Speciation and thermodynamic parametric study on complexation behaviour of Sm(III), Eu(III), Gd(III) and Tb(III) with aminopyridines in aqueous and mixed equilibria

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ABSTRACT

The determination of formation constants of binary Lanthanone(III) complexes (ML), where M = Sm (III) or Eu (III) or Gd (III) or Tb (III) and L = 2-aminopyridine or 3-aminopyridine or 4-aminopyridine have been carried out using Irving – Rossotti titration technique in aqueous media at different temperatures and at ionic strength. To understand more about the nature of equilibrium involving lanthanide(III) complexes with aminopyridines the effect of dielectric constants on the stability of these complexes at different percentage of solvent variation and at different solvent systems has been studied.. The formation constant ($\log\beta_n$) have been calculated on IBM computer using BEST Program. The S_{min} values are also calculated. Thermodynamic parameters (ΔG, ΔH & ΔS) are also evaluated, negative ΔG & ΔH values and positive ΔS values indicate that complex formation is favorable at ordinary temperatures. Species distribution curves of complexes have been plotted as function of pH using Fortran IV program SPE PLOT to visualize the equilibria systems in pH range of 2-12 pH. The metal ligand formation constant values of selected aminopyridine were in the order 4-aminopyridine > 2-aminopyridine > 3-aminopyridine. The order of stability for metals is Sm < Eu < Gd < Tb. These orders can be explained on the basis of basicity of ligand, protonation of ligand, electronic configuration of metal ions, size and ionic potential of tripositive ion, charge/size ratio of metal ions and species distribution diagrams. The mechanism through which protonation and complex formation takes place have been also discussed and shown by chemical reactions.

Key words: Binary complexes, formation constant, aminopyridine, ionic strength

INTRODUCTION

Lanthanone (III) plays an important role in various biochemical reactions[1-8]. -NH_2 group has a wide variety of applications in medicine, biology and other fields of chemistry[9-11]. Many binary complexes of transition and inner transition metals have been studied potentiometrically[12-16].

So the present study was undertaken to determine the formation constants and thermodynamic parameters of Sm(III), Eu(III), Gd(III) and Tb(III) with 2-aminopyridine or 3-aminopyridine or 4-aminopyridine at 303K, 313K, 323 ± 0.1 & at ionic strength, μ = 0.05M, 0.10M, 0.15M & 0.25M ($NaClO_4$). The nature of complexes were ascertained by species distributed curves. To derive more information somewhat detailed study is carried out on stability of these complexes in different percentage of solvent variation and at different solvent system.

EXPERIMENTAL

All chemicals used were of A.R. grade. All solutions were prepared in the conductivity water. Metal solution was prepared and standardized complexometrically. Perchloric acid was

standardized with standard NaOH solution and constant ionic strength was maintained with an inert electrolyte sodium perchlorate ($NaClO_4$) (Reidol). pH-metric titration were carried out with systronic-µ pH meter 361 having combined glass electrode & temperature probe with readability ± 0.1°C. Temperature was maintained with thermostate High Precision Water Bath Cat. No. MSW-274 with readability ± 0.1°C. The titration solutions were prepared in conductivity water. The double walled glass cell is used in nitrogen atmosphere to avoid any side reactions.

The method of Bjerrum & Calvin as modified by Irving & Rossotti [17] has been used to determine pL values. The experimental procedure involved potentiometric titration of the following sets of solutions.

The following three sets were prepared for titrations:
1. acid [2 milimole]
2. acid [2 milimole] + Aminopyridine [0.5 milimole]
3. acid [2milimole] +Aminopyridine [0.5 milimole] + metal perchlorate [0.05 milimole].

Total volume used in the cell was 50 ml & ionic strength was maintained 0.2 M [$NaClO_4$] temperature at 30 ± 0.1°C in all sets. Titrations were carried out with carbonate free standardized 0.2 M NaOH solution.

From the above titration curves of solution (i), (ii) & (iii), the values of β_n were calculated with BEST program[18] run on personal computer. The weighted least squares treatment determines that set of β_n values of which metal the formation

$$U = \sum_{n=0}^{N} (y - x - nz) \quad \beta_n X^n$$

nearst to zero by minimizing the formation's'

$$S = \sum_{i=1}^{l} U^2 \ (x_i y_i z_i)$$

with respect to variation of β_n in the above equation y is the total concentration, x is total concentration of unbound ligand, z is the total ion concentration & β_n denotes stability constants.

We report here, the S minimum values for the different metal complexes, S_{min} in the same statistical distribution as x^2 with K degrees of freedom and with weights reported in accordant with Powell & Fetcher [19-22], S minimum can be equated to x^2.

RESULTS AND DISCUSSION

The formation constants of the binary complexes formed due to interaction of trivalent
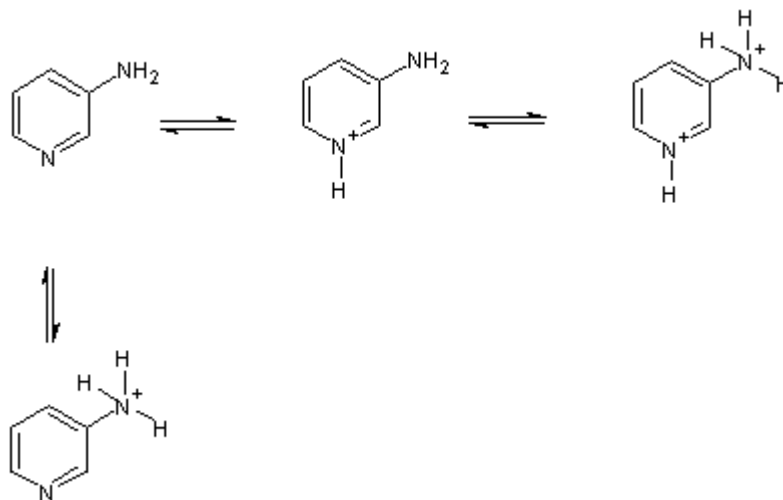
Scheme 1

Sm(III) or Eu(III) or Gd(III) or Tb(III) ion with aminopyridine such as 2-aminopyridine or 3-aminopyridine or 4-aminopyridine were calculated by measuring the magnitude of the proton liberated during the titration of the ligand in absence and presence of metal against standard sodium hydroxide solution. The proton ligand formation constant and metal ligand formation constant values are presented table 1.

The metal ligand formation constant values of selected aminopyridine is in the following order, 4-aminopyridine > 2-aminopyridine > 3-aminopyridine

This order is explained on the basis of basicity of ligand and Protonation of ligand. This order is same as the proton ligand formation constant values.

Table 1: Formation constants of trivalent lanthanide complexes of aminopyridine in aqueous medium at different ionic strength & at temperature 25 ± 0.1°c

Metal ion		Stability Constant	Ionic strength μ				log K°
			0.05	0.10	0.15	0.25	
2-amino	pK_2		6.91	6.87	6.80	6.70	
Pyridine	pK_1		11.32	11.29	11.27	11.20	
Sm(III)		$logk_1$	5.47	5.41	5.32	5.30	5.48
		S_{min}	0.0195	0.1652	0.143	0.003	
Eu(III)		$logk_1$	5.56	5.50	5.42	5.36	5.70
		S_{min}	0.0832	0.0033	0.038	0.0384	
Gd(III)		$logk_1$	5.94	5.89	5.84	5.80	5.93
		S_{min}	0.1559	0.0470	0.4560	0.1937	
Tb(III)		$logk_1$	6.40	6.32	6.27	6.20	6.40
		S_{min}	0.0234	0.0249	0.0753	0.0399	
3-amino	pK_2		6.20	6.14	6.08	6.01	
Pyridine	pK_1		11.30	11.28	11.26	11.19	
Sm(III)		$logk_1$	5.32	5.25	5.21	5.16	5.33
		S_{min}	0.0210	0.0270	0.5320	0.4274	
Eu(III)		$logk_1$	5.36	5.32	5.29	5.24	5.36
		S_{min}	0.0096	0.0745	0.0675	0.2759	
Gd(III)		$logk_1$	5.47	5.39	5.34	5.30	5.45
		S_{min}	0.0125	0.0359	0.1025	0.0726	
Tb(III)		$logk_1$	6.57	6.47	6.41	6.38	6.53
		S_{min}	0.0477	0.0698	0.0725	0.2684	
4-amino	pK_2		9.25	9.10	9.01	8.91	
Pyridine	pK_1		11.47	11.34	11.30	11.22	
Sm(III)		$logk_1$	5.55	5.51	5.48	5.35	5.62
		S_{min}	0.2598	0.0699	0.0698	0.3548	
Eu(III)		$logk_1$	5.61	5.55	5.49	5.40	5.65
		S_{min}	0.0625	0.1235	0.3542	0.3452	
Gd(III)		$logk_1$	6.11	5.96	5.90	5.83	6.04
		S_{min}	0.0233	0.0132	0.3252	0.2631	
Tb(III)		$logk_1$	7.27	7.21	7.14	7.09	7.29
		S_{min}	0.3510	0.6512	0.2431	0.6540	

Table 2: Formation constants of trivalent lanthanide complex of aminopyridine at ionic strength 0.2m NaClo$_4$ at different temperature with free energy, enthalpy & entropy changes

Metal ion	Stability Constant	Temperature			ΔG K.Cal.mole^{-1}			ΔH K.Cal.mole^{-1}		ΔS K.Cal.mole^{-1}	
		303K	313K	323K	$\Delta G_1$303K	$\Delta G_1$313K	$\Delta G_1$323K	303K	313K	303K	313K
2-amino pK$_2$		6.72	6.67	6.60							
Pyridine pK$_1$		11.25	11.14	11.10							
Sm(III)	logk$_1$	5.3154	5.2030	5.1454	-7.37	-7.45	-7.48	-4.87	-6.55	0.0082	0.0029
	S$_{min}$	0.0712	0.1954	0.1951							
Eu(III)	logk$_1$	5.3454	5.2802	5.1357	-7.41	-7.56	-7.59	-2.82	-6.67	0.0151	0.0028
	S$_{min}$	0.1256	0.3615	0.3697							
Gd(III)	logk$_1$	5.7781	5.6541	5.5031	-8.01	-8.09	-8.13	-5.37	-6.97	0.0087	0.0036
	S$_{min}$	0.9855	0.2579	0.1138							
Tb(III)	logk$_1$	6.3627	6.2570	6.0712	-8.82	-8.96	-8.97	-4.58	-8.58	0.0044	0.0016
	S$_{min}$	0.0926	0.0743	0.2187							
3-amino pK$_2$		6.01	5.89	5.83							
Pyridine pK$_1$		11.20	11.17	11.10							
Sm(III)	logk$_1$	5.1156	4.9600	4.8200	-7.09	-7.10	-7.12	-6.74	-6.46	0.0012	0.0020
	S$_{min}$	0.0216	0.0551	0.0032							
Eu(III)	logk$_1$	5.1957	5.0621	4.9300	-7.20	-7.25	-7.28	-5.79	-6.05	0.0047	0.0038
	S$_{min}$	0.1727	0.1143	0.0396							
Gd(III)	logk$_1$	5.2655	5.2234	5.1200	-7.30	-7.48	-7.56	-1.82	-4.77	0.0180	0.0086
	S$_{min}$	0.1136	0.0015	0.2714							
Tb(III)	logk$_1$	6.3361	6.1920	6.0100	-8.78	-8.86	-8.89	-6.24	-8.03	0.0084	0.0026
	S$_{min}$	0.0012	0.0103	0.7511							
4-amino pK$_2$		8.97	8.67	8.36							
Pyridine pK$_1$		11.26	11.16	11.12							
Sm(III)	logk$_1$	5.4269	5.3010	5.1520	-7.52	-7.59	-7.61	-5.45	-6.88	0.0068	0.0023
	S$_{min}$	0.0064	0.1063	0.1456							
Eu(III)	logk$_1$	5.6082	5.4574	5.3102	-7.77	-7.81	-7.84	-6.53	-6.80	0.0041	0.0032
	S$_{min}$	0.0014	0.1152	0.1571							
Gd(III)	logk$_1$	5.8964	5.7384	5.5713	-8.17	-8.21	-8.23	-6.84	-7.72	0.0044	0.0016
	S$_{min}$	0.1354	0.2642	0.3215							
Tb(III)	logk$_1$	7.2723	7.1211	6.9321	-10.0	-10.2	-10.2	-6.55	-8.73	0.0116	0.0047
	S$_{min}$	0.2351	0.0514	0.1126							

Since there are two nitrogen atoms in the aminopyridines it might be anticipated that they could be dibasic due to two protonation constants. The equilibrium stoichiometry of 3-aminopyridine is shown as under.

The formation of structure (III) could be a stepwise process and preferred intermediate structure is (II) or (IV). In forming structure (IV) proton reacts with the π electron of the amino nitrogen and converts it to tetrahedral state. This modifies the unsaturated system by removing nitrogen and its two π electrons. To form structure (II) only π electrons of the ring are distributed over seven atoms is unchanged. So structure (II) will be preferred. So in the dilute acidic solution preferred and stable structure is (II). Second proton may be accepted in concentrated acidic solution. Ultraviolet spectra of 2-, 3- and 4-aminopyridine in dilute acid solutions is different from that of concentrated acidic solution [23].

In the present study two pK_a values are obtained, may be due to strong acidic conditions but ML type of complexes are formed. The values of protonation constants of ligands (pK_a) decrease
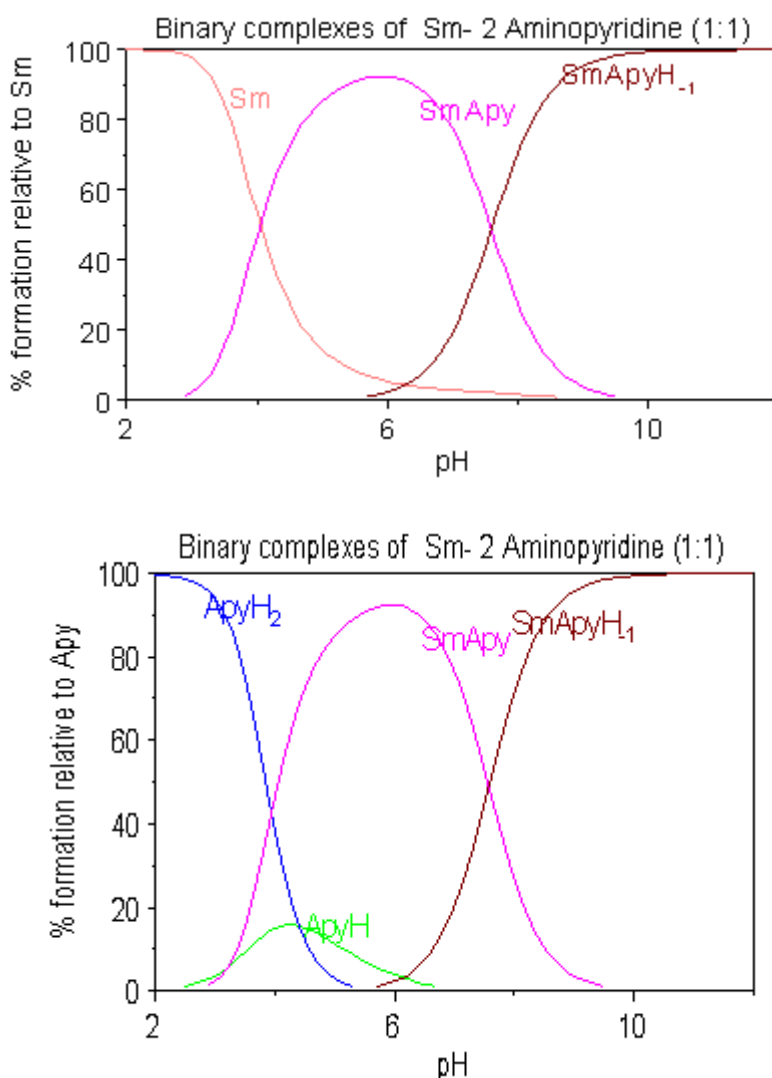

Fig. 1: Species distribution diagrams for sm(iii)- 2-aminopyridines

with increase in ionic strength of medium, which is in agreement with Debye Huckel treatment [24]. Thermodynamic stability constant (log K°) obtained by extrapolating the linear plot of log K_1 vs $\sqrt{\mu}$ to zero ionic strength are given in table 1. The values of stability constants in table 2 reveal that stability constants decrease with increase in temperature along with the pK_H values. The high temperatures does not favour the formation of stable complexes. There results are good agreement with those of Pitzer [25-30]. Thermodynamic parameters were calculated and reported in table 2. The negative values of ΔG & ΔH indicate the complex formation reactions are favorable at ordinary temperature. ΔS is positive for all the complexes reveal that entropy is favorable for the formation of all these

Table: 3 Formation constants of trivalent lanthanide complexes of aminopyridine in different % of solvent and in various solvet system at ionic streangth μ =0.1M NaClO$_4$ and at temperatuer 30±0.1°C

Metal ion	Stability Constant	Different % solvent			Different sovent system		
		10%	20%	30%	10%	20%	30%
2-amino	pK_2	6.82	7.04	7.14	7.70	8.10	6.92
Pyridine	pK_1	11.30	11.45	11.52	11.66	11.580	11.40
Sm(III)	$logk_1$	5.44	5.97	6.20	6.40	6.80	5.67
	S_{min}	0.0016	0.9368	0.0488	0.1550	0.0212	0.0124
Eu(III)	$logk_1$	5.46	5.99	6.27	6.58	6.92	5.67
	S_{min}	0.1347	0.619	0.01437	0.1904	0.0506	0.650
Gd(III)	$logk_1$	5.85	6.20	6.45	6.60	7.14	5.93
	S_{min}	0.0178	0.0815	0.0182	0.0390	0.1842	0.0145
Tb(III)	$logk_1$	6.86	7.29	7.45	7.62	7.95	7.13
	S_{min}	0.0787	0.0094	0.0381	0.4915	0.0390	0.1842
3-amino	pK_2	6.48	6.79	6.95	7.23	7.97	7.02
Pyridine	pK_1	11.29	11.32	11.46	11.51	11.74	11.22
Sm(III)	$logk_1$	5.42	5.87	6.05	6.23	6.54	6.01
	S_{min}	0.0006	0.0014	0.0045	0.0032	0.0054	0.0002
Eu(III)	$logk_1$	5.41	5.89	6.15	6.49	6.62	5.72
	S_{min}	0.0011	0.0004	0.0134	0.0413	0.0521	0.0103
Gd(III)	$logk_1$	5.74	6.01	6.22	6.53	6.71	5.83
	S_{min}	0.0013	0.0145	0.0361	0.0054	0.0032	0.0144
Tb(III)	$logk_1$	6.81	7.20	7.39	7.59	7.02	7.00
	S_{min}	0.1106	0.1574	0.0325	0.0539	0.3984	0.5614
4-amino	pK_2	9.10	9.47	9.89	10.01	10.25	9.97
Pyridine	pK_1	11.40	11.87	11.81	12.08	12.60	11.58
Sm(III)	$logk_1$	5.87	6.04	6.35	6.57	6.94	6.35
	S_{min}	0.0814	0.6581	0.2540	0.0251	0.3610	0.8410
Eu(III)	$logk_1$	5.94	6.40	6.63	6.93	7.20	6.09
	S_{min}	0.2543	0.5272	0.0747	0.0372	0.5467	0.1258
Gd(III)	$logk_1$	6.17	6.43	6.66	6.99	7.29	6.29
	S_{min}	0.0518	0.0512	0.2560	0.0742	0.5213	0.3540
Tb(III)	$logk_1$	6.97	7.18	7.87	7.98	8.29	7.59
	S_{min}	0.1108	0.3240	0.0356	0.0324	0.0421	0.3251

complexes. These factors indicate that these are major driving force for the formation of binary complexes. The enthalpy decrease accompanying the complexastion of metal ion in solution is the characteristic property of heat of the reaction and measures entropy difference between the metal ligand & metal water coordinated bonds. The results obtained in the present case suggested that the metal – ligand bonds are fairly strong as evidenced by their negative enthalpy changes.

The entropy changes accompanying the formation of metal complexes can be related to number of reacting species in the system and changes in the solvation of reactant & product species. During to the formation of metal chelates in solution, the ligand species get coordinated to the solvated metal ions by displacing the water molecules from the aqua– complex, [$M(H_2O)]^{3+}$ as shown in the following equation :

$$[M^{3+}(H_2O)n] + L\,(aq) \rightleftharpoons \quad ML^{3+}\,(aq) \,+\, n\,H_2O$$
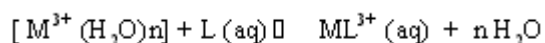
Thus there will be an increase in number of particles in system leading to increases in disorderliness of system.

The values of protonation constant & formation constant of complexes of trivalent metal ions with aminopyridines at temperature $30 \pm 0.1°$ C & 0.2M ionic strength has been evaluated in mixed aqua – organic solvents & given in table 3. It is clear that pK_H values of ligand increases with increase in organic content of aqua-organic solvent. These may be due to decrease in dielectric constant of medium, hydrogen bonding & increase in proton solvation of organic solvent. The data in table 3 show that metal ligand formation constant increases with increase in percentage of organic solvent in medium respectively.

10 % methanol – 90 % water < 20 % Methanol – 80 % water < 30 % methanol – 70 %

water. For a particular type of compounds in various aqua – organic solvent systems, it has been observed that pK_H & stability constant of metal complexes are following the order 20 % butanol > 20 % ethanol > 20 % methanol > 20 % DMF.

In general, stability of complexes containing O-H or N-M link increases with increase in organic solvent which is due to decrease in dielectric constant of bulk solution. As dielectric constant decreases the ion –ion interaction involving proton (or metal ion) & the ligand increases to a greater extent than ion dipole interaction between protons. Higher stability in butanol – water medium is due to decrease in hydrogen – bonded structure in water. The hydrogen bonded structure is less prevalent in butanol than either in methanol and is absent in dimethylformaide. The order of stability for binary complexes with respect to metal ions is found as Sm < Eu < Gd < Tb. This order can be explained by considering electronic configuration, size and ionic potential of tri positive ion, charge / size ratio.

Species distribution study as function of pH (2 -12) pointed that the formation of ML started around pH ~ 3.0. As pH increased beyond ~ 3.0, the % of complex so formed also increased up to pH ~ 6. In this and was maximum (~ 98%); after which concentration of complex decreased fell to zero at pH around ~ 9.8 (fig**.**1).

CONCLUSION

pH-metric studies on lanthanide(III) complexes with 2-aminopyridine, 3-aminopyridine, 4-aminopyridine reveal that pyridines contain two dissociable protons in highly acidic medium but species distribution curves and calculations show that ML type of binary complexes are formed. Thermodynamic studies have shown that the reactions are exothermic in nature & favoured by enthalpy change. The positive values of ∆S indicate that complexastion reactions are entropically favoured under experimental conditions.

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