

Solvent effects on complexation of molybdenum(VI) with nitrilotriacetic acid in different aqueous solutions of methanol

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Abstract

The formation constants of the species formed in the systems $H^+ + Mo(VI) +$ nitrilotriacetic acid and $H^+ +$ nitrilotriacetic acid have been determined in different aqueous solutions of methanol at 25 °C and constant ionic strength 0.1 mol dm⁻³ sodium perchlorate, using spectrophotometric and potentiometric techniques. The composition of the complex was determined by the continuous variations method. It was shown that molybdenum(VI) forms a mononuclear 1:1 complex with nitrilotriacetic acid of the type MoO_2L^{-3} at $-\log[H^+] = 5.8$. The formation constant in various media was analyzed in terms of Kamlet and Taft's parameters. Single-parameter correlations of the formation constant, K_S , versus α (hydrogen-bond donor acidity) and π^* (dipolarity/polarizability) are poor in all solutions, except for β (hydrogen-bond acceptor basicity), but multi-parameter correlations represent significant improvement with regard to the single-parameter models. Linear relationship is observed when the experimental $\log K_S$ is plotted versus the calculated ones, while all the Kamlet and Taft's parameters are considered. Finally, the results are discussed in terms of the effect of solvent on complexation.

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1. Introduction

Chemists are usually interested to understand solvent effects on the overall solution capabilities that depend on all possible intermolecular interactions between solute and solvent molecules. The search for finding a correlating factor goes back to the work of Thomson and Nernst [1,2] who suggested a connection between the dielectric constant of a solvent and its dissociating power. A more theoretical approach to using the dielectric constant as a parameter in describing any solvent system may be found in the Bjerrum-Fuoss ion-pair model [3,4]. Denison and Ramsey [5] have constructed a model by assuming that two oppositely charged ions exist either in contact as an associated ion-pair, or at such a large distance apart that the coulombic force between them is negligible. Van Uitert et al. showed that the negative logarithm of the dissociation constant of some β -diketonates is a linear function

of the mole fraction of dioxane in dioxane–water mixtures of low dioxane concentration [6].

The influence of solvent on solute molecule has been intensively studied but the problem is yet far from being completely understood. At present, there are two more important approaches to the quantitative description of this effect. The theoretical approach describes the solvent as an isotropic environment of dissolved particles and characterizes it by its bulk properties. Unfortunately, this approach involves only the influence of the nonspecific interactions. The other approach is based on the description of the solvent effect by suitably chosen empirical parameters measuring specific and nonspecific interactions. The drawback of this approach is that such parameters are not universal and depend on each other. The interactions between solvent and solute molecules are separated in literature into specific and nonspecific. As a result, linear functions with few parameters for description of the solvent effect are proposed [7–11]. One of the most interesting is that proposed by Kamlet and Taft [12].

Recently, solvent effects on transition metal complexes are reviewed [13] and more attention has been paid to binary

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solvent mixtures in this field [14,15]. Solute–solvent interactions are much more complex in mixed solvent systems than in pure solvents due to the possibility of preferential solvation by any of the solvents present in the mixtures. Moreover, the solvent–solvent interactions produced in solvent mixtures can affect the solute–solvent interactions and therefore they can also affect preferential solvations [16].

In the present work, we have chosen a well-understood system, the complexation of molybdenum(VI) with nitrilotriacetic acid, nta [17], in different solutions of methanol+water to show how the solvents and their mixtures with various dielectric constants affect the formation of such a complex.

2. Experimental

2.1. Reagents

Methanol was obtained from Merck as analytical reagent grade material and was used without further purifications. Nitrilotriacetic acid, nta, (Fluka, analytical reagent grade) was recrystallized from hot water, washed with ethanol and dried over P_2O_5 . Equivalent weights were checked by titration against a standard alkali. The NaOH solution was prepared from titrisol solution (Merck) and its concentration was determined by several titrations with standard HCl. Perchloric acid, sodium perchlorate and sodium molybdate were supplied from Merck (analytical reagent grade) and were used without further purification. Dilute perchloric acid solution was standardized against standard NaOH solution. All dilute solutions were prepared from double-distilled water with a specific conductance equal to $1.3 \pm 0.1 \mu\Omega^{-1} \text{ cm}^{-1}$.

2.2. Apparatus

An Eyela pH meter, PHM 2000, was used for pH measurements. The hydrogen ion concentration was measured with an Ingold UO 3234 glass electrode and an Ingold UO 3236 calomel electrode. Spectrophotometric measurements were performed using a UV–Vis Shimadzu 2100 spectrophotometer with a GDU-20 computer and thermostated matched 10 mm quartz cells.

2.3. Measurements

All measurements were carried out at $25 \pm 0.1^\circ \text{C}$. The ionic strength was maintained at 0.1 mol dm^{-3} with sodium perchlorate. The pH-meter was calibrated for the relevant H^+ concentration with a solution of 0.01 mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate (for adjusting the ionic strength to 0.1 mol dm^{-3}). For this standard solution, we set $-\log[H^+] = 2.00$ [18,19]. Junction potential corrections have been calculated from Eq. (1).

$$-\log[H^+]_{\text{real}} = -\log[H^+]_{\text{measured}} + a + b[H^+]_{\text{measured}} \quad (1)$$

a and b were determined by measuring the hydrogen ion concentration for two different solutions of $HClO_4$ with sufficient $NaClO_4$ to adjust the ionic media.

2.4. Procedure

For each experiment two solutions of $Mo(VI) + nta$ have been prepared with the same concentration, $2.5 \times 10^{-2} \text{ mol dm}^{-3}$, but the ionic strength of the first was maintained with sodium perchlorate, and that of the second, with sodium hydroxide or perchloric acid, both with the same mole fraction of methanol. The first solution was then titrated with the second. The pH and absorbance were measured after addition of a few drops of titrant and this procedure extended up to the required pH. In all cases, the procedure was repeated at least three times and the resulting average values and corresponding standard deviations are shown in the text and tables.

2.5. Calibration of the glass electrode

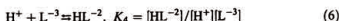
The term pH has significance only in aqueous media [20]. The glass electrode potential in an aqueous solution differs from that in the solution of mixed solvents and a liquid-junction potential of uncertain magnitude may affect the results. To overcome this difficulty, it was necessary to calibrate the glass electrode in different solvent mixtures. The experimental method outlined by Van Uiter and Hass [21] was employed for this purpose. The pH meter reading B in methanol+water media was converted into $[H^+]$ using the equation

$$-\log[H^+] = B + \log \mu_H \quad (2)$$

where the concentration factor $\log \mu_H$ was obtained for the ionic strength 0.1 mol dm^{-3} $NaClO_4$ from the expression $\log \mu_H = \log \mu_H^\circ + \log \gamma_\pm$. The value of μ_H° is independent of ionic concentration but is dependent on solvent composition and γ_\pm is the mean activity coefficient of perchloric acid in the solvent mixtures. In this work, the values of B were recorded in various solvent mixtures containing known concentration of perchloric acid and sufficient sodium perchlorate to give a constant ionic strength of 0.1 mol dm^{-3} . The difference between the logarithm of known hydrogen-ion concentrations and the corresponding values of B was used to calculate values of the correction term $\log \mu_H = \log(\mu_H^\circ \gamma_\pm)$ [22].

3. Results and discussion

The following species of nta may exist in solution at different $-\log[H^+]$, L^{-3} , HL^{-2} , H_2L^{-} , H_3L and H_4L^+ , where L^{-3} represents the fully dissociated ligand anion. The protonation constants of nta have been extensively studied in different kinds of background electrolytes and the results are reported in the literature. The following equilibria were considered.



Where K_1 , K_2 and K_3 refer to the protonation constants of the carboxyl, and K_4 to the amino groups of nta, respectively. The protonation constant values have been determined using potentiometric technique under the same condition of temperature, ionic media and mole fraction of methanol as mentioned before and calculated using a computer program, which employs a least-squares method [23]. The release of the first and second protons from nta, Eqs. (3) and (4), occurs at very low pH and is not considered further. The protonation constant values, expressed in log unit, are collected in Table 1 together with the values reported in the literature [17,24].

3.1. Complexation of molybdenum(VI)

The occurrence of molybdenum polymerization in acidic media complicates the study of molybdenum complexation with nta [25,26]. Due to the stability constants of the polymerization, equilibria are not well known, the region from pH>5 is useful for spectrophotometric determination. Using the continuous variations method, we determined the absorbances of solutions of Mo(VI) and nta with total concentration 5.0×10^{-3} mol dm⁻³ in the UV range 260–280 nm at a constant $-\log[H^+]$ of 5.8. The observed absorbances were corrected for unreacted Mo(VI) from Eq. (7) and are plotted in Fig. 1.

$$A_C = A_{obs} - \epsilon_{Mo} [Mo(VI)] \quad (7)$$

Raymond et al. [27] synthesized Na[MoO₃(L)]H₂O, among other molybdenum chelate complexes, where L refers to a tridentate amino acid as ligand. The IR spectrum of those compounds crystallized at $-\log[H^+] = 6$ shows the tridentate ligands coordinated to a *cis*-trioxo molybdenum core. As well, Cruywagen et al. [28] have demonstrated the acid dissociation of molybdic acid as



Assuming that H₂MoO₄ is equivalent to MoO₃, H₂O, we can write the molybdenum(VI) chelate formation as Eq. (9). The same conclusion has been obtained before by Zare et al. [17]. So, the composition of the complex indicated by the spectrophotometric measurements at $-\log[H^+] = 5.8$ is

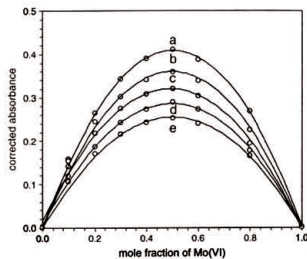
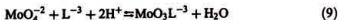


Fig. 1. Continuous variations plots of corrected absorbances of MoO₃L⁻³ versus mole fraction of Mo(VI) at 25 °C, ionic strength 0.1 mol dm⁻³ NaClO₄, $X_{methanol} = 0.0$ and different wavelengths: (a) 260, (b) 265, (c) 270, (d) 275 and (e) 280 nm.

MoO₃L⁻³. The formation of a 1:1 complex with nta, thus, has Mo/ligand/proton equal to 1:1:2 stoichiometry as



with the stability constant, K_S , as

$$K_S = [MoO_3L^{-3}] / [MoO_4^{2-}] [L^{-3}] [H^+]^2 \quad (10)$$

Thus, equations can be written for the total concentration of Mo, C_M and the total concentration of the ligand, C_L , at the maximum point on the plot, where its concentration is maximum (Fig. 1):

$$C_M = [Mo] + [C] \quad (11)$$

$$C_L = [L] + [C] \quad (12)$$

Combining Eqs. (7) and (11), (12) in Eq. (10) and solving for K_S gives the stability constant of Eq. (9), and its average values at different wavelengths are shown in Table 2 together with the values reported before.

Table 1

Protonation constants of the carboxylic, K_3 , and the amino, K_4 , groups of nta at 25 °C, ionic strength 0.1 mol dm⁻³ sodium perchlorate and different mole fractions of methanol, $X_{methanol}$

$X_{methanol}$	Log K_3	Log K_4	Experimental condition	Ref.
0.00	2.66±0.05	10.41±0.08	3 M NaClO ₄ , $t = 25$ °C	This work
0.03	2.71±0.05	10.62±0.09	1 M NaClO ₄ , $t = 25$ °C	This work
0.05	2.75±0.03	10.70±0.07		This work
0.07	2.77±0.04	10.72±0.05		This work
0.10	2.78±0.06	10.76±0.06		This work
0.15	2.79±0.08	10.80±0.10		This work
0.20	2.81±0.04	10.86±0.09		This work
0.25	2.86±0.06	10.94±0.10		This work
0.30	2.89±0.04	11.02±0.09		This work
0.00	2.63	9.17	3 M NaClO ₄ , $t = 25$ °C	[17]
0.00	2.39	9.10	1 M NaClO ₄ , $t = 25$ °C	[24]

Table 2

The formation constants of Mo(VI)+nta in different solutions of methanol+water at 25 °C and Kamlet and Taft's solvatochromic parameters

Mole fraction of methanol	Log K_S	π^{**}	α^a	β^b	Dielectric constant ^c
0.00	17.85±0.06	1.140	1.260	0.190	78.74
0.03	18.02±0.04	1.130	1.214	0.208	76.88
0.05	18.08±0.11	1.125	1.188	0.222	74.93
0.07	18.16±0.09	1.120	1.164	0.238	73.08
0.10	18.20±0.10	1.110	1.130	0.260	70.47
0.15	18.61±0.11	1.091	1.088	0.308	66.51
0.20	18.97±0.09	1.068	1.055	0.353	62.97
0.25	19.90±0.09	1.042	1.031	0.397	59.79
0.30	19.41±0.08	1.013	1.016	0.436	56.92
0.00	18.6 ^d				78.74

a, b, c and d were obtained from Refs. [14,17,22,29], respectively.

Table 3
The percentage contribution of Kamlet and Taft's parameter on the effect of different media on complexation at 25 °C and ionic strength 0.1 mol dm⁻³ NaClO₄

π	β	π^*
0.46	82.44	17.10

3.2. Solvent effect

Solvent effects on formation constants are often defined in terms of the polarity of the organic solvent. Solvent polarity is a commonly used term related to the capacity of the solvent for solvating dissolved charged or dipolar species. Attempts to express it quantitatively involved mainly physical solvent properties such as dielectric constant of the solvent. However, this approach is often inadequate since dielectric constant regards solvents as a non-structured system, which is not composed of individual molecules with their own solvent-solvent and solvent-solute interactions such as hydrogen-bonding interactions, which often play a dominating role in any reaction. The problem is to identify and to assess the relative importance of these various factors on the solvent effects.

Recently, a quantitative measurement of the solvent polarity has been introduced by Kamlet and Taft [9,12]. Kamlet and Taft's solvatochromic parameters have been used in one-, two- or three-parameter correlation involving different combinations of these parameters, which are called linear solvation energy relationships. In general, all these parameters constitute more comprehensive measures of solvent polarity than the dielectric constant or any other single physical characteristic, since they reflect more reliably the complete picture of all intermolecular forces acting between solute and solvent molecules. Using the solvatochromic solvent parameters, the multi-parameter Eq. (13) has been proposed

$$\log K_S = A_0 + p(\pi^* + d\delta) + a\alpha + b\beta \quad (13)$$

where A_0 represents the regression value and π^* is the index of the solvent dipolarity/polarizability, which is a measure of the ability of a solvent to stabilize a charge or a dipole by its own dielectric effects. The π^* scale was selected to run from 0.0 for cyclohexanone to 1.0 for dimethylsulfoxide. The α coefficient represents the solvent hydrogen-bond donor (HBD) acidity; in other words, it describes the ability of a solvent to donate a proton in a solvent to a solute hydrogen-bond. The α scale extends from 0.0 for non-HBD solvents to about 1.0 for methanol. The β coefficient is a measure of a solvent hydrogen-bond acceptor (HBA) basicity and describes the ability of a solvent to accept a proton in a solute to a solvent hydrogen-bond. The β scale was selected to extend from 0.0 for non-(HBA) solvents to about 1.0 for hexamethylphosphoric acid triamide. δ is a discontinuous polarizability correction term equal to 0.0 for non-chlorine substituted aliphatic solvents, 0.5 for poly-chlorine substituted aliphatics and 1.0 for aromatic solvents [15]. The regression coefficients, p , d , a and b in Eq. (10) measure the relative susceptibilities of solvent-dependent $\log K_S$ to the indicated solvent parameters.

The solvent polarity parameter of media, π^* , increases with increasing the mole fraction of water in aqueous solutions of methanol. If the π^* of media was the only factor for the solvent effect on the complexation, it may be expected that $\log K_S$ in water should be greater than those of all the other aqueous solutions of methanol. However, the formation constant increases with increasing the solvent hydrogen-bond acceptor basicity parameter, β , and decreases with increasing the solvent polarity π^* , as well as increases with decreasing the hydrogen-bond donor acidity parameter of the solvents, α .

In order to explain the obtained $\log K_S$ values through Kamlet and Taft's solvent parameter, the formation constants were correlated with solvent properties by means of single and multiple linear regression analysis by a suitable computer program [23]. We used the Gauss-Newton linear least-squares method in the computer program to refine the $\log K_S$ by minimizing the error squares sum from Eq. (14):

$$S = \sum (a_i - b_i)^2 \quad (14)$$

Where a_i is a quasi-experimental formation constant and b_i is the calculated one. Single-parameter correlations of $\log K_S$ in terms of individually with α or π^* did not give a good result, Eqs. (15) and (16).

$$\log K_S = 19.90 - 1.17\alpha \quad (n = 9, r = 0.30) \quad (15)$$

$$\log K_S = 32.55 - 12.85\pi^* \quad (n = 9, r = 0.97) \quad (16)$$

So, we thought it interesting to correlate $\log K_S$ versus a multi-parametric equation involving α , β and π^* . The result presented in Eq. (17), multi-parametric equation, indicates significant improvement with regard to the single-parameter models.

$$\log K_S = 14.71 + 0.04\alpha + 7.23\beta + 1.5\pi^* \quad (n = 9, r = 0.9993) \quad (17)$$

The coefficients of π^* , α and β in Eq. (17) are very different to each other and are in the order of $\beta > \pi^* > \alpha$, and indicate that the hydrogen-bond acceptor basicity parameter is the most important one. The polarity parameter power of the solvent plays a relatively small role and finally the hydrogen-bond donor acidity parameter nearly has no significance in changing the formation constant of the Mo(VI)+nta system in the proposed various aqueous solutions of methanol. From the

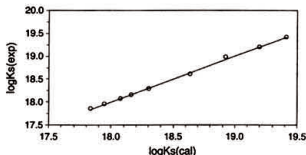


Fig. 2. Plot of the experimental values of $\log K_S$ versus the calculated ones from Eq. (15).

magnitude of the coefficients a , b and p , the percentage contribution of the Kamlet and Taft's solvatochromic parameters on the effect of different media on complexation were calculated and are given in Table 3.

In order to show the efficiency of the suggested multi-parameter correlations, experimental values of $\log K_s$ are plotted versus their calculated ones from Eq. (17) for different aqueous solutions of methanol. It can be seen (Fig. 2) that the experimental and calculated values of $\log K_s$ are in good agreement with each other, $r=0.9993$.

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