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Thermodynamic studies on the interaction between some amino acids with some rare earth metal ions in aqueous solutions

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Abstract

The interactions between the amino acids (glycine and L-threonine) with some rare earth metal ions (Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+} and Yb^{3+}) were studied at a wide range from ionic strengths (0.07–0.32 M KNO_3) and temperatures (25–45 °C) in aqueous solutions by using Bjerrum potentiometric method. The stoichiometric and thermodynamic stability constants were calculated as well as the standard thermodynamic parameters (ΔG°, ΔH° and ΔS°) for all possible reactions that occur. The degree of formation ($\bar{n}$) for all studied systems was determined and discussed. The thermodynamic parameters differences ($\Delta\Delta G^\circ$, $\Delta\Delta H^\circ$ and $\Delta\Delta S^\circ$) were calculated and discussed to determine the factors which control these complexation processes from the thermodynamic point of view.

Keywords: Thermodynamics; Amino acids; Rare earth metal

1. Introduction

In the end of 20th century, many authors directed their researches to physical studies on the complexation processes between the amino acids and different metal ions [1–4]. A special interest for these studies was carried out on the interactions between the amino acids and the rare earth metal ions [4,5]. According to what previously said, this work studies the different possible reactions between two important amino acids (glycine and L-threonine) with seven rare earth metal ions (Pr^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Ho^{3+} and Yb^{3+}). This work presents a new thermodynamic treatment for these reactions. The reactions were studied at a wide range from ionic strengths μ (0.07, 0.12, 0.17, 0.22 and 0.32 M KNO_3) and temperature ($t =$ 25, 30, 35, 40 and 45 °C). The stoichiometric stability constants of these reactions were determined by using Bjerrum pH-titration method [6] in aqueous solutions. Based on these data, the thermodynamic stability constants (K°) and the standard thermodynamic parameters (ΔG°, ΔH° and ΔS°) were calculated to determine the factors that affect these complexation processes.

2. Experimental

2.1. Materials

All the reagents used were of A.R. grade. All the solutions in this study were prepared by using conductivity water. The lanthanone trivalent metal ion nitrates were analyzed by complexometric methods [7]. Sodium glycinate and sodium threoninate were

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Table 1
Ionization constants of the amino acids [14,15]

Amino acids	Temperature (°C)	pK_1 values					pK_2 values				
		$\mu = 0.07$	$\mu = 0.12$	$\mu = 0.17$	$\mu = 0.22$	$\mu = 0.32$	$\mu = 0.07$	$\mu = 0.12$	$\mu = 0.17$	$\mu = 0.22$	$\mu = 0.32$
Glycine	25	2.39	2.37	2.41	2.42	2.42	9.63	9.61	9.59	9.57	9.57
	30	2.49	2.48	2.42	2.43	2.40	9.58	9.56	9.54	9.53	9.51
	35	2.33	2.39	2.36	2.37	2.37	9.53	9.50	9.49	9.47	9.45
	40	2.31	2.37	2.30	2.34	2.33	9.43	9.41	9.39	9.38	9.36
	45	2.22	2.18	3.18	2.18	2.17	9.26	9.24	9.22	9.21	9.19
L-Threonine	25	2.23	2.21	2.23	2.24	2.24	9.14	9.11	9.08	9.05	9.00
	30	2.29	2.28	2.24	2.24	2.22	9.10	9.07	9.04	9.02	8.99
	35	2.19	2.22	2.21	2.21	2.21	8.86	8.81	8.75	8.73	8.68
	40	2.17	2.22	2.16	2.18	2.18	8.72	8.66	8.65	8.62	8.58
	45	2.10	2.06	2.06	2.06	2.05	8.60	8.56	8.53	8.50	8.46

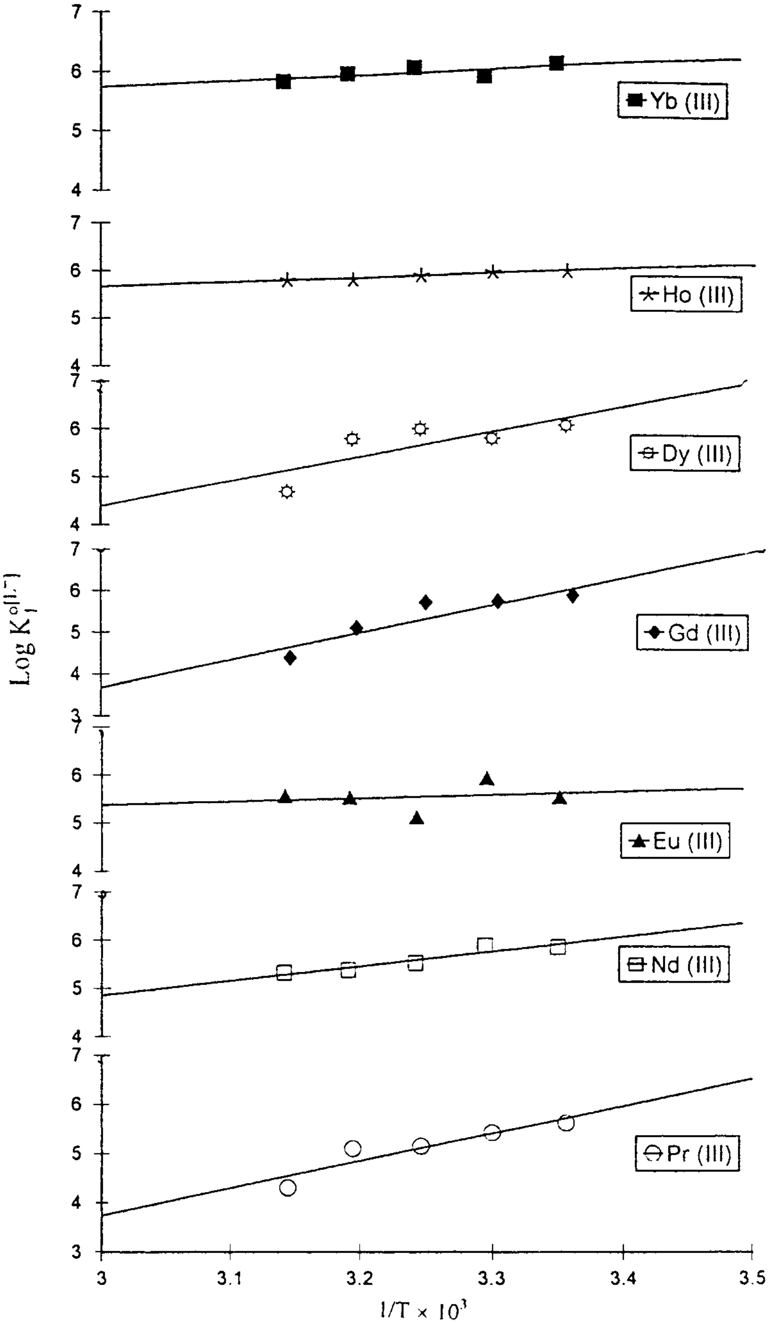


Fig. 1. $\log K_1^{\circ[L^-]}$ vs. $1/T$ for complexes of glycine with different metal ions.

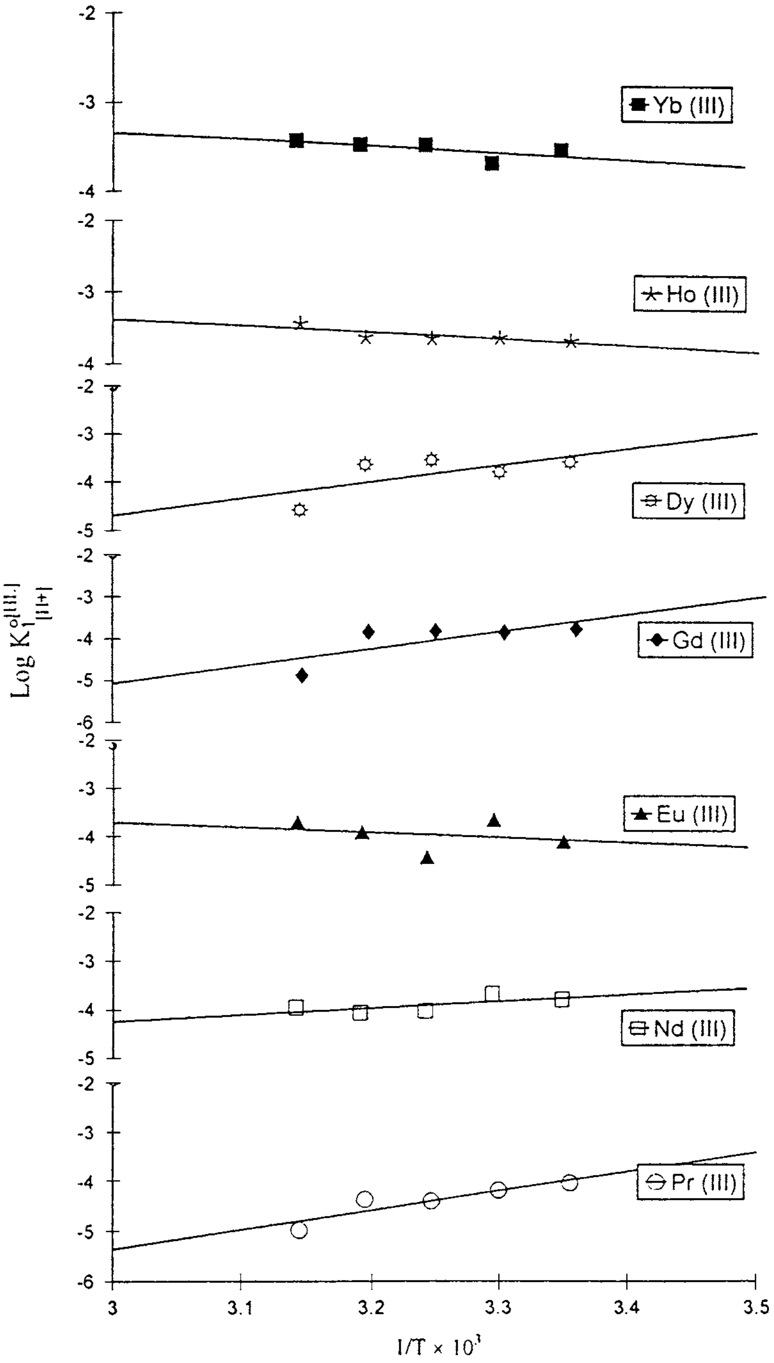


Fig. 2. log $K^{\circ[\mathrm{HL}]}_{1[\mathrm{H}^{+}]}$ vs. 1/T for complexes of glycine with different metal ions.

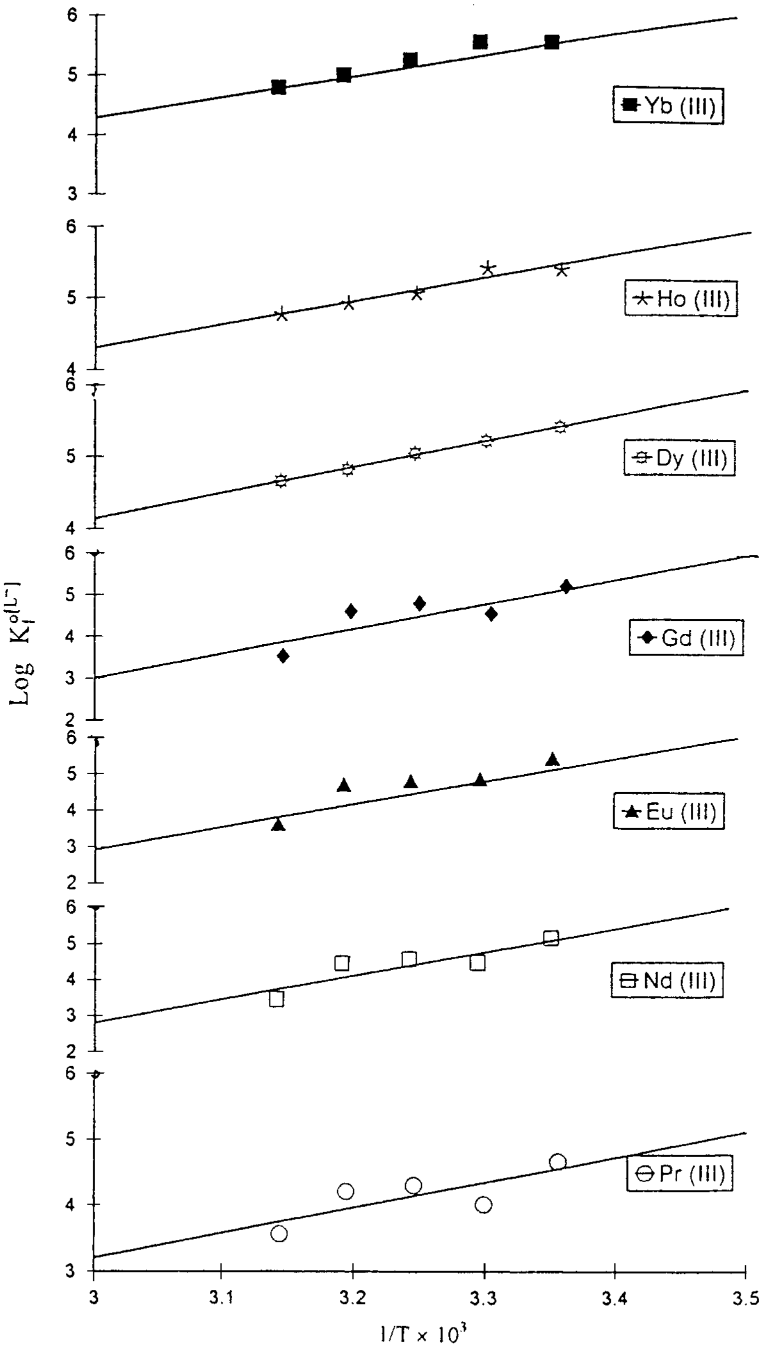


Fig. 3. $\log K_1^{\circ[L^-]}$ vs. $1/T$ for complexes of L-threonine with different metal ions.

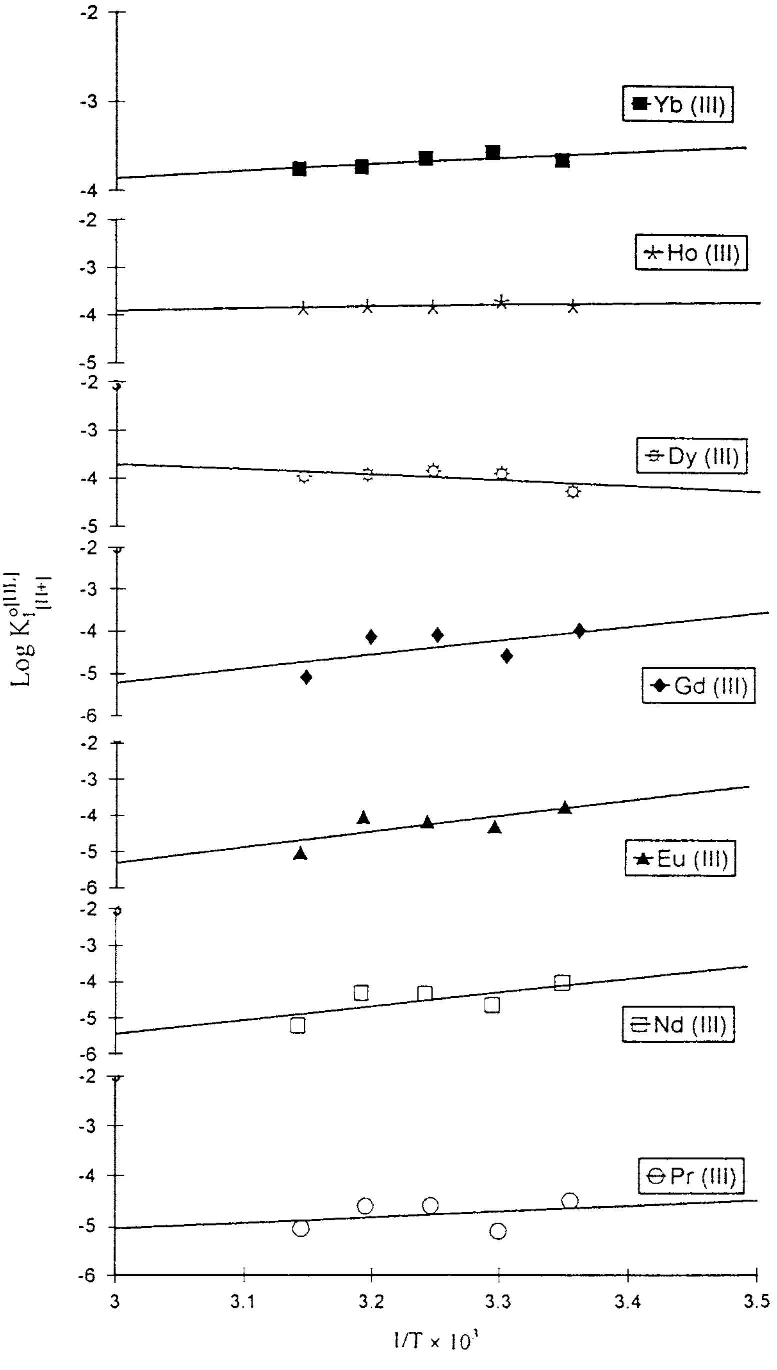


Fig. 4. $\log K^{\circ[\mathrm{HL}]}_{1[\mathrm{H}^+]}$ vs. $1/T$ for complexes of L-threonine with different metal ions.

prepared by the addition of equivalent amounts from NaOH solution (standardized by potassium hydrogen phthalate) to pure glycine and L-threonine, respectively.

2.2. Procedure

The pH measurements were carried out with an Orion Research ionalyzer pH meter which standardized against buffers pHs: 4, 7 and 10. The pH values were accurate to ±0.01 pH unit by using a correction value as follows:

$$\mathrm{pH} = 7.00 + (\mathrm{pH}_{\mathrm{meter}} - 700)C_{\mathrm{meter}} \qquad (1)$$

There will be a correction factor (C_{meter}) in acidic range and another factor in alkaline range [8,9].

According to Bjerrum pH-titration technique [6], a 100 ml solution containing 0.001 M $M(NO_3)_3$ (M = Pr, Nd, Eu, Gd, Dy, Ho or Yb) and 0.001 M HNO_3 and sufficient amount from 1 M KNO_3 to fix the ionic strength [10] (at $\mu = 0.07, 0.12, 0.17, 0.22$ and 0.32) was thermostated at the desired temperatures ($t = 25$, 30, 35, 40 and 45 °C). The solution then titrated against 0.1 M monosodium salt of the amino acid (glycine or L-threonine). The pH is recorded after each addition from the titrant. These measurements were carried out in aqueous media.

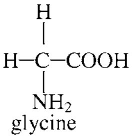
2.3. Calculations

The use of Bjerrum technique in this study (mineral acid + metal salt titrated with sodium salt of the amino acid) is a prerequisite to the occurrence of the following equilibria [11–13]:

$$H_2L^+ \overset{K_1}{\rightleftharpoons} HL + H^+, \quad K_1 = \frac{[H^+][HL]}{[H_2L^+]} \qquad (2)$$

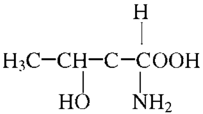
$$HL \overset{K_2}{\rightleftharpoons} L^- + H^+, \quad K_2 = \frac{[H^+][L^-]}{[HL]} \qquad (3)$$

where H_2L^+, HL and L^- are the diprotonated, monoprotonated and the amino acid anion, respectively, i.e. HL for the studied ligands represented by the following structures:



$$\mathrm{H{-}\underset{NH_2}{\overset{H}{C}}{-}COOH}$$

glycine



$$\mathrm{H_3C{-}\underset{HO}{CH}{-}\underset{NH_2}{\overset{H}{C}}{-}COOH}$$

L-threonine

The values of pK_1 and pK_2 were determined [14,15] (and reported in Table 1) to calculate the concentrations of H_2L^+, HL and L^- which present in the reaction medium. Most previous studies consider that the complexation processes were carried out by one of these species. This study takes into account that all of these species could act as a ligating species. Due to the presence of three positive charges of the studied metal ions, an expected repulsion between the reacting species H_2L^+ and M^{3+} may occur. For this reason, the diprotic species H_2L^+ were excluded as a ligating species. In this case, the most probable ligating species are HL and/or L^-, the stoichiometric stability constants of the possible suggested reactions were calculated as follows.

Table 2
Summary of $\bar{n}$ data of M^{3+}–amino acid complexes at $\mu = 0.07$

Amino acid	M^{3+}	t (°C)	$\bar{n}$	pH	$[H_2L^+]$	[HL]	$[L^-]$
Glycine	Pr^{3+}	30	0.00	3.46	5.9710×10^{-5}	4.4564×10^{-4}	2.7000×10^{-10}
			0.00	5.39	1.5550×10^{-6}	9.8790×10^{-4}	5.0944×10^{-8}
			6.50×10^{-4}	6.21	2.3562×10^{-7}	9.8889×10^{-4}	3.3689×10^{-7}
			0.40	6.46	1.3205×10^{-7}	9.8555×10^{-4}	5.9707×10^{-7}
			0.60	6.61	9.3323×10^{-8}	9.8383×10^{-4}	8.4191×10^{-7}
			0.80	6.65	6.7485×10^{-8}	9.8207×10^{-4}	1.1601×10^{-6}
L-Threonine	Nd^{3+}	25	0.00	3.74	2.7824×10^{-5}	7.1635×10^{-4}	2.3000×10^{-9}
			0.00	6.15	1.5000×10^{-7}	9.9334×10^{-4}	8.1920×10^{-7}
			0.20	6.71	4.1084×10^{-8}	9.8788×10^{-4}	2.9581×10^{-6}
			0.40	6.93	2.4711×10^{-8}	9.8610×10^{-4}	4.9004×10^{-6}
			0.60	7.37	8.9573×10^{-9}	9.8448×10^{-4}	1.3474×10^{-6}
			0.75	7.89	2.6964×10^{-9}	9.8133×10^{-4}	4.4475×10^{-5}

2.3.1. Reaction (I)

The deprotonated amino acid anion L^- could acts as a ligating species according to the following equilibria:

$$M^{3+} + L^- \overset{\beta_1^{[L^-]}}{\rightleftharpoons} ML^{2+}, \quad \beta_1^{[L^-]} = \frac{[ML^{2+}]}{[M^{3+}][L^-]} \tag{4}$$

$$M^{3+} + 2L^- \overset{\beta_2^{[L^-]}}{\rightleftharpoons} ML_2^+, \quad \beta_2^{[L^-]} = \frac{[ML_2^+]}{[M^{3+}][L^-]^2} \tag{5}$$

where $\beta_1^{[L^-]}$ and $\beta_2^{[L^-]}$ are the overall stability constants of the complexes formed from the reaction between L^- and M^{3+}. In this case, $[L^-]$ can be calculated from Eqs. (2) and (3) and substituted in Eqs. (4) and (5), where [16] $[L^-] = K_1K_2[H_2L^+]/[H^+]^2$.

2.3.2. Reaction (II)

The monoprotic amino acid HL could acts as interacting ligating species and the complexation process

Table 3
Stability constants of M^{3+}–glycine complexes

Metal ion	μ	$\log K_1^{[L^-]}$					$\log K_{1[H^+]}^{[HL]}$				
		$t = 25\,°C$	$t = 30\,°C$	$t = 35\,°C$	$t = 40\,°C$	$t = 45\,°C$	$t = 25\,°C$	$t = 30\,°C$	$t = 35\,°C$	$t = 40\,°C$	$t = 45\,°C$
Pr^{3+}	0.07	5.62	5.41	5.14	5.09	4.34	−4.02	−4.17	−4.39	−4.34	−4.92
	0.12	5.57	5.46	5.11	4.74	3.85	−4.04	−4.10	−4.39	−4.67	−5.39
	0.17	5.60	5.39	5.12	5.07	4.14	−3.99	−4.15	−4.37	−4.32	−5.07
	0.22	5.55	5.44	5.09	4.72	3.83	−4.02	−4.09	−4.38	−4.66	−5.38
	0.32	5.55	5.42	5.07	4.70	3.81	−4.02	−4.09	−4.37	−4.66	−5.38
Nd^{3+}	0.07	5.85	5.88	5.52	5.37	5.31	−3.78	−3.70	−4.01	−4.06	−3.95
	0.12	5.87	5.86	5.41	5.26	5.16	−3.74	−3.70	−4.09	−4.15	−4.08
	0.17	5.83	5.86	5.50	5.35	5.29	−3.76	−3.58	−3.99	−4.04	−3.93
	0.22	5.84	5.84	5.39	5.24	5.14	−3.73	−3.69	−4.07	−4.14	−4.07
	0.32	5.84	5.82	5.38	5.22	5.12	−3.73	−3.69	−4.07	−4.14	−4.07
Eu^{3+}	0.07	5.54	5.94	5.12	5.53	5.56	−4.09	−3.64	−4.41	−3.90	−3.70
	0.12	5.57	5.95	4.96	5.55	5.51	−4.04	−3.61	−4.54	−3.86	−3.73
	0.17	5.52	5.92	5.10	5.51	5.54	−4.07	−3.62	−4.39	−3.88	−3.68
	0.22	5.54	5.93	4.94	5.53	5.49	−4.03	−3.60	−4.53	−3.85	−3.72
	0.32	5.54	5.91.	4.92	5.51	5.47	−4.03	−3.60	−4.53	−3.85	−3.72
Gd^{3+}	0.07	5.88	5.73	5.71	5.10	4.38	−3.75	−3.85	−3.82	−4.33	−4.88
	0.12	5.87	5.77	5.66	5.01	4.68	−3.74	−3.79	−3.84	−3.40	−4.56
	0.17	5.86	5.74	5.69	5.08	4.36	−3.73	−3.80	−3.80	−4.31	−4.86
	0.22	5.84	5.75	5.64	4.99	4.66	−3.73	−3.78	−3.83	−4.39	−4.55
	0.32	5.84	5.73	5.62	4.97	4.65	−3.72	−3.78	−3.83	−4.39	−4.54
Dy^{3+}	0.07	6.06	5.79	5.99	5.79	5.02	−3.57	−3.79	−3.54	−3.64	−4.24
	0.12	6.04	5.76	5.94	5.79	4.68	−3.57	−3.80	−3.56	−3.62	−4.56
	0.17	6.04	5.77	5.98	5.77	3.65	−3.55	−3.77	−3.51	−3.62	−5.57
	0.22	6.01	5.74	5.92	5.77	4.66	−3.56	−3.79	−3.55	−3.61	−4.55
	0.32	6.01	5.72	5.90	5.75	4.64	−3.56	−3.79	−3.55	−3.61	−4.55
Ho^{3+}	0.07	5.96	5.95	5.89	5.80	5.82	−3.67	−3.63	−3.64	−3.63	−3.44
	0.12	5.95	5.94	5.87	5.79	5.82	−3.65	−3.62	−3.63	−3.62	−3.42
	0.17	5.95	5.93	5.88	5.78	5.80	−3.64	−3.61	−3.61	−3.61	−3.42
	0.22	5.93	5.92	5.85	5.77	5.80	−3.64	−3.61	−3.62	−3.61	−3.41
	0.32	5.93	5.90	5.84	5.75	5.78	−3.64	−3.61	−3.61	−3.61	−3.41
Yb^{3+}	0.07	6.10	5.90	6.05	5.95	5.82	−3.53	−3.68	−3.48	−3.48	−3.44
	0.12	6.11	5.91	6.04	7.92	5.82	−3.50	−3.65	−3.46	−3.49	−3.42
	0.17	6.08	5.88	6.03	7.93	5.80	−3.51	−3.66	−3.46	−3.46	−3.42
	0.22	6.08	5.89	6.02	7.91	5.80	−3.49	−3.64	−3.45	−3.47	−3.41
	0.32	6.08	5.87	6.00	5.89	5.78	−3.49	−3.64	−3.45	−3.47	−3.41

could proceeds with proton release as follows:

$$M^{3+} + HL \overset{\beta^{[HL]}_{1[H^+]}}{\rightleftharpoons} ML^{2+} + H^+,$$

$$\beta^{[HL]}_{1[H^+]} = \frac{[ML^{2+}][H^+]}{[M^{3+}][HL]} \qquad (6)$$

$$M^{3+} + 2HL \overset{\beta^{[HL]}_{2[H^+]}}{\rightleftharpoons} ML_2^+ + 2H^+,$$

$$\beta^{[HL]}_{2[H^+]} = \frac{[ML_2^+][H^+]^2}{[M^{3+}][HL]^2} \qquad (7)$$

where $\beta^{[HL]}_{1[H^+]}$ and $\beta^{[HL]}_{2[H^+]}$ are the overall stability constants of the complexes formed from the reaction between HL and M^{3+} with proton release. In this case, [HL] can be calculated from Eq. (2) and substituted in Eqs. (6) and (7), where $[HL] = K_1[H_2L^+]/[H^+]$.

In general, the overall stability constants β's can be calculated from the following equation [6,17]:

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2\frac{(2-\bar{n})}{(1-\bar{n})}[L] + \sum_{i=3}^{j}\frac{(i-\bar{n})}{(1-\bar{n})}\beta_i[L]^{i-1} \qquad (8)$$

Table 4
Stability constants of M^{3+}–L-threonine complexes

Metal ion	μ	$\log K_1^{[L^-]}$					$\log K^{[HL]}_{1[H^+]}$				
		$t = 25\,^\circ C$	$t = 30\,^\circ C$	$t = 35\,^\circ C$	$t = 40\,^\circ C$	$t = 45\,^\circ C$	$t = 25\,^\circ C$	$t = 30\,^\circ C$	$t = 35\,^\circ C$	$t = 40\,^\circ C$	$t = 45\,^\circ C$
Pr^{3+}	0.07	4.63	3.99	4.26	4.11	3.53	−4.51	−5.11	−4.60	−4.62	−5.07
	0.12	4.85	3.98	4.23	4.06	3.55	−4.25	−5.09	−4.57	−4.59	−5.01
	0.17	4.59	3.96	4.18	4.05	3.47	−4.49	−5.09	−4.58	−4.54	−5.06
	0.22	4.81	3.95	4.17	4.03	3.48	−4.24	−5.08	−4.57	−4.59	−5.02
	0.32	4.76	3.91	4.11	3.83	3.44	−4.24	−5.08	−4.57	−4.56	−5.03
Nd^{3+}	0.07	5.11	4.44	4.52	4.42	3.40	−4.03	−4.65	−4.33	−4.31	−5.21
	0.12	5.09	4.44	4.59	4.41	4.08	−4.01	−4.63	−4.22	−4.24	−4.49
	0.17	5.07	4.41	4.45	4.36	3.35	−4.01	−4.63	−4.32	−4.29	−5.19
	0.22	5.05	4.41	4.52	4.39	4.03	−4.00	−4.62	−4.21	−4.23	−4.47
	0.32	5.00	4.37	4.47	4.34	3.99	−4.00	−4.62	−4.21	−4.23	−4.47
Eu^{3+}	0.07	5.40	4.84	4.77	4.69	3.58	−3.74	−4.25	−4.10	−4.03	−5.02
	0.12	5.38	4.82	4.83	4.74	4.25	−3.73	−4.33	−3.98	−3.92	−4.31
	0.17	5.36	4.81	4.69	4.64	3.53	−3.72	−4.23	−4.31	−4.01	−5.00
	0.22	5.33	4.79	4.76	4.71	4.20	−3.72	−4.23	−3.97	−3.91	−4.30
	0.32	5.28	4.76	4.71	4.67	4.16	−3.72	−4.23	−3.97	−3.91	−4.30
Gd^{3+}	0.07	5.18	4.52	4.76	4.59	3.49	−3.98	−4.58	−4.10	−4.14	−5.11
	0.12	5.15	4.65	4.73	4.46	4.17	−3.96	−4.42	−4.07	−4.20	−4.39
	0.17	5.14	4.49	4.69	4.53	3.44	−3.94	−4.56	−4.08	−4.12	−5.09
	0.22	5.10	4.62	4.67	4.43	4.12	−3.95	−4.41	−4.06	−4.19	−4.38
	0.32	5.06	4.58	4.61	4.38	4.08	−3.95	−4.41	−4.06	−4.19	−4.38
Dy^{3+}	0.07	5.37	5.20	5.01	4.80	4.63	−3.77	−3.90	−3.85	−3.93	−3.97
	0.12	5.34	5.08	4.98	4.82	4.68	−3.77	−3.98	−3.83	−3.84	−3.88
	0.17	5.33	5.17	4.93	4.74	4.58	−3.75	−3.88	−3.83	−3.91	−3.95
	0.22	5.29	5.05	4.92	4.79	4.63	−3.76	−3.97	−3.81	−3.83	−3.87
	0.32	5.24	5.02	4.86	4.75	4.59	−3.76	−3.97	−3.81	−3.83	−3.87
Ho^{3+}	0.07	5.35	5.39	5.03	4.91	4.74	−3.79	−3.71	−3.83	−3.82	−3.86
	0.12	5.36	5.37	5.03	4.89	4.75	−3.75	−3.70	−3.78	−3.77	−3.81
	0.17	5.31	5.37	4.96	4.85	4.69	−3.77	−3.67	−3.81	−3.80	−3.84
	0.22	5.31	5.33	4.97	4.86	4.70	−3.74	−3.69	−3.77	−3.76	−3.80
	0.32	5.26	5.30	4.91	4.81	4.66	−3.74	−3.69	−3.77	−3.76	−3.80
Yb^{3+}	0.07	5.49	5.53	5.22	4.99	4.84	−3.65	−3.57	−3.64	−3.74	−3.76
	0.12	5.50	5.53	5.20	4.95	4.78	−3.61	−3.54	−3.61	−3.70	−3.78
	0.17	5.45	5.50	5.15	4.93	4.76	−3.63	−3.55	−3.62	−3.72	−3.77
	0.22	5.45	5.50	5.13	4.92	4.73	−3.60	−3.53	−3.60	−3.69	−3.77
	0.32	5.40	5.46	5.08	4.88	4.69	−3.60	−3.53	−3.60	−3.69	−3.77

Table 5
Thermodynamic stability constants of M^{3+}–amino acid complexes

Amino acid	M^{3+}	$\log K_1^{\circ[L^-]}$					$\log K_{1[H^+]}^{\circ[HL]}$				
		$t = 25\,^\circ C$	$t = 30\,^\circ C$	$t = 35\,^\circ C$	$t = 40\,^\circ C$	$t = 45\,^\circ C$	$t = 25\,^\circ C$	$t = 30\,^\circ C$	$t = 35\,^\circ C$	$t = 40\,^\circ C$	$t = 45\,^\circ C$
Glycine	Pr^{3+}	5.62	5.42	5.15	5.10	4.30	−4.02	−4.17	−4.39	−4.35	−4.97
	Nd^{3+}	5.86	5.89	5.53	5.38	5.32	−3.78	−3.67	−4.02	−4.06	−3.95
	Eu^{3+}	5.55	5.95	5.13	5.54	5.57	−4.09	−3.64	−4.41	−3.90	−3.70
	Gd^{3+}	5.89	5.75	5.72	5.11	4.39	−3.75	−3.84	−3.82	−3.84	−4.88
	Dy^{3+}	6.07	5.80	6.00	5.80	4.69	−3.57	−3.79	−3.54	−3.64	−4.58
	Ho^{3+}	5.97	5.96	5.90	5.81	5.83	−3.67	−3.63	−3.64	−3.63	−3.44
	Yb^{3+}	6.11	5.91	6.06	5.96	5.83	−3.53	−3.68	−3.48	−3.48	−3.44
L-Threonine	Pr^{3+}	4.67	4.02	4.30	4.21	3.57	−4.51	−5.11	−4.60	−4.61	−5.06
	Nd^{3+}	5.15	4.47	4.56	4.44	3.44	−4.03	−4.65	−4.33	−4.31	−5.20
	Eu^{3+}	5.44	4.86	4.81	4.71	3.62	−3.74	−4.29	−4.16	−4.03	−5.01
	Gd^{3+}	5.21	4.55	4.80	4.61	3.53	−3.97	−4.58	−4.10	−4.14	−5.10
	Dy^{3+}	5.41	5.22	5.05	4.82	4.66	−4.26	−3.90	−3.85	−3.93	−3.97
	Ho^{3+}	5.39	5.42	5.07	4.93	4.77	3.79	−3.71	−3.83	−3.82	−3.86
	Yb^{3+}	5.53	5.56	5.26	5.01	4.80	3.65	−3.57	−3.64	−3.74	−3.77

where [L] is the concentration of free ligand (i.e. it varies according to the suggested reaction) and $\bar{n}$ is the ligand number (or the degree of complexation) which to be defined as the average number of ligand bound per metal ion concentration C_{M} and expressed as follows [17]:

$$\bar{n} = \frac{\text{bound ligand}}{\text{total metal ion concentration}} = \frac{\text{L}_{\text{bound}}}{C_{\text{M}}} = \frac{\text{L}_{\text{total}} - \text{L}_{\text{free}}}{C_{\text{M}}} \tag{9}$$

Details of the calculation of $\bar{n}$ and [L] values have been previously described [17,18].

The application of Eq. (8) on the suggested reaction (I) yields the equation:

$$\frac{\bar{n}}{(1-\bar{n})[\text{L}^-]} = \beta_1^{[\text{L}^-]} + \beta_2^{[\text{L}^-]} \frac{(2-\bar{n})[\text{L}^-]}{(1-\bar{n})} \tag{10}$$

A plot of $\bar{n}/(1-\bar{n})[\text{L}^-]$ against $(2-\bar{n})[\text{L}^-]/(1-\bar{n})$ gives an intercept equal to $\beta_1^{[\text{L}^-]}$ and a slope equal to $\beta_2^{[\text{L}^-]}$. Similarly, applying Eq. (8) on the suggested reaction (II) we obtain:

$$\frac{\bar{n}[\text{H}^+]}{(1-\bar{n})[\text{HL}]} = \beta_{1[\text{H}^+]}^{[\text{HL}]} + \beta_{2[\text{H}^+]}^{[\text{HL}]} \frac{(2-\bar{n})[\text{HL}]}{(1-\bar{n})[\text{H}^+]} \tag{11}$$

A plot of $\bar{n}[\text{H}^+]/(1-\bar{n})[\text{HL}]$ versus $(2-\bar{n})[\text{HL}]/(1-\bar{n})[\text{H}^+]$ gives an intercept equal to $\beta_{1[\text{H}^+]}^{[\text{HL}]}$ and a slope equal to $\beta_{2[\text{H}^+]}^{[\text{HL}]}$.

The relationship between the overall stability constant β_n and the successive stability constants K_n values is given by [19]

$$\beta_n = K_1 K_2 \cdots K_n \tag{12}$$

In this work, the degree of complexation of the system lies in the range $0.0 < \bar{n} \lesssim 1$ (i.e. the complexes formed were 1:1). Hence, $\beta_1 = K_1$ and the thermodynamic stability constant K° can be calculated by plotting $\log K$ values versus μ. Extrapolating the straight line to zero gives $\log K^\circ$ at each temperature. From these data, the standard free energy change ΔG° can be calculated from the equation:

$$\Delta G^\circ = -2.303RT \log K^\circ \tag{13}$$

Similar to the previous potentiometric studies, the standard enthalpy change ΔH° can be determined by using temperature dependence method [20–22]. In this case, ΔH° can be calculated from the straight line slope [18] (which equal to $-\Delta H^\circ/2.303R$) obtained by plotting $\log K^\circ$ against the reciprocal of absolute temperature $(1/T)$as shown in Figs. 1–4. Then, the standard entropy change ΔS° can be calculated from Eq. (14):

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} \tag{14}$$

All of the above calculations were carried out by a special designed computer programs (using P.C.).

3. Results and discussion

Because of the richness of $\bar{n}$ data obtained in this work, a selected two simple examples are summarized in Table 2. Examining these data, we observed that at low pH range [(3.46 < pH < 6.46 for glycine complexes) and (3.74 < pH < 6.93 for L-threonine complexes)] H_2L^+ has a relatively high concentration, and no complexation or only weak interactions were taking place, this is obvious from the very low $\bar{n}$ values ($\bar{n} < 0.5$). In this pH region, we note that the $\bar{n}$ values were sometimes equal to zero, this means that all reacting species present in the solution were free, i.e. this meaning seems to be clear from the expression of $\bar{n}$ function in Eq. (9). A continuous addition of the ligand increases the pH reading as well

Table 6
Comparison of results with those from literature for reaction (I) of M^{3+}–amino acid complexes at 25 °C

Amino acid	M^{3+}	μ	$\log K_1^{[\text{L}^-]}$	Reference
Glycine	Pr^{3+}	0.22	5.55	This work
		0.20	4.40	[24]
		0.20	6.25	[25]
	Nd^{3+}	0.22	5.84	This work
		0.20	4.50	[24]
		0.20	6.31	[25]
	Gd^{3+}	0.22	5.84	This work
		0.20	4.64	[24]
		0.20	6.11	[25]
L-Threonine	Pr^{3+}	0.22	4.81	This work
		0.20	4.90	[26]
	Nd^{3+}	0.22	5.05	This work
		0.20	5.03	[26]

as that of [L^-] conversely [H_2L^+] decreases while [HL] is a high and seem to be constant. In this pH range [($6.46 < \mathrm{pH} \leq 6.65$ for glycine complexes) and ($6.93 < \mathrm{pH} \leq 7.89$ for L-threonine complexes)] 1:1 complexes were formed (i.e. $0.5 < \bar{n} \lesssim 1$). This means that the most possible reactions between M^{3+} with L^- and HL species were carried out according to the reactions (I) and (II).

The stoichiometric and thermodynamic stability constants of the two studied amino acid complexes for a suggested reactions (I) and (II) are represented in Tables 3–5. The stability constants values show that $\log K_1^{[L^-]} \ggg \log K_{1[H^+]}^{[HL]}$. This is attributed to the contribution of the amino acid ionization constants in reaction (II) according to the following equation [23]:

$$\beta_{1[\mathrm{H}^+]}^{[\mathrm{HL}]} = \beta_1^{[\mathrm{L}^-]} K_2(\text{amino acid}) \qquad (15)$$

Table 6 gives a comparison between our data for reaction (I) with those reported in literature. In general,

Table 7
Standard thermodynamic parameters of M^{3+}–glycine complexes

M^{3+}	t (°C)	Reaction (I)			Reaction (II)		
		$-\Delta G^\circ$ (kJ/mol)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/K mol)	ΔG° (kJ/mol)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/K mol)
Pr^{3+}	25	32.07	106.80	250.77	22.94	75.07	328.89
	30	31.44		284.71	24.19		327.59
	35	30.37		248.15	25.89		327.79
	40	30.56		243.58	27.15		326.58
	45	26.18		253.52	30.26		331.23
Nd^{3+}	25	33.44	57.70	81.41	21.57	26.66	161.85
	30	34.17		77.66	21.29		158.25
	35	32.61		81.46	23.71		163.54
	40	32.24		81.34	24.33		162.91
	45	32.39		79.59	24.05		159.47
Eu^{3+}	25	31.67	13.70	−60.30	23.34	−18.42	16.51
	30	34.52		−68.71	21.12		8.91
	35	30.25		−53.73	26.01		24.64
	40	33.20		−62.30	23.37		15.81
	45	33.91		−63.55	22.53		12.92
Gd^{3+}	25	33.61	131.04	326.95	21.40	80.86	343.15
	30	33.36		322.38	22.28		340.40
	35	33.73		315.94	22.53		335.68
	40	30.62		320.83	23.01		331.85
	45	26.73		328.02	29.71		347.70
Dy^{3+}	25	34.63	98.93	215.77	20.37	66.80	292.52
	30	33.65		215.45	21.99		293.04
	35	35.38		206.33	20.88		284.68
	40	34.76		205.02	21.81		283.10
	45	28.56		221.89	27.89		297.77
Ho^{3+}	25	34.06	15.62	−61.88	20.94	−16.50	14.90
	30	34.58		−62.57	21.06		15.05
	35	34.79		−62.24	21.47		16.14
	40	34.82		−61.34	21.75		16.77
	45	35.50		−62.52	20.95		13.99
Yb^{3+}	25	34.86	18.44	156.31	20.14	−13.68	21.68
	30	34.29		155.61	21.35		25.31
	35	35.74		148.38	20.52		22.21
	40	35.72		143.77	20.86		22.94
	45	35.50		144.47	20.95		22.86

the published stability constant data of glycine complexes were not unanimous [24,25]. Then, our results seem rather to be intermediate in case of glycine complexes, while the comparison shows the good agreement with literature in case of L-threonine complexes [26].

Tables 7 and 8 give the standard thermodynamic parameters ΔG°, ΔH° and ΔS° for all complexation processes. Reading ΔG° data, one can conclude that the complexation process in reaction (I) is more spontaneous than the complexation process in reaction (II). This spontaneity for reaction (I) is due to its high negative ΔG° values. It is to be attributed to the electrostatic attraction between the positive lanthanide ion M^{3+} and the negative deprotonated amino acid anion L^-.ΔH° values indicate that all complexation processes are exothermic due to their negative values (with exception of some cases in reaction (II) for the

Table 8
Standard thermodynamic parameters of M^{3+}–L-threonine complexes

M^{3+}	t (°C)	Reaction (I)			Reaction (II)		
		$-\Delta G^\circ$ (kJ/mol)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/K mol)	ΔG° (kJ/mol)	$-\Delta H^\circ$ (kJ/mol)	$-\Delta S^\circ$ (J/K mol)
Pr^{3+}	25	26.65	72.73	154.63	25.73	21.65	158.99
	30	23.32		163.07	29.65		169.31
	35	25.36		153.80	27.13		158.38
	40	25.23		151.76	27.63		157.44
	45	21.74		297.08	30.81		164.97
Nd^{3+}	25	29.38	124.69	319.83	22.99	72.09	319.06
	30	25.93		325.94	26.98		326.96
	35	26.89		317.53	25.53		316.95
	40	26.61		313.36	25.83		312.84
	45	20.95		326.23	31.66		326.26
Eu^{3+}	25	31.04	136.89	355.20	21.34	82.23	374.55
	30	28.20		358.71	24.89		353.53
	35	28.37		352.34	24.53		346.62
	40	28.23		347.16	24.15		339.87
	45	22.04		361.16	30.50		354.50
Gd^{3+}	25	29.73	119.00	299.56	22.65	65.33	295.23
	30	26.40		305.61	26.57		303.30
	35	28.31		294.45	24.18		290.61
	40	27.63		291.92	24.81		287.99
	45	21.49		306.64	31.05		303.08
Dy^{3+}	25	30.87	68.93	127.72	24.31	−20.51	12.75
	30	30.28		127.56	22.63		7.00
	35	29.78		127.11	22.71		7.14
	40	28.89		127.92	23.55		9.71
	45	28.37		127.55	24.17		11.51
Ho^{3+}	25	30.75	62.66	107.08	21.63	9.00	102.78
	30	31.44		103.04	21.52		100.73
	35	29.90		106.36	22.59		102.57
	40	29.55		105.78	22.89		101.89
	45	29.04		105.72	23.50		102.20
Yb^{3+}	25	31.55	72.67	138.00	20.83	14.73	119.33
	30	32.26		133.37	20.71		116.96
	35	31.02		135.23	21.47		117.53
	40	30.03		136.23	22.41		118.66
	45	29.23		136.60	22.96		118.85

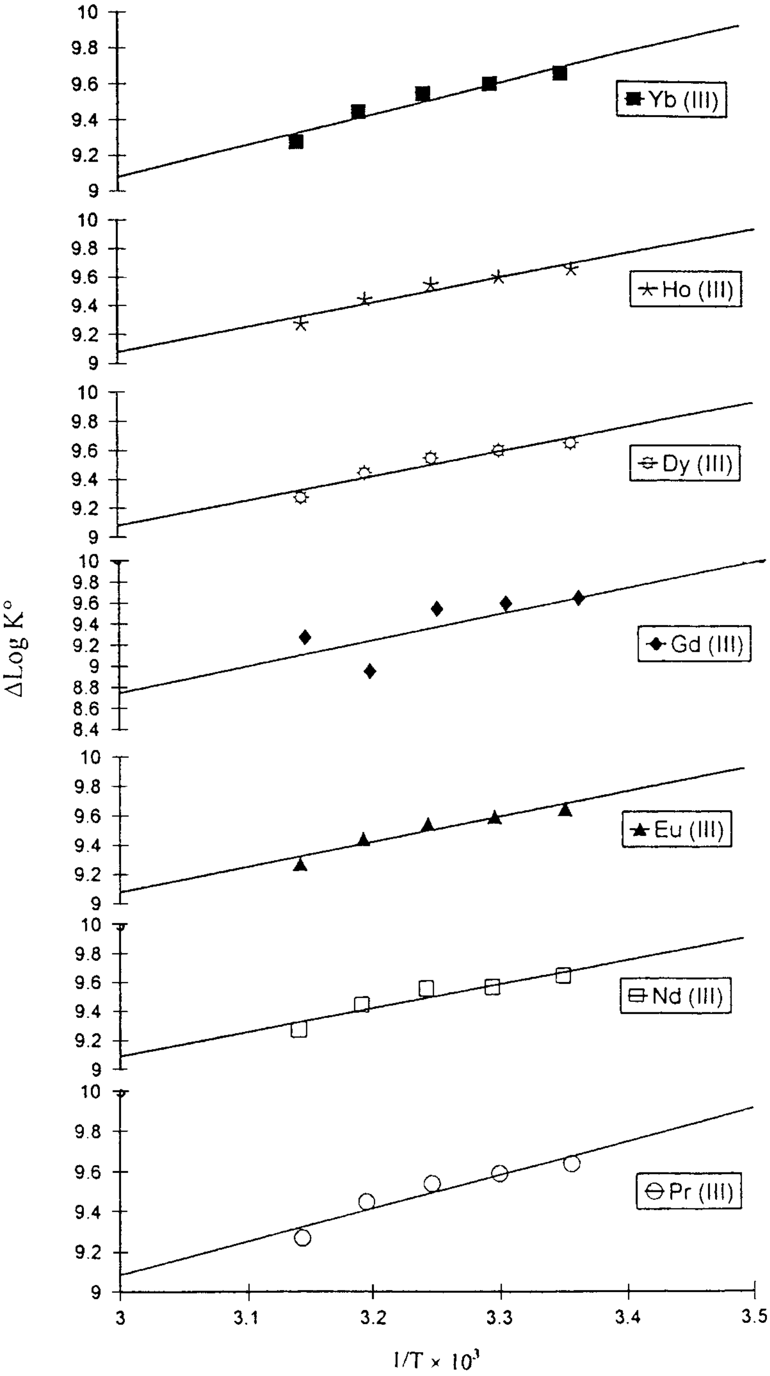


Fig. 5. $\Delta \log K^\circ$ vs. $1/T$ for complexes of glycine with different metal ions.

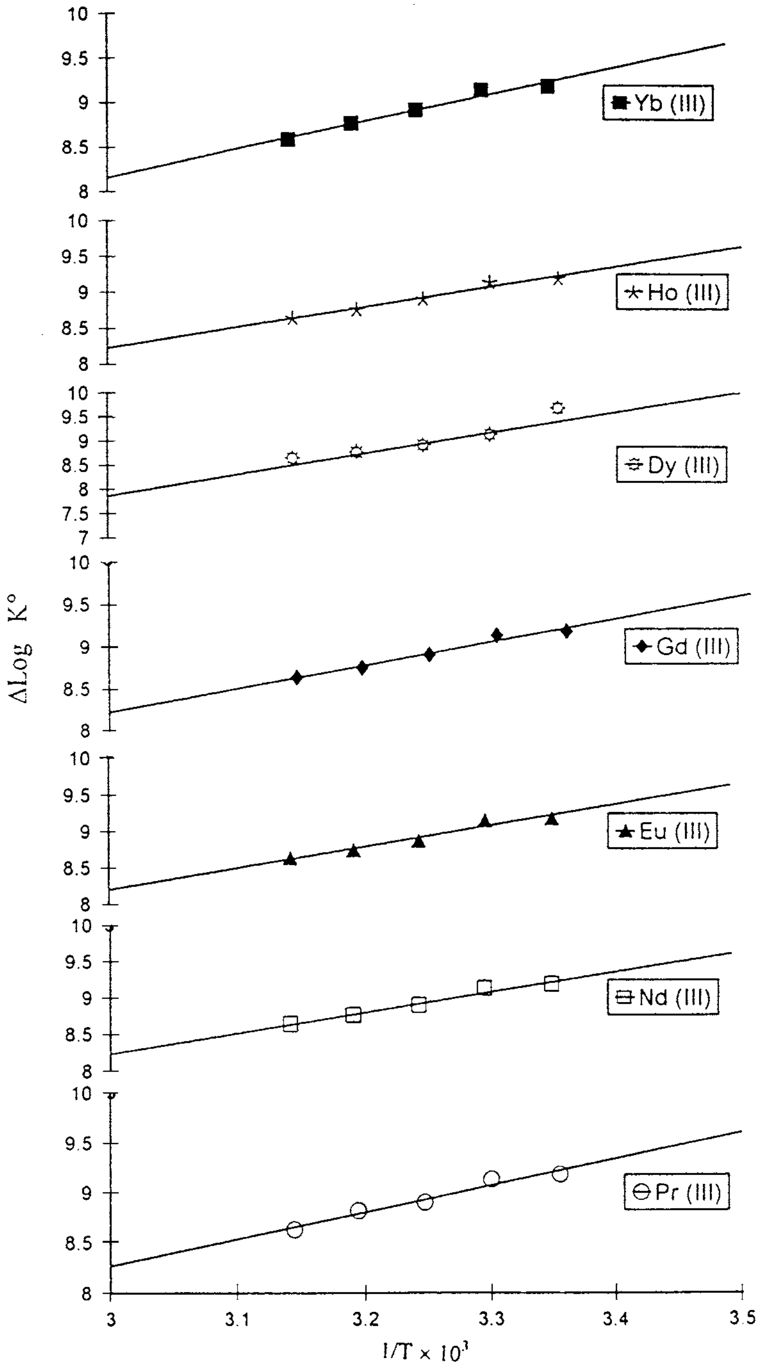


Fig. 6. $\Delta \log K^\circ$ vs. $1/T$ for complexes of L-threonine with different metal ions.

interactions between L-threonine with Dy^{3+} as well as the interactions between glycine with Eu^{3+}, Ho^{3+} and Yb^{3+} which have positive ΔH° values).

In most cases, ΔS° values were negative (with exception of some cases in reaction (I) for the complexations between glycine with Eu^{3+} and Ho^{3+} which have positive ΔS° values). Inspecting ΔS° values, we found that, in most cases ΔS° values for reaction (I) are higher than those for reaction (II). This reflects the more spontaneity of reaction (I) which is characterized by its negative ΔH° values.

Therefore, the high negative ΔG° values for reaction (I) is attributed to the higher contribution of ΔH° term (which indicate that these complexation processes are enthalpy favored processes). If we considered that

$$\Delta \log K^\circ = \log K^\circ(\text{reaction(I)}) - \log K^\circ(\text{reaction(II)}) \tag{16}$$

$$\Delta\Delta G^\circ = \Delta G^\circ(\text{reaction(I)}) - \Delta G^\circ(\text{reaction(II)}) \tag{17}$$

Table 9
The difference of thermodynamic parameters for M^{3+}–glycine complexes

M^{3+}	t (°C)	$\Delta \log K^\circ$	$-\Delta\Delta G^\circ$ (kJ/mol)	$-\Delta\Delta H^\circ$ (kJ/mol)	$\Delta\Delta S^\circ$ (J/K mol)
Pr^{3+}	25	9.64	55.01	31.73	78.19
	30	9.59	55.63		42.88
	35	9.54	56.26		79.64
	40	9.45	57.71		83.30
	45	9.27	56.44		77.71
Nd^{3+}	25	9.64	55.01	31.04	80.44
	30	9.56	55.46		80.59
	35	9.55	56.32		82.08
	40	9.44	56.57		81.57
	45	9.27	56.44		79.88
Eu^{3+}	25	9.64	55.01	32.12	76.81
	30	9.59	55.64		77.62
	35	9.54	56.26		78.37
	40	9.44	56.57		78.11
	45	9.27	56.44		76.47
Gd^{3+}	25	9.64	55.01	50.18	16.20
	30	9.59	55.64		18.02
	35	9.54	56.26		19.74
	40	8.95	53.63		11.02
	45	9.27	56.44		19.68
Dy^{3+}	25	9.64	55.00	32.10	76.75
	30	9.59	55.64		77.59
	35	9.54	56.26		78.35
	40	9.44	56.57		78.08
	45	9.27	56.45		75.88
Ho^{3+}	25	9.64	55.00	32.12	76.78
	30	9.59	55.64		77.62
	35	9.54	56.26		78.38
	40	9.44	56.57		78.11
	45	9.27	56.45		76.51
Yb^{3+}	25	9.64	55.00	32.12	−134.63
	30	9.59	55.64		−130.30
	35	9.54	56.26		−126.17
	40	9.44	56.58		−126.83
	45	9.27	56.45		−121.61

Table 10
The difference of thermodynamic parameters for M^{3+}–L-threonine complexes

M^{3+}	t (°C)	$\Delta \log K^\circ$	$-\Delta\Delta G^\circ$ (kJ/mol)	$-\Delta\Delta H^\circ$ (kJ/mol)	$\Delta\Delta S^\circ$ (J/K mol)
Pr^{3+}	25	9.18	52.38	51.08	4.36
	30	9.13	52.97		6.24
	35	8.90	52.76		4.58
	40	8.82	52.86		5.68
	45	8.63	52.55		4.62
Nd^{3+}	25	9.18	52.37	52.60	−0.77
	30	9.12	52.91		1.02
	35	8.89	52.42		−0.58
	40	8.75	52.44		−0.52
	45	8.64	52.61		0.03
Eu^{3+}	25	9.18	52.38	54.66	−7.65
	30	9.13	52.97		−5.18
	35	8.90	52.49		−5.72
	40	8.75	52.44		−7.29
	45	8.63	52.54		−6.66
Gd^{3+}	25	9.18	52.38	53.67	−4.33
	30	9.15	53.08		−2.31
	35	8.87	52.90		−3.84
	40	8.74	52.38		−3.93
	45	8.63	52.54		−3.56
Dy^{3+}	25	9.67	55.18	48.42	−114.97
	30	9.12	52.91		−120.56
	35	8.90	52.49		−119.97
	40	8.75	52.44		−118.21
	45	8.63	52.54		−116.04
Ho^{3+}	25	9.18	52.38	53.66	−4.30
	30	9.13	52.96		−2.31
	35	8.90	52.49		−3.79
	40	8.75	52.44		−3.89
	45	8.63	52.54		−3.52
Yb^{3+}	25	9.18	52.38	57.94	−18.67
	30	9.13	52.97		−16.41
	35	8.90	52.49		−17.70
	40	8.75	52.44		−17.57
	45	8.57	52.19		−17.75

$$\Delta\Delta H^\circ = \Delta H^\circ(\text{reaction(I)}) - \Delta H^\circ(\text{reaction(II)}) \tag{18}$$

$$\Delta\Delta S^\circ = \Delta S^\circ(\text{reaction(I)}) - \Delta S^\circ(\text{reaction(II)}) \tag{19}$$

to get an idea about the difference between the two suggested reactions.

Figs. 5 and 6 represent the relation between $\Delta \log K^\circ$ against $1/T$. It is obvious a high similarity with those obtained from the plot of $\log K_1^{\circ[L^-]}$ versus $1/T$ (as shown in Figs. 1 and 3).

Tables 9 and 10 include the obtained $\Delta \log K^\circ$, $\Delta\Delta G^\circ$, $\Delta\Delta H^\circ$ and $\Delta\Delta S^\circ$ values. From these data, we feel that the most predominant reaction is reaction (I), this is evidence from the nearly behavior of these functions with those obtained from reaction (I) (i.e. $\log K^\circ$, ΔG°, ΔH° and ΔS° for reaction (I)). Where $\log K^{\circ[L^-]}$ and $\Delta \log K^\circ$ have a similar decrease with increasing the temperature as well as the negative values for ΔG° (for reaction (I)) and $\Delta\Delta G^\circ$. The negative $\Delta\Delta H^\circ$ values reflected the more exothermic nature for reaction (I) than reaction (II), also, the high positive values of $\Delta\Delta S^\circ$ indicate the high disorder of reaction (I) than reaction (II). Therefore, we shall center our research on the study of reaction (I) to gain a better understanding of the factors that control the complexation processes between the different ligands and metal ions under study. Patel and Joshi [5] have been reported that the calculated metal–ligand formation constant values are in agreement with the proton–ligand formation constants of the amino acids. This corresponds to our results, where the interaction of glycine anion with the studied lanthanides ions is comparatively more spontaneous than the corresponding L-threonine anion due to the effective basicity of glycinate ion [5].

Fig. 7 represents the plot of $-\Delta G^\circ$ (at 25 °C) against the ionic radii of the lanthanone(III) ions. In general, we notice that the spontaneity (and stability) of the complex formations were increased with the ionic radii decreased. But in some cases, we found a slight exchange in the position of some metal ion complexes (specially for Eu^{3+} and Gd^{3+} complexes). The electronic configuration of Eu: (Xe) $4f^7$ $6s^2$ and Gd: (Xe) $4f^7$ $5d^1$ $6s^2$, the 4f orbital in each Eu and Gd is half filled, and added to that the interference of 5d orbital in the configuration, so the unlikely situation of Eu and Gd is believed to be due to a change in the spin part of the ground state stabilization energy which causes a much greater reduction in formation constant values [26,27], in order that, a smaller stabilities for Eu^{3+} and Gd^{3+} complexes were expected.

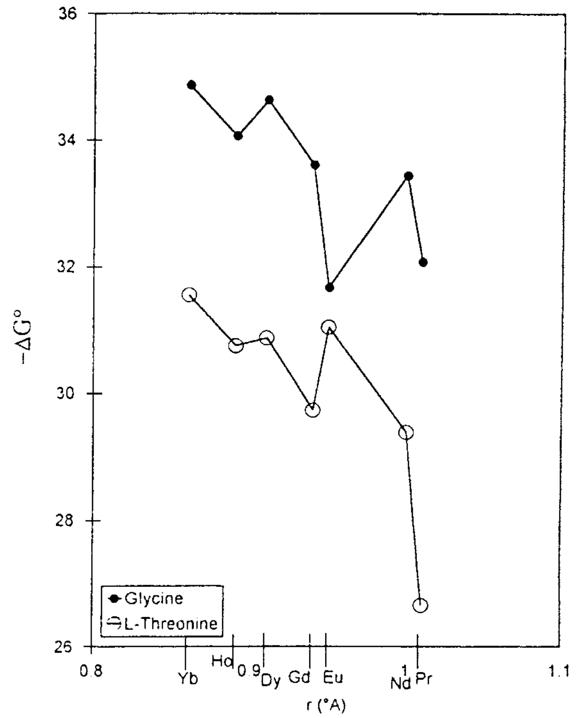


Fig. 7. $-\Delta G^\circ$ ionic radii of lanthanone(III) ions for (●) glycine and (○) L-threonine complexes at 25 °C.

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