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CONDUCTOMETRIC STUDIES ON METAL COMPLEXES OF ISONICOTINIC ACID HYDRAZIDE

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The conductometric studies on complexes of isonicotinic acid hydrazide (INH) with nitrates of Fe(III), Al(III) and biotoxic metals Cd(II), Hg(II) were carried out in aqueous-ethanolic solutions. The titrations having transition metal nitrate : INH ratio 1 : 2 and 1 : 1 while Al(III) formed 1 : 3 and 1 : 2 complexes with the ligand (INH).

INTRODUCTION

Conductometric techniques have been used frequently to study the formation of complex compounds and in many cases to confirm the structure of complex compounds. The conductometric titrations are not only simple but also give reproducible results. The conductometric measurements have special advantage over other ordinary methods because of the possibility of the study in dilute solutions, aqueous or non-aqueous, the only requisite being exchange, displacement, addition or removal of ions of different mobility. Using conductivity measurements, Werner and Miolate for the first time established the structures of metal ammine complexes. Since then large number of works have been done to study (a) the formation of complexes even in those cases where the isolation of the compound was either impossible or involved tedious operations (b) to find out the stoichiometric requirements of the substances and thus to assign a simple structure to the complexes. The equivalence point of a conductometric titrations is not characterised by an abrupt change in conductivity against the volumes of titrant added and the end point is obtained by extrapolating the lines obtained at the beginning and at the end of the titration.

A number of acid hydrazides and their derivatives have been reported [1-13] to display important role in various micro-organism and hence are of pharmacological importance. The therapeutic use of pyridine-4-carboxylic acid hydrazide or isonicotinic acid hydrazide (INH) interested us to study their complexing behaviour with nitrates of bi- and trivalent metals.

MATERIALS AND METHODS

Nitrates of Al(III), Fe(III), Cd(II), Hg(II) etc. used were of E-merk/BDH/AnalaR grade. The nitrate of Fe(III) was prepared in the laboratory from freshly precipitated and well washed ferric hydroxide.

A 0.005 M solution of isonicotinic acid hydrazide (INH) was prepared in conductivity water containing 25% (by volume) ethanol. Ethanol was used to help formation of coarse precipitate, otherwise micro-crystalline precipitate of the complex formed, which were insoluble in water such as those of Cd(II), Hg(II) and Fe(III). A 0.05M solutions of the metal nitrates were prepared separately in the same solvent. 40 ml of the ligand (INH) was placed in a small beaker and a conductivity cell was vertically placed in it. The metal nitrate solution was taken with the help of a 10 ml microburette. For conductometric titration, the metal salt solution was added gradually in lots of 0.1 or 0.5 ml in the ligand solution. The solution in the beaker after each addition was stirred on magnetic stirrer for five minutes and then allowed to stand for about 5-10 minutes. The conductivity cell was placed in the solution and after five more minutes the conductivity of the solution was determined by means of a conductivity meter. Dilution corrections were applied to the observed conductivity values. The corrected conductivity values were plotted against the volume (in ml) of the titrant (metal nitrate solution) added.

$$\text{Corrected conductivity } \frac{V_1 + V_2}{V_1} \times \text{observed conductance.}$$

(Where V_1 = initial volume of the ligand solution taken, V_2 = Volume of the titrant added).

Experimental observations : The results of the conductometric titrations are given in Table 1-4 and the corresponding plots of conductivity against volume (in ml) of metal nitrate solution added are shown in Fig. 1 & 2.

Conductometric titration of INH with Cadmium nitrate solution :

Strength of Cd(II) nitrate solution = 0.05M, Strength of INH solution = 0.005M

Temperature of the experiment = (30 ± 0.5)ºC, Volume of INH solution = 40 mL

Table – 1

Volume of metal salt solution (in mL)	Corrected conductance (in mhos × 10^{-5})	Volume of metal salt solution (in mL)	Corrected conductance (in mhos × 10^{-5})
0.00	0.2	4.50	8.9
0.50	1.2	5.00	9.7
1.00	2.2	5.50	10.3
1.50	3.5	6.00	11.0
2.00	4.9	6.50	11.6
2.50	5.8	7.00	12.6
3.00	6.6	7.50	12.8
3.50	7.5	8.00	13.4

1st break, Cd(II) : INH = 1 : 2 2nd break, Cd (II) : INH = 1 : 1

Table – 2. Conductometric titration of INH with Mercuric nitrate solution

Volume of metal salt solution (in mL)	Corrected conductance (in mhos ×10^{-5})	Volume of metal salt solution (in mL)	Corrected conductance (in mhos ×10^{-5})
0.00	0.2	3.50	12.5
0.50	2.5	4.00	13.8
0.80	3.8	4.50	14.5
1.00	5.0	5.00	15.3
1.50	7.4	5.50	16.0

2.00	9.5	6.00	16.5
2.50	10.5	6.50	17.0
3.00	11.5	7.00	17.8

1st break, Hg(II) : INH = 1 : 2 2nd break, Hg(II) : INH = 1 : 2

Strength of Al(III) nitrate solution = 0.05M, Strength of INH solution = 0.005M

Temperature of the experiment = (30 ± 0.5)ºC, Volume of INH solution = 40 mL

Table - 3

Volume of metal salt solution (in mL)	Corrected conductance (in mhos × 10^{-5})	Volume of metal salt solution (in mL)	Corrected conductance (in mhos ×10^{-5})
0.00	0.2	2.40	15.9
0.50	6.5	2.60	16.3
0.70	8.2	3.00	17.0
1.00	10.8	3.50	17.8
1.20	12.5	4.00	18.7
1.30	13.4	4.50	19.4
1.50	13.9	5.00	20.4
1.60	14.2	5.50	21.3
1.70	14.8	6.00	22.0
2.00	15.2	6.50	23.0
2.20	15.6	7.50	24.5

1st break, Hg(II) : INH = 1 : 3 2nd break, Al(III) : INH = 1 : 2

Strength of Fe(III) nitrate solution = 0.05 M, Strength of INH solution = 0.005 M

Temperature of the experiment = (30 ± 0.5)ºC, Volume of INH solution = 40 mL

Table - 4

Volume of metal salt solution (in mL)	Corrected conductance (in mhos × 10^{-5})	Volume of metal salt solution (in mL)	Corrected conductance (in mhos × 10^{-5})
0.00	0.2	3.20	19.2
0.50	10.5	3.50	19.3
0.70	11.5	4.00	19.8
1.00	13.0	4.20	20.3
1.30	14.5	4.50	20.9
1.50	15.55	4.70	21.2
1.80	17.1	5.00	21.7
2.20	18.0	5.50	22.5
2.50	18.4	6.00	23.5
2.80	18.7	7.00	25.0
3.00	18.9	7.00	25.0

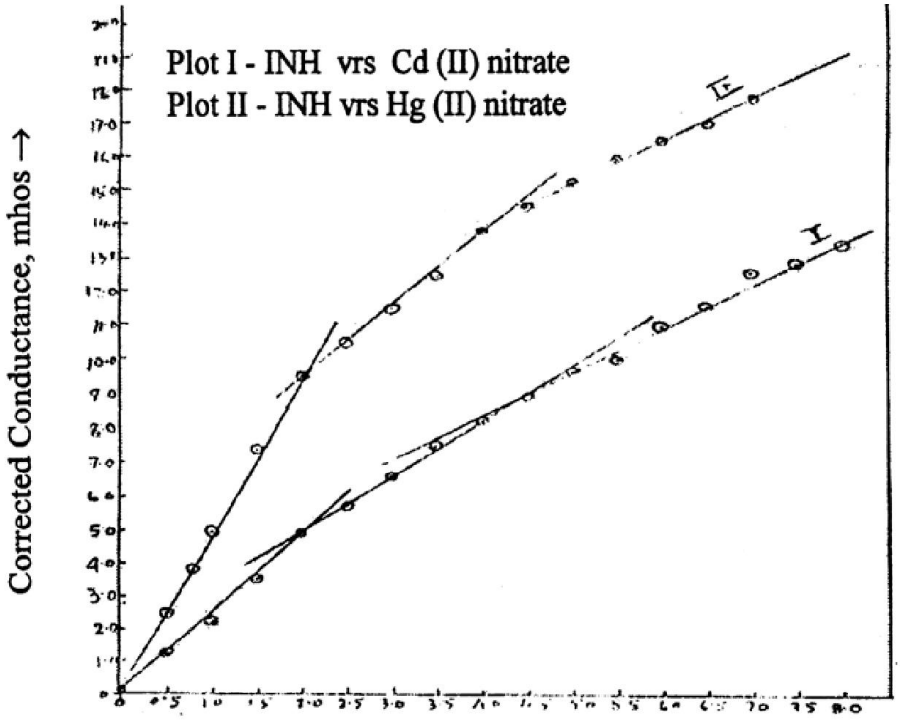
1st break, Fe(III) : INH = 1 : 2 2nd break, Hg(II) : INH : 1 : 1

Discussion

It is evident from Fig. 1 & 2 that in all the cases two breaks are obtained, the conductance which is initially very low shows a rapid increase linearly with the addition of the metal nitrate solution. The slope becomes less when the first compound is formed corresponding to the first break. Further addition of the metal nitrate solution gives a second well defined break which corresponds to the formation of the second new compound after which the increase in conductance is small. It appears that the first compound is an addition product(complex compound) formed with excess of the organic ligand, which breaks up to give the second addition product with excess of the metal nitrate solution. Al(III) form complex with metal : ligand (INH) ratio of 1 : 3 corresponding to the first break. None of the other metal taken for study, forms complexes of this stoichiometry. However, Cd(II), Hg(II) and Fe(III) form complexes with metal : ligand ratio of 1 : 2 corresponding to the first break in their conductance curve. The second break in conductivity curves correspond to metal : ligand ratio of 1 : 2 in case of Al(III) and 1 : 1 in case of Cd(II), Hg(II) and Fe(III). These observations suggest that the following complexes are formed in aqueous-alcohol solution :

(a) In case of Al(III), $Al(NO_3)_3.3[INH]$ and $Al(NO_3)_3.2[INH]$

(b) In cases of Cd(II), Hg(II) and Fe(III) : $Cd(NO_3)_2.2[INH]$ and $Cd(NO_3)_2.[INH]$
$Hg(NO_3)_2.2[INH]$ and $Hg(NO_3)_2.[INH]$



Volume of metal nitrate solution in mL

Fig. 1

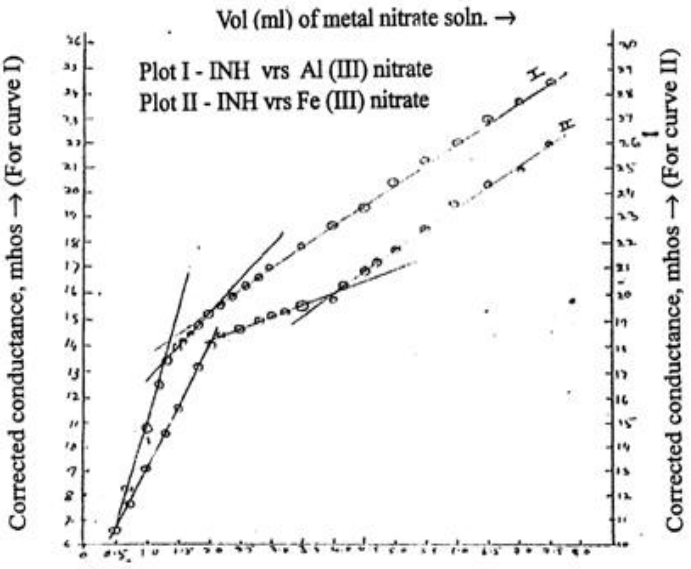


Fig. 2

Conclusion

Conductometric titration of isonicotinic acid hydrazide (INH) suggested that Al(III) nitrate form 1 : 3 and 1 : 2 complexes with the organic ligand (INH) while Cd(II), Hg(II) and Fe(III) nitrates form 1 : 2 and 1 : 1 complexes in aqueous-ethanol (25% by vol.) solution.

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