

Equilibrium Studies on Mixed Ligand Complexes of Some Tripositive Rare Earth Ions

RASHMI VIMAL, MAMTA SINGH and RAM NAYAN*

Department of Chemistry

Hindu College, Moradabad–244 001, India

Interaction of the rare earth ions, La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+} with the pair of ligands 1-amino-2-naphthol-4-sulphonic acid (an, H_2A) and *o*-aminophenol (ap, HB) have been studied in aqueous solution at 25°C ($\mu = 0.1 \text{ M KNO}_3/\text{NaCl}$). Equilibrium constants of the reactions involving the formations of the mixed ligand species MAB, MA_2B^{2-} , MB_2A^- (M = metal ion) and the binary complexes containing up to three ligand molecules have been evaluated from the pH-metric data, and coordinating behaviour of the ligands in the formation of the mixed ligand complexes has been discussed.

INTRODUCTION

Studies on mixed ligand complex formation reactions in aqueous solution, involving primary and secondary ligands, have widely been reported¹. But, the systems where two ligand molecules combine with metal ion, specially the rare earth ions, in a single step have not sufficiently been investigated²⁻⁴. Also, the informations on the formation of such complexes containing more than two ligand molecules are rare⁵.

In a mixture of metal ion M with coordination number more than three and two different types of bidentate ligands A and B of comparable metal binding affinity, in 1:1:1 ratio, kinds of complexes expected to be present in appreciable amount are MA, MA_2 , MB, MB_2 and MAB. Similarly, three types of mixed ligand complexes, MAB, MA_2B and MAB_2 , would be expected to be present in significant amount along with free metal, free ligand and binary complex species in the mixture containing the tripositive rare earth ions or any other metal capable of combining with three ligand molecules, in 1:1:2 or 1:2:1, M-A-B molar ratio^{2,6,7}. Here, quantitative studies of mixed ligand equilibria involving the rare earth ions, La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+} and the ligands, 1-amino-2-naphthol-4-sulphonic acid (an, H_2A) and *o*-aminophenol (ap, HB) have been made introducing amounts of the reactants in different molar ratios as described earliest² in pH-metric measurements to obtain information on MAB, MA_2B and MAB_2 type complexes.

EXPERIMENTAL

Mono-sodium salt of 1-amino-2-naphthol-4-sulphonic acid was used to prepare 0.01 M of its aqueous stock solution, by direct weighing. Sodium hydroxide (0.1786 N), potassium nitrate/potassium chloride (1.0 M), nitric acid/hydrochloric acid (0.07856 N), metal nitrate, *o*-aminophenol solutions were obtained by the previously described procedure⁸.

1:1, 1:2, 1:3, metal-ap/an ($[ap/an] = 5.0 \times 10^{-4}$ M) and 1:1:1, 1:2:1, 1:1:2, metal-ap-an ($[M] = 5.0 \times 10^{-4}$ M) mixtures were prepared and titrated against 0.1786 N sodium hydroxide solutions at 25°C, using Systronic 335 pH-meter as described earlier^{2,9}. All the reactions except those of Ce^{3+} were studied in nitrate medium at an ionic strength of 0.1 M KNO_3 . The Ce^{3+} systems were investigated in chloride medium keeping the ionic strength 0.01 M KCl.

RESULTS AND DISCUSSION

Proton-ligand dissociation

The titration curve of 1-amino-2-naphthol-4-sulphonic acid (monosodium salt) lies between $a = 1$ and -1 , in the pH-range 3.0–11.0. A steep inflection in the curve at $a = 0$ indicates that two protons are liberated in steps, respectively from the protonated amino group and the phenolic group. The stepwise proton-ligand dissociation constants are $K_1^H = 10^{-2.80 \pm .01}$ and $K_2^H = 10^{-8.87 \pm .04}$. Initially, at low pH values, the colour of the ligand is red. A gradual colour change, red to orange, takes place between pH 2.6 and 4.6 (below $a = 0$) due to deprotonation of the protonated ligand. The steep inflection in the titration curve (Fig. 1) confirms that the ligand (monoanion) is orange. A further colour change (light brown) appears at pH 6.5. The intensity of brown colour gradually increases with increase in dianionic ligand concentration up to pH *ca.* 10.0 where the value of a is *ca.* 1.0. Details of proton-*o*-aminophenol equilibria have been described in earlier publication⁸.

Formation of binary complexes

1:1 Metal-an complex species MA^+ ($A =$ ligand dianion) is expected to exist in solution at low pH-values as indicated by pH vs a curves (Fig. not given). Above pH *ca.* 7.6, 7.2, 7.1, 6.8, 6.3 and 6.1 mixtures of La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+} , respectively with an (1:1) remain turbid where the turbidity does not allow any calculation. From the evaluated K_1 values, reported in Table-1, it is concluded that complexing tendency of the metal ions increases with decrease in ionic size. Thus, the stability constant follows the order: $La^{3+} < Ce^{3+} < Pr^{3+} < Nd^{3+} < Sm^{3+} < Eu^{3+}$.

1:2 Metal-an mixtures turn turbid from pH *ca.* 7.8, 7.3, 7.2, 7.0, 7.0 and 6.8, respectively in La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+} systems. Existence of both 1:1 and 1:2 metal-an species in solution below these pH values, is evident from the titration curves (Fig. 1, Nd^{3+} system). The K_2 is smaller than the K_1 of the corresponding system. Further, the stability constant for the reaction between MA^+ and A^{2-} follows the order: $LaA^+ < CeA^+ < PrA^+ < NdA^+ < SmA^+ < EuA^+$.

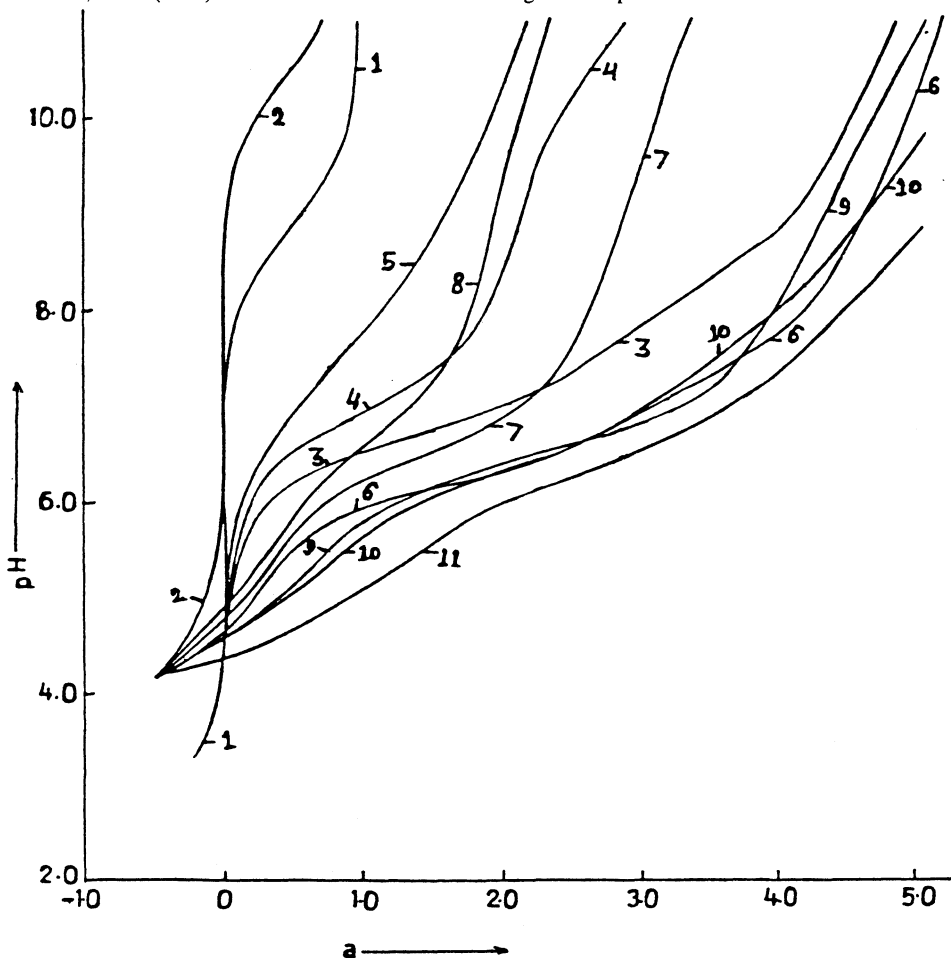


Fig. 1. pH vs a curves for Nd^{3+} -1-amino-2-naphthol-4-sulphonic acid (H_2A)- o -aminophenol (HB) complex systems (1) H_2A (2) HB, (3) $\text{N}^{3d} - \text{H}_2\text{A}$, (4) $\text{N}^{3d} - 2\text{HA}$, (5) $\text{Nd}^{3+} - 3\text{H}_2\text{A}$, (6) $\text{Nd}^{3+} - \text{HB}$, (7) $\text{Nd}^{3+} - 2\text{HB}$, (8) $\text{Nd}^{3+} - 3\text{HB}$, (9) $\text{Nd}^{3+} - \text{H}_2\text{A} - \text{HB}$, (10) $\text{Nd}^{3+} - 2\text{H}_2\text{A} - \text{HB}$, (11) $\text{Nd}^{3+} - \text{H}_2\text{A} - 2\text{HB}$. [H_2A -used as mono sodium salt].

Appearance of turbidity has also been noted in 1:3 metal-an mixtures at higher pH-values (*i.e.*, at pH *ca.* 7.8, 7.3, 7.2, 7.1, 7.0, 6.9, respectively, for La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} and Eu^{3+} systems). Equilibrium constant K_3 calculated below pH of turbidity formation and the corresponding K_1 and K_2 (Table-1) indicate that stepwise equilibrium constants follow the trend $K_3 < K_2 < K_1$. Difference of $\log K_1$ and $\log K_2$ is greater than that for $\log K_2$ and $\log K_3$ in each metal system. Also, simultaneous existence of MA^+ , MA_2^- and MA_3^{3-} is exhibited by small difference in K_1 , K_2 and K_3 values and the absence of sharp inflections in the titration curves. Comparing the equilibrium constant values (Table-1) of metal-an system with the corresponding values of metal- o -aminophenol, reported earlier by the authors⁸, we observed the complexing tendency of $\text{ap} > \text{an}$. Smaller values of equilibrium constant for 1-amino-2-naphthol-4-sulphonic acid complexes than the cor-

TABLE-1
EQUILIBRIUM CONSTANT OF BINARY AND TERNARY COMPLEXES
OF an (H₂A) AND ap (HB) (25°C, $\mu = 0.1$ M KNO₃)

Reaction	log K						
	La ³⁺	[†] Ce ³⁺	Pr ³⁺	Nd ³⁺	Sm ³⁺	Eu ³⁺	
M ³⁺ + A ²⁻ ⇌ MA ⁺	4.84 ± .14	5.17 ± .06	5.24 ± .08	5.53 ± .08	5.71 ± .02	5.89 ± .05	
MA ⁺ + A ²⁻ ⇌ MA ₂	3.98 ± .06	4.42 ± .14	4.95 ± .10	5.11 ± .11	5.18 ± .21	5.51 ± .04	
MA ₂ + A ²⁻ ⇌ MA ₃ ⁻	3.60 ± .18	4.15 ± .24	4.67 ± .09	4.77 ± .28	5.01 ± .05	5.35 ± .05	
M ³⁺ + B ⁻ ⇌ MB ²⁺	8.01 ± .14	8.17 ± .12	8.27 ± .10	8.41 ± .10	8.54 ± .12	8.64 ± .06	
MB ²⁺ + B ⁻ ⇌ MB ₂ ⁺	7.08 ± .08	7.36 ± .03	7.78 ± .07	8.07 ± .09	8.38 ± .06	8.58 ± .03	
MB ₂ ⁺ + B ⁻ ⇌ MB ₃	6.22 ± .14	7.07 ± .09	7.40 ± .21	7.66 ± .12	7.94 ± .11	8.28 ± .05	
M ³⁺ + A ²⁻ + B ⁻ ⇌ MAB	13.20 ± .43	13.58 ± .31	13.85 ± .25	14.37 ± .28	14.65 ± .24	15.14 ± .20	
MA ⁺ + B ⁻ ⇌ MAB	8.36	8.41	8.61	8.84	8.94	9.25	
MB ²⁺ + A ²⁻ ⇌ MAB	5.19	5.41	5.58	5.96	6.11	6.50	
M ³⁺ + 2A ²⁻ + B ⁻ ⇌ MA ₂ B ²⁻	18.81 ± .54	19.20 ± .43	19.68 ± .43	20.13 ± .54	21.26 ± .52	21.49 ± .16	
M ³⁺ + 2B ⁻ + A ²⁻ ⇌ MB ₂ A ⁻	21.04 ± .36	21.40 ± .69	20.99 ± 1.85	22.59 ± .78	22.34 ± 1.14	23.54 ± .75	
MA ₂ + B ⁻ ⇌ MA ₂ B ²⁻	9.90	9.61	9.49	9.49	10.37	10.09	
MB ₂ ⁺ + A ²⁻ ⇌ MB ₂ A ⁻	5.95	5.87	4.94	6.11	5.42	6.32	
MA ⁺ + 2B ⁻ ⇌ MAB ₂	16.20	16.23	15.75	17.06	16.63	17.65	
MB ²⁺ + 2A ²⁻ ⇌ MBA ₂ ²⁻	10.80	11.03	11.41	11.72	12.72	12.85	
MAB + A ²⁻ ⇌ MA ₂ B ²⁻	5.61	5.62	5.83	5.76	6.61	6.35	
MAB + B ⁻ ⇌ MAB ₂	7.84	7.82	7.41	8.22	7.69	8.44	

*Values from earlier publication⁸.

[†] $\mu = 0.1$ M KCl

responding value for *o*-aminophenol complex may be regarded as a result of its poor electron donating property due to the larger size of ligand and electron-withdrawing nature of sulphonic acid group.

Formation of ternary complexes

Turbidity appears from pH *ca.* 7.5, 6.6, 6.5, 6.6, 6.5, 6.6, respectively in 1:1:1 metal (La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+})-an-ap mixtures. However, a comparison of the titration curves indicates the formation of ternary complexes in solution below the pH of turbidity formation. The pH vs *a* curve of the mixed ligand complex system deviates in the right direction from the composite pH vs *a* curve of one ligand and 1:1 metal-other ligand in each metal system. The calculated equilibrium constant values are reported in Table-1. By comparing the equilibrium constants of binary and ternary complex systems it is inferred that the formation constant values for the addition of a ligand to the 1:1 metal-ligand complex with other ligand are comparable in magnitude with values for the aqua-ion. A parallel effect has been noted by Perrin and coworkers¹⁰ in studying the ternary complexes of some biologically important ligands, *e.g.*, ethylenediamine, histamine, serine, salicylic acid with Cu^{2+} ; similar results have recently been reported by Singh in Th^{4+} -salicylic acid(sa)-5-sulphosalicylic acid(ss), UO_2^{2+} (sa)(ss) and Th^{4+} -ap-catechol(ca) complex systems⁵.

Formation of 1:1:2 or 1:2:1 metal-ap-an complexes is evident from a comparison of the titration curves (Fig. 1). The composite pH vs *a* curve of 1:1:1, metal-an-ap and ap or an deviates, respectively, from 1:1:2 or 1:2:1 metal-an-ap system, as described earlier in 1:1:1 metal-ligand pair systems. In addition, weak inflections also appear in pH vs *a* curves (at *a* = 3) of each system. Equilibrium constants evaluated by the method described earlier⁹ are given in Table-1. Analysis of the data could not be made at higher pH values, in all the systems, due to appearance of turbidity from pH *ca.* 6.3, 6.3, 6.2, 6.2, 6.0, 5.8 and 6.3, 6.0, 5.9, 5.9, 6.0, 5.9 respectively in 1:1:2 mixtures of tripositive rare earth ions (La^{3+} , Ce^{3+} , Pr^{3+} , Nd^{3+} , Sm^{3+} , Eu^{3+}) with an-ap and ap-an.

Table-1 indicates that stability constant for addition of an to $\text{M}(\text{an})_2$ or $\text{M}(\text{an})(\text{ap})$ or aqua rare earth ion are very close to each other. Slightly higher values for mixed ligand system may be regarded due to ligand-ligand interaction. Similarly, difference in the values for interaction of ap to $\text{M}(\text{an})(\text{ap})^+$ and the corresponding aqua ion is very low. Equilibrium constant for addition of ap^- to $\text{M}(\text{an})_2^+$ is considerably higher than the value for its addition to $\text{M}(\text{an})(\text{ap})$, probably due to more interaction between reacting ap^- and two coordinated an molecules of $\text{M}(\text{an})_2^+$, than the one coordinated an molecule of $\text{M}(\text{an})(\text{ap})^+$ in spite of a greater steric effect. Higher value of equilibrium constants for reaction $\text{MA}_2 + \text{B} \rightleftharpoons \text{MA}_2\text{B}$ than corresponding aqua ion have earlier been reported on mixed ligand complexes of Ni^{2+} (with pair of serine, ethylenediamine, histamine)¹⁰ and the heavy rare earths (with pair of adenine, xanthine and hypoxanthine)². Almost similar trend is followed in addition of ap^- , ss^{3-} to $\text{Th}(2\text{-nitroso-1-naphthol})(\text{ap})^{2+}$, $\text{Th}(2\text{-nitroso-1-naphthol})(\text{ss})$ and $\text{Th}(\text{ap})(\text{ca})^+$, respectively.

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