

## EFFECT OF TEMPERATURE AND IONIC STRENGTH ON THE FORMATION CONSTANTS OF 2-ACETILPYRIDINE(N-BENZOYL)GLYCINE HYDRAZONE WITH LANTHANIDE(III) IONS

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### Abstract

Formation of 2-Acetylpyridine(N-Benzoyl)Glycine Hydrazone, 2-ApBzGH with Ln(III) ions (Ln = La, Pr, Nd, Sm, Eu, Gd) was studied pHmetrically at temperatures 283, 293, 303, 313 and 323 K and ionic strengths 0.05, 0.10, 0.15, 0.20 M using KNO<sub>3</sub> as the background electrolyte. The pH titration and the proton-ligand formation curves of the ligand showed the presence of one ionizable proton in the ligand. The ligand formed 1:1 and 1:2 complexes with La(III) ion while 1:1, 1:2 and 1:3 complexes were formed with other Ln(III) ions in 30 % (v/v) aqueous-dioxane medium and the corresponding formation constants (log  $K_f$ ) were determined from the formation curves. The formation constant values decreased with increase in temperature and ionic strength indicating that complex formation was more favorable at lower temperature and ionic strength. The trend in the constants along the lanthanide series was: La < Pr < Nd < Sm < Eu > Gd, showing a break at Gd. Changes in free energy, enthalpy and entropy associated with the protonation and complexation reactions were evaluated. All reactions were spontaneous, exothermic and enthalpy-driven processes.

**Key Words:** Formation constants, lanthanide complexes, pHmetric, hydrazone

### INTRODUCTION

The chemical properties of hydrazones having N,O-donor atoms have been intensively investigated in several research areas. The interest in the study of these compounds arose from their tendency to form chelates with transition metals, lanthanides, and main group metals, and their interactions have served as model systems for the study of many biomolecules and metalloproteins. There are several reports on metal complexes of hydrazones having a variety of applications in medicine, analytical, industrial, and organic synthesis [1-7].

Recent years showed an increased interest in the study of the lanthanide complexes of hydrazones. The interactions between such polydentate N, O-donor hydrazones and trivalent lanthanide ions have always been related with anionic or proton ionizability of these ligands as they have the ability to displace more effectively the hydration sphere of the metal cation, providing more kinetically stable complexes. However, to understand the interactions and activities of these ligands and their complexes, it is necessary to have detailed knowledge about the extent to which they bind to metal ions, the

concentration of metal complexes in equilibrium mixture, and thermodynamic and solution equilibria involved in the reactions. These are conveniently obtained through the determination of stability constants. Moreover, owing to the unique properties of the lanthanide ions, lanthanides have often been effectively employed as active Ca<sup>2+</sup> and Mg<sup>2+</sup> substitutes in many metalloproteins, as chiral NMR shift reagents, MRI contrast agents, and also luminescent probes of metal binding in biological systems [1,8-10].

Thus, keeping the above facts in mind and in continuation of our earlier work [10-14], we carried out a solution study on the complexation of 2-acetylpyridine (N-benzoyl)glycyl hydrazone (2-ApBzGH, Fig. 1) with some trivalent lanthanides. The effects of temperature and ionic strength on the interaction of the hydrazone with the lanthanides were also studied because such a study would help to explain the nature and driving forces for the interactions of lanthanides with a ligand. We report herein the dissociation constant of the hydrazone, the stability constants of the complexes, and the thermodynamic parameters that were calculated based on the formation constants.

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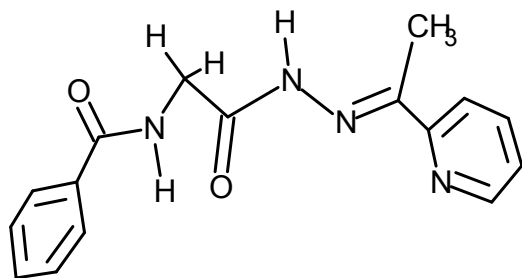


Figure 1 Structure of the ligand

## MATERIALS AND METHODS

2-Acetylpyridine, N-Benzoylglycine and  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  ( $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd}$ ) were purchased from Sigma while 1,4-dioxane was obtained from Merck. All the other chemicals and solvents used in this study were of AR or equivalent grade.

All the solutions of metal salts, KOH,  $\text{HNO}_3$  and  $\text{KNO}_3$  were prepared in double distilled water. KOH solution used for the standardization of  $\text{HNO}_3$  was standardized [15] with standard oxalic acid solution (0.05 M). The metal salt solutions were also standardized [16]. The ligand solution was prepared in aqueous 1,4-dioxane.

### Potentiometric titration

Potentiometric titration was carried out using an Eutech Cyberscan pH 1100 model with a glass calomel electrode at five different temperatures 283, 293, 303, 313 and 323 K, and ionic strengths 0.05, 0.10, 0.15, 0.20 M  $\text{KNO}_3$ . The pH-meter was standardized with standard buffer solutions of pH 4.00, 7.00 and 9.00. All the titrations were thermostated with a Circular D<sub>8</sub>-G Haake Mess Technik.

### Preparation of solutions

The following three sets of reaction mixtures were prepared and titrated potentiometrically against standard 0.02 M KOH solution:

- ❖ mL  $\text{HNO}_3$  (0.001 M) + 1.25 mL  $\text{KNO}_3$  (0.05 M)
- ❖ solution (a) + 1.00 mL 2-ApBzGH (0.0003 M) and
- ❖ solution (b) + 2.5 mL  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (0.00015 M)

The volume of each set was made up to 25 mL with 30 % (v/v) aqueous - dioxane mixture. The ionic strength of each reaction mixture was maintained at 0.05, 0.10, 0.15, 0.20 M using 0.1 M  $\text{KNO}_3$  solution as the background electrolyte. The pH-titrations were terminated when the pH readings became unstable upon formation of complexes. In all cases, no calculations have been performed beyond the precipitation point. Therefore, the hydroxyl species

likely to be formed beyond this point could not be studied.

### Preparation and characterization of the ligand

Acetylpyridine (N-Benzoyl) Glycine Hydrazone was prepared as reported [14] and the structure and purity of the compound was confirmed from elemental, IR, NMR and mass spectral analysis.

## RESULTS AND DISCUSSIONS

### Titration curves

2-ApBzGH was pHmetrically titrated with standard KOH at four different ionic strengths 0.05, 0.10, 0.15, 0.20 M  $\text{KNO}_3$  and at five different temperatures 283, 293, 303, 313 and 323 K.

Figure 2 represents the pHmetric equilibrium curves at 303 K at a constant ionic strength 0.10 M  $\text{KNO}_3$  where curve (a) represents acid titration curve, curve (b), the ligand curve and curves (c-h), the metal-ligand titration curves for La(III), Pr(III), Nd(III), Sm(III), Eu(III) and Gd(III) complexes, respectively. The acid curve started at pH 2.8 and extended upto pH 12.4. The ligand curve also would start at pH 2.8, however, it diverged from the acid curve at about pH 5.0 extending upto pH 12.0. The divergence of the ligand curve from the acid curve was due to the liberation of proton(s) from the ligand at this pH-range. A single inflection was observed in the equilibrium curve of the ligand at pH 5.0-11.5 corresponding to the neutralization of one proton of the ligand in the aqueous -dioxane solution at this pH range. This observation is in consistence with the reported monobasic character of the ligand [14] which would be represented as  $[\text{HL} \leftrightarrow \text{H}^+ + \text{L}^-]$ .

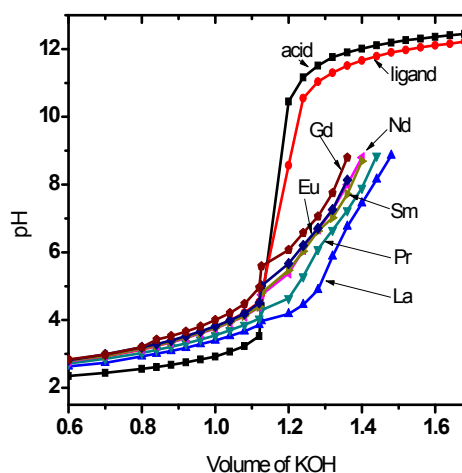


Figure 2 Titration curves of 2-ApBzGH and Ln(III) complexes at 303 K and 0.1 M ionic strength.

Addition of metal ion to the free ligand solution caused a shift in the buffer region of the ligand to a lower pH value as observed in the curves (c-h). It is because complex formation would proceed by releasing proton from the base. Wide separation resulting in the shift of the complex curves to the right side of the ligand indicated release of the dissociable proton due to complex formation. The curves also showed that all metals were complexed and complexation occurred at pH range 4.0 – 8.5.

Similar curves were obtained for the pH-metric titrations of the complexes carried out at other temperatures and different ionic strengths. However, they differ at the pH ranges at which the complexation occurs.

### Protonation Constant

The average number of protons,  $\bar{n}_H$ , associated with 2-ApBzGH at various pH-meter readings were calculated from acid and ligand titration curves using the relationship (2) given by Irving and Rossotti [17,18]:

$$\bar{n}_H = Y - \frac{(V_L - V_A)(N + E^0)}{(V_0 + V_A)T_L^0} \quad (2)$$

where Y is the number of dissociable protons present in the ligand.  $V_L$  and  $V_A$  are the volumes of KOH of concentration N (0.02 M) consumed by solutions (b) and (a), respectively, for the same pH reading and  $(V_L - V_A)$  measures the displacement of the ligand curve with respect to the acid curve.  $V_0$  is the initial volume of the reaction mixture (25 cm<sup>3</sup>), and  $E^0$  and  $T_L^0$  are the resultant concentrations of nitric acid (0.001 M) and 2-ApBzGH (0.0003 M) in the reaction mixture, respectively.

The protonation curves for the proton- ligand systems at different temperatures and ionic strengths (Figure 3) were obtained by plotting  $\bar{n}_H$  vs pH. According to Bjerrum's half integral method [19], the pH value corresponding to  $\bar{n}_H=0.5$  gives the first protonation constant, the value corresponding to  $\bar{n}_H=1.5$  gives the second protonation constant, and so on. It was observed from the figure that the curves did not extend beyond 1.0 on the  $\bar{n}_H$  scale showing the presence of only one dissociable proton in the ligand. The protonation constant of 2- ApBzGH ( $\log K_1^H$ ) thus obtained was used for computation of the stability constant of the Ln(III) complexes. The protonation constants of the ligand evaluated from the curves at different temperatures and different ionic strengths are collected in Table 1 and 2. The

tables show a gradual decrease in the protonation constant of the ligand with increase in temperature and ionic strength indicating that dissociation of the ligand was favorable at lower temperature and ionic strength.

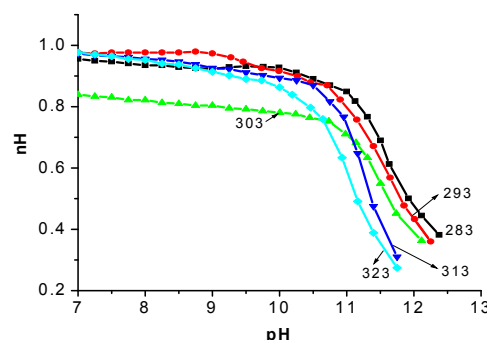


Figure 3 Protonation curves of the ligand at 0.1 M ionic strength at different temperatures (K).

Table 1 Protonation constants of the ligand and stepwise formation constants of Ln(III) complexes at 313 K at different ionic strengths. All the values were obtained after polynomial fitting.

Ligand/Metal Ions	Stability Constant	Ionic strength				
		0.00	0.05	0.10	0.15	0.20
2-ApBzGH	$\log K_1^H$	-	11.52	11.40	11.30	11.22
	$\log K_1^{La}$	8.69	8.07	7.81	7.62	7.45
La	$\log K_2^{La}$	7.72	7.12	6.85	6.70	6.53
	$\log K_3^{La}$	-	-	-	-	-
Pr	$\log K_1^{Pr}$	8.80	8.17	7.90	7.70	7.52
	$\log K_2^{Pr}$	7.74	7.20	6.90	6.80	6.65
	$\log K_3^{Pr}$	-	-	6.23	-	-
Nd	$\log K_1^{Nd}$	8.85	8.23	7.97	7.80	7.60
	$\log K_2^{Nd}$	7.87	7.32	7.08	6.92	6.73
	$\log K_3^{Nd}$	-	7.29	7.00	-	-
Sm	$\log K_1^{Sm}$	8.90	8.30	8.05	7.85	7.70
	$\log K_2^{Sm}$	7.96	7.40	7.17	7.03	6.82
	$\log K_3^{Sm}$	-	7.37	7.06	-	-
Gd	$\log K_1^{Gd}$	8.98	8.40	8.14	7.93	7.75
	$\log K_2^{Gd}$	8.01	7.45	7.20	7.10	6.84
	$\log K_3^{Gd}$	-	6.49	6.92	-	-
Eu	$\log K_1^{Eu}$	9.05	8.44	8.22	8.02	7.81
	$\log K_2^{Eu}$	8.02	7.51	7.25	7.12	6.90
	$\log K_3^{Eu}$	-	7.20	7.22	-	-

\*Standard deviation ( $\pm 0.02 - 0.05$ )

**Table 2** Protonation constants of the ligand ( $\log K_1^H$ ), stepwise formation constants of the complexes ( $\log K_i^{Ln}$ ) and thermodynamic parameters ( $\Delta G$ ,  $\Delta H$ ,  $\Delta S$ ) at 0.1 M ionic strength at different temperatures.

Ligand/ Metal Ions	Stability Constant	Temperatures, K					(-) $\Delta G^\circ$ kcal $\cdot$ mol $^{-1}$	(-) $\Delta H$ kcal $\cdot$ mol $^{-1}$	(-) $\Delta S$ cal $\cdot$ deg $^{-1}$ $\cdot$ mol $^{-1}$
		283	293	303	313	323			
2-ApBzGH	$\log K_1^H$	11.70	11.60	11.40	11.21	10.92			
	(-) $\Delta G$ kcal $\cdot$ mol $^{-1}$	15.17	15.57	15.82	16.07	16.12	-	11.25	+16.89
La	$\log K_1^{La}$	8.54	8.24	7.81	7.67	7.50	12.06		
	$\log K_2^{La}$	7.30	7.03	6.85	6.45	6.10	10.71		
	$\log K_3^{La}$	-	-	-	-	-	-	24.15	12.21
	(-) $\Delta G$	20.51	20.47	20.45	20.28	20.10			
Pr	$\log K_1^{Pr}$	8.60	8.30	7.90	7.78	7.62	12.21		
	$\log K_2^{Pr}$	7.43	7.10	6.90	6.57	6.20	10.74		
	$\log K_3^{Pr}$	6.32	(6.32)	6.23	-	-	-	24.41	12.50
	(-) $\Delta G$	20.76	20.65	20.62	20.55	20.43			
Nd	$\log K_1^{Nd}$	8.74	8.42	7.97	7.89	7.70	12.28		
	$\log K_2^{Nd}$	7.50	7.22	7.08	6.71	6.36	10.92		
	$\log K_3^{Nd}$	7.05	7.20	7.00	6.77	-	-	24.51	11.76
	(-) $\Delta G$	21.03	20.97	20.95	20.91	20.78			
Sm	$\log K_1^{Sm}$	8.86	8.55	8.05	7.93	7.80	12.35		
	$\log K_2^{Sm}$	7.62	7.36	7.17	6.82	6.45	11.05		
	$\log K_3^{Sm}$	7.49	7.43	7.06	6.42	-	-	24.96	12.04
	$-\Delta G$	21.34	21.33	21.31	21.13	21.06			
Gd	$\log K_1^{Gd}$	8.87	8.56	8.14	7.96	7.82	12.46		
	$\log K_2^{Gd}$	7.64	7.38	7.20	6.84	6.50	11.12		
	$\log K_3^{Gd}$	7.78	7.27	6.92	6.76	-	-	22.88	5.41
	(-) $\Delta G$	21.38	21.37	21.35	21.20	21.14			
Eu	$\log K_1^{Eu}$	8.94	8.62	8.22	8.08	7.90	12.56		
	$\log K_2^{Eu}$	7.70	7.44	7.25	6.90	6.54	11.13		
	$\log K_3^{Eu}$	7.61	7.16	7.62	6.65	-	-	25.17	12.04
	(-) $\Delta G$	21.55	21.53	21.52	21.46	21.34			

Standard deviation ( $\pm 0.02 - 0.05$ )

### Metal ligand formation constant

The average number of ligands attached per metal ion,  $\bar{n}$  and the free ligand exponent,  $pL$  were determined using the expressions (3) and (4) [17,18] :

$$\bar{n} = \frac{(V_M - V_L)(N + E^0)}{(V_0 + V_A)T_M^0 n_H} \quad (3)$$

$$pL = \log_{10} \left[ \frac{\sum_{n=0}^{n=j} \beta_n H \left( \frac{1}{\text{anti log } pH} \right)^n}{T_L^0 - \bar{n} T_M^0} \times \frac{V_0 + V_M}{V_0} \right] \quad (4)$$

where  $N$ ,  $E^0$ ,  $V_L$ ,  $V_0$  and  $V_A$  have the same meaning as in (2).  $V_M$  is the volume of alkali added to solution (c) to attain the  $pH$  reading as that of  $V_L$  and  $T_M^0$  is the

metal ion concentration (0.00015 M) in the reaction mixture.

The maximum value of  $\bar{n}$  evaluated for the complexes varies from 2.2 to 3.2 at pH range 7.0 to 9.0, which is approximately the hydrolysis pH range of the rare earth metal ions. It indicates that Ln(III) complexes having different metal-ligand stoichiometries were formed. At pH > 9.0, precipitation occurred and  $\bar{n}$  calculations were done before the point of precipitation. The values of  $\bar{n}$  is (0.2 <  $\bar{n}$  < 1.5) for La(III) chelate and (0.2 <  $\bar{n}$  < 3.5) for other Ln(III) chelates suggesting that 1:1 and 1:2 La(III) complexes were formed while the remaining Ln(III) formed 1:1, 1:2 and 1:3 complexes. Thus, La(III) ion was not able to coordinate to a third ligand. This is in consistent with the formation of 1:2 complexes of 2-ApBzGH with transition metal ions [14]. Expansion of coordination number and formation of 1:3 chelates with Ln(III) ions might be explained in the light of their large size and high positive charge coupled with their tendency to attain higher coordination number.

The metal-ligand formation curves were obtained by plotting  $\bar{n}$  vs pL and Figure 4 represents the metal-ligand formation curves at different temperatures at ionic strength 0.1 M KNO<sub>3</sub>. The first, second and third formation constants ( $\log K_i^{Ln}$ ) of the complexes were evaluated [19] from the complex formation curves and the values so obtained at different temperatures and ionic strengths are included in Tables 1 and 2.

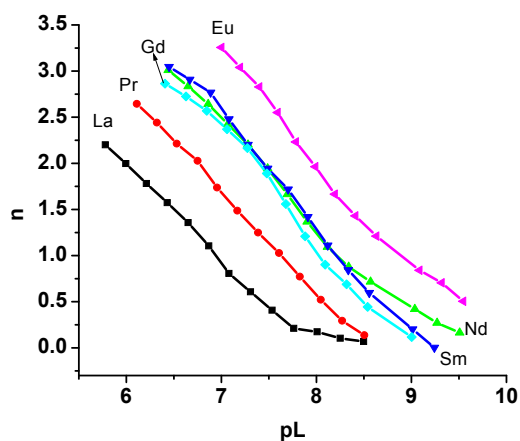


Figure 4 Formation curves of Ln(III) complexes at 303 K at 0.1 M ionic strength

An examination of these values shows that the complexation was more favored at lower temperature and ionic strength and the tendency of the ligand for complex formation decreased with increase in temperature and ionic strength. The existence of intramolecular hydrophobic interaction may be examined in terms of the relation,  $\Delta \log K_i^{Ln}$

$= \log K_1^{Ln} - \log K_2^{Ln}$ . Positive values of  $\Delta \log K_i^{Ln}$  for these Ln(III)-(2-ApBzGH) system may be regarded as an evidence of hydrophobic interactions responsible for relatively greater stabilization of the Ln(III) complexes.  $\Delta \log K_i^{Ln}$  values for the formation of 1:1 and 1:2 complexes is about unity indicating stepwise formation of these complexes while the  $\Delta \log K_i^{Ln}$  values for the formation of 1:2 and 1:3 complexes are small ( $\ll 1.0$ ) suggesting simultaneous bonding of second and third ligand molecules. At a constant temperature, the stability of the metal chelates increases in the order: La<sup>3+</sup> < Pr<sup>3+</sup> < Nd<sup>3+</sup> < Sm<sup>3+</sup> < Eu<sup>3+</sup> > Gd<sup>3+</sup>. The steady increase in stability constants from La<sup>3+</sup> to Eu<sup>3+</sup> may be due to decrease in size with subsequent increase in ionic potential of the Ln<sup>3+</sup> along the series [20]. The decrease of the values of the stability constants with temperature (Table 2) shows that the complex formation process was exothermic in nature and more favorable at lower temperature. Ln (III) ions except La(III) ion were able to coordinate to three ligand molecules at lower temperature so as to saturate their coordination numbers but none of the Ln(III) ions could not form 1:3 complexes at 323 K. A plot of overall stability constants,  $\log \beta$ , where  $\log \beta = \log K_1^{Ln} + \log K_2^{Ln}$  vs  $Z^2/r$  where Z is the charge and r is the ionic radii of the lanthanide ions (Figure 5) indicates that the formation constants of metal chelates increased with decrease in atomic number with a break at gadolinium, the half-filled shell ion which is in accordance with the tetrad effect reported by earlier workers [8,21,22]. The abnormal behavior of Gd(III) known as the 'Gd break' may be attributed to (i) zero field stabilization energy, (ii) unavailability of the well shielded 4f electron for bond formation and (iii) a structural change in the hydration sphere of lanthanide ions near the middle of series [23,24].

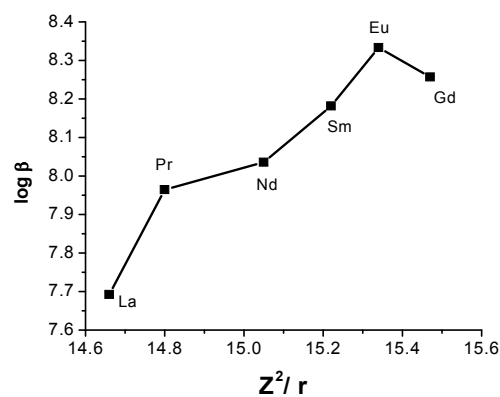


Figure 5 Plot of  $\log \beta$  vs  $Z^2/r$  for Ln(III) chelates.  $\log \beta = \log K_1^{Ln} + \log K_2^{Ln}$ .



### Effect of Temperature

The change in free energy ( $\Delta G$ ) was calculated from the formation constant values ( $\log K$ ) at various temperatures using the following equation:

$$\Delta G = -2.303RT \log K \quad (5)$$

where  $R$  (ideal gas constant) =  $8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$ ;  $K$  = Dissociation constant of 2-ApBzGH or stability constant of the complexes;  $T$  = Absolute temperature. The enthalpy change ( $\Delta H$ ) for the dissociation of 2-ApBzGH and complexation process was evaluated from the slope of the plot ( $\log K_1^H$  or  $\log K_i^{Ln}$  vs  $1/T$ ) using the graphical representation of Van't Hoff's equation (6) and the change in entropy ( $\Delta S$ ) could then be calculated using the relationship (7):

$$\Delta G = \Delta H - T\Delta S \quad (6)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (7)$$

Plot of  $\log \beta$  vs  $1/T$  is a straight line (Figure 6) showing  $\log \beta$  decreases with increase in temperature. This suggests that the interaction of metal ions with the ligand was exothermic in nature. The calculated thermodynamic parameters for the dissociation of 2-ApBzGH and complexation reactions are included in Table 2. It is observed from the table that all the values of the thermodynamic parameters were negative. The negative  $\Delta G$  values indicate that both dissociation of the ligand and the complexation process were spontaneous. Negative  $\Delta H$  also accounts for the exothermic nature of the complexation and the metal-ligand binding process was enthalpy driven.  $\Delta S$  values for the complexation reactions were negative except for the protonation of the ligand which showed that the complexation reactions had unfavorable change of entropy.

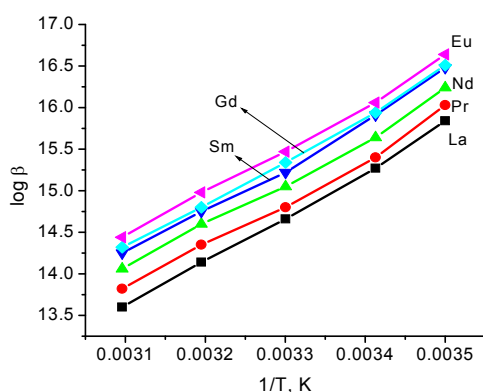


Figure 6 Plot of  $\log \beta$  vs  $1/T$ ;  $T$  in absolute scale.

An extensive solvation of metal chelates in aqueous-organic medium [22] for all the Ln(III) complexes might also be responsible for the negative  $\Delta S$  values. These values have no sharp behavior with temperature showing the independent nature of the reactions with respect to temperature [25].

### Effect of ionic strength

The data obtained for  $\log K_1^H$  or  $\log K_i^{Ln}$  could be utilized to study the thermodynamic dissociation constants at zero ionic strength and to know the mechanism of complexation equilibria, since the complexation reactions involve ions or reactant product sites. The validity of Bronsted equation was tested for various systems by plotting the graph  $\log K_i^{Ln}$  vs  $\sqrt{I}$  which is a straight line (Figure 7). Extrapolation of  $K_i^{Ln}$  to zero ionic strength gives thermodynamic  $K_0^{Ln}$  values and the symbols  $K_i^{Ln}$  and  $K_0^{Ln}$  refer to the negative logarithm of the ionization constants at finite ionic strength and at zero ionic strength. The protonation constant of the ligand and stability constants of all the complexes of 2-ApBzGH showed a steady decrease with increasing ionic strength, which is in agreement with Debye-Huckel equation [26].

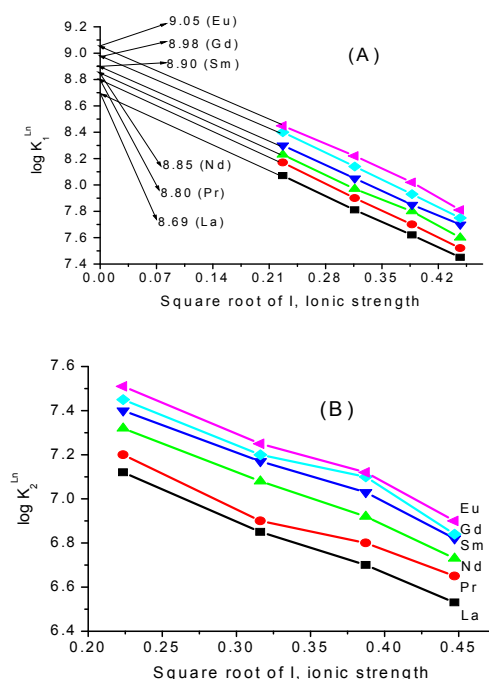


Figure 7 Plots of  $\log K_i^{Ln}$  vs  $\sqrt{I}$  for Ln(III) chelates (A) for  $\log K_1^{Ln}$  and (B) for  $\log K_2^{Ln}$ ;  $\log K$  values at  $I=0$  are indicated with arrows on the respective curves. Similar values are also noted down from (B). The values obtained on extrapolation of the curves are given in the table.

### Thermodynamic Parameters of Complexation as a Function of Ionic Radii of the Lanthanides

The correlation between the thermodynamic parameters of the complexation with the ionic radii of the metal ions may be analyzed from Table 2 and it is important to see how the ionic size of the lanthanides affects the stability constants and the changes in free energy, enthalpy and entropy. Both  $\Delta H$  and  $\Delta S$  values decrease and  $\Delta G$  value increases with decrease in the ionic size from lanthanum to europium with a break at gadolinium. A small break is also observed in the  $\Delta H$  and  $\Delta S$  values at praseodymium. Such patterns of the thermodynamic data against ionic size are generally true for complexes of Ln series [8].

### CONCLUSION

On the basis of the foregoing discussion, 2-*ApBzGH* is found to possess only one dissociable proton and forms stable deprotonated complexes with Ln(III) ions in which the ligand exhibits tautomerism and acts as a uninegative bidentate species bonding through the iminol oxygen and azomethine nitrogen in aqueous-dioxane medium. While La(III) ion forms only 1:1 and 1:2 complexes, other Ln(III) ions are able to expand their coordination numbers and can bind upto three ligand molecules forming 1:1, 1:2 and 1:3 species. Since the ligand is a monobasic ligand, formation of 1:2 complexes would not satisfy the charge of La(III) ion and therefore, it is probable that the metal ion is bonded to other charge anion in order to balance its charge. The trend in the stability constants of the complexes,  $\text{La}^{3+} < \text{Pr}^{3+} < \text{Nd}^{3+} < \text{Sm}^{3+} < \text{Eu}^{3+} > \text{Gd}^{3+}$  shows gadolinium break due to tetrad effect and the values decrease with increase in temperature and ionic strength. Both protonation and complex formation of the ligand are spontaneous and exothermic. All reactions are enthalpy-driven.

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