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Kinetic Studies of the Interaction of Pr(III) with some amino acids in Aqueous Medium using pH meter: Evaluation of Pre- exponential Factor and Activation Energy

Juliana Sanchu, M. Indira Devi
Department of Chemistry, Nagaland University; Lumami, Nagaland

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ABSTRACT

Kinetic studies of the Complexation of Pr(III) with some amino acids (L-Aspartic acid, L-Histidine and L-Valine) in aqueous solvents were carried out at different temperatures (room temperature and higher temperatures) using pH meter. Different thermodynamic parameters (ΔEa, ΔSº, ΔGº and ΔHº) of the Complexation have been evaluated. It was found that the value of pH increases with time which shows that the rate of the reaction of Pr (III) with different amino acids in aqueous medium increases with time.

Keywords - Praseodymium, Amino acids, Thermodynamic Parameters, Oscillator Strength, Judd-Ofelt.

I. INTRODUCTION

Because of their special qualities, lanthanide-based reporters—also known as lanthanide labels or lanthanide probes—are being used more often in a wide range of applications [1]. The interest in employing trivalent lanthanide ions Ln(III) as structural probes in biological systems gave rise to the study of the chemical bonds between amino acids and peptides [2-3]. In-depth reviews of the interactions of several lanthanides with a variety of proteins have been conducted [4]. O>N>S and F>Cl are the donor atoms that lanthanides prefer, demonstrating their strong affinity for oxygen donor atoms [5]. The bonding between Ln(III) and amino acids is most likely made with the oxygen of the carboxylate group, and it is highly improbable that it would occur via the nitrogen of the amino group, at least in the pH range up to 5.6 [6-7] The role of solvents in the complexation of lanthanides and ligands is also discussed using a variety of solvents and their equimolar combinations [8]. Lanthanide complexes are used in solution spectrum investigations using a kinetic and thermodynamic method to learn more about the mechanism, reaction routes, chemical bonds, and conformations. When forming complexes, the lanthanide complexes' stability rises as their atomic number does [9]. Due to their well-defined spectroscopic and magnetic characteristics, lanthanide (III) complex research has gained prominence recently [10-14]

The present paper investigates the kinetic studies for the interaction between Praseodymium (III) and some selected amino acid (L-Aspartic acid, L-Histidine and L-Valine) in aqueous solvents using pH meter. The reaction dynamics of the interaction of Praseodymium (III) with some selected amino acid at various time intervals and in different temperatures could enable us to analyze systematically, the nature

of the chemical reaction pathways as well as the thermodynamic behaviour by computing the parameters like specific rate constant/rate constant (k), pre-exponential factor (A), ΔH^0, ΔS^0 and ΔG^0.

II. EXPERIMENTAL WORKS

Materials and methods:

A) Materials

Praseodymium (III) nitrate Hexahydrate [$Pr(NO_3)_3.6H_20$] of 99.99% purity was purchased from alfa aesar, Ligands (L-Aspartic acid, L-Histidine and L-Valine) were purchased from HIMEDIA, the solvent DMF of A.R grade was purchased from Merck, distilled water and the instrument used was pH 700 (pH electrode, meter with ATC probe) Eutech instrument.

B) Methods

Theoretical

The kinetic studies of 0.1 N solution of Praseodymium(III) nitrate hexahydrate and 0.1 N of amino acids (L-Aspartic acid, L-Histidine and L-Valine) in aqueous organic medium is recorded at different temperatures and time intervals. The activation energy for the complexation of Pr (III): Ligand (L-Aspartic acid, L-Histidine and L-Valine) in DMF is calculated from the plot of log k (k= rate constant) against 1/T by using Arrhenius rate equation [13].

$$\log k = \log A - \frac{E_a}{2.303R} \times \frac{1}{T} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where, A is the pre-exponential factor or frequency factor.

From the slope the activation energy E_a is calculated as

$$E_a = -\text{Slope} \times 2.303 \times R \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where R is the universal gas constant

The thermodynamic parameters for the complexation of Pr^{3+}: Ligands (L-Aspartic acid, L-Histidine and L-Valine) are calculated by using Van't Hoff (14) equation of ln k against 1/t

$$\ln k = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T}\right] + \frac{\Delta S^\circ}{R}$$

$$\text{or } \ln k = -\frac{\Delta G^\circ}{RT} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

III. CALCULATIONS

A) Pr(III):L-Aspartic acid complex

Table 1 : pH values at different time interval (10 mins)

TIME	pH (at 25°C / 298 K)	pH (at 35°C / 308 K)
0	5.32	5.89
10	5.57	5.92
20	5.68	5.95
30	5.77	5.98
40	5.83	6.00
50	5.91	6.02
60	5.97	6.03

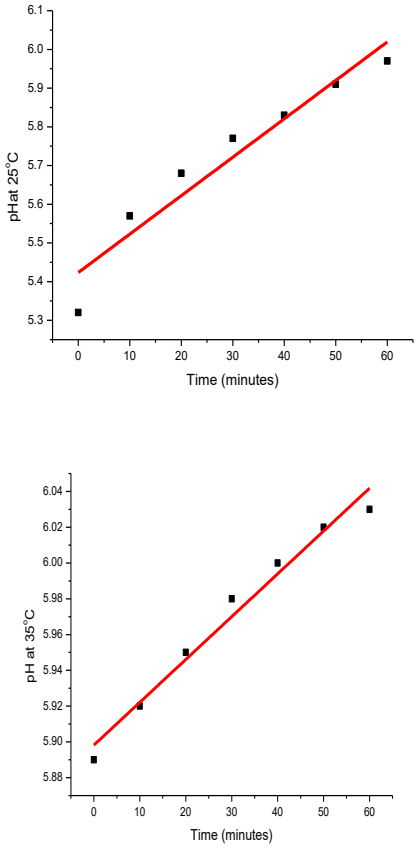

Fig 1: Plot of Time in minutes versus pH for Pr (III) : L-Aspartic acid complex at two different temperatures.

Table 2 : Reaction Rate at different temperatures (298 K and 308 K) and Activation Energy for Pr (III): L-Aspartic acid complex

Temp.(T)	$1/T \times 10^3$	Rate constant (k)	log k	Activation energy (ΔEa)
298	3.35571	2.75833	0.44065	-108.69545
308	3.24675	0.66389	-0.17790	

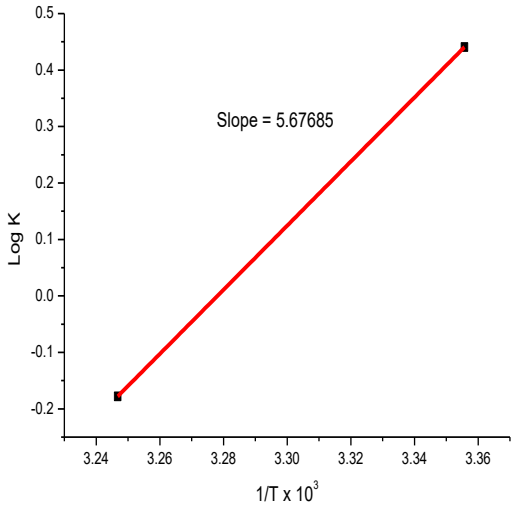

Fig 2 : Plot of log K versus (1/T) × 10^3 for the complexation of Pr (III): L-Aspartic acid in solution.

Table 3 : Thermodynamic parameters for the complexation of Pr (III): L-Aspartic acid complex in solution.

Temperature	log k	ΔH	ΔG	ΔS
298	0.44065	-108.69545	-2.51428	-0.35631
308	-0.17790		1.04913	-0.35631

B) Pr(III):L-Histidine complex

Table 4: *pH values at different time interval (10 mins)*

TIME	pH (at 25°C / 298 K)	pH (at 35°C / 308K)
0	5.90	5.92
10	5.94	5.95
20	5.96	5.97
30	5.98	6.06
40	6.01	6.08
50	6.03	6.11
60	6.04	6.15

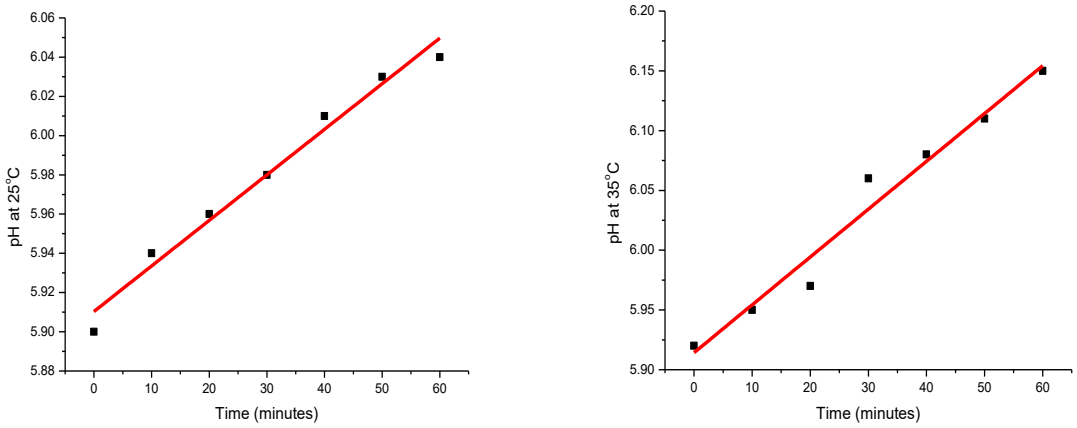

Fig 3: Plot of Time versus pH value for Pr(III): L-Histidine complex at two different temperatures.

Table 5 : Reaction Rate at different temperatures (298 K and 308 K) and Activation Energy for Pr (III): L-Histidine complex

Temp. (T)	1/T× 10^3	Rate constant (k)	log k	Activation energy (ΔEa)
298	3.35571	0.64444	-0.19082	41.57342
308	3.24675	1.11111	0.04576	

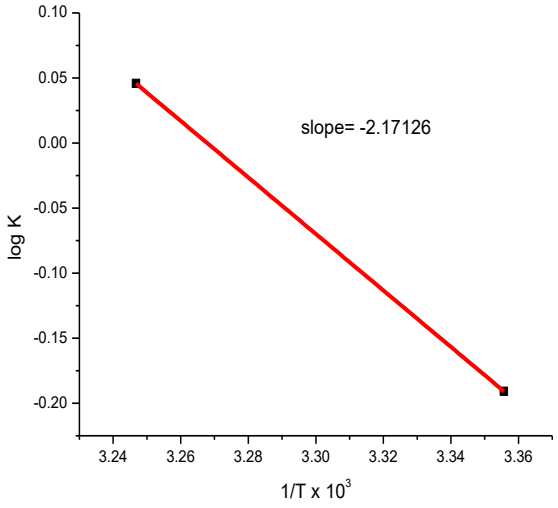

Fig 4: Plot of log K versus (1/T) X 10^3 for the Complexation of Pr (III): L-Histidine complex in solution.

Table 6 : *Thermodynamic parameters for the complexation of Pr (III): L-Histidine complex in solution.*

Temperature	log k	ΔH	ΔG	ΔS
298	-0.19082	41.57342	1.08879	0.13585
308	0.04576		-0.26986	0.13585

C) Pr(III):L-Valine complex

Table 7 *: pH values at different time interval (10 mins)*

TIME	pH (at 25^{0}C / 298 K)	pH (at 35^{0}C / 308 K)
0	5.59	6
10	5.63	6.09
20	5.69	6.15
30	5.74	6.20
40	5.84	6.26
50	5.95	6.33
60	6.07	6.40

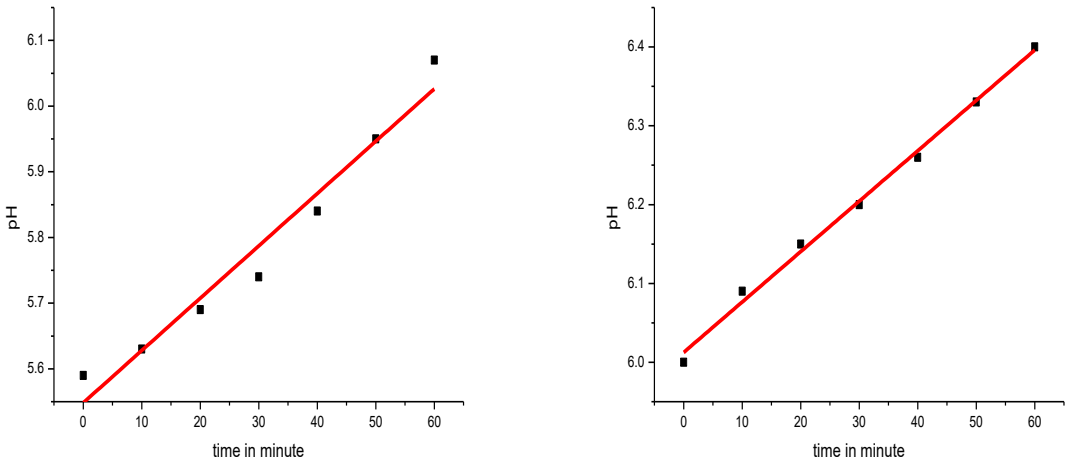

Fig 5 : Plot of Time versus pH for Pr(III) : L-Valine complex at two different temperatures.

Table 8: Reaction Rate at different temperatures (298 K and 308 K) and Activation Energy for Pr (III): L-Valine complex.

Temp. (T)	1/T×10^3	Rate constant (k)	log k	Activation energy (ΔEa)
298	3.35571	2.21111	0.34461	16.78362
308	3.24675	1.77500	0.24910	

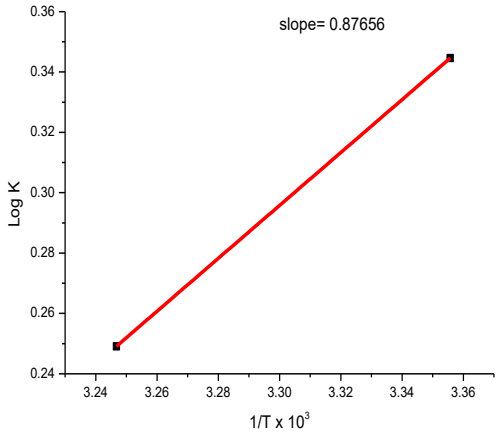

Fig 6 : Plot of log K versus (1/T) × 10^3 for the complexation of Pr (III): L-Valine complex in solution.

Table 9 : Thermodynamic parameters for the complexation of Pr (III): L-Valine complex in solution.

Temperature	log k	ΔH	ΔG	ΔS
298	0.34461	16.78362	-1.96629	0.06292
308	0.24910		-1.42132	0.05910

Table 10 : Pre-exponential factor of the reaction of Pr (III) with amino acids (L-Aspartic acid, L-Histidine and L-Valine).

Sl.no.	Complex	Pre –exponential factor	Temperature
1.	Pr (III): L-Aspartic acid complex	5.42357	25⁰C
		5.89821	35⁰C
2.	Pr (III): L-Histidine complex	5.91036	25⁰C
		5.91429	35⁰C
3.	Pr (III): L-Valine complex	5.54821	25⁰C
		6.01250	35⁰C

Table 11 : *Comparative pH values of Pr (III) L-Aspartic acid, Pr (III): L-Histidine and Pr (III): L-Valine complexes at 25° C/ 298 K.*

Time (in min.)	pH (at 25⁰C / 298 K) Pr (III): L-Aspartic acid complex	pH (at 25⁰C / 298 K) Pr (III): L-Histidine complex	pH (at 25⁰C / 298 K) Pr (III): L-Valine complex

0	5.32	5.90	5.59
10	5.57	5.94	5.63
20	5.68	5.96	5.69
30	5.77	5.98	5.74
40	5.83	6.01	5.84
50	5.91	6.03	5.95
60	5.97	6.04	6.07

Table 12 *: Comparative pH values of Pr (III) Nitrate with Pr (III): L-Aspartic acid, Pr (III): L-Histidine and Pr (III): L-Valine complex at 35° C/ 308 K.*

Time (in min.)	pH (at 35^{0}C / 308 K) Pr (III): L-Aspartic acid complex	pH (at 35^{0}C / 308 K) Pr (III): L-Histidine complex	pH (at 35^{0}C / 308 K) Pr (III): L-Valine complex
0	5.89	5.92	6
10	5.92	5.95	6.09
20	5.95	5.97	6.15
30	5.98	6.06	6.20
40	6.00	6.08	6.26
50	6.02	6.11	6.33
60	6.03	6.15	6.40

IV. RESULTS AND DISCUSSION

pH value has been evaluated using pH-meter for Pr (III) L-Aspartic acid, Pr (III): L-Histidine and Pr (III): L-Valine complexes at different time interval of 10 minutes as shown in table 1, 4 and 7. From the study we found out that the value of pH increases with time which shows that the rate of the reaction of Pr (III) with amino acids in aqueous DMF medium increases with time, following the Arrhenius concept.

Graphs have been plotted as pH versus time and from the graphs we evaluate the frequency factor (A) or pre-Exponential factor from the intercept of the plot (from figure 1, 3 and 5). Slope of the plot of log k versus 1/T x 10^3 gives Slope = E_a/2.303 from which we can calculate the value of activation energy (E_a) which is found to be;

1)

rom the values of ΔH in the three different tables, it is found that ΔH value of

Pr (III) L-Aspartic acid > Pr (III): L-Histidine > Pr (III): L-Valine complexes.

2) Again, from the study of the value of ΔS values we get,

Pr (III): L-Valine < Pr (III): L-Histidine < Pr (III) L-Aspartic acid complexes.

Which signifies the crystal structure of these three complexes in the order of,

Pr (III): L-Valine > Pr (III): L-Histidine > Pr (III) L-Aspartic acid complexes.

From table 6 and 9 ΔH signifies that the Complexation is endothermic and table 3 shows that the complexation is exothermic reaction. The reaction is favoured one shown by the –ve value of ΔG both at higher and lower temperatures, even the negligible ΔS

value also reveals for the formation of complexes and the positive value of ΔS says that the complexation reaction is an entropy driven one.

Table 10 reflects the pre-exponential factor of the formation of Pr-amino acids complexes and it signifies how quickly and oftenly / frequently a reaction can happen, the reaction favourable order is given below,

L-Histidine > L- Aspartic acid > L-Valine.

Again, when we look into separately of the different Pr-amino acids complexes, there is enhancement of the frequency factor at higher temperature for all the cases i.e., in the case of L-Aspartic acid at 25º C the value is 5.42357 at 25º C which is less than 5.89821 at 35º C which follows the theoretical prediction of Arrhenius equation.

V. CONCLUSION

From the systematic study of Pr (III) with amino acids: L-Aspartic acid, L-Histidine and L-Valine, it may be concluded that:

- The reactions are fast reactions which are conveyed for the low values of activation energies.
- Negative value of ΔG signified that the reaction is favourable and spontaneous.
- Positive value of ΔH shows that the reaction is endothermic as in the case of L-Histidine and L-Valine (table 6 and 9).
- Negative value of ΔH shows that the reaction is exothermic as in case of L- Aspartic acid (from table 3)
- Negative value of ΔS signifies that the reaction is entropy driven reaction.
- Negative value of ΔE_a signifies that the reaction is instantaneous.

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