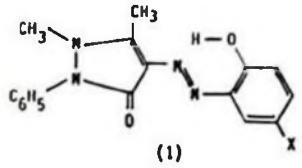
Chelate Stability Constants of Lanthanide Ions with some Azoantipyrines

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Complexation of lanthanide (III) cations with three ortho-hydroxyphenyl azo antipyrine derivatives (x-HAAP) has been studied by potentiometric and spectrophotometric methods. The protonation constant (pK_{11}) for the three ligands is in the order: (II) > (I) > (III). This corresponds to the effect of substitutents on the phenyl-azo moiety of the ligand. The sequence of the stability constants of the complexes for a given lanthanide ion is also in the same order. These ligands behave as uni-negative, tri-dentates; the carbonyl oxygen, the phenolic oxygen and one of the nitrogens of the azo group are the potential donor sites.

As a continuation of our investigation on complexes of rare earth metal ions with pyrozolyl-5-one derivatives [1-4], a new series of 2-hydroxy phenyl azo antipyrine dyes (x-HAAP) were prepared. The dissociation constants of these ligands as well as the stability constants of their complexes with lanthanide(III) cations have been determined by pH-metric and spectrophotometric methods. The effect of solvents on the electronic spectra of the ligands was also studied.



(I)

Chemical formula of 1-phenyl, 2,3-dimethyl, 4(x-phenylazo) - 5 - pyrazolone known as (x-Hydroxy Azoantipyrin) (x-HAAP)
Ligand I, x = 2-hydroxy-;
Ligand II, x = 2-hydroxy-5-methyl- ;
Ligand III, x = 2-hydroxy-5-chloro;

EXPERIMENTAL

Material and Methods

All metal nitrates used in this study were of analytical reagent grade and solutions were prepared in carbonate - free, double distilled water. The metal ions were standardized using the appropriate method of analysis [5]. An aqueous solution of KOH (Merck) was standardized by potentiometric titration against potassium hydrogen phthalate. EDTA solutions were prepared from the disodium salt of EDTA (AR) and the stock solution was stored in a polyethylene bottle. The ligands were prepared by coupling antipyrine (BDH) in a sodium acetate medium with the diazonium salt of 2-aminophenol, 2-amino-4-methyl phenol and 2-amino-4-chloro phenol. The crude products were recrystallized from ethanol. Purity of these ligands was confirmed by elemental and IR analysis. All the solvents used in this investigation were purified using the recommended methods [6].

Measurements

A China pH-meter model-25 (with accuracy ± 0.02 pH) was calibrated by means of standard buffer solutions (Burrough's

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Wellcome & Co., England). Potentiometric titrations were perfomed in 75%(v/v) dioxan - water mixture under inert atmosphere (nitrogen) at 30°C and at an ionic strength < 0.1 M. Known volumes of standard KOH solution was added to the titrating solution, allowed to reach a constant pH meter reading and readings were noted.

The ultraviolet and visible spectra were recorded at room temperature using a Perkin - Elmer 550 S Spectrophotometer in the range of 200 - 1000 nm using 1 cm matched quartz or glass cell.

RESULTS AND DISCUSSION

Potentiometric Studies

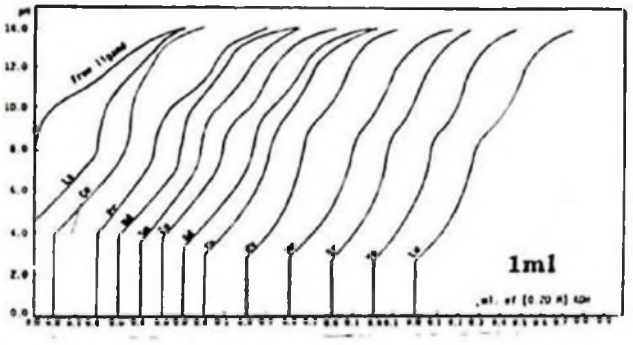
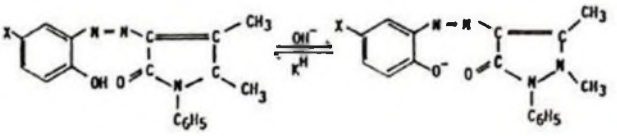


Fig.1 Potentiometric titration curves of 4-(2-hydroxypheny pheylazo antipyrine (2.5 mM) in absence/presence of Ln ion (1.25 mM)

T 30° C : I = 0.01M : V_o = 30ml 75% dioxan - water

Typical titration curves of 2-hydroxyphenyl azo antipyrine in absence and presence of Ln^{3+} ion (Ln = La, Ce, Pr, ...Lu) are illustrated in Fig. 1. The appearance of only one inflection in the titration curves of the free ligands (in absence of the lanthanide ion) after m = 1 (m = number of moles of KOH added per mole of ligand), corresponds to complete neutralization of the phenolic proton in a single step as:



The protonation constant of the ligands (AAP) (=L) is defined as follows:

$$pK_{II} = B + 0.28 + \log [HL]/[L^-]$$

where B = pH meter reading, 0.28 is the correction factor for pH reading in dioxan - water mixture [7]. The pK_w in 75% v/v dioxan - water was taken as 18.7 [8]. $[OH^-]$ was considered negligible and the values of log $[HL]/[L^-]$ were calcualted from the titration curves of the free ligand.

The value of pK_{II} for ligand II (11.32) is higher than that of parent ligand (pK_{II} of ligand I is 11.02), because of the presence of electron repelling methyl group in the para-position with respect to the OH group. This increases the charge density on the hydroxyl oxygen and lowers its acidity. The chloro atom in the para position in ligand III decreases this charge leading to higher acidity, resulting in lower pK_{II} value (9.92).

The titration curves of the ligands are greatly altered in the presence of Ln(III) cations as a result of complex formation. The inflection point which occurs on the curves at m = 2 indicated the complete formation of a bis-chelate:

$$2\ HL + Ln^{3+} <=====> (LnL_2)^+$$

The liberation of the proton of the phenolic group from these ligands by the lanthanide ion, indicates the participation of the phenolic oxygen in chelate formation.

The stability constants of Lanthanide complexes were calculated using Irving and Rossotti [9] expressions:-

$$\log [\ \bar{n} / (1-\bar{n})] = \log K_1 + pL \quad ....(1)$$

$$\log [\ (\bar{n}-1) / (2-\bar{n})\ ] = \log K_2 + pL \quad ....(2)$$

where $\bar{n}$ is the average number of ligand molecules bound to a metal ion and L is the concentration of the free ligand.

The accurate values of the stability constants - log K_1 and log K_2 - were computed using the least square line fitting program for the Irving and Rossotti expression. The experimental data giving $\bar{n}$ values ranging between 0.95 and 1.05 were neglected since they were too sensitive to slight experimental errors. Correlation coefficients of the obtained data were also calculated using the rest of the values by the same program. The results are presented in Table 1.

Table 1

Stability Constants and Free Energies of Lanthanide Complexes with 4-(x-phenyl azo)-anthipyrine

Medium 75% dioxan-water; Ionic strength 0.01 M; Temp = 30°C.

Metal ion	log K_1	$-\Delta G^{\circ}_1$ [a]	log β	Δlog K [b]
x = 2-hydroxy- pK_{II} = 11.02 ± 0.03				
La^{3+}	8.33	47.65	16.07	0.59
Ce^{3+}	8.84	50.56	16.98	0.70
Pr^{3+}	8.78	50.22	16.86	0.70
Nd^{3+}	8.94	51.14	17.11	0.77
Sm^{3+}	9.21	52.68	17.62	0.80
Eu^{3+}	9.15	52.34	17.45	0.85
Gd^{3+}	9.60	54.91	18.38	0.82
Tb^{3+}	9.90	56.63	18.90	0.90
Dy^{3+}	10.10	57.77	19.03	1.17
Ho^{3+}	10.20	58.34	19.28	1.12
Er^{3+}	10.25	58.34	19.25	1.15
Yb^{3+}	10.40	59.49	19.62	1.18
Lu^{3+}	10.50	60.06	19.91	1.09
x = 2-hydroxy-5-methyl- pK_{II} = 11.32 ± 0.14				
La^{3+}	9.08	51.94	17.01	1.15
Ce^{3+}	9.19	52.57	17.39	0.99
Pr^{3+}	9.22	52.74	17.50	0.94
Nd^{3+}	9.47	54.17	18.04	0.90
Sm^{3+}	9.48	54.23	18.19	0.77
Eu^{3+}	9.45	52.34	17.99	0.91
Gd^{3+}	9.65	55.20	18.51	0.79
Tb^{3+}	9.84	56.28	18.91	0.77
Dy^{3+}	9.83	56.23	18.97	0.69
Ho^{3+}	9.86	56.40	18.99	0.73
Er^{3+}	9.94	56.86	19.04	0.84
Yb^{3+}	10.20	58.34	19.68	0.72
Lu^{3+}	10.10	57.77	19.26	0.94
x = 2-hydroxy-5-chloro- pK_{II} = 9.92 ± 0.56				
La^{3+}	6.95	37.69	13.32	0.50
Ce^{3+}	7.14	40.84	13.69	0.59
Pr^{3+}	6.70	38.32	12.70	0.70
Nd^{3+}	6.89	39.41	13.13	0.65
Sm^{3+}	7.11	40.67	13.55	0.67
Eu^{3+}	7.17	41.01	13.78	0.56
Gd^{3+}	7.55	43.19	14.40	0.70
Tb^{3+}	7.62	43.59	14.70	0.54
Dy^{3+}	7.89	45.13	15.28	0.50
Ho^{3+}	8.22	47.02	15.91	0.53
Er^{3+}	8.26	47.25	15.92	0.60
Yb^{3+}	8.59	49.13	16.51	0.67
Lu^{3+}	8.38	47.93	16.03	0.73

The uncertainty in the stability constants ranged between ± 0.03 to 0.06 and the correlation coefficient ranged between 0.94 to 0.96

log K_1 = stability constant of the first complex (M:L = 1:1)

log K_2 = stability constant of the second complex (M:L = 1:2)

log β = The overall stability constant (log K_1 + log K_2)

a ΔG_1 = K. Joule/mole

b Δlog K = log K_2 - log K_1

Correlation of chelate stability with the nature of metal ion

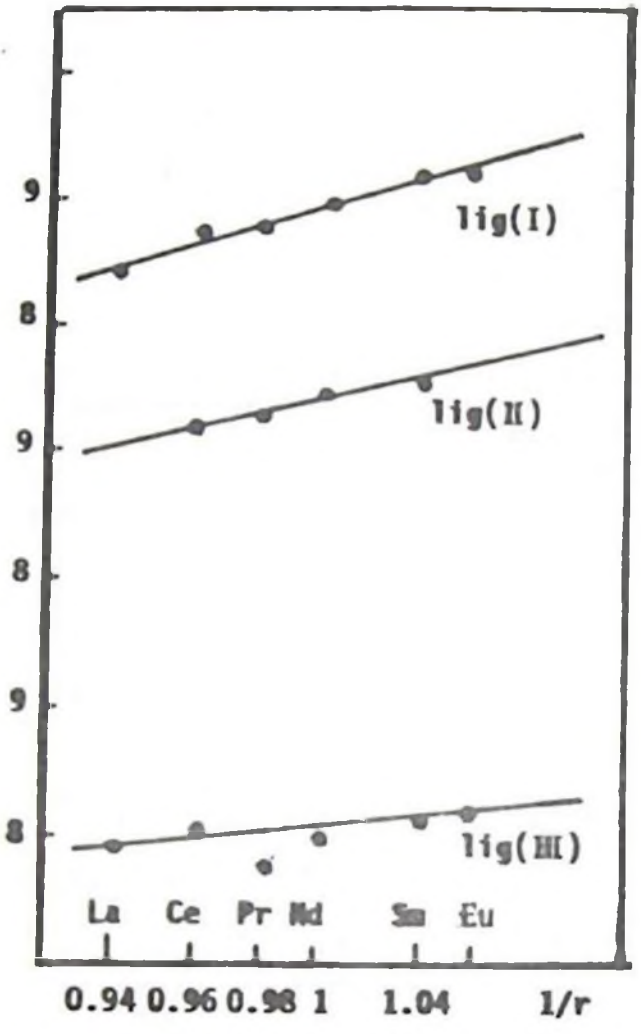


Fig.2. Correlation of stabilities of rare erth complexes *vs* 1/r

Ligands as described in text

A plot of log K_1 of various light rare earth chelates against the reciprocal of ionic radius (Fig.2) is more or less linear. Similar relationships were obtained with picolinate, EDTA, DCTA [10-12] and phenyl hydrozo-β-diketones [13] - ligands containing nitrogen and oxygen as coordinating sites. In this study all rare earth ions are in the +3 oxidation states and are more or less of the same size. Accordingly, the electrostatic contribution of metal ligand bond is assumed to be nearly the same. Therefore, log K_1 values for the lighter metal complexes with different ligands were also plotted against the respective overall ionization potentials of Ln^{3+} to find the effect of the electron affinity of the rare earth on the stability of the formed complexes. The plots of log K_1 *vs* z^2/r were similar to that in fig. 2 - linear for each ligand.

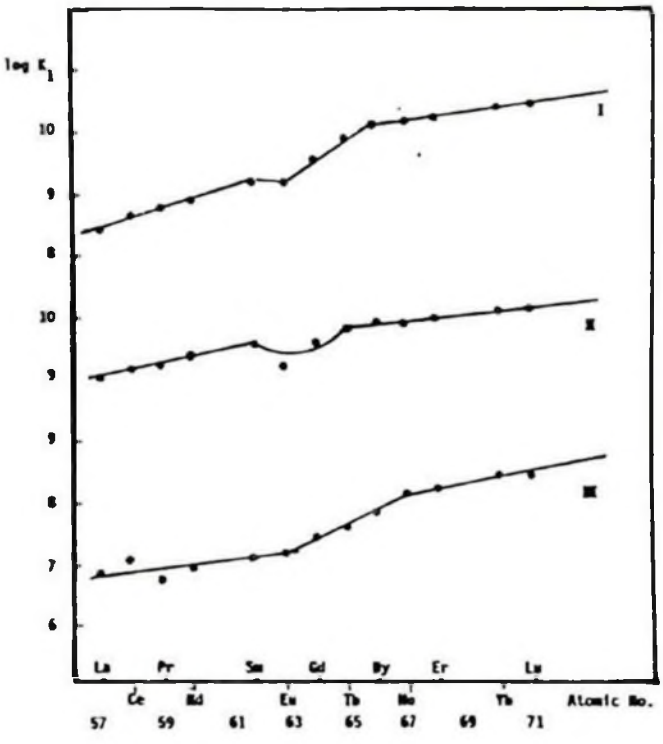


Fig.3. Log K_1 as a funciton of Atomic number

Fig.3 shows the correlation of log K_1 of complexes with the atomic number of the central lanthanide metal. The first part of this plot (La^{3+} - Eu^{3+}) shows a linear increase indicating that the stability of the first complex formed with each ligand was directly proportional to the total ionization potential of the central atom. The second part of the curve (Eu^{3+}- Lu^{3+}) shows a buffer region near the Gd^{3+} area (gadolinium break) and the stability starts

to show gradual increase from Dy^{3+} to Lu^{3+}. The hydration effects [14,15] would explain the variation observed in the properties of rare earth complexes.

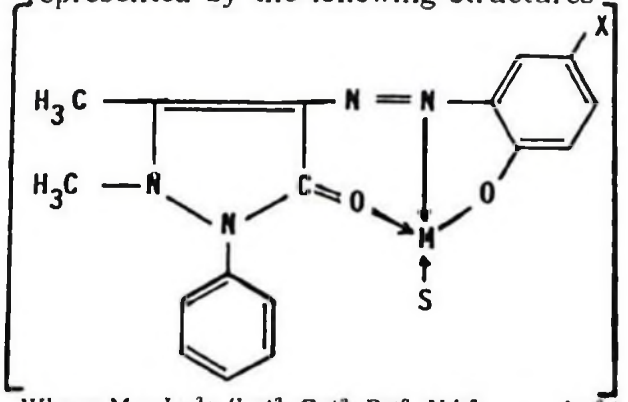
The Ratio of Successive Stability Constants

As the tendency of metal ion to bind to the ligand is proportional to the number of vacant sites, the ratio between consecutive constants, is determined, to a certain extent, statistically [16]. For an ionic ligand, the coulombic attraction is more for M^{3+} as compared to ML^{2+}. Thus, $\Delta\log K$ ($\log K_1 - \log K_2$) values are usually positive (Table 1) and lie within 0.08 - 1.67 log units.

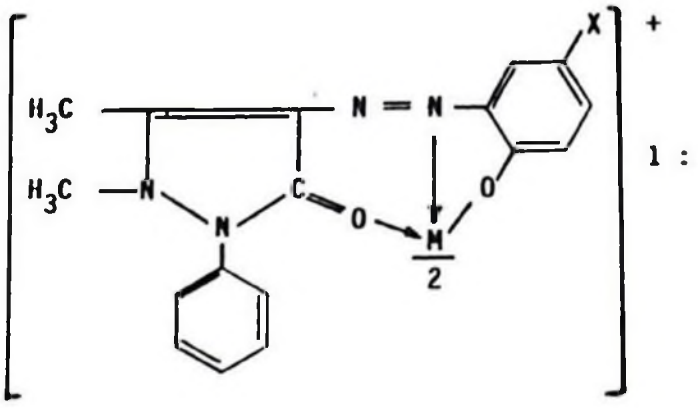
Correlation with the nature of the ligand

Stability constants of the complexes are in the order Ln-Lig II > Ln-Lig I > Ln-Lig III. A plot of $\log K_1$ of the complex with ligand II vs that with ligand I gave a straight line: the same was case with other pairs (Fig.4). The intercepts were 0.3, 1.1, and 1.4 units respectively. This is expected from the differences in the protonation constants of these ligands.

The probable strucutre of the 1:1 and 1:2 (Metal : ligand) complexes can be represented by the following structures



Where M = Ln^{3+} (La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3} .....Lu^{3+})
x = H, CH_3 or Cl, S = solvent



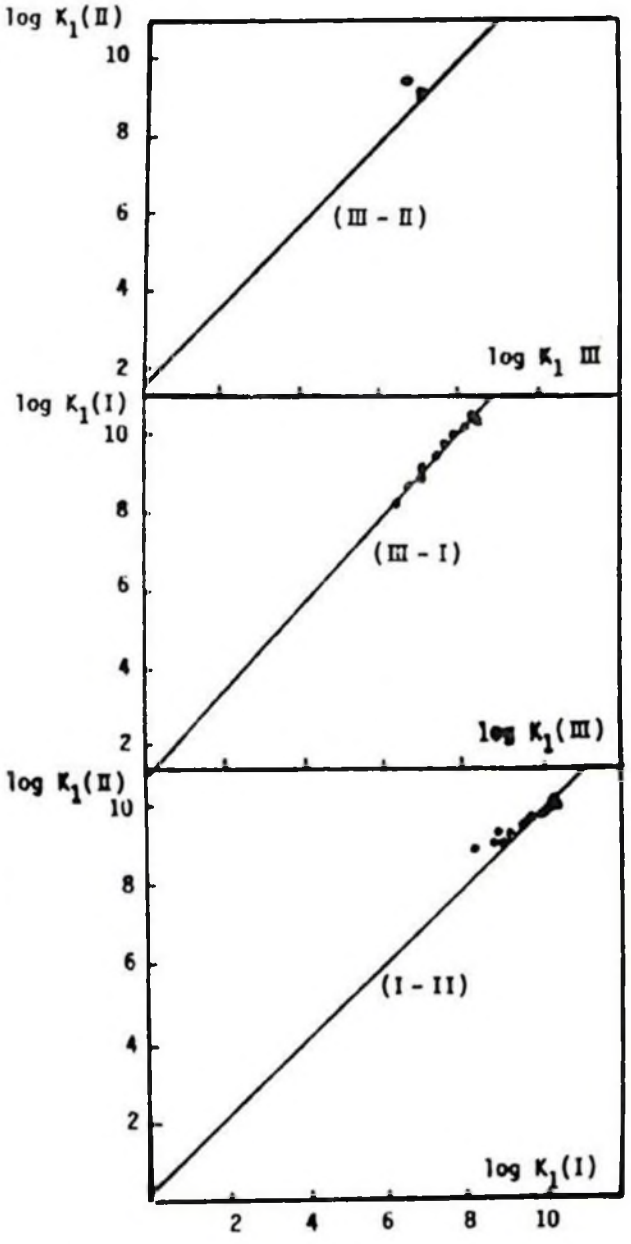


Fig.(4): Stabilities of Trivalent Lanthanide Ions with (I), (II) and (III) Ligands.

Spectrophotometric Studies

The Electronic Absorption Spectra of the Organic Ligands

The electronic spectra of the hydroxy azo antipyrine derivatives show four adsorption bands - A, B, C and D - starting from the shorter wave length side. These bands are characterized by high molar absorptivity (log ε = 3.82 - 4.83), which shows that they are of π - π* and CT transition types.

Effect of solvents on the electronic spectra of the organic ligands

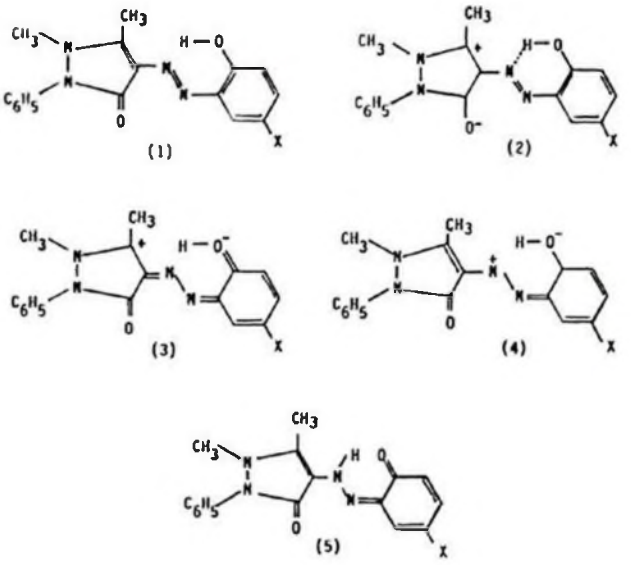
The effect of solvents of different polarities on the spectra of the ligands reveals the following results:

1. All bands show red shift on going from non-polar to polar solvents(π-π* transitions) which is in agreement with the observation of Bayliss and other workers [18,19].

2. The spectrum does not change its feature by the change of polarity of the solvent. This denotes the presence of one tautomer. One exception to this behaviour is in case of ethanol where the spectrum suffers high red shift as compared to carbon tetrachloride.

3. The polar structures make a large contribution to the excited state of the ligands. It has been shown that solvents of low dielectric constants stabilize the non-polar contributions [20], while solvents of high dielectric constants lower the excited state energies of polar structures leaving those of the nonionic structures unchanged. This appears clearly in case of the intramolecular charge transfer band (D) which is more solvent sensitive than the other bands in the spectrum.

4. The decrease in excitation energy in methanol and ethanol solvents results in the observed bathochromic (red) shifts which is higher than in case of other solvents with lower dielectric constants (upto D = 18.30).



: Polar structures of hydroxyazoantipyrine

The effect of the dielectric constant of the medium is governed by the relation of Suppan [21]:

$$F(D) = \frac{2D - 2}{2D + 1} \quad \text{or} \quad \Phi(D) = \frac{D - 1}{D + 1}$$

The plot of shift in frequency of the band D at λ_{max} in different solvents against the function F(D) or Φ (D) (Figs.5-A, 5-B) is

not linear indicating that the dielectric constant is not the main factor governing the excitation energy. The deviation can be explained on the basis that solute - solvent interactions. Effectiveness of bonding of the solvent with solute are more predominant compared to the dielectric effect. These effects can enhance or retard the charge transfer due to the formation of intermolecular hydrogen bonds of various types. The bonding can occur with more than one centre; carbonyl and -N=N- group can act as proton acceptor; the OH group can act as both proton donor or proton acceptor (cf polar structures).

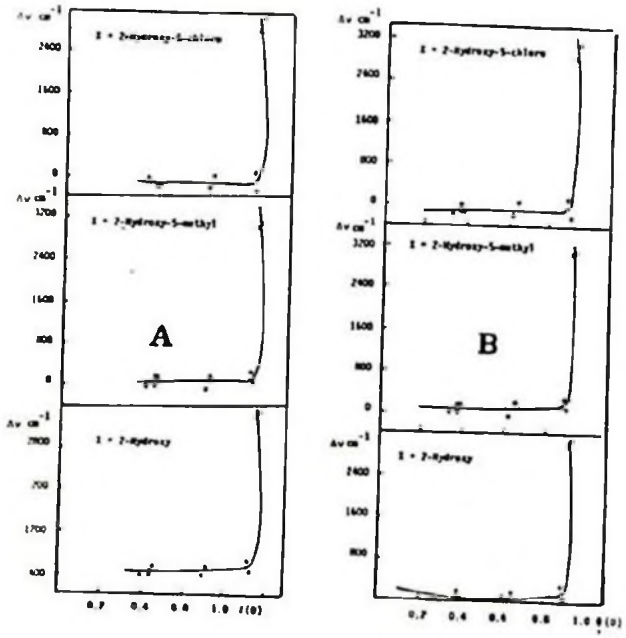
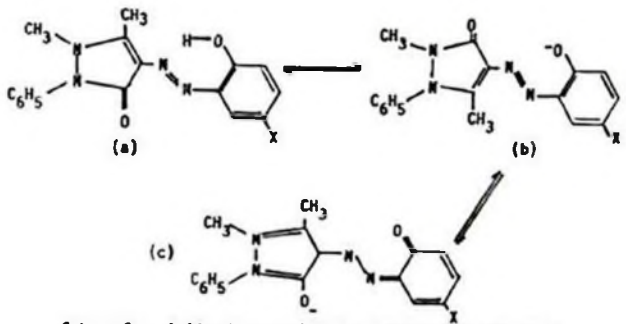


Fig.5 Relation between Dielectric function and Δvcm^{-1} of D band of ligands in different organic solvents.
(A) F(D), (B) ϕ(D)

Effect of pH on the spectra of the organic ligands

The absorption spectra of these ligands were studied in solutions of pH-range 5.75 to 12.50. The spectra at pH 5.75 are characterized by three bands- λ_{max} 255, 312, 472 nm for ligand I, λ_{max} 255, 312, 522 nm for ligand II and λ_{max} 302, 468 for ligand III and the colour of the solution is red. When the pH of the medium rises from pH 5.75 till pH = 11 [till pH = 8.5 in case of ligand III], the intensities of these bands decrease and suffer bathochromic shifts to longer wave length with the formation of isosbestic points at 255, 286, 348, 411, 540 nm for ligand I, at 255, 287, 358, 436, 565 nm for ligand II and at 283, 355, 530 nm for ligand III and the colour of the solutions becomes blue.

The presence of these isobestic points indicates the presence of an acid-base equilibrium over the pH-range 5.75-11 for ligands I and II and 5.75-8.5 for ligand III. The equilibrium corresponds to the elimination of proton from the OH group in alkaline media.



Scheme 5 : Acid - base equilibria of hydroxyazoantipyrine

Determination of the protonation constants of the organic ligands

From the data obtained, it can be seen that the relations between the absorbance and the pH values for each ligand take the form of one S shaped curve denoting the presence of one ionizable hydrogen. From this the pK_{II} can be determined by the methods described earlier [22] and presented in Table 2.

The protonation constant is increasing in the order: 2-hydroxy-5-methyl- > 2-hydroxy- > 2-hydroxy-5-chloro-.

The order is the same as found in 75% dioxan-water media by pH metry. The behaviour in 75% and 50% dioxan are the same.

Determination of the Composition and Stability Constants of Sm^{3+}, Eu^{3+}, Yb^{3+}

In these studies, the absorbance was measured with the ligands as reference because the Ln^{3+} complexes absorb in the same visible region as the ligands. The data obtained using molar ratio and continuous variation methods [23,24] for the determination of Ln^{3+} complexes indicate the probable formation of different complexes ranging from the 1:1 to the 1:3 (metal : ligand) types (Fig.6). The stability constants of Sm^{3+}, Eu^{3+} and Yb^{+3} - complexes formed with ligands I, II and III were determined with the aid of the Limiting Logarthmic [25], Haymann [26] and Molar Ratio methods [23]. The avearage values of the formation constants

Table 2

pK_{II} values of 4(x-phenyl azo) antipyrine
Medium: 50% dioxan-Universal buffer (0.04 M).

Method	Ligand I	Ligand II	Ligand III
Limiting Absorbance	8.950	9.380	7.930
Lim. Abs. modified	8.950	9.383	7.986
Half height	8.950	9.345	7.990
Collector	8.890	9.350	7.900
Mean Value	8.960±0.016	9.370±0.019	7.950±0.034

Table 3

Stability Constant (log K_1) Values for Ln-complexes (Calculated by different methods)

x=2-hydroxy (ligand I)			x=2hydroxy-5-methyl (ligand II)			x=2-hydroxy-5-chloro (ligand III)		
Sm^{3+}	Eu^{3+}	Yb^{3+}	Sm^{3+}	Eu^{3+}	Yb^{3+}	Sm^{3+}	Eu^{3+}	Yb^{3+}
Limiting logarthmic method								
8.73	8.74	8.69	9.12	9.10	9.00	7.45	7.48	7.66
Hayman method								
9.23	8.99	8.66	9.07	9.07	9.14	7.14	7.54	6.85
Molar ratio method								
9.24	9.90	10.59	9.77	10.75	11.10	7.98	8.33	9.12
Average								
9.07	9.21	9.31	9.32	9.64	9.74	7.53	7.78	7.88

are tabulated in Table 3 which agree with the normal behaviour of substituted ligands with respect to their basicity.

Use of these Ligands in Analysis of Rare Earths

Estimation of Sm^{3+}, Eu^{3+} and Yb^{3+} as hydroxyazoantipyrine complexes

This spectrophotometric method was used for quantitative deterination of Ln^{3+} ions as their coloured complexes in 75% dioxan-water (v/v) at pH=6, acetate buffer (0.04 M). Solutions containing 2 x 10^{-4}M ligand and varying concentrations of Ln^{3+} were prepared and their absorbances were measured against solutions of the same concentration of the ligand and under the same conditions. The plotted results show a straight line over a range of concentrations which denotes that Beer's law was obeyed.

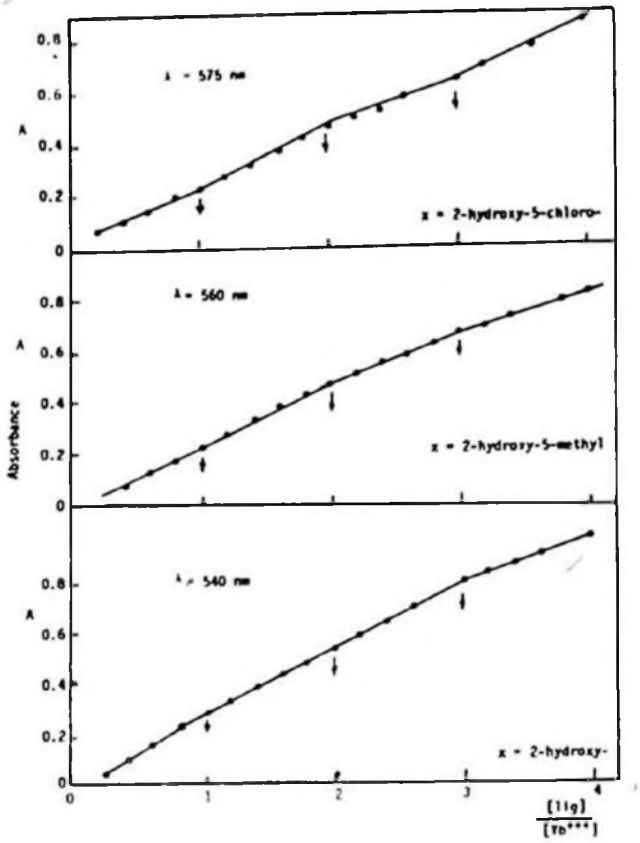


Fig.6 Molar ration method Yb^{3+} -4- (X-Phenylaz) Antipyrine complexes

The results are presented in Table 4

Table 4

Spectroscopy of Lanthanide Complexes in Analysis

Solvent 75% dioxan; Buffer 0.04 M acetate of pH 6;
Molar absorptivity in mol^{-1} cm^{-1} at specified wave length

	Ligand I	Ligand II	Ligand III
Sm^{3+} Complex	5 x10^{-5} M	6x10^{-5} M	4x10^{-5} M
Beers law limit	12187 at 533 nm	8192 at 550 nm	8173 at 550 nm
Absorptivity	10466 at 550 nm	5476 at 645 nm	6876 at 560 nm
Eu^{3+} Complex	4x10^{-5} M	5x10^{-5} M	4x10^{-5} M
Beers law limit	10207 at 550 nm	10200 at 550 nm	7433 at 550 nm
Absorptivity	7004 at 625 nm	5583 at 640 nm	7278 585 nm
Yb^{3+} Complex	3x10^{-5} M	3x10^{-5} M	3x10^{-5} M
Beer law limit	27668 at 540 nm	21645 at 560 nm	10154 at 580 nm
Absorptivity	8804 at 625 nm	8480 at 636 nm	7502 at 600 nm

These results indicate that it is possible to use Sm^{3+}, Eu^{3+} and Yb^{3+} hydroxyazoantipyrine complexes for the estimation of micro amounts of these metals spectrophotometrically with sufficient accuracy and rapidity.

Spectrophotometric Titration of Ln^{3+} with EDTA using Hydroxy azo antipyrine Ligands as Indicators

The additon of successive volumes of EDTA [from 0.1 to 0.9 ml of 2 x 10^{-3} M] to a certain volume of metal salt solution [0.5 ml of 2 x 10^{-3} M] at pH 6 [0.04 M acetate buffer], followed by the addition of ligand [1 ml of 2 x 10^{-3} M for ligand I or 2 ml of 2 x 10^{-3} M for ligands II and III] in 75% dioxan-water solvent affords another method for the estimation of the metal concentration.

A relation between ml. added of EDTA and the corresponding absorbance is drawn in Fig.7. The concentration of metal cation can be determined with fair accuracy from these calibration graphs.

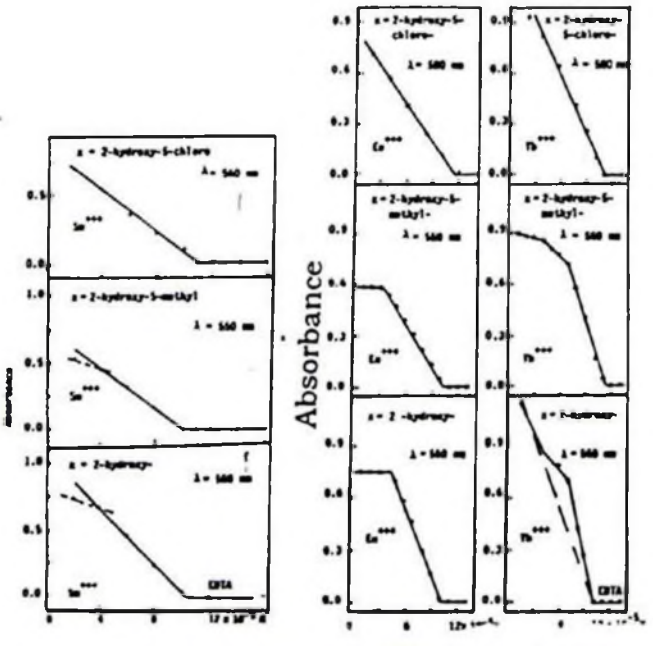


Fig.7. Spectrophotometric Titration of Metal Ian using 4- (x-Phenylazo) Antipyrine as incictor

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