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Speciation of Binary Complexes of Pb(II), Cd(II) and Hg(II) with L-Valine in Low Dielectric Media

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Abstract: ***Speciation of binary complexes of Pb(II), Cd(II) and Hg(II) in 0.0-60.0% v/v 1, 2-Propanediol-water mixtures with L-valine at an ionic strength of 0.16 mol L^{-1} and 303.0 K was studied pH metrically. The approximate formation constants obtained by classical methods are refined using MINIQUAD75 computer program. The binary species confirmed are ML and ML_2 for Pb(II), Cd(II) and Hg(II). The species distribution, which gave the important information regarding the extent of formation various species with pH and the effect of influential parameters on stability constants were also studied.***

Keywords: Binary species, L-valine, 1, 2-Propanediol, MINIQUAD75.

1. Introduction

Speciation profoundly influences both the toxicity and bioavailability of an element. Reliable speciation knowledge can be used to optimize drug efficacy, to minimize side reactions and to predict undesirable clinical side effects. The speciation studies of toxic metal ion complexes are useful to identify those metal species that are likely to have adverse effect on biota therefore different exposure standards should be established for different metal species. For all these reasons, the toxic metals (Pb^{2+}, Cd^{2+} and Hg^{2+}) are chosen for the speciation study. Better computing and analytical methods lead to an understanding of the speciation underlying many chemical reactions, with interesting conclusions, in industry, medicine and in environmental studies.

The reaction of any metal with ligands in the concentrated bioligands background gives binary complexes. Obviously, studies on formation of binary complexes under physiological conditions are important. Hence in recent years researchers show interest in the study of metal ions interaction with various ligands[1-4].

Lead enters the human body through multiple routes and gets distributed and stored in almost every organ resulting in the defective functions of the organ[5-7]. Findings of biochemical and toxicological effects of lead studies in detail by many workers have indicated deleterious effects to hematopoietic, renal, neurological, reproductive and skeletal systems[8-10].

Cadmium causes iron deficiency by binding to cysteine, glutamate, aspartate, and histidine ligands[11]. Cadmium inhibits enzymes that participate in bilirubine conjunction[12]. Mercury is one of the most toxic elements and has negative health effects in human populations, highly dependent on fish consumption[13,14].

L-Valine is a nonpolar essential amino acid. It has wide applications in the field of pharmaceutical and food industry[15]. It is a bidentate ligand and formation of its binary complexes of with metals was reported earlier, using polrographic study[16], batch equilibrium method with cation exchange resin[17], potentiometric titration method[18] and pH metric titration method[19]. Stability constants were evaluated with the computer program SCOGS[20], CHEMEQ[21] and SUPERQUAD[22]. Norvaline (an isomer of L-valine) binary complexes with Co (II) and Cu(II) were also reported using paper electrophoretic[23] and ionophoretic[24] techniques.

1,2-Propanediol also known as propylene glycol (PG) is a clear, viscous, colorless, odorless liquid with a dielectric constant of 30.2[25]. It is completely miscible with water.

2. Materials and Solutions

Aqueous solutions of L-valine (SRL, India), Pb(II), Cd(II) and Hg(II) nitrates (Qualigens, India) were prepared in triple distilled water by maintaining 0.05 mol L^{-1} nitric acid concentration to increase the solubility. 1, 2-Propanediol (Qualigens, India) was used as received. The strengths of acid and alkali were determined using Gran plot method[26]. To assess the errors that might have crept in to the determination of the concentrations, the data were subjected to analysis of variance of one way classification (ANOVA)[27].

Apparatus

The titrimetric data were obtained with a calibrated Systronics MK-VI digital pH meter, which was calibrated with potassium hydrogen phthalate (0.05 mol L^{-1}) in acidic region and borax (0.01 mol L^{-1}) in basic region. The glass electrode was equilibrated for several days in a well stirred PG-water mixture containing inert electrolyte. 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 effect of variations in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor[28].

Procedure

For the determination of stability constants of metal-ligand binary species, initially titrations of strong acid with alkali were carried out at regular intervals to check whether complete equilibration was achieved. Then the calomel

electrode was refilled with PG-water mixture of equivalent composition as that of the titrand. 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[29].

Modeling Strategy

The computer program SCPHD[30] 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.

3. Results and Discussion

Alkalimetric titration curves in PG-water mixtures revealed that the acido-basic equilibria of L-valine (LH_2^+ and LH) were active in the pH range 1.5-11.0. Based on the active forms of the ligands in this pH range, models containing various numbers and combination of complex species are fed to the MINIQUAD75 along with the alkalimetric titration data. The best-fit model was selected using the statistical parameters[31] of the least squares residuals. The final models along with the statistical parameters are given in Table1. The low standard deviation in the model parameters illustrates the adequacy of the models.

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[32]. Hence the plausible binary metal-ligand complexes can be predicted from this data. The present investigation reveals the existence of ML and ML_2 for Pb(II), Cd(II) and Hg(II).

The formation of various L-valine complexes species is shown in the following equilibria.

$$M(II) + LH_2 \rightleftharpoons ML + 2H^+ \quad (1)$$
$$M(II) + LH \rightleftharpoons ML + H^+ \quad (2)$$
$$M(II) + 2LH \rightleftharpoons ML_2 + 2H^+ \quad (3)$$
$$ML + LH \rightleftharpoons ML_2 + H^+ \quad (4)$$

ML and ML_2 species are formed in the pH range 6.0-9.0 for Pb(II) and Cd(II), 2.0-5.0 for Hg(II) and their percentages increase in the same order (Figure 1). ML species can be formed by the interaction of metal ion with LH_2 (Equilibrium 1) and the interaction of metal ion with LH (Equilibrium 2). ML_2 species is formed by the interaction of metal ion with LH (Equilibrium 3), and ML with LH (Equilibrium 4).

Table 1: Parameters of the best-fit chemical models 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)		NP	$U_{corr}*10^8$	χ^2	Skewness	Kurtosis	R-factor	pH
	ML	ML_2							
Pb(II)									
0.0	4.65(24)	7.69(33)	37	17.23	34.37	0.24	4.18	0.0407	3.0-9.5
10.0	4.67(13)	7.94(16)	52	4.56	35.08	0.93	6.81	0.0179	2.5-9.5
20.0	4.91(16)	8.73(17)	55	4.89	28.60	-0.01	4.38	0.0181	2.5-9.5
30.0	5.28(19)	9.1(23)	27	7.08	7.99	0.10	5.60	0.0261	3.5-9.2
40.0	5.01(10)	8.81(12)	34	2.42	29.76	0.04	5.31	0.0141	3.0-9.0
50.0	5.68(15)	10.11(18)	51	4.82	28.70	-0.67	3.96	0.0176	2.5-9.0
60.0	6.19(82)	10.93(99)	75	11.97	74.47	1.42	4.96	0.0699	2.5-9.0
Cd(II)									
0.0	3.38(43)	6.36(26)	84	15.73	13.11	0.80	2.74	0.0249	2.0-9.5
10.0	3.59(15)	6.79(09)	33	1.74	8.56	0.67	4.41	0.0129	3.0-9.5
20.0	3.78(46)	7.33(28)	84	15.36	84.63	-1.08	3.49	0.0243	2.0-9.5
30.0	3.87(39)	7.88(17)	23	6.86	55.17	0.09	6.88	0.0247	3.5-9.0
40.0	4.18(32)	7.88(22)	31	7.86	11.34	0.27	3.33	0.0237	3.0-8.9
50.0	4.54(13)	8.56(09)	52	1.14	40.51	0.80	3.04	0.0078	2.5-8.9
60.0	5.83(84)	9.76(99)	49	4.0	75.86	0.99	4.33	0.0496	3.0-9.5
Hg(II)									
0.0	8.18(16)	13.68(37)	55	4.53	16.77	0.57	3.42	0.0554	2.5-9.5
10.0	8.77(07)	13.37(15)	52	14.4	6.97	0.09	2.87	0.0311	2.5-9.5
20.0	8.22(14)	16.52(10)	55	8.91	9.88	0.61	4.30	0.0226	2.5-9.0
30.0	8.69(14)	16.44(14)	21	6.42	5.95	0.17	3.30	0.0244	3.0-8.6
40.0	9.46(03)	16.82(08)	50	1.61	8.72	-0.37	2.43	0.0105	2.5-9.5
50.0	9.93(03)	17.96(09)	114	3.76	17.44	2.26	4.54	0.0095	1.8-8.8
60.0	10.39(04)	19.64(06)	86	4.80	13.26	1.08	5.18	0.0135	2.0-8.0

U_{corr} = U/ (NP-m); m = number of species; NP = number of experimental points; SD= Standard deviation

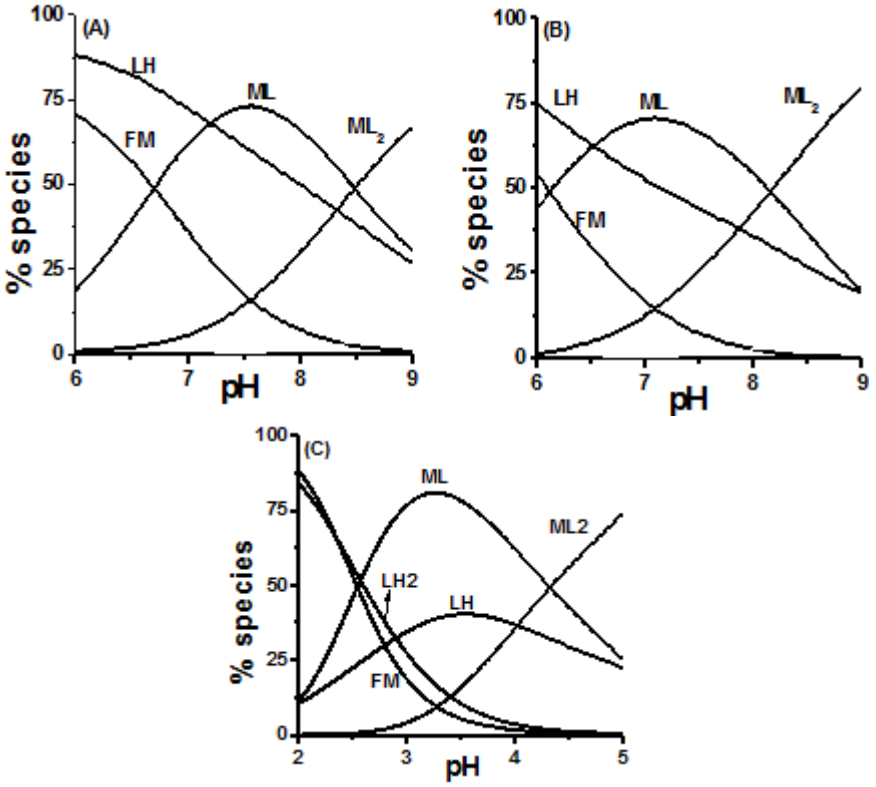

Figure 1: Distribution diagrams of binary complexes of valine in 50% v/v PG-water mixture: (A) Pb(II), (B) Cd(II) and (C) Hg(II).

Effect of influential parameters on stability constants

Any variation in the parameters (the concentrations of ingredients) affects the magnitudes of stability constants. Such parameters are called influential parameters. In order to rely upon the best fit chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, Pb(II)-valine system in 10% v/v PG-water mixture was studied by introducing errors in the concentrations of ingredients (mineral acid, ligand, metal and alkali). These results (Table 2) emphasize that errors in the concentrations of acid and alkali affect more than other factors. Increase in the standard deviations with the introduction of errors infers the appropriateness of experimental conditions and correctness of analytical concentrations.

4. Conclusions

1) L-Valine forms unprotonated complexes in the pH range 1.8-9.0.
2) The common species formed due to the interaction of L-valine with the metals are ML and ML_2. These models are validated by statistical treatment of data.
3) The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is acid > alkali > metal > ligand > log F.
4) The stability order of binary complexes is Pb(II) < Cd(II) << Hg(II).

Table 2: Effect of errors in influential parameters on the stability constants of Cd(II)-valine binary complexes in 30% v/v PG-water mixture

Reagent	% Error	log β_{mlh} (SD)	
		ML	ML_2
	0	3.87(39)	7.88(17)
Alkali	-5	7.67(36)	12.46(43)
	-2	4.40(31)	8.74(16)
	+2	3.43(69)	7.12(28)
	+5	2.36(394)	6.07(51)
Acid	-5	2.44(286)	5.83(63)
	-2	3.47(62)	7.05(28)
	+2	4.35(36)	8.77(17)
	+5	Rejected	9.90(37)
Ligand	-5	3.84(46)	7.96(17)
	-2	3.86(41)	7.91(18)
	+2	3.89(38)	7.85(18)
	+5	3.90(36)	7.81(18)
Metal	-5	3.81(50)	7.97(18)
	-2	3.85(43)	7.92(18)
	+2	3.89(36)	7.85(17)
	+5	3.92(33)	7.80(17)
Log F	-5	3.87(39)	7.88(18)
	-2	3.87(39)	7.88(17)
	+2	3.87(39)	7.88(17)
	+5	3.87(39)	7.88(18)

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