Complexation of molybdenum(VI) with methyliminodiacetic acid in different water + methanol solutions

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Abstract: The complexation of molybdenum(VI) with methyliminodiacetic acid (MIDA) at pH 6.00, T = 298 K, I = 0.1 mol dm^{-3} of sodium chloride and different water + methanol solutions (0–45 vol. %) was studied using potentiometric and UV spectrophotometric measurements. The values of the stability constants were calculated and their trends interpreted using the Kamlet––Abboud–Taft (KAT) model in order to investigate the role of different specific and non-specific interactions in aqueous solutions of methanol.

Keywords: methyliminodiacetic acid; Kamlet–Abboud–Taft equation; solvent effect.

INTRODUCTION

Investigation of the solvent effect in complex formation reactions is the subject of ongoing research[1–4] aimed at comparing the new results with previous data in aqueous solutions[5–10] and understanding the contribution of the solvent in various interactions in alcoholic and ionic liquid solutions. The study of the solvent effect could be considered as a kind of simulation for the cases where the solvent polarity decreases.[11] The solvent polarity at a protein–water surface or in the active site cavities of metalloenzymes are reduced in comparison to pure bulk water.[11] Therefore, it is well known that different types of water exist in cells.[11]

For the second and third transition periods, molybdenum and tungsten, respectively, are the most abundant metals in the oceans.[12] This correlates with the fact that molybdenum and tungsten are the only elements of their respective periods that have known biological functions.[12] To what extent this abundance is responsible for the extensive usage of Mo in biology, as opposed to its unique chemistry, is not entirely clear.[12] Molybdenum is a trace element and most molybdenum enzymes catalyze a conversion, the net effect of which is to add an

oxygen atom to, or remove an oxygen atom from the substrate.[12] Molybdenum enzymes have a considerable strategic significance in the biosphere and are found in all forms of life, from bacteria, through higher plants and animals to humans.[12] Molybdenum complexes can catalyze reactions that involve oxygen atom transfer.[12]

Aminopolycarboxylic acids have been used with the aim of removing toxic metals and preventing metal precipitation at least for the last fifty years. They have vast applications in different fields, such as textile production, metal electroplating, waste treatment, pharamaceuticals, cosmetics, agriculture, cleaning operations, food products and photography.[13] A new generation of bifunctional aminopolycarboxylic acids have been investigated for magnetic resonance imaging (MRI) and photometric or radioactive imaging and therapy.[13] They can be attached to biological macromolecules through a covalent bond.[13]

The stability constants data for the complexation of molybdenum(VI) with methyliminodiacetic acid (MIDA) at $T = 298$ K and different ionic strengths of sodium perchlorate ($0.1 < I < 1.0$ mol dm^{-3}) were reported previously.[6] Therefore, in this research, molybdenum(VI) complexation with MIDA was studied in different aqueous solutions of methanol (0–45 vol. %) at $I = 0.1$ mol dm^{-3} of sodium chloride and 298 K. The solvent dependence of the dissociation and stability constants was fitted to the Kamlet–Abboud–Taft (KAT) equation in order to derive the solvatochromic regression coefficients. All of the UV measurements for the complex formation reaction in the current work were performed at pH 6.00 in order to avoid the hydrolysis of molybdenum and to ensure the existence of MoO_4^{2-} in the solution.[6,14]

EXPERIMENTAL

Sodium chloride, 99.5 %; hydrochloric acid titrazole (1 mol dm^{-3}), sodium hydroxide titrazole (1 mol dm^{-3}), sodium molybdate, 99.5 %; sodium carbonate anhydrous, 99.5 %; methanol, 99.9 %; potassium hydrogen phthalate, minimum 99.9 % were purchased from Merck and MIDA, 99 % (Fig. 1) from Aldrich and were used without further purification. The NaOH solutions were prepared from titrazole solutions and their concentration was determined by several titrations with potassium hydrogen phthalate. The HCl solution was standardized with sodium carbonate solution (Na_2CO_3). Sodium chloride and sodium carbonate were dried in an oven at 383 K for 2 h. All chemicals were analytical reagent grade. The specific conductance of double-distilled water was 1.3±0.1 μS cm^{-1}.
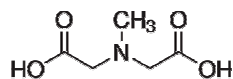
 Fig. 1. The chemical structure of MIDA.

All of the spectrophotometric and potentiometric measurements were performed at 298 K and an ionic strength 0.1 mol dm^{-3} of sodium chloride. A Metrohm pH-meter, model 827, was used for the pH measurements. The pH-meter had a sensitivity of 0.001 units. The hydrogen ion concentration was measured with a Metrohm combination electrode, model 6.0228.010. A 0.01 mol dm^{-3} hydrochloric acid solution containing 0.09 mol dm^{-3} sodium

chloride (for adjusting the ionic strength to 0.1 mol dm^{-3}) was employed as a standard solution of the hydrogen ion concentration.

Calibration of the glass electrode for different methanol mixtures was realized according to the literature.[11,15,16] Thus, the calibration was performed using buffers (pH 4.00, 7.00) from Metrohm, Herisau, Switzerland, similar to the work of Sigel[11] and then correction factors[15,16] were applied for the different solvent mixtures. Many glass electrodes show the theoretical response to hydrogen ions, at least up to alcohol concentrations near 90 weight percent.[15] Definition of acidity in alcohol–water solvents in terms of the experimental quantity (pH) is possible by several units, but from the practical point of view, the pm_H unit is unsatisfactory in water + alcohol media.[15] The pa_H* was related directly to the experimental quantity using the following equation:[15]

$$p a_H^* = pH - \delta \tag{1}$$

where a_H^* is the hydrogen ion activity referred to the standard state in the mixed solvent.[15] pa_H* is a useful quantity that plays a simple and distinct role in chemical equilibria in alcoholic media.[15] In the present research, the values of the experimental quantity (pH) were obtained in different methanol mixtures containing known concentrations of HCl and NaCl to give a constant ionic strength of 0.1 mol dm^{-3}.[15] The standard solutions of known pa_H* having the same solvent composition as the unknowns were used to calculate the values of the correction term δ.[15] The value of δ is substantially constant for a solvent medium of given composition.[15] The values of δ are small up to about 80 weight percent methanol and their values for different water + alcohol solutions are available in the literature.[15] Potentiometric titrations were performed with 0.2 mol dm^{-3} sodium hydroxide in thermostatted vessels with a magnetic stirrer. Thus, 25 cm^{-3} solution in the thermostatted titration vessel contained the reagents with final concentrations: sodium chloride, 0.1 mol dm^{-3}; hydrochloric acid, 0.016 mol dm^{-3}; MIDA, 0.01 mol dm^{-3} and the desired amount of methanol and water for each volume fraction of methanol.

Spectrophotometric measurements were performed with a PerkinElmer Lambda 25 UV– –Vis spectrophotometer between 245 and 280 nm in thermostatted 10-mm quartz cells at 298 K and an ionic strength 0.1 mol dm^{-3} of sodium chloride.[5-8,10] The measurement cell was of the flow type.[5-8,10] In order to measure the absorbance and pH of the solution simultaneously, a Masterflux pump was used which allowed the circulation of the solution under study between the potentiometric and spectrophotometric cells.[5-8,10] Measurements were performed for different metal, ligand concentrations and ligand/metal mole ratios but the best results were obtained with $c_L = c_M = 0.007$ mol dm^{-3}. The Job method was used for different water + methanol solutions (0–45 vol. %).[5-8,10]
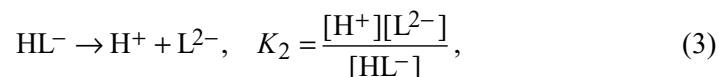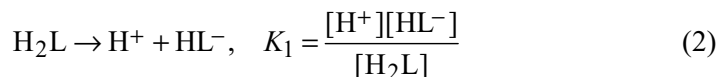
Using the Job method, the absorbances of the solutions of the Mo(VI) + MIDA complex at total concentration of 0.0028 mol dm^{-3} in the UV range (260 to 270) nm at a constant pH of 6.00 and different volume fractions of methanol were measured and the results are gathered in Tables S-I–S-X of the Supplementary material. The plot for 35 % methanol is shown in Fig. 2. The experimental procedure for the Job method was described in detail in a previous paper.[6]

RESULTS AND DISCUSSION

Complexation of molybdenum (VI) with MIDA in different aqueous solutions of methanol

The dissociation reactions of MIDA were reviewed in the literature.[13] The values of MIDA dissociation constants at 298 K, at $I = 0.1$ mol dm^{-3} of NaClO$_4$

and different water + methanol solutions (0–45 vol. %) were gathered in Tables I and II of a previous work.[16] In the current work, the values of the dissociation constants were calculated based on the following equilibria (L = MIDA):

$$H_2L \rightarrow H^+ + HL^-, \quad K_1 = \frac{[H^+][HL^-]}{[H_2L]} \tag{2}$$

$$HL^- \rightarrow H^+ + L^{2-}, \quad K_2 = \frac{[H^+][L^{2-}]}{[HL^-]}, \tag{3}$$

The values of dissociation constants determined in this work that were obtained at different volume fractions of methanol (0–45 vol. %), I = 0.1 mol dm^{-3} of NaCl using the potentiometric technique and the Hyperquad 2013 program[17] are reported in Table I together with the literature data. Three titrations were performed for each aqueous solution of methanol and approximately 110 points were used for the calculations at each volume fraction of methanol.

TABLE I. Average experimental values of log K_1 at I = 0.1 mol dm^{-3} of NaCl and different aqueous solutions of methanol for MIDA, T = 298 K

Methanol content, vol. %	log K_1	log K_2
0	2.29±0.10	9.21±0.04
5	2.46±0.03	9.25±0.02
10	2.56±0.02	9.30±0.01
15	2.60±0.05	9.30±0.02
20	2.66±0.04	9.40±0.02
25	2.74±0.03	9.49±0.02
30	2.87±0.04	9.56±0.02
35	2.87±0.02	9.58±0.01
40	3.11±0.04	9.68±0.02
45	3.17±0.05	9.78±0.03
0	2.12±0.09[a]	9.65±0.07[a]
0	2.28±0.02[b]	9.59±0.02[b]
0	2.32±0.03[c]	9.43±0.03[c]
0	2.4±0.1[d]	9.46±0.03[d]
0	2.54±0.04[e]	9.48±0.06[e]
5	2.58±0.02[f]	9.67±0.10[f]
10	2.68±0.03[g]	9.68±0.06[g]
15	2.64±0.01[h]	9.70±0.06[h]
20	2.65±0.02[i]	9.76±0.01[i]
25	2.72±0.02[j]	9.83±0.08[j]
30	2.76±0.01[k]	9.87±0.07[k]
35	2.79±0.02[l]	9.95±0.12[l]
40	2.85±0.01[m]	9.97±0.10[m]
45	2.95±0.01[n]	10.06±0.07[n]

[a]I = 0.1 mol dm^{-3} KCl, T = 298 K; [b]I = 0.5 mol dm^{-3} NaClO$_4$, T = 298 K; [c]I = 0.5 mol dm^{-3} KNO$_3$, T = 298 K; [d]I = 1.0 mol dm^{-3} NaClO$_4$, T = 298 K (a, b, c and d data were taken from the literature[13]); [e-n]I = 0.1 mol dm^{-3} NaClO$_4$, T = 298 K (e, f, g h, i, j, k, l, m and n data were taken from the literature[16])

Errors for pH and volume in the Hyperquad 2013 program were 0.001. The speciation diagram and fitted titration curves from Hyperquad 2013 program are presented in Figs. 2 and 3, respectively, for 25 % methanol.
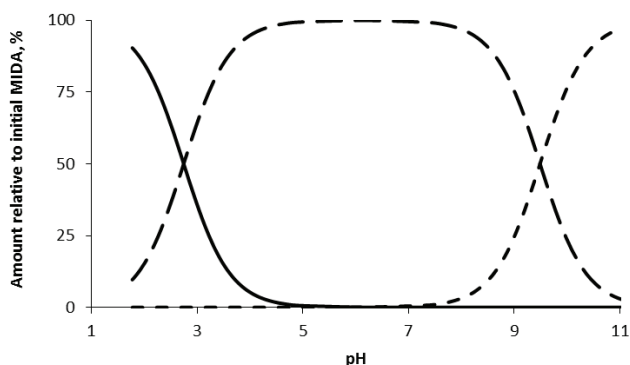

Fig. 2. Speciation diagram for MIDA (L) at 298 K, $I = 0.1$ mol dm^{-3} NaCl and 25 % methanol; $c_L = 0.01$ mol dm^{-3}; solid line H$_2$L; long dashed line HL$^-$; short dash line free L.

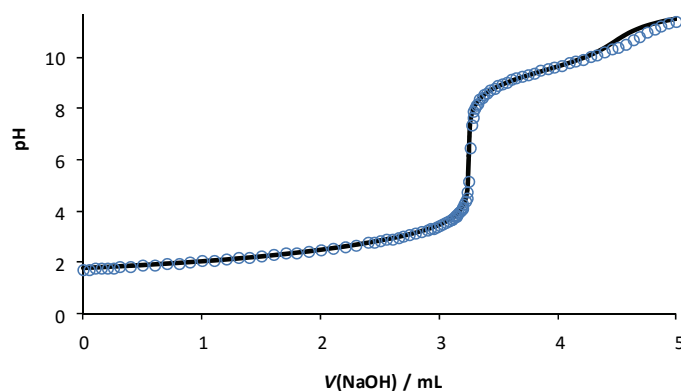Fig. 3. Potentiometric titration of MIDA (L) at 298 K, $I = 0.1$ mol dm^{-3} NaCl and 25 % methanol; $c_L = 0.01$ mol dm^{-3} *vs.* volume of NaOH. The continuous line represents the calculated pH refined with the Hyperquad 2013 program, considering H$_2$L and HL$^-$ species. Circles show the experimental pH values.

MoO$_4^{2-}$ binds with this tridentate ligand as a 1:1 complex:[5–8,10]

$$x\text{MoO}_4^{2-} + (y+2x)\text{H}^+ + z\text{L}^{2-} \rightarrow (\text{MoO}_3)_x\text{H}_y\text{L}_z^{(2z-y)-} + x\text{H}_2\text{O} \tag{4}$$

$$\beta_{xyz} = \frac{[(\text{MoO}_3)_x\text{H}_y\text{L}_z^{(2z-y)-}]}{[\text{MoO}_4^{2-}]^x[\text{H}^+]^{(y+2x)}[\text{L}^{2-}]^z} \tag{5}$$

where $x = 1$, $y = 0$ and $z = 1$. Thus, the stability constants for the complex species, MoO$_3$L^{2-}, was calculated at different volume fractions of methanol by combination of the following equations according to previous works:[5–8,10]

$$A_c = A_{obs} - \varepsilon_0[\text{MoO}_4{}^{2-}] \tag{6}$$

$$[\text{MoO}_3\text{L}^{2-}] = \frac{A_c}{\varepsilon_1} \tag{7}$$

$$C_M = [\text{MoO}_4{}^{2-}] + [\text{MoO}_3\text{L}^{2-}] \tag{8}$$

$$C_L = [\text{L}] + [\text{MoO}_3\text{L}^{2-}] \tag{9}$$

A_c, A_{obs}, and ε_0 are the corrected absorbance of the complex, the observed absorbance and the molar absorptivity of $\text{MoO}_4{}^{2-}$, respectively. The ε_0 values are calculated at $X_{metal} = 1.0$. The molar absorptivity values of the complex, ε_1, were calculated at low mole fraction of the metal, where all the metal ions were in the form of a complex. $[\text{MoO}_3\text{L}^{2-}]$, which is the concentration of the complex, was calculated at $X_{metal} = 0.5$ where the maximum absorbance was observed (Fig. 4). The value of [L] was used for the calculation of $[\text{L}^{2-}]$ according to the definition of dissociation constants. The values of the conditional stability constants were obtained by inserting the values of $[\text{MoO}_3\text{L}^{2-}]$, $[\text{MoO}_4{}^{2-}]$, $[\text{H}^+]$ and $[\text{L}^{2-}]$ into Eq. (5). Their values together with the literature values are shown in Table II. Microsoft Excel 2010 was used for the calculations in Eqs. (5)–(9).
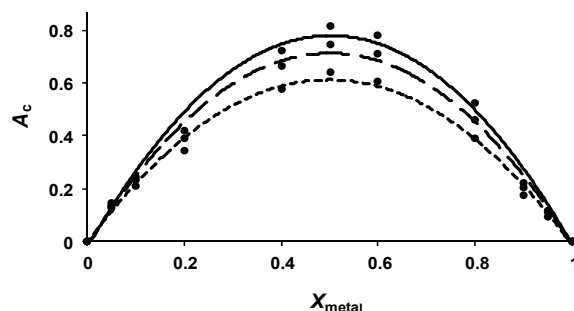

Fig. 4. Corrected absorbance data, A_c, for $\text{MoO}_3\text{MIDA}^{2-}$ vs. the mole fraction of Mo(VI), X_{metal}, at 298 K, an ionic strength of 0.1 mol dm^{-3} NaCl, 35 % methanol and different wavelengths: solid line 260 nm; long dashed line 265 nm; and short dashed line 270 nm. All of the lines were obtained based on the best fit to the corrected absorbance data.

TABLE II. Average experimental values of $\log \beta_{101}$ at pH 6.00, $I = 0.1$ mol dm^{-3} of NaCl and different aqueous solutions of methanol for the complexation of molybdenum(VI) with MIDA, $T = 298$ K

Methanol content, vol. %	$\log \beta_{101}$
0	18.30±0.03
5	18.40±0.04
10	18.44±0.04
15	18.46±0.06
20	18.53±0.10
25	18.64±0.01
30	18.76±0.03

TABLE II. Continued

Methanol content, vol. %	$\log \beta_{101}$
35	18.84 ± 0.02
40	18.86 ± 0.06
45	18.89 ± 0.10
0	18.2^a
0	19.09 ± 0.14^b
0	18.78 ± 0.18^c
0	18.67 ± 0.20^d
0	18.85 ± 0.15^e
0	18.91 ± 0.40^f

[a]This value was not at a fixed ionic strength and was obtained by the NMR technique. The concentrations are usually high in NMR (minimum of 0.1 mol dm^{-3} in metal and ligand[18]); [b]$I = 0.1$ mol dm^{-3} NaClO$_4$, $T = 298$ K, $c_L = c_M = 0.01$ mol dm^{-3}; [c]$I = 0.3$ mol dm^{-3} NaClO$_4$, $T = 298$ K, $c_L = c_M = 0.01$ mol dm^{-3}; [d]$I = 0.5$ mol dm^{-3} NaClO$_4$, $T = 298$ K, $c_L = c_M = 0.01$ mol dm^{-3}; [e]$I = 0.7$ mol dm^{-3} NaClO$_4$, $T = 298$ K, $c_L = c_M = 0.01$ mol dm^{-3}; [f]$I = 1.0$ mol dm^{-3} NaClO$_4$, $T = 298$ K, $c_L = c_M = 0.01$ mol dm^{-3} (b, c, d, e and f data were taken from the literature[6])

Comparison with literature data

The original and further first works about the complexation of molybdenum(VI) with different aminopolycarboxylic acids were reported by Kula and coworkers.[18–21] A literature survey showed that although there are only a few reports about the complexation of molybdenum(VI) with ethylenediamine-*N*,*N*′--diacetic acid (EDDA) in methanol–water[22,23] and complexation of tungsten(VI)[24] and molybdenum(VI)[25] with EDDA in propanol–water mixtures, no paper was found on stability constants data in different water + methanol solutions for the interaction of molybdenum(VI) with MIDA. It was seen from literature data[22–25] that the stability constants increased with decreasing polarity of alcohol–water mixtures, which confirms the pattern that was obtained in the current research. The concentration of Mo(VI) and MIDA and the kind of background electrolyte ($c_L = c_M = 0.007$ mol dm^{-3}, NaCl) in this research were different from that used in a previous work ($c_L = c_M = 0.01$ mol dm^{-3}, NaClO$_4$),[6] therefore the values of stability constants at 0 % methanol ($I = 0.1$ mol dm^{-3}) in the two works were not the same (Table II).

Application of the KAT model for the study of the solvent effect

Although linear Gibbs energy relationships such as the Hammett equation are well established and are known to perform very well for substituent effects, solvent effects are more complicated processes that require a more detailed investigation. Therefore, a more generally applicable treatment of multiple interacting solvent effects was designed by Kamlet, Abboud and Taft (KAT).[26] In their treatment, it is necessary to consider non-specific and specific solute–solvent interactions separately. Specific solute–solvent interactions were subdivided into solvent Lewis-basicity interactions (hydrogen bond donor (HBD) solute/

/(hydrogen bond acceptor (HBA) solvents) and solvent Lewis acidity interactions (hydrogen bond acceptor (HBA) solute/(hydrogen bond donor (HBD) solvents). Thus, the following multiparameter equation was suggested for application in linear solvation energy relationships (LSER):[26–44]

$$\log K = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \tag{10}$$

LSER have been used in various fields, such as, ionic liquids, solubility, thermochemistry, NMR chemical shifts, pharmaceuticals, *etc*. Equation (10) has been used in the correlation analysis by multiple regression of numerous reaction rates and equilibria, spectroscopic data and various other solvent dependent processes. The value of α shows the solvent HBD acidity and is a measure of the proton transfer from the solvent to the solute for hydrogen bond formation. The α values lie between zero for non-HBD solvents up to 1.0 for methanol (Table III).[16] The ability of the solvent to accept a proton from a solute in order to form a hydrogen bond is indicated by the value of β, which is called the solvent HBA basicity. The β values vary from zero for non-HBD solvents up to 1 for hexa-methylphosphoric acid triamide (HMPT).[16] The solvation parameters α and β have been used for the interpretation of intermolecular hydrogen bonding. The value of π^* is an index of solvent dipolarity/polarizability. In other words, it is the capability of the solvent regarding charge, dipole and dielectric contributions. The π^* value is 0.00 and 1.00 for cyclohexane and dimethylsulfoxide, respectively.[16] The value of δ is a discontinuous polarizability correlation term. The value of δ is 0.0 for non-chloro substituted aliphatic solvents, 0.5 for poly-chloro--substituted aliphatics, and 1.0 for aromatic solvents.[16] In the current work, δ value was zero. A_0 is the value for log K in the setup when α, β, δ and π^* are equal to zero. The KAT equations given in Table IV were obtained using Microsoft Excel 2010 software.

TABLE III. Solvatochromic parameters for different aqueous solutions of methanol from the literature[16]

Methanol content, vol. %	α	β	π^*
0	1.17	0.47	1.09
5	1.16	0.48	1.05
10	1.15	0.49	1.04
15	1.14	0.50	1.02
20	1.13	0.51	0.99
25	1.12	0.52	0.97
30	1.11	0.53	0.94
35	1.10	0.54	0.92
40	1.09	0.55	0.89
45	1.07	0.56	0.85

TABLE IV. Different KAT equations with one and two solvatochromic parameters together with their standard errors and square values of the correlation coefficients (r^2) for the dissociation and stability constants at $T = 298$ K, $I = 0.1$ mol dm^{-3} of NaCl and different aqueous solutions of methanol. α, hydrogen bond donor acidity; β, hydrogen bond acceptor basicity; π^*, dipolarity/polarizability. $n = 10$

KAT equation	r^2
$\log K_1 = (12.33\pm0.59) - (8.54\pm0.52)\alpha$	0.97
$\log K_1 = -(1.92\pm0.29) + (9.04\pm0.56)\beta$	0.97
$\log K_1 = (6.25\pm0.18) - (3.60\pm0.19)\pi^*$	0.98
$\log K_1 = (5.81\pm10.83) - (4.64\pm6.50)\alpha + (4.14\pm6.88)\beta$	0.97
$\log K_1 = (4.06\pm4.90) + (3.06\pm6.84)\alpha - (4.88\pm2.87)\pi^*$	0.98
$\log K_1 = (5.89\pm4.66) + (0.40\pm5.18)\beta - (3.44\pm2.05)\pi^*$	0.98
$\log K_2 = (16.18\pm0.33) - (5.98\pm0.29)\alpha$	0.98
$\log K_2 = (6.21\pm0.19) + (6.31\pm0.37)\beta$	0.97
$\log K_2 = (11.91\pm0.11) - (2.52\pm0.11)\pi^*$	0.98
$\log K_2 = (16.67\pm6.17) - (6.28\pm3.70)\alpha - (0.31\pm3.92)\beta$	0.98
$\log K_2 = (12.97\pm3.00) - (1.48\pm4.19)\alpha - (1.90\pm1.76)\pi^*$	0.98
$\log K_2 = (12.09\pm2.84) - (0.20\pm3.15)\beta - (2.60\pm1.25)\pi^*$	0.98
$\log \beta_{101} = (25.97\pm0.57) - (6.54\pm0.51)\alpha$	0.95
$\log \beta_{101} = (15.01\pm0.22) + (7.00\pm0.42)\beta$	0.97
$\log \beta_{101} = (21.30\pm0.19) - (2.76\pm0.19)\pi^*$	0.96
$\log \beta_{101} = (5.66\pm7.61) + (5.61\pm4.56)\alpha + (12.91\pm4.83)\beta$	0.98
$\log \beta_{101} = (19.29\pm5.07) + (2.81\pm7.08)\alpha - (3.94\pm2.97)\pi^*$	0.96
$\log \beta_{101} = (14.76\pm4.13) + (7.27\pm4.58)\beta + (0.11\pm1.82)\pi^*$	0.97

CONCLUSIONS

The KAT equations obtained in this research (Table IV) could be used for the calculation of the dissociation constants of MIDA and the stability constants for the complexation of Mo(VI) with MIDA at pH = 6.00, $T = 298$ K, $I = 0.1$ mol dm^{-3} of sodium chloride in the desired range of methanol (0–45 %) without any further experimental work. The values of dissociation and stability constants increased with a mild slope as the volume fraction of methanol increased, because the solvation decreased and stability increased (Tables I and II).[11,45,46] The standard errors for A_0, a, b and p are too high for the two parameter KAT equation in comparison to the one parameter equation (Table IV), which is due to the linear increase of solvatochromic parameters for methanol (Table III). The trend that was obtained in this research is in agreement with previous findings[1,2,16] and therefore it is predicted that it could probably be valid for the complexation of molybdenum(VI) with other aminopolycarboxylic acids.

SUPPLEMENTARY MATERIAL

The absorbances of the solutions of the Mo(VI) + MIDA complex at total concentration of 0.0028 mol dm^{-3} in the UV range (260 to 270) nm at a constant pH of 6.00 and different volume fractions of methanol are available electronically from http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

И З В О Д

ФОРМИРАЊЕ КОМПЛЕКСА МОЛИБДЕНА(VI) СА МЕТИЛИМИНОДИАЦЕТАТНОМ КИСЕЛИНОМ У РАЗЛИЧИТИМ ВОДА + МЕТАНОЛ РАСТВОРИМА

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Формирање комплекса молибдена(VI) са метилиминодиацетатном киселином (MIDA) при pH 6,00, T = 298 K и I = 0,1 mol dm^{-3} натријум-хлорида и различитим вода + метанол растворима (0–45 запр. %) је испитивано потенциометријским и UV спектро-фотометријским мерењима. Вредности константи стабилности су израчунате и њихови трендови интерпретирани применом Kamlet–Abboud–Taft (KAT) модела да би се испитала улога специфичних и неспецифичних интеракција у воденим растворима метанола. За прорачуне су коришћени софтвери Hyperquad 2013 и Microsoft Excel 2010.

(Примљено 23. октобра, ревидирано 30. децембра 2015, прихваћено 12. јануара 2016)

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