

# Potentiometric Studies of Complex Formation of Mn(II), Co(II), Ni(II), Cu(II) & Zn(II) with *o*-Hydroxyacetophenone Oxime & Its Derivatives

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The stability constants of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of some substituted *o*-hydroxyacetophenone oximes have been determined potentiometrically in water-dioxane (25-75% v/v) at  $\mu \sim 0.1M$  ( $NaClO_4$ ) and  $30 \pm 0.1^\circ$  using the Bjerrum-Calvin pH titration technique as adopted by Irving and Rossotti. The validity of (i) linear relations between metal-ligand stability constants and proton-ligand stability constants, (ii) Irving-Williams order, and (iii) Hammett equation have been examined for 1:1 complexes.

THOUGH the formation of metal chelates of *o*-hydroxyacetophenone oxime, resacetophenone oxime and 2-hydroxy-5-methylacetophenone oxime has been indicated<sup>1-4</sup> but these studies were mainly concerned with the use of those reagents as analytical reagents. The present work deals with a systematic potentiometric study of proton-ligand constants of some substituted *o*-hydroxyacetophenone oximes and stability constants of its chelates with transition metal ions.

## Materials and Methods

The details regarding preparation of ligands and the experimental technique employed for the Bjerrum-Calvin titration are given in an earlier communication<sup>5</sup>.

## Metal Salt Solutions

In view of the ability of  $SO_4^{2-}$  ion to complex to the same extent with the metal ions studied in the present investigation and comparatively high the metal-ligand stability, it was considered desirable to employ sulphates of transition metal ions (BDH, Analar) for the present study<sup>6</sup>. The solution of Cu(II) and Ni(II) were standardized by titrating the metal solutions with aq. sodium EDTA using murexide as an indicator. Mn(II) and Zn(II) were estimated using Erio. T indicator as described by Schwarzenbach<sup>7</sup>. The amount of Co(II) was determined by the method followed by Schwarzenbach<sup>7</sup>.

## Calculations

For the calculation of stability constants it was assumed that factors like hydrolysis of metal ions and presence of polynuclear hydrogen and hydroxyl bearing complexes were absent. The assumptions were justified on the following grounds: (i) The solutions employed being very dilute, the probability of polynuclear species under experimental conditions was not expected to be significantly high, (ii) the metal-reagent curves show departure from the reagent curve at  $B$  values (pH meter readings) much lower than the  $B$  values of hydrolysis of metal ions,

and (iii) the metal-ligand stability constants being comparatively very high, the anion complexing will not vitiate the relative stability values because this factor remains common throughout. Values of  $\bar{n}$  (metal-ligand formation number) were calculated using the Irving-Rossotti<sup>8</sup> expression.

**Cobalt(II) system** — The  $B$  values of hydrolysis of Co(II) was 5.5. The departure of metal-complex titration curve from the reagent curve commenced at  $B = 2.75$ . The variation of  $\bar{n}$  was continuous and symmetrical up to  $B = 6.5$ . The highest value of  $\bar{n}$  was 2 before hydrolysis commenced. This indicates formation of 1:1 and 1:2 complexes. The formation curve was not symmetrical. The part of the curve between  $0 < \bar{n} < 2$  was treated by the pointwise calculation. The values showed continuous drift. The  $\log K$  values were calculated by the method of pointwise calculation  $\log K_1 = \log \bar{n} / (1 - \bar{n}) + pHL$ ,  $\log K_2 = \log (\bar{n} - 1) / (2 - \bar{n}) + pHL$  and the half integral method.

**Manganese(II) system** — The  $B$  value of hydrolysis of Mn(II) could not be determined accurately as the solution became opaque at  $B = 5.6$ . The deviation of metal complex titration curve from the reagent curve was observed from  $B = 3.7$  to 4.5, depending on the reagent. The variation of  $\bar{n}$  is continuous and symmetrical up to  $B = 6$ . The highest value of  $\bar{n}$  was 2 with a few ligands, while with most of the ligands the maximum value of  $\bar{n}$  was 1.00. The methods of pointwise calculation and of half integrals were used for the calculation of  $\log K$  values.

**Nickel(II) system** — The  $B$  of hydrolysis of Ni(II) was 7. The departure of metal-complex titration curve from the reagent curve was seen from  $B = 5$ . The variation of  $\bar{n}$  was continuous and symmetrical up to  $B = 7$ , and then changed abruptly. Values of  $\bar{n}$  greater than unity were observed at and above the  $B$  value of hydrolysis. This indicated the formation of 1:1 complex and that of 1:2 complex was uncertain. The  $\log K$  values for 1:1 complex were obtained by the method of pointwise calculation.

**Copper(II) systems** — It was observed that (i) in all copper systems, except in the case of 2-hydroxy-5-

TABLE 1 — METAL-LIGAND STABILITY CONSTANTS

Ligand	log $PK_2^H$	(Temp. $30^\circ \pm 0.1^\circ$ )							
		Mn(II)		Co(II)		Ni(II)	Cu(II)		Zn(II)
		log $K_1$	log $K_2$	log $K_1$	log $K_2$	log $K_1$	log $K_1$	log $K_2$	log $K$
OHAPO	11.86	10.26	7.92	11.43	9.43	7.80	10.99	10.42	9.19
RAPO	11.14	9.24	6.04	10.65	7.29	8.23	11.10	10.67	8.46
5-Methyl-OHAPO	12.11	7.86	—	9.20	8.11	8.14	11.33	10.71	8.85
3-Methyl-OHAPO	12.05	8.67	—	8.89	—	7.97	11.47	10.93	9.03
5-Chloro-OHAPO	11.28	9.06	6.54	11.17	7.57	7.59	10.77	10.34	8.42
5-Bromo-OHAPO	11.27	9.30	7.65	11.22	8.34	7.57	10.78	10.17	8.26
3-Chloro-OHAPO	10.77	7.78	—	10.35	7.20	7.97	10.99	9.01	7.76
3-Bromo-OHAPO	11.04	9.66	—	10.37	7.69	8.02	11.19	10.12	8.24
5-Iodo-OHAPO	11.16	8.31	—	11.04	7.41	7.44	10.68	9.97	8.09
5-Nitro-OHAPO	8.97	6.17	—	9.26	6.39	6.36	—	—	5.53

\*Taken from an earlier paper [*Indian J. Chem.*, **13** (1975), 605].

OHAPO=*o*-hydroxyacetophenone oxime; RAPO=resacetophenone oxime.

nitroacetophenone oxime where precipitation was noticed at  $B = 2.2$  and measurements were not carried out, a distinct colour change was observed on the addition of reagent around  $B = 3.4$ , (ii) the departure of metal-complex titration curve from the reagent curve was always seen at  $B$  values less than  $B$  of hydrolysis, 4.9 and (iii) the highest value of  $\bar{n}$  was around 1.8, indicating the formation of 1:1 and 1:2 complexes. The hydrolysis effects were ignored while calculating the metal-ligand stability constants as the complex formation took place at a lower  $B$  value than that of hydrolysis.

The values in low  $\bar{n}$  and  $[L]$  range are not available and even if obtained would be suspect on account of anion complexing at the low  $B$  values. This permits the use of only the least squares treatment or pointwise calculation method of Hearon and Gilbert<sup>9</sup>. In the latter method log  $K_1K_2$  is obtained either by least squares method<sup>10</sup> using Eq. (1).

$$\frac{\bar{n}}{(\bar{n}-1)[L]} = \frac{(2-\bar{n})[L]}{(\bar{n}-1)} K_1K_2 - K_1 \quad \dots(1)$$

or from the relation log  $K_1K_2 = 2 pHL_{\bar{n}-1}$  and log  $K_1$  is then calculated using Eq. (2).

$$K_1 = \frac{(2-\bar{n})[L]^2 K_1K_2 - \bar{n}}{[L](\bar{n}-1)} \quad \dots(2)$$

The least square value of log  $K_1$  was too low as compared to most of the corresponding values obtained by the pointwise calculation. This discrepancy is due to negative values of log  $K_1$  at  $\bar{n} < 0.5$  which were obtained in the calculations carried out assuming log  $K_1K_2 = 2 pHL_{\bar{n}=1}$ . These negative values might be either due to inaccuracies in the estimation of  $\bar{n}$  at such low  $B$  values where  $v_{(3)} - v_{(2)}$  is quite small or due to anion complexing at low  $B$  values of the order of 3. This would cause the experimental values of  $\bar{n}$  to be lower than the true ones.

In the treatment by the method of least squares, it has been suggested that the values are better estimated with the help of the slope rather than the intercept. The value of log  $K_1K_2$  was, therefore, obtained by this method. log  $K_2$  was obtained by the pointwise calculations independently. The value of log  $K_1$  was then obtained by taking the difference.

The values of log  $K_1$  and log  $K_2$  so obtained are in agreement with those obtained from the half-integral method.

*Zinc(II) system* — The deviation of metal complex titration curve from the reagent curve starts at  $B = 5.5$ . The value of  $\bar{n} = 1$  at  $B$  value of hydrolysis 6.1, show the formation of only 1:1 complex.

## Results and Discussion

The metal-ligand stability constants of the various metal systems studied presently are given in Table 1.

*Relation between log  $K_1$  and log  $PK_2^H$  ( $pK_2^H$ )* — The validity of the linear relation between metal-ligand stability constants and proton-ligand stability constants has been examined for transition metal complexes of substituted *o*-hydroxyacetophenone oximes (OHAPOs) by plotting log  $K_1$  against log  $PK_2^H$ . It will be seen a single line passing through all the points is not possible. In particular, the points corresponding to 5-methyl-, 3-methyl-, 5-nitro-, 3-chloro- and 3-bromo-OHAPOs show significant deviation from linearity. Jones *et al.*<sup>11</sup> have suggested that correlations of this type are not generally valid. In the present case for oximes with dissociation constants close to each other the points, roughly fall on a linear plot, while 5-methyl-, 3-methyl- and 5-nitro-OHAPOs whose log  $PK_2^H$  are widely different, the points deviate from linearity. However deviation from linearity exhibited 3-chloro- and 3-bromo-OHAPOs may be due to steric interaction.

*Relation between log  $K$  values of two similar metal ions with the same ligand* — A comparison of the metal-ligand stability constants of two similar metals having the same coordination number was suggested by Irving and Rossotti<sup>13</sup>. Plots obtained for the systems Cu(II)-Zn(II), Cu(II)-Ni(II), Mn(II)-Zn(II) and Ni(II)-Zn(II) show that except for Cu(II) complexes the relation of Freiser and coworkers<sup>12</sup> does not show much improvement over the log  $K_1$  versus  $pK_{OH}$  relation.

*Irving-Williams order for stability constants* — The log  $K$  values of the metal complexes do not follow the Irving-Williams<sup>14</sup> order. They also do not

agree with the order of the  $pH$  values of incipient precipitation of metal ions given by Flagg and Furman<sup>15</sup> for salicylaldehyde or by Bandyopadhyaya and Ray<sup>16</sup> for salicylamidoxime.

The Irving-Williams order which is essentially the order of crystal field stabilization energies (CFSE) of transition metal ions will ideally hold for octahedral spin-free transition metal complexes if the various factors such as metal ligand bond energies, polarization energies of the ligands, hydration energies, etc., contributing to standard enthalpy change, vary uniformly, except the differences in ligand field stabilization energies. The work on solid transition metal complexes of substituted, OHAPOs<sup>17</sup> indicated that Cu(II), Ni(II) and Co(II) complexes are square planar and the last two are spin-paired. The exceptions to the Irving-Williams order have been attributed to spin-pairing in strong crystal fields as one of the probable causes since this factor influences the relative CFSE in a different way than in spin-free complexes<sup>18</sup>. Further, Co(II) and Mn(II) ions are known for their tendency to get oxidized in alkaline medium in the presence of nitrogen donors. It, therefore, appears that unless one has exact knowledge of the contribution of various factors which influence the CFSE of metal complexes, it would be futile to discuss the order of stability constants vis-à-vis the Irving-Williams order.

*Application of Hammett equation to metal-ligand system*—May and Jones<sup>19</sup> on the lines of the Hammett relation proposed the relation  $\log K/K^0 = \sigma$  for metal-complexes, where  $K$  and  $K^0$  are the stability constants of the complexes with substituted and unsubstituted acids,  $\sigma$  is Hammett constant and  $\sigma$  is a constant characteristic of the reaction. They found that the above relation was valid for seventeen Cu(II) complexes of substituted benzoic acids but failed for a series of pyridine adducts of Cu(II) acetyl acetonates. Tate and Jones<sup>20</sup> also could not get a satisfactory linear relation for sulphonate complexes of cadmium. The values of  $\sigma$  were obtained by Hammett from a great variety of data and have, in some cases, a rather large probability spread. These values for dioxane-water solvent are not available. It was, therefore, thought

that one could justify the use of alternative  $\sigma$  values given by the ratio of dissociation constants of substituted OHAPOs to that of OHAPO. These  $\sigma$  values were employed to test the linear relation suggested by May and Jones. It was found that the points corresponding to 5-methyl-, 5-chloro-, 5-bromo- and 5-iodo-OHAPOs roughly fall on a linear plot and those corresponding to 3-methyl-, 3-chloro-, 3-bromo- and 5-nitro-OHAPOs show significant deviation from linearity. The deviation observed in the case of first three oximes may be attributed to the *ortho* effect. The nitro substituted compound gives anomalous results probably because of the possibility of direct conjugation of the nitro group with the phenoxide ion.

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