Alkaline-earth Metal Complexes of
N-Phosphonomethyl Glycine

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The proton-ligand formation constants of N-phosphonomethyl glycine (NPMG) and the complexation equilibria of its corresponding binary and ternary chelates with alkaline-earth metal ions, *viz.*, Mg(II), Ca(II) and Sr(II) inolving some other O–O, N—N, N—O—O and N—O donors like catechol (Cat), oxalic acid (Oxa), 5-sulphosalicylic acid (5SSA), 1,10-phenanthroline (Phen), 2,2'-bipyridyl (Bipy), iminodiacetic acid (imda), glycine (Gly) and β-alanine (Ala) have been determined potentiometrically at a constant temperature (30°C) and ionic strength (0.10 M KNO_3) in aqueous medium. In presence of all the other chelating agents, except Gly and Ala, NPMG behaves as a secondary ligand while in the presence of Gly and Ala, it coordinates simultaneously with all the above mentioned metal ions. The binary and ternary stability constants (log K_1 and log K'_T or log K_T), the differences in stability constants (D.S.C.) of 1 : 1 : 1 ternary and 1 : 1 secondary metal complexes (Δ log K' or Δ log K), the percentages of relative stabilization ([% R.S.]) values and the distribution of metal ions in different chelated species have been evaluated and discussed.

INTRODUCTION

N-phosphonomethyl glycine (NPMG) is a potential herbicide and its chemistry has an immense importance in the fields of industry, agriculture, biology and medicine[1,2]. It is a tridentate ligand and was found suitable for binding even to the most basic cations like alkaline-earth metal ions[3]. Literature survey shows that except for a few sporadic references[3,4] on binary systems, no work has been done on NPMG with these metal ions in different systems. Thus, two main factors, one the strong chelating tendency of NPMG and second the existence of Mg(II), Ca(II) and Sr(II) in agricultural soil and hard water, have motivated us to select these systems for the present work.

EXPERIMENTAL

The ligand NPMG was prepared by the method of Franz[5] and the metal ion solutions were standardized by chelatometric titrations and gravimetric analysis. The proton-ligand and metal-ligand binary formation constants were determined by the graphical method of Irving and Rossotti[6] and those of ternary systems by Santappa and Ramamoorthy[7]. The ionic strength was maintained at 0.10 M by adding calculated amounts of 1.0 M KNO_3 solution.

RESULTS AND DISCUSSION

The value of first acid dissociation constant of NPMG (2.23) was found to be

much lower than the pH range of complexation and hence was not considered in the calculations of stability constants. The values of second and third pK_as were found to be 5.60 and 10.00 respectively. These metal ions form only 1:1 (and not 1:2) metal complexes with NPMG as is evidenced by the values $\tilde{n}$ (average number of ligand molecules bound per metal ion) which lie in between 0.10 and 0.90. Mg(II) and Ca(II) ions were found to have the same stability constant value of 3.50 while Sr(II) possesses a lesser log K_1 value of 3.35.

The ternary systems of the type M-L'-A and M-A-L, where M = Mg(II), Ca(II) or Sr(II), A = NPMG, L' = catechol (Cat), 5-sulphosalicylic acid (5-SSA), 1,10-phenanthroline (Phen), 2,2'-bipyridyl (Bipy), iminodiacetic acid (imda) and L = glycine (Gly) or β-alanine (Ala) have been studied in which M-L'-A systems follow stepwise equilibria with NPMG functioning as a secondary ligand while those of M-A-L systems follow simultaneous equilibria. Ca(II) ion forms insoluble precipitate with oxalic acid. In the former stepwise formation systems, the mixed ligand [M-L'-A] curves follow those of 1:1 [M-L'] binary curves in the lower pH region until the protons of the primary ligands are neutralized indicating the formation of only binary [M-L'] complexes and non-coordination of L' with M(II) ions in this region. The divergence of the ternary M-L'-A curves from the binary curves above this region reveals their formation in two distinct steps. This was further supported by the non-superimposable nature of the theoretical composite curves in the region of mixed ligand complex formation[8]. The formation of either stepwise or simultaneous equilibria also becomes distinctly clear from the distribution of total metal among the various chelated species as a function of pH as calculated by a computer programme BEST due to Martell and Motekaitis[9].

The ternary formation constants (log K_T or log K_T) along with other related parameters, *viz.*, the differences in 1:1:1 ternary and 1:1 binary stability constants, D.S.C., (Δ log K' or Δ log K) and their relative stabilization ([% R.S.]) values at a given temperature and ionic strength are listed in Table-1. Larger negative values of ([% R.S.]) indicate lesser stabilization of the ternary complexes in solution. Such a lowering of stabilities may be due to a greater destabilization effect[8, 10] caused by the ligand repulsion in the mixed ligand complexes than those in the binary systems coupled with the availability of lesser number of coordination sites for the second ligand on the primary complex [M-L'] compared to free M(II) ion[11]. However, electrostatic attractions between primary complex [M-L'] and the secondary ligand A facilitates to some extent the formation of ternary complexes. The positive values of Δ log K prevailing in simultaneous equilibria indicate the formations of stronger ternary complexes. A comparison of these statistical considerations reveals that the order of ternary stabilities with respect to "the other chelating agents", L' follow the order, Cat > 5-SSA > imda > Phen > Bipy > Oxa and with respect to L, Ala > Gly. This is in accordance with their basicity order and denticity nature, because for a series of similar ligands, the higher the basicity of the ligand, the greater is the stability of the metal complexes[10]. The sequence of ternary stabilities with different metal ions follows Irving-William order[12] *i.e.*, Mg(II) = Ca(II) > Sr(II).

TABLE-1

TERNARY COMPLEXES FORMATION CONSTANT, D.S.C. AND [% R.S.] VALUES OF
NPMG METAL COMPLEXES INVOLVING OTHER CHELATING AGENTS IN
AQUEOUS MEDIUM AT 30°C AND 0.10 M (KNO$_3$) IONIC STRENGTH

STEPWISE EQUILIBRIA

Other chelating agent	Mg(II)			Ca(II)			Sr(II)		
	S.C. log K'_T	D.S.C. Δ log K (−ve)	[% RS] (−ve)	S.S. log K'_T	D.S.C. Δ log K (−ve)	[% RS] (−ve)	S.C. log K'_T	D.S.C Δ log K (−ve).	[% RS] (−ve)
Cat	3.48	0.02	0.57	3.49	0.01	0.28	2.87	0.47	14.00
5-SSA	3.04	0.46	13.14	3.04	0.46	13.14	2.70	0.65	19.40
imda	2.86	0.64	18.28	2.89	0.61	17.42	2.69	0.66	19.70
Phen	2.83	0.66	18.85	2.79	0.71	20.28	2.50	0.85	25.37
Bipy	2.81	0.68	19.42	2.96	0.54	15.42	2.38	0.97	28.95
Oxa	2.61	0.89	25.42	------ forms ppt. ------			2.35	1.00	29.85

SIMULTANEOUS EQUILIBRIA

	S.C. log K_T	D.S.C. Δ log K (+ve)	[% RS] (+ve)	S.S. log K_T	D.S.C. Δ log K (+ve)	[% RS] (+ve)	S.C. log K_T	D.S.C. Δ log K (+ve)	[% RS] (+ve)
Ala	8.87	0.76	21.71	7.78	1.08	30.85	7.48	0.44	13.12
Gly	5.99	0.42	11.99	5.91	0.36	10.28	5.74	1.49	44.00

S.C. = Stability constant; D.S.C. = Differences in stability constant values of 1 : 1 : 1 ternary and
1 : 1 binary systems; [% RS] = Per cent relative Sabilization values.

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