Potentiometric studies on serine and Asparagin complexe with Cd^{+2} and pb^{+2}

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A B S T R A C T

Potentiometric studies were carried out on Serine and L-asparagin complexes with Cd^{+2}, pb $^{+2}$. IR were used to identify the structure of the studied complexes. The ΔH, ΔS, ΔG and stability constants were determined for the prepared complex . The results showed that the ligands (Asparagin and Seraine) have protonation is endothermic, non-spontaneous and increases on heating but with (Pb- Asparagin , Pb-Seraine and Cd- Asparagin complexes) the dissociation is exothermic, spontaneous at low T and decreases on heating , but in the case Cd- Seraine the dissociation is endothermic, non-Spontaneous and increases on heating. All the stability constants in the order of Cd^{2+} < Pb^{2+}.

Keywords: Potentiometric studies and preparation of complexes.

INTRODUCTION

Metal complexes are widely used in various fields such as biological processes, pharmaceuticals, analytical processes, separations techniques, etc. Metal complexes play a vital role in nature, they have been extensively used in clinical applications as enzyme inhibitors [1], anti-bacterial [2,3], antiviral [4-6] and as anti-cancerous [7-10].

Metal complexes containing optically active ligands frequently exhibit stereoselective effects upon the formation of their diastereoisomers [11]. Complex formation of metal ions of biological importance with drug and amino acid and their derivatives are of great significance as many of these systems can offer simple model of complexes of metal drug and amino acid equilibria in different enzymatic processes. At low pH the drug enalpril maleate undergoes dissociation and metallation at carbonyl group of oxygen atom and deprotonation of secondary amine at slight higher pH [12]. Amino acids are organic molecules containing amino group (-NH$_2$) and carboxylic acid group(-COOH) both attached to the same carbon atom called α – carbon. Since amino acids are the building blocks of proteins and also many other biologically occurring amino acids serve other functions in cells, it is then necessary to determine their dissociation constants and their stability constants for the formation of complexes with essential metals. The dissociation constant, pKa is used to explain the strength of the acids because it is a quantitative measure of the strength of the acids in all its reactions [10].

The complexation behaviour of ligand with different metals Cd(II), pb(II) have been studied by many workers but literature is quite silent about the studies of metal ligand complexes of Serine and L-asparagin. Hence the present work has been undertaken for the study. The overall formation constants of the resulting complexes in aqueous medium have been evaluated graphically by DeFord-Hume's method [13]. The overall formation constants of the complexes have also been calculated using mathematical method of Mihailov [14].

Experimental part
Synthesis of (Cd , pb) amino acids complexes:
   0.008 mmol of Ligand L-Asparagin (0.15g) and DL-Serine (0.10g) were dissolved in 50 ml of distilled water , dissolution took place only with slow heating. For deprotonation of amino acids 0.06 mmol (9.00g) were dissolved in 50 ml of distilled water. Then 4 mmol of the metal salt Lead Chloride (22.24 g), 4 mmol of the metal salt Cadmium Chloride (14.66 g), all of them in 50 ml of distilled water for each one , and was added to the deprotonated amino acid solution under stirring for several minutes. The precipitate was filtered, washed with water several times, and dried in air[15].

Infrared spectra:
IR spectra were taken with (Type thermo FT-IR 380 Nicolet company) spectrophotometer in 400–4000 cm^{-1} range.

Potentiometric Analysis :
   All pH titration were performed using automatictitrator, coupled with thermostat, the reactions were carried out in two different temperature 25 and 35 C^0.

PH- Titration:
   Sodium hydroxide solution 0.02 M was prepared, standard solution HCl 0.01M, KCl 0.01M Was prepared . Metal salts with concentration 0.01M (Cd , Pb) also prepared with ligand solution has concentration (0.1M) For the determination of acid dissociation constant of the ligand, on aqueous solution (0.1M),Of the protonated was titrated with 0.02 M NaOH at 25°Cunder nitrogen atmosphere and ionic strength of 0.1M KCl [16].

RESULTS AND DISCUSSION

Thermodynamic parameters :

Table 1. Thermodynamic parameters for ligand(L-Asparagin)

T^0K	PKa	GΔ	HΔ	SΔ
298	8.01	45.72		
308	7.33	43.23	119.64	-248.07

Table 2. Thermodynamic parameters for ligand (L-Seraine):

T^0K	PKa	GΔ	HΔ	SΔ
298	9.15	52.22		
308	7.81	46.08	235.28	-614.29

Table 3. Thermodynamic parameter for Asparagin–pb

T^0K	PKa	GΔ	HΔ	SΔ
298	5.15	29.38		
308	7.18	42.36	-357.52	1298.33

Table 4. Thermodynamic parameter for Seraine – pb complex:

T^0K	PKa	GΔ	HΔ	SΔ
298	5.82	33.21		
308	6.19	36.52	-65.44	331.03

Table 5. Thermodynamic parameter for Asparagin – Cd complex:

T^0K	PKa	GΔ	HΔ	SΔ
298	7.03	40.12		
308	7.16	42.20	-21.77	207.71

Table 6. Thermodynamic parameter for Seraine – Cd complex:

T^0K	PKa	GΔ	HΔ	SΔ
298	8.14	46.44		
308	6.50	38.32	288.37	-811.83

   In general from these tables all equilibrium reversible processes occurs at ΔS =0. In contrast, spontaneous irreversible are always associated with positive total entropy changes. Non spontaneous processes that require work to force them to take place have $\Delta S < 0$.

When chemical reaction occurs, heat almost always either released to or absorbed from the surrounding . In former case , we term the reaction exothermic, in the latter case, the reaction is said to be endothermic . In thermodynamic term , exothermic reaction are associated with processes for which $\Delta H < 0$, whereas endothermic reaction have $\Delta H > 0$. Irreversible process associated when $\Delta G < 0$, for reversible process $\Delta G = 0$, and at $\Delta G > 0$ non spontaneous processes was occurred [17] . whereas ligand (Asparagin, Seraine) the protonation is endothermic, non-spontaneous and increases on heating but with (Pb- Asparagin , Pb-Seraine and Cd- Asparagin complexes) are the dissociation is exothermic, spontaneous at low T and decreases on heating but in the case Cd- Seraine the dissociation is endothermic, non-Spontaneous and increases on heating. All the stability constants in the order of $Cd^{2+} < Pb^{2+}$. It is expected that all these metal ion build a chelate with amino acids over carboxyl- and amine groups [18] .
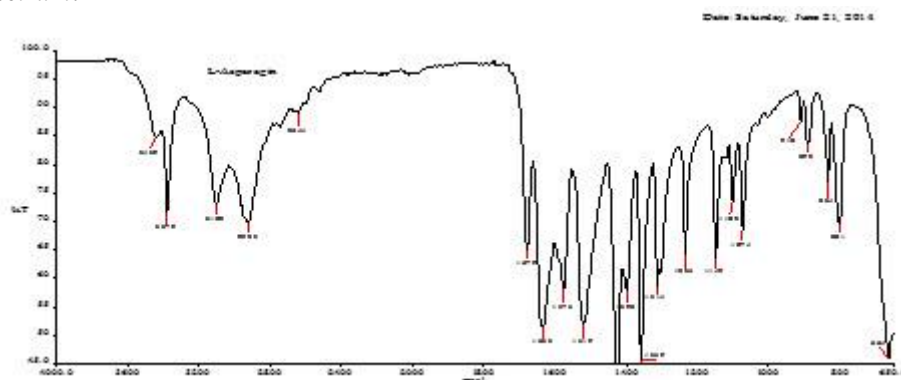
The results of IR spectrum:

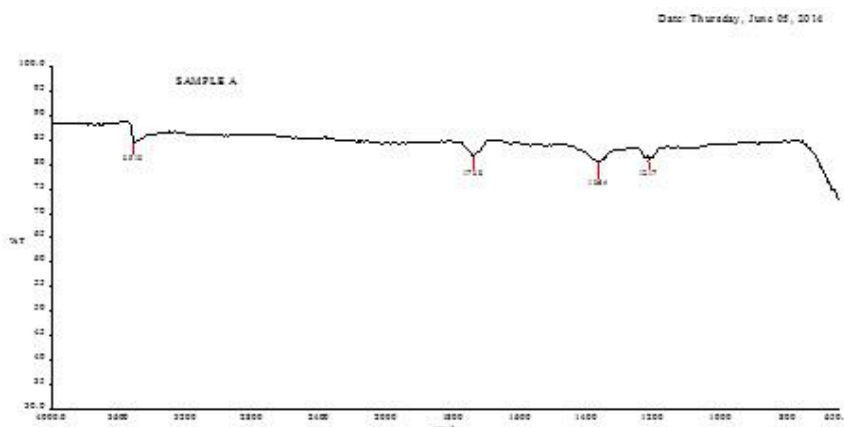Figure 1. IR spectrum for L-Asparagin
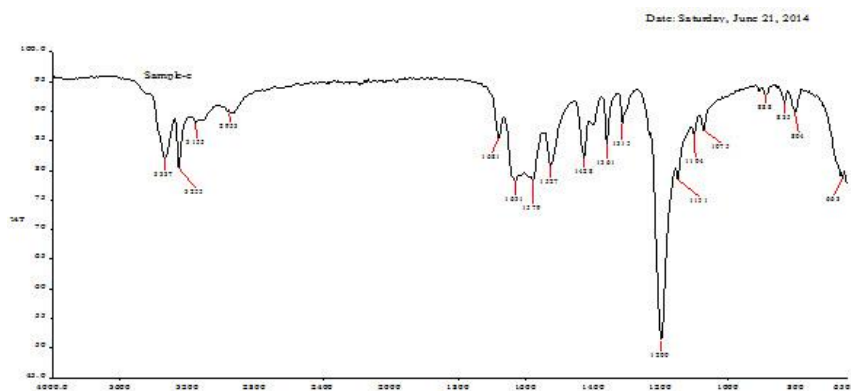

Figure 2. IR spectrum for Pb-Asparagin complex

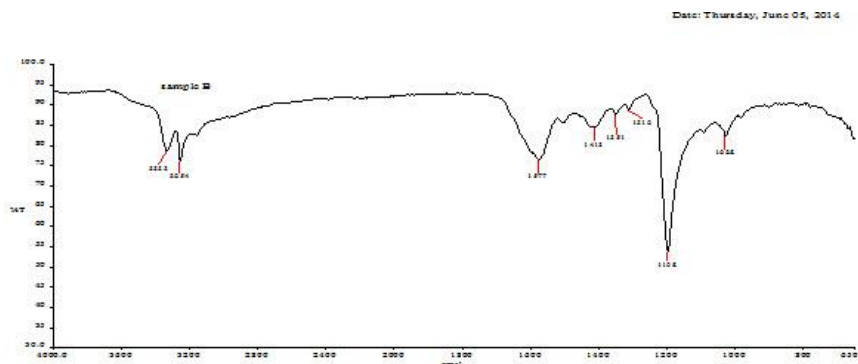Figure 3. IR spectrum for Cd-Asparagine complex
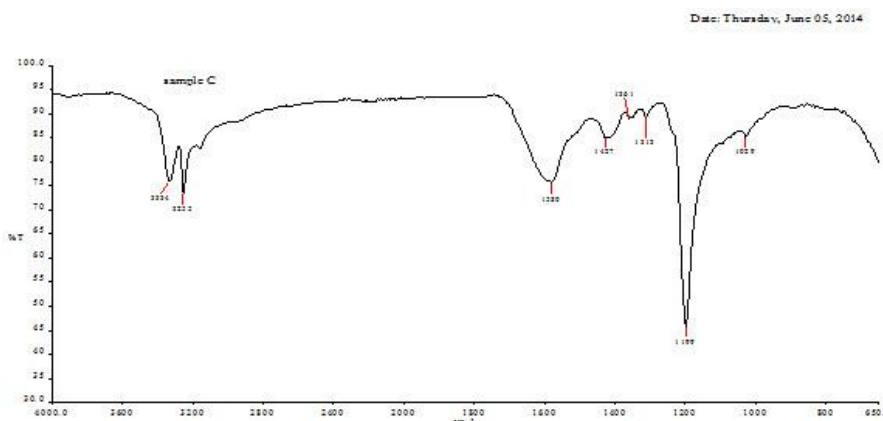
Figure 4. IR spectrum for Seraine

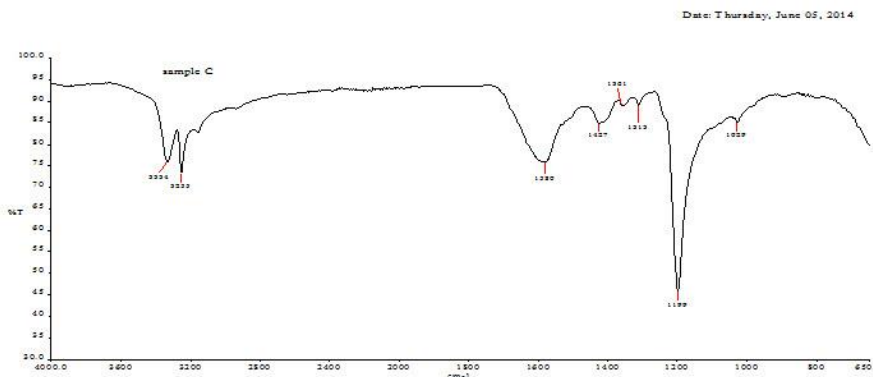Figure 5. IR spectrum for Pb-serine complex

Figure 6. IR spectrum for Cd-serine complex

The figures (Figs.1–6) show the main peaks of the IR spectra and are presented the most important absorption bands In the spectra of the ligand (Asparagin) and (Serine), the (N–H) stretching vibrations appear at (2940 cm^{-1}) bands appear to be shifted toward higher frequencies in the spectra the complexes at (3510 cm^{-1}) this for (Pb–Asparagin complex), (3255cm^{-1}) for (Pb–Serine complex) and (3254cm^{-1}) for (Cd- Serine complex) and (3255 cm^{-1}) for (Cd- Asparagin complex)[19].

The absorption band at (1633 cm^{-1}) was attributed to the carbonyl stretching vibration in the ligand (Serine) spectrum and appears to be shifted to (1681cm^{-1}) for (pb- Serine complex), and in the other two complexes (Cd – phenylalanine complex) are shifted toward lower frequencies in the spectrum to (1577 cm^{-1}), this displaying a well-resolved high-intensity signal, which involves the carboxylic group in covalent bonding to the Pb , Cd ion. The (O–H) stretching vibration appear at (3337 cm^{-1}) was attributed to the - (O–H) vibration and appears to be shifted in the spectrum of the (Pb– Serine complex) , (Cd – Serine complex) to (3333 cm^{-1} , 3359 cm^{-1}) respectively , meaning that the O–H band is not involves in hydrogen bonding.

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