Articles

Thermodynamic Complexation of Dopamine with Molybdenum(VI) in Media with Different Dielectric Constants

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The complexation of Mo(VI) with dopamine has been investigated by spectrophotometric measurements in a mixed solvent system at an ionic strength of 0.2 mol·dm^{-3} sodium chloride, employed [(15, 25, or 35 ± 0.1) °C] at pH ranges of ~4 to ~7 with a high ratio of ligand to metal. 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 are the stability and dielectric constants, respectively.

Introduction

Dopamine is a neurotransmitter, which activates dopamine receptors in the brain, and disorders of this dopaminergic system affect movement control and cause a decline in neurocognitive functions.[1,2] The action of dopamine is terminated primarily through its binding to a dopamine transporter (DAT) and the following translocation of the ligand back into dopaminergic neurons.[3,4] To increase the amount of dopamine in the brains of patients with diseases such as Parkinson's disease[5−7] and dopa-responsive dystonia, L-DOPA (levodopa), which is the precursor of dopamine, can be given because it can cross the blood-brain barrier.

As a member of the catecholamine[8] family, dopamine is a precursor to epinephrine (adrenaline) and then norepinephrine (noradrenaline) in the biosynthetic pathways for these neurotransmitters.

Neurotransmitters are frequently organic bases, which form adducts with systems of electron acceptors such as metal ions, proteins, and components of protein by direct or indirect interactions. For example, the operations of neurotransmitters are distorted if they react with heavy metals such as Pb, Hg, or lanthanides that frequently act as hard acids. The coordination chemistry of these compounds is complicated by their ability to act as ambidentate or bridging ligands.[9,10]

Dopamine, a brain chemical associated with addiction to cocaine, alcohol, and other drugs, may also play an important role in obesity, according to researchers from Brookhaven National Laboratory's (BNL) Medical and Chemistry Departments.

In a study appearing in *The Lancet* of February 3, 2001, researchers announced that, compared with the brains of normal-weight people, obese people's brains have fewer receptors for dopamine, a neurotransmitter that helps produce feelings of satisfaction and pleasure.

BNL scientists have done extensive research showing that dopamine plays an important role in drug addiction. They have found that addictive drugs increase the level of dopamine in the brain, and that addicts have fewer dopamine receptors than normal subjects. "Since eating, like the use of addictive drugs, is a highly reinforcing behavior, inducing feelings of gratification and pleasure, we suspected that obese people might have abnormalities in brain dopamine activity as well," Volkow said.[11]

"It's possible that obese people have fewer dopamine receptors because their brains are trying to compensate for having chronically high dopamine levels, which are triggered by chronic overeating," says Wang.[11] "However, it's also possible that these people have low numbers of dopamine receptors to begin with, making them more vulnerable to addictive behaviors including compulsive food intake." But, exercise, which has other obvious benefits in weight control, is another way obese subjects might be able to stimulate their dopamine pleasure and satisfaction circuits, the researchers suggest. The results of such studies may provide useful information in aiding in rational drug design, medicinal chemistry, biochemistry, and molecular biology.

In the last few decades there has been a continuous expansion in the work of metal complexes associated with biological applications. There are few reports on the study of the coordination chemistry of catecholamines in the literature.[12−14] Heavy-metal stains such as osmium tetraoxide and uranyl salts have been used to help in the location of catechol amine-rich sites in brain tissue. El-Hendawy et al. studied the reactions of the five most important biological catecholamines with OsO_4 and uranyl salts, ($[MoO_4]^{2-}$) and ($[WO_4]^{2-}$).[15]

An important finding is the demonstration that alcohol can affect the function of specific neurotransmitters.[16] Specifically, alcohol can act as a depressant by increasing inhibitory neurotransmission, by decreasing excitatory neurotransmission or through a combination of both. Alcohol has been shown to activate dopamine systems in certain areas of the brain through an interaction with glutamate receptors.[17] Interestingly, endogenous opitate systems could cause a decrease in the acting of dopamine systems that occurs during alcohol withdrawal.

Current research strongly suggests that alcohol affects multiple neurotransmitter systems in the brain. Virtually all brain functions depend on a delicate balance between excitatory and

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10.1021/je9001619 CCC: $40.75
Published on Web 10/16/2009

inhibitory neurotransmission. Alcohol consumption may affect multiple neurotransmitter systems to influence behavior.

Stability constants of chelate compounds and protonation constants of chelateing ligands have often been measured in mixed solvents. The search for a correlating factor dates back to the work of Thomson and Nernst, who suggested a connection between the dielectric constant of a solvent and its dissociating power. Recently, solvent effects on transition metal complexes were reviewed,[18] and more attention was paid to binary solvent mixtures in this field.[19,20] Solute−solvent interactions are much more complex in mixed solvent systems than in pure solvents because of the possibility of preferred solvation by any of the solvents present in mixtures.

In this paper we evaluate the stability constants and thermodynamic parameters for Mo(VI) binding to dopamine in cosolvent systems of ethanol and water using a combination of potentiometric and spectrophotometric methods.[21−23]

Experimental Section

Reagents. Dopamine, sodium molybdate, ethanol, sodium dihydrogen phosphate, disodium hydrogen phosphate, and sodium chloride were supplied from the Merck Chemical Co. and were used without further purification. The NaOH solutions were prepared from titrasol solutions.

Measurements. All measurements were carried out at [(15, 25, and 35 ± 0.1) °C] and at an ionic strength of 0.2 mol·dm^{-3} which was controlled with sodium chloride. For each experiment, solutions of Mo(VI) + dopamine were prepared with the different concentrations but the same ionic strength. The ligand concentrations were 1.2 mmol·dm^{-3}, and the MoO_4^{2-} concentrations were (0.4, 0.6, and 1.2) mmol·dm^{-3} with ligand to MoO_4^{2-} molar ratios of 3, 2, and 1. The pH of the solutions were controlled with phosphate buffers.

A Horiba D-14 pH meter was employed for pH measurements. The hydrogen ion concentrations were measured using an Ingold UO3234 glass electrode and an Ingold UO3236 calomel electrode. It is essential that the system be calibrated routinely for various solvent mixtures of known hydrogen ion concentration.[24−28]

Spectrophotometric measurements were conducted using an UV−visible Shimadzu 2101 spectrophotometer equipped with a Acermate 486 SX/25D computer and thermostatically matched 10 mm quartz cells.

The dielectric constants D of mixed solvent systems of ethanol in water were measured by comparing the capacitance of a capacitor with and without the sample present (C and C_0, respectively), using $D = C/C_0$. Dielectric constant measurements were carried out using a Lurton-DM-9023 capacitance meter.

In all cases, the procedure was repeated at least four times, and the resulting average values and corresponding standard deviations are shown in the text and tables.

Results and Discussion

The complex $M_xH_yL_z^{(nx+y-z)+}$ formed is characterized by its stoichiometry (x:y:z) where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of the complexation or the protonation, eq 2 is defined by β_{xyz}:

$$xM^{n+} + yH^+ + zL^- \rightleftharpoons M_xH_yL_Z^{(nx+y-z)+} \quad (1)$$

$$\beta_{xyz} = [M_xH_yL_z^{(nx+y-z)}]/[M^{n+}]^x[H^+]^y[L^-]^z \quad (2)$$

The protonation constants of dopamine have been used for computation of stability constants, β_{xyz}. The protonation constants for a 1 mmol·dm^{-3} concentration ligand in water and in mixed solvent systems of ethanol and water were obtained from potentiometric titrations with 0.1 mol·dm^{-3} NaOH, employing a computer-programmed nonlinear least-squares method. Values of the constants obtained are listed in Table 1 and agree with those obtained from the literature ($pK_{a1} = 8.89$, $pK_{a2} = 10.41$, and $pK_{a3} = 13.1$ at 25 °C).[29−31] We assume that deprotonation occurs in the following order with increasing pH: the paraphenolic group, the ammonium group, and then the second OH group for dopamine. The protonation constants are K_{1a}, K_{2a}, K_{3a}. These values are listed in Table 1.

Table 1. Average Values of Protonation Constants of Dopamine with Standard Deviations, in (x) water + (1 − x) Ethanol at Different Temperatures and I = 0.2 mol·dm^{-3}

x (molar fraction)	log k_{3a}	log k_{1a}	$pK_{13} + pK_1$
	t = 15 °C		
1.000	9.03 ± 0.01	13.15 ± 0.01	21.78 ± 0.02
0.979	9.06 ± 0.02	13.16 ± 0.01	21.82 ± 0.03
0.930	9.10 ± 0.01	13.16 ± 0.01	21.86 ± 0.02
0.901	9.14 ± 0.01	13.18 ± 0.01	21.92 ± 0.02
	t = 25 °C		
1.000	8.89 ± 0.02	13.10 ± 0.02	21.59 ± 0.04
0.979	8.94 ± 0.01	13.10 ± 0.01	21.64 ± 0.02
0.930	8.99 ± 0.01	13.11 ± 0.01	21.70 ± 0.02
0.901	9.03 ± 0.01	13.12 ± 0.01	21.75 ± 0.02
	t = 35 °C		
1.000	8.86 ± 0.02	13.05 ± 0.02	21.51 ± 0.04
0.979	8.91 ± 0.01	13.06 ± 0.01	21.57 ± 0.02
0.930	8.96 ± 0.01	13.09 ± 0.01	21.65 ± 0.02
0.901	8.98 ± 0.01	13.09 ± 0.01	21.67 ± 0.02

The method of determination of the stability constant based on the relationship, $A = f$ (pH) was employed, on account of the high stability of the complexes studied. Absorbance measurements were made for solutions containing Mo(VI) and dopamine with different molar ratios in pH of ∼4 to ∼7 in different solvent systems.

Considering that absorbance is a function of pH, the values of the molar absorptivities of Mo(VI), ε_0 (and for dopamine, ε_1), at different wavelengths and various dielectric constants are shown in Table 2. To determine ε_1 and ε_0, solutions were prepared by a similar method and conditions, but in the absence of metal and ligand ions as described, respectively.

To determine ε_2, the formation constant of the complex can be expressed as follows:

$$MoO_4^{2-} + H_3L^+ \rightleftharpoons MoO_3(HL)^- + H_2O \quad (3)$$

The absorbance at a wavelength is given by:

$$A = \varepsilon_0[MoO_4^{2-}] + \varepsilon_1[H_3L^+] + \varepsilon_2[MoO_3(HL)^-] \quad (4)$$

where ε_0, ε_1, and ε_2 are the molar absorptivities of the Mo(VI) ion, dopamine, and complex, respectively.

Thus, considering material balance, the equilibrium constant for the formation reaction of complex can be expressed as follows:

$$A + \varepsilon_1 C_{MoO_4^{2-}} - \varepsilon_1 C_{H_3L^+}/C_{MoO_4^{2-}} = \varepsilon_2 + \frac{(\varepsilon_0 + \varepsilon_1 - \varepsilon_2)(-A + \varepsilon_1 C_{H_3L^+} + \varepsilon_0 C_{MoO_4^{2-}})}{C_{MoO_4^{2-}}(A - \varepsilon_0 C_{MoO_4^{2-}} - \varepsilon_2 C_{H_3L^+} + \varepsilon_0 C_{H_3L^+})[H^+]K^H_{MoO_3(HL)^-}} \quad (5)$$

The values of $K^H_{MoO_3(HL)^-}$ were determined from the slope of the straight line plots of $A + \varepsilon_1 C_{MoO_4^{2-}} - \varepsilon_1 C_{H_3L}/C_{MoO_4^{2-}}$ (Y) against

$(-A + \varepsilon_1 C_{H_3L^+} + \varepsilon_0 C_{MoO_4^{2-}})/C_{MoO_4^{2-}}[H^+]$ (X). The intercept of linear fit yields ε_2 (Figure 1).

The equilibrium reaction of complex formation is:

$$MoO_3(HL)^- + H_3L^+ \rightleftharpoons MoO_2(HL)_2 + H_2O \quad (6)$$

The absorbance at a wavelength is given by:

$$A = \varepsilon_0[MoO_4^{2-}] + \varepsilon_1[H_3L^+] + \varepsilon_2[MoO_3(HL)^-] + \varepsilon_3[MoO_2(HL)_2] \quad (7)$$

$$MoO_4^{2-} \approx 0 \quad (8)$$

Table 2. Values of Molar Absorptivities of MoO_4^{2-} ($\cdot 10^{-4}$ ε_0), Dopamine ($\cdot 10^{-4}$ ε_1), $MoO_3(HL)^-$ ($\cdot 10^{-4}$ ε_2), and MoO_2 $(HL)_2$ ($\cdot 10^{-4}$ ε_3) in (x) Water + (1 − x) Ethanol at Different Temperatures and I = 0.2 mol·dm^{-3}

λ		λ/nm				
x	ε	260	265	270	275	280
			t = 15 °C			
1.000	ε_0	1015.8	550.38	320	265	50.31
	ε_1	212	156	137	126	117
	ε_2	1921.7	1360.5	1237.8	1150.5	1081.1
	ε_3	2096.9	1722.9	1647	1417.3	1341
0.979						
	ε_0	1115.2	616.65	333.16	170.3	68.6
	ε_1	402	399	353	280	276
	ε_2	1954.4	1383.2	1254.8	1170.1	1090.5
	ε_3	2102.9	1741.8	16675.2	1425	1362
0.930						
	ε_0	1190.7	620	353	182.2	76.03
	ε_1	609	515	473	422	410
	ε_2	2052.3	1466	1347.4	1200.7	1150.1
	ε_3	2119.4	1824.5	1697.7	1491.7	1480
0.901						
	ε_0	1398.7	622.06	388.65	184.26	82.33
	ε_1	710	609	599	560	530
	ε_2	2138.3	1508.6	1473.8	1301.6	1240.1
	ε_3	2225.7	1916.7	1790.3	1547.2	1515.7
			t = 25 °C			
1.000	ε_0	1055	570	328.58	170	54.61
	ε_1	279	272	265	260	256
	ε_2	1027.4	580.07	465.35	460.5	454.7
	ε_3	2076.6	1694.1	1318.3	1160.5	1034
0.979	ε_0	1135	584.52	335.46	172.03	70.49
	ε_1	545	411	315	292	208
	ε_2	1892.6	1160.9	1120.6	1090.7	1064.2
	ε_3	2044.1	1578	1518	1383	1300.3
0.930	ε_0	1200	533.35	360	191.54	80.15
	ε_1	916	775	753	573	567
	ε_2	2016.5	1270.5	1225.6	1185.2	1121.8
	ε_3	2056.3	1554.2	1540	1513	1408.6
0.901	ε_0	1400	700	443.1	298.50	84.65
	ε_1	1488	1265	1053	929	901
	ε_2	2122.9	1390.5	1320.8	1290.6	1210.5
	ε_3	2210	1601	1577.5	1561.2	1506.4
			t = 35 °C			
1.000	ε_0	1060	600	349.7	186.9	60.25
	ε_1	373	309	247	218	207
	ε_2	1007.6	574.2	454.3	442.2	430.5
	ε_3	2003.3	1590	1308	1256	1000.5
0.979	ε_0	1140.8	639.69	350.38	173.46	72.3
	ε_1	583	460	300	235	226
	ε_2	1824.6	1145.5	1110.6	1038.8	1020.5
	ε_3	2037.5	1564	1480	1325.5	1113
0.930	ε_0	1230	660	367.8	200.69	84.63
	ε_1	1122	877	779	659	627
	ε_2	1895.6	1178.8	1150.6	1089.2	1045.1
	ε_3	2082.4	1530	1505	1421	1202.9
0.901	ε_0	1407.9	780.39	452.9	222.71	86.84
	ε_1	1706	1189	1030	972	955
	ε_2	1956.2	1245.3	1185.5	1140.6	1112.9
	ε_3	2110	1587	1575.9	1467.2	1410.5

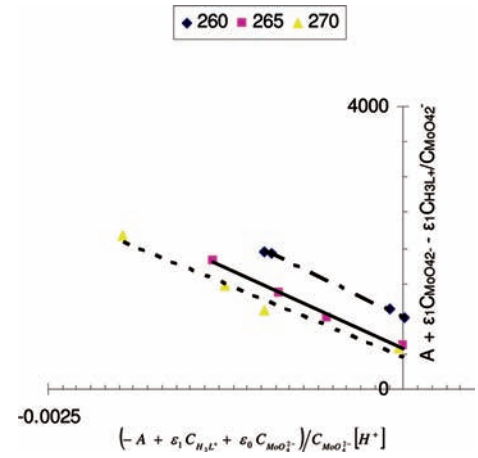

Figure 1. Plot of $A + \varepsilon_1 C_{MoO_4^{2-}} - \varepsilon_1 C_{H_3L}/C_{MoO_4^{-2}}$ versus $(-A + \varepsilon_1 C_{H_3L^+} + \varepsilon_0 C_{MoO_4^{2-}})/C_{MoO_4^{2-}}[H^+]$ for x = 1 and different wavelengths: (1) 260 nm, (2) 265 nm, and (3) 270 nm at 25 °C.

$$A = \varepsilon_1[H_3L^-] + \varepsilon_2[MoO_3(HL)^-] + \varepsilon_3[MoO_2(HL)_2] \quad (9)$$

where ε_0, ε_1, ε_2, and ε_3 are the molar absorptivities of the Mo(VI) ion, dopamine, and their complexes.

For the molar balance of Mo(VI) and dopamine:

$$[MoO_4^{2-}] = [MoO_3(HL)^-] + [MoO_2(HL)_2] \quad (10)$$

$$[H_3L^+] = C_{H_3L^+} + [MoO_3(HL)^-] + 2[MoO_2(HL)_2] \quad (11)$$

where C_{MoO4}^{2-} and $C_{H_3L^+}$ are the total concentrations of Mo(VI) and dopamine. Thus, the equilibrium constant for formation of the complex can be expressed as follows:

$$(-A + \varepsilon_1 C_{H_3L^+} - 2\varepsilon_1 C_{MoO_4^{2-}})/C_{MoO_4^{2-}} = (\varepsilon_3 - \varepsilon_2 - \varepsilon_1)(A - \varepsilon_1 C_{H_3L^+} + \varepsilon_1 C_{MoO_4^{2-}} - \varepsilon_2 C_{MoO_4^{2-}}) - \varepsilon_3 + \frac{}{K^H_{MoO_2(HL)_2}(\varepsilon_3 C_{H_3L^+} - \varepsilon_2 C_{H_3L^+} - A - \varepsilon_3 C_{MoO_4^{2-}} + 2\varepsilon_2 C_{MoO_4^{2-}})(C_{MoO_4^{2-}})[H^+]} \quad (12)$$

Considering that A is a function of pH, the values of molar absorptivities are shown in Table 2. The values of $K^H_{MoO_2(HL)_2}$ were determined from the intercept of the straight line plots of $-A + \varepsilon_1 C_{H_3L^+} - 2\varepsilon_1 C_{MoO_4^{2-}}/C_{MoO_4^{2-}}$ (Y) against $(A - \varepsilon_1 C_{H_3L^+} + \varepsilon_1 C_{Mo_4^{2-}} - \varepsilon_2 C_{MoO_4^{2-}})/C_{MoO_4^{2-}}[H^+]$ (X) and are shown in Table 2. The intercept of the lines yields ε_3 (Figure 2).

To properly interpret the overall stability constants, we must consider the form of the ligand chelating to the metal ion. In the case of dopamine pK_{a3} corresponds almost exclusively to the ionization of the second phenolic group. As vertified by several techniques, the macroconstants K_{1a} and K_{2a} cannot be assigned exclusively to the first phenolic and ammonium group deprotonation constants but are mixtures of them. Kiss and Gergely[29−31] define the microscopic acidity constants for the first two deprotonations. They approximate its concentration by estimating the microconstant k_{13} for loss of the second phenolic proton from the microspecies with a protonated ammonium group. They correct pK_3 assigned exclusively to the second phenolic ionization in the molecule with a deprotonated amino

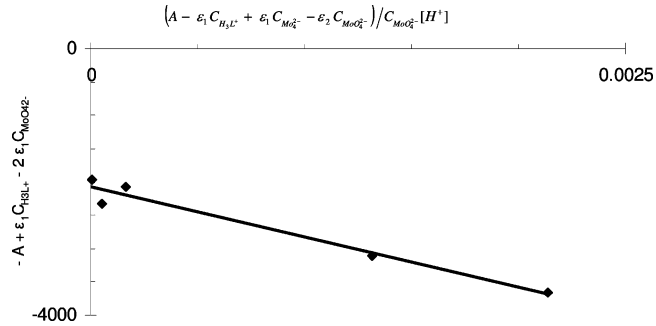

Figure 2. Plot of $-A + \varepsilon_1 C_{H_3L^+} - 2\varepsilon_1 C_{Mo^{6+}}$ versus $(A - \varepsilon_1 C_{H_3L^+} + \varepsilon_1 C_{Mo_4^{2-}} - \varepsilon_2 C_{MoO_4^{2-}})/C_{MoO_4^{2-}}[H^+]$ for $x = 1$ and $\lambda = 260$ nm at 25 °C.

Table 3. Average Values of log $K_{MoO_2(HL)_2}$, log $K^{H}_{MoO_2(HL)_2}$, $\Delta G°$, and $\Delta S°$ of Molybdenum with Dopamine with Standard Deviations, in (x) Water + (1 − x) Ethanol at Different Temperatures and I = 0.2 mol·dm^{-3}

X (molar fraction)	log $K_{MoO_2}(HL)_2$	log $K^{H}_{MoO_2(HL)_2}$	$-\Delta G°$, kJ/mol	$\Delta S°$, J/mol·K
		t = 15 ° C		
1.000	51.48 ± 0.02	7.92 ± 0.02	246.53 ± 0.15	740.46 ± 0.15
0.979	51.94 ± 0.04	8.30 ± 0.03	248.73 ± 0.15	748.11 ± 0.15
0.930	52.07 ± 0.03	8.35 ± 0.02	249.35 ± 0.15	750.27 ± 0.15
0.901	52.42 ± 0.02	8.48 ± 0.02	251.03 ± 0.15	756.10 ± 0.15
		t = 25 ° C		
1.000	51.08 ± 0.05	7.90 ± 0.04	291.05 ± 0.10	864.99 ± 0.10
0.979	51.56 ± 0.01	8.28 ± 0.02	293.81 ± 0.10	874.27 ± 0.10
0.930	51.70 ± 0.05	8.30 ± 0.03	294.61 ± 0.10	876.94 ± 0.10
0.901	51.93 ± 0.02	8.43 ± 0.02	295.92 ± 0.10	881.34 ± 0.10
		t = 35 ° C		
1.000	50.66 ± 0.04	7.64 ± 0.03	298.37 ± 0.20	860.68 ± 0.20
0.979	51.40 ± 0.01	8.26 ± 0.01	302.73 ± 0.20	874.84 ± 0.20
0.930	51.53 ± 0.01	8.23 ± 0.01	303.50 ± 0.20	877.32 ± 0.20
0.901	51.54 ± 0.02	8.20 ± 0.01	303.55 ± 0.20	877.75 ± 0.20

group by the difference for the ligand according to $pK_{13} = pK_3 - (pk_{21} - pK_1)$. The sum $pK_1 + pk_{13}$ is now used to calculate the concentration of the microspecies with two anionic phenolates and protonated ammonium group.

The stability constant of the $MoO_2(HL)_2$ complex was calculated by combining the protonation constants of dopamine with the formation constants of the complexes (Table 3)

$$\log_{10} K_{MoO_2(HL)_2} = \log_{10} K^{H}_{MoO_2(HL)_2} + 2(pK_{13} + pK_1) \quad (13)$$

The calculated stability constants are in good agreement with the results obtained in previous papers.[12−15,29−31]

In this study, we evaluate stability constants for Mo(VI) binding to dopamine and the effect of solvent systems on protonation and complexation. The ionic strength was constant (0.2 mol·dm^{-3}). A dipositive ion such as Mo(VI) prefers oxygen donors and is expected to chelate to the catecholate locus of catecholamines rather than bind at the amino group. The effect of a protonated ammonium group on a phenolic ionization may be expressed as the difference $pk_{21} - pK_1 \approx 0.4$. In neutral solutions the ligand is protonated, and Mo(VI) must compete with with protons for catecholate binding sites on the ligand.

Solvent effects on formation constants are often described in terms of the polarity of organic solvents. Solvent polarity is a commonly used term related to the ability of the solvent to solvate dissolved charged or dipolar species. Attempts to describe it quantitatively mainly involve physical solvent properties such as the dielectric constant of the solvent.

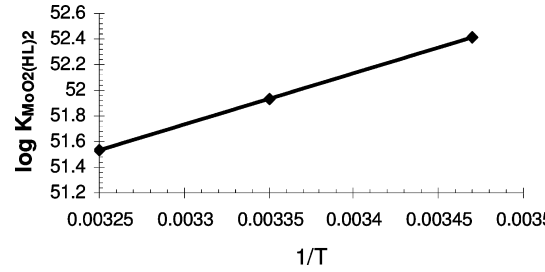

Figure 3. log $K_{MoO2(HL)^2}$ versus 1/T for (x) water + (1 − x) ethanol.

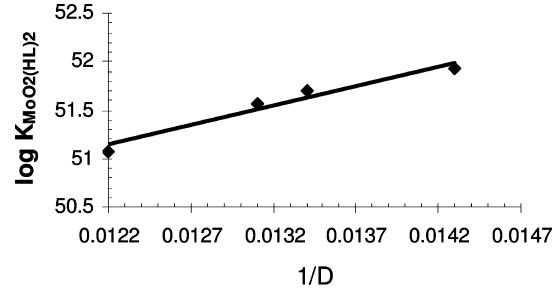

Figure 4. log $K_{MoO2(HL)^2}$ versus 1/D for (x) water + (1 − x) ethanol at 25 °C.

However, this approach is often inadequate, because dielectric constants describe solvents as unstructured systems not composed of individual molecules with their own solvent−solvent and solvent−solute interactions such as hydrogen-bond interactions which often play a predominant role in reactions. The problem is to identify and assess the relative importance of these various factors for solvent effects.

Recently, a quantitative measure of solvent polarity was introduced by Kamlet and Taft.[20] Using the solvatochromic solvent parameters, a multiparameter equation was proposed:

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

where A_0 represents the regression value and π^* is the index of solvent dipolarity/polarizability which is a measure of ability of solvent to stabilize a charge or a dipole by its own dielectric effects. The α coefficient represents solvent hydrogen bond donor acidity; in other words, it describes the ability of a solvent to donate a proton to a solute with hydrogen-bond formation. The β coefficient is a measure of solvent hydrogen bond acceptor basicity and describes the ability of a solvent to accept a proton from a solute with solvent hydrogen bond formation. The δ value is a discontinuous polarizability correction. The solvent polarity parameter of media, π^*, increases with the increasing mole fraction of water in aqueous solutions of ethanol. If the π^* value of media was the only factor determining the solvent effect on complex formation, it might be expected that the log K_s value in water should be larger than that of all the other aqueous solutions of ethanol. However, the formation constant increases with increasing of the solvent hydrogen bond acceptor basisity parameter, β, and decreases with increasing of the solvent polarity π^*. It also increases with decreasing of the hydrogen bond donor acidity parameter of solvent, α.

Water is substituted by ethanol which has a lower dielectric constant. Thus, the electrostatic force of attraction between ions of opposite charge is reduced. Adding ethanol decreases the dielectric constant of solution, resulting in a greater attraction force and hence larger formation and protonation and formation constants.

To compare all thermodynamic parameters, the change in standard Gibbs free energy (ΔG) should be calculated according

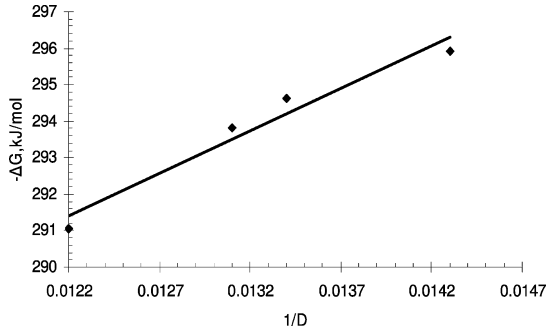

Figure 5. $-\Delta G^\circ$ versus $1/D$ for (x) water + (1 − x) ethanol at 25 °C.

to $\Delta G = -RT \ln K$. Enthalpy changes were obtained by plotting log K versus $1/T$ (the van't Hoff equation, Figure 3). The value of ΔH obtained was -4002.7 J·mol^{-1}. Figure 3 represents the linear relation between log K of the complex and $1/D$ of the solvent in the ethanol and water system, where D is the dielectric constants of the system.

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 Figures 4 and 5 and Table 3).

Acknowledgment

This work was supported by the Chemistry Department of Science and Research Branch of the Islamic Azad University.

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Received for review June 9, 2008. Accepted October 2, 2009.

JE9001619