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# STABILITY CONSTANTS OF $\text{UO}_2^{2+}$ , $\text{Th}^{4+}$ AND $\text{Ce}^{3+}$ WITH L-ASPARAGINE AND THERMODYNAMIC PARAMETERS

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The stability constants of L-asparagine and its complexes formed with  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  ions were determined potentiometrically using the Calvin–Bjerrum technique as adopted by Irving and Rossotti at different temperatures (290, 298 and 310 K), in 0.1 M KCl. The stability constants were computed using the least-squares treatment method in EXCEL program for proton–ligand and metal–ligand at the temperatures given above. The protonation constants of L-asparagine ( $\log \beta_2$ ) were found to be  $13.07 \pm 0.01$ ,  $12.58 \pm 0.10$ ,  $12.28 \pm 0.16$  at 290, 298 and 310 K, respectively. In addition, the thermodynamic parameters  $\Delta H$ ,  $\Delta G$  and  $\Delta S$  of L-asparagine and its complexes with metal ions were evaluated and discussed at the same temperatures.

*Keywords:* Stability constants; Potentiometry; L-Asparagine;  $\text{Th}^{4+}$ ;  $\text{Ce}^{3+}$ ;  $\text{UO}_2^{2+}$

## INTRODUCTION

L-Asparagine, a well-known amino acid forms complexes with many metal ions, has an amide group in its structure which differs from other amino acids. L-Asparagine acts as a tridentate ligand toward metal ions, with three donor sites on the terminal amino and carboxyl as well as the amide groups on the side chain of the molecule so that it makes 6-membered rings [1,2]. One of the most important questions about the complexes formed between metal ions and peptides is to determine whether the oxygen or nitrogen in the amide group works as a donor atom. The study of the asparagine complexes may provide further evidence about the nature of the peptide complexes. In addition, L-asparagine plays an important role in living organisms since it affects the reproduction of certain cancer cells [3].

Complex formation stability constants of some metal ions with some amino acids have been studied by many workers [1–10]. Most of these studies have been carried out according to the potentiometrically Irving–Rossotti method [11]. Irving–Rossotti is still the most commonly used method to compute stability constants by a

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potentiometry method. Some of the computer codes such as SCOG, LETAGROP, PKAS, MINQUAD, SUPERQUAD, HYPERQUAD have been used for the computation of the stability constants upto now [24–26]. However, the increase in the use of PCs makes EXCEL more convenient than the others [14]. For that reason, we used EXCEL program in this work as previously [15].

In this study, potentiometric titrations were carried out for different temperatures at 290, 298 and 310 K in KCl media due to the use of amino acids in biological applications. The proton–ligand stability constants of L-asparagine and stability constants of  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  metal complexes formed with L-asparagine were determined potentiometrically using the Calvin–Bjerrum technique [12,13] as adopted by Irving–Rossotti [11] at these temperatures. Besides, thermodynamic parameters were evaluated at the same temperatures.

## EXPERIMENTAL

### Materials

L-Asparagine and all other chemicals were purchased from the Merck Chemical Co. pH Titrations were carried out by Metrohm-665 Dozimat.

### Potentiometric Titrations

0.1 M HCl, 1 M KCl, 0.004 M  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ , 0.004 M  $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 0.004 M  $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  solutions were prepared in bidistilled water supplied from Millipor (Milli-Q Gradient A-10) water purification instrument. 0.1 M NaOH was prepared in 20% dioxane–water.

The proton–ligand and metal–ligand stability constants were obtained from the data obtained by titrating solutions containing *Titration*  $V_1$ : 10 mL 1 M KCl + 5 mL 0.1 M HCl, *Titration*  $V_2$ : 10 mL 1 M KCl + 5 mL 0.1 M HCl + 10 mL 0.02 M ligand solution, *Titration*  $V_3$ : 10 mL 1 M KCl + 5 mL 0.1 M HCl + 10 mL 0.02 M ligand + 10 mL 0.004 M metal solution ( $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$ ), *Titration*  $V_4$ : 10 mL 1 M KCl + 5 mL 0.1 M HCl + 10 mL 0.004 M metal solution ( $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$ ), maintained at a constant volume of 100 mL in 20% (v/v) dioxane–water medium in each case, against carbonate free standard 0.1 M NaOH in the pH range 2.5–10.00 ( $\pm 0.01$ ) under argon atmosphere specially designed Metrohm-665 Dozimat beaker. Figure 1 shows titration curves for  $\text{Th}^{4+}$ . All measurements were made in a thermo-controlled waterbath maintained at the desired temperature ( $\pm 0.1$  K). The ionic strength was maintained at 1 M with KCl solution.

### Calculations

The average number of protons associated with the anionic ligand,  $n_A$ , is given by the below equation:

$$n_A = y + \frac{(V_1 - V_2)(N^0 + E^0)}{(V^0 + V_1)(B_T^0)} \quad (1)$$

where  $y$  is the total proton number associated with the original ligand,  $V_1$  is the total volume of 0.1 M NaOH solution used for the titration of acid solution corresponding

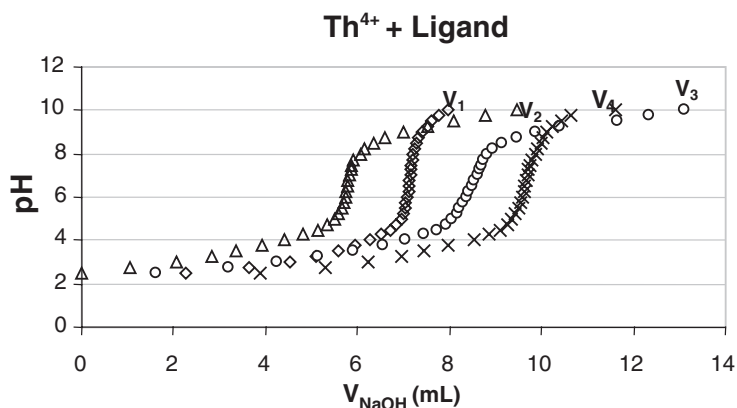


FIGURE 1 Titration curves for acid, ligand, metal–ligand and metal titration for complex of  $\text{Th}^{4+}$  with L-asparagine at 298 K ( $\diamond$   $V_1$ : acid,  $\Delta$   $V_2$ : acid + ligand,  $\circ$   $V_3$ : acid + ligand + metal,  $\times$   $V_4$ : acid + metal solution).

to a given pH value,  $V_2$  is the total volume of 0.1 M NaOH solution used for the titration of acid + ligand solution corresponding to the same pH given above,  $V^0$  is the initial volume of the acid + ligand solution,  $N^0$  is the concentration of NaOH solution,  $E^0$  is the initial free acid concentration and  $B_T^0$  is the total initial concentration of the ligand. Using this equation,  $n_A$  values *versus* pH were obtained and plotted.

#### Least-squares Treatment Method

This method is given by Corsini and Billo [16]. According to this method,

$$\frac{n_A}{(n_A - 1)[\text{H}^+]} = \frac{(2 - n_A)[\text{H}^+]}{(n_A - 1)} K_1 K_2 - K_1 \quad (2)$$

must give a straight line.  $K_1$  and  $K_2$  can be found from the intercept and slope. However the method is very sensitive to experimental errors close to integer values of  $n_A$ , therefore the points close to integer of  $n_A$  were rejected in this treatment.

#### Metal–Ligand Stability Constants

Irving–Bjerrum method gives the following equation for the complex formation function,  $n_i$ , i.e., average number of ligands bound to metal cation

$$n_i = \frac{[(V_4 - V_1) - (V_3 - V_2)](N^0 + E^0)}{(V^0 + V_1)n_A M_T^0} \quad (3)$$

where  $V_3$  is the volume of 0.1 M NaOH solution used for the titration of acid + ligand + metal solution,  $V_4$  is the volume of 0.1 M NaOH solution used for the titration of acid + metal solution,  $M_T^0$  is the initial concentration of metal cation  $n_A$ ,  $N^0$ ,  $E^0$ ,  $V^0$ ,  $V_1$ ,  $V_2$  have the same definitions as given in Eq. (1),  $n_i$  values were obtained for different pH values from this equation and  $pL$  is the inverse of logarithm of the free ligand concentrations that can be found from Eq. (4),

$$pL = \log \frac{\sum_{n=0}^{n=j} \beta_n^H \{1/\text{antilog}(\text{pH})\}^n V^0 + V_3}{(L_T - n_i M_T) V^0}, \quad (4)$$

where  $L_T$  is the total ligand concentration,  $n_i$  is the ligand number associable with metal cation;  $M_T$  is the total metal ion concentration;  $V^0$  is the initial volume;  $V_3$  is the NaOH volume that is spent for acid + ligand + metal solution and  $\beta_n$  is the total proton–ligand stability constants upto  $n$ .

Metal–ligand formation constants were found by least-squares treatment method.

### ***Least-squares Treatment***

According to this method,

$$\frac{n_i}{(n_i - 1)[L]} = \frac{(2 - n_i)[L]}{(n_i - 1)} K_1 K_2 - K_1 \quad (5)$$

must give a straight line and intercept gives  $-K_1$  [17]. However values between  $0.95 < n_i < 1.05$  are very sensitive to experimental errors. The points in this small region are therefore best rejected in this treatment [17]. The  $K_1$  and  $K_2$  values were obtained by using Eq. (5).

## **RESULTS**

### **Potentiometric Studies**

#### ***Proton–Ligand Stability Constants***

The average number of protons associated with L-asparagine,  $n_A$ , at different pH was calculated as reported previously [15,18–20]. The least squares computational method was applied to evaluate proton–ligand stability constants ( $\log K_1$ ,  $\log K_2$  and  $\log \beta_2$ ). The average values obtained at 290, 298 and 310 K are listed in Table I.

#### ***Metal–Ligand Stability Constants***

The average number of ligands attached per metal ion,  $n_i$ , were calculated according to Irving and Rossotti [11,15–20]. The metal–ligand stability constants ( $\log K_1$ ,  $\log K_2$  and  $\log \beta_2$ ) of  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  ion complexes were found to be at 290, 298 and 310 K, respectively by the least-squares treatment method and the results are given in Table II.

Dioxane has the advantage of a very low dielectric constant, thus it can be used for potentiometric titrations as reported by other researchers [15–17,25] and it prevents decomposition of the metal complex. For that reason 20% (v/v) dioxane was used in this study.

### ***Thermodynamic Studies***

As well as determining the stability constants of L-asparagine and its complexes with  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  at 290, 298 and 310 K, thermodynamic parameters were also calculated using  $\log K$  values at relevant temperatures. The graphs,  $\log K$  versus

TABLE I The average proton–ligand stability constants in 0.1 M KCl at different temperatures

<i>T</i> (K)	$\log K_1$	$\log K_2$	$\log \beta_2$
290	9.24 ± 0.02	3.83 ± 0.02	13.07 ± 0.01
298	9.13 ± 0.01	3.45 ± 0.02	12.58 ± 0.10
330	8.98 ± 0.02	3.30 ± 0.14	12.28 ± 0.16

TABLE II Metal–ligand stability constants of UO<sub>2</sub><sup>2+</sup>, Th<sup>4+</sup> and Ce<sup>3+</sup> with L-asparagine in 0.1 M KCl at different temperatures

<i>Metal ion</i>	290 K		298 K		310 K	
	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$	$\log K_1$	$\log \beta_2$
Ce <sup>3+</sup>	7.49 ± 0.01	8.44 ± 0.13	7.03 ± 0.01	8.01 ± 0.14	6.32 ± 0.21	7.05 ± 0.05
UO <sub>2</sub> <sup>2+</sup>	9.45 ± 0.17	9.84 ± 0.10	8.81 ± 0.01	9.78 ± 0.10	8.01 ± 0.22	8.42 ± 0.08
Th <sup>4+</sup>	9.78 ± 0.01	10.95 ± 0.12	9.51 ± 0.01	10.87 ± 0.01	8.43 ± 0.01	8.43 ± 0.01

TABLE III Thermodynamic parameters of L-asparagine for proton–ligand

<i>T</i> (K)	$\log \beta_2$	$\Delta H$ (kJ/mol)	$\Delta G$ (kJ/mol K)	$\Delta S$ (J/mol K)
290	13.07 ± 0.01	−65.02	−72.57	26.06
298	12.58 ± 0.10		−71.78	22.70
310	12.28 ± 0.16		−72.89	25.40

TABLE IV Thermodynamic parameters of L-asparagine complexes with UO<sub>2</sub><sup>2+</sup>, Th<sup>4+</sup> and Ce<sup>3+</sup>

<i>Metal ion</i>	<i>T</i> (K)	<i>Enthalpy change</i>	<i>Free energy change</i>	<i>Entropy change</i>
		(kJ/mol)	(kJ/mol K)	(J/mol K)
Ce <sup>3+</sup>	290	−118.43	−46.86	−246.77
	298		−45.70	−244.04
	310		−41.85	−247.03
UO <sub>2</sub> <sup>2+</sup>	290	−124.52	−54.64	−240.98
	298		−55.80	−230.60
	310		−49.98	−240.46
Th <sup>4+</sup>	290	−116.40	−54.31	−214.11
	298		−54.26	−208.50
	310		−50.04	−214.06

1/*T*, were plotted for proton and complex formation of L-asparagine. With the help of graphs, enthalpy change ( $\Delta H$ ) values were found for the proton and complex formation processes, respectively. The free energy change ( $\Delta G$ ) and entropy change ( $\Delta S$ ) were calculated using the well-known Gibbs Helmholtz equation. All thermodynamic parameters of L-asparagine and its complexes were given in Tables III and IV. In addition, Fig. 2 shows the complex formation of the related metal ions with L-asparagine at the given temperatures.

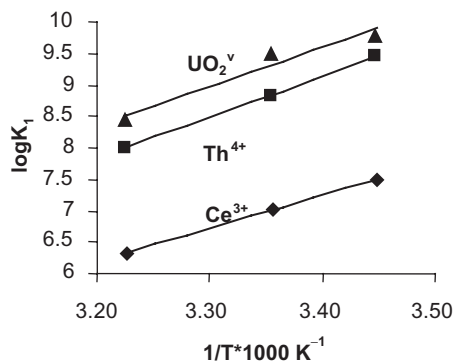


FIGURE 2  $\log K_1$  vs.  $1/T$  graph of  $\text{Ce}^{3+}$ ,  $\text{UO}_2^{2+}$  and  $\text{Th}^{4+}$  complexes with L-asparagine.

## DISCUSSION

In metal–ligand stability constants, the values change with respect to metal complexes formed with relevant metal ions. There is a relationship between the ionic radii and ionic charge of metals. Increasing ionic radius and decreasing ionic charge of metals increase the ability of the formation of complexes. The order of stability constants of the metal complexes of L-asparagine was found to be  $\text{Th}^{4+} > \text{UO}_2^{2+} > \text{Ce}^{3+}$ . This order is inversely related to the radius of the metal ions. This agrees with ionic radii of these metal ions. The similar conclusion has been reported in the study of other metal–ligand complexes [15,21,22]. The other factor that affects the stability is the size of the complexes. Metal–ligand stability weakens with the increasing size of the complex. For example Abu-Eittah reported that metal–ligand stability constants of  $\text{Th}^{4+}$  with some amino acid anions L-alaninate, L-phenylalaninate and L-histidinate have higher metal–ligand stability constants than  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  [23].

There are some reports indicating stability constants of some metal ions with L-asparagine [1,10]; however, thermodynamic parameters for these metal complexes are limited. According to our results  $\log \beta_2$  values decreased with increasing temperature for both proton–ligand and metal–ligand. The  $\Delta H$  values were found to be negative for  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  complexes. This shows that these processes are exothermic and favorable at lower temperatures for these metal complexes. The negative values of  $\Delta G$  for the complex formation of  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  with L-asparagine suggests a spontaneous nature of such process. The positive values of  $\Delta S$  for proton–ligand constants show entropically favorable process. The  $\Delta S$  values for the complex formation of L-asparagine with  $\text{UO}_2^{2+}$ ,  $\text{Th}^{4+}$  and  $\text{Ce}^{3+}$  are entropically unfavorable. As seen in Fig. 2, the complex of  $\text{Ce}^{3+}$  was separated from  $\text{Th}^{4+}$  and  $\text{UO}_2^{2+}$ . Consequently, there is a discrepancy between complexes of lanthanide and actinide series.

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