((n = 2)\); \(\varepsilon\) is the true molar absorptivity.

The true molar absorptivity \(\varepsilon\) 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.

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.

\[
K_D = \frac{A_1}{A_3}
\]
$K_D = \frac{[\text{INT}]_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]\}_2]}{[\text{INT}]_2\{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]\}_2]}(\text{aq})$

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

$$R\% = 100 \frac{K_D}{(K_D + 1)} \quad (8)$$

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

(i) $\log K_{ex} = \log K_D + \log \beta \quad (9)$

where $\beta$ was determined by the method of Komar-Tolmachev.

(ii) the method of Likussar-Boltz.

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):

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

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

The values of the equilibrium constants and the recovery factor are presented in Table 3.

**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 ($\beta$), the distribution constant ($K_D$), the extraction constant ($K_{ex}$), the recovery factor ($R$), the apparent molar absorptivity ($\epsilon'$), the true molar absorptivity ($\epsilon$), 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-H$_2$O-CHCl$_3$, it can be concluded that the ion-associate formed between

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

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

<table>
<thead>
<tr>
<th>Equilibrium constant and recovery factor</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium (equation 3) – Association constant $\beta$</td>
<td>$\log \beta = (9.93 \pm 1.38)^a$</td>
</tr>
<tr>
<td>$\beta = ([\text{INT}]_2{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}_2]) / {[[\text{INT}]]^2(\text{aq})} \beta {\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}^2(\text{aq})}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium (equation 4) - Distribution constant $K_D$</td>
<td>$\log K_D = (1.23 \pm 0.01)^b$</td>
</tr>
<tr>
<td>$K_D = ([\text{INT}]_2{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}_2])(\text{org}) / {[[\text{INT}]]^2(\text{aq})} \beta {\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}^2(\text{aq})}$</td>
<td></td>
</tr>
<tr>
<td>Equilibrium (equation 5) – Extraction constant $K_{ex}$</td>
<td>$\log K_{ex} = (10.95 \pm 0.15)^c$</td>
</tr>
<tr>
<td>$K_{ex} = ([\text{INT}]_2{\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}_2])(\text{org}) / {[[\text{INT}]]^2(\text{aq})} \beta {\text{MoO}_2[\text{O}_2\text{C}_6\text{H}_2(\text{NO}_2)_2]}^2(\text{aq})}$</td>
<td></td>
</tr>
<tr>
<td>Recovery factor $R%$</td>
<td>$R = (94.39 \pm 0.05)^e$</td>
</tr>
</tbody>
</table>

* Calculated by Komar-Tolmachev method (equation 6); † Calculated by equation (7); ‡ Calculated by equation (9), where $\beta$ is determined by the Komar-Tolmachev method; § Calculated by Likussar-Boltz method (equation (10)); ¶ Calculated by equation (8).
the anionic chelate of Mo(VI)-3,5-DNC and the monomer tetrazolium cation allows determinations of Mo(VI) with a high sensitivity. The presence of hydrophobic substituents, phenyl groups in the molecule of the monomer tetrazolium 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)·[MoO₄(O₃C₆H₄(NO₂))₂]. A corresponding reaction scheme and a structure of the complex were also suggested.

5. Acknowledgements

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