Asian Journal of Chemistry; Vol. 24, No. 5 (2012), 2301-2303

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Study on the Thermodynamic Spectroscopy Methods of Dopamine with V(V), Ni(II) and Co(III)

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(*Received*: 8 June 2011; *Accepted*: 21 December 2011) AJC-10886

Dopamine is a member of ketcol amine groups. Dopamine is a hormone in body and acts as a nerve transferor in brain. Shortage of dopamine can lead to Parkinson disease so thermodynamic study using spectroscopy methods is an important issue for recognition of dopamine in blood and biological and pharmaceutical liquids. In this study, the interactions of water soluble metallic ions of V(V), Ni(II) and Co(III) with dopamine have been investigated using UV-VIS spectroscopy technique, SQUAD program as well as thermodynamic studies. The obtained results indicate the formation of 1:1 complex of V(V), Ni(II) and Co(III) with dopamine. Doing experiments at six different temperatures and analyzing the data helped us to thermodynamic analysis based on Vant Hoff equation. Results showed that reaction is exothermic and process is enthalpy and entropy driven.

Key Words: Dopamine ($C_8H_{11}NO_2$), Van't Hoff equation, Exothermic.

INTRODUCTION

Dopamine (DA) is a hormone produced in brain and causes to increase the heartbeat and blood pressure and strengthening the wishes and joy in human that released with phenyl ethyl amine[1,2]. Dopamine ($C_8H_{11}NO_2$) (Fig. 1) with molecular mass of 181.53 g mol^{-1} is a member of ketcol amines group[3,4]. Ketcol amines (such as dopamine) and ketcol amino acids are the most important intermediaries in many biological and neurological reactions[5,6]. The brain hormone of dopamine causes to have more ability and energy and its shortage causes to weariness and impatience while serotonin increases the optimism satisfaction feeling and decreases the tension[7,8]. Dopamine is an amine biogen and is one of the most important biochemical materials which transfer information from nerve cells to each other[2].

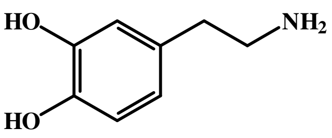

Fig. 1. Structure of dopamine

Biochemical and pharmacological Knowledge of dopamine in brain leads to improvement and effective therapy of Parkinson disease[9]. Aroid Carlson in 1959 mentioned that the reason of Parkinson tremor in mice is due to rapid decreasing of dopamine contents of tailed nucleus of brain[10]. A new method for producing ketcol amines is based on oxidation of system using ascorbic acid-O_2-Cu^{2+} in aqueous solution[11,12]. These materials effect on C-O bond in 2-aloxy phenols and the initial substance change to katcol using the carboxyl accepting method with high selective power (output is 100 %)[13,14]. Dopamine is also produced with biological method[15].

In this study, the interaction of water soluble metallic ions of V(V), Ni(II) and Co(III) with dopamine were investigated using UV-VIS spectroscopy techniques. The equilibrium constants were determined using SQUAD program. We could determine all thermodynamic parameters of interaction using equilibrium constants at different temperatures and based on Vant Hoff equation. Amounts of calculated parameters can give us valuable information about molecular mechanism of interaction.

EXPERIMENTAL

All used materials containing dopamine (DA), cobalt acetate, nickel acetate, vanadium acetate; $NaH_2PO_4\cdot 12H_2O$, $Na_2HPO_4\cdot 2H_2O$, NaOH, KCl, K_2HPO_4 and KH_2PO_4 were obtained from Fluka, Merck and Aldrich. All solutions were freshly prepared by double distilled water before using.

General procedure: Spectral measurements were carried out on a Carry 100 Scan UV-VIS-NIR double beam spectrophotometer with a thermostat cell compartment. The AE 160 digital balance with accuracy of 0.0001 g was used for weighing the materials and F-12 pH meter from Metrohm Company was used for adjusting the pH.

Detection method

Preparing the 1 mM buffer solution of phosphate: 0.676 mg K_2HPO_4 and 41.41 mg KH_2PO_4 were placed in a 1000 mL volumetric flask and reached to volume. the pH of solution was adjusted to pH = 7 using pH-meter and concentrated solution of NaOH and HCl.

Preparing the stock solution of dopamine: In order to preparing 1 L stock solution of dopamine (40 μM), 6.127 mg dopamine (m.w. = 181.53 g mol^{-1}) and buffer of phosphate (1 mM, pH = 7) were placed in a 1000 mL volumetric flask and reached to volume.

Preparing the stock solution of KCl: 1.8637 g KCl were dissolved by phosphate buffer (pH = 7) and the volume of solution were reached to 250 mL the concentration of this solution is 0.01 M. This solution was used for titration experiments of dopamine and V(V), Ni(II) and Co(III).

Preparing the solution of V(V), Ni(II) and Co(III): The aqueous solutions of V(V), Ni(II) and Co(III) (1.5×10^{-3} M) were prepared using acetate salts of vanadium, nickel and cobalt.

RESULTS AND DISCUSSION

The titration experiment of dopamine on the absorption spectrum of V(V), Ni(II) and Co(III): 1800 μL of water soluble metallic ions of V(V), Ni(II) and Co(III) with a given concentration were placed in sample cell and the volumes of 20 μL of dopamine solution (40 μM) were added gradually. After each addition, the solution of cell was mixed for 1 min and then the spectrum was recorded. The effect of dilution on the obtained spectrum was exerted and corrected spectrum was determined. This experiment was carried out at pH = 7 and temperatures of 20, 25, 35, 40 and 45 ºC. Results are shown in Figs. 2-4.

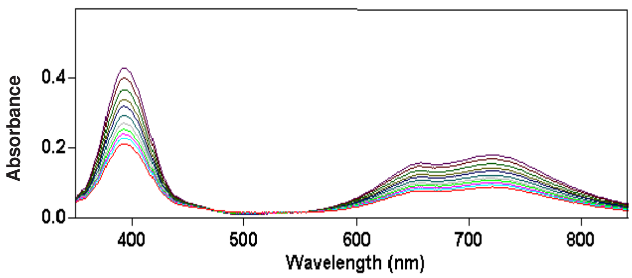

Fig. 2. Absorption spectrum of aqueous solution of Ni[II] at different concentrations of dopamine in 1 mM phosphate buffer and at different temperatures

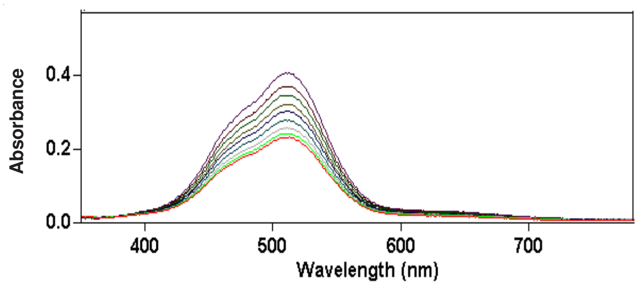

Fig. 3. Absorption spectrum of aqueous solution of Co[III] at different concentrations of dopamine in 1 mM phosphate buffer and at different temperatures

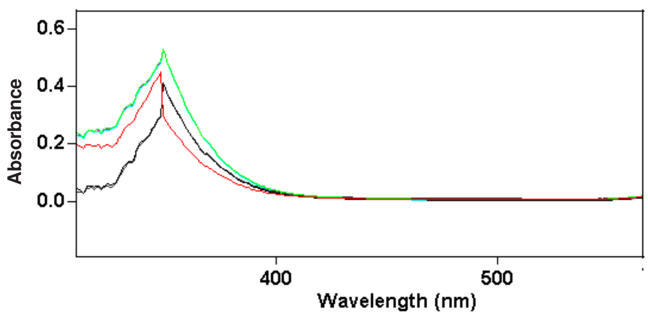

Fig. 4. Absorption spectrum of aqueous solution of V[V] at different concentrations of dopamine in 1 mM phosphate buffer and at different temperatures

Interaction of dopamine with V(V), Ni(II) and Co(III): In absorption spectrum of dopamine there is a maximum in 276 nm that is related to electron transitions of π bonds (π→π*) of aromatic cycle of dopamine so the created changes in UV-VIS spectrum of metallic ions and DA mixture in 300-800 nm is related to complex of metallic ions with dopamine. Figs. 1-3 show the changes in absorption spectra of solutions of metallic ions of V(V), Ni(II) and Co(III) in various concentrations of DA and at different temperatures of 20, 25, 30, 35, 40 and 45 ºC. As these figures show, when the concentration of dopamine increases the absorption intensity decreases. Existence of isobestic points in some regions indicates a 1:1 equilibrium between metallic ions of V(V), Ni(II) and Co(III) and dopamine. The obtained spectral data can be analyzed in order to attain equilibrium constant. In this regard we used SQUAD program.

Analyzing the binding process of V(V), Ni(II) and Co(III) to dopamine: As we know thermodynamic analysis of a process is carried out based on three basic quantities of Gibbs free energy (ΔGº), enthalpy changes (ΔHº) and entropy changes (ΔSº). Fig. 5 shows variations of ln K *versus* 1/T of the 1:1 binding process of metallic ions to dopamine. The high linear correlation coefficient of curve indicates acceptable approximation at considering ΔHº being constant with temperature. It seems that ΔC_P of binding process is negligible and with

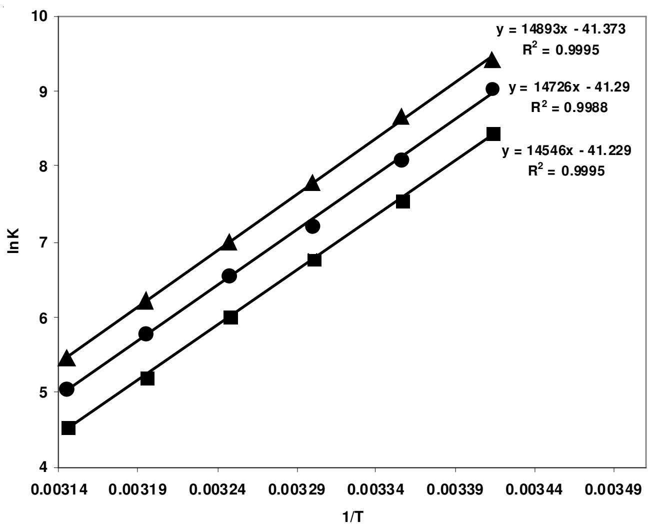

Fig. 5. Variations of ln K *versus* 1/T (Vant Hoff diagram) of Ni[II] (▲), Co[III] (●) and V[V] (■) with dopamine in 1 mM phosphate buffer (pH = 7) and at different temperatures

TABLE-1
THERMODYNAMIC PARAMETERS OF BINDING OF Ni[II] TO DOPAMINE IN 1 mM PHOSPHATE BUFFER (pH = 7) AT DIFFERENT TEMPERATURES

t (ºC)	ln K	$\Delta G^0 \pm \Delta\Delta G^o$ (KJ mol^{-1})	$\Delta H^o \pm \Delta\Delta H^o$ (KJ mol^{-1})	$\Delta S^o \pm \Delta\Delta S^o$ (JK^{-1} mol^{-1})
20	9.41	-22.93 ± 0.111	-120.94 ± 0.181	-334.51 ± 0.612
25	8.66	-21.46 ± 0.102	-120.94 ± 0.181	-333.83 ± 0.635
30	7.79	-19.62 ± 0.084	-120.94 ± 0.181	-334.38 ± 0.681
35	6.99	-17.90 ± 0.071	-120.94 ± 0.181	-334.54 ± 0.712
40	6.21	-16.16 ± 0.068	-120.94 ± 0.181	-334.76 ± 0.721
45	5.45	-14.41 ± 0.074	-120.94 ± 0.181	-335.00 ± 0.693

TABLE-2
THERMODYNAMIC PARAMETERS OF BINDING OF Co[III] TO DOPAMINE in 1 mM PHOSPHATE BUFFER (pH = 7) AT DIFFERENT TEMPERATURES

t (ºC)	ln K	$\Delta G^0 \pm \Delta\Delta G^o$ (KJ mol^{-1})	$\Delta H^o \pm \Delta\Delta H^o$ (KJ mol^{-1})	$\Delta S^o \pm \Delta\Delta S^o$ (JK^{-1} mol^{-1})
20	9.03	-21.99 ± 0.072	-122.43 ± 0.022	-342.79 ± 0.555
25	8.10	-20.07 ± 0.068	-122.43 ± 0.022	-343.49 ± 0.547
30	7.22	-18.19 ± 0.091	-122.43 ± 0.022	-344.02 ± 0.521
35	6.55	-16.77 ± 0.110	-122.43 ± 0.022	-343.05 ± 0.513
40	5.77	-15.02 ± 0.075	-122.43 ± 0.022	-343.16 ± 0.521
45	5.04	-13.33 ± 0.088	-122.43 ± 0.022	-343.08 ± 0.534

TABLE-3
THERMODYNAMIC PARAMETERS OF BINDING OF V[V] TO DOPAMINE IN 1 mM PHOSPHATE BUFFER (pH = 7) AT DIFFERENT TEMPERATURES

t (ºC)	ln K	$\Delta G^0 \pm \Delta\Delta G^o$ (KJ mol^{-1})	$\Delta H^o \pm \Delta\Delta H^o$ (KJ mol^{-1})	$\Delta S^o \pm \Delta\Delta S^o$ (JK^{-1} mol^{-1})
20	8.45	-20.58 ± 0.063	-123.82 ± 0.012	-352.35 ± 0.727
25	7.55	-18.71 ± 0.074	-123.82 ± 0.012	-352.71 ± 0.707
30	6.77	-17.05 ± 0.091	-123.82 ± 0.012	-352.38 ± 0.768
35	6.01	-15.39 ± 0.076	-123.82 ± 0.012	-342.05 ± 0.669
40	5.21	-13.56 ± 0.122	-123.82 ± 0.012	-352.27 ± 0.851
45	4.55	-12.03 ± 0.141	-123.82 ± 0.012	-351.54 ± 0.735

specifying the amount of ΔHº based on the slope of Fig. 5 (vant Hoff diagram) and using related equations we can calculate all thermodynamic parameters of binding of metal ions to dopamine. Amounts of these parameters are shown in Tables 1-3.

Results show that binding process is exothermic and affinity of binding increases upon decreasing the temperature. It seems that process is enthalpy and entropy driven. Amount of K confirms correctness of calculations and formation of 1:1 complex.

Conclusion

The obtained experimental results of UV-VIS spectroscopy were analyzed using SQUAD program. Obtained results indicate that the most spectra of mixture of free and bound complex have isobestic points indicating the 1:1 equilibrium between free and bound complex. With choosing 50 wavelength and 15 spectra, 750 absorption data were extracted from titration experiments and were used for estimating the stability constants of complex of metal ions with dopamine. The data were analyzed based on 1:1, 1:2 and 2:1 models and results indicated that 1:1 complex has the least uncertainty. Existence of isobestic points in metallic ions of V(V), Ni(II) and Co(III) indicates an equilibrium and analysis results of spectral data by SQUAD program confirmed the 1:1 equilibrium and also determined amounts of equilibrium constants. Doing experiments at six different temperatures and analyzing the data made it possible to analyze thermodynamically based on Vant Hoff equation. Results indicate that interaction is exothermic and process is enthalpy and entropy driven.

ACKNOWLEDGEMENTS

The authors gratefully thank Shahreza Branch, Islamic Azad University for financial support.

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