



pH-Metric Studies of (2-pyrrole)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone with Inner Transition Metals



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Abstract

The reaction of (2-pyrrole)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone with trivalent 4f lanthanide metal ions (La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III) and Yb(III)) and 5f actinide metal ion UO₂(II) has been studied potentiometrically in 75% (v/v) dioxane-water; at 283, 293, 303 and 313K. The ligand behaves as mono-protic species with the dissociation of hydrazo group proton and reacts with metal ion in molar ratio 1:2; M:L in solution. The formation constants were calculated, which decrease as temperature increases. The negative values of ΔH° and ΔG° indicate that the complexation process is exothermic and proceeds spontaneously, respectively. The electrostatic forces are weaker than non-electrostatic forces, where $-\Delta G^\circ_{\text{non}}$ is lower than $-\Delta G^\circ_{\text{el}}$. $\Delta G^\circ_{\text{el}}$ has negative comparable values and suggests that the complexation process is affected by the temperature and environment. The higher negative value of $\Delta H^\circ_{1\text{non}}$ than $\Delta H^\circ_{2\text{non}}$ for UO₂-complex would reflect that the bond strength from ligand to UO₂ ion, which is stronger in the 1st coordination than the 2nd coordination.

Keywords: pyrrole, hydrazone, triazine, pH-metric studies.

1. Introduction

Hydrazones and their metal complexes play a central role in many fields [1-8]. They are used in biomedical field and wastewater remediation [9], Photoresponse [10], optoelectronic [11], catalytic [12], analytical [13] and cytotoxicity [14,15] studies. Also, they are used as antimicrobial, antitumor [16], anticancer [17], antioxidant [18], antiproliferative [19] and chemotherapeutic agent [20]. Lanthanides and actinides and their complexes have attracted a great interest as a result of their antimicrobial, antioxidant, antitumor, DNA binding, electro-optical, nephelauxetic, luminescent properties [21-35]. Pyrrole is important heterocyclic compound, where porphyrins (haem), chlorines (chlorophyll) and corrin (vitamin B12) contain pyrrole ring [36]. This is

extension to work on the ligand, (2-pyrrole)-(5,6-diphenyl-[1,2,4]-triazin-3-yl)hydrazone, HPT, where in our previous studies, the binary and ternary complexes of Ni(II) and Co(II) complexes were isolated and characterized [37]. On the other hand, the pH-metric studies of the free ligand, Ni(II) and Co(II) ions have been discussed in our previous study [37]. The aim of this study is the interaction of the studied ligand with trivalent 4f lanthanide metal ions (La(III), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III) and Yb(III)) and 5f actinide metal ion UO₂(II) potentiometrically in 75% (v/v) dioxane-water; at 283, 293, 303 and 313K using 0.1 M KNO₃ as a supporting electrolyte.

2. Experimental

2.1. Materials

Hydrazine hydrate (100%), thiosemicarbazide, benzil, glacial acetic acid, pyrrole and POCl₃ were

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either Aldrich, BDH or Merck products. Organic solvents were reagent grade chemicals and were used without further purification.

2.2. Preparation of metal ions solutions

Solutions of Ln(III)-nitrates were prepared by dissolving their corresponding oxides in nitric acid and evaporating till dryness. The resulting nitrates were dissolved in the appropriate volume of water. The pH value of the resulting nitrate solution was checked and found to be ~ 4.5. The solutions of Ln(III) ions were standardized by EDTA using xylenol orange indicator and acetate buffer of pH= 5.

2.3. Preparation of the organic ligand solution

Solution of 0.02 M ligand was prepared for pH-metric titrations by dissolving the accurate weight of the ligand in the proper volume of the purified solvent.

2.4. Preparation of KOH solution

A concentrated solution of potassium hydroxide was prepared from the solid (BDH) in carbon dioxide-free boiled bidistilled water. The solution was stored in a stoppered polyethylene bottle for some days with occasional shaking to obtain a carbonate-free hydroxide. The solution of base of the required molarity was standardized against oxalic acid, potassium hydrogen phthalate.

2.5. Synthesis of HPT ligand and pH-metric measurements

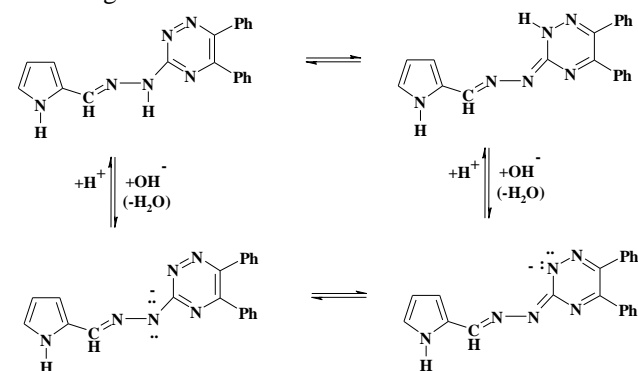
The ligand was prepared as described in previous publication [37]. The Jenway Instrument, model 3505 pH- ion selective electrode meter fitted with a combined glass electrode is used for pH-metric measurements. A stream of purified nitrogen gas was passed during the entire titration. The thermostat model Lauda, Heizung Chauffage heater is used to keep temperature constant. The pH-metric titrations were carried out in 75% (v/v) dioxane- water at 283, 293, 303 and 313 K. The standard solutions of metal nitrates (0.001 mol L^{-1}) and the ligand (0.003 mol L^{-1}) were titrated against 0.065 mol L^{-1} KOH solution. The total volume was 30 mL. The investigated solution was adjusted to 0.1 M ionic strength using KNO_3 and maintained at a constant temperature by circulated water through a sealed-jacketed cell. An inelt tube in the cell kept the solution under stream of purified nitrogen gas by passing it through two

alkaline pyrogallol bubblers. The pH-readings were taken after addition of each increment of base and the reading became constant.

3. Results and discussion

3.1. Dissociation constants

The tautomerism and ionized forms of the investigated ligand (HPT) are shown in the following Scheme 1:



Scheme 1 Tautomeric and ionized forms of HPT.

The pH-titration curves are shown in Fig. 1 for the free HPT ligand and Sm(III) complex at different temperatures (283, 293, 303 and 313K) and constant ionic strength 0.1 M KNO_3 , in 75% (v/v) dioxane-water. Under these conditions, the ligand behaves as mono-protic species with the dissociation of hydrazo group proton [37]. The detailed calculation of pK^{H} [37] of the free HPT at different temperatures (283, 293, 303 and 313K) are presented graphically in Fig. 2 [38].

3.2. Formation constants

For calculation of the stepwise formation constants, the method adopted by Irving-Rossotti [39] has been employed to calculate the parameter \bar{n} (average number of ligand ions attached / one metal ion) and pL (free ligand exponent).

$$\begin{aligned} \log(\bar{n}/1 - \bar{n}) &= \log K_1 - \text{pL} & \bar{n} < 1.0 \\ \log(\bar{n} - 1/2 - \bar{n}) &= \log K_2 - \text{pL} & 1.0 < \bar{n} < 2.0 \end{aligned}$$

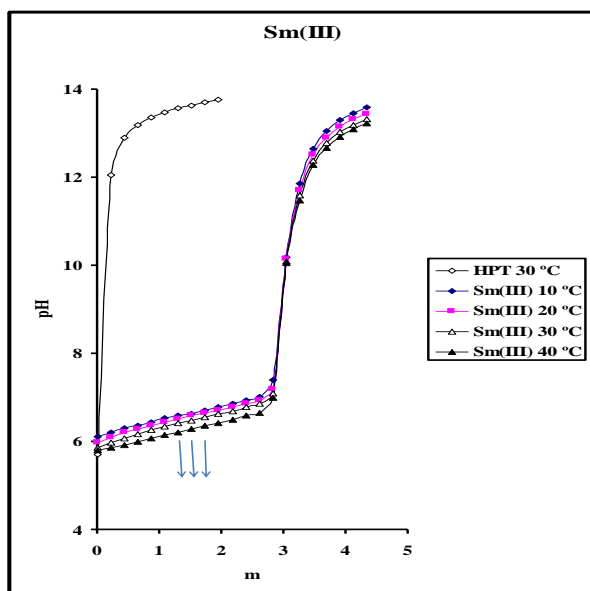


Fig. 1. pH-Metric titration curves of HPT (3×10^{-3} M) [36] in presence of Sm(III) (1×10^{-3} M) in 75% (v/v) dioxane-water at different temperatures and $V_0 = 30$ mL.

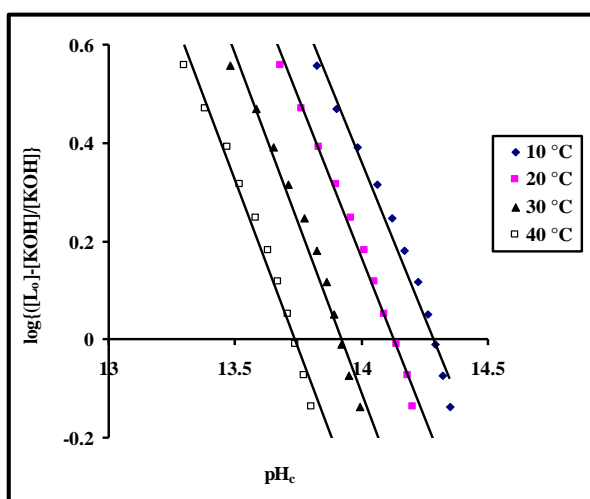


Fig. 2. Evaluation of the $pK^{H'}$'s of HPT [36] in 75% (v/v) dioxane-water at different temperatures.

It is evident that the degree of metal-ligand formation \bar{n} extends between 0.1 – 1.9, suggesting that the higher species in solution is 1: 2; M: L. The formation constants were summarized in Table 1 and represented graphically in Fig. 3.

The values of the logarithms of the formation constants were refined using the least-squares method. The error limits were calculated after subjecting the data to least-squares analysis and represent the standard deviation of an individual run.

Inspection of the titration curves given in Fig. 1 reveals the following:

- (i) The formation of higher complex species more than ML_2^{+n-2} was checked by the titration of (1:3) M:L ratio. The titration curves (in pervious study on Ni and Co ions) show only a sharp inflection at $m = 2.0$ corresponding to the formation of ML_2^{+n-2} as higher formed species. In this study, $m = 3.0$, where this refers that formation of hydroxo complex. Hence, the formation of higher species such as ML_3^{+n-3} could be excluded due to the bulkness of the ligand.
- (ii) Values of $\log K_2$ for the bis-chelates of Ln(III) ions with HPT are not included in Table 1 because of the tendency of these species to hydrolyze in the region of its formation as indicated in Fig. 1.

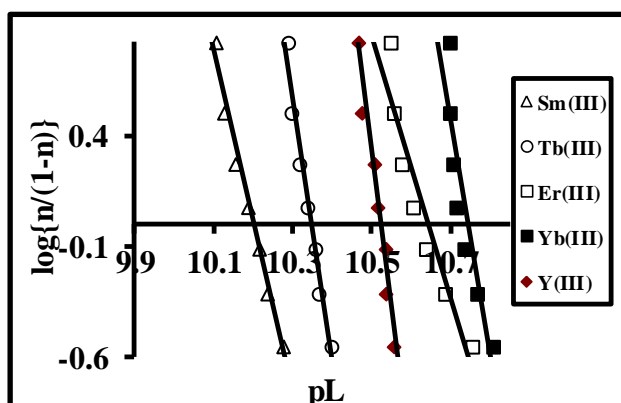


Fig. 3. Evaluation of the formation constants ($\log K_1$) of the HPT-complexes in 75% (v/v) dioxane-water at 303K.

The dissociation constants of the ligand [37] and its stepwise formation constants with metal ions in 75% dioxane-water are summarized in Table 1. $\log K_1 > \log K_2$ for UO_2 complex. This is consistent with the fact that the Coulombic attractions between M^{2+} and L^- are higher than those between ML^+ and L^- , in addition to some steric hindrance for the second coordination (Table 1). The formation constants of the divalent oxygenated cation complexes $UO_2(II)$ have higher values. This may be attributed to the bonded oxygen atoms which may increase the electrostatic attraction between the metal ion and the coordinated ligand and overcome any steric hindrance afforded by the oxygen of the oxygenated cations. Many attempts have been made to find

Table 1 Formation constants and thermodynamic functions* of the complexes of HPT ligand [36], in 75% (v/v) dioxane-water.

Cation	283K	293K	303K	313K	Thermodynamic functions			Cation	283K	293K	303K	313K	Thermodynamic functions		
	logK1	logK1	logK1	logK1	-ΔG°1	-ΔH°1	ΔS°1		logK2	logK2	logK2	logK2	-ΔG°2	-ΔH°2	ΔS°2
UO ₂ (II)	12.08	11.99	11.83	11.74	16.38	4.77	38.32	UO ₂ (II)	11.84	11.79	11.58	11.56	16.03	4.25	38.88
Cation	283K	293K	303K	313K	Thermodynamic functions			Cation	283K	293K	303K	313K	Thermodynamic functions		
	logK1	logK1	logK1	logK1	-ΔG°1	-ΔH°1	ΔS°1	logK1	logK1	logK1	logK1	logK1	-ΔG°1	-ΔH°1	ΔS°1
H(I) [36]	14.33	14.17	13.98	13.79	-19.36	-7.31	-39.90	Gd(III)	10.46	10.30	10.13	10.01	14.03	6.16	25.96
La(III)	10.24	10.14	10.06	10.02	13.93	3.01	36.03	Tb(III)	10.50	10.42	10.34	10.26	14.32	3.24	36.58
Pr(III)	10.37	10.30	10.15	10.04	14.05	4.6	31.20	Dy(III)	10.59	10.47	10.40	10.33	14.4	3.45	36.14
Nd(III)	10.58	10.40	10.36	10.32	14.35	3.35	36.27	Ho(III)	10.58	10.30	10.04	9.91	13.9	9.22	15.45
Sm(III)	10.33	10.26	10.19	10.16	14.11	2.36	38.79	Er(III)	10.78	10.70	10.63	10.58	14.72	2.72	39.61
Eu(III)	10.78	10.52	10.35	10.18	14.33	7.99	20.92	Yb(III)	11.09	10.83	10.74	10.62	14.87	6.11	28.93

* ΔG° and ΔH° are in kcal mol⁻¹, while ΔS° is in cal mol⁻¹ K⁻¹ (r = 0.969- 0.999 except r=0.933 for Nd(III)-complex).

general relationships to investigate the factors affecting the stability of the chelate formation.

3.3. Effect of temperature

In an attempt to calculate the thermodynamic parameters, the formation constants of the HPT ligand with metal-ions were determined pH-metrically in 75% (v/v) dioxane-water at various temperatures *viz.* 283, 293, 303 and 313 K (Table 1). The thermodynamic functions (Table 1) are calculated by using the well-known relations:

(i) $\Delta G^\circ = -4.57 T \log K$, where ΔG° is in cal mol⁻¹.

(ii) $\log K = (-\Delta H^\circ / 4.57 T) + (\Delta S^\circ / 4.57)$.

Thus, on plotting $\log K$ vs. $1/T$, one gets a straight line whose slope = $-\Delta H^\circ / 4.57$ and its intercept = $\Delta S^\circ / 4.57$.

As it is clear from Table 1 the free energy ΔG° for HPT ligand is positive, indicating that the dissociation process is not spontaneous. The ΔH° values are positive indicating that the dissociation is accompanied by absorption of heat and the process is endothermic. ΔS° value of HPT ligand is negative which may be due to the fact that the degree of reorientation and partially immobilization of dioxane and water molecules by [H⁺], the neutral and anionic species are greater in these mixed solvents [37].

From the values of formation constants (Table 1), it is clear that the stepwise formation constants decrease with the rise in temperature indicating that the formation equilibria are exothermic. This is also born out by the fact that ΔG° and ΔH° are both negative. The negative values of ΔG° indicate that the complexation proceeds spontaneously.

The large entropy contribution as a major driving force for the metal-ligand coordination is

substantiated by relatively large magnitude of ΔS°_1 and ΔS°_2 (Table 1).

The entropy changes associated with the metal-chelate formation (Table 1) of the studied systems are relatively high and positive for the 1:1 and 1:2 (M:L) complexes which could be attributed to a companion of:

- An increase in ΔS° values owing to release of water of hydration.
- A decrease in entropy of translation on the formation of one chelate from two species.
- A decrease in configuration entropy of the ligand on complex formation.

For the reaction of a metal ion with charged donor groups (the ligand under investigation behaves as monoprotic species. i.e. HL), the entropy changes associated were predominate, because of the neutralization of charge on the metal ion. This results in greater release of water of hydration and hence greater distortion of the partially immobilized and oriented water dipoles.

In order to provide information of the nature of bonding in the complexes, the values of ΔG°_n , ΔH°_n and ΔS°_n (n = 1 or 2) given in Table 1, have been separated into their electrostatic (el) and non-electrostatic or cratic components (Table 2). Electrostatic (el) or (environment) components represent long-range electrostatic forces depending upon environment and temperature; while non-electrostatic (non) or (cratic) components represent short-range or quantum-mechanical forces; covalent forces insensitive to environment and independent of temperature.

The separated values ΔG°_{el} , ΔG°_{non} , ΔH°_{el} , ΔH°_{non} and ΔS°_{el} are calculated for all complexes under investigation and given in Table 2. ΔS°_{non} is constant

and equals to -8 cal/mol.K. Inspection of the data (Table 2) reveals the following;

- I. ΔG_{el}° has negative comparable values and suggests that the complexation process is affected by the temperature and environment.
- II. $-\Delta G_{non}^{\circ} < -\Delta G_{el}^{\circ}$. This order remains almost constant in all systems, indicating that the electrostatic forces are weaker than non-electrostatic forces. This reflects thereby that metal chelation reactions occur by similar mechanism.

III. ΔH_{el}° has positive values, this is consistent with $T = 303K > \theta = 219K$ and results in an endothermic contribution to the total change of enthalpy. $\Delta H_{el}^{\circ} = (T - \theta) \Delta S_{el}^{\circ}$

IV. $(-\Delta H_{1non}^{\circ}) > (-\Delta H_{2non}^{\circ})$. The higher negative value of ΔH_{1non}° than ΔH_{2non}° for UO_2 -complex would reflect that the bond strength from ligand to UO_2 ion which is stronger in the 1st coordination than the 2nd coordination.

Table 2 Electrostatic and non-electrostatic thermodynamic functions^{a,b} of HPT-chelates.

Complex	1 st coordination				ΔS_{el}°	Complex	2 nd coordination				ΔS_{el}°
	$-\Delta G_{el}^{\circ}$	ΔG_{non}°	ΔH_{el}°	ΔH_{non}°			$-\Delta G_{el}^{\circ}$	$-\Delta G_{non}^{\circ}$	ΔH_{el}°	ΔH_{non}°	
UO₂(II)	10.14	6.24	3.89	8.66	46.32	UO₂(II)	10.27	5.77	3.94	8.19	46.88
Complex	1 st coordination				ΔS_{el}°	Complex	1 st coordination				ΔS_{el}°
	$-\Delta G_{el}^{\circ}$	ΔG_{non}°	ΔH_{el}°	ΔH_{non}°			$-\Delta G_{el}^{\circ}$	$-\Delta G_{non}^{\circ}$	ΔH_{el}°	ΔH_{non}°	
Y(III)	10.01	4.56	3.84	6.98	45.71	Gd(III)	7.44	6.59	2.85	9.01	33.96
La(III)	9.64	4.29	3.69	6.71	44.03	Tb(III)	9.76	4.56	3.74	6.98	44.58
Pr(III)	8.58	5.47	3.29	7.89	39.20	Dy(III)	9.67	4.73	3.71	7.16	44.14
Nd(III)	9.69	4.65	3.72	7.07	44.27	Ho(III)	5.14	8.77	1.97	11.20	23.45
Sm(III)	10.25	3.86	3.93	6.29	46.79	Er(III)	10.43	4.29	3.99	6.72	47.61
Eu(III)	6.33	8.00	2.43	10.40	28.92	Yb(III)	8.09	6.78	3.10	9.21	36.93

^a ΔG_{ox} , ΔH_{ox} are in k cal. mol⁻¹, while ΔS_{ox} is in cal. mol⁻¹ K⁻¹ (x = el or non).

^b $\Delta S_{non} = \text{constant} = -8 \text{ cal. mol}^{-1} \text{ K}^{-1}$ (not included in the Table).

In general, ΔH_{non}° arises by the changes in the ligand field stabilization accompanying the complex-formation and reflects the covalent nature of bonding and also the structural changes upon complexation [40]. Also, this order is in good agreement with the softness/hardness of these metal ions in solution towards a specific ligand (HPT).

As might be expected from the high stabilities obtained for most M^{n+} -HPT complexes in 75% (v/v) dioxane-water medium, the enthalpies are not greatly exothermic. This is because the exothermic ΔH_{non}° value is compensated by the endothermic ΔH_{el}° value. All the bivalent and trivalent metal ions are nearly similar numerically in ΔH_{el}° (Table 2) in comparison with ΔH_{non}° . ΔH_{1el}° for $UO_2(II)$ equals 3.89 Kcal/mol and the quantitative inspection of ΔH_{el}° and ΔH_{non}° makes it seem that the order in the magnitude of ΔH° among metal ions carrying the same charge is determined directly by the magnitude of ΔH_{non}° .

The ΔH_{non}° values reflect the covalency of the bonding and structural changes on complexation [41]. Regarding the covalency, the softer metal ion has a greater affinity for the softer donors [42]. Values of ΔH_{non}° are plotted against the quantity E_n^* , introduced by Klopman [43] as a measure of hardness and softness of metal ions in aqueous solution. A soft metal is characterized by large negative value in E_n^* and *vice versa*. In general, E_n^* value above 2ev hard, 2 to -2 intermediate and below -2 ev soft. ΔH_{el}° values are surprisingly constant, this is ascribed to the nearly constant ionic radii of these metals.

3.4. Tetrads

It is easy to notice that the correlation between the values of the formation constants data of Ln^{3+} -HPT complexes (Table 1) with the third ionization potential ($\sum_1^3 I$) and $(1/r)$ according to eqns. i and ii were examined. The graph which illustrates these correlations is shown in Fig 4 and Table 3. In most cases the first step (1:1) are more correlated by the

third ionization potential ($\sum_1^3 I$) than by $(1/r)$ (see Table 3) as indicated by comparison of the corresponding correlation coefficients (R) of each relationship. It seems that the bonding in these complexes possesses more covalent character. This might result from the polarizing power of the lanthanide ion and thus an increasing tendency to form covalent bonds with HPT ligand, therefore, the correlations are determined by the ionization potentials ($\sum_1^3 I$).

$$\frac{\log K^* - \log K}{\log K^*} \neq \frac{\sum_1^3 I^* - \sum_1^3 I}{\sum_1^3 I^*} \quad (i)$$

$$\frac{\log K^* - \log K}{\log K^*} \neq \frac{(1/r^*) - (1/r)}{(1/r^*)} \quad (ii)$$

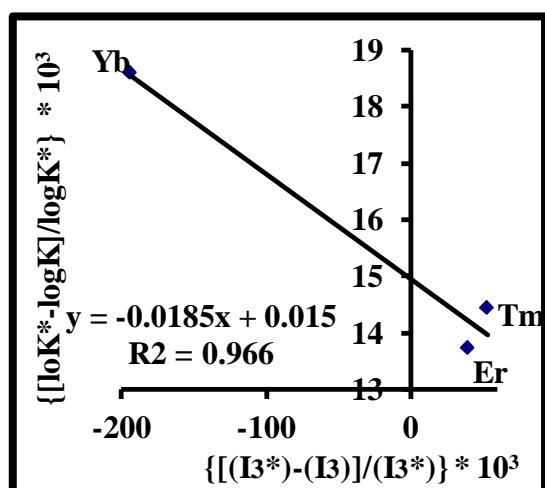
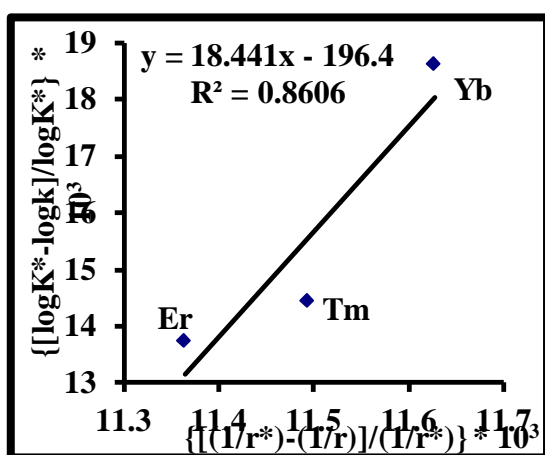


Fig. 4. Dependence of the formation constants of Ln^{3+} - HPT complexes on the ionic radius or ionization potential in 75% (v/v) dioxane-water at 283K.

Conclusions

The current ligand (HPT) behaves as monobasic species (HL) towards the metal ions in solution as evidenced from the titration curves. The maximum \tilde{n} values were found to be ≈ 2 , revealing that both ML and ML_2 species are formed in solution. For UO_2 complex; $\log K_1 > \log K_2$ indicating that the vacant sites of the metal ions are more freely available for binding of a first ligand than second one. The presence of 5-membered chelate rings accompanied by resonance stabilization. The formation constants were calculated, which decrease as temperature increases. The negative values of ΔH° and ΔG° indicate that the complexation processes are exothermic and proceeds spontaneously, respectively. $\Delta G_{\text{non}}^\circ$ is lower than $-\Delta G_{\text{el}}^\circ$, so that the electrostatic forces are weaker than non-electrostatic forces. The complexation process is affected by the temperature and environment, where $\Delta G_{\text{el}}^\circ$ has negative comparable values.

Table 3. Formation constants of trivalent lanthanide metal ions with HPT and their periodical change (tetrads) in 75% dioxane-water at different temperatures.

Cation	HPT				Tetrad	(Eqn. i)			(Eqn. ii)		
	283 K	293 K	303 K	313 K		a	b	R ²	a	b	R ²
283 K											
La(III)	10.24	10.14	10.06	10.02	La-Nd	-	0.0252	0.8607	-0.8087	0.0290	0.2681
Ce(III)					Pm-Gd	0.3149	0.0058	0.5307	-1.7903	0.0245	0.0750
Pr(III)	10.30	10.22	10.10	10.03	Gd-Ho	0.1803	0.1051	0.0003	0.4171	-0.6763	0.0160
Pr(III)	10.37	10.30	10.15	10.04	Gd-Ho	0.1051	0.0003	0.4171	-0.6763	0.0160	0.7939
Nd(III)	10.58	10.40	10.36	10.32	Er-Lu	-	0.0150	0.9660	18.4410	-	0.8606
					Er-Lu	0.0185				0.1964	
293 K											
Pm(III)	10.45	10.33	10.27	10.25	La-Nd	-	0.0104	0.9157	-0.0921	0.0105	0.1942
Sm(III)	10.33	10.26	10.19	10.16	Pm-Gd	0.0435	0.1192	0.0028	0.5882	-0.8938	0.0112
Eu(III)	10.78	10.52	10.35	10.18	Gd-Ho	0.1192	0.5009	-	0.9865	-0.8006	0.0144
Gd(III)	10.46	10.30	10.13	10.01	Gd-Ho	0.5009	0.0167				0.1160
					Er-Lu	0.0098	0.0056	0.9308	-7.2287	0.0883	0.4512
303 K											
Tb(III)	10.50	10.42	10.34	10.26	La-Nd	-	0.0265	0.8650	-0.9338	0.0307	0.2627
Dy(III)	10.59	10.47	10.40	10.33	La-Nd	0.3683	0.1000	-	0.6506	-0.5061	0.0023
Dy(III)	10.59	10.47	10.40	10.33	Pm-Gd	0.1000		0.0014			0.0239
Ho(III)	10.58	10.30	10.04	9.91	Gd-Ho	1.0004	-	0.9906	-1.5094	0.0240	0.1038
Er(III)	10.78	10.70	10.63	10.58	Gd-Ho	0.0365	1.0004	-	0.9906	-1.5094	0.0240
					Er-Lu	-	0.0054	0.6998	6.7874	-	0.9999
					Er-Lu	0.0054				0.0724	
313 K											
Tm(III)	10.93	10.76	10.68	10.60	La-Nd	-	0.0380	0.8990	-1.4015	0.0413	0.2176
Yb(III)	11.09	10.83	10.74	10.62	La-Nd	0.6192	0.0528	-	0.7098	-0.1515	0.0084
					Pm-Gd	0.0528		0.0062			0.0059
Lu(III)	11.30	10.87	10.79	10.64	Gd-Ho			-	0.9915	-1.7650	0.0281
					Gd-Ho	1.1878	0.0432				0.1007
					Er-Lu	2x10 ⁻⁵	0.0019	0.7035	-0.0268	0.0022	0.9999

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