J. Indian Chem. Soc.,
Vol. 74, March 1997, pp. 222-224

NOTE

Potentiometric Studies on Mixed Ligand Complexes in Aqueous Solution: M(II) + Neutral or Charged Primary Ligand + Amino Acid Systems

A. K. PATEL and J D. JOSHI*

Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388120

Manuscript received 7 June 1995, accepted 27 October 1995

The introduction of synthetic organic chelating agents into the environment can have a marked effect on the translocation and bioavailability of trace metal ions[1]. The synthetic ligand may form complexes that are most soluble, more toxic or more readily absorbed than the predominant naturally occurring species. Because these ligands must compete with natural complexing agents. To understand the driving forces leading to mixed ligand complexes in biological systems, ternary complexes of the type M(II)AL, where M(II) = Ni, Zn or Cd; A = 2,2′-bipyridyl, *o*-phenanthroline, 2,2′-bipridylamine, histidine or iminodiacetic acid; L = glycylglycine, phenylalanine or aspartic acid, have been investigated.

Results and Discussion

The potentiometric titration curves at 25° for 1 : 1 : 1 MAL involving Ni^{II}-histidine-aspartic acid was drawn (figure not shown). It is evident from histidine and Ni^{II}-histidine curves that 1 : 1 complex is formed at low pH and stable up to higher pH. This is because the horizontal distance between these curves remains constant upto pH ~7.5. Similar behaviour has been observed in case of 1 : 1 Ni-IMDA complex. While in cases of Zn-hist, Cd-hist, Zn-IMDA and Cd-IMDA, 1 : 1 complexes are formed at low pH and stable upto pH ~8.0, ~8.25, ~7.5 and ~7.75 respectively. In case of neutral primary ligands 2,2′-bipy, *o*-phen and 2,2′-bipya, 1 : 1 MA [Ni^{II}, Zn^{II} or Cd^{II}] complexes are formed at low pH and stable upto pH ~7.5.

The mixed ligand complex formation MAL takes place in all the cases only after complete formation of [MA]. The mixed ligand complex MAL is stable upto higher pH, above which the curve starts converging indicating absence of hydrolysis or hydroxo complex formation. In case of secondary ligand (aspartic acid) curve, one or two equivalents of extra perchloric acid have been added to account for the hydrogen ions liberated as a result of complexation of hist or IMDA with Ni^{II}, Zn^{II} and Cd^{II} in Ni^{II}-histidine-aspartic acid curve. The titration curve of the mixed ligand complex is well separated from the secondary ligand (L). Thus, replacement of H^+ ion is due to complexation of $[MA]^{2-n}$ or $[MA]^{2+}$ with ligand (L).

The stability constants of the ternary metal ion complexes containing MAL were calculated for the equilibria shown in equation (3), using data obtained in potentiometric pH-titrations,

$$M + A \rightleftharpoons MA \quad (1)$$

$$MA + L \rightleftharpoons MAL \quad (2)$$

$$M + A + L \rightleftharpoons MAL \quad (3)$$

$$\log K_{MAL}^{MA} = \frac{[MAL]}{[M][L][A]} \quad (4)$$

Average number of ligand molecules $\bar{n}$, attached per metal ion and free ligand exponent values pL were calculated[2,3]. Precise value of mixed ligand formation constants were determined by the method of averages[4]. The results are in good agreement with the previously reported values[3]. The relative stabilities of ternary complexes compared with the corresponding binary complexes can be qualitatively expressed in many different ways. We have expressed the relative stabilities in terms of $\Delta \log K_T$

$$\Delta \log K_T = \log K_{MAL}^{MA} - \log K_{ML}^{M}$$

The advantages of using $\Delta \log K_T$ for comparison of the stability of binary and ternary complexes have been reviewed[5]. The values obtained are presented in Tables 1–4.

The electronegativity order of [MA] is found to be as follows : $[M(aq)]^{2+} \sim [M(2,2'\text{-bipy})]^{2+} \sim [M(o\text{-phen})]^{2+} \sim [M(2,2'\text{-bipya})]^{2+} < [M(hist)]^{+} < [M(IMDA)]^{o}$. The stability of the metal ions with glycylglycine, phenyl alanine and aspartic acid follows the order : $Ni^{2+} > Zn^{2+} > Cd^{2+}$ respectively. The mixed ligand formation constant in the MA amino acid systems are in the order : glycylglycine < phenylalanine < aspartaic acid, same as in the binary system. This is in expected order of the decreasing basicities of ligand.

The most important aspect of the study is that the values of $\log K_{MAL}^{MA}$ are slightly lower than $\log K_{ML_1}^{M}$ and higher than $\log K_{ML_2}^{ML}$, which is due to the fact that the tendency of L to get bound with aquated metal ion $[M(aq)]^{2+}$ is more than to combine with the metal ion already bound with A. From statistical consideration also the driving force for the binding of the secondary ligand with $[MA]^{2-n}$ should be less than for the binding of L with $[M(aq)]^{2+}$ in binary system.

2,2′-Bipyridyl, *o*-phenanthroline and 2,2′-bipyridylamine molecules are neutral in behaviour and bound to the

*Present address : Department of Chemistry, North Gujarat University, Patan-384 265

TABLE 1–DISSOCIATION OF FREE LIGAND AND STABILITIES OF THE BINARY M(II)-AMINO ACID COMPLEXES*

Temp. = 25 ± 0.1°, μ = 0.2 *M* ($NaClO_4$)

Ligand	pK_1^H	pK_2^H	$\log K_{NiL}^{Ni}$	$\log K_{Ni.L_2}^{NiL}$	$\log K_{Zn.L}^{Zn}$	$\log K_{Zn.L_2}^{ZnL}$	$\log K_{Cd.L}^{Cd}$	$\log K_{Cd\,L_2}^{Cd}$
Glycylglycine	8.12	3.21	4.33	3.41	3.78	2.74	3.27	2.73
Phenylalanine	8.80	2.20	5.20	4.62	4.70	3.72	3.88	3.15
Aspartic acid	9.60	3.60	7.17	5.32	5.74	4.09	4.53	3.50

*Constant Values accurate to ± 0.05 units.

TABLE 2–FORMATION CONSTANTS OF THE 1 · 1 : 1 TERNARY COMPLEX OF METAL IONS WITH VARIOUS PRIMARY LIGAND AND SECONDARY LIGANDS

Temp. = 25 ± 0.1°, μ = 0.2 *M* ($NaClO_4$)

Ligand	$\log K_{M.bipy\,L}^{M.bipy}$			$\log K_{M.o.Phen.L}^{M.o.Phen}$			$\log K_{M-2,2'-bipy.a.L}^{M-2,2'-bipy.a}$			$\log K_{M.hist.L}^{M.hist}$			$\log K_{M\,IMDA.L}^{M\,IMDA}$		
	Ni	Zn	Cd	Ni	Zn	Cd	Ni	Zn	Cd	Ni	Zn	Cd	Ni	Zn	Cd
Glycylglycine	3.88	3.36	3.26	4.19	3.73	3.20	4.00	3.57	3.26	3.96	3.32	3.15	4.02	3.25	3.19
Phenylalanine	4.49	4.09	3.79	4.81	4.39	3.82	4.89	4.14	3.64	4.01	3.81	3.76	3.95	3.66	3.51
Aspartic acid	6.04	4.89	4.29	6.47	5.68	4.57	6.74	5.24	4.49	4.73	4.69	4.40	5.09	4.97	4.47

*Constant values accurate to ± 0.05 units

TABLE 3–VALUES OF Δ log K_T OF THE 1 : 1 : 1 TERNARY METAL COMPLEXES OF NEUTRAL PRIMARY LIGANDS WITH VARIOUS LIGANDS

Temp = 25 ± 0.1°, μ = 0.2 *M* ($NaClO_4$)

Ligand	Ni-2,2'-bipy.L	Zn-2,2'-bipy.L	Cd-2,2'-bipy.L	Ni-*o*-Phen.L	Zn-*o*-Phen.L	Cd-*o*-Phen.L	Ni-2,2'-bipy-A.L	Zn-2,2'-bipy-A.L	Cd-2,2'-bipy-A.L
Glycylglycine	–0.45	–0.42	–0.24	–0.14	–0.05	–0.07	–0.33	–0.21	–0.01
Phenylalanine	–0.71	–0.61	–0.09	–0.39	–0.31	–0 06	–0.31	–0.56	–0.24
Aspartic acid	–1.13	–0.85	–0.24	–0.70	–0.06	+0.04	–0.43	–0.50	–0.04

*Constant values accurate to ± 0.05 units.

TABLE 4–VALUES OF Δ log K_T OF THE 1 : 1 : 1 TERNARY METAL COMPLEXES OF CHARGE PRIMARY LIGANDS WITH VARIOUS SECONDARY LIGANDS

Temp. = 25 ± 0.1°, μ = 0.2 *M* ($NaClO_4$)

Ligand	Ni. hist.L	Zn. hist.L.	Cd. hist.L.	Ni. IMDA.L.	Zn. IMDA.L.	Cd. IMDA.L
Glycylglycine	–0.37	–0.46	–0.12	–0.31	–0.53	–0.08
Phenylalanine	–1.19	–0.89	–0.12	–1.25	–1.04	–0.37
Aspartic acid	–2 44	–1.05	–0.13	–2.08	–0.77	–0.06

*Constant values accurate to ± 0.05 units.

metal ion by σ-bonding. Hence, electronegativity in case of $[M(H_2O)_n]^{2+}$, $[M(2,2'\text{-bipy})]^{2+}$, $[M(O\text{-phen})]^{2+}$ and $[M(2,2'\text{-bipya})]^{2+}$ is almost same. Therefore, it is expected that log K_{MAL}^{MA} should be near to log K_{ML}^{M}. However, in case of *o*-phenanthroline, log K_{MAL}^{MA} values are lower compared to 2,2'-bipyridyl and 2,2'-bipyridylamine. This is due to bigger size of the *o*-phenanthroline molecule. Besides, there is also π-bond formation by the back donation of π-electrons from metal to the ligand. The *dπ-pπ* interaction has been observed in metal-2,2'-bipyridyl and -*o*-phenanthroline complex by earlier workers[6]. The *dπ-pπ* interaction does not allow to concentrate electron density significantly. In other words, positive charge on the metal ion in $[MA]^{2+}$, where A = 2,2'-bipy, *o*-phen or 2,2'-bipya is almost same as in $[M(aq)]^{2+}$ complex.

2,2'-Bipyridylamine as the primary ligand has shown that in the presence of an aromatic nitrogen donor metal ion becomes more selective and discriminating to the donor groups on the incoming[7] secondary ligand. The behaviour of 2,2'-bipyridylamine is similar to that of 2,2'-bipyridyl and *o*-phenanthroline. However, log K_{MAL}^{MA} values in case of 2,2'-bipyridylamine is higher than 2,2'-bipyridyl and *o*-phenanthroline. This is due to presence of one more nitrogen atom in 2,2'-bipyridylamine molecule.

In case of hist or IMDA, the values of log K_{MAL}^{MA} are significantly lower than the values of log K_{MA}^{M}. This can be explained to be due to the negative charge existing on hist (-1) and IMDA (–2) ions. Histidine exhibits bi- or tridentate character[8], coordination taking place from COO^- and from nitrogen of the imidazole group or two nitrogens from both imidazole and amino groups. Histidine has one negative charge and being a bigger molecule exerts more repulsion on the incoming ligand. Therefore, there is a decrease in the stability of mixed ligand complex. IMDA behaves as tridentate[9] ligand, the coordination taking place from the nitrogen atom and two carboxylate groups. It has two negative charges and hence tendency of the secondary ligand to combine with [Ni(IMDA)] will be less than to combine

with $[M(aq)_n]^{2+}$. Therefore, $\log^{MA}_{MAL}$ values are lower in case of M.IMDA.L complexes.

It is observed that $\Delta\log K_T$ values are smaller in cases of 2,2′-bipyridyl, *o*-phenanthroline and 2,2′-bipyri-dylamine, while in case of hist or IMDA, with phenyla-lanine or aspartic acid the $\Delta\log K_T$ values are bigger. The observed values of $\Delta\log K_T$ agree with nature of the A and L.

Experimental

The amino acids glycylglycine, phenylalanine and aspartic acid (all AnalaR), sodium perchlorate (Fluka), perchloric acid (Baker analysed) and sodium hydroxide (AnalaR) were used.

Stock solutions (2×10^{-2} mol dm^{-3}) of Ni^{II}, Zn^{II} and Cd^{II} perchlorates were prepared and standardised[10]. The carbonate-free sodium hydroxide was prepared and standardised[11]. Double-distilled water was used throughout. The formation constants of ternary metal complexes were determined by potentiometric titrations[12] of different mixtures agaisnt standard carbonate-free sodium hydroxide. An APX-175 pH meter was used. Solutions (2×10^{-2} mol dm^{-3}) of ligands A and L were used for the determination of ternary formation constants. For the mixed ligand system, the total volume was raised to 50.0 ml and ionic strength initially raised to 0.2 mol dm^{-3} using sodium perchlorate as an inert electrolyte. The following mixtures were titrated : (a) $HClO_4$, (b) $HClO_4$ + primary ligand (A), (c) $HClO_4$ + secondary ligand (L), (d) $HClO_4$ + M(II) + primary ligand (A) and (e) $HClO_4$ + M(II) + primary ligand (A) + secondary ligand (L).

Acknowledgement

The authors thank Prof. M. N. Patel, Head, Department of Chemistry, S. P. University, Vallabh Vidyanagar, for facilities.

References

1. E. A. Jenne and S. N. Lumoa, ERDA Symp. Ser., 1977, **42**, 110; A. Siegel in "Organic Compounds in Aquatic Environments", eds S. D. Faust and J. V. Hunter, Marcel Dekker, New York, 1971, p 265
2. H. Irving and H. Rossotti, *J. Chem. Soc.*, 1953, 3397.
3. M. R. Patel, N. Patel, M. Patel and J. D. Joshi, *J. Indian Chem. Soc.*, 1993, **70**, 569.
4. R C. Mehrotra and S. N. Dubey, *J. Indian Chem. Soc.*, 1970, **47**, 881.
5. R. B. Martin and R. Prados, *J. Inorg. Nucl. Chem.*, 1974, 1665.
6. R. Griesser, B Prijs and H. Sigel, *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 443; D H. Busch and J. C. Bailer, *J. Am. Chem. Soc.*, 1956, **78**, 1137; D. J. Hathway, M. J. Bew, D. E. Billina, R. J. Dudley and P. Nicholls, *J. Chem Soc.*, 1969, 2312.
7. M. S. Mohan, D. Bancroft and E. H. Abbott, *Inorg. Chem.*, 1979, **18**, 344; G. F Condike and A. E. Martell, *J. Inorg. Nucl. Chem.*, 1969, **31**, 2455; M. S. Mohan, *Indian J. Chem., Sect. A*, 1981, **20**, 252.
8. T. Nortia, *Suomen Kemistillehti (B)*, 1960, **33**, 161
9. B. B. Smith and T. D Sawyer, *Inorg. Chem.*, 1968, **7**, 1526.
10. H. A Flaschka, "EDTA Titrations", Pergamon, Oxford, 1964.
11. G. Schwarzenbach and R. Biederman, *Helv. Chim. Acta*, 1948, **31**, 331.
12. H. M. Irving and H. S. Rossotti, *J. Chem Soc.*, 1954, 2904; I P. Mavani, C R. Jejurkar and P. K. Bhattacharya, *J. Indian Chem. Soc.*, 1972, **49**, 469