

## THERMODYNAMIC PARAMETERS AND STABILITIES OF SOME RARE-EARTH METAL ION CHELATES OF $\alpha$ -VALINE

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Solution equilibria for some rare-earth metal ions with valine have been studied potentiometrically in aqueous medium at temperatures from 25 to 55° and ionic strengths (I) from 0.1 to 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub>. The thermodynamic parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  for the formation processes were evaluated in terms of temperature, ionic strength and nature of metal ion present. The stability of the complexes was found to be: La(III) < Nd(III) < Gd(III) < Eu(III) < Yb(III) < Lu(III).

**Key words:** Formation constant, Thermodynamic parameters, Rare-earths.

### Introduction

Amino acids play a significant role in biochemistry and chemical industry as starting material for manufacturing, proteins, peptide, coenzyme, drugs and antibiotics [5-10]. However, there have only been a few studies on their complexes with rare earth metal ions [11-13]. In the present work the interaction of  $\alpha$ -valine as with the example of  $\alpha$ -amino carboxylic acids rare-earths La(III), Nd(III), Eu(III), Gd(III), Yb(III) and Lu(III) in aqueous medium have been studied potentiometrically at different temperatures and ionic strengths. The stability constants of the complexes were evaluated employing different methods [14,15, 19]. As well as the corresponding thermodynamic parameters  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  for the formation processes have been calculated and discussed in order to give information about the nature of the complexes.

### Experimental

All chemical used in this work were of BDH or Analar grade. The metal content in the solutions was determined as recommended [16], solutions of lower concentration were obtained by dilutions. The measurement of pH values were carried out using pH meter (HANNA instrument, Italy) with accuracy of 0.02 log unit and sensitivity  $\pm 0.01$ , temperature was controlled by a thermostated water-bath ( $\pm 0.1^\circ$ ).

The proton-ligand and metal-ligand thermodynamic stability constant were calculated from the results of the following solutions against standardised carbonate-free KOH solution (0.159 mol dm<sup>-3</sup>).

- (i). HClO<sub>4</sub> (0.02 mol dm<sup>-3</sup>) + NaClO<sub>4</sub> (2 mol dm<sup>-3</sup>)
- (ii). Solution (i) + valine (0.02 mol dm<sup>-3</sup>)
- (iii). Solution (ii) + metal solution (0.004 mol dm<sup>-3</sup>)

The total volume was made to 50 cm<sup>3</sup> in each case with doubly distilled water and the titrations were carried out in a specially designed double-walled beaker (250 cm<sup>3</sup>, Pyrex)

using the Calvin-Bejerrum [17] titration technique as modified by Irving and Rossotti [14,15] and performed in duplicate in order to establish reproducibility.

### Results and Discussion

In order to examine the influence of temperature and ionic strength of the medium on the dissociation process of  $\alpha$ -valine, the potentiometric curves of  $\alpha$ -valine solutions at temp. from 25 to 55° and ionic strengths from 0.1 to 1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> were determined (Fig. 1). The value obtained were in good agreement with those reported in the literature [9,11]. From these curves and by the application of Bejrrum's method and its modifications [14,15,17] the values of pK<sub>a</sub> were calculated (Table 1). The values obtained were in good agreement with those reported in the literature [9,11]. The results, indicate that pK<sub>a</sub> values increases with the increase in ionic strength. On the other hand, pK<sub>a</sub> values decrease with a rise in temperature in accordance with the weak acidic nature of valine. Decreasing pK<sub>a</sub> values with rise in temperature support the hypothesis that, the dissociation process is favourable at higher temperature.

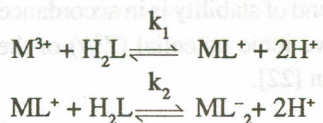
Plotting log K<sub>a</sub> vs the square root values of ionic strength (I<sup>1/2</sup>), a straight line was obtained, its extrapolation at I = 0, log k<sub>o</sub> value was evaluated. The free energy  $\Delta G^\ddagger$  values of the dissociation process can be obtained from the relation:

$$\Delta G^\ddagger = -2.303 RT \log k_o$$

The  $\Delta G^\ddagger$  values were positive; therefore, the dissociation process is non-spontaneous.  $\Delta G^\ddagger$  values increases with increase in temperatures (Table 1). A straight line was obtained of plots of log k<sub>o</sub> -1/T for each ionic strength. The slope and intercept of the line give the correspondence  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for the dissociation process respectively (Table 1). The enthalpy changes  $\Delta H^\ddagger$  were positive values as expected for the weak acid nature of  $\alpha$ -valine and the dissociation process is an endothermic reaction. On the other hand, entropy change

values  $\Delta S^\ddagger$  were negative; this means that the dissociation process was accompanied by the decrease in the disorder of the system. This observation may be due to the solvation effect and Zweiter ion formation [19].

The interaction of rare-earths ( $M^{3+}$ ) with  $\alpha$ -valine ( $H_2L$ ) may be represented as:



To investigate the effect of the working condition on the  $pK_a$ , value series of pH-metric titration of  $\alpha$ -valine ( $H_2L$ )-in aqueous medium at different temperature from 25 to 55° and varying ionic strength 0.1-1.0 mol dm<sup>-3</sup> NaClO<sub>4</sub> were carried out as an example (Fig. 1). The average number of proton associated with  $\alpha$ -valine was calculated according to the following equation.

$$\bar{n}_A = Y + \frac{(V_1 - V_2) N^\circ + E^\circ}{(V_0 + V_1) T_L}$$

The average number of  $\alpha$ -valine per metal ion, PL, were calculated using the following equations

$$\bar{n} = \frac{(V_3 - V_2) N^\circ + E^\circ}{(V_0 + V_1) \bar{n}_A \cdot T_M}$$

$$pL = \log \left[ \frac{\sum_{n=0}^{n=1} \beta_n (\log [H^+])^n}{T_L - \bar{n} T_M} \right] \frac{V_0 + V_3}{V_0}$$

The parameters  $\bar{n}$ ,  $n_A$  and  $pL$  having the same definitions and meanings given by Irving-Rossotti [14,15], where  $T_L$ ,  $T_M$

TABLE 1. INFLUENCE OF THE TEMPERATURE AND IONIC STRENGTH OF THE MEDIUM ON  $pK_a$  VALUES OF  $\alpha$ -VALINE, AS WELL AS SOME THERMODYNAMIC PARAMETERS FOR ITS DISSOCIATION PROCESS.

Ionic strength mol dm <sup>-3</sup>	$pK_a$ values (°C)				$\Delta H^\ddagger$ (kJ mol <sup>-1</sup> )	$-\Delta S^\ddagger$ (JK <sup>-1</sup> mol <sup>-1</sup> )
	25°	35°	45°	55°		
0.1	9.45	9.36	9.28	9.21	14.99	130.6
0.2	9.47	9.39	9.31	9.24	14.35	133.17
0.4	9.51	9.44	9.36	9.29	13.72	136.04
0.8	9.56	9.50	9.42	9.35	13.10	137.04
1.0	9.58	9.53	9.45	9.38	12.48	141.00
$pK_a$	9.37	9.28	9.20	9.14	-	-
$\Delta G^\ddagger$ (kJ mol <sup>-1</sup> )	53.46	54.73	56.01	57.39	-	-

and  $\beta$  are the total concentration of ligand, metal and the overall stability constant of complexes respectively. The values of  $n$  for all complexes varying between 0.2 – 1.9 thereby indicating the formation of 1:1 and 1:2 (M:L) complexes.

Plot ( $\bar{n}$ -PL) diagrams for the complexes at different ionic strengths give the formation curves represented in Fig. 2. From these curves  $\log k_1$  and  $\log k_2$  can be evaluated at  $n$  equal to 0.5 and 1.5 respectively. Values of the overall stability constant  $\beta$  ( $\beta = k_1 k_2$ ) of the complexes were further refined by using calculation method graphical, least-square and the mid-point methods calculation methods. The final values of the overall stability constant ( $\log \beta$ ) for the complexes are given in (Table 2). The results are in good agreement with those from similar studies [11-13].

The results indicate that the stability constant decreases with the increases in temperature and thus lower temperatures favour complex formation. On the other hand ( $\log \beta$ ) values decrease with the increases in the ionic strength. This observation may be due to the decrease in the metal ion activity for the complexation with the ligand in the presence of other foreign ions in the system i.e. the metal ions are screened by the other

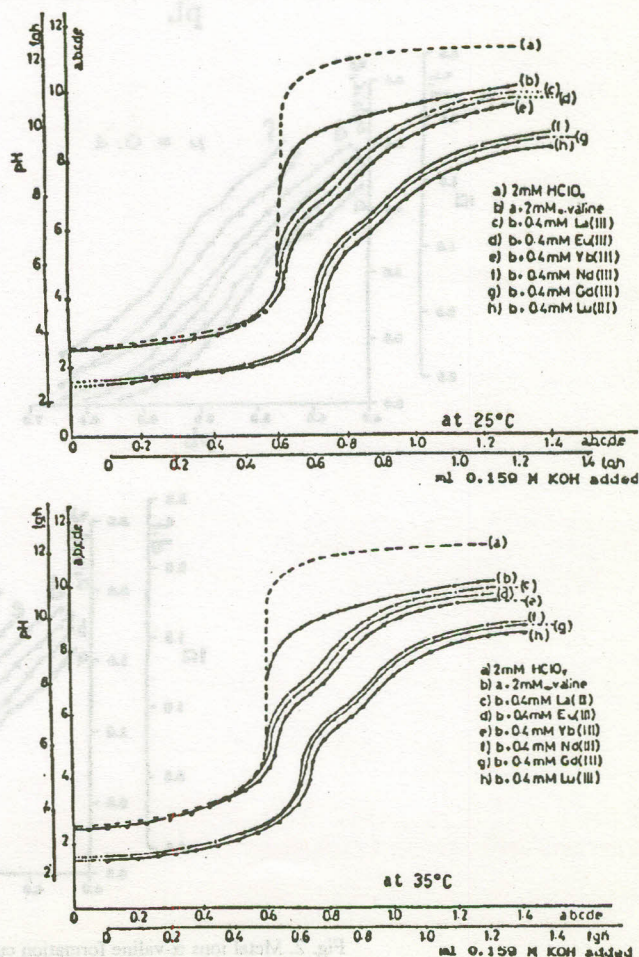


Fig. 1. Potentiometric titration curves at  $\mu = 0.1M$  for  $\alpha$ -valine with metal ions

ions, this conclusion is in accordance with similar findings reported by Hückel [20].

The values of the overall stability constant for the complexes increased in the order: La(III) < Nd(III) < Gd(III) ≤ Eu(III) < Yb(III) < Lu(III), which is in accordance with the Irving-Williams rule [21]. A plausible explanation for this trend is that, rare-earth metal ions differ in the number of 4f electrons which are effectively shielded from the interaction with the ligand orbitals by the electrons in 5s and 6p orbitals.

Figure 3 shows that the difference in stability constants of rare earth metal ion complexes and the positive nuclear charge of metal ions e.g. Gd(III) ion has completely half filled thus configuration leads to a shielding of the nuclear charges of such ion from the interaction with the ligand and hence to decrease its (log β) than that of Eu(III) the next metal ion in series. The trend of stability is in accordance with the increase of the effective ionic potential ( $Z^2/r$ ) of the metal ion in the same direction [22].

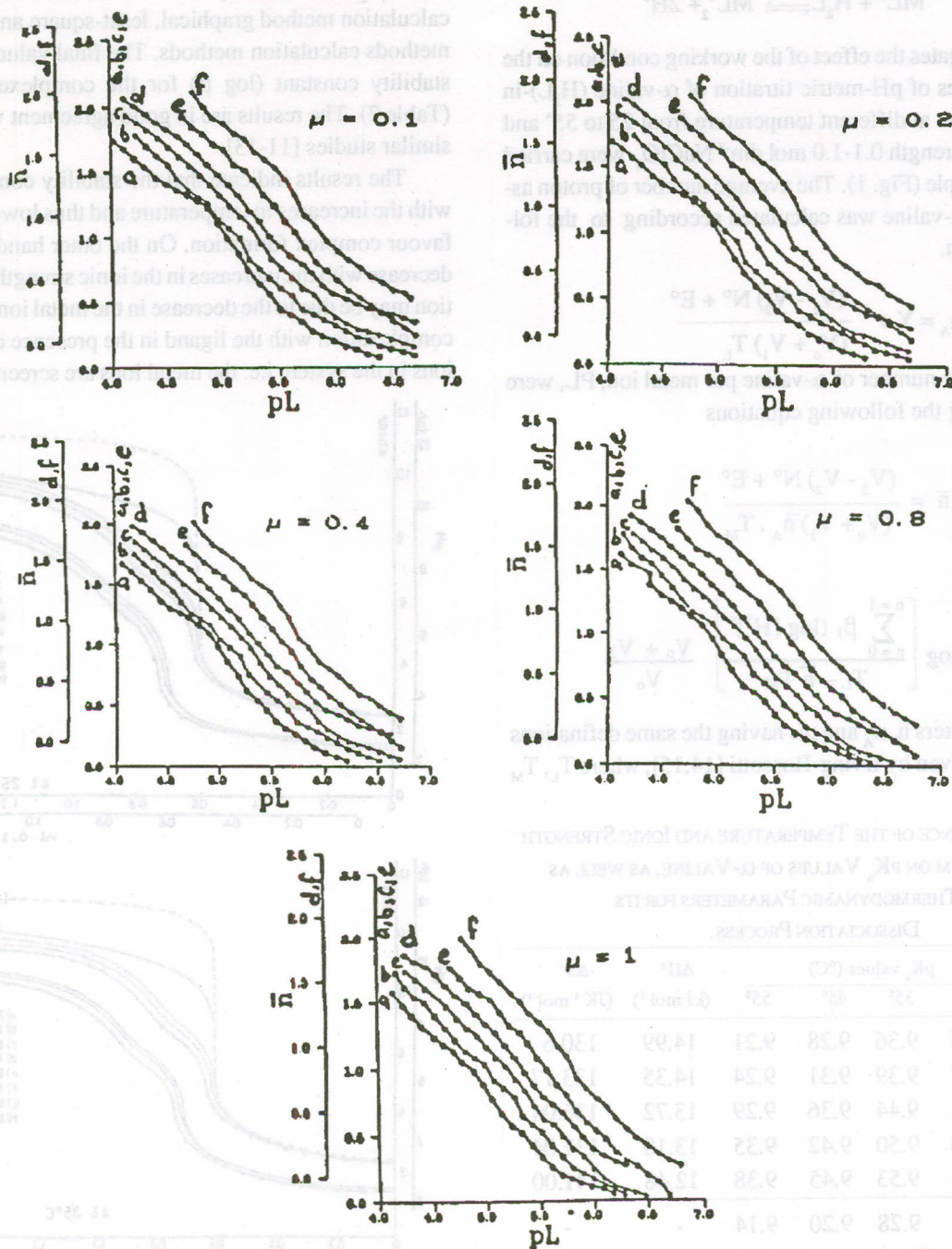


Fig. 2. Metal ions  $\alpha$ -valine formation curves at  $t^\circ\text{C} = 25$  and different ionic strengths. (a) La (III); (b) Nd (III), (c) Eu (III), (d) Gd (III), (e) Yb (III), (f) Lu (III).

TABLE I. INFLUENCE OF THE TEMPERATURE AND IONIC STRENGTH OF THE MEDIUM ON  $\text{pK}_a$  VALUES OF  $\alpha$ -VALINE, AS WELL AS SOME THERMODYNAMIC PARAMETERS FOR ITS DISSOCIATION PROCESS.

mol dm <sup>-3</sup>	ionic strength		$\text{pK}_a$ values ( $^\circ\text{C}$ )		All $\Delta G^\circ$ (kJ mol <sup>-1</sup> )	
	0.1	1.0	25	35	25	35
0.1	9.45	9.36	9.28	9.21	14.99	14.32
0.2	9.47	9.39	9.31	9.24	14.32	13.72
0.4	9.51	9.44	9.36	9.29	13.72	13.12
0.8	9.56	9.50	9.42	9.35	13.12	12.52
1.0	9.58	9.53	9.45	9.38	12.52	11.92
	9.57	9.52	9.40	9.34	11.92	11.32

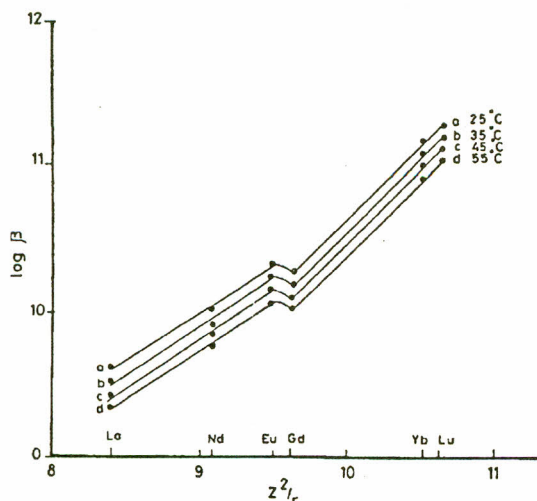


Fig. 3. Log  $\beta$  as a function of ionic potential ( $Z^2/r$ ) for valine-lanthanide complexes at  $I = 1 \text{ mol dm}^{-3} \text{ NaClO}_4$  and different temperatures.

The thermodynamic functions  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  for the complex formation were calculated using the standard equations as followed: Plotting  $\log \beta$  vs  $I^{1/2}$  gave a straight line, interrupted the Y-axis at  $\log \beta_0$  which was substituted in the following equation to obtain the values of free energy  $\Delta G^\circ$ .

$$\Delta G^\circ = -2.303 RT \log \beta_0$$

All obtained values were negative (Table 3) which indicated the spontaneous reaction nature of valine with lanthanide ions and  $\Delta G^\circ$  increases from La(III) to Lu(III) which indicated that the stability of the complexes increase in the same order.

Plotting,  $\log \beta$  vs  $1/T$  gave a straight line (Fig. 4) its slope and ordinate yield  $\Delta H^\circ$  and  $\Delta S^\circ$  for the complexation process respectively, according to the reaction:

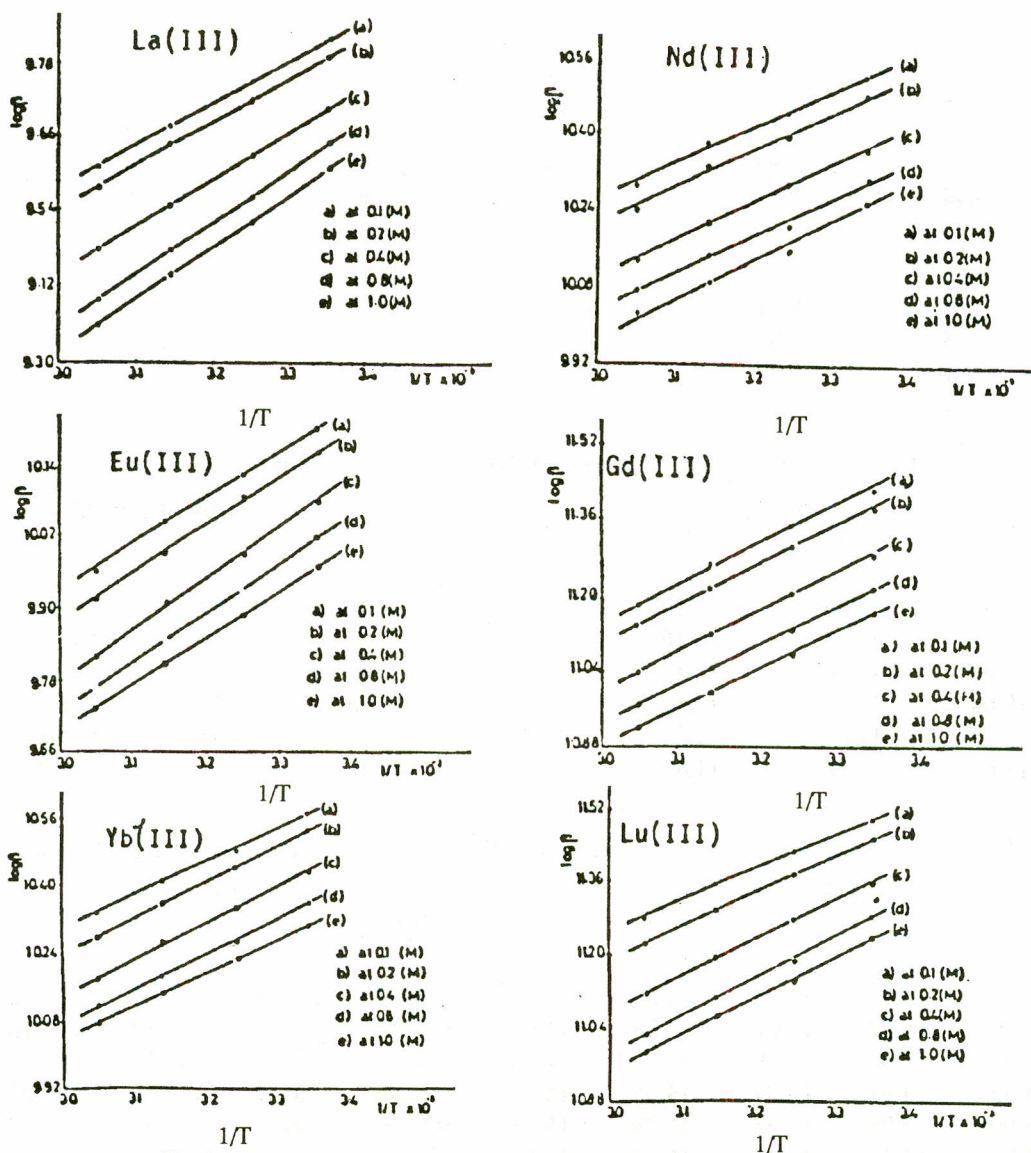


Fig. 4. Relation of  $\log \beta - 1/T$  for  $\alpha$ -valine complexes at different ionic strengths.

TABLE 2. THE OVERALL STABILITY CONSTANTS ( $\log \beta$ ) OF 1:2  $M^{3+}$  VALINE COMPLEXES AT DIFFERENT IONIC STRENGTHS AND TEMPERATURE.

Metal ion (III) I (mol dm <sup>-3</sup> ) t(°C)	La	Nd	Eu	Gd	Yb	Lu
25°C						
0.1	9.82	10.21	10.57	10.52	11.43	11.50
0.2	9.79	10.17	10.53	10.48	11.39	11.46
0.4	9.71	10.08	10.43	10.36	11.29	11.36
0.8	9.65	10.02	10.36	10.30	11.22	11.29
1.0	9.61	9.97	10.31	10.25	11.17	11.24
35°C						
0.1	9.75	10.13	10.48	10.44	11.35	11.43
0.2	9.72	10.09	10.44	10.39	11.31	11.38
0.4	9.63	9.99	10.35	10.29	11.21	11.28
0.8	9.56	9.93	10.27	10.20	11.33	11.19
1.0	9.52	9.89	10.23	10.15	11.08	11.15
45°						
0.1	9.68	10.05	10.41	10.38	11.27	11.36
0.2	9.65	9.99	10.36	10.33	11.22	11.30
0.4	9.55	9.91	10.27	10.21	11.12	11.20
0.8	9.48	9.85	10.19	10.14	11.05	11.11
1.0	9.44	9.81	10.15	10.08	11.00	11.07
55°						
0.1	9.61	9.96	10.34	10.29	11.18	11.28
0.2	9.58	9.91	10.28	10.24	11.14	11.23
0.4	9.48	9.82	10.18	10.13	11.04	11.12
0.8	9.40	9.77	10.02	10.07	10.97	11.03
1.0	9.36	9.73	10.08	10.02	10.92	10.99

TABLE 3. THERMODYNAMIC CONSTANTS AND FREE ENERGY CHANGE ( $\Delta G^*$ ) OF METAL ION-VALINE COMPLEXES AT DIFFERENT TEMPERATURES.

Metal t(°C) ion	$\log K_o$				$-\Delta G^*$ (kJ mol <sup>-1</sup> )			
	25	35	45	55	25	35	45	55
La (III)	9.92	9.86	9.79	9.72	56.58	58.13	59.62	61.10
Nd (III)	10.32	10.24	10.16	10.07	58.90	60.40	61.87	63.22
Eu (III)	10.69	10.60	10.53	10.46	61.00	62.49	64.12	65.70
Gd (III)	10.64	10.57	10.52	10.41	60.74	62.36	64.05	65.41
Yb (III)	11.55	11.47	11.39	11.30	65.90	67.67	69.38	70.97
Lu (III)	11.62	11.56	11.49	11.41	66.30	68.17	69.98	71.68

TABLE 4. ENTHALPY AND ENTROPY CHANGE OF METAL ION-VALINE COMPLEXES AT DIFFERENT IONIC STRENGTHS.

I (mol dm <sup>-3</sup> ) Metal ion	$-\Delta H^*$ (kJ mol <sup>-1</sup> )					$-\Delta S^*$ (kJ mol <sup>-1</sup> )				
	0.1	0.2	0.4	0.8	1.0	0.1	0.2	0.4	0.8	1.0
La (III)	13.10	12.79	14.35	15.60	15.28	144.06	143.48	137.77	132.40	132.62
Nd (III)	15.60	16.22	15.91	15.28	14.97	143.16	140.30	139.52	140.46	140.65
Eu (III)	14.35	15.60	15.28	14.97	14.93	154.23	149.28	148.30	148.12	149.26
Gd (III)	15.35	14.97	14.04	14.35	14.66	153.28	150.42	151.16	149.07	147.07
Yb (III)	15.59	15.28	14.97	15.28	15.31	166.51	166.70	165.74	164.40	162.48
Lu (III)	13.72	14.34	14.97	16.22	15.60	174.14	171.27	167.27	161.67	162.88

$$\log \beta = \frac{-\Delta H^*}{2.303 R} \frac{1}{T} + \frac{\Delta S^*}{2.303 R}$$

The  $\Delta H^*$  and  $\Delta S^*$  values for all complexes are summarized in Table 4. From Table 4, it is clear that the values of  $\Delta H^*$  for all cases are negative which means that the complexation processes are exothermic reactions and are favourable at lower temperatures. On the other hand,  $\Delta S^*$  values for all complexes are positive, which suggests that, on account of the complexation processes the disorder of the system increases and the entropy factor is the principle driving force for the complex.

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