Mixed ligand complexes of Cu(II) with reactive methylene compounds of malonamic acid series and oxalic acid

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ABSTRACT

The mixed ligand complexes of N-(2-ethoxy) phenyl malonamate (EPM$^-$), N-(4-methyl phenyl malonamate (MPM$^-$) and oxalate (OX^{2-}) with Cu(II) have been studied polarographically at constant ionic strength μ =2.0 (NaNO$_3$) and pH 5.6 at 25±0.1°C. The reduction of simple and mixed complexes has been found to be reversible and diffusion-controlled. The stability constant of simple system has been determined before the study of mixed ligand complex by the method of De-Ford and Hume[1]. The stability constants of the mixed ligand complexes [Cu(OX)(MPM)]$^-$ and [Cu(OX)(EPM)]$^-$ are found to be log β_{11}=12.25 and log β_1=10.82 respectively. Oxalic acid, N-(2-ethoxy) and N-(4-methyl) phenyl malonamic acid are abbreviated as OX^{2-}, EPM$^-$ and MPM$^-$ respetively.

Key words: Polarogrpahic study, mixed ligand complexes, Malonamic acid, oxalic acid.

The use of polarographic data for the study of complexation is well known[1-6]. Reactive methylene compounds[7] have been found to be excellent starting materials for the synthesis of various types of chemotherapeutic and AnalR grade. It appears that polarographic studies of mixed complexes of Cu(II) with Oxalic acid, (N-ethoxy0 phenyl malonamic acid and N-(4-mehyl) phenyl malonamic acid have not been reported so far. With this end in view the present study has been undertaken.

All the chemicals used were of analytical grade. Their stock solutions were prepared in conductivity water. The concentration of Cu(II) (from CuSO4) was maintained 1.0×10^{-3} M. Sodium salts of oxalic acid was used as source of oxalata (OX^{2-}) ion. KCl was used as a supporting electrolyte and also to maintained a constant μ = 2.0. Polarograms of the solutions were obtained by means of a Toshniwal CLO-2A in conjunction with Toshniwal (PL-50) polyflex galvanometer. Purified nitrogen was used for removing the dissolved oxygen. All the measurements were made at 25±01°C. A saturated calomel electrode (S.C.E.) was used as a reference electrode. The d.m.e. had the following characteristics m 2.404 mg/sec, t=3.4 sec, $m^{2/3} t^{1/6}$=2.2 mg$^{2/3}$ sec$^{-1/2}$ (in 2.0 M KCl, open circuit), h$_{corr}$ = 64.8 cm.

The polarographic reduction of Cu(II) in Ox, $^{2-}$EPM$^-$, MPM$^-$ separately were found to be reversible and diffusion controlled. The slopes of linear plots of log(i/i$_d$-i) vs E$_{d.e.}$ were of the order of 32±1 mV.

Cu(II)-OX^{2-} system

A plot of E½ vs log[Ox^{2-}] is a straight line which shows the formation of single complex. The value of coordination number J comes out to be 2, using Lingane's method[6]. The composition of complex [Cu(OX$_2$)]$^{2-}$ and its stability constant is log β_2= 9.73.

Cu(II)-EPM$^-$ and Cu(II)-MPM$^-$ system
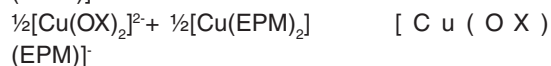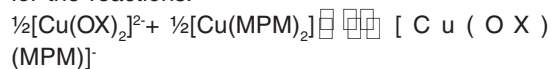
The plots of E$_{½}$ vs log [EPM]$^-$ and E$_{½}$ vs log [MPM]$^-$ were staight lines showing the formation

of simple complex in each case. The value of coordination number J comes out to be 2 in both the cases. Therefore, the composition of the complexes formed were $[Cu(MPM)_2]$ and $[Cu(EPM)_2]$ with stability constants log β_2=10.75 and β_2=8.50 respectively.

Cu(II)-OX^{2-} -MPM$^-$ and Cu(II)-OX^{2-} EPM$^-$ mixed systems

In each case single well defined reverisble and diffusion controlled wave was obtained, and E$_{\frac{1}{2}}$ values were more negative than those obtained in the absence of MPM$^-$ and EPM$^-$ showing the formation of mixed ligand complexes. Schaap and McMasters[8] method has been used to determine the composition and stability constants of mixed complexes (Table 1).

A comparative study of both the systems shows that the mixed system [Cu(II)-OX^{2-}MPM]$^-$ in more stable than [Cu(II)-OX^{2-}MPM]$^-$ in more stable than [Cu(II)-OX^{2-}-EPM]$^-$ which is further proved by the larger positive log value of mixing constant (K$_M$) for the reactions.

$\frac{1}{2}[Cu(OX)_2]^{2-}$+ $\frac{1}{2}[Cu(MPM)_2]$ ⇌ $[Cu(OX)(MPM)]^-$

$\frac{1}{2}[Cu(OX)_2]^{2-}$+ $\frac{1}{2}[Cu(EPM)_2]$ $[Cu(OX)(EPM)]^-$

The positive log K$_M$ values in both the cases also indicate the stability of mixed complexes over the simple complexes.

Table 1: Composition and stability constant of mixed complexes of Cu(II) with , OX^{2-}, MPM$^-$ and EPM$^-$ ion

Temp.= 25±0.1°C

System	Composition	Stability constant ⇌ log β_{11}	Mixing constant log K$_M$
Cu(II)-OX^{2-}-MPM$^-$	[Cu(OX) (MPM)]$^-$	12.25	3.25
Cu(II)-OX^{2-}-EPM$^-$	[Cu(OX) (EPM)]$^-$	10.82	1.25

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