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Research Article

Speciation study of Mercaptosuccinic acid complexes of Pb(II), Cd(II) and Hg(II) in Acetonitrile-water mixtures

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Abstract
Equilibrium study on complex formation of Mercaptosuccinic acid with Pb(II), Cd(II) and Hg(II) has been investigated pH metrically in acetonitrile - water mixtures 0.0-60% v/v at 303 K and 0.16 M ionic strength. The predominant species detected for Pb(II), Cd(II) and Hg(II) are MLH_2. Models containing different numbers of species were refined by using the computer program MINIQUAD75. The best-fit chemical models were arrived at based on statistical parameters. The trend in variation of complex stability constants with change in the dielectric constant of the medium is explained on the basis of electrostatic and non-electrostatic forces.

Keywords: Complex equilibria, Chemical speciation, Mercaptosuccinic acid, Acetonitrile, Metals.

Introduction:

The speciation study of toxic metal ion complexes is useful to understand the role played by the active site cavities in biological molecules and the bonding behavior of protein residues with the metal ion. The species refined and their relative concentrations under the experimental conditions represent the possible forms of amino acids in bio fluids. Due to its numerous uses and high persistence, lead is a major environmental contaminant[1]. Lead is toxic even at low concentrations for living organisms, which can absorb it in various ways[2]. Lead intake by humans can be due to the consumption of crop plants grown on soils with high plant-available metal concentrations[3]. Cadmium causes iron deficiency by binding to cysteine, glutamate, aspartate, and histidine ligands[4]. Cadmium inhibits enzymes that participate in bilirubin conjunction[5]. It increases urine Ca^{2+} excretions which can cause severe bone pathology[6]. Mercury is one of the most toxic elements and has negative health effects in human populations, highly dependent on fish consumption[7]. Recent research concluded that neither vitamin B_{12} nor the acetyl-CoA pathways are required for bacterial methylation of mercury[8].

Mercaptosuccinic acid (MSA) or thiomalic acid (HOOC–CH(SH)-CH2-COOH) is a dicarboxylic acid containing a thiol functional group (-SH group) instead of an –OH group in malic acid[9]. MSA is a tridentate ligand which has the ability to form strong complexes with many metal ions in natural environment and within cells[10] and it has three replaceable hydrogen ions (two from the carboxylic and one from the sulfhydryl functional groups).

Acetonitrile (AN) is a colorless polar aprotic solvent[11]. It behaves as a weaker base[12] and as a much weaker acid[13] than water. It has a dielectric constant of 36 and autoprotolysis constant of 33.6. AN also acts as a strongly differentiating solvent with a modest solvating power for many polar ionic solutes[14].

Hence MSA is selected for speciation studies of its complexes with Pb(II), Cd(II) and Hg(II) in AN-water mixtures. The protonation constants of MSA in AN-water mixtures were reported earlier[15].

EXPERIMENTAL

Materials

Acetonitrle (Merck, Mumbai) was used as received. Aqueous solutions of MSA and sodium nitrate (E-Merck, Germany) were prepared. Metal solutions of Pb(II), Cd(II), Hg(II) nitrates were prepared. To increase the solubility of MSA and to suppress the hydrolysis of metal salts, the mineral acid concentration in the above solutions was maintained at 0.05 M. To assess the errors that might have crept into the determination of the con-

centrations, the data have been subjected to analysis of variance of one way classification (ANOVA). The strength (concentration) of alkali has been determined using the Gran plot method[16, 17].

Apparatus

The titrimetric data were obtained with a calibrated ELICO (Model L1-120) pH-meter (readability 0.01) which can monitor the changes in H^+ concentration. The pH meter was calibrated with 0.05 M potassium hydrogen phthalate in acidic region and 0.01 M borax solution in basic region. The glass electrode was equilibrated in a well-stirred AN-water mixture containing inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of AN (0-60.0 % v/v) maintaining an ionic strength of 0.16 M 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[18].

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 AN-water mixture of equivalent composition as that of titrand. In each of the titrations, the titrand consisted of approximately 1 mmol mineral acid in a total volume of 50 mL. Titrations with different ratios (1:2.5, 1:3.75 and 1 : 5.0 in the case of Pb(II) , Cd(II) and (1:5, 1:7.5, 1:10) for Hg(II) of metal-ligand were carried out with 0.4 M sodium hydroxide. Other experimental details are given elsewhere[19].

Modeling Strategy

The computer program SCPHD[20] was used to calculate the correction factor. By using the pH-metric titration data, the binary stability constants were calculated with the computer program MINIQUAD75[21], which exploits the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor and the protonation constants of MSA are fixed. The variation of stability constants with the dielectric constant of the medium was analyzed on electrostatic grounds on the basis of solute-solute and solute-solvent interactions.

RESULTS AND DISCUSSION

For an ideal normal distribution, the values of kurtosis and skewness should be three and zero, respectively. Kurtosis is a measure of the peakedness of the error distribution near a modal value. For an ideal normal distribution kurtosis value should be three (mesokurtic). If the calculated kurtosis is less than three, the peak of the error distribution curve is flat (platykurtic) and if the kurtosis is greater than three, the distribution shall have sharp peak (leptokurtic). The kurtosis values in the present study indicate that the residuals form leptokurtic as well as platykurtic patterns. The values of skewness recorded in the tables are between -1.62 and 4.53. These data evince that the residuals form part of a normal distribution. Hence, the least-squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R-value recorded. These statistical parameters thus show that the best-fit models portray the metal-ligand species in AN-water mixture.

Effect of Systematic Errors on Best-Fit Model

In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the influential parameters[22] like concentrations of alkali, mineral acid, ligand and metal (Table 2). The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > ligand > metal. Some species are even rejected when errors are introduced in the concentrations. This study confirms the appropriateness of the chosen best-fit models. This study also indicates the relative sensitivities of model parameters.

Table 1: Parameters of best-fit chemical models of Pb(ll), Cd(ll) and Hg(ll) –MSA complexes in acetonitrile-water mixture.(No. of titrations in each percentage=3, Temp=303 K)

%v/v AN	Logβmlh(SD)	NP	U_{corr}	Skewness	Kurtosis	χ^2	R-Factor	pH range
	1 1 2							
Pb(ll)								
0	16.81(07)	91	1.65	-0.86	6.41	86.41	0.0029	1.6-3.5
10	18.42(40)	108	13.27	1.42	8.40	50.47	0.0096	1.5-2.5
20	17.14(39)	102	762.9	4.53	103.56	702.10	0.0707	1.5-2.8
30	17.58(20)	98	18.96	0.10	4.29	56.42	0.011	1.5-3.0
40	18.51(58)	89	78.29	-0.40	5.34	79.10	0.0235	1.4-2.5
50	18.95(23)	62	20.98	-0.08	3.56	45.40	0.0134	1.4-2.8
60	18.45(36)	87	78.13	-1.62	7.42	181.21	0.0231	1.4-2.8
Cd(ll)								
0	17.00(39)	36	28.34	0.01	1.77	8.30	0.0294	1.6-5.0
10	18.06(14)	140	12.23	-.33	4.74	73.52	0.0113	1.6-7.0
20	17.46(25)	101	34.5	1.19	5.22	91.38	0.017	1.6-3.2
30	18.25(41)	35	27.97	1.41	4.91	21.25	0.02	1.8-3.0
40	18.09(45)	89	91.25	-0.47	5.69	96.60	0.0255	1.7-3.0
50	18.40(40)	47	54.78	1.38	5.00	38.35	0.0248	1.8-3.0
60	19.16(35)	63	35.64	1.42	4.84	40.88	0.0191	1.7-3.0
Hg(ll)								
0	17.65(21)	108	3.63	1.37	7.66	76.84	0.0045	1.6-2.8
10	18.40(34)	94	12.47	0.64	4.11	31.82	0.0095	1.6-2.5
20	17.58(41)	136	29.85	1.42	7.07	207.80	0.0162	1.59-4.2
30	18.55(53)	91	28.22	0.41	5.63	47.03	0.0146	1.6-2.5
40	18.48(62)	74	97.80	1.04	4.03	56.63	0.0472	1.8-3.5
50	18.14(24)	165	98.17	1.40	4.73	346.64	0.0310	1.6-7.0
60	18.11(73)	58	93.33	1.82	7.39	127.15	0.0392	2.1-4.8

U_{corr}=U/ (NP-m) X10^8;NP= Number of points; m= number of protonation constants; SD= Standard deviation.

Table 2: Effect of errors in influential parameters on the complex stability constants in 30% (v/v) AN-water mixture (MSA)

Ingredient	% of error	MLH_2
Acid	-2	18.50(17)
	+2	Rejected
	-5	Rejected
	+5	Rejected
	0	17.58(20)
Alkali	-2	Rejected
	+2	18.04(15)
	-5	Rejected
	+5	18.46(16)
Ligand	-2	17.69(19)
	+2	17.54(20)
	-5	17.66(19)
	+5	17.48(21)
Metal	-2	17.61(18)
	+2	17.57(18)
	-5	17.65(18)
	+5	17.54(18)

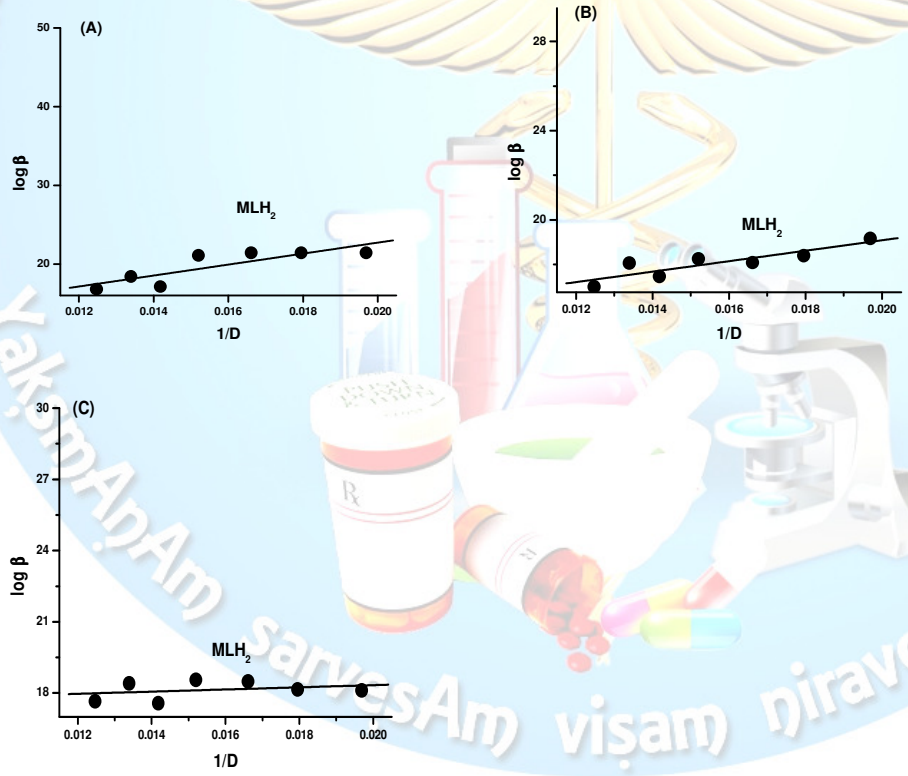


Figure 1: Variation of stability constant values of metal-MSA complexes with reciprocal of dielectric constant (1/D) in AN-water mixtures at temperature = 303 K and ionic strength = 0.16 M. (A) Pb(II), (B) Cd(II) and (C) Hg(II); (●) log β_{112}

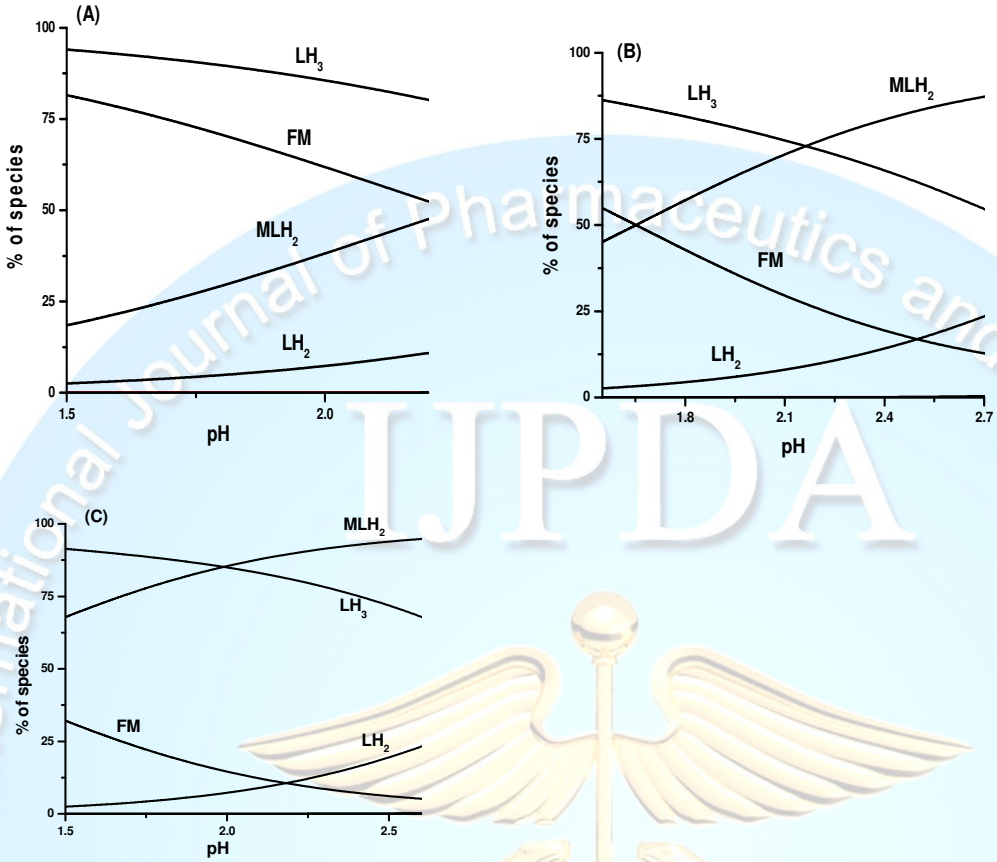


Figure 2: Distribution diagrams of MSA complexes in 30% v/v AN-water mixture Temperature = 303 K , ionic strength = 0.16 M. (A) Pb(II), (B) Cd(II) and (C) Hg(II).

Effect of Solvent

Variation of logarithmic values of stability constants (log β) with reciprocal of dielectric constant (1/D) are shown in Figure 1. AN is a protophilic, dipolar aprotic and coordinating solvent. It is a structure breaker of water and disrupts the water structure to form AN-water complex[23] of the formula AN. When small amount of AN is added to water, the water structure breaks down resulting in more basic monomeric water molecules. Hence water molecules compete with the ligands for coordination with metal ions, decreasing the stability of the complexes. But the formation of solvent-water complex decreases the coordinating power of water. 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. Born's classical treatment[24] 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 1/D 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.

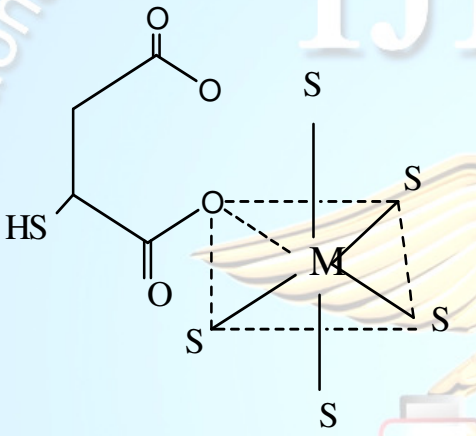
Distribution Diagrams

MSA is a tridentate ligand which has the ability to form strong complexes with many metal ions in natural environment and within cells[10] and it has three replaceable hydrogen ions (two from the carboxylic and one from the sulfhydryl functional groups). The different forms of MSA are LH_3, LH_2^-,

LH^{2-} and L^{3-} the pH ranges 2.0-4.3, 2.0-8.0, 3.0-11.8, and greater than 6.5, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of MLH_2 for Pb(II), Cd(II) and Hg(II). Whose formation is shown in the following equilibrium. The species distribution diagrams are shown in Figure 2.

$$M(II)+LH_3^{+} \rightleftharpoons MLH_2^{+}+H^{+}$$

Depending on the active sites in the ligand and the nature of the metal ions, the structures were proposed for the species detected as shown in Figure 3.



CONCLUSIONS

1. The present biomimetic studies of metal ion complexes with MSA in AN-water mixtures indicated that the complexes were protonated in acidic pH values. The species detected was MLH_2.
2. The log β values linearly increased with 1/D of the medium, indicating the dominance of electrostatic forces over non-electrostatic forces.
3. The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations was alkali > acid > ligand > metal.

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