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Interaction of Transition Metal Ions with some Biologically Active Ligands

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Mn(II), Co(II) and Ni(II) complexes with biologically active ligands viz. 2-methoxybenzoic acid, 3-methoxybenzoic acid and 4-methoxybenzoic acid have been studied by paper electrophoresis at 25°C, 35°C and 45°C and a fixed ionic strength $\mu = 0.1$ M $HClO_4$. The stability constant values of the complexes have also been reported.

INTRODUCTION

The chemistry of methoxybenzoic acids and their metal complexes is of considerable interest due to their biological activities[1,2]. Derivatives of methoxybenzoic acids are known to act as antimycotic agents[2]. Copper complexes containing methoxybenzoates have been synthesised and shown to possess anti-inflammatory and antipyretic activities[1]. Few metal complexes of 2-methoxybenzoic acid have been prepared and characterised by IR spectra and X-ray diffraction[3]. There are no reports, however, on the electrophoretic studies of these complexes. Hence it was worthwhile to examine the reactions of Mn(II), Co(II) and Ni(II) with 2-methoxybenzoic acid (2-MBA), 3-methoxybenzoic acid (3-MBA) and 4-methoxybenzoic acid (4-MBA) at different temperatures.

EXPERIMENTAL

All the chemicals used were of AnalaR grade. Fresh solutions of metal ions were prepared by dissolving metal carbonates in perchloric acid and standardizing it by usual methods[4]. The final concentrations of metal and ligand solutions were kept at 5.0×10^{-3} M and 1.0×10^{-2} M, respectively. Ethanolic solution of 1-(2-pyridylazo)-2-naphthol was used as locating reagent. Systronics paper electrophoresis equipment No. 604 (India) and two types of pH indicator and accessories (Leeds and Northup, and Elico LI-110), having glass and calomel electrode assembly, were employed after duly calibrating it with pH 4 and pH 9.2 buffer solutions. The calibration was checked after each set of experiments.

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Electrophoretic observations were recorded as earlier reported methods[5] at temperatures 25°C, 35°C and 45°C, ionic strength being maintained at 0.1.

RESULTS AND DISCUSSION

Stability constants were calculated with the help of pH vs. mobility curve and dissociation constants of the ligands[6]. The values are presented in Table 1.

TABLE 1

STABILITY CONSTANT VALUES OF THE COMPLEXES

Ionic strength $\mu = 0.1$ M $HClO_4$

Ligand	Temp (°C)	Mn(II)	Co(II)	Ni(II)
	25	3.40	3.69	3.79
2-MBA	35	2.85	3.12	3.21
	45	2.40	2.61	2.68
	25	3.41	3.69	3.79
3-MBA	35	2.85	3.12	3.22
	45	2.40	2.61	2.68
	25	3.38	3.67	3.77
4-MBA	35	2.83	3.10	3.19
	45	2.39	2.59	2.67

Two plateaus are obtained in all the metal(II)–2-MBA, -3-MBA and -4-MBA systems in which the first plateau represents the region of uncomplexed metal ion whereas the second plateau indicates formation of 1 : 1 species. That no further complexation is taking place is supported by the constant value of mobility after the second plateau.

The order of stability constant values is Ni > Co > Mn which finds support from the work of Irving and Williams[7].

In view of the ligands, the order of stability constant values is found to be 2-MBA $\simeq$ 3-MBA > 4-MBA.

A plausible explanation for this trend is based upon the ability of deprotonation of the ligands.

Methoxy group is an electron donating group and this is more pronounced from *para* position than from *meta* position. So, higher electron density will be manifested at the oxygen atom of the —OH group due to increased electron density at the carbon atom of the carboxyl group. Consequently, proton release will be difficult, decreasing the acid strength and hence, 4-MBA will be expected to be weaker than 3-MBA. 2-MBA and 3-MBA have equal acidic strength as is evident from their pKa values[6]. The stronger acidic character of 2-MBA and 3-MBA than 4-MBA is responsible for the higher values of stability constants of M(II)–2-MBA and M(II)–3-MBA complexes. However, a negligible difference in some cases of M(II)–2-MBA and M(II)–3-MBA has been noticed.

It has also been observed that the values decrease with the increase of temperature which is not unusal.

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