

## Polarographic studies of mixed ligand complexes of cadmium(II) and lead(II) employing ligands of biochemical interest

V R MUNDRA, G N RAO\* and C S R MURTHY

Chemistry Department, Indian Institute of Technology, New Delhi 110016, India

MS received 14 November 1983; revised 26 March 1984

**Abstract.** Stability constants of various mixed ligand complexes of cadmium(II) and lead(II) have been determined employing the polarographic technique of Schaap and McMasters. Evidence has been obtained for the formation of ten mixed ligand complexes in the presence of glycine, aspartic acid, mono-ethanolamine and diethanolamine which are of biochemical interest.

**Keywords.** Mixed ligand complexes; mixing constants; stabilization constants.

### 1. Introduction

Whenever two different suitable ligands are present along with the metal ion in solution, mixed ligand complexes are always formed. Marcus and Eliezer (1969) have reviewed the work on the stability of mixed complexes in solution. Mixed ligand complexes are very likely to be formed in biological fluids since potential ligands like aminoacids, peptides, proteins etc., are present along with metal ions usually in the complexed form.

Rao and Subrahmanya (1964) studied the mixed ligand complexes of cadmium-glycine-ammonia and cadmium-alanine-ammonia system. Fridman *et al* (1963) reported the work on mixed ligand complexes of cadmium(II) and glycine using monodentate ligands like, thiosulphate, thiourea, thiocyanide, iodide, bromide and chloride. Schaap and McMasters (1961) worked on cadmium(II)-ethylenediamine and oxalate system. Sharma *et al* (1978) have studied the mixed ligand complexes of cadmium(II) with propylenediamine and malonate. It is therefore evident that not much work has been done on the mixed ligand complexes of cadmium(II) with alkanolamines and aminoacids.

### 2. Theory

Schaap and McMasters (1961) have extended the method developed by Deford and Hume to determine the formation constants of mixed ligand complexes. According to them the  $F_{00}(X, Y)$  function for all formation constants of the mixed ligand complexes is denoted by

$$F_{00}(X, Y) = \text{anti log } (0.4343nF/RT) [(E_{1/2})_s - (E_{1/2})_c + \log \frac{I_M}{I_c}]. \quad (1)$$

\*To whom all correspondence should be addressed.

By Leden's approach, the  $F_{00}(X, Y)$  function can be factored and written in the form

$$F_{00}(X, Y) = A + B[X] + C[X]^2 + D[X]^3 \quad (2)$$

where

$$A = \beta_{00} + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3; B = \beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2; \\ C = \beta_{20} + \beta_{21}[Y]; D = \beta_{30}$$

The value of the constant  $A$  at a given concentration of  $Y$  can be calculated if the consecutive formation constants are known for the simple system containing the metal ion with  $Y$  alone. This  $A$  value may be compared with the  $A$  value obtained by plotting  $F_{00}$  vs  $[X]$  at the same value of  $[X]$ . The plot represents a cubic equation whose intercept at  $[X] = 0$  is  $A$  and the limiting slope at  $[X] = 0$  is  $B$ .

If the intercept value  $A$  is subtracted from  $F_{00}$  and the resulting quantity divided by  $[X]$  it gives the  $F_{10}$  value and the plot of  $F_{10}$  vs  $[X]$  represents a quadratic equation whose intercept is  $B$  and the limiting slope is  $C$ .

$$F_{10} = \frac{F_{00}(X, Y) - A}{[X]} = B + C[X] + D[X]^2$$

Continuing this procedure it is seen that the function  $F_{20}$  is linear with the intercept  $C$  and slope  $D$ , and the plot for  $F_{30}$  function is horizontal to the  $[X]$ -axis.

### 3. Experimental

The amino acids and alkanolamines used were BDH England or Eastman Kodak chemicals. To check the purity of the ligands, techniques like pH-titration with standard hydrochloric acid and comparison of the observed pK values of the ligand with literature and titration with standard hydrochloric acid to get the neutral equivalent by mixed indicator method have been employed. Strength of the stock solution of cadmium sulphate was determined by complexometric titration.

The ionic strength of the solution is maintained at unity by using potassium nitrate solution, which also serves as the supporting electrolyte. To suppress the maxima, 0.005% Triton X-100 was used and the polarograms were obtained manually at 25°C using Toshniwal polarograph type CL02A.

### 4. Results

Suitable concentrations of the ligands were chosen from the stability constants of the pure complexes of cadmium(II) formed by these ligands. In all these systems the metal ion concentration is kept at 1 mM. Stability constants of mixed ligand complexes have been calculated by the method of Schaap and McMasters (1961). Estimated error in the logarithmic values of stability constants is  $\pm 0.1$  unit.

#### 4.1 Cadmium-glycine-aspartic acid system

The effect of varying the concentration of aspartic acid from 0.1–1 M on the half-wave potential of cadmium has been studied while keeping the concentration of glycine constant at 0.1 M and 0.2 M. Polarographic measurements and  $F_{ij}$  values of this system

**Table 1.** Polarographic measurements and  $F_{ij}$  values of cadmium-glycine-aspartic acid system.

$g$	$a$	$-E_{1/2}$	$i_d$	$F_{00}$ ( $\times 10^9$ )	$F_{10}$ ( $\times 10^9$ )	$F_{20}$ ( $\times 10^9$ )	$F_{30}$ ( $\times 10^9$ )
0	0	0.571	9.1	—	—	—	—
0.1	0.10	0.792	8.6	0.0318	0.2597	1.5975	1.975
	0.20	0.805	8.2	0.0920	0.4307	1.6536	1.268
	0.40	0.824	7.7	0.4308	1.0622	2.4055	2.5137
	0.60	0.833	7.2	0.9390	1.5385	2.3975	1.6625
	0.80	0.841	6.8	1.8347	2.2860	2.7325	1.6656
	1.00	0.847	6.3	3.1607	3.1540	3.0540	1.6504
0.2	0.10	0.806	8.5	0.0959	0.5004	2.0440	2.4400
	0.20	0.815	8.1	0.2031	0.7878	2.4390	3.1950
	0.40	0.822	7.5	0.6040	1.3963	2.7405	2.3512
	0.60	0.838	7.2	1.3716	2.2100	3.1837	2.3060
	0.80	0.847	6.6	3.0170	2.7143	4.2678	3.0847
	1.00	0.852	6.3	4.6660	4.6204	4.3204	2.5207

For  $g = 0.1$  M,  $A = 5.894 \times 10^6$ ,  $B = 1 \times 10^8$ ,  $C = 1.4 \times 10^9$ ,  $D_{av} = 1.789 \times 10^9$ .

For  $g = 0.2$  M,  $A = 4.555 \times 10^7$ ,  $B = 3 \times 10^8$ ,  $C = 1.8 \times 10^9$ ,  $D_{av} = 2.649 \times 10^9$ .

are given in table 1. Tables for other systems are not given as they are similar. The waves are reversible as the difference of  $E_{1/4}$  and  $E_{3/4}$  lies between 29 and 35 mV. Evidence has been obtained for the formation of the species of the type  $Cd(g)(a)$ ,  $Cd(g)_2(a)$  and  $Cd(g)(a)_2$ . The log values of the stability constants are 8.7, 9.7 and 9.8 respectively. All final values of stability constants of mixed complexes in this paper have been rounded off to the second decimal place.

#### 4.2 Cadmium-glycine-monoethanolamine system

In this case, concentration of ethanolamine was maintained constant at 0.15 M and 0.25 M and the concentration of glycine was varied from 0.05 M to 0.25 M to note the change in the half-wave potential of cadmium. The waves are reversible. Evidence has been obtained for the formation of the species  $Cd(e)(g)$ ,  $Cd(e)_2(g)$  and  $Cd(e)(g)_2$ . The log values of stability constants are 6.81, 7.28 and 8.90 respectively. Ethanolamine is coordinated as neutral molecule under the conditions employed in these studies.

#### 4.3 Cadmium-glycine-diethanolamine system

Mixed complex formation with cadmium has been studied keeping the diethanolamine concentration constant at 0.15 M and 0.25 and varying the glycine concentration from 0.05 M to 0.25 M. Existence of the species of the type  $Cd(d)(g)$ ,  $Cd(d)_2(g)$  and  $Cd(d)(g)_2$  has been confirmed and the log values of stability constants are 7.17, 7.71 and 8.48 respectively. Diethanolamine is coordinated as neutral molecule under these experimental conditions.

#### 4.4 Lead(II)-glycine-aspartic acid system

Formation of mixed ligand complexes with lead(II) in solution has been studied by measuring the  $E_{1/2}$  values of lead while varying the concentration of glycine from 0.05 M to 0.5 M and keeping the aspartic acid concentration constant at 0.1 M and 0.2 M. Evidence for the formation of only one species *i.e.*  $Pb(g)(a)$  has been obtained. The logarithmic value of the stability constant of this complex obtained using Schaap and McMasters method is 7.96. Detailed studies confirmed that hydroxyl group does not participate in complex formation.

Attempts to obtain evidence for the mixed complexes of lead(II) in systems containing ethanolamine and diethanolamine as in cadmium(II) did not succeed as precipitation was observed in many experiments.

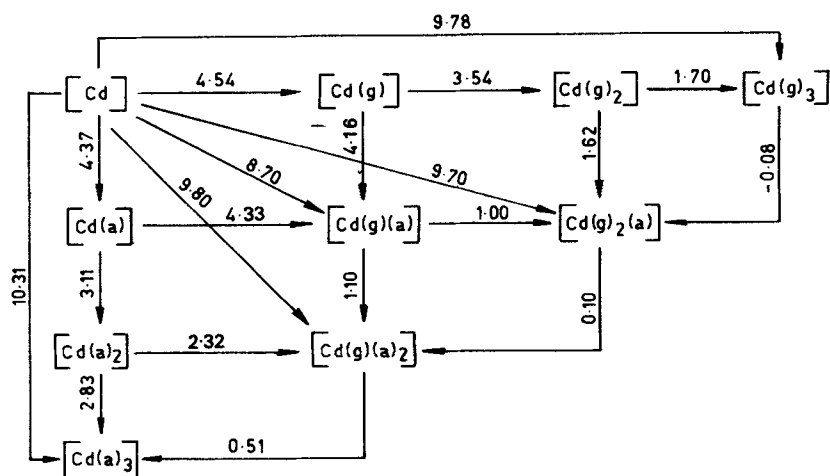
### 5. Discussion

Mixed complexes of cadmium(II) in solution state exist in the equilibria as shown in figures 1–3. Following the treatment of Marcus and Eliezer (1969) the stability of mixed complexes can be discussed on the basis of 'mixing constant'  $K_{M(ij)}$  and 'stabilization constant'  $K_s$ . The dimensionless mixing constant for the formation of one mole of mixed complex is defined by the equilibrium



$$K_{M(ij)} = \beta_{ij} / \beta_{n0}^{i/n} \beta_{0n}^{j/n}.$$

The statistical effect has a plausible explanation for the relative stabilization of mixed complex but in the first theoretical treatments of mixed ligand complexes and ion association it was found that 'the mixtures make a better than statistical use of their additional opportunities . . . and are . . . generating a more than statistical proportion



**Figure 1.** Equilibria involving mixed complexes of cadmium(II) with glycine and aspartic acid with log  $K$  values. (In this and other figures charges of the species are omitted to simplify the diagrams).

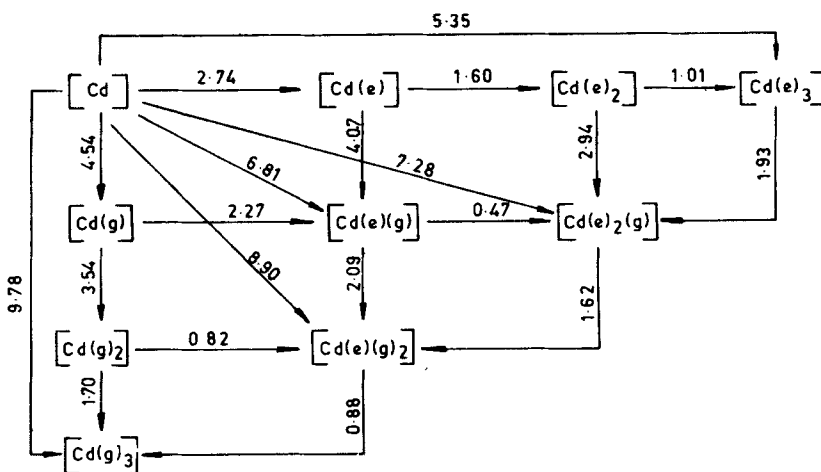


Figure 2. Equilibria involving mixed complexes of cadmium(II) with glycine and monoethanolamine with log  $K$  values.

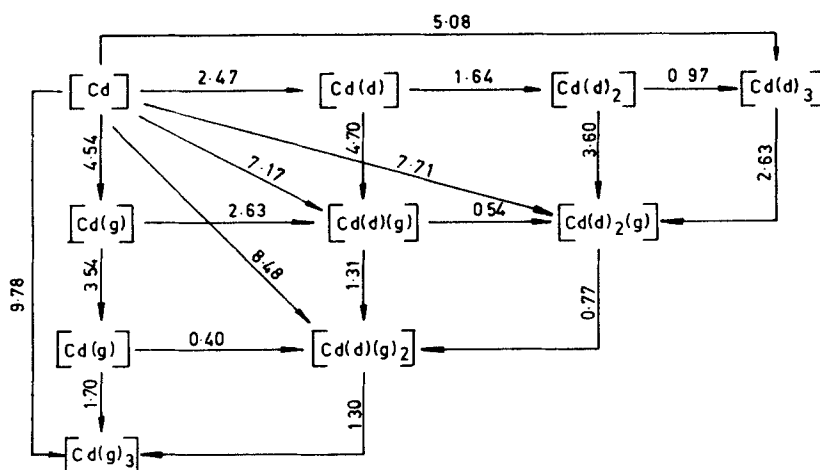


Figure 3. Equilibria involving mixed complexes of cadmium(II) with glycine and diethanolamine with log  $K$  values.

of mixed ions' (Hughes *et al* 1957). In other words it is found that the experimental  $K_M$  values agreed with those calculated from statistical consideration in very few complexes only. Usually  $K_M$  is larger, though there are some cases where it is smaller than the calculated value.

As a major contribution to  $K_{M(ij)}$  comes from statistical reasons, another constant  $K_s$  has been defined for ligands of equal denticity as

$$\log K_s = \log K_M - \log (n/i).$$

It may be noted that most of the ligands employed in the present study are bidentate.

Table 2. Relative stabilities of mixed complexes.

Complex	ligand A	ligand B	log $K_M$	log $K_s$
Cd AB	glycine	aspartic acid	0.98	0.68
Cd A <sub>2</sub> B			-0.25	-0.73
Cd AB <sub>2</sub>			-0.33	-0.81
Pb AB			0.73	0.43
Cd AB	diethanolamine	glycine	1.08	0.78
Cd A <sub>2</sub> B			1.07	0.59
Cd AB <sub>2</sub>			0.27	-0.21
Cd AB	ethanolamine	glycine	0.60	0.30
Cd A <sub>2</sub> B			0.46	0.02
Cd AB <sub>2</sub>			0.60	0.12

On the above basis values of log  $K_M$  and log  $K_s$  have been calculated for various mixed complexes. Table 2 presents the data. The values of stability constants ( $\beta_{n0}$ ,  $\beta_{0n}$ ) for the pure complexes which are required for calculating log  $K_M$  are taken from Rao and Subrahmanya (1964) and Migal and Pushnyak (1960) for glycine and aspartic acid, ethanolamine and diethanolamine respectively. For most of the mixed complexes, the value of log  $K_M$  is positive indicating the compatibility of the ligands. However, for the mixed complexes ( $MA_2B$  and  $MAB_2$  type) involving aspartic acid which can function as a tridentate ligand under the experimental conditions employed, values of log  $K_M$  were negative. Here of course the coordination level is not maintained constant, since both the ligands do not have the same denticity. The reason for this is not clear at present but it is interesting to note that Bennet (1959) obtained negative values of log  $K_M$  and log  $K_s$  for the mixed complex CuAB where A and B are *l*-aspartate and *d*-aspartate respectively. However for Cd(*a*)(*g*) and Pb(*a*)(*g*), the values of log  $K_M$  and log  $K_s$  are positive.

## 6. Conclusions

The results obtained in this study show that cadmium(II) forms mixed ligand complexes in systems containing (a) glycine and aspartic acid (b) glycine and diethanolamine and (c) glycine and ethanolamine. Values of stability constants have been calculated.

Positive values of mixing constants in general indicate the compatibility of the ligands in forming the mixed ligand complexes.

## References

- Bennet W E 1959 *J. Am. Chem. Soc.* **81** 246  
 Fridman Y D, Veresova R A, Dolgasheva N V and Sorochan R I 1963 *Zh. Neorg. Khim.* **8** 676  
 Hughes E D, Ingold C K, Patai S and Pocker Y 1957 *J. Chem. Soc.* 1206  
 Marcus Y and Eliezer I 1969 *Coord. Chem. Rev.* **4** 273  
 Migal P K and Pushnyak A N 1960 *Zh. Neorg. Khim.* **5** 610  
 Rao G N and Subrahmanya R S 1964 *Proc. Indian Acad. Sci. (Chem. Sci.)* **60** 165  
 Schaap W B and McMasters D L 1961 *J. Am. Chem. Soc.* **83** 4699  
 Sharma R S, Baghel S C and Gaur J N 1978 *Trans. SAEST* **13** 37