

Leucine Complexes with Cerium: Stability Constants and Thermodynamic Parameters

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ABSTRACT: The complexation of leucine (Leu) with Ce^{3+} was investigated using the potentiometric method at different ionic strengths ($I = (0.10 \text{ and } 1.00) \text{ mol dm}^{-3}$) in KCl medium at elevated temperatures. The stability constants of the leucine complexes with Ce^{3+} at metal:ligand (M:L) molar ratios of 1:1, 1:3, and 1:5 were determined. From the data obtained, stability constants were calculated using the program HYPERQUAD2006 for proton–ligand and metal–ligand species. The formation of monomeric species was taken into consideration for Ce^{3+} at (25, 37, and 45) °C. Thermodynamic parameters were calculated for all possible leucine complexes. In conclusion, it is indicated that the formation of complexes change the value of the stability constants at various ionic strengths and temperatures.

INTRODUCTION

Amino acids are important low molecular weight ligands in humans and other biosystems. In addition, the reactivity of amino acids and other small organic molecules is often modified when they form complexes with metal ions. In principle, acidic, polar, and basic amino acids can bind metal ions through a mixture of available donor groups that include α -carboxylate and α -amino groups. Amino acids have been used as primary ligands and a large amount of research concerning metal amino acid complexation has been reported. There are many areas of application in chemistry, biology, and medicine. Also the importance of amino acid–metal ion interactions is well-known in medicinal chemistry.^{1,2} Stability constants provide information required to calculate the concentrations of the complexes in solution. Stability constant values are exploited in a wide variety of applications. 2-Amino-4-methylpentanoic acid, leucine (Leu), is a very important bioligand for the health of humans and animals. Leu, an exogenous amino acid including one carboxyl group and one amino group (Figure 1), exists in several proteins. Every free amino acid has at least two pK_a values: the one associated with the protonation of the carboxylate and the other associated with the deprotonation of the amine group.³

There have been many studies aimed at designing ligands remove to actinides and lanthanides from biological systems. The complexes of various metal ions with amino acids, and other ligands have been reported by several workers. In addition, it is well-known that lanthanide ions form strong complexes with organic ligands. Cerium, Ce^{3+} , is a subject of increasing interest in bioinorganic and coordination chemistry.⁴

The present paper reports on studies of the stability constants of complexes of leucine with, Ce^{3+} potentiometrically at elevated temperatures in a KCl medium. The stability constants of the complexation species of leucine with Ce^{3+} were simulated using the HySS program⁵ and were computed with the aid of the HYPERQUAD2006 computer program.⁶ Furthermore, thermodynamic parameters were derived and discussed by utilizing this data.

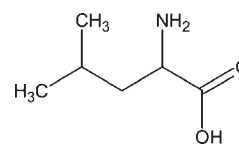


Figure 1. Structural formula of leucine.

EXPERIMENTAL SECTION

Materials and Solutions. Leucine, the nitrate salt of cerium, potassium chloride, hydrochloric acid, and sodium hydroxide were of analytical grade from Merck. All solutions were prepared with bidistilled and carbon dioxide-free water. The aqueous stock solutions of leucine were prepared daily and stored in the dark. KCl was used to adjust the ionic strength of the media.

Apparatus and Procedure. Potentiometric measurements of the pH were performed on a titrator (Schott Titroline Alpha) with a pH-combination electrode (Schott BlueLine). The electrode was also equipped with a temperature probe. The electrode system was calibrated daily with buffer solutions prepared from Merck buffer powders at pH 4.00 and 7.00 at 25 °C. Potentiometric titrations were carried out in a magnetically stirred, water-jacketed cell of 100 cm³ (Schott). It was loosely fitted with a special cover, through which could be inserted the tip of titrator's dosing unit, the electrode and nitrogen inlet and outlet tubes. When water from a thermostat (Grant W14) was circulated through the jacket of the cell, the temperature of the solution to be titrated was kept constant. The titrations were carried out in an inert atmosphere by bubbling purified nitrogen through the solutions.

The results of strong acid versus alkali titrations were analyzed using a computer program named GLEE (glass electrode evaluation).

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Table 1. Summary of the Numerical Values for Complexation Species of Leu with Ce^{3+} Ion at (25, 37, and 45) °C^a

<i>I</i> (mol dm ⁻³)	metal:ligand (M:L) molar ratio	pH range		
		<i>t</i> = 25 °C	<i>t</i> = 37 °C	<i>t</i> = 45 °C
0.10	1:1	2.77–11.00 (130 data)	2.60–10.74 (133 data)	3.27–10.54 (125 data)
	1:3	2.76–11.00 (223 data)	2.77–10.77 (214 data)	2.68–10.62 (231 data)
	1:5	3.08–9.80 (150 data)	3.00–9.98 (174 data)	2.96–9.83 (185 data)
1.00	1:1	2.75–10.83 (158 data)	2.73–10.99 (195 data)	2.70–11.05 (214 data)
	1:3	2.76–10.11 (203 data)	2.73–10.10 (212 data)	2.73–10.10 (209 data)
	1:5	3.11–9.88 (201 data)	3.04–10.01 (217 data)	3.05–10.11 (227 data)

^a Concentration of leucine was 0.25 mmol dm⁻³ for protonation in the pH range 2.98–9.37 (for 62 data) at 25 °C, 2.97–9.54 (for 62 data) at 37 °C, and 3.01–9.12 (for 58 data) at 45 °C for *I* = 0.10 mol dm⁻³ KCl; 2.83–9.89 (for 159 data) at 25 °C, 3.04–9.53 (for 140 data) at 37 °C, and 2.96–9.57 (for 127 data) at 45 °C for *I* = 1.00 mol dm⁻³ KCl.

The GLEE program has been developed as part of the HYPERQUAD suite of programs for stability constant determination. The ionic strength (*I*) of all the titration mixtures was adjusted to (0.10 and 1.00) mol dm⁻³ by adding the requisite volume of KCl solution and a constant volume of 25 mL was maintained. The values of $\text{p}K_w$ were confirmed using GLEE for each ionic medium.⁷ ($\text{p}K_w = 13.78$ at 25 °C, 13.46 at 37 °C and 13.16 at 45 °C for *I* = 0.10; $\text{p}K_w = 13.75$ at 25 °C, 13.52 at 37 °C, and 13.29 at 45 °C for *I* = 1.00). Before performing the titrations, titration conditions were simulated using the HySS2006 computer program. The potentiometric titrations in aqueous solution were carried out and evaluated for proton–ligand and metal–ligand stability constants.

Titrations for Proton–Ligand Stability Constants. The protonation constants of Leu were determined by titrating 25 mL of aqueous solution in the presence of appropriate amounts of Leu with 0.1 M NaOH. KCl was used in a sufficient amount to adjust to (0.10 and 1.00) ionic strength. The pH measurements were done automatically using a Schott Titroline Alpha by recording the pH measurements at suitable time intervals for Leu. A summary of the titrations used in the numerical analysis, for the three temperatures is given in Table 1.

Titrations for Metal Hydrolysis Constants. For the determination of stability constants, a few preliminary titrations were performed to investigate the effects of experimental variables such as the time interval between consecutive titration readings and varying concentrations of Ce^{3+} ion at appropriate pH ranges and at the desired temperatures. To determine the hydrolysis constants of the Ce^{3+} ion at 1.00 mol dm⁻³ ionic strength, experiments were designed and carried out at (25, 37, and 45) °C according to the method reported before. The hydrolysis constants of Ce^{3+} ion at 0.1 mol dm⁻³ ionic strength were obtained from a previous study.⁸ Finally, the potentiometric results were transferred to HYPERQUAD2006 computer program and stability constants were calculated.

Titrations for Metal–Ligand Stability Constants. The metal–ligand titration conditions were simulated considering the hydrolytic behavior of the Ce^{3+} ion, using the HySS2006 computer program, and then the pH measurements were done by recording the pH measurements at suitable time intervals for the Ce^{3+} ion. For determination of the metal–ligand stability constant a 25 mL aqueous solution in the presence of 0.05 mmol of Ce^{3+} and a suitable amount of HCl were titrated with 0.1 M NaOH automatically. The titrations for complex formation were performed with a solution containing metal:ligand (M:L) molar ratios of 1:1, 1:3, and 1:5.

Table 2. Proton–Ligand Stability Constants of Leucine and Literature Data

<i>t</i> (°C)	log K_1	data type ^b	
	log β_2		
15	9.81 ± 0.03	pot.	ref 1 ^c
	12.20 ± 0.05		
25	9.52 ± 0.02	pot.	ref 3 ^d
	11.86 ± 0.02		
37	9.29 ± 0.01	pot.	this work, <i>I</i> = 0.10 mol dm ⁻³ KCl
	11.62 ± 0.01		
45	9.11 ± 0.02	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	11.44 ± 0.02		
60	8.80 ± 0.1	pot.	this work, <i>I</i> = 0.10 mol dm ⁻³ KCl
	11.20 ± 0.1		
15	9.66	pot.	this work, <i>I</i> = 0.10 mol dm ⁻³ KCl
25	9.54		
35	9.42	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
25	9.64 ± 0.05		
37	11.68 ± 0.13	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	9.5 ± 0.17		
45	11.50 ± 0.10	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	9.47 ± 0.03		
25	11.26 ± 0.04	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	9.45 ± 0.10		
37	11.84 ± 0.06	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	9.32 ± 0.02		
45	11.58 ± 0.01	pot.	this work, <i>I</i> = 1.00 mol dm ⁻³ KCl
	9.21 ± 0.04		
	11.47 ± 0.06		

^b pot.: potentiometric. ^c Medium: 0.1 M KNO_3 , titration data of experiments were analyzed by the nonlinear least-squares program CHEMEQ. ^d Medium: 0.10 M NaClO_4 , titration data of experiments were analyzed by the Irving–Rossotti method (calculated by a PC using MS Excel).

Each set of titrations were repeated at least three times at (25, 37, and 45) °C for each metal:ligand molar ratio and each ionic strength.

Calculations. The data from each titration were imported into the program HYPERQUAD and treated by nonlinear least-squares refinement.⁶

The weights of the titrant were input directly into the HYPERQUAD2006 program as independent variables and the pH values as

Table 3. Hydrolysis Constants for Ce^{3+} in KCl

I (mol dm ⁻³)	t (°C)	log β			
		$(p, q) = (2, -1)$	$(p, q) = (2, -2)$	$(p, q) = (1, -3)$	$(p, q) = (2, -5)$
0.10 ^a	25	-4.02 ± 0.49	-11.51 ± 0.36	-23.65 ± 0.82	-35.70 ± 0.80
	37	-3.39 ± 0.39		-21.67 ± 1.19	-32.99 ± 1.40
	45	-3.20 ± 0.34		-20.81 ± 1.66	-31.95 ± 1.61
1.00 ^b	25	-4.26 ± 0.38	-12.60 ± 0.35	-24.47 ± 0.31	-37.58 ± 0.11
	37	-4.35 ± 0.05	-11.78 ± 0.62	-23.37 ± 0.49	-35.58 ± 0.21
	45	-4.42 ± 0.41		-23.31 ± 0.88	-34.34 ± 0.11

^a The data taken from Teksoz et al.'s study.^{8b} Measurements were taken in the pH range 3.15–10.58 (for 85 data) at 25 °C, 3.75–10.58 (for 82 data) at 37 °C, and 4.52–9.99 (for 82 data) at 45 °C for $I = 1.00$ mol dm⁻³ KCl.

Table 4. Results of Potentiometric Measurements of Leucine Complexes with Ce^{3+} ^a

I (mol dm ⁻³)	t (°C)	log β				
		$(p, q, r) = (1, 0, 1)$	$(p, q, r) = (1, 1, 1)$	$(p, q, r) = (1, 2, 1)$	$(p, q, r) = (1, 0, 2)$	$(p, q, r) = (1, 0, 3)$
0.10	25	6.80 ± 0.24	14.78 ± 0.32	21.90 ± 0.45	11.83 ± 0.57	13.78 ± 0.80
	37	7.08 ± 0.78	14.95 ± 0.79	22.27 ± 0.64	12.56 ± 0.70	14.56 ± 0.52
	45	7.89 ± 0.19	15.02 ± 0.46	22.54 ± 0.97	13.19 ± 0.77	15.75 ± 0.11
1.00	25		12.16 ± 0.32	18.49 ± 0.10	9.05 ± 0.11	11.62 ± 0.20
	37		12.26 ± 0.55	19.40 ± 0.85	9.75 ± 0.30	12.24 ± 0.55
	45		12.52 ± 0.30	19.71 ± 0.34	10.17 ± 0.77	12.42 ± 0.34

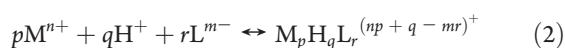
^a Initial total $[\text{Ce}^{3+}] = 0.5$ mmol dm⁻³.

the dependent variables. While the log β for the proton–ligand or metal–ligand species are calculated for acceptable conditions in the solution, others worsen the statistical parameters and are rejected as being negative or excessive by the HYPERQUAD program. Errors in fixed values are not introduced in HYPERQUAD, so that error propagation is not considered in optimizing the protonation constants. Statistical data refer to protonation constants: N = total number of experimental data points used; χ^2 = observed statistical parameter based on weighted residuals of the pH readings (values <12.6 indicate a confidence level >95%), σ = ratio of the root-mean-square of the weighted residuals to the estimated error in the actual working conditions (σ_V and σ_E).⁸

In the current study, the proton–ligand constants for the overall reaction, β_n , are described as

$$\beta_n = K_1 \cdot K_2 \cdots K_n = \frac{[\text{H}_n\text{L}]}{[\text{H}]^n [\text{L}]} \quad (1)$$

For metal–ligand complexation, formation constants, β_{pqr} , are generally represented by eq 2:



The equilibrium constants for the overall reaction are described as

$$\beta_{pqr} = \frac{[\text{M}_p\text{H}_q\text{L}_r]}{[\text{M}]^p [\text{H}]^q [\text{L}]^r} \quad (3)$$

where $\text{M}^{n+} = \text{Ce}^{3+}$ in this study.

Table 5. Thermodynamic Parameters of Leucine

I (mol dm ⁻³)	t (°C)	(p, q, r)	thermodynamic parameters		
			ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹)
0.10	25	(0, 1, 1)	-18.46 ± 1.84	-55.06 ± 0.28	122.74 ± 5.23
		(0, 2, 1)	-32.73 ± 1.26	-66.42 ± 0.36	112.97 ± 3.01
	37	(0, 1, 1)		-55.52 ± 0.25	119.49 ± 5.13
		(0, 2, 1)		-68.29 ± 0.58	114.63 ± 2.17
	45	(0, 1, 1)		-57.68 ± 0.17	123.28 ± 5.25
		(0, 2, 1)		-68.59 ± 0.25	112.69 ± 3.15
1.00	25	(0, 1, 1)	-16.81 ± 1.06	-53.66 ± 0.16	123.58 ± 4.12
		(0, 2, 1)	-34.04 ± 0.77	-67.56 ± 0.36	112.42 ± 1.38
	37	(0, 1, 1)		-55.31 ± 0.12	124.13 ± 3.84
		(0, 2, 1)		-68.73 ± 0.04	111.86 ± 2.37
	45	(0, 1, 1)		-56.10 ± 0.25	123.49 ± 4.16
		(0, 2, 1)		-68.84 ± 0.38	112.51 ± 1.22

RESULTS AND DISCUSSION

The numerical values for complexation species of Leu with the Ce^{3+} ion have been evaluated pH metrically at (25, 37, and 45) °C and are summarized in Table 1. The mean values of the protonation constants (the log values) with the associated experimental parameters obtained from this study including literature data are given in Table 2. The hydrolysis constants for Ce^{3+} are given in Table 3. The calculated log β values for leucine complexes of Ce^{3+} are displayed in Table 4.

Also the thermodynamic parameters of leucine and complexation species of leucine with Ce^{3+} ion have been calculated and summarized in Table 5 and 6, respectively. In addition, percent

Table 6. Thermodynamic Parameters of Leucine with Cerium

I (mol dm ⁻³)	t (°C)	(p, q, r)	thermodynamic parameters		
			ΔH (kJ mol ⁻¹)	ΔG (kJ mol ⁻¹)	ΔS (J mol ⁻¹)
0.10	25	(1, 0, 1)	94.29 ± 6.79	-38.90 ± 0.52	446.77 ± 24.54
		(1, 1, 1)	50.31 ± 0.10	-84.06 ± 0.12	450.68 ± 0.08
		(1, 2, 1)	147.77 ± 1.26	-121.65 ± 0.04	903.63 ± 4.36
		(1, 0, 2)	148.66 ± 2.54	-65.16 ± 0.38	717.14 ± 8.47
		(1, 0, 3)	215.85 ± 7.28	-76.27 ± 0.48	979.79 ± 22.79
	37	(1, 0, 1)		-40.80 ± 1.30	435.68 ± 17.70
		(1, 1, 1)		-88.54 ± 0.42	447.69 ± 1.67
		(1, 2, 1)		-129.19 ± 1.68	892.98 ± 1.36
		(1, 0, 2)		-71.16 ± 4.05	708.76 ± 15.10
		(1, 0, 3)		-85.96 ± 0.13	973.12 ± 23.07
	45	(1, 0, 1)		-48.43 ± 1.38	448.62 ± 25.68
		(1, 1, 1)		-93.23 ± 0.22	451.17 ± 0.37
		(1, 2, 1)		-140.29 ± 0.43	905.41 ± 5.31
		(1, 0, 2)		-79.94 ± 0.27	718.54 ± 8.53
		(1, 0, 3)		-96.22 ± 0.04	980.90 ± 22.75
1.00	25	(1, 1, 1)	70.49 ± 1.07	-67.51 ± 1.09	462.84 ± 0.07
		(1, 2, 1)	166.10 ± 0.20	-104.81 ± 0.08	908.65 ± 0.93
		(1, 0, 2)	106.18 ± 2.04	-51.01 ± 0.12	527.22 ± 7.24
		(1, 0, 3)	66.58 ± 0.97	-65.14 ± 0.81	441.76 ± 5.96
	37	(1, 1, 1)		-73.28 ± 0.67	463.55 ± 1.28
		(1, 2, 1)		-117.11 ± 0.67	913.13 ± 2.80
		(1, 0, 2)		-58.91 ± 0.25	532.30 ± 7.38
		(1, 0, 3)		-69.66 ± 0.01	439.25 ± 3.12
	45	(1, 1, 1)		-76.72 ± 1.16	462.72 ± 0.30
		(1, 2, 1)		-122.75 ± 0.01	907.90 ± 0.61
		(1, 0, 2)		-61.28 ± 0.26	526.37 ± 7.22
		(1, 0, 3)		-74.11 ± 1.08	442.18 ± 6.43

distribution diagrams of the complexation species of leucine with Ce³⁺ at certain temperatures are shown in Figures 2 and 3. These figures were drawn using the IUPAC Stability Constants Database (SC-Database).^{9,10}

Relationships among metal concentrations and other variables were analyzed by multivariate statistics using the SPSS 13 program (Univariate Variance Analyses and (Chicago, IL) Pearson Correlation). Correlation is significant at $p < 0.01$ for the 99% confidence level. While $\log \beta$ values were chosen as dependent variables, independent variables were temperature and ionic strength.

Proton–Ligand Stability Constants for Leucine. The average proton–ligand values ($\log K_1$, $\log \beta_2$) obtained at (25, 37, and 45) °C are listed in Table 2. Also Table 2 includes the reported values about the protonation constants for leucine at given temperatures by other workers.^{1–3} The proton binding sites of the amino acids have been established between amino and carboxyl groups for leucine. Leucine has two acidic groups so dissociation takes place in two steps. As reported by other workers, in this study the first deprotonation occurs from the amino side and the second deprotonation occurs from the carboxyl side of leucine.^{1,2} The structural formula of leucine is given in Figure 1.

Taking into account the results of the concentration range used, there is a significant correlation between the $\log \beta$ values of leucine and temperature, as seen in Table 2. Statistical results

show that $\log \beta$ ($p < 0.01$, $r^2 = 0.79$) correlated well with temperature in the $I = 0.10$ mol dm⁻³ KCl medium. Also both $\log K_1$ ($p < 0.01$, $r^2 = 0.82$) and $\log \beta_2$ ($p < 0.01$, $r^2 = 0.93$) correlated well with temperature in the $I = 1.00$ mol dm⁻³ KCl medium.

When we discussed the effect of ionic strength, there is a meaningful agreement between the ionic strength and $\log K_1$ values ($p < 0.05$, $r^2 = 0.38$).

Also the thermodynamic parameters for leucine and its metal complexes have been calculated using the Gibbs and van't Hoff equations and summarized in Tables 5 and 6.

In view of the thermodynamic data in Table 5, the entropy values of leucine are positive at all temperatures but the enthalpy changes and Gibbs energy changes are negative. Thus, it can be concluded that protonation is favorable for all temperatures.

Complex Formation of Leucine with Ce³⁺. Stability constants of leucine complexes with cerium at (25, 37, and 45) °C were computed from the imported data by potentiometry. Ligand protonation constants and cerium hydrolysis constants were held constant for all three titrations with leucine. Cerium hydrolysis constants were calculated in a previous study for $I = 0.1$.⁸ Measurements were carried out to determine the hydrolytic constants of Ce³⁺ ion at a 1.00 mol dm⁻³ ionic strength, and the hydrolysis constants were calculated from obtained data at (25, 37, and 45) °C. Leu coordinates metals via their amino and

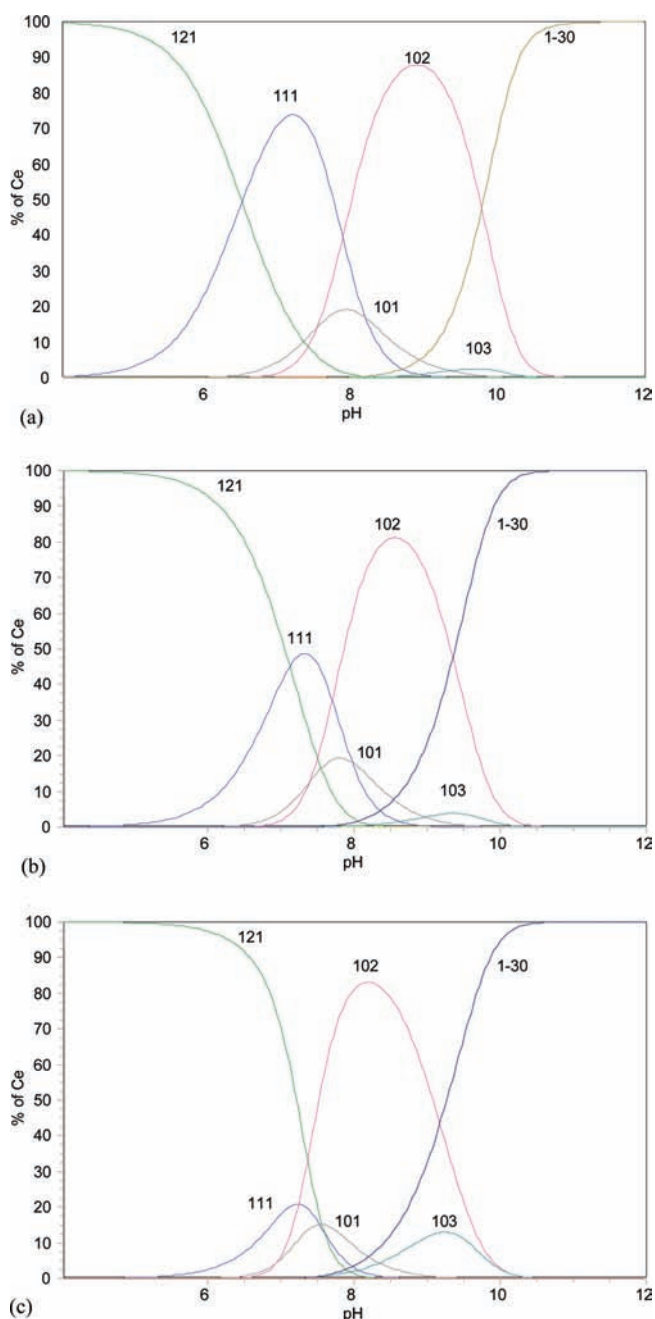


Figure 2. Species distribution of Ce^{3+} with leucine at a 1:5 metal:ligand molar ratio $I = 0.10 \text{ mol dm}^{-3} \text{ KCl}$: (a) at $25 \text{ }^\circ\text{C}$; (b) at $37 \text{ }^\circ\text{C}$; (c) at $45 \text{ }^\circ\text{C}$.

carboxyl groups as reported in previous studies.^{1–3} In the current study, it was found that mononuclear complexes of leucine represented as ML_2 and ML_3 were calculated for both ionic strengths. On the other hand ML was observed only in the $I = 0.10 \text{ mol dm}^{-3} \text{ KCl}$ medium. The computed $\log \beta$ values for leucine are given in Table 4 shown as $\log \beta_{101}$, $\log \beta_{102}$, and $\log \beta_{103}$. Also, $\log \beta_{111}$ and $\log \beta_{121}$ values were found for species formed with leucine in solution. These species are exhibited as MHL and MH_2L .

The percent distribution curves of Ce – Leu species vs pH were plotted for each ionic strength at (25, 37, and 45) $^\circ\text{C}$ (Figures 2 and 3).

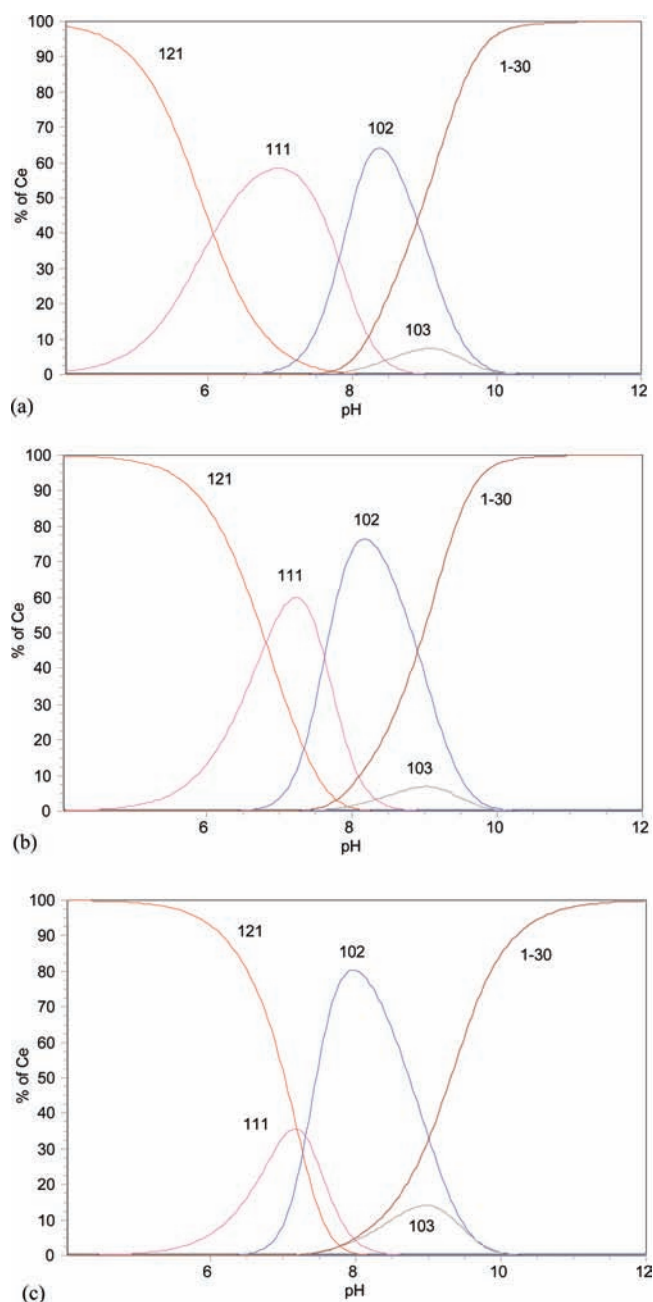


Figure 3. Species distribution of Ce^{3+} with leucine at a 1:5 metal:ligand molar ratio $I = 1.00 \text{ mol dm}^{-3} \text{ KCl}$: (a) at $25 \text{ }^\circ\text{C}$; (b) at $37 \text{ }^\circ\text{C}$; (c) at $45 \text{ }^\circ\text{C}$.

Results of $I = 0.10 \text{ mol dm}^{-3} \text{ KCl}$. The percent distribution curves of Ce – leucine species vs pH were plotted for each temperature at $I = 0.10 \text{ mol dm}^{-3} \text{ KCl}$ (Figure 2). As shown in the curve, the formation of metal–ligand and metal–ligand proton and hydrolyzed metal ligand species are found over a wide pH range in the solution. The (1, 2, 1) species dominates between pH 4 and 6, (1, 1, 1) forms in the 6–8 pH range, the (1, 0, 1) species exists at pH 8 whereas (1, 0, 2) is the most abundant between pH 8 and 10, and (1, 0, 3) is established at pH 10. The hydrolytic species (1, –3, 0) can be observed at pH > 9 at $25 \text{ }^\circ\text{C}$. As seen in the figure, while the percent distribution of the (1, 1, 1) species decreases, the (1, 0, 3) species increases with increasing temperature.

When we discussed the effect of temperature, there is meaningful agreement between temperature and $\log \beta$ values. According to multiple linear regression results, (1, 0, 1) ($p < 0.05$, $r^2 = 0.29$), (1, 2, 1) ($p < 0.01$, $r^2 = 0.32$), (1, 0, 2) ($p < 0.01$, $r^2 = 0.40$), and (1, 0, 3) ($p < 0.01$, $r^2 = 0.70$) correlated well with temperature in the $I = 0.10 \text{ mol dm}^{-3}$ KCl.

Results of $I = 1.00 \text{ mol dm}^{-3}$ KCl. Figure 3 shows the species distribution diagram for Ce–leucine at $I = 1.00 \text{ mol dm}^{-3}$ KCl. While (1, 1, 1) and (1, 0, 2) species are dominant between pH 6 and 10, (1, 2, 1) is the dominant species at low pH. The (1, 0, 3) species is observed between pH 8–10 at 25 °C. As seen, the hydrolytic species of $\text{Ce}(\text{OH})_3$ can be observed at $\text{pH} > 8$. As seen in Figure 3, the percent distribution of the (1, 0, 3) species increases with increasing temperature. There is no significant difference between the speciation curves at the various temperatures for the other species.

According to multiple linear regression results, the $\log \beta$ values of (1, 2, 1) ($p < 0.01$, $r^2 = 0.48$), (1, 0, 2) ($p < 0.01$, $r^2 = 0.50$), and (1, 0, 3) ($p < 0.01$, $r^2 = 0.47$) correlate well with temperature. Also there is no significant correlation for the $\log \beta$ values of (1, 1, 1).

When we discussed the effect of ionic strength, there is meaningful agreement between ionic strength and the $\log \beta$ values. According to multiple linear regression results, the $\log \beta$ values of (1, 2, 1) ($p < 0.01$, $r^2 = 0.71$), (1, 1, 1) ($p < 0.01$, $r^2 = 0.86$), (1, 0, 2) ($p < 0.01$, $r^2 = 0.74$), and (1, 0, 3) ($p < 0.01$, $r^2 = 0.58$) correlated well with ionic strength.

In view of the thermodynamic data, the complexation of all cerium species is endothermic, and all species have positive entropy values at all temperatures and ionic strengths as given in Table 6.

In the literature, the stability constants of the metal ion complexes formed with amino acids at different ionic strengths and temperature have been reported. Mohamed et al. studied complexation of phenylglycine with some transition metal ions with changing ionic strength and temperature. They concluded that there is an ionic strength dependence of the ionization constant values at each temperature.¹¹

CONCLUSION

- The results summarized in this study show that ionic strength and temperature affected the formation of complexes as would be expected.
- The entropy change values of leucine are positive at all temperatures, but the enthalpy change and Gibbs energy change are negative.
- In this study, calculation of metal ligand stability constants at various temperatures and thermodynamic parameters contribute significantly to the understanding of the complexation behavior of leucine with Ce^{3+} .
- In this respect, it could be important to gain more data about complexation of lanthanide ions with leucine due to a widespread interest from nuclear waste to biological systems.

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