Polarography of Pyridine Complexes with Cobalt(II) & Manganese(II)

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The possibility of obtaining hexacoordinated complexes of pyridine with Co(II) and Mn(II) has been investigated polarographically. The effects of temperature and addition of small amounts of formamide and DMF on the formation constants of these complexes have been studied.

Pyridine forms a variety of complexes with different metal ions. Atkinson et al.1 and Bjerrum2 have established that Mn(II) and Co(II) form four and two stepwise complexes respectively. It was felt that since Mn(II) and Co(II) have a maximum coordination number of six, polarographic investigation of the existence of higher complexes should be carried out. The present investigation was, therefore, undertaken to explore this possibility polarographically and to study the effect of temperature and addition of organic solvents such as formamide and DMF on the formation constants of the complexes.

Since Co(II) and Mn(II) form complexes which are irreversibly reducible at D.M.E., the indicator ion method as developed by Ringbom and Erikson3,4 was used. A suitable indicator ion whose complex should be reducible at sufficiently more positive potential than the ions under investigation, is essential in this method.

In practice, a series of \( E_{1/2} \) values are first obtained for the indicator ion, N, as a function of wide [ligand] range. The entire set of measurements is repeated in presence of fixed concentrations of metal ion, M. In each case \( E_{1/2} \) would be less negative than the corresponding value for indicator ion alone. The \( E_{1/2} \) values obtained in two sets are plotted against the analytical concentration of the ligand, \( C_x \). At higher concentrations of \( C_x \), the two curves become parallel to each other indicating that the maximum coordination number has been achieved. The concentration of M is kept \( \sim 10^3 \) times greater than that of N to make the positive shift measurable.

The ligand number \( \bar{n} \) for the system MX is given by Eq. 1,

\[
\bar{n} = \frac{C_x - [X]}{C_M} \quad \ldots \ (1)
\]

Where \( C_x \) = total ligand concentration, \([X]\) = free ligand concentration and \( C_M = \) total concentration of M.

From the two \(-E_{1/2}\) versus \( C_x \) plots, free ligand concentration \([X]\) for the system MX can be determined. Knowing \([X]\), \( \bar{n} \) can be calculated from Eq. 1.

The formation curve \( \bar{n} \) versus \([X]\) was drawn and integrated graphically to get \( F_0(X) \) data.

The stability constants were obtained from \( F_0X \) data using Fronaeus's5 and Leden's methods6.

All the reagents used were of AR grade. Cd(II) sulphate was used as the indicator while Co(II) and Mn(II) nitrates were used as metal ions for complexation studies. All the solutions were made in conductivity water. Sodium perchlorate was used as the supporting electrolyte while 0.002% gelatin was used to suppress the maxima. The \( iR \) drop correction was applied wherever applicable. The capillary characteristics measured in open circuit were: 2.24 mg/s and \( t = 3.03 \) s.

The test solution was placed in a thermostated \((\pm 0.1^\circ C)\) H cell coupled with a saturated calomel electrode. Just prior to polarographic examination of each solution, purified nitrogen was passed through it for 15 min to expel dissolved oxygen. The variation in current was recorded on a scalamp galvanometer while increasing the applied potential gradually.

The polarograms were first taken with 0.6 m M Cd(II) + 0.5 M sodium perchlorate + 0.002% gelatin and varying amounts of pyridine (0.00 to 2.0 M). The polarograms were again taken after adding 0.12 M of the metal ion under investigation. The concentration of sodium perchlorate was proportionately decreased to keep ionic strength at 0.5. For each concentration of pyridine, the half-wave potential was more positive in the presence of added metal ion than in its absence. Both the systems i.e., Co(II)-pyridine and Mn(II)-pyridine were then studied at higher temperatures and in the presence of 10% and 20% of formamide and DMF when similar results were obtained.

The formation curves were plotted (Fig. 1) and integrated graphically to get \( F_0(X) \) functions. The formation constants obtained from these \( F_0(X) \) functions are shown in Table 1.

The larger stabilities observed for Co(II) complexes in comparison to those for Mn(II) are justified from the Irving Williams sequence7,8. The variation of stepwise stability constants with increasing coordination is, in some cases, somewhat irregular. However, on the basis of statistical considerations alone, the stepwise constants should decrease fairly regularly. This trend is
expected for systems in which changes in stereochemistry, \( \pi \)-bonding and ground state of the central metal ion do not occur. The irregular trends in the stepwise stability constants of Mn(II) and Co(II) complexes under investigation indicate changes in mode of formation of the complex species as the number of coordinated ligands is increased. These fluctuations are necessarily encountered when any one of the factors noted above is operative. In the present studies, the effects due to change in stereochemistry and extent of \( \pi \)-bonding appear to have the predominating influence. Similar irregular trends in stepwise constants for Ni(II) complexes with pyridine and pyrazoles have been reported.

Interestingly, the present results indicate the formation of five stepwise complexes for Co(II)-pyridine system and six for Mn(II)-pyridine system. After making due allowance for variation in experimental conditions, it can be concluded that the stability constant values obtained are in good agreement with those obtained by Atkinson et al. and Bjerrum for the common complexes. However, Mn(II)-pyridine complexes show a marked decrease in their stabilities in presence of DMF. Similar anomalous decrease has been observed for pyridine and picoline complexes with Cd(II) and Zn(II) ions, though a satisfactory explanation is not available.

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References