Comparison Studies on Complexation of Molybdenum(VI) with Aspartic Acid And Glutamic Acid in Different Dielectric Constants[1]

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ABSTRACT

Equilibria of the reaction of molybdenum(VI) with L-aspartic acid (Asp) and L- Glutamic acid (Glu) have been studied by spectrophotometric measurements in mixed solvent systems at an ionic strength of 0.2 mol/dm^3 sodium perchlorate, employed (15, 20, 25, 30± 0.1°C) at pH ranges of 3.2 to 5.5 with a high ratio of ligand to metal. The stability constants of the complexes and the resulting free energy changes are presented. The effect of solvent systems on protonation and complexation are discussed. Linear relationships are observed by plotting log$K$ versus $1/D$, where K and D show stability and dielectric constants, respectively.

INTRODUCTION

So far , few investigation about the complexation of a molybdate ion in mixed solvent systems has been performed. The biochemical aspect and importance of molybdenum in enzymes present in microorganisms, plants, and animals have been investigated by Kendrick *et al.* [1]. The equilibria of Mo(VI) in an aqueous solution are complex, and various polynuclear species are formed in acidic solution (pH < 4.5) [2–10]. The complexation of molybdenum and aspartic acid & glutamic acid play an important role in animal and plant metabolism particularly in reactions involving transformation and transfer of amino group. Due to this fact, complexation with transitional elements and consideration of the stability of the complex could be of great value [11-13].

In this research project, the complexation of molybdenum(VI) with aspartic acid and glutamic acid have been investigated using a combination of potentiometric and spectrophotometric means in mixed solvent systems of CH_3OH and H_2O with a high ratio of ligand to metal employing pH ranges of 3.2 to 5.5 .

EXPERIMENTAL

Perchloric acid Sodium perchlorate, methanol, and sodium hydroxide were supplied from Merck Chemical Co., L-aspartic acid, L-glutamic acid and sodium molybdate were purchased from Aldrich Chemical Co., and Riedel–De Haenayseelze– Hannover, respectively. Dilute perchloric acid solution was standardized against $KHCO_3$. A 50% sodium hydroxide solution free from carbonate was prepared from analytical grade material followed by filtration through a G4 Jena glass filter and stored in a polyethylene bottle. Dilute solution was prepared from double distilled water with a specific conductivity of (1.3 ± 0.1) $\mu\Omega^{-1}cm^{-1}$ and standardized against $HClO_4$.

All measurements were carried out at 15, 20, 25, and 30 ± 0.1°C. The ionic strength was maintained at 0.2 mol/dm^3 using sodium perchlorate. A Horiba D-14 pH meter was employed for pH measurements. The hydrogen ion concentration was measured using an Ingold UO3234 glass electrode and an Ingold UO3236 calomel electrode. It is essential to calibrate the system routinely for various solvent mixtures of known hydrogen ion concentration and constant ionic strength to determine the hydrogen ion concentration [14-16].

Spectrophotometric measurements were conducted using an UV-Vis Shimadzu 2101 spectrophotometer equipped with a Acermate 486 SX/25D computer and thermostatically matched 10 mm quarts cells, employing a flow type cell and masterflex pump allowing the circulation of the solution from the potentiometric cell to the spectrophotometric cell. The absorbance and pH of the solution were measured simultaneously.

The dielectric constant of mixed solvent systems of methanol in water were measured by comparing the capacitance of a capacitor with and without the
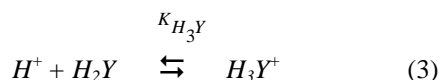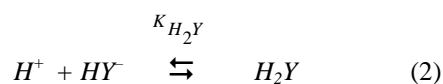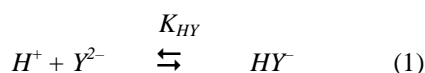

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sample present (C and C_0, respectively), using $D = C/C_0$. Dielectric const ant measurements were carried out using a Lutron-DM-9023 capacitance meter.

RESULTS AND DISCUSSION

The stability constants of protonation equilibria of Asp and Glu in water and in mixed solvent systems of methanol + water were determined prior to the metal aminopolycarboxylate complex study. The protonation equilibria of Ligands have been extensively studied in aqueous solution [17]; however, little is known about the protonation equilibria of Asp and Glu in different dielectric media [18-20].

Consider the following equilibria:

$$H^+ + Y^{2-} \overset{K_{HY}}{\rightleftharpoons} HY^- \qquad (1)$$

$$H^+ + HY^- \overset{K_{H_2Y}}{\rightleftharpoons} H_2Y \qquad (2)$$

$$H^+ + H_2Y \overset{K_{H_3Y}}{\rightleftharpoons} H_3Y^+ \qquad (3)$$

Where Y^{2-} represents a fully dissociated Asp and Glu anion. The results, means of average values of at least three determinations with corresponding standard deviations are presented in Table 4, where the protonation constants have been determined by potentiometric techniques employing a computer programmed nonlinear least-squares method.

Complexation of molybdenum (VI) with Asp and Glu

Complexation equilibria of a molybdate ion with both of the ligands have been studied employing a method based on the relation of absorbance as a function of pH, $A = f(pH)$, considering the high stability of complexes [21, 22]. Absorbance measurements were performed for solutions containing Mo(VI) (10^{-4}mol/dm^3) with a large excess of Asp and Glu (10^{-2} mol/dm^3) of various pH ranges (3.2–5.5) in different solvent systems. Considering that the absorbance is a function of concentrations(Fig.1) ,the values of the molar absorptivities of molybdenum(VI), ε_0, at different wavelengths and various dielectric constants are shown in Table 3, where under these experimental conditions, the hydrolysis of molybdenum(VI) ion was negligible; however, ε_0 has been determined using other methods [23].

The equilibrium reaction and complex formation of aspartic acid and glutamic acid with tetraoxymolybdenum in an acidic environment follows:

$$MoO_4^{2-} + H^+ + HY^- \rightleftharpoons MoO_3Y^{2-} + H_2O, \qquad (4)$$

$$A = \varepsilon_0 [\, MoO_4^{2-} \,] + \varepsilon_1 [\, MoO_3Y^{2-} \,] \qquad (5)$$

Where ε_1 is the molar absorptivity of the complex. Considering the mass balance equilibrium,

$$[\, MoO_4^{2-} \,] = c_{Mo(VI)} - [\, MoO_3\,Y^{2-} \,], \qquad (6)$$

$$[HY] = (c_{HY} - [MoO_3Y^{2-}\,]\,)\, \alpha_{HY}, \qquad (7)$$

Where $c_{Mo(VI)}$ and c_{HY} are the total concentrations of Mo (VI) and Asp or Glu, respectively, and α_{HY} is the mole fraction of HY presented as a free ligand given by

$$\alpha_{HY} = \frac{K_{HY}K_{H_2Y}[H^+]}{[H^+]^3 + K_{HY}[H^+]^2 + K_{HY}K_{H_2Y}[H^+]^3 + K_{HY}K_{H_2Y}K_{H_3Y}}$$

In Equation (8), the formation constant, is derived from equation (1):

$$K_c = \frac{[MoO_3Y^{2-}]}{[MoO_4^{2-}][H^+][HY^-]} \qquad (8)$$

Considering the concentration of ligand to metal and insertion of equation (5) in (6) and (7) and simplifying the result equation (9) is derived:

$$\frac{C_{Mo(VI)}}{A} = \frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_1 K_C(C_{HY} - \dfrac{A}{\varepsilon_1 - \varepsilon_0})} \times$$

$$\frac{(A - \varepsilon_0 C_{Mo(VI)})}{A\alpha_{HY}[H^+]} \qquad (9)$$

Plotting $C_{Mo(VI)}/A$ against $(A - \varepsilon_0 C_{Mo(VI)})/A\alpha_{HY}[H^+]$ shows a straight line where formation constants and molar absorptivity of the complexes are calculated from the slope and intercept, respectively (see Fig 2).

The absorbance of MoO_3Y^{2-} at different pH and wavelengths in methanol, the molar absorptivity of the complex, and formation constants are listed in Tables 1–4 respectively.

Table 1. Absorbance, A, of solutions at different pH values and wavelengths in (x) water + (1-x) methanol
$c_{Mo} = 10^{-4}$ M, I =0.2 M, Asp = 10^{-2} M.

	λ / nm								λ / nm						
PH	250	255	260	265	270	275	280	pH	250	255	260	265	270	275	280
T = 15°C															
x =1.000								**x = 0.899**							
3.68	0.234	0.175	0.139	0.116	0.095	0.077	0.061	3.77	0.309	0.249	0.204	0.169	0.142	0.118	0.095
4.03	0.228	0.168	0.131	0.108	0.088	0.072	0.055	4.51	0.279	0.214	0.173	0.142	0.120	0.101	0.082
4.29	0.217	0.157	0.121	0.098	0.079	0.064	0.050	4.85	0.260	0.196	0.155	0.127	0.107	0.089	0.072
4.64	0.196	0.117	0.103	0.080	0.065	0.052	0.039	5.16	0.236	0.172	0.133	0.107	0.088	0.073	0.060
5.49	0.146	0.089	0.058	0.027	0.020	0.013	0.013	5.62	0.199	0.139	0.101	0.077	0.062	0.050	0.042
6.10	0.135	0.080	0.048	0.019	0.013	0.008	0.008	6.12	0.176	0.117	0.181	0.059	0.046	0.036	0.03
x = 0.952								**x = 0.839**							
3.69	0.267	0.205	0.168	0.138	0.115	0.094	0.076	3.81	0.361	0.298	0.249	0.208	0.177	0.149	0.125
4.23	0.252	0.190	0.151	0.125	0.103	0.083	0.069	4.27	0.335	0.271	0.223	0.188	0.160	0.134	0.113
4.49	0.238	0.175	0.138	0.12	0.092	0.074	0.061	4.79	0.308	0.240	0.195	0.164	0.141	0.119	0.100
5.03	0.200	0.139	0.104	0.080	0.063	0.051	0.041	5.34	0.265	0.199	0.158	0.130	0.111	0.092	0.079
5.60	0.160	0.101	0.069	0.048	0.035	0.026	0.022	5.62	0.227	0.161	0.122	0.097	0.081	0.067	0.058
6.14	0.151	0.092	0.060	0.039	0.028	0.020	0.016	6.25	0.203	0.140	0.102	0.079	0.065	0.053	0.047
T = 20°C															
x = 1.000								**x = 0.899**							
3.74	0.232	0.147	0.138	0.113	0.093	0.075	0.059	3.70	0.314	0.252	0.207	0.175	0.144	0.121	0.091
4.21	0.222	0.163	0.127	0.102	0.083	0.067	0.053	4.00	0.304	0.239	0.195	0.162	0.136	0.113	0.092
4.48	0.211	0.151	0.114	0.090	0.072	0.057	0.045	4.51	0.283	0.218	0.175	0.145	0.122	0.102	0.084
5.01	0.180	0.121	0.086	0.065	0.049	0.038	0.030	4.04	0.245	0.179	0.140	0.113	0.093	0.018	0.065
5.55	0.156	0.099	0.065	0.045	0.031	0.022	0.016	5.72	0.193	0.131	0.094	0.070	0.055	0.046	0.039
6.01	0.147	0.090	0.058	0.037	0.029	0.015	0.011	6.26	0.175	0.115	0.079	0.057	0.043	0.034	0.030
x = 0.952								**x = 0.839**							
3.73	0.260	0.202	0.162	0.135	0.113	0.091	0.074	3.89	0.354	0.286	0.241	0.203	0.169	0.142	0.118
4.49	0.234	0.173	0.135	0.110	0.091	0.074	0.059	4.25	0.335	0.268	0.221	0.187	0.158	0.132	0.110
4.82	0.214	0.154	0.117	0.093	0.077	0.061	0.049	4.86	0.300	.231	0.188	0.156	0.132	0.112	0.094
5.15	0.188	0.130	0.095	0.073	0.057	0.046	0.037	5.07	0.287	0.219	0.178	0.148	0.124	0.106	0.089
5.57	0.164	0.106	0.072	0.051	0.039	0.030	0.023	5.30	0.269	0.202	0.161	0.132	0.112	0.095	0.079
6.01	0.149	0.092	0.060	0.040	0.029	0.020	0.016	6.26	0.204	0.140	0.103	0.078	0.064	0.053	0.045
T = 25°C															
x = 1.000								**x = 0.899**							
3.34	0.228	0.173	0.137	0.114	0.094	0.077	0.061	3.11	0.308	0.251	0.208	0.174	0.147	0.122	0.102
4.09	0.214	0.154	0.119	0.096	0.078	0.062	0.049	4.28	0.282	0.218	0.174	0.144	0.122	0.102	0.083
4.62	0.183	0.124	0.089	0.069	0.053	0.042	0.033	4.9	0.242	0.179	0.139	0.112	0.093	0.077	0.063
5.01	0.160	0.102	0.070	0.050	0.036	0.027	0.021	5.21	0.218	0.156	0.117	0.090	0.075	0.062	0.051
5.69	0.139	0.084	0.052	0.034	0.032	0.015	0.011	5.53	0.197	0.136	0.099	0.075	0.061	0.050	0.041
6.12	0.134	0.079	0.048	0.029	0.018	0.012	0.008	6.02	0.181	0.120	0.085	0.061	0.048	0.039	0.033
x = 0.952								**x = 0.839**							
3.02	0.259	0.201	0.165	0.138	0.116	0.096	0.077	3.23	0.356	0.295	0.249	0.208	0.176	0.147	0.122
4.10	0.244	0.181	0.143	0.116	0.095	0.079	0.064	4.20	0.341	0.277	0.231	0.193	0.164	0.135	0.113
4.57	0.222	0.161	0.123	0.098	0.081	0.066	0.051	4.81	0.286	0.219	0.177	0.146	0.124	0.105	0.087
5.08	0.185	0.124	0.089	0.068	0.052	0.041	0.031	5.02	0.273	0.206	0.164	0.135	0.115	0.097	0.082
5.3	0.173	0.113	0.078	0.057	0.042	0.034	0.027	5.99	0.206	0.141	0.105	0.079	0.065	0.054	0.046
6.34	0.150	0.092	0.058	0.039	0.028	0.020	0.014	6.49	0.196	0.132	0.095	0.069	0.057	0.047	0.040
T = 30°C															
x = 1.000								**x = 0.899**							
3.95	0.219	0.160	0.125	0.102	0.083	0.067	0.052	3.82	0.301	0.236	0.193	0.160	0.135	0.112	0.092
4.26	0.203	0.144	0.109	0.087	0.070	0.059	0.043	4.50	0.266	0.202	0.160	0.132	0.110	0.092	0.074
4.62	0183	0.124	0.089	0.069	0.053	0.042	0.033	4.90	0.242	0.179	0.139	0.112	0.093	0.077	0.063
5.01	0.160	0.102	0.070	0.050	0.036	0.027	0.021	5.21	0.218	0.156	0.117	0.090	0.075	0.062	0.051
5.69	0.0139	0.082	0.052	0.034	0.032	0.015	0.011	5.53	0.197	0.136	0.099	0.075	0.061	0.050	0.041
6.12	0.134	0.079	0.048	0.029	0.018	0.012	0.008	6.02	0.181	0.120	0.085	0.061	0.048	0.039	0.033
x = 0.952								**x = 0.839**							
3.90	0.253	0.191	0.152	0.125	0.104	0.085	0.068	3.78	0.342	0.277	0.231	0.192	0.163	0.135	0.113
4.10	0.244	0.181	0.183	0.116	0.095	0.079	0.064	4.20	0.341	0.277	0.230	0.193	0.164	0.135	0.113
4.57	0.222	0.161	0.123	0.098	0.081	0.066	0.051	4.81	0.286	0.219	0.177	0.146	0.124	0.105	0.087
5.08	0.185	0.124	0.089	0.068	0.052	0.041	0.031	5.02	0.273	0.206	0.164	0.135	0.115	0.097	0.082
5.30	0.173	0.113	0.078	0.057	0.042	0.034	0.027	5.37	0.245	0.178	0.139	0.112	0.094	0.078	0.066
6.34	0.150	0.092	0.058	0.039	0.028	0.020	0.014	5.99	0.206	0.141	0.105	0.079	0.065	0.054	0.046

Table 2. Absorbance, A, of solutions at different pH values and wavelengths in (x) water + (1-x) methanol
$c_{Mo} = 10^{-4}$ M, I =0.2 M, Glu = 10^{-2} M.

	λ / nm								λ / nm						
PH	250	255	260	265	270	275	280	pH	250	255	260	265	270	275	280
								T = 15°C							
			x =1.000								x = 0.899				
3.63	0.186	0.104	0.106	0.006	0.072	0.059	0.047	3.81	0.246	0.196	0.159	0.131	0.115	0.097	0.079
4.00	0.159	0.106	0.079	0.059	0.049	0.037	0.028	4.01	0.233	0.173	0.139	0.111	0.094	0.077	0.065
4.20	0.152	0.100	0.069	0.048	0.039	0.030	0.023	4.22	0.204	0.149	0.116	0.093	0.077	0.064	0.054
4.61	0.140	0.086	0.057	0.039	0.025	0.018	0.013	4.06	0.177	0.125	0.091	0.066	0.053	0.044	0.036
4.94	0.138	0.081	0.052	0.033	0.023	0.017	0.013	5.05	0.169	0.11	0.077	0.053	0.043	0.035	0.027
5.31	0.132	0.080	0.050	0.030	0.022	0.015	0.012	6.03	0.158	0.100	0.068	0.043	0.035	0.028	0.022
			x = 0.952								x = 0.839				
3.60	0194	0.143	0.113	0.095	0.080	0.068	0.051	3.77	0.315	0.263	0.224	0.188	0.160	0.138	0.120
3.91	0.172	0.123	0.092	0.071	0.054	0.050	0.038	3.94	0.301	0.247	0.207	0.173	0.149	0.128	0.111
4.20	0.159	0.103	0.074	0.053	0.041	.033	0.024	4.27	0.262	0.208	0.163	0.136	0.118	0.108	0.087
4.57	0.147	0.093	0.063	0.041	0.033	0.024	0.018	4.46	0.246	0.189	0.151	0.120	0.101	0.085	0.075
5.09	0.140	0.086	0.053	0.033	0.024	0.018	0.011	5.02	0.218	0.155	0.120	0.091	0.075	0.064	0.056
6.00	0.140	0.086	0.054	0.033	0.023	0.019	0.011	6.40	0.206	0.140	0.104	0.077	0.063	0.056	0.050
								T = 20°C							
			x = 1.000								x = 0.899				
3.63	0.168	0.120	0.093	0.075	0.063	0.048	0.041	3.73	0.253	0.203	0.166	0.139	0.121	0.098	0.082
3.91	0.147	0.098	0.069	0.053	0.039	0.030	0.021	4.15	0.207	0.157	0.123	0.099	0.081	0.065	0.054
4.20	0.135	0.086	0.055	0.037	0.026	0.017	0.013	4.34	0.189	0.135	0.103	0.079	0.063	0.053	0.041
4.57	0.125	0.075	0.045	0.029	0.018	0.009	0.007	4.70	0.177	0.121	0.086	0.065	0.052	0.040	0.032
5.09	0.121	0.068	0.042	0.023	0.012	0.009	0.004	5.30	0.166	0.110	0.076	0.054	0.040	0.030	0.026
6.00	0.117	0.067	0.037	0.022	0.011	0.005	0.004	6.26	0.161	0.104	0.070	0.047	0.037	0.028	0.025
			x = 0.952								x = 0.839				
3.75	0.194	0.144	0.116	0.093	0.078	0.062	0.051	3.77	0.291	0.237	0.198	0.167	0.144	0.121	0.103
4.09	0.167	0.120	0.086	0.067	0.053	0.043	0.034	4.19	0.242	0.187	0.152	0.122	0.103	0.086	0.070
4.39	0.153	0.102	0.070	0.051	0.037	0.027	0.021	4.43	0.218	0.162	0.127	0.099	0.081	0.067	0.055
4.72	0.145	0.089	0.061	0.039	0.028	0.021	0.016	4.82	0.198	0.143	0.103	0.079	0.065	0.052	0.044
5.07	0.138	0.084	0.053	0.034	0.021	0.018	0.013	5.05	0.187	0.131	0.093	0.071	0.054	0.049	0.039
6.42	0.135	0.077	0.046	0.027	0.017	0.012	0.010	6.38	0.177	0.116	0.082	0.058	0.044	0.038	0.032
								T = 25°C							
			x = 1.000								x = 0.899				
3.62	0.168	0.117	0.092	0.074	0.063	0.052	0.040	3.69	0.235	0.185	0.155	0.131	0.106	0.080	0.073
4.09	0.145	0.094	0.065	0.044	0.034	0.027	0.022	4.19	0.194	0.141	0.113	0.100	0.086	0.057	0.046
4.45	0.130	0.080	0.051	0.032	0.023	0.014	0.011	4.48	0.179	0.122	0.093	0.091	0.054	0.042	0.034
4.86	0.129	0.072	0.042	0.025	0.015	0.011	0.008	4.98	0.163	0.107	0.075	0.073	0.040	0.028	0.023
5.18	0.122	0.069	0.038	0.020	0.013	0.006	0.006	5.22	0.160	0.103	0.070	0.055	0.037	0.025	0.022
6.05	0.120	0.065	0.037	0.018	0.011	0.005	0.004	6.63	0.151	0.092	0.061	0.043	0.031	0.019	0.016
			x = 0.952								x = 0.839				
3.65	0.199	0.149	0.120	0.099	0.080	0.069	0.055	3.80	0.272	0.221	0.181	0.152	0.127	0.109	0.094
4.24	0.160	0.111	0.078	0.060	0.043	0.039	0.030	4.21	0.234	0.183	0.145	0.118	0.096	0.080	0.069
4.50	0.153	0.10	0.067	0.050	0.035	0.030	0.024	4.50	0.215	0.162	0.123	0.098	0.078	0.068	0.056
4.96	0.142	0.090	0.057	0.039	0.026	0.022	0.019	4.92	0.197	0.142	0.104	0.079	0.063	0.052	0.044
5.23	0.138	0.084	0.054	0.034	0.022	0.019	0.015	5.36	0.186	0.126	0.089	0.066	0.052	0.044	0.039
6.20	0.135	0.081	0.049	0.032	0.020	0.016	0.011	6.27	0.178	0.121	0.084	0.060	0.047	0.040	0.035
								T = 30°C							
			x = 1.000								x = 0.899				
3.67	0.167	0.120	0.093	0.078	0.064	0.050	0.040	3.82	0.225	0.173	0.139	0.113	0.095	0.082	0.063
3.98	0.157	0.105	0.076	0.060	0.045	0.035	0.028	4.23	0.197	0.149	0.113	0.085	0.074	0.061	0.047
4.19	0.142	0.091	0.064	0.046	0.034	0.024	0.017	4.55	0.183	0.132	0.097	0.070	0.056	0.048	0.038
4.50	0.131	0.080	0.050	0.034	0.022	0.015	0.011	4.95	0.169	0.116	0.079	0.055	0.044	0.037	0.027
4.99	0.122	0.070	0.042	0.026	0.014	0.007	0.004	4.42	0.166	0.109	0.075	0.050	0.039	0.032	0.027
5.36	0.121	0.067	0.038	0.022	0.011	0.006	0.003	6.93	0.161	0.104	0.069	0.047	0.036	0.028	0.023
			x = 0.952								x = 0.839				
3.76	0.184	0.138	0.108	0.085	0.072	0.059	0.045	3.92	0.264	0.209	0.176	0.142	0.120	0.103	0.088
4.25	0.159	0.106	0.077	0.055	0.042	0.033	0.026	4.08	0.251	0.201	0.161	0.136	0.113	0.095	0.082
4.50	0.149	0.095	0.064	0.044	0.032	0.024	0.019	4.32	0.233	0.181	0.142	0.113	0.096	0.082	0.070
5.00	0.139	0.082	0.051	0.032	0.022	0.016	0.013	4.59	0.218	0.163	0.129	0.096	0.085	0.070	0.062
5.30	0.137	0.082	0.051	0.031	0.022	0.014	0.011	4.93	0.208	0.148	0.112	0.085	0.072	0.060	0.054
6.09	0.135	0.081	0.049	0.031	0.021	0.015	0.014	5.32	0.199	0.153	0.101	0.072	0.064	0.054	0.044
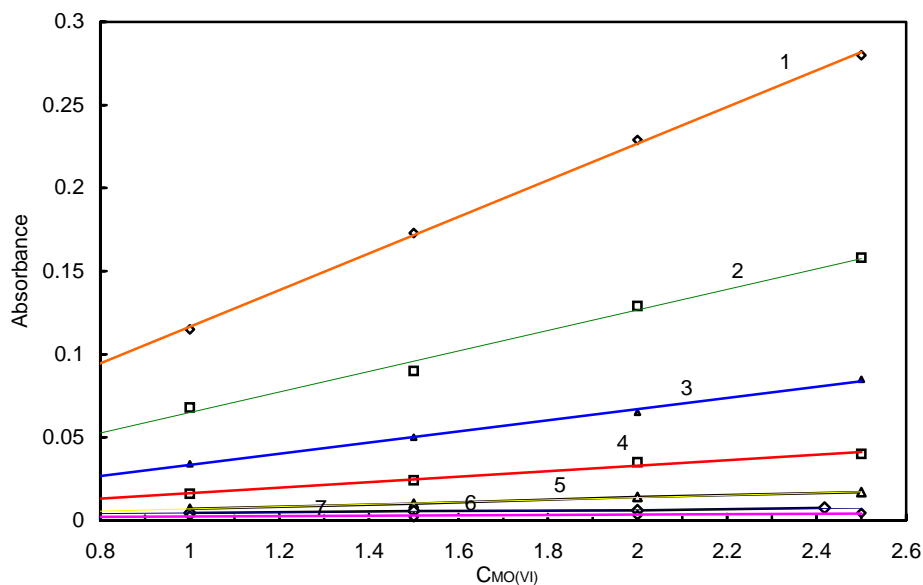
Fig. 1. Absorbance versus $c_{Mo(VI)}$ at different wavelengths:(1) 250, (2) 255, (3)260,(4)265, (5) 270,(6) 275 and (7) 280 nm at 25°C for (x) water + (1-x) methanol mixed solvent: x =1.000 .
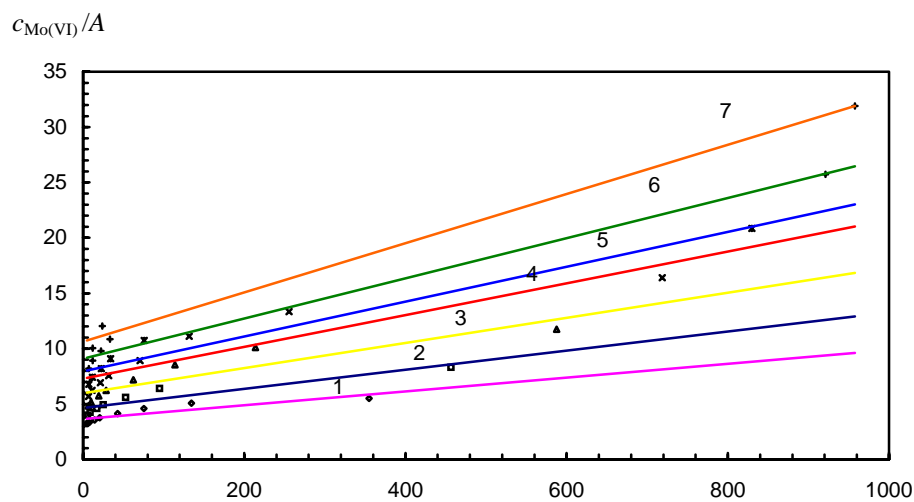
$(A-\varepsilon_0\ c_{Mo(VI)}) / A\alpha_{HY}\ [H^+]$

Fig. 2. $c_{Mo(VI)}$ /A versuse $(A-\varepsilon_0\ c_{Mo(VI)})/A\alpha_{HY}\ [H^+]$ for (x) water + (1-x) methanol mixed solvent at different wavelengths:(1)250,(2)255,(3)260,(4)265,(5)270,(6) 275 and (7)280 nm^{-1} at 25°C ,x = 0.899

Table 3. Values of molar absorptivities of molybdenum ($10^{-2}\,\varepsilon_0$) and MoO_3Y^{-2} (10^{-3}) in mixed solvent system (x) water + (1-x) methanol.

X	ε	250	255	260	265	270	275	280
					λ / nm			
					$T=15°C$			
1.000	ε_0	11.00	5.86	2.92	1.48	0.62	0.14	0.10
	ε_1	2.755	1.802	1.517	1.238	1.045	0.913	0.709
0.952	ε_0	11.50	6.42	3.40	1.70	0.70	0.20	0.10
	ε_1	2.841	2.841	1.988	1.678	1.470	1.228	1.050
0.899	ε_0	11.86	6.78	3.70	1.80	0.78	0.37	0.12
	ε_1	3.049	3.049	2.717	2.541	2.110	1.919	1.821
0.839	ε_0	11.28	5.98	3.14	1.60	0.780	0.210	0.200
	ε_1	4.016	3.472	3.058	2.659	2.358	2.150	1.880
					$T=20°C$			
1.000	ε_0	11.40	6.10	3.340	1.680	0.660	0.380	0.120
	ε_1	2.309	1.764	1.534	1.272	1.075	0.933	0.824
0.952	ε_0	11.62	6.440	3.420	1.720	0.750	0.320	0.120
	ε_1	2.571	1.848	1.587	1.447	1.244	0.973	0.810
0.899	ε_0	11.96	6.780	3.700	1.880	0.980	0.430	0.220
	ε_1	3.401	3.145	2.591	2.320	1.876	1.698	1.420
0.839	ε_0	12.17	6.090	3.840	1.940	1.000	0.480	0.280
	ε_1	3.649	3.311	2.841	2.445	2.193	1.961	1.715
					$T=25°C$			
1.000	ε_0	11.000	6.180	3.360	1.660	0.680	0.200	0.120
	ε_1	1.927	1.297	1.064	0.851	0.764	0.714	0.656
0.952	ε_0	11.700	6.460	3.52	1.96	0.80	0.38	
	ε_1	2.069	1.667	1.326	1.136	0.953	0.912	0.810
0.899	ε_0	12.00	6.80	3.76	1.94	1.02	0.49	0.30
	ε_1	2.500	2.053	1.855	1.658	1.422	1.328	1.138
0.839	ε_0	12.20	6.74	4.10	2.06	1.06	0.50	0.30
	ε_1	2.717	2.278	1.901	1.689	1.490	1.333	1.171
					$T=30°C$			
1.000	ε_0	11.60	6.20	3.40	1.70	0.60	0.28	0.12
	ε_1	1.645	1.200	1.015	0.781	0.616	0.580	0.517
0.952	ε_0	11.80	6.68	3.58	1.84	0.86	0.40	0.19
	ε_1	1.727	1.228	1.076	0.877	0.812	0.665	0.570
0.899	ε_0	12.00	6.80	3.90	2.00	1.06	0.50	0.30
	ε_1	2.169	1.730	1.353	1.084	1.014	0.883	0.709
0.839	ε_0	12.50	6.90	4.69	2.10	1.08	0.52	0.31
	ε_1	2.544	2.188	1.721	1.543	1.375	1.222	1.072

The stability constant of MoO_3Y^{2-} complex is calculated by combining the protonation constants of aspartic acid and glutamic acid with the formation constants of the complexes:

$$K_{MoO_3Y^{2-}} = \frac{[MoO_3Y^{2-}]}{[MoO_4^{2-}][Y^-]} = K_C K_{HY} K_{H_3Y} \quad (10)$$

where the mean values are shown in Table 4.

Water, which has a higher dielectric constant, is substituted by methanol; therefore, the electric force of attraction between two ions of opposite charge is considerably reduced. Adding an organic solvent decreases the dielectric constant of the solution, resulting in a greater attraction force and, hence, larger formation and protonation constants. Enthalpy changes were obtained by plotting $\log K$ versus $1/T$. Figure 3 represents the linear relation between $\log K$ of aspartic acid & glutamic acid and $1/D$ of a solvent in a methanol and water system. It has been noted that such a plot yields curves of different slope for each solvent system. The fact that the linear plots of the obtained values of free-energy changes, as a function of $1/D$ show that our results agree with the above speculation(see Fig. 4 and Table 5). Comparison of thermodynamic studies Asp and Glu has been resulted that Asp gives more negative and stability free energy than Glu.

Table 4. Average values of K_c and $\log K_{MoO_3Y^{2-}}$ and the protonation constants for Asp & Glu with standard deviations (± 0.01), in (x) water + (1 - x) methanol at different temperatures and I =0.2 M.

x = 1.000	1/D	$\log K_c$		$\log K_{MoO_3Y^{-2}}$		$\log K_{H_3Y}$		$\log K_{H_2Y}$		$\log K_{HY}$	
		Asp	Glu	Asp	Glu	Asp	Glu	Asp	Glu	Asp	Glu
				$T = 15°C$							
1.000	0.0122	7.430	6.311	19.000	18.141	2.03	2.12	3.75	4.31	9.73	9.71
0.952	0.0130	7.455	6.707	19.155	18.587	2.06	2.15	3.83	4.37	9.82	9.73
0.899	0.0140	7.748	7.140	19.568	19.090	2.10	2.17	3.84	4.42	9.85	9.78
0.839	0.0146	7.756	7.180	19.639	19.260	2.21	2.24	3.90	4.34	9.91	9.84
				$T = 20°C$							
1.000	0.0124	7.435	6.151	19.115	17.871	2.01	2.09	3.73	4.24	9.71	9.63
0.952	0.0131	7.683	6.517	19.443	18.307	2.05	2.11	3.78	4.26	9.77	9.68
0.899	0.0141	7.722	6.595	19.572	18.455	2.10	2.14	3.81	4.27	9.82	9.72
0.839	0.0149	7.742	7.008	19.682	18.948	2.16	2.20	3.84	4.31	9.85	9.74
				$T = 25°C$							
1.000	0.0126	7.155	5.947	18.875	17.577	1.99	2.05	3.71	4.18	9.69	9.58
0.952	0.0133	7.207	6.287	19.027	17.987	2.04	2.09	3.73	4.21	9.72	9.61
0.899	0.0145	7.712	6.507	19.632	18.277	2.09	2.12	3.76	4.22	9.76	9.65
0.839	0.0151	7.948	6.541	19.984	18.411	2.13	2.20	3.79	4.30	9.81	9.67
				$T = 30°C$							
1.000	0.0128	6.954	6.291	18.714	17.871	1.96	2.02	3.69	4.16	9.61	9.56
0.952	0.0134	7.113	6.392	18.993	18.052	2.01	2.07	3.72	4.20	9.69	9.55
0.899	0.0147	7.411	6.507	19.361	18.247	2.06	2.12	3.75	4.22	9.76	9.62
0.839	0.0153	7.448	6.756	19.568	18.536	2.08	2.15	3.76	4.25	9.80	9.63
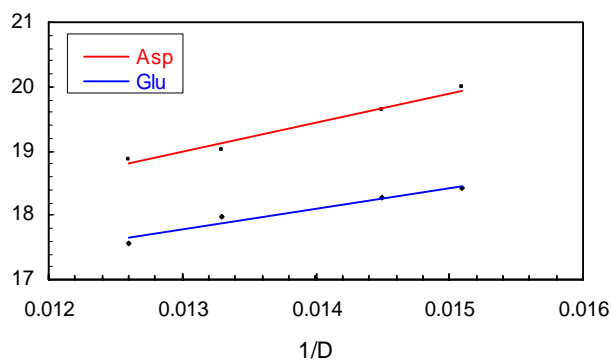
$\log K_{MoO_3Y^{2-}}$

Fig .3. $\log K_{MoO_3Y^{2-}}$ versus 1/D for (x) water + (1 - x) methanol at 25 $^{\circ}$C

$-\Delta G^{\circ}/J.mol^{-1}$

1/D
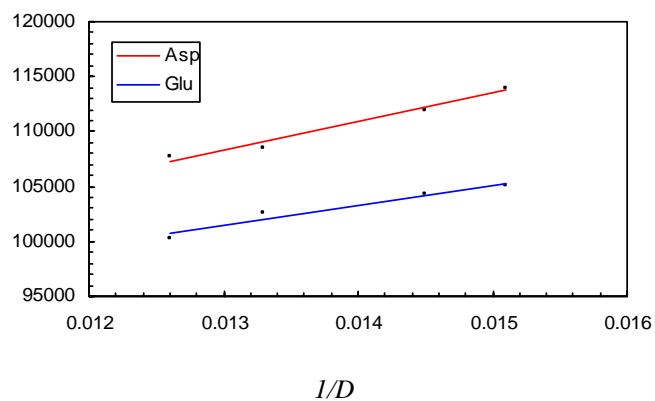
Fig. 4. $\Delta G°$ versus 1/D for (x) water + (1 - x) methanol at 25 $^{\circ}$C.

Table 5. Values of ΔG°, ΔH° and ΔS° of the molybdenum with Asp & Glu complex formation in aqueouse and mixed solvent systems for (x) water + (1-x) methanol at different temperature and I =0.2 M.

x	$\Delta G^\circ / J.mol^{-1}$		$\Delta H^\circ / J.mol^{-1}$		$\Delta S^\circ / J.mol^{-1}.K^{-1}$	
	Asp	**Glu**	**Asp**	**Glu**	**Asp**	**Glu**
	T=15°C					
1.000	-104754	-100018	-1047	-947	360.09	343.99
0.952	-105609	-102477	-1047	-947	363.06	352.53
0.899	-107886	-105250	-1047	-947	370.97	362.16
0.839	-108277	-106188	-1047	-947	372.33	365.42
	T=20°C					
1.000	-107218	-100240	-1047	-947	362.36	338.88
0.952	-109058	-102686	-1047	-947	368.64	347.23
0.899	-109781	-103516	-1047	-947	371.10	350.06
0.839	-110398	-106281	-1047	-947	373.21	359.50
	T=25°C					
1.000	-107678	-100274	-1047	-947	357.82	333.31
0.952	-108546	-102612	-1047	-947	360.73	341.16
0.899	-111997	-104267	-1047	-947	372.31	346.71
0.839	-114005	-105031	-1047	-947	379.05	349.27
	T=30°C					
1.000	-108551	-103661	-1047	-947	354.79	338.99
0.952	-110170	-104711	-1047	-947	360.14	342.45
0.899	-112304	-105842	-1047	-947	367.18	346.19
0.839	-113505	-107519	-1047	-947	371.15	351.72

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