EFFECTIVE ANALYSIS ASSOCIATED WITH STABILITY CONSTANTS OF TERNARY COMPLEXES

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ABSTRACT

Concurrent equilibrium studies are of most extreme imperative to manage organic, medicinal and ecological issues emerging because of cutting edge specialized improvements. But in manufactured blends experienced in research facilities, metal ions or ligands never exist in secluded form requiring a top to bottom investigation of multi-metal and multi-ligand equilibria in solution. Accordingly the significance of such studies is acknowledged, as intensive investigation of the considerable number of species existing in biosystem may not be conceivable because of the limitations of the present accessible test strategies to screen the degree of complexation. The metal ions exist in various forms in various biofluids like blood serum, intestinal liquid, cerebrospinal liquid, gastric juice and so forth. They can be in non-

replaceable structure, inexactly bound to some natural ligands and in equilibrium with an assortment of bioligands with comparable metal ions in solution, and in aquated structure. Hence, the foundation of synchronous equilibria including an assortment of metal ions and ligands is conceivable in natural liquids. In this way, demonstrating ponders including ternary and quaternary edifices picked up significance. It implies that the number and concentrations of ligands exceed those of the metal ions in numerous biofluids. So the investigation of ternary edifices containing a metal ion and two distinct ligands drew the attention of a few analysts.

INTRODUCTION

Mixed ligand complexes can be considered as models for apoenzymemetal ion-substrate complexes. In peptides, proteins and amino acids, amide group is one of the important binding sites for the coordination of the metal ions. Another application of ternary complexes is in surgical cases wherein it becomes necessary to depend on the Total Parenteral Nutrition (TPN) for a sufficiently lengthy period.

If proper mineral balance is not maintained in the fluids, the metal ions that are present in the physiological system will be gradually depleted. Hence, it is a must that every nutritive solution should contain trace metal ions such that their optimum concentrations in the body fluids are maintained. The preparation of such a nutritive mixture requires the knowledge of precise free metal ion concentration in body fluids and a computer based reliable distribution of each metal ion in the presence of a number of ligands and other metal ions present in different concentrations.

Stability constants

Stability constants are based on the general equilibrium4 where M is the central metal ion, H is the proton, L and X are first and second ligands, respectively, in the complex and m, l, x, h and t are stoichiometric coefficients.

$$mM + hH + lL + xX + tH_2O \rightleftharpoons M_m H_h L_l X_x (H_2O)_t$$

The corresponding stability constant is defined as Stability constants for the inorganic metal complexes and minerals showed reasonable agreement between several independent and critically reviewed sources. In contrast to the inorganic metal complexes and minerals, few data were available for metal complexes with aspartic, citric, malonic, salicylic and tricarboxylic acids that comprised the fatty acid models.

REVIEW OF LITERATURE

Literature survey shows that many of the earlier investigations confined to the systems, whose pH regions for the formation of binary and ternary species were widely different. In such cases the concentrations of the binary complexes were assumed to be equal to the total concentration of the metal ion. The formation constant of ternary complexes was calculated in a similar way using modified Irving equation.

Simplified equations were arrived at by Ramamoorthy and Santappa for the calculation of formation constants of mixed ligand complexes, when the two ligands simultaneously interacted with the metal ion. These are valid only if the protonation constants of primary and secondary ligands are comparable. But non-linear least squares algorithms were found to be suitable for studying the unprotonated or protonated mixed ligand complexes, even though the corresponding binary systems contain hydroxylated and/or protonated species. Formation constants of mixed ligand complexes of Cu(II), Ni(II), Co(II) and Zn(II) with Aspartic or glutamic acid as primary ligand and imidazole as secondary ligand were determined potentiometrically by Sinha et al.

Voltametric technique was used to study the binary and ternary complexes of cadmium with L-lysine, L-ornithine, L-threonine, L-serine, L-phenylalanine, L-glutamic acid and L-aspartic acid as primary ligands and L-ascorbic acid as secondary ligand.

Venkataiah et al. studied the ternary complexes of Cu(II) with N-(1-naphthyl) ethylenediamine, (N-N donors) and a series of amino acids (alanine, phenylalanine, tryptophan, lysine, serine, threonine, aspartic acid or histidine and ethylenediamine potentiometrically. Polarographic technique was used to determine the stability constants of ternary complexes of Zn(II) with L-lysine, L-ornithine, L-threonine, L-serine, Lphenylglycine, L-phenylalanine, L-glutamic acid and L-aspartic acid as primary ligands and γ-picoline as secondary ligand.

Iman Ahmed determined the ternary systems of Zn(II), Ni(II), Co(II), Cd(II), Pb(II), UO22+, Ce(III) and La(III) pH-metrically with N[tris(hydroxyl methylmethyl]glycine(tricine), N-(2-acetamido)iminodi acetic acid and dicarboxylic amino acids (aspartic and glutamic) as primary ligands and 3-amino-5-mercapto-1, 2, 4-triazole as a secondary ligand.

Jussara and Judith studied ternary complexes of Cu(II) with guanidinoacetic acid, glutamic and aspartic acids. Koteswar Rao and Srinivas Mohan18 investigated ternary complexes of D- and L- aspartic acid containing polyacrylamides and Cu(II) bovine serum albumin.

Potentiometric measurements have been made on the interaction of glycine, serine, methionine, aspartic acid, glutamic acid and Lhistidine with Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) in the presence of biologically important secondary ligand zwitterionic buffers β-hydroxymorphocinepropanesulfonic acid (MOPS) and 3-bis(hydroxymethyl) amino-2-hydroxypropanesulfonic acid (TAPSO).

Christine and Frantisek studied the ternary complexes of aspartic acid with Cu(II) and phenanthroline ligands.

The speciation of selected environmentally relevant elements (H, Na, K, Ca, Mg, Fe, Mn, U, Al, Pb, Zn, Cu, and Cd) in aqueous system, with models of fulvic acid like aspartic, citric, malonic, salicylic and tricarboxylic acids was studied.

Venkataiah et al. studied the interaction of adenosine-5–triphosphate (ATP) with a series of binary Cu(II) complexes (MLn) [(where L = O-phenanthroline (Phen), 5- nitrophenanthroline (NPhen), 5-methyl phenanthroline (Mphen), 2, 9- dimethyl-phenanthroline (Dphen), 2, 9-dimethyl-4, 7-diphenyl phenanthroline (Dphphen), oxalic acid (Ox), glycine (Gly), alanine (Ala), valine (Val), phenylalanine (Phe), tryptophan (Trp), methionine (Met), histidine (His) or aspartic acid (Asp)] to form ternary complexes by pHmetric technique. With respect to the nitrogen donor ligands the stability of the ternary complexes decreased in the order Nphen > Phen > Mphe > Dphen > Dphphen, whereas in ternary complexes containing amino acids the stability decreased in the order Phe > Trp > Ala > Gly > Val > Met > His > Asp.

Mixed ligand complexation of Cu(II) with pyridoxine, isoleucine, aspartic acid, glutamic acid and valine was studied by Saxena et al. who reported only MLX species.

Janarthan et al. studied the mixed ligand complexes of UO22+ with aspartic acid as primary ligand and oxalic, succinic, malonic and lactic acids as secondary ligands potentiometrically. Although the mixed ligand complexes reported earlier were of the type, M(bipy)(amino acid) or M(amino acid)(catechol), during the last decade there was increased interest in systems with two amino acids, one serving as primary and the other as secondary ligand.

Sakurai et al. studied the ternary complexes of Asp, L-lysine, L-ornithine, glumatic acid and L-arginine.

Scheller et al. studied the ternary complexes of Cu(II) with Asp as primary ligand and cytidine-5-monophosphate (CMP) as secondary ligand.

Venkatachalapathi et al.27 studied about the Cr(III) complexes with Asp as primary ligand and Glu or L (+)-cysteine as secondary ligand. Both the protonation and binary complexes of Laspartic acid and ethylenediamine in solvents Dox and PG were already studied in our laboratory. Some of the present values are comparable with those reported earlier studies.

Alkalimetric titration data

A preliminary investigation of the alkalimetric titration data inferred that these two ligands do not form any condensed species. Assuming that there is no expansion of the coordination sphere and three bidentate ligands are sufficient to satisfy the coordination number of the metal ion, the total number of primary and secondary ligands together was restricted to a maximum of three in generating the ternary species for modeling.

Table 1 – Ternary Complexes

Constraints: 1. Maximum number of primary ligands = 2
2. Maximum number of secondary ligands = 2
3. Primary + Secondary ligands = 3

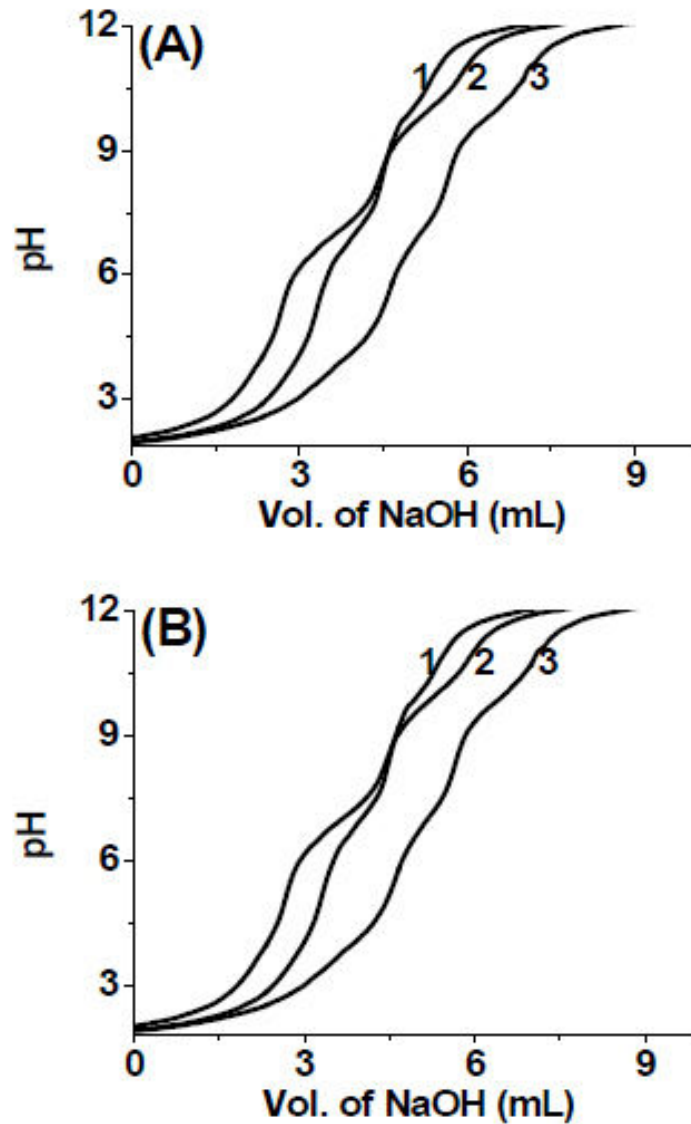| S. No.	Ligand form		Ligand number		
	Primary	Secondary	2	3	
1	LH_3	XH_2	$MLXH_3$	ML_2XH_5	MLX_2H_4
2	LH_3	XH	$MLXH_2$	ML_2XH_4	MLX_2H_2
3	LH_2	XH_2	$MLXH_2$	ML_2XH_3	MLX_2H_3
4	LH_2	XH	$MLXH$	ML_2XH_2	MLX_2H
5	LH	XH_2	$MLXH$	ML_2XH	MLX_2H_2
3	LH	XH	MLX	ML_2X	MLX_2

Figure 1 - Alkalimetric titration curves of Asp-M(II)-en ternary complexes in aqueous medium.
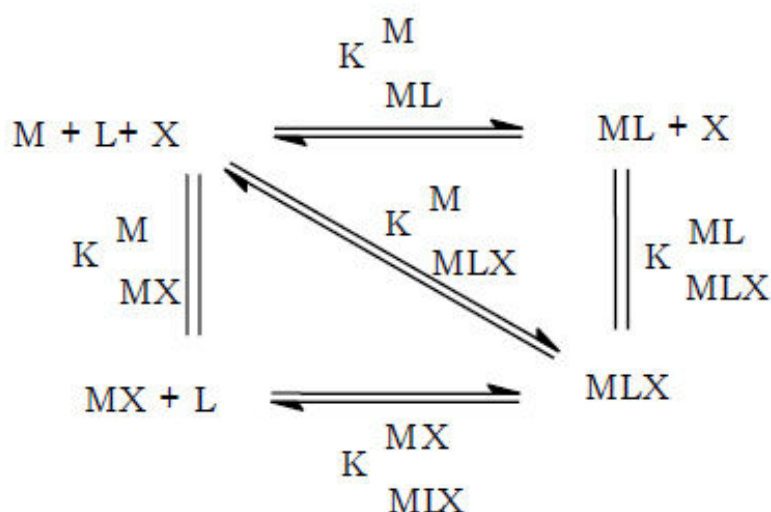
SELECTION OF MODELS

The qualitative evidence for the formation of mixed ligand complexes was obtained from the shift of the precipitation point of mixed ligand systems compared to those of the corresponding binary systems. In all these systems, the pH for precipitation of the mixed ligand systems was

found to be more than that for any of the binary system. The formation constants for acido-basic equilibria of both the primary and the secondary ligands and those for the binary metal complexes were fixed in testing various chemical models using MINIQUAD7540 program.

Stability of ternary complexes

The formation of mononuclear unprotonated binary and ternary complexes from a mixture of metal ion (M) and primary (L) and secondary (X) ligands.

$$M + L + X \; \underset{}{\overset{K^{M}_{ML}}{\rightleftharpoons}} \; ML + X$$

$$MX + L \; \underset{}{\overset{K^{MX}_{MLX}}{\rightleftharpoons}} \; MLX$$

with K^{M}_{MX}, K^{M}_{MLX}, K^{ML}_{MLX} relating the equilibria toward MLX.

EFFECT OF CO-SOLVENT

Variation of logarithmic values of stability constants (log β) are shown for both Dox- and PG-water mixtures. These plots indicate the nature of electrostatic and non-electrostatic forces operating in the equilibria. The linear trend indicates that either the dielectric constant or the long range interactions are responsible for the trend in stability. This linear trend in log β values indicates the dominance of the structure forming nature of Dox/PG over the complexing ability. The Dox-water mixtures are the combination of aprotic and protic solvents with a wide range of dielectric constant and with high solubility for polar as well as non-polar solutes.

The increased basicity of Dox54 water mixtures, induced by co-solvent, stabilizes the protons. At the same time the coordinating solvent (Dox) competes with the ligands for coordination with the metal ions and this property of Dox decreases the stability of the complexes. Hence, the stability of the complex is expected to either increase or decrease. PG is an amphiprotic solvent. It is a structure former and it enhances the water structure in PG-water mixtures; hence, it removes water from the coordination sphere of metal ions, making them more reactive towards the ligands. As a result, the stability of the complexes is expected to increase. At the same time, it is a coordinating solvent and it competes with the ligands for coordinating the metals. This decreases the stability of the complexes. Hence, the stability of the complexes is expected to either increase or decrease linearly.

The variation of overall stability constants with co-solvent content depends upon electrostatic and non-electrostatic factors. Born's classical treatment holds good in accounting for the electrostatic contribution to the free energy change. According to this treatment, the energy of electrostatic interaction is related to dielectric constant. Hence, the $\log \beta$ values should vary linearly as a function of reciprocal of the dielectric constant (1/D) of the medium.

CONCLUSION

The existing work suggests that Co(II), Ni(II) and Cu(II) complexes shall be octahedral. Amino nitrogen can associate with hydrogen ions in physiological pH ranges. Hence, there is often significant competition between hydrogen and metal ion for this donor site. This situation results in the simultaneous existence of a number of equilibria producing an array of protonated complexes, which are detected in the present study. Asp acts as bidentate or tridentate ligand depending on the experimental conditions and en acts as bidentate ligand.

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