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Influence of Dielectric Constant on The Speciation of Pb(II), Cd(II) and Hg(II) With L-Valine in 1, 2-Propanediol-Water Mixtures.

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ABSTRACT

Potentiometric technique with glass electrode as a probe was employed for data acquisition under carefully designed experimental conditions. The Calvin-Wilson titration technique as modified by Irving and Rossetti will be used for the primary data acquisition. The stability constants of Pb(II), Cd(II) and Hg(II) with L-valine in 1, 2- Propanediol-water mixtures were refined using computer program MINIQUAD75. The stability constants increased linearly with decreasing dielectric constant of the medium due to dominance of electrostatic forces and structure forming nature of 1, 2- Propanediol. The plausible structures of the species were also presented.

KEYWORDS : Potentiometric technique, L-valine, 1, 2-propanediol, MINIQUAD75

Introduction

The toxic heavy metal (Pb^{2+}, Cd^{2+} and Hg^{2+}) ions are potential enzyme inhibitors because they are easily bound to enzyme donor groups. The toxicity of heavy metals is due to the replacement of essential metal ion from the corresponding enzyme. These metals disturb the natural functions of the biological system. Toxic metals have cumulative deleterious effects that can cause chronic degenerative changes. Studies on formation of binary complexes under physiological conditions are important to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ion. Hence in recent years researchers show interest in the study of metal ions interaction with various ligands[1-4]. Lead is a toxic element, which effects renal, neurological, reproductive and skeletal systems[5-7]. Cadmium causes iron deficiency by binding to cysteine, glutamate, aspartate, and histidine ligands[8]. Cadmium inhibits enzymes that participate in bilirubine conjunction[9]. Mercury is one of the most toxic elements and has negative health effects in human populations, highly dependent on fish consumption[10,11].

L-valine is a bidentate ligand and formation of its binary complexes of with metals was reported earlier, using polrographic study[12], batch equilibrium method with cation exchange resin[13], potentiometric titration method[14] and pH metric titration method[15]. Stability constants were evaluated with the computer program SCOGS[16], CHEMEQ[17] and SUPERQUAD[18]. 1,2-Propanediol also known as propylene glycol (PG) is a clear, viscous, colorless, odorless liquid with a dielectric constant of 30.2[19]. It is completely miscible with water.

Procedure

All the titrations were carried out in the medium containing varying compositions of PG (0.0-60.0% v/v) maintaining an ionic strength of 0.16 mol L^{-1} with sodium nitrate at 303.0±0.1 K. The titrimetric data were obtained with a calibrated Systronics MK-VI digital pH meter. Titrations with different ratios (1: 2.5, 1: 3.75 and 1: 5.0 in the case of Pb(II) and Cd(II) and 1: 7.5, 1: 8.5 and 1: 10.0 in the case of Hg(II)) of metal-to-ligand were carried out with 0.4 mol L^{-1} sodium hydroxide. Other experimental details are given elsewhere[20].

Modeling Strategy

The computer program SCPHD[21] was used to calculate the correction factor. The binary stability constants were calculated from the pH metric titration data using MINIQUAD75, which exploits the advantage of constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor, protonation constants of ligand were fixed.

Results, Discussion and Conclusion

In solutions containing several metal ions and ligands such as bio-fluids, the speciation study becomes complex due to the formation of a large number of different species. These include simple, mono-nuclear, poly-nuclear, protonated and hydroxylated species. Ordinary mathematical procedures fail to analyze such a complex system, where several species coexist. Therefore, one has to resort to modern Chemo metric methods to determine the nature and extent of formation of each species. Potentiometric technique with glass electrode as a probe will be employed for data acquisition under carefully designed experimental conditions. The Calvin-Wilson titration technique as modified by Irving and Rossetti will be used for the primary data acquisition. The approximate formation constants obtained by classical methods will be refined using Miniquad-75 computer program. Using the best-fit models thus obtained, species distribution diagrams, which give the important information regarding the extent of formation various species against pH will be generated.

L-Valine is a bidentate ligand that has one dissociable and one associable protons. The different forms of L-valine are LH_2^+, LH and L^- in the pH ranges 1.5-4.0, 4.0-9.0 and 9.0-11.0, respectively[22]. Hence the plausible binary metal-ligand complexes can be predicted from this data. The present investigation reveals the existence of ML and ML_2 species for Pb(II), Cd(II) and Hg(II) in 1, 2- Propanediol-water mixtures (Table 1). We studied the effect of solvent the speciation of Pb(II), Cd(II) and Hg(II) with L-valine in 1, 2- Propanediol-water mixtures.

Effect of solvent

PG is an amphiprotic and coordinating solvent. It removes water from 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 competes with the ligands for coordinating the metals. This decreases the stability of the complexes. Hence the stability of the complex is expected to either increase or decrease. Variation of logarithmic values of stability constants (log β) or change in free energy with co-solvent content depends upon two factors, viz., electrostatic and non-electrostatic forces. Born's classical treatment[23] 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 β values should vary linearly as a function of the reciprocal of the dielectric constant of the medium. The linear trend observed in the present study (Figure 1) indicates that electrostatic forces are dominating the equilibrium process under the present experimental conditions.

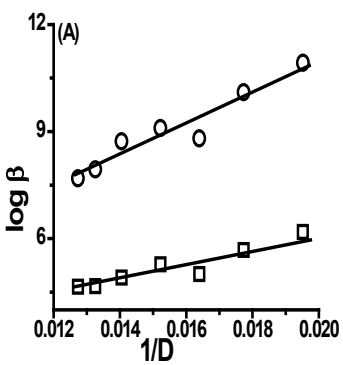
Structures of complexes

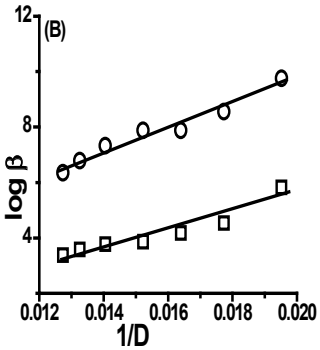
In aqueous solutions metal ions are coordinated by six water molecules. Bidentate or tridentate amino acids replace water molecules slowly and form metal-amino acid complexes. Depending upon the nature of the ligands and metal ions and based on the basic chemi-

cal knowledge tentative structures of the complexes are proposed as shown in Figure 2. Carboxyl oxygen and amino nitrogen of L-valine are coordinated to the metal ions.

Table 1. Stability constants of L-valine complexes of Pb(II), Cd(II) and Hg(II) in PG-water mixtures. (temperature = 303K, ionic strength = 0.16 mol L-1)

PG (% V/V)	log β_{mlh} (SD)		pH
	ML	ML_2	
Pb(II)			
0.0	4.65(24)	7.69(33)	3.0-9.5
10.0	4.67(13)	7.94(16)	2.5-9.5
20.0	4.91(16)	8.73(17)	2.5-9.5
30.0	5.28(19)	9.1(23)	3.5-9.2
40.0	5.01(10)	8.81(12)	3.0-9.0
50.0	5.68(15)	10.11(18)	2.5-9.0
60.0	6.19(82)	10.93(99)	2.5-9.0
Cd(II)			
0.0	3.38(43)	6.36(26)	2.0-9.5
10.0	3.59(15)	6.79(09)	3.0-9.5
20.0	3.78(46)	7.33(28)	2.0-9.5
30.0	3.87(39)	7.88(17)	3.5-9.0
40.0	4.18(32)	7.88(22)	3.0-8.9
50.0	4.54(13)	8.56(09)	2.5-8.9
60.0	5.83(84)	9.76(99)	3.0-9.5
Hg(II)			
0.0	8.18(16)	13.68(37)	2.5-9.5
10.0	8.77(07)	13.37(15)	2.5-9.5
20.0	8.22(14)	16.52(10)	2.5-9.0
30.0	8.69(14)	16.44(14)	3.0-8.6
40.0	9.46(03)	16.82(08)	2.5-9.5
50.0	9.93(03)	17.96(09)	1.8-8.8
60.0	10.39(04)	19.64(06)	2.0-8.0





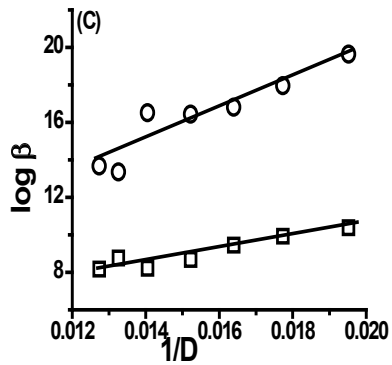


Figure 1. Variation of stability constant values of metal-valine complexes with reciprocal of dielectric constant (1/D) of PG-water mixtures: (A) Pb(II), (B) Cd(II), (C) Hg(II);

(□) log β_{ML}, (O) log β_{ML2} .

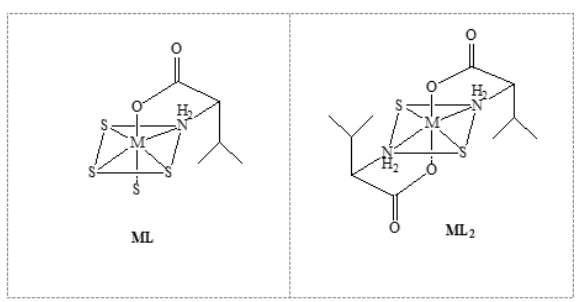


Figure 2. Proposed structures of L-valine complexes, where S is either solvent or water molecule.

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