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Stability Constants and Thermodynamic Parameters of Complexes of Lanthanide Ions and (±)-Norvaline

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The protonation constants of (±)-norvaline and the stability constants of complexes between lanthanide ions and (±)-norvaline at various ionic strengths (I_c/mol·dm^{-3} = 0.05, 0.10, and 0.15) at 300 K and at different temperatures (T/K = 300, 310, and 320) at I_c = 0.05 mol·dm^{-3} were determined potentiometrically. The potassium nitrate solution was used to maintain the ionic strength. The stability constants show an inverse relationship with ionic strengths. The thermodynamic parameters based on these formation constants were calculated. The values of enthalpy change and entropy change are positive for all systems. The stability order obtained was La(III) < Pr(III) < Nd(III) < Tb(III). The formula of the complex is given and acid−ligand curves are interpreted. The thermodynamic stability constants (log K_n^T) obtained for the complexes of (±)-norvaline with La(III), Pr(III), Nd(III), and Tb(III) were 5.57, 5.94, 5.96, and 6.55, respectively.

Introduction

Amino acids are the structural units of proteins; hence the study of metal−amino acid complexes may lead to a better understanding of structure and binding sites in metalloproteins (Spaulding and Brittain, 1985). The interaction between various metal ions and valine and norvaline has been studied, and the stability constants of these complexes have been determined using different electroanalytical techniques (Palrecha and Gaur, 1979; Matsui, 1981; Arbad and Jahagirdar, 1986; Khuspe and Nemade, 1986; Rao and Mohan, 1989). However, no studies have been reported on the thermodynamics of the complexation reaction between (±)-norvaline and lanthanide ions. The present work deals with the study of complexes of La(III), Pr(III), Nd(III), and Tb(III) with (±)-norvaline at different temperatures and various ionic strengths. The Calvin (1945) and Bjerrum (1957) pH titration technique as modified by Irving and Rossotti (1954) has been employed.

Experimental Section

Materials and Solutions. All the solutions were prepared in double-distilled CO$_2$-free water on mass by volume basis. Metal nitrates were prepared from the corresponding oxides of Analar grade (BDH Laboratory Chemicals, Bombay), and their solutions were standardized by the EDTA method (Schwarzenbach and Flaschka, 1969). The ligand, (±)-norvaline obtained from Fluka, and all other Analar grade inorganic salts were used without further purification. A fresh ligand solution (0.04 mol·dm^{-3}) was prepared just before use. A potassium nitrate solution (2.5 mol·dm^{-3}) was used to maintain constant ionic strength throughout each titration. Carbon-dioxide-free sodium hydroxide solution (0.1515 mol·dm^{-3}) was prepared by Vogel's (1978) method. The concentration of nitric acid (AR) solution was checked against the sodium hydroxide solution and was found to be 0.28 mol·dm^{-3}.

pH Measurements. The pH was measured by a Systronics digital pH-meter 335 using a glass−calomel combined electrode of PPC type CL 51. The pH-meter had a sensitivity of 0.01 units. The pH-meter was calibrated using potassium hydrogen phthalate (0.05 mol·dm^{-3}) in the acidic range and borax solution (0.01 mol·dm^{-3}) in the basic range, before every titration. All titrations were carried out in a double-jacketed glass cell. The temperature was maintained by circulating water from the thermostat

Table 1. Determination of Proton−Ligand Stability Constants (pK_{1a}) at $\bar{n}$ = 1.5

pH	V_A	V_L	$V_L - V_A$	$\bar{n}_{A(expt)}$	$\bar{n}_{A(cal)}$
I_c = 0.05 mol·dm^{-3}; T = 300 K					
2.2	5.850	5.100	−0.750	1.593	1.605
2.3	6.275	5.563	−0.712	1.559	1.550
2.4	6.650	6.000	−0.650	1.507	1.494
2.5	6.925	6.363	−0.562	1.436	1.439
2.6	7.125	6.638	−0.487	1.377	1.383
I_c = 0.10 mol·dm^{-3}; T = 300 K					
2.10	5.000	4.275	−0.725	1.582	1.595
2.15	5.300	4.600	−0.700	1.559	1.570
2.20	5.600	4.900	−0.700	1.556	1.545
2.25	5.850	5.150	−0.700	1.554	1.521
2.30	6.075	5.450	−0.625	1.492	1.496
2.35	6.300	5.700	−0.600	1.471	1.471
2.40	6.500	5.950	−0.550	1.430	1.446
I_c = 0.15 mol·cm^{-3}; T = 300 K					
2.00	4.200	3.450	−0.750	1.611	1.604
2.05	4.600	3.875	−0.725	1.587	1.584
2.10	5.000	4.300	−0.700	1.562	1.565
2.15	5.325	4.650	−0.675	1.539	1.545
2.20	5.625	4.975	−0.650	1.516	1.526
2.25	5.860	5.225	−0.635	1.502	1.506
2.30	6.100	5.475	−0.625	1.492	1.487
2.35	6.300	5.700	−0.600	1.471	1.467
2.40	6.475	5.900	−0.575	1.450	1.448
2.45	6.650	6.100	−0.550	1.429	1.428
2.50	6.800	6.275	−0.525	1.408	1.409
I_c = 0.05 mol·dm^{-3}; T = 310 K					
2.10	5.700	4.938	−0.763	1.605	1.606
2.20	6.163	5.450	−0.713	1.561	1.551
2.30	6.500	5.875	−0.625	1.489	1.495
2.40	6.775	6.225	−0.550	1.428	1.440
2.50	7.020	6.513	−0.508	1.394	1.384
I_c = 0.05 mol·dm^{-3}; T = 320 K					
1.70	3.700	2.825	−0.875	1.720	1.797
1.80	4.550	3.675	−0.875	1.709	1.694
1.90	5.250	4.375	−0.875	1.700	1.590
2.00	5.710	5.100	−0.610	1.484	1.487
2.10	6.075	5.590	−0.485	1.382	1.383
2.20	6.300	6.000	−0.300	1.235	1.280

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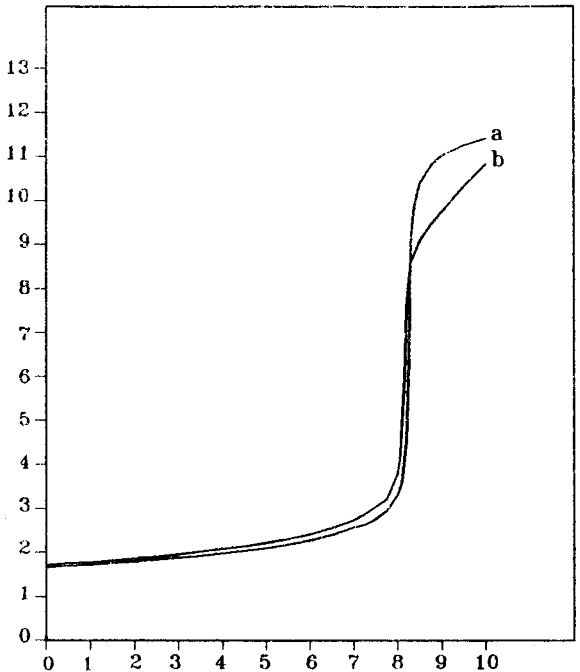


Figure 1. pH against volume of 0.1515 mol·dm^{-3} NaOH at I_c = 0.10 mol·dm^{-3} and at 300 K: (a) 2.52 × 10^{-2} mol·dm^{-3} nitric acid; (b) (a) + 4 × 10^{-3} mol·dm^{-3} (±)-norvaline.

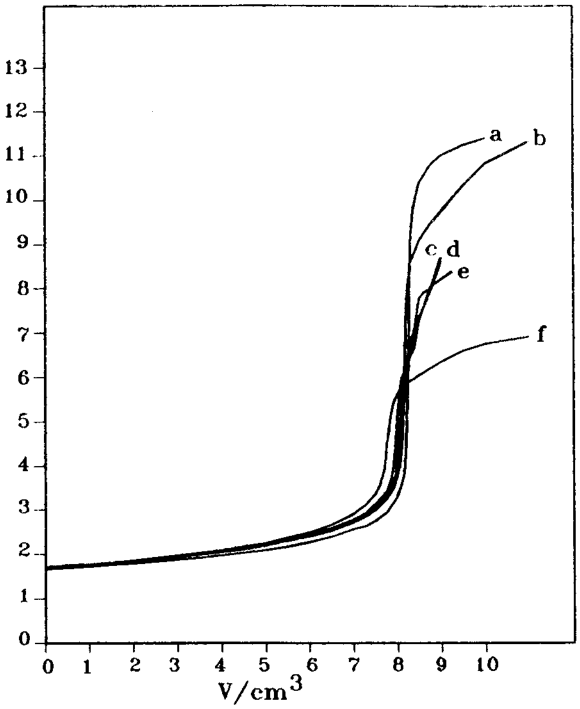


Figure 2. pH against volume of 0.1515 mol·dm^{-3} NaOH at I_c = 0.10 mol·dm^{-3} and at 300 K: (a) 2.52 × 10^{-2} mol·dm^{-3} nitric acid; (b) (a) + 4 × 10^{-3} mol·dm^{-3} (±)-norvaline; (a) + (b) + 1 × 10^{-3} mol·dm^{-3} metal ion solution of (c) La(III), (d) Pr(III), (e) Nd(III), or (f) Tb(III).

through the outer jacket of the cell. The thermostat was constant to 0.1 K. The following three sets of titrations were carried out in sequence:

(a) Acid titration: 4.5 cm^3 of nitric acid (0.28 mol·dm^{-3}). (b) Ligand titration: 4.5 cm^3 of nitric acid (0.28 mol·dm^{-3}) + 5 cm^3 of ligand solution (0.04 mol·dm^{-3}). (c) Metal titration: 4.5 cm^3 of nitric acid (0.28 mol·dm^{-3}) + 5 cm^3 of ligand solution (0.04 mol·dm^{-3}) + 5 cm^3 of metal solution (0.01 mol·dm^{-3}).

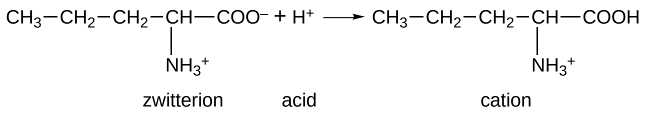
Table 2. Determination of Proton–Ligand Stability Constants (pK_{2a}) at $\bar{n}$ = 0.5

pH	V_A	V_L	$V_L - V_A$	$\bar{n}_{A(expt)}$	$\bar{n}_{A(cal)}$
I_c = 0.05 mol·dm^{-3}; T = 300 K					
09.50	8.295	8.704	0.409	0.690	0.689
09.60	8.303	8.798	0.495	0.625	0.625
09.70	8.308	8.888	0.580	0.561	0.561
09.80	8.310	8.975	0.665	0.496	0.497
09.90	8.320	9.067	0.747	0.434	0.433
10.00	8.335	9.168	0.833	0.369	0.369
I_c = 0.10 mol·dm^{-3}; T = 300 K					
09.50	8.330	8.770	0.440	0.667	0.666
09.55	8.330	8.815	0.485	0.633	0.636
09.60	8.335	8.855	0.520	0.606	0.606
09.65	8.340	8.900	0.560	0.576	0.575
09.70	8.345	8.945	0.600	0.546	0.545
09.75	8.350	8.995	0.645	0.512	0.515
09.80	8.355	9.023	0.668	0.494	0.485
09.85	8.363	9.090	0.728	0.449	0.455
09.90	8.370	9.130	0.760	0.425	0.425
I_c = 0.15 mol·dm^{-3}; T = 300 K					
09.50	8.330	8.890	0.560	0.576	0.577
09.55	8.340	8.935	0.595	0.549	0.547
09.60	8.345	8.985	0.640	0.515	0.517
09.65	8.350	9.025	0.675	0.489	0.487
09.70	8.360	9.080	0.720	0.455	0.456
09.75	8.368	9.125	0.757	0.427	0.426
09.80	8.375	9.175	0.800	0.395	0.396
I_c = 0.05 mol·dm^{-3}; T = 310 K					
09.40	8.222	8.738	0.516	0.608	0.610
09.50	8.240	8.815	0.575	0.564	0.560
09.60	8.260	8.905	0.645	0.511	0.509
09.70	8.287	9.010	0.723	0.452	0.459
09.80	8.330	9.110	0.780	0.409	0.408
09.90	8.363	9.210	0.847	0.359	0.357
I_c = 0.05 mol·dm^{-3}; T = 320 K					
09.30	8.233	8.777	0.545	0.587	0.586
09.35	8.235	8.820	0.585	0.556	0.557
09.40	8.240	8.860	0.620	0.530	0.529
09.45	8.242	8.902	0.660	0.499	0.501
09.50	8.245	8.943	0.698	0.471	0.472
09.55	8.249	8.980	0.731	0.446	0.444

The mole ratio of metal to ligand was kept 1:4 in order to fulfill the maximum coordination number of the metal ion. In every set of titrations, the required volume of the potassium nitrate solution (stock solution of 2.5 mol·dm^3) was added to maintain constant ionic strength. The total volume of the reaction mixture was made to 50 cm^3 using double-distilled CO$_2$-free water, and then the reaction mixture was titrated against standard NaOH (0.1515 mol·dm^{-3}). Every titration was carried out three times, and the average was used for further calculations.

Results and Discussion

Figure 1 shows the nature of the acid curve and ligand curve. In the initial stages of titration the pH values of the ligand curve are slightly higher than the corresponding values of the acid curve at the same low volume of alkali added. This is due to the formation of the cation of (±)-norvaline (Yonezawa et al., 1964; Sandhu and Kalia, 1979) resulting in the decrease in H$^+$ ion concentration of the reaction mixture in the ligand titration.



$$CH_3-CH_2-CH_2-\underset{NH_3^+}{\underset{|}{CH}}-COO^- + H^+ \longrightarrow CH_3-CH_2-CH_2-\underset{NH_3^+}{\underset{|}{CH}}-COOH$$

This cation of the amino acid has two dissociable protons, one from the carboxylate group and another from the ammonium group.

Table 3. Proton−Ligand Stability Constants of (±)-Norvaline

T/K	I_c/mol·dm^{-3}	pK_{1a}	pK_{2a}
300	0.05	2.39	9.80
300	0.10	2.29[a]	9.78[a]
300	0.15	2.26	9.63
310	0.05	2.29	9.62
320	0.05	1.98	9.45

[a] The reported values of proton−ligand stability constants are pK_{1a} = 2.30, pK_{2a} = 9.80 at I_c = 0.10 mol·dm^{-3} and 298 K (Sekhon and Chopra, 1973).

Table 4. Determination of Metal−Ligand Stability Constants at T = 300 K and I_c = 0.05 mol·dm^{-3}

pH	V_A	V_L	V_M	$V_M - V_L$	$\bar{n}_{(expt)}$	$\bar{n}_{(cal)}$	pL
La(III)							
6.80	8.192	8.082	8.230	0.148	0.450	0.448	5.515
6.90	8.195	8.085	8.248	0.163	0.496	0.494	5.421
7.00	8.196	8.090	8.265	0.175	0.532	0.541	5.326
7.10	8.200	8.094	8.288	0.194	0.590	0.586	5.233
7.20	8.203	8.098	8.306	0.208	0.633	0.632	5.139
Pr(III)							
6.40	8.184	8.057	8.197	0.140	0.425	0.412	5.912
6.50	8.186	8.064	8.212	0.148	0.450	0.463	5.815
6.60	8.188	8.070	8.236	0.166	0.504	0.511	5.722
6.70	8.190	8.076	8.260	0.184	0.559	0.560	5.629
6.80	8.192	8.082	8.285	0.203	0.617	0.609	5.536
Nd(III)							
6.30	8.183	8.050	8.155	0.105	0.319	0.353	5.999
6.40	8.184	8.057	8.202	0.145	0.440	0.423	5.914
6.50	8.186	8.064	8.240	0.176	0.535	0.496	5.825
6.60	8.188	8.070	8.260	0.190	0.577	0.574	5.731
6.70	8.190	8.076	8.282	0.206	0.626	0.651	5.637
Tb(III)							
5.80	8.169	8.007	8.133	0.126	0.383	0.372	6.506
5.90	8.173	8.015	8.173	0.158	0.480	0.491	6.416
6.00	8.175	8.025	8.221	0.196	0.595	0.606	6.333
6.10	8.178	8.034	8.273	0.239	0.726	0.718	6.250
6.20	8.180	8.042	8.317	0.275	0.835	0.833	6.165

Table 5. Determination of Metal−Ligand Stability Constants at T = 300 K and I_c = 0.10 mol·dm^{-3}

pH	V_A	V_L	V_M	$V_M - V_A$	$\bar{n}_{(expt)}$	$\bar{n}_{(cal)}$	pL
La(III)							
6.70	8.255	8.173	8.290	0.117	0.355	0.347	5.584
6.80	8.257	8.177	8.310	0.133	0.404	0.411	5.490
6.90	8.258	8.180	8.334	0.154	0.468	0.474	5.398
7.00	8.260	8.183	8.360	0.177	0.538	0.536	5.307
7.10	8.263	8.187	8.385	0.198	0.602	0.598	5.216
Pr(III)							
6.50	8.252	8.167	8.274	0.107	0.325	0.334	5.781
6.60	8.253	8.170	8.310	0.140	0.425	0.426	5.693
6.70	8.255	8.173	8.348	0.175	0.531	0.516	5.606
6.80	8.257	8.177	8.380	0.203	0.616	0.608	5.517
6.90	8.258	8.180	8.407	0.227	0.689	0.702	5.426
Nd(III)							
6.30	8.247	8.160	8.240	0.080	0.243	0.227	5.971
6.40	8.249	8.163	8.279	0.116	0.352	0.347	5.884
6.50	8.252	8.167	8.308	0.141	0.428	0.473	5.793
6.60	8.253	8.170	8.364	0.194	0.589	0.583	5.713
6.70	8.255	8.173	8.409	0.236	0.716	0.698	5.630
Tb(III)							
5.85	8.236	8.146	8.200	0.054	0.164	0.147	6.412
5.90	8.238	8.148	8.260	0.112	0.340	0.370	6.382
5.95	8.238	8.149	8.331	0.182	0.552	0.548	6.358
6.00	8.240	8.151	8.396	0.245	0.743	0.734	6.333

Table 6. Determination of Metal−Ligand Stability Constants at T = 300 K and I_c = 0.15 mol·dm^{-3}

pH	V_A	V_L	V_M	$V_M - V_L$	$\bar{n}_{(expt)}$	$\bar{n}_{(cal)}$	pL
La(III)							
6.90	8.210	8.178	8.315	0.137	0.417	0.402	5.242
7.00	8.213	8.188	8.338	0.150	0.456	0.462	5.147
7.10	8.216	8.200	8.365	0.165	0.502	0.522	5.053
7.20	8.218	8.210	8.398	0.188	0.573	0.579	4.963
7.30	8.223	8.220	8.434	0.214	0.652	0.636	4.873
Pr(III)							
6.60	8.203	8.148	8.280	0.132	0.401	0.418	5.540
6.70	8.205	8.158	8.319	0.161	0.489	0.475	5.451
6.80	8.208	8.168	8.348	0.180	0.547	0.536	5.358
6.90	8.210	8.178	8.375	0.197	0.599	0.596	5.265
7.00	8.213	8.188	8.400	0.212	0.645	0.656	5.171
Nd(III)							
6.40	8.195	8.128	8.214	0.086	0.261	0.309	5.723
6.50	8.201	8.138	8.276	0.138	0.419	0.398	5.642
6.60	8.203	8.148	8.323	0.175	0.532	0.493	5.556
6.70	8.205	8.158	8.365	0.207	0.629	0.589	5.468
6.80	8.208	8.168	8.380	0.212	0.644	0.696	5.371
Tb(III)							
5.90	8.155	8.078	8.130	0.052	0.158	0.141	6.211
5.95	8.160	8.082	8.180	0.098	0.298	0.309	6.177
6.00	8.163	8.086	8.235	0.149	0.453	0.467	6.145
6.05	8.168	8.091	8.290	0.199	0.605	0.620	6.114
6.10	8.171	8.095	8.350	0.255	0.775	0.753	6.087

Table 7. Determination of Metal−Ligand Stability Constants at T = 310 K and I_c = 0.05 mol·dm^{-3}

pH	V_A	V_L	V_M	$V_M - V_A$	$\bar{n}_{(expt)}$	$\bar{n}_{(cal)}$	pL
La(III)							
6.40	8.073	8.028	8.166	0.138	0.420	0.405	5.731
6.50	8.082	8.043	8.188	0.145	0.441	0.450	5.634
6.60	8.085	8.055	8.215	0.160	0.487	0.492	5.540
6.70	8.101	8.063	8.236	0.173	0.527	0.536	5.445
6.80	8.107	8.069	8.257	0.188	0.573	0.578	5.351
6.90	8.110	8.074	8.282	0.208	0.634	0.620	5.259
Pr(III)							
6.10	8.050	7.988	8.110	0.122	0.371	0.371	6.025
6.20	8.058	8.000	8.145	0.145	0.441	0.444	5.933
6.30	8.065	8.015	8.185	0.170	0.518	0.516	5.843
6.40	8.073	8.028	8.222	0.194	0.591	0.588	5.752
6.50	8.082	8.043	8.259	0.216	0.658	0.661	5.661
Nd(III)							
6.00	8.043	7.975	8.103	0.128	0.390	0.395	6.127
6.05	8.047	7.981	8.125	0.144	0.438	0.437	6.083
6.10	8.050	7.988	8.148	0.160	0.487	0.480	6.039
6.15	8.054	7.994	8.167	0.173	0.527	0.524	5.994
6.20	8.058	8.000	8.185	0.185	0.563	0.569	5.948
Tb(III)							
5.35	8.002	7.927	8.065	0.138	0.420	0.422	6.780
5.40	8.005	7.928	8.089	0.161	0.490	0.490	6.739
5.45	8.008	7.930	8.115	0.185	0.563	0.559	6.698
5.50	8.011	7.933	8.139	0.206	0.627	0.629	6.656
5.55	8.014	7.936	8.165	0.229	0.697	0.698	6.615

In the present study, the proton−ligand stability constants for (±)-norvaline and the metal−ligand stability constants for the complexes of La(III), Pr(III), Nd(III), and Tb(III) with (±)-norvaline were determined by carrying out the acid, ligand, and metal titrations initially by keeping the temperature constant to 300 K and varying the ionic strengths (I_c/mol·dm^{-3}) = 0.05, 0.10, and 0.15) and later by maintaining the ionic strength at I_c = 0.05 mol·dm^{-3} and changing the temperature to 310 K and 320 K. Figure 2 exhibits a set of acid, ligand, and four metal titration curves at I_c = 0.10 mol·dm^{-3} and T = 300 K. At higher volumes of alkali added, the relatively large drop in pH in metal titrations (curves c−e) with respect to the ligand titration (curve b) and the appearance of precipitate both confirm the formation of the metal complex (Martell and Calvin, 1956).

The acid dissociation constant (pK_a) has an inverse relationship with the protonation constant (pK^H) (Irving and Rossotti, 1954). Hence, in the present work pK_1^H equals pK_{2a} and pK_2^H is the pK_{1a}. These protonation constants were determined from the graph of $\bar{n}_{A(cal)}$ v/s pH (half-integral method) where the pH values at $\bar{n}_A = 0.5$ and

Table 8. Determination of Metal−Ligand Stability Constants at $T = 320$ K and $I_c = 0.05$ mol·dm^{-3}

pH	V_A	V_L	V_M	$V_M - V_A$	$\bar{n}_{(expt)}$	$\bar{n}_{(cal)}$	pL
				La(III)			
6.10	7.970	7.962	8.070	0.108	0.329	0.295	5.850
6.20	7.982	7.965	8.090	0.125	0.381	0.396	5.756
6.30	7.995	7.970	8.123	0.153	0.466	0.491	5.666
6.40	8.009	7.981	8.157	0.176	0.537	0.588	5.575
6.50	8.023	7.987	8.225	0.238	0.726	0.668	5.500
				Pr(III)			
5.90	7.944	7.956	8.099	0.143	0.436	0.415	6.062
5.95	7.950	7.957	8.120	0.163	0.497	0.518	6.020
6.00	7.955	7.959	8.155	0.196	0.598	0.611	5.982
6.05	7.964	7.960	8.190	0.230	0.701	0.700	5.946
6.10	7.970	7.962	8.225	0.263	0.802	0.790	5.909
				Nd(III)			
5.50	7.895	7.950	8.100	0.150	0.458	0.440	6.465
5.60	7.908	7.950	8.110	0.160	0.488	0.482	6.369
5.70	7.919	7.953	8.120	0.167	0.509	0.526	6.271
5.80	7.931	7.955	8.133	0.178	0.543	0.568	6.176
5.90	7.944	7.956	8.150	0.194	0.592	0.609	6.082
6.00	7.955	7.959	8.183	0.224	0.683	0.648	5.994
				Tb(III(			
4.70	7.820	7.923	8.055	0.132	0.403	0.362	7.259
4.75	7.825	7.925	8.070	0.145	0.442	0.474	7.213
4.80	7.828	7.928	8.100	0.172	0.525	0.569	7.174
4.85	7.833	7.930	8.145	0.215	0.656	0.651	7.140
4.90	7.835	7.934	8.185	0.251	0.766	0.736	7.105

Table 9. Metal−Ligand Stability Constants at Various Ionic Strengths and $T = 300$ K

	log K_1			
I_c/mol·dm^{-3}	La(III)	Pr(III)	Nd(III)	Tb(III)
0.05	5.41 ± 0.02	5.74 ± 0.01	5.82 ± 0.04	6.41 ± 0.02
0.10	5.36 ± 0.01	5.62 ± 0.01	5.77 ± 0.02	6.36 ± 0.00
0.15	5.09 ± 0.02	5.41 ± 0.02	5.55 ± 0.04	6.14 ± 0.00

Table 10. Metal−Ligand Stability Constants at Various Temperatures and $I_c = 0.05$ mol·dm^{-3}

	log K_1			
T/K	La(III)	Pr(III)	Nd(III)	Tb(III)
300	5.41 ± 0.02	5.74 ± 0.01	5.82 ± 0.04	6.41 ± 0.02
310	5.52 ± 0.02	5.86 ± 0.00	6.02 ± 0.01	6.73 ± 0.00
320	5.66 ± 0.04	6.03 ± 0.02	6.33 ± 0.05	7.20 ± 0.01

$\bar{n}_A = 1.5$ designate pK_1^H and pK_2^H, respectively (Bjerrum, 1957). The $\bar{n}_{A(expt)}$ values were calculated from the following equation (Tables 1 and 2).

$$\bar{n}_{A(expt)} = Y - \frac{(V_L - V_A)(N + E°)}{(V_o + V_A)T_L^{\circ}} \qquad (1)$$

where Y denotes the number of dissociable protons initially present on the ligand; in the present case it is 1. N is the concentration of sodium hydroxide (0.1515 mol·dm^{-3}). $V_L - V_A$ is the measure of the displacement of the ligand curve relative to the acid curve where V_L and V_A are the volumes of alkali added to reach the same pH reading. To get accurate values of $V_L - V_A$, the titration curves were drawn on an enlarged scale. To avoid errors, those portions of the curves where separation between these curves was very small, were rejected. $E°$ and T_L° are the resultant concentrations of nitric acid (0.0252 mol·dm^{-3}) and (±)-norvaline (0.004 mol·dm^{-3}) in the reaction mixture, respectively. V_o is the initial volume of the reaction mixture (50 cm^3). $\bar{n}_{A(expt)}$ values were refined by applying the linear least squares method and thus the $\bar{n}_{A(cal)}$ values were calculated. The standard deviation in terms of $\Delta\bar{n}_A$ (Irving and Rossotti, 1953) had a maximum value of ±0.016. The practical protonation constants were then confirmed by Schwarzenbach's (1947) graphical method. As expected, the practical proton−ligand stability constants show an inverse relationship with ionic strength as well as temperature (Table 3), and the values so obtained are in good agreement with the reported work (Sekhon and Chopra, 1973).

Similarly, the metal−ligand stability constants were determined by the half-integral method by plotting $\bar{n}_{(cal)}$ v/s pL. The experimental $\bar{n}$ values were determined using the expression

$$\bar{n}_{(expt)} = \frac{(V_M - V_L)(N + E°)}{(V_o + V_A)T_M^{\circ}\bar{n}_H} \qquad (2)$$

N, $E°$, V_o, V_A, and V_L have the same significance as in eq 1. $V_M - V_L$ gives the relative shift in the titration curves of the metal and the ligand curve, where V_M is the volume of alkali added in the metal titration to attain the given pH reading and T_M° (0.001 mol·dm^{-3}) is the concentration of metal ion in the reaction mixture. However, values of Bjerrum's (1957) formation function $\bar{n}_H$ were determined from the following equation:

$$\bar{n}_H = \frac{pK_1^H(1/\text{antilog } B) + 2pK_1^H pK_2^H(1/\text{antilog } B)^2}{1 + pK_1^H(1/\text{antilog } B) + pK_1^H pK_2^H(1/\text{antilog } B)^2} \qquad (3)$$

These $\bar{n}_H$ values were considered up to the sixth decimal place so as to get a good difference between consecutive $\bar{n}_H$ values. The pL values were calculated from the relation

$$\text{pL} = \log\{[1 + pK_1^H(1/\text{antilog } B) + pK_1^H pK_2^H(1/\text{antilog } B)^2[(V_o + V_L)/V_o]/[T_L^{\circ} - [T_M^{\circ}\bar{n}_{(expt)}]]\} \qquad (4)$$

The $\bar{n}_{(expt)}$ values (Tables 4−8) remain within the range of 0.10 to 0.90, indicating the formation of a 1:1 complex. $\bar{n}_{(expt)}$ is the degree of formation of the complex, and it gives the average number of the ligands attached to the metal ion. The $\bar{n}_{(expt)}$ values were also refined by the linear least squares method to get $\bar{n}_{(cal)}$ values. Out of all the metal complexes studied Nd−norvalinate at 300 K and $I_c = 0.15$ mol·dm^{-3} shows the maximum standard deviation in terms of $\Delta\bar{n}$ ($\sigma = \pm 0.041$). The pL values corresponding to $\bar{n}_{(cal)} = 0.5$ are taken as log K_1 where K_1 is the stoichiometric stability constant. These log K_1 values were confirmed by the linear plot method as per the equation log K_1 = pL − log(1 − $\bar{n}/\bar{n}$). The stoichiometric stability constant values so obtained increase from La(III) to Tb(III) independent of

Table 11. Metal−Ligand Stability Constants and the Thermodynamic Parameters of Complexes of (±)-Norvaline at Various Temperatures and $I_c = 0.05$ mol·dm^{-3}

	−Δ$G°$/kJ·mol^{-1}			+Δ$H°$/kJ·mol^{-1}	+Δ$S°$/J·mol^{-1}·K^{-1}
complex	300 K	310 K	320 K	310 K	310 K
La−(±)-norvalinate	31.08 ± 0.12	32.76 ± 0.12	34.68 ± 0.25	22.98 ± 1.82	180.00 ± 10.00
Pr−(±)-norvalinate	32.97 + 0.06	34.78 ± 0.00	36.95 ± 0.13	26.64 ± 0.89	200.00 ± 0.00
Nd−(±)-norvalinate	33.43 ± 0.23	35.73 ± 0.06	38.78 ± 0.31	46.84 ± 0.86	270.00 ± 0.00
Tb−(±)-norvalinate	36.82 ± 0.11	39.95 ± 0.00	44.12 ± 0.07	72.57 ± 0.95	360.00 ± 0.00

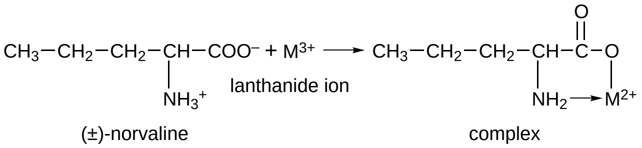
Table 12. Thermodynamic Metal−Ligand Stability Constants at $T = 300$ K

complex	log K^{T}_{n}
La−(±)-norvalinate	5.57
Pr−(±)-norvalinate	5.94
Nd−(±)-norvalinate	5.96
Tb−(±)-norvalinate	6.55

temperature or ionic strength (Tables 9 and 10); hence the stability order can be written as La(III) < Pr(III) < Nd(III) < Tb(III) which is in the natural order of their ionic radii (Shannon and Prewitt, 1970). A glance at Table 9 shows that the metal−ligand stability constants decrease on increasing the ionic strength, which is in agreement with Debye−Huckel limiting law; however, the rise in temperature favors the complexation reaction (Table 10).

The $\Delta G°$ values evaluated using the relationship $\Delta G° = -2.303RT \log K_1$ are negative; hence the complexation reaction is spontaneous (Table 11). The $\Delta H°$ values determined from the slope of the graph of log K_1 vs T^{-1} are positive, exhibiting the endothermic nature of the reaction. The $\Delta S°$ values calculated using Gibb's equation are positive, confirming that the chelation effect is essentially an entropy effect (Sekhon and Chopra, 1973). The thermodynamic stability constants log K^{T}_{n} were determined by extrapolating the graph of log K_1 v/s $(I_c)^{1/2}$ to zero ionic strength (Table 12).

The chelation of peptide with lanthanide ion appears to be through the terminal nitrogen forming the coordinate covalent bond and the peptide oxygen forming the covalent bond as follows (Martell and Calvin, 1956).



$$CH_3{-}CH_2{-}CH_2{-}\underset{NH_3^+}{CH}{-}COO^- + M^{3+} \longrightarrow CH_3{-}CH_2{-}CH_2{-}\underset{NH_2 \rightarrow M^{2+}}{CH}{-}\overset{O}{\overset{\|}{C}}{-}O$$

These complexes may find an application in the separation of rare-earth metals (Lal, 1972), and as copper−valinate complexes (Namasivayam and Natarajan, 1983) these complexes may be tried as initiators in vinyl polymerization.

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