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Synthesis of Metal Oxide Nanoparticles of Nickel(II), Vanadium(V) and Potentiometric Determination of the Stability Constants of Their Complexes with Histidine and Glutamine at Different Temperatures in Aqueous Solutions

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In this research, the stability constants of complexes of L-histidine and glutamine with metal ions and nanoparticles of nickel(II) and vanadium(V) at four different temperatures of 25, 30, 35 and 40 ºC using Bjerrum procedure were determined potentiometrically. In generating the data, GRC Beta software, which is an improved version of BEST routine and developed in our laboratory was used. The parameters affecting the stability constants and behaviour of nanopartiocles with respect to corresponding bulk metallic ions have been discussed. Furthermore, thermodynamics parameters *i.e.*, ΔH, ΔS, ΔG for the complexes were also evaluated.

Key Words: Nanoparticles, Amino acid complex, Stability constant, Potentiometric titration, Thermodynamic parameters.

INTRODUCTION

The interaction of nanoparticles with biomolecules has attracted attention of many chemists and biochemist. The dimensional similarities of nanoparticles with biological molecules have lead to intensive research in this area. Nanostrucutred materials possess unique characteristics, namely, size and surface effects. Amino acids which are the building blocks of proteins are fascinating compounds. Among the amino acids, L-histidine is one the strongest metal coordinating ligand and plays an important role in the binding of metal ions by proteins. Glutamine is the most abundant amino acid in the body and is involved in more metabolic processes than any other amino acid.

One feasible method for studying the interaction of metal ions with ligands of biological interest is through complexation. Martell *et al*. have been pioneers in this field[1-4]. The interaction between metal ions and amino acids is of considerable attention as models for metal-protein reactions and models in a variety of biological systems[5,6]. There have been different methods to study these kinds of interactions. Potentiometric titration is one of practical methods in calculating the stability constants. Amino acids (Fig. 1) also occupy a special place in the coordination chemistry of transition metal ions[7,8]. In most of these complexes, amino acid ligands are bound to a metal center in a unidentate fashion by amino nitrogen. In acidic medium, where the amino group is protonated, the formation of oxygen-bound species is observed. It has been shown that the imidazole group of histidine is the most important binding site for metal ions. In most of the enzymes with metal ions, only the functional groups of the side chains of the peptides coordinate to metal ions[9]. Glutamine has been studied extensively over the past fifteen years and has been shown to be useful in the treatment of serious illnesses, injury, trauma, burns and treatment-related side-effects of cancer as well as in wound healing for postoperative patients. Vanadium is a trace bio-element that plays an important role in several metabolic and mitogenic processes. The biological roles of vanadium in amino acids complexation and in smaller peptides are good example of such studies[10,11].

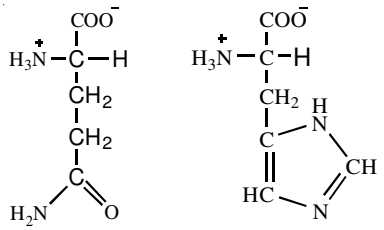

Fig. 1. Glutamine and histidine structures

In this research work, first vanadium(V) and nickel(II) metal oxide nanopartices were synthesized, then histidine and glutamine complexes of metal ions of vanadium(V) and nickel(II) were investigated, their interactions with nanoparticles, were examined, stability constants of corresponding complexes and the thermodynamic parameters were calculated.

EXPERIMENTAL

Amino acids of histidine and glutamine were with purity of 99 %. Vanadyl acetylacetonate (M = 265.16 amu), urea, $CO(NH_2)_2$, $Ni(NO_3)_2 \cdot 6H_2O$ all were analytical grade. Methanol and ethanol, sodium hydroxide, hydrochloric acid titrisol 0.1 mol/L (HCl), perchlorate acid, nitric acid and sodium nitrate were purchased from Merck. All experiments were conducted in deionized water.

The pH potentiometric titrations were performed using pH meter Schott, thermostat MLW16, glass cell, magnetic stirrer, micro-buret, X-ray diffraction spectrometer, transmission electron microscopy, IR, UV-VIS and FTIR spectrophotometers.

Synthesis of Vanadium(V) oxide nanoparticles: 3 g (0.037 mol) of vanadyl acetylacetonate, $VO(C_5H_7O_2)_2$, was dissolved in 300 mL of deionized water, then concentrated nitric acid was added in drop wise (about 1 mL) to adjust the pH of the solution to 2. The solution was stirred at 50 ºC for 48 h and allowed the orange precipitate to form. The precipitate transferred into a round-bottom flask, 120 mL of methanol was added and aged for 24 h at room temperature, which caused a colour change from light to dark orange. After that, it was filtered off, washed with deionized water to remove the possible absorbed ions and also to reduce agglomeration. Finally it was dried in an oven at 90 ºC for 3 h[12]. The structure of product was confirmed by IR, X-ray diffraction patterns (Fig. 2) and TEM image (Fig. 3).

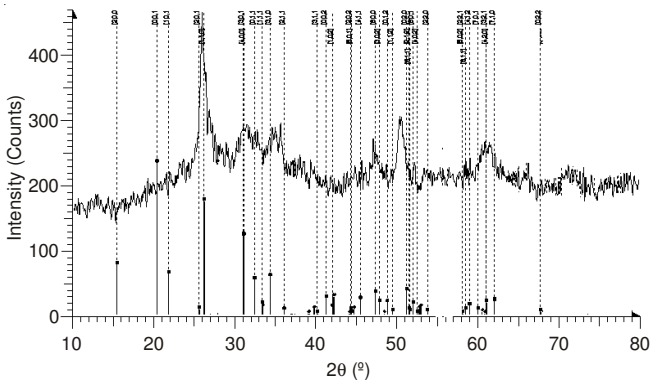

Fig. 2. XRD patterns of V_2O_5 nanoparticles. Size range of nanocrystals has been calculated from Scherrer's formula: $d = 0.89l/(\beta.\cos\theta)$; where, d represents the average particle size, β stands for the full with at half height of the peaks λ, represents the wavelength of X- ray and θ the diffraction angle of the peak. The sample has been irradiated with X-rays at 26.04º, 31.35º, 50.56º and 61.19º. Nanocrystals of orthorhombic structure with size of 7-11 nm was obtained

Synthesis of nickel oxide nanoparticles: In molar ratio of 1:4, 5.23 g of nickel(II) nitrate and 4.32 g urea was dissolved separately in beakers containing 30 mL of deionized water. Then the first solution was added to the second, stirred with magnetic bar for 2 h to mix thoroughly. After that the magnet was removed and the solution was placed in oil bath at temperature of 110 ºC and refluxed for 90 min. During this process a green precipitate was developed. Using a sinter-glass funnel the precipitate was filtered, the filtered was dried in vacuum and then it was placed in an oven at 400 ºC for 1 h, following, which it was left intact in vacuum oven for 1 h to calcinate. The product was calcinated NiO nanoparticles[13]. The structure of desired compound was confirmed by IR, X- ray diffraction patterns (Fig. 4) and TEM image (Fig. 5).

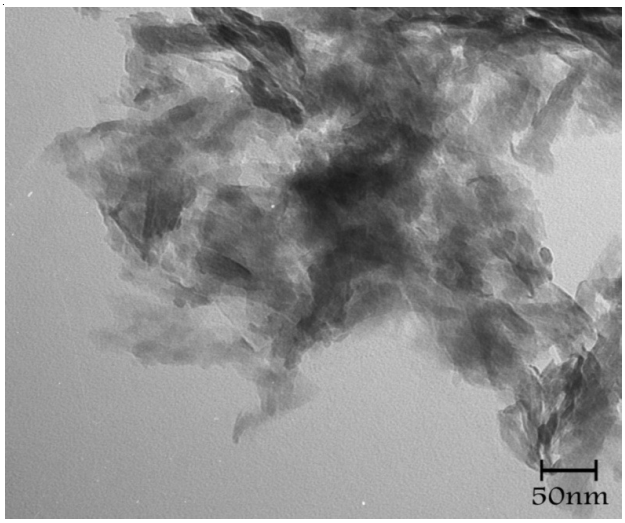

Fig. 3. TEM image of V_2O_5 nanoparticles; The size of nanoparticles is between 12-19 nm

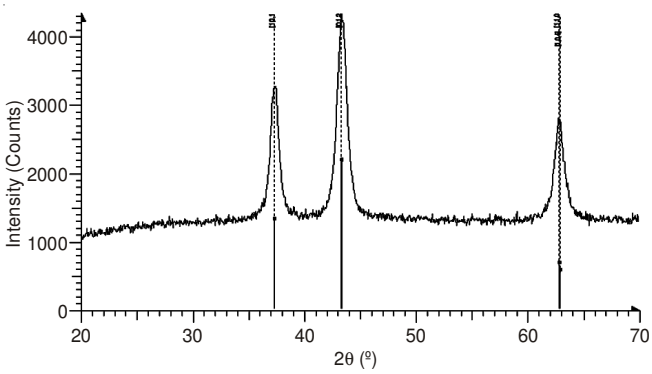

Fig. 4. XRD patterns of NiO nanoparticles after the precursors have been calcined. The peak positions appearing at 32.28º, 43.28º, 62.88º

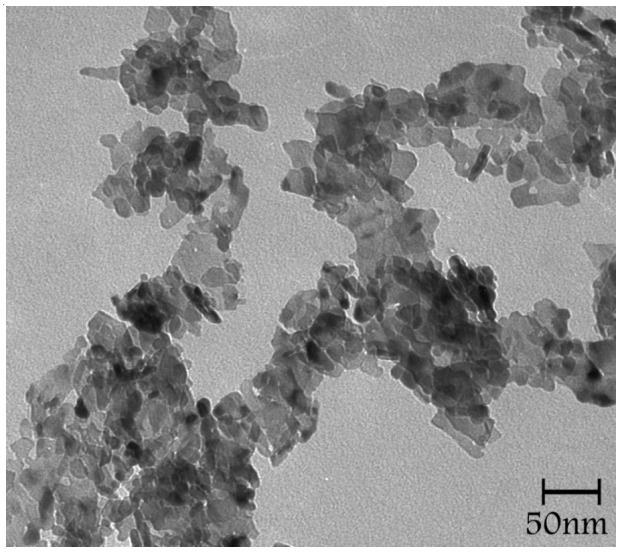

Fig. 5. TEM image of NiO nanoparticles; The size of each nanoparticle is between 7-18 nm

Calculation of stability constant of metal-complexes: Here, histidine and glutamine act as a ligand. The stability of

a complex is due to electrostatic forces between the metal ions and the ligand. In general, an amino acid forms zwitter ion at pH 7. The NH_2 group accepts a proton and the COOH group loses a proton.

Disassociation of an amino acid (H_2L^+) can be shown as:

$$H_2L^+ \rightleftharpoons HL + H^+ \quad K_{a_1} = \frac{[HL][H^+]}{H_2L^+} \tag{1}$$

$$HL_{(aq)} \rightleftharpoons L^-_{(aq)} + H^+_{(aq)} \quad K_{a2} = \frac{[L^-][H^+]}{[HL]} \tag{2}$$

The deprotonated histidine and glutamine anion L^- could act as an interacting ligating species as follows:

$$M^{2+} + HL \rightleftharpoons ML^+ + H^+ \quad K_{f1} = \frac{[ML^+][H^+]}{[M^{2+}][HL]} \tag{3}$$

$$ML^+ + L^- \rightleftharpoons ML_2 \qquad K_{f2} = \frac{[ML_2]}{[ML^+][L^-]} \tag{4}$$

$$L_{free} = [H_2L^+] + [HL] + [L^-] \tag{5}$$

where, K_{f1} and K_{f2} are the overall stability constants of the complexes formed from the suggested reactions[14,15].

We define as the average number of ligands bound per metal ion concentration.

$$\bar{n} = \frac{\text{bound ligand}}{\text{total metal ion concentration}} = \frac{\text{L bound}}{\text{CM}} = \frac{L_{total} - L_{free}}{\text{CM}} \tag{6}$$

Ligand concentration L_{free} was calculated by:

$$L_{free} = [H_2L] + [HL] + [L^-] \tag{7}$$

The bound ligand concentration (L_{bound}) was then estimated as:

$$L_{bound} = L_{total} - L_{free} \tag{8}$$

$$\bar{n} = \frac{T_{H_{2L^+}} - [H_2L^+] - [HL] - [L^-]}{T_{Zn^{2+}}} \tag{9}$$

$$\bar{n} = \frac{[ML^+] + 2[ML_2]}{[M^{2+}] + [ML^+] + [ML_2]} \tag{10}$$

According to mass balance relation we have:

$$T_M = [M^{2+}] + [ML^+] + [ML_2] \tag{11}$$

$$T_{HL} = [HL] + [L^-] + [ML^+] + 2[ML_2] \tag{12}$$

$$[ClO_4] = T_{HClO_4} + 2T_M \tag{13}$$

$$[ML^+] + 2[ML_2] = [Na^+] - T_{HClO_4} + [H^+] \tag{14}$$

$$\bar{n} = \frac{[Na^+] - [HClO_4] + [H^+]}{T_M} \tag{15}$$

$$[HL] = \frac{K_a(T_{H_2L^+} - \bar{n}T_M)}{k_a + [H^+]} \tag{16}$$

To calculate the stability of respective complexes $\bar{n}$ should be plotted *versus* p_{HL}.

By making assumption that $[M^{2+}] = [ML^+]$ we can write:

$$K_{f1} = \frac{1}{[HL]_{\bar{n}=\frac{1}{2}}} \tag{17}$$

$$K_{f2} = \frac{1}{[HL]_{\bar{n}=\frac{3}{2}}} \tag{18}$$

It means that the inverse of [HL] at $\bar{n} = 0.5$ gives K_{f1} and the inverse of [HL] at $\bar{n} = 1.5$ produces K_{f2}.

To perform these calculations more precisely, we have developed a new software program that brings into account all possible existing species concentrations. The software displays a plot of pH reading *versus* the concentration of added standardized sodium hydroxide.

For calculating thermodynamic parameters we need to consider the following:

The Gibb's free energy, ΔG, can be calculated from the equation below:

$$\Delta G = -RT \ln K_f \tag{19}$$

$$\frac{d \ln K_f}{dT} = \frac{1}{R}\frac{d}{dT}\left(\frac{\Delta G}{T}\right) \tag{20}$$

$$\frac{d}{dT}\left(\frac{\Delta G}{T}\right) = -\left(\frac{\Delta H}{T^2}\right) \tag{21}$$

$$\frac{d \ln k_f}{dT} = \left(\frac{\Delta H}{RT^2}\right) \tag{22}$$

The enthalpy change, ΔH and the entropy change, ΔS, were calculated using a temperature dependence method, where the plot of log K_f *versus* 1/T produces a line with slope equals to -ΔH/R and the intercept equals to ΔS/R.

Determination of stability constant of metal-complexes: In a home-made glass reactor as a titrand, a 30.00 mL mixture solution, which was 1.000×10^{-3} M with respect to the metal ion, 5.000×10^{-3} M with respect to the amino acid and 0.0169 M with respect to the $HClO_4$, was prepared. A flow of nitrogen gas was provided through solution. Next, potentiometric titration was conducted using standardized sodium hydroxide as a titrant and pH glass electrode as the working electrode. Reference electrode was a saturated calomel electrode. Our software program produces a scheme in which the pH at the intersection of the potentiometric titration curve with these two points will give K_{f1} and K_{f2} respectively (Fig. 6). In each potentiometric titration about 6.00 mL of the titrant was added. The experiment was repeated five times.

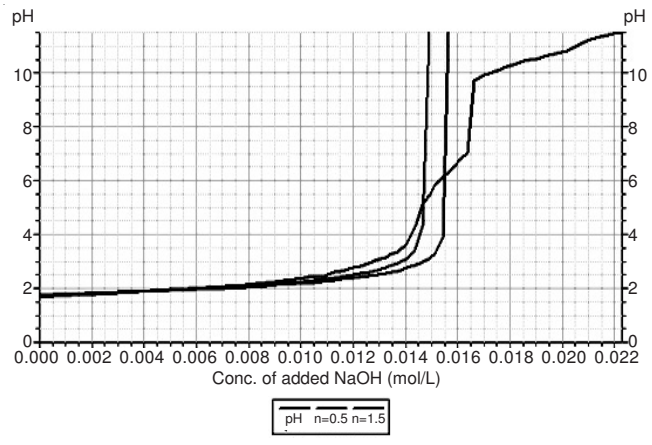

Fig. 6. Plot of pH *versus* concentration of added standardized NaOH for nano Ni(II)-Gln complex in an aqueous solution at 25 ºC

RESULTS AND DISCUSSION

By controlling temperature and in oxygen-free medium, potentiometric titrations were performed. The titration curve for each complex has three platforms *i.e.* three inflecion points. The first one is due to neutralization of extra $HClO_4$ in solution with titrant. In the second, the -COOH is titrated. And the third is due to $-NH_3^+$. It was found out that the stability constant values of glutamine complexes are larger than histidine. This is due to more steric hindrance of histidine with regard to glutamine. In all of the complexes, $K_{f1} > K_{f2}$ is owing to electrostatic repulsions and steric hindrance among substituted ligands. These are important factors in reducing stepwise formation constants of the complexes[16]. Tables 1 and 2 listed log K_{f1} and log K_{f2} values for complexes of histidine and glutamine with vanadium and nickel bulk metal ions and with their nanoparticles respectively.

TABLE-1
STABILITY CONSTANTS VALUES OF METAL-COMPLEXES OF HISTIDINE AND GLUTAMINE WITH THE RESPECTIVE METAL IONS IN AQUEOUS SOLUTION AT FOUR DIFFERENT TEMPERATURES

Complex	Stability constant	T (ºC)			
		25	30	35	40
V(IV)-His	log Kf_1	4.85	4.77	4.70	4.63
	log$K f_2$	2.68	2.66	2.63	2.59
Ni(II)- His	log Kf_1	6.57	5.46	5.00	4.66
	log$K f_2$	4.73	3.62	3.06	2.64
V(IV)-Gln	log Kf_1	7.93	7.65	7.09	6.53
	log$K f_2$	7.03	6.70	3.83	2.83
Ni(II)-Gln	log Kf_1	8.48	8.30	7.87	5.46
	log$K f_2$	2.69	2.66	2.65	2.62

TABLE-2
STABILITY CONSTANTS VALUES OF METAL-COMPLEXES OF HISTIDINE AND GLUTAMINE WITH METAL OXIDE NANOPARTICLES IN AN AQUEOUS SOLUTION AT FOUR DIFFERENT TEMPERATURES

Complex	Stability Constant	T (ºC)			
		25	30	35	40
V(IV)-His	log Kf_1	7.80	7.60	7.49	7.31
	log$K f_2$	6.99	6.75	6.42	6.14
Ni(II)-His	log Kf_1	9.27	8.11	7.25	6.40
	log$K f_2$	8.46	7.83	7.02	6.05
V(IV)-Gln	log Kf_1	8.21	8.12	7.62	7.57
	log$K f_2$	4.29	3.81	3.00	2.64
Ni(II)-Gln	log Kf_1	8.98	8.88	8.73	8.6
	log$K f_2$	8.31	8.07	7.06	5.91

With increasing temperature from 25 to 40 ºC, the stability constant values of respective complexes decreases, because the complex reactions are exothermic. Also, the stability constant of complexes of nanoparticles versus bulk metal ions have greater values. In nanoparticles there is an increase for ratio of surface area to volume which dominates the behaviour atoms in the surface in comparison with inner atoms. This phenomenon affects the properties of particles and causes the reactions to proceed faster. On the other hand ionic potential (q/r) which is an important parameter in formation of bound is raised, leading to an increase in the rate of reactions[17-19].

$$K_{fV(V)\text{ - His}} < K_{f\,V(V)\text{-Gln}}$$

$$K_{fNi(II)\text{-His}} < K_{fNi(II)\text{-Gln}}$$

The enthalpy change values of complexes of Ni(II) with histidine and glutamine are smaller than that of V(V) as shown in Table-3, while the reverse trend has been observed for the mentioned complexes with nanoparticles (Table-4). Increased change in degree of disorder is indicative of the spontaneity of the reaction. The Gibbs free energies of all complexes are negative indicating the spontaneity of the complex reactions. In our experiments, all of enthalpy changes and entropy changes are positive, but ΔS values are greater than ΔH values, so ΔGs have negative values (Table-5).

TABLE-3
ΔH AND ΔS VALUES OF HISTIDINE AND GLUTAMINE COMPLEXES WITH RESPECTIVE METAL IONS IN AN AQUEOUS SOLUTION AT FOUR DIFFERENT TEMPERATURES

Complex		ΔS (J $k^{-1}mol^{-1}$) T (ºC)					ΔH (kJ mol^{-1})
		25	30	35	40		
V(V)-His	ΔS_1	92.87	89.05	88.80	88.63	ΔH_1	11.30
	ΔS_2	51.30	50.96	50.96	50.88	ΔH_2	7.50
Ni(II)-His	ΔS_1	125.83	104.54	95.73	89.25	ΔH_1	10.80
	ΔS_2	93.85	69.35	58.60	48.92	ΔH_2	4.65
V(V)-Gln	ΔS_1	149.9	149.0	135.80	125.1	ΔH_1	18.40
	ΔS_2	128.4	134.7	73.6	54.3	ΔH_2	7.8 0
Ni(II)-Gln	ΔS_1	155.65	149.33	145.92	143.26	ΔH_1	9.06
	ΔS_2	50.6	50.3	50.5	50.5	ΔH_2	6.08

TABLE-4
ΔH AND ΔS VALUES OF COMPLEXES OF GLUTAMINE AND HISTIDINE WITH NICKEL OXIDE AND VANADIUM OXIDE NANOPARTICLES IN AN AQUEOUS SOLUTION AT FOUR DIFFERENT TEMPERATURES

Complex		ΔS (J.$k^{-1}mol^{-1}$) T (ºC)					ΔH (kJ.mol^{-1})
		25	30	35	40		
V(V)-His	ΔS_1	152.98	145.33	141.43	139.93	ΔH_1	12.16
	ΔS_2	133.79	129.22	122.90	117.58	ΔH_2	5.52
Ni(II)-His	ΔS_1	177.55	155.53	138.65	122.61	ΔH_1	18.2
	ΔS_2	162.01	150.12	134.57	115.86	ΔH_2	15.4
V(V)-Gln	ΔS_1	157.23	150.50	145.92	144.93	ΔH_1	11.05
	ΔS_2	82.18	72.95	57.24	50.58	ΔH_2	4.64
Ni(II)-Gln	ΔS_1	162.43	158.94	150.71	104.56	ΔH_1	18.18
	ΔS_2	133.32	131.90	121.93	95.65	ΔH_2	13.06

TABLE-5
ΔG_1 AND ΔG_2 (KJ.MOL^{-1}) VALUES OF COMPLEXES OF HISTIDINE AND GLUTAMINE WITH NICKEL OXIDE AND VANADIUM OXIDE AT TEMPERATURES OF 25, 30, 35 AND 40 ºC

Complex	–ΔG (KJ.mol^{-1}) T (ºC)	Complex	–ΔG (KJ.mol^{-1}) T (ºC)
	25, 30, 35, 40		25, 30, 35, 40
V(V)-His	$-\Delta G_1 = 27.69$	Nano-V(V)-His	$-\Delta G_1 = 44.12$
	$-\Delta G_2 = 15.43$		$-\Delta G_2 = 38.40$
Ni (II)-His	$-\Delta G_1 = 31.62$	Nano-Ni (II) -His	$-\Delta G_1 = 45.24$
	$-\Delta G_2 = 20.45$		$-\Delta G_2 = 42.81$
V(V)-Gln	$-\Delta G_1 = 42.62$	Nano-V(V)-Gln	$-\Delta G_1 = 46.04$
	$-\Delta G_2 = 29.61$		$-\Delta G_2 = 20.01$
Ni(II)-Gln	$-\Delta G_1 = 43.89$	Nano-Ni(II)-Gln	$-\Delta G_1 = 51.42$
	$-\Delta G_2 = 15.52$		$-\Delta G_2 = 42.80$

By plotting log K_f *versus* 1/T for a given complex we are able to calculate its stability constant at any temperature. As examples, plots of log K_{f1} *versus* 1/T for complexes of Ni(II)-Gln, bulk metal ions and V(IV)-His, nanoparticles in aqueous solutions at four different temperatures have been demonstrated in Figs. 7 and 8.

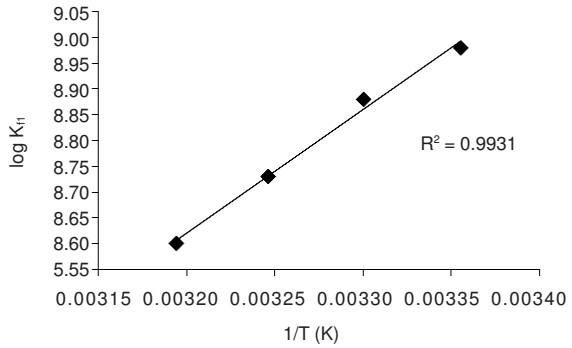

Fig. 7. Plot of log K_{f1} *versus* 1/T for complex of nano Ni(II)-Gln in aqueous solutions at four different temperatures

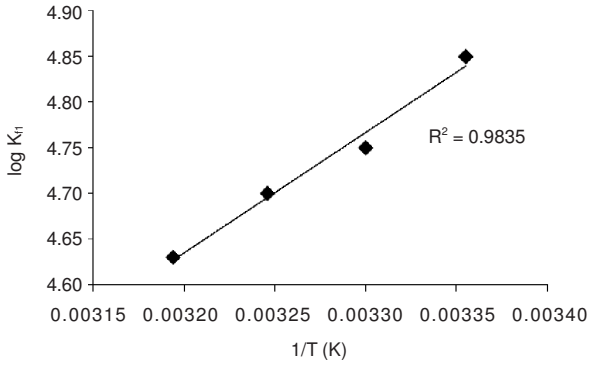

Fig. 8. Plot of log K_{f1} *versus* 1/T for complex of V(V)-His in an aqueous solution at four different temperatures

In UV-visible spectra of histidine complex with bulk vanadium metal ions (Fig. 9) it is observed that the spectra of the ligand have been concealed in complex spectra, a new peak appeared indicating the formation of the complex.

The TEM image of formed complex of glutamine with NiO nanoparticles has been shown in Fig. 10.

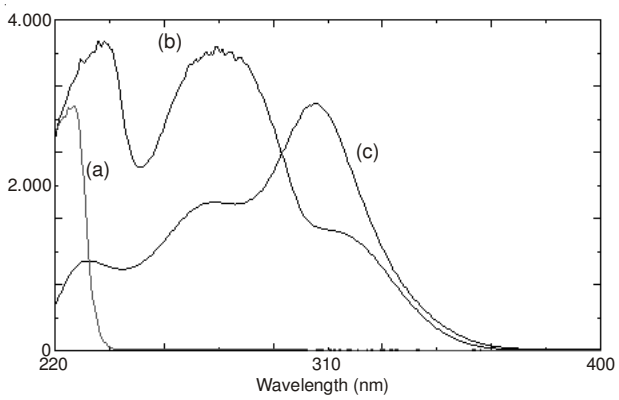

Fig. 9. UV-visible spectra of a) histidine, (b) vanadium (V), c) V(V)-histidine complex

Conclusion

Potentiometric titration was performed to determine the stability constant of histidine and glutamine complexes with V_2O_5 and NiO nanoparticles and corresponding bulk metal ions. The results illustrated that stability constants values are greater for histidine complexes than glutamine in both cases of nanoparticles and bulk metal ions. Stability constants values

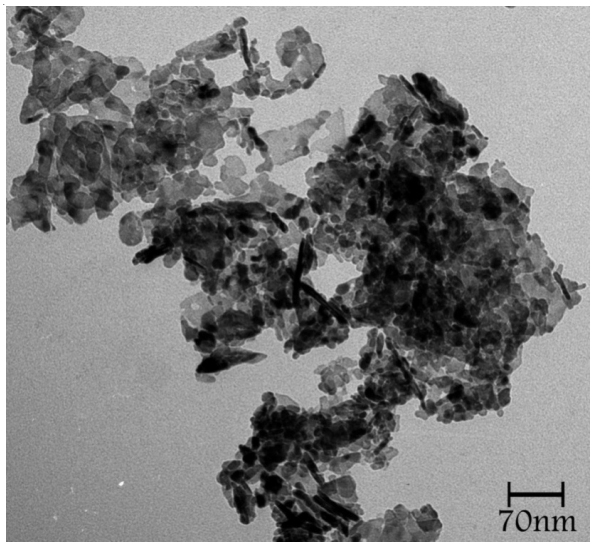

Fig. 10. TEM image of glutamine complex with NiO nanoparticles; The size of a nanoparticle is between 12-25 nm

for nanoparticles were not as high as we expected. There is a possibility that some kind of adsorption is involved. More research is in progress in our lab to understand the existing mechanism in the complex formation process for metal oxide nanoparticles. Moreover thermodynamics parameters for respective complexes have been calculated which are in agreement with related data in the literature.

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