Thermodynamic Properties of Some Lanthanide Metal Ion Complexes of Newly Mono- and Dioximes in Dioxan-water mixtures

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The protonation constants of monoxime HL^1 and dioxime H_2L^2, derived from 1-(o-hydroxybenzoyl)propane-1,2-dione were determined by pH-metric method. The stability constants of their complexes with a series of lanthanide metal ions increase in the order of Gd(III) < Nd(III) < Dy(III) < Sm(III) < Tb = Er(III) < La(III) < Eu(III) at M:L ratio of 1:3 at different temperatures (20, 30, and 40 °C) and constant ionic strength in dioxin-water mixtures (25-75% v/v). The thermodynamic parameters were determined and indicated that the ligand dissociation and complex formation reactions were exothermic.

Keywords: Oximes; Lanthanide metal ion complexes; potentiometry; protonation constants ; stability constants.

1. INTRODUCTION

Metal complexes of *o*-hydroxyoximes received a considerable attention to their structural feature which have general interest [1-5]. These features include short intramolecular hydrogen bonds and packing configuration which give raise to unusual optical properties hydroxyoximes and oxime derivatives used as commercial reagents in extractive metallurgy in both solvent extraction and forth flotation [6-8]. Oximes are used also as analytical reagents [9,10] and serves as models for biological systems such as vitamin B_{12}, oxygen carrier and as semiconducting material [11], as well as catalysts

in chemical process [12,13]. Dioximes are successful sequestering agents for transition metals and other ions, as well as semiconducting materials [14]. The chemistry of monooxime HL^1 and dioxime H_2L^2, derived from 1-(o-hydroxybenzoyl) propane-1,2-dione [15,16] with some lanthanide metal ions is reported with special reference to their formation and structure in solution. The acidity constants, K_a of the ligands and the stability constants, $\log 10\ K_{st}$, of their obtained metal complexes were determined using pH-metric titration in in aqueous media 75-25% v/v dioxane-water with different ratios and at different temperatures.
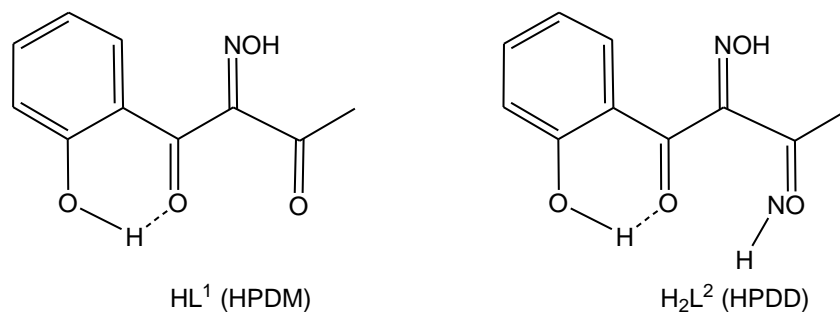
Scheme 1. The structures of the ligands HL^1 and H_2L^2

2. EXPERIMENTAL

2.1. Materials and reagents

All chemical used were of Merk or BDH. Hydroxylamine hydrochloride was commercial grade. Metal salts $Ln(NO_3)_3.xH_2O$ and UO(II) nitrates, and Ru(III) chlorides were BDH and solvents used in pH-metric titrations 1,4-dioxane, methanol and DMF were HPLC.

2.2. Procedure of Potentiometric titration:

Lanthanide salts were prepared in redistilled water. HNO_3 solution was standardized with KOH according to Gran´s method [17]. Carbonate free potassium hydroxide solution was standardized with standard potassium hydrogen phthalate. The metal salts solutions were standardized using EDTA titration (acetate buffer, xylenol orange as indicators). The ligand solutions were prepared in 1,4-dioxane, methanol and DMF (HPLC). Potentiometric titrations were carried out using a Digital meter-Delta 320 pH-meter with combined electrode, buffers adjusted with BDH, pH (4.00, 7.00, 9.00). All the titrations were thermostatted with a circular D_8-G. Haake Mess techinink at 3 different temperature (20, 30 and 40°C): Three sets of reaction mixtures were prepared and titrated against KOH 0.1 M solution in 75% v/v solvent-water: **(i)** 2.5 ml KNO_3 (0.1M) + 5 ml HNO_3 (0.01 M); (ii) 2.5 ml KNO_3 (0.1 M) + 5 ml HNO_3 (0.01 M) + 5 ml ligand (0.01 M), **c-**2.5 ml KNO_3 (0.1 M) + 5 ml HNO_3 (0.01 M) + 5 ml ligand (0.01 M) + 1 ml metal nitrate (0.01 M). The volume of each set was made up to 50 ml,

with 75% dioxane water mixture, 75% v/v methanol-water, 75% v/v DMF-water. The ionic strength of each reaction mixture was maintained at 0.10 M using KNO_3.

3. RESULTS AND DISCUSSION

### 3.1. Stability constant of metal complexes in aqueous solution

3.1.1. pH-metric titration

The monoxime ligand HL^1 and dioxime H_2L^2 (Scheme 1) were potentiometrically titrated with a standard solution KOH at IS = 0.1 (KNO_3) at three temperatures 20, 30 and 40°C. The equilibrium curves (Figures 1 and 2) at 20ºC represent the acid titration curve and metal ligand titration curves of La(III), Nd(III), Eu(III), Er(III), Tb(III), Dy(III) Sm(III) and Gd(III), respectively. Similar curves were obtained at the other temperatures.
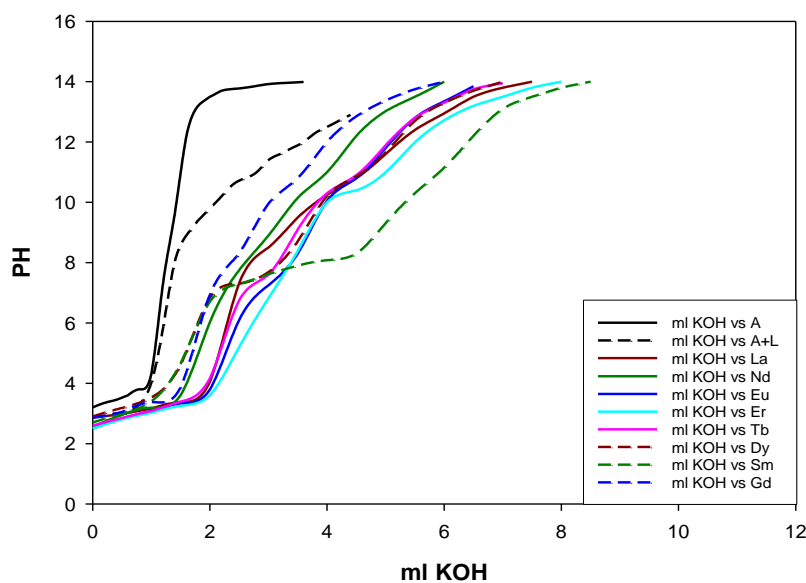
Figure 1. Titration Curves of HL^1 with some Ln^{+3} ions in 1,4 Dioxane (75%, v/v)at 20 °C .

The stability constants log b of HL^1 and H_2L^2 with some lanthanide ions in dioxane -water at (75 %, v/v) at 20 , 30 and 40 °C are shown in Table 1. The titration curves in presence of metal ions give infliction between $a = 0$ to $a = 2$ indicating formation of bis-chelate ML_2. The curves also show steady state at pH 7.5 to 9.0 due to formation of hydroxo complex as no precipitate formed during titration.
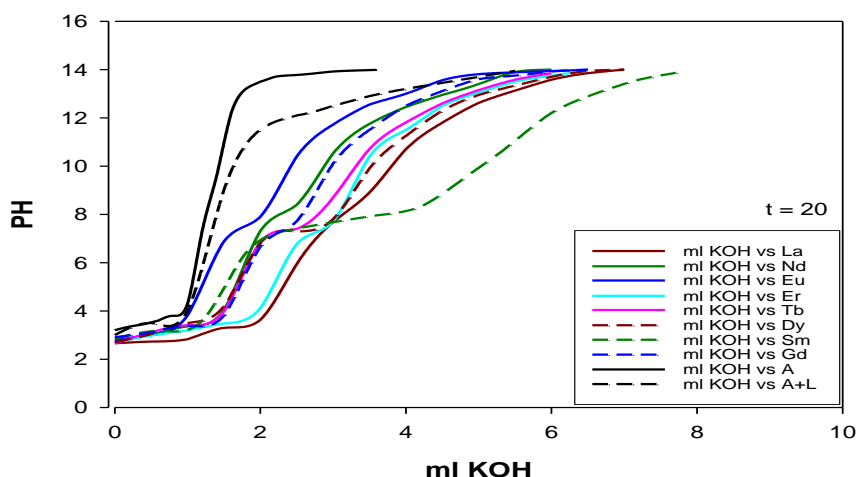
Figure 2. Titration Curves of H_2L^2 with some 1,4 Dioxane (75%, v/v) at (20°C)

Table 1. the stability constants log b of HL^1 and H_2L^2 with some lanthanide ions in dioxane -water at (75 %, v/v) at 20 , 30 and 40 °C

Ln^{3+}	H_2L^2			HL^1
	20 °C	40 °C	30 °C	20 °C
La	33.45	31.30	31.0	26.35
Nd	33.90	32.50	31.05	25.15
Sm	33.80	33.35	33.00	25.75
Eu	34.50	33.88	33.00	26.60
Gd	33.40	32.25	30.90	24.90
Tb	36.15	3295	32.50	25.90
Dy	36.30	34.50	33.10	25.25
Er	34.9	34.00	31.60	25.90

The librated protons may be due to phenolic protons ($pK_a = 9.62$) as its more acidic than oximic proton ($pK_a = 12.1$). The small difference between log K_1 and log K_2 can be explained in terms of spontaneous formation of ML_1, ML_2. Titration curves of HL^1 fig. (1), with Ln^{3+} indicate formation of tris-chelate as inflection at n = 2.66 $\bar{n}$ 3. The stability constants increase in the order La(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Dy(III) < Er(III). The presence of two inflictions at pH 2.5 – 12.5, in the H_1L^1 and H_2L^2 curves figures 3 and 4. which corresponds to neutralization of two proton in the aqueous solution. Addition of metal ions to the free ligand shifts the buffer region to lower pH. This prove that complex formation proceeds by releasing phenolic protons and then one of oximic hydrogen [18].
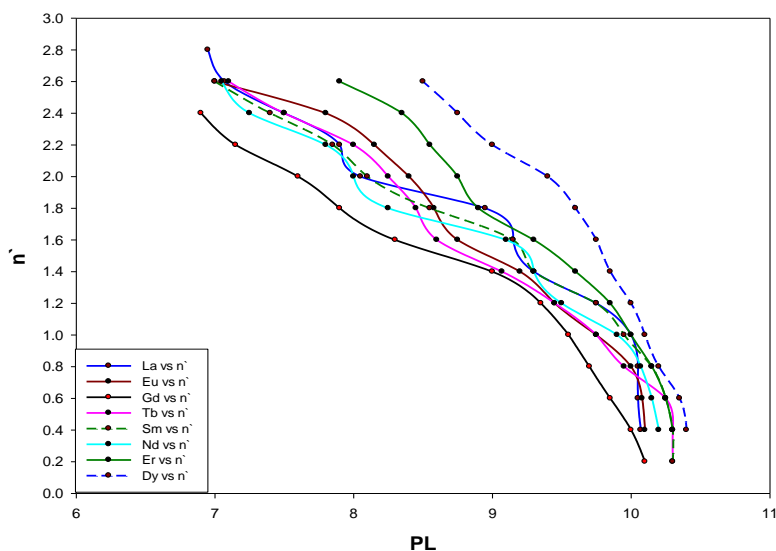
Figure 3. Relation between n` and pL of HL^1 with Ln^{+3} in 1,4 Dioxane (75%, v/v) at 20 °C.
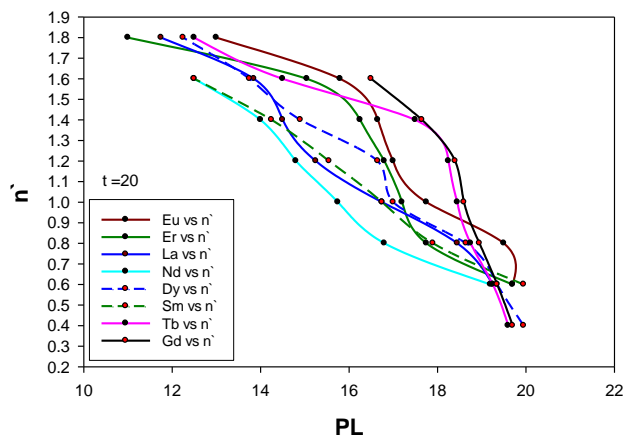
Figure 4. Relation between n` and pL of H$_2$L^2 (HPDD) with Ln^{+3} in 1,4 Dioxane (75%, v/v) at (20°C) .

3.1.2. Ligand Protonation constant

The proton dissociation constants (pK_a) and the stability constant of metal-ligand complexes log K_1, log K_2 were determined from acid-ligand titration curves using the Irving-Rossoti technique [19]. The average number of proton, $\bar{n}_H$ associated with ligands at various pH-meter readings was calculated from acid and ligands titration curves using the relation:

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

Where Y is the number of dissociable protons present in the ligand. V_L and V_A are the volumes of NaOH of concentration N(0.05 M) consumed by solutions (b) and (a) respectively, for the same pH

reading and $(V_L - V_A)$ measures the displacement ,of ligand curve with respect to acid curve. V_0 is the initial volume of the reaction mixture (25 cm^3), E^0 and T_L^0 are the resultant concentration of HNO$_3$ and ligand in the reaction mixture, respectively. The protonation curves for proton-ligand systems at temperatures 20, 30 and 40ºC (Supplementary Materials) where obtained by plotting $\bar{n}_H$ Vs pH. The curves is extend presence of two dissociable in the ligand. The protonation constants (β) of the ligands at different temperature were evaluated from the curve using βjerrum´s half integral method, the results were illustrated in Table (1). The increase in dissociation constants as the temperature increase indicate that dissociation of ligand in favorable at high temperature and the reaction is endothermic.

3.1.3. Metal ligand formation constant: $\bar{n}$

The formation curves for the metal complexes were determined from metal-ligand titration curves by plotting the average number of ligands attached per metal ion n verses the free ligand exponent pL, according to Irving and Rosotti [20]. $\bar{n}$ and pL can be calculated using the equation:

$$\bar{n} = \frac{(V_3 - V_2)(N^0 + E^0)}{(V^0 - V_1)(T^0 \cdot \bar{n}_A)}$$

And $$pL = \log \frac{\sum \beta_n^H (\frac{1}{anti\log} pH)^n}{C_L^0 - n C_M^0} \times \frac{V^0 + V_3}{V^0}$$

Where pL the free ligand exponent, C_M^0 is the total concentration of metal ions present in the solution, β_n^H is the overall stability constant, V_1, V_2 and V_3 are the volume of alkali required to reach the same pH on titration curves of nitric acid, ligand and complex, respectively. The values of $\bar{n}$ 1.8-2.0 indicate that the formed dioxime complexes were in the 1:2 metal ligand stoichiometry.

3.1.4. Effect of temperature on the stability of Ln^{3+} complexes:

The change in free energy (ΔG), was calculated from the formation constants log β at various temperature using Gibbs energy equation

ΔG = -2.303 RT log K

ΔS = ΔH – ΔG/T

The enthalpy change ΔH for oximes dissociation and complex formation process calculated from the slops of the plot pK_a or log$K$ vs 1/T using graphical representation of vanthoff equation

ΔH = 2.303 RT. Slop

Where R is gas constant = 8.314 JK^{-1} mol^{-1}

The +ve ΔH values (table (2)) indicate that the process is endothermic.

Table 2. Thermodynamic parameters of the ligand and its complexes with some lanthanide metal ions.

	log β			40 °C			30 °C			20 °C		
	20 °C	30 °C	40 °C	KJmol^{-1}	Jmol^{-1}	K^{-1}	KJmol^{-1}	Jmol^{-1}	K^{-1}	KJmol^{-1}	Jmol^{-1}	K^{-1}
				$-\Delta H$	$-\Delta G$	ΔS	$-\Delta H$	$-\Delta G$	ΔS	$-\Delta H$	$-\Delta G$	ΔS
H$_2$L^2	21.90	23.30	23.7	16.52	93.69	246.57	15.99	135.11	393.14	15.47	132.89	400.77
Nd	33.90	32.70	31.05	25.04	203.06	568.77	24.24	189.62	545.8	23.44	190.09	568.77
Eu	33.00	33.88	34.50	18.21	197.67	573.37	17.46	196.46	590.77	17.05	193.45	602.06
Gd	30.90	32.25	33.40	30.05	185.09	495.35	29.08	187.01	521.22	28.13	187.28	543.17
Tb	32.50	33.95	36.15	45.52	194.68	476.55	44.07	196.87	504.29	42.62	202.70	564.35
Dy	33.10	35.00	36.30	41.56	198.27	500.68	40.24	202.96	537.02	39.06	203.54	561.39
Er	32.50	34.00	34.9	22.53	194.68	550.00	21.81	197.16	578.71	21.09	195.98	596.89

The metal–ligand formation curve for Ln^{3+} dioxime complexes at various temperature Figure(4) were obtained by plotting $\bar{n}$ vs. pL. The maximum value for $\bar{n}$ 2.66 corresponding to formation of ML$_3$, ML$_2$, ML complexes and n≈2.0 − 1.8 of dioxime. The stability constant, log$K$, of the complexes evaluated are given in Table (1). At constant temperature the log$K$ increase in the order La^{3+} > Nd^{3+} > Sm^{3+} > Eu^{3+} < Gd^{3+} < Dy^{3+}, Er^{3+}.

The steady increase from La^{3+} to Eu^{3+} may be due to a decrees in size with increase ionic potential in the Ln^{3+} series i.e. the acidity increase as temperature increase. The decrease of log K as temperature increase indicate that oximes dissociation reaction is exothermic, also the complex formation process is exothermic, more favorable at lower temperature. A plot of log K$_1$, log K$_2$ or log β vs 1/r (Fig. (5)) indicate that the stability constants of metal chelate increase with atomic number and a break at Gd^{3+}, is in accordance with earlier results [19,20], known as Gd break. This is due to zero filed stabilization energy, unavailability of the well-shilded 4f electron for band formation and structured change in the hydration sphere of lanthanides ions near the widdle of series 1:1, 1:2
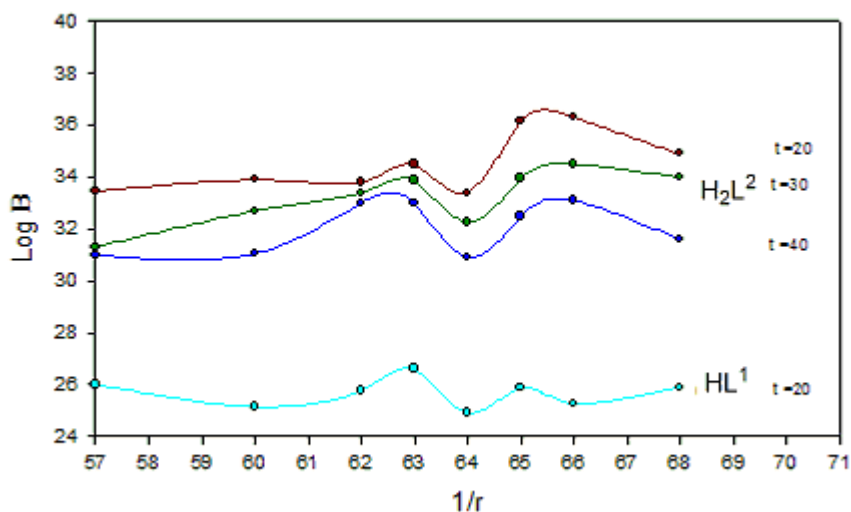
Figure 5. Relation between Log β and Z^2/r of HL^1 at 20 °C and H$_2$L^2 at (20, 30, and 40°C) with Ln^{+3} in 1,4 Dioxane (75%, v/v).

3.1.5. Effect of dielectric constant of the medium on stability of HL[1] complexes

The determination of formation constants of HL[1] with 3d ions Cu(II), Ni(II), Co(II), Fe(III), La(III), Gd(III), and VO(II) also carried out potentiometricaly, metal-lignd molar ratio 1:3, I.S 0.1 KNO$_3$ at 20±1 in 75% DMF, dioxane, methanol-water to study the effect of dielectric constant (ε). Titration curves are shown in fig. (6). The division in titration curves of Cu(II) at pH=4 and Co(II), Ni(II), Zn(II), Mn(II) and Fe(III) at pH=6 from the titration curves of the ligands alone implied the formation of metal complexes, inflection at $a = 0$ to $a = 2$ (where a = indicat formation of ML$_2$ (bis-chelate).
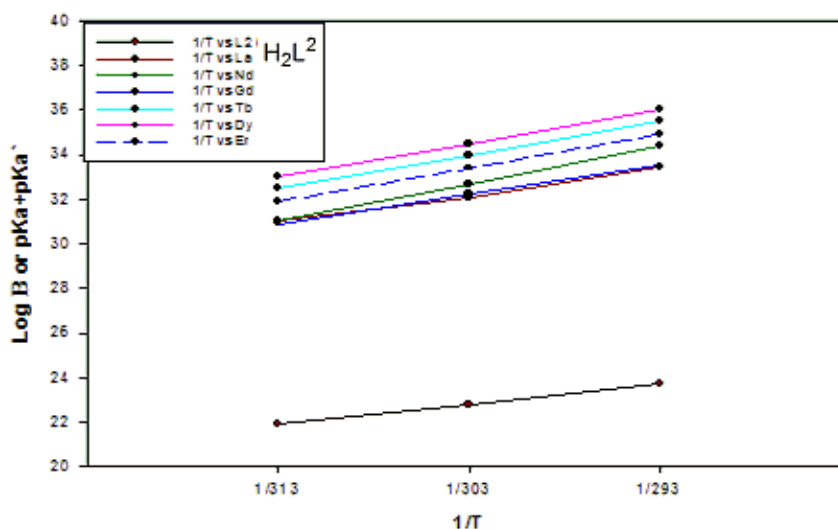
Figure 6. Relation between log β or pK_a + pK_a and 1/T of H$_2$L^2 with Ln^{+3} in 1,4 Dioxane (75%, v/v) at (20,30,40°C).

The curves show steady state zone indicating formation of hydroxo complexes as no precipitate formed during titration [21,22], this result show that the stability increase in the order Dioxane > methanol >DMF this means that decreasing dielectric constant lead to increase in stability because the coordination ability of the solvents may decrease and increase in the basicity of the ligand.

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