

COMPARATIVE POLAROGRAPHIC STUDIES OF Cd(II) COMPLEXES OF GLYCINE IN AQUEOUS AND AQUEOUS-NONAQUEOUS MEDIA

Suresh Kumar, Meena, Akhil K. Barjatya and O.D. Gupta*

Department of Chemistry, University of Rajasthan, Jaipur-302004 (India) *E-mail: gupta_od@yahoo.com

ABSTRACT

The stability constants for the Cd(II)-glycine binary complex system have been determined using polarographic measurements in DMF-water mixture lonic strength was maintained with KCI (μ =1.0M) and TritoX-100 was used as maxima suppressor. The study shows that the tendency of glycine to form complex with Cd(II) ions is greater in DMF-water mixture as compared to that in only water. **Keywords:** Cd(II)-glycine binary complex; polarographic measurements.

INTRODUCTION

Mostly the inorganic polarographic investigation have been carried out in aqueous media and rare are the reports¹ citing advantages by carrying out such investigations in media other than aqueous. Mixed ligand complexes of transition metals with several amino acids have been studied by many workers²⁻⁸. Vast data are available on the stability constants of amino acids complexes in aqueous media⁹⁻¹¹. Despite this, little is known about the chemistry of amino acids and metal complexes in nonaqueous media and mixed solvents¹²⁻¹⁴. The present communication deals with the studies of binary complexes of Cd(II) with glycine in DMF-water mixture.

EXPERIMENTAL

All reagents used were analytical grade and their solutions were prepared in conductivity water. The ionic strength was maintained constant at $\mu = 1.00$ using KCl as supporting electrolyte. The concentration of Cd(II) was maintained at 5×10^{-4} M. Polarograms were obtained by means of a manual polarograph. All the measurements were obtained at 300K. A saturated calomel electrode was used as references electrode. The d.m.e. had the following characteristics m = 2.30 mg/sec., t = 3.20 sec. and h = 40 cm.

RESULTS AND DISCUSSION

All the plots of log (i/i_d-i) vs $E_{d.e.}$ yielded straight line with slopes ($30\pm1mV$) which established two electron reversible reduction. Linear plots of i_d vs h^{1/2} passed through the origin, established the diffusion controlled nature, of the reduction at the electrode. When increasing amounts of glycine added to solutions containing 5×10^{-4} M Cd(II), requisite quantity of KCl and different percentages of DMF, a shift in the half-wave potential towards negative side and decrease in the diffusion current were observed. These indicate complex formation. The polarographic measurements and $F_j[X]$ functions, as determined by DeFord and Hume's method, have been recorded in Tables 1 to 3 for 10%, 20% and 30% DMF-water mixtures, respectively and shown graphically in Figures 1 to 3. The stability constants have been determined by DeFord and Hume's method which are redorded in Table 4. The values of stability constants for Cd(II)-glycine system in aqueous medium are summarized in Table 5. The results show that the stability constants are higher in DMF-water mixtures than in purely aqueous medium. This is expected because water has a high dielectric constant of about 80, so the electrostatic force of attraction between two ions of opposite charge in considerably reduced. Addition of organic solvent as DMF decreases the dieletric constant of the media, resulting in a greater attraction force and hence larger stability constants.

| [gly] | $\Delta E_{1/2}$ | logI _m /I _c | $F_0[X] \ge 10^4$ | $F_1[X] \ge 10^6$ | $F_2[X] \ge 10^8$ | F ₃ [X]x |
|---------------------|------------------|-----------------------------------|-------------------|-------------------|-------------------|---------------------|
| mol L ⁻¹ | | | | | | 10 ¹⁰ |
| 0.001 | 0.0885 | 0.1104 | 0.1220 | 1.2191 | 7.2902 | 9.8012 |
| 0.002 | 0.1037 | 0.1461 | 0.4289 | 2.1441 | 8.2703 | 9.8014 |
| 0.003 | 0.1140 | 0.1587 | 0.9796 | 3.2650 | 9.2550 | 9.8000 |
| 0.004 | 0.1214 | 0.1850 | 1.8394 | 4.5983 | 10.2706 | 9.9017 |
| 0.005 | 0.1275 | 0.1988 | 3.0474 | 6.0947 | 11.2094 | 9.7989 |
| 0.006 | 0.1322 | 0.2278 | 4.6846 | 7.8076 | 12.1961 | 9.8102 |
| 0.007 | 0.1366 | 0.2430 | 6.8002 | 9.7145 | 13.1779 | 9.8113 |
| 0.008 | 0.1403 | 0.2588 | 9.4484 | 11.8104 | 14.1505 | 9.8007 |

Table-1: Polarographic measurements and $F_j[X]$ values for the Cd(II)-glycinate system in 10% DMF. [Cd(II)] = 5x 10⁻⁴ M, $E_{1/2}$ of Cd(II) = - 0.6090 V vs SCE, $i_d = 49$ div., $\mu = 1.0$ M KCl, temp. = 300K.

Table-2: Polarographic measurements and $F_j[X]$ values for the Cd(II)-glycinate system in 20% DMF. $[Cd(II)] = 5x \ 10^{-4} M$, $E_{1/2}$ of Cd(II) = - 0.6090 V vs SCE, $i_d = 49$ div., $\mu = 1.0 M$ KCl, temp. = 300K.

| [gly] mol L ⁻¹ | $\Delta E_{1/2}$ | logI _m /I _c | F ₀ [X] x 10 ⁴ | F ₁ [X] x 10 ⁶ | F ₂ [X] x 10 ⁸ | F ₃ [X] x 10 ¹⁰ |
|------------------------------|------------------|-----------------------------------|--------------------------------------|--|--------------------------------------|--|
| 0.001 | 0.0933 | 0.1217 | 0.1812 | 1.8110 | 10.1600 | 12.1000 |
| 0.002 | 0.1083 | 0.1481 | 0.6139 | 3.0690 | 11.3700 | 12.1002 |
| 0.003 | 0.1183 | 0.1618 | 1.3713 | 4.5708 | 12.5860 | 12.1204 |
| 0.004 | 0.1253 | 0.1908 | 2.5243 | 6.3106 | 13.7890 | 12.0986 |
| 0.005 | 0.1313 | 0.2060 | 4.1616 | 8.3230 | 15.0560 | 12.2134 |
| 0.006 | 0.1357 | 0.2382 | 6.3148 | 10.5246 | 12.2160 | 12.1103 |
| 0.007 | 0.1399 | 0.2552 | 9.0928 | 12.9897 | 17.4210 | 12.1007 |
| 0.008 | 0.1436 | 0.2730 | 12.6111 | 15.7638 | 18.7110 | 12.2008 |

Table-3: Polarographic measurements and $F_j[X]$ values for the Cd(II)-glycinate system in 30% DMF. $[Cd(II)] = 5x \ 10^{-4} M$, $E_{1/2}$ of Cd(II) = - 1.6085V vs SCE, $i_d = 41$ div.,

 $\mu = 1.0$ M KCl, temp. = 300K.

| [gly] | $\Delta E_{1/2}$ | logI _m /I _c | $F_0[X] \ge 10^4$ | $F_1[X] \ge 10^6$ | $F_2[X] \ge 10^8$ | F ₃ [X] x |
|---------------------|------------------|-----------------------------------|-------------------|-------------------|-------------------|-----------------------------|
| mol L ⁻¹ | | | | | | 10 ¹⁰ |
| 0.001 | 0.1126 | 0.0943 | 0.7565 | 7.5649 | 26.6490 | 14.4998 |
| 0.002 | 0.1246 | 0.1357 | 2.1041 | 10.5200 | 28.1000 | 14.5000 |
| 0.003 | 0.1319 | 0.1814 | 4.1296 | 13.7653 | 29.5510 | 14.5016 |
| 0.004 | 0.1381 | 0.1978 | 6.9202 | 17.3004 | 31.0010 | 14.5020 |
| 0.005 | 0.1431 | 0.2148 | 10.5751 | 21.1500 | 32.5000 | 14.6004 |
| 0.006 | 0.1467 | 0.2510 | 15.1444 | 25.2406 | 33.9010 | 14.5012 |
| 0.007 | 0.1495 | 0.2906 | 20.7555 | 29.6506 | 35.3580 | 14.5123 |
| 0.008 | 0.1525 | 0.3117 | 27.5047 | 34.3808 | 36.8510 | 14.5632 |

Table-4: Successive stability constants for ML, ML₂ and ML₃ complexes of Cd(II) - glycinate in various percentages of DMF - water mixture.

| Stability constants | 10% DMF | 20% DMF | 30 DMF |
|---------------------|---------|---------|---------------|
| $\log \beta_1$ | 5.69 | 5.90 | 6.69 |
| $\log \beta_2$ | 3.80 | 8.90 | 9.40 |
| $\log \beta_{13}$ | 10.99 | 11.08 | 11.16 |







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Fig. 3 : Plot of F_i[X] vs [GLY] : Cd(II)-glycinate system in 30% DMF at 300K.

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Table-5: Successive stability constants for ML, ML₂ and ML₃ complexes of Cd(II)-glycinate at 300K.

| Temeprature | Stability constant | | | |
|--------------------------|--------------------|----------------------|--------------------|--|
| | $[Cd(gly)]^{+1}$ | $[Cd(gly)_2]$ | $[Cd(gly)_3]^{-1}$ | |
| | $\log \beta_1$ | $\log \beta_2$ | $\log \beta_3$ | |
| 300K | 4.30 | 7.70 | 9.85 | |
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