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Speciation studies of mercaptosuccinic acid complexes of Pb(II), Cd(II), Hg(II) in dimethylformamide –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 Dimethylformamide –water mixtures of 0.0 – 60.0% v/v at 303 K and maintaining 0.16 mol dm⁻³ ionic strength. The predominant species refined are MLH₂ for Pb(II), MLH₂ and ML₂H for Cd(II) and ML₂H and MLH for Hg(II). Models containing different number of species were refined by using the computer program MINIQUAD75. The best fit chemical models were arrived based on the 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: Mercaptosuccinic acid, Chemical speciation, Dimethylformamide, complex equilibria, Metals

1. Introduction

Mercaptosuccinic acid (MSA) or thiomalic acid is (HOOCCH(SH)CH₂COOH) is a dicarboxylic acid containing thiol functional group (-SH group) instead of -OH group in malic acid [1]. It is an important organic compound with multifunctional intermediate in organic synthesis. MSA is widely applied in industry and technology as corrosion inhibitor, electrolyte for electroplating bath, and components of bleachfixing baths for photographic films and as active materials for depilatories and hair straightening [2].

Heavy metals such as lead, cadmium and mercury are toxic substances which exert adverse effects on neurological, reproductive and renal and hemotological systems in humans and animals. Organo-mercury and lead compounds exhibit toxic effect on central nervous system [3]. Similarly cadmium exhibits various chronic and acute disorders like testicular atrophy, hypertension, damage to kidneys and bones, anemia and itai- itai [4-8]. Hence the stability constants of the binary complexes of Pb(II), Cd(II) and Hg(II) have been determined pH metrically. These values are potentially useful to environmental and biological problems [9-11]. In this study water was substituted by Dimethylformamide (dmf) that has lower dielectric constant to mimic the permittivity of bio-active sites. Thus the dmf-water mixtures produce the conditions that exist at the active sites of enzymes and side chains of proteins. The present paper describes the complexation of Pb(II), Cd(II) and Hg(II) with MSA in dmf-water mixtures.

Materials and methods

Reagents and preparation

Mercaptosuccinic acid (MSA), nitrates of lead, cadmium and mercury, dmf, mineral acid (HNO₃), sodium nitrate and sodium hydroxide were of analytical grade reagents. Dmf was used as received. Aqueous solutions of MSA, metal salt solutions, nitric acid, a carbonate free sodium hydroxide and sodium nitrate were prepared by dissolving samples in triple distilled water. To increase the solubility of MSA and to suppress the hydrolysis of metal salts, the nitric acid concentration was maintained at 0.05 mol dm⁻³. The solutions were standardized by employing standard methods. The data were subjected to ANOVA [12], to assess the errors that might have crept into the determination of the concentrations. Gran plot [13] method was employed to determine the strength of the alkali.

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Apparatus

Elico LI 120 pH meter was used for the pH measurements. Potassium hydrogen phthalate solution (0.05 mol dm^{-3}) in the acidic region and borax solution (0.01 mol dm^{-3}) in the basic region were used to calibrate the pH meter. The pH meter was equilibrated in a well stirred dmf-water mixture containing the electrolyte. The effects of variations in the asymmetry potential, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of the glass electrode were accounted for in the form of correction factor ^[14-15].

Measurements

All measurements were carried out at 303 K and at an ionic strength of 0.16 mol dm^{-3} which was maintained with sodium nitrate. The electrode was kept usually for 2-3 days, in the required solvent system for equilibration. To verify whether the electrode was equilibrated or not, a strong acid was titrated with the alkali every day until no appreciable differences were observed between the pH values of two titrations at the corresponding volumes of the titrant. Then the electrode was said to be equilibrated. Free acid – base

titrations were performed to calculate the correction factor. In each of these titrations, titrand consisted of 1-3 mmol of mineral acid in a total volume of 50 cm^3 . Titrations with different metal to ligand ratios (1:2.5,1:3.75,1:5) in case of lead and cadmium and (1:5,1:7.5,1:10) in case of mercury (as the solubility of mercury is low) were carried out with 0.40 mol dm^{-3} sodium hydroxide. The analytical concentrations of the ingredients are given in Table 1. Other experimental details were given elsewhere ^[16].

Model strategy

The approximate complex stability constants were calculated using the computer program SCPHD ^[17]. By following some heuristics in the refinement of the stability constants, the best fit chemical models for each system were arrived at using the computer program MINQUAD75 ^[18].

Results and discussion

Alkalimetric titration curves in dmf–water mixtures reveal that the acido-basic equilibria of MSA are active in the pH range of 2.0 -10.0.

Table 1: Total initial concentrations of ingredients (in mmol) of titrands in dmf–water mixtures [NaOH]= 0.4 mol dm^{-3} ; $V_0=50.0 \text{ cm}^3$; temp=303 K; ionic strength= 0.16 mol dm^{-3} ; mineral acid= 0.2 mmol .

% v/v dmf	TM0		TL0 MSA	TL0:TM0	TM0	TL0	TL0:TM0
	Pb(II)	Cd(II)			Hg(II)	MSA	
0.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
10.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
20.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
30.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
40.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
50.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0
60.0	0.099	0.094	0.250	2.50	0.045	0.250	5.00
			0.375	3.75		0.375	7.50
			0.500	5.00		0.500	10.0

Based on the active forms of the ligand in this pH range, models containing various numbers and combinations of complex species were generated using an expert system package CEES ^[19]. These models were inputted to

MINQUAD75 along with the alkalimetric titration data. The best fit model was selected using the statistical parameters of the least square residuals. The final values of the stability constants of the complexes are given in Table 2.

Table 2: Parameters of best fit chemical models, of MSA complexes of Pb(II), Cd(II) and Hg(II) in dmf-water mixtures. Temperature =303K, Ionic strength =0.16 mol dm⁻³

%v/v DMF	Logβ _{mlh} (SD) 1 1 1, 1 1 2, 1 2 1			NP	U _{corr}	χ ²	Skewness	R factor	Kurtosis	pH range
Pb (II)										
0		17.43(11)		89	19.21	208.36	-3.28	0.009	22.85	1.6-2.5
10		17.44(30)		10	6.53	6.27	-0.86	0.008	4.39	1.9-2.1
20		17.61(47)		9	27.12	15.37	-0.8	0.021	15.37	2.1-2.5
30		19.56(12)		11	1.66	8.94	-0.26	0.004	4.33	1.9-2.2
40		21.66(28)		17	5.98	16.61	-0.16	0.008	4.54	2.0-2.5
50		21.66(28)		17	5.99	16.61	-0.16	0.008	4.54	2.0-2.3
60		23.12(29)		17	5.91	16.92	-0.15	0.008	4.52	2.0-2.3
Cd (II)										
0		17.00(39)	18.69(40)	36	29.19	8.30	0.1	0.029	1.77	4.0-7.0
10		17.19(13)	18.24(16)	32	3.30	23.50	1.76	0.011	7.48	3.6-6.5
20			18.40(11)	32	1.48	37.33	0.16	0.007	4.73	4.0-7.5
30			18.15(40)	49	42.73	138.33	2.27	0.028	7.04	3.0-7.5
40		17.76(46)	18.79(30)	27	51.2	26.75	1.78	0.035	5.48	3.5-7.0
50		18.68(42)	23.96(22)	13	89.99	10.03	1.11	0.010	5.71	3.5-4.6
60			28.70(15)	5	3.55	16.47	2.34	0.006	8.95	3.5-3.9
Hg(II)										
0			18.38(32)	194	47.09	315.43	1.11	0.020	3.80	4.0-9.0
10			18.22(47)	59	174.3	27.70	-0.86	0.119	3.49	4.0-9.5
20			19.02(26)	37	13.02	13.90	0.54	0.028	2.63	4.0-7.0
30	14.19(37)		22.86(30)	83	4.85	67.69	0.78	0.011	6.78	2.5-9.5
40	14.68(49)		25.37(38)	68	22.42	47.61	0.73	0.028	5.61	3.1-7.0
50	14.42(48)		24.94(18)	41	2.58	76.64	-0.13	0.031	4.53	3.5-5.0
60	15.34(43)			67	127.1	78.68	1.98	0.046	6.25	3.0-5.5

$$U_{\text{corr}} = U / (\text{NP} - m) * 10^8, m - \text{number of species} ; \text{NP} = \text{number of experimental points}$$

Effect of systematic errors on the best fit model

In order to rely upon the best fit model for critical evaluation and application under varied experimental conditions with different accuracies of data acquisition, a study was made by employing pessimistic errors into influential parameters, such as the concentration of alkali, mineral acid, ligand and metal (Table 3). The order of constituents that influence the magnitudes of the stability constants due to incorporation of errors are alkali>acid>ligand>metal. The rejection of some species and increased standard deviations in the stability constants on introduction of errors confirm the appropriateness of the best fit models. This study supports that the experimental concentrations are appropriate and the proposed models are adequate for the experimental data.

Table 3: Effect of errors in concentrations of ingredients on stability constants of Pb (II) –MSA complexes in 30% v/v dmf-water mixtures

ingredient	% of error	Logβ
		1 1 2
alkali	0	19.27(12)
	-5	Rejected
	-2	19.10(14)
	+5	Rejected
	+2	20.08(17)
acid	-5	Rejected
	-2	20.31(23)
	+5	Rejected
	+2	20.31(23)
ligand	-5	19.59(12)
	-2	19.57(12)
	+5	19.52(12)
	+2	19.57(12)
Metal	-5	19.62(13)
	-2	19.58(13)
	+5	19.50(12)
	+2	19.53(12)

Effect of dielectric constant

Addition of dmf to water decreases the dielectric constant of the medium. The dielectric constants of the medium at different percentages (0-60% v/v) of dmf were taken from literature [20]. The change in overall stability constants or change in free energy with change in co-solvent depends on two factors, viz., electrostatic and non electrostatic. As basicity of dmf is lower than that of water, the non electrostatic effect seems to decrease proton accepting power of the ligand. Addition of more dmf removes water molecules from hydration sphere of metal ion making it more susceptible to react with the ligand. According to Born's equation [21] the energy of electrostatic interactions is related to dielectric constant of the medium and log β versus 1/D (D is the dielectric constant) should be linear. So the log β should increase/decrease linearly in dielectric constant of the medium (with increase in dmf content) if the interaction between metal and ligand is electrostatic in nature.

According to this treatment, the energy of electrostatic interaction is related to dielectric constant. The linear and non-linear trend observed in the present study (Fig.1) indicate that non electrostatic forces are dominating the equilibrium process in Cd(II) under the present experimental conditions (fig 1B) and electrostatic forces are dominating equilibrium process in Pb(II) and Hg(II). The linear increase indicates the dominance of the structure-forming nature of dmf over complexing ability. The cation stabilizing nature of co-solvents, specific solvent-water interactions, charge dispersion and specific interactions of co-solvent with solute (indicated by the changes in the solubility of different species in the aqua-organic mixtures) account for little deviation from the linear relationship.

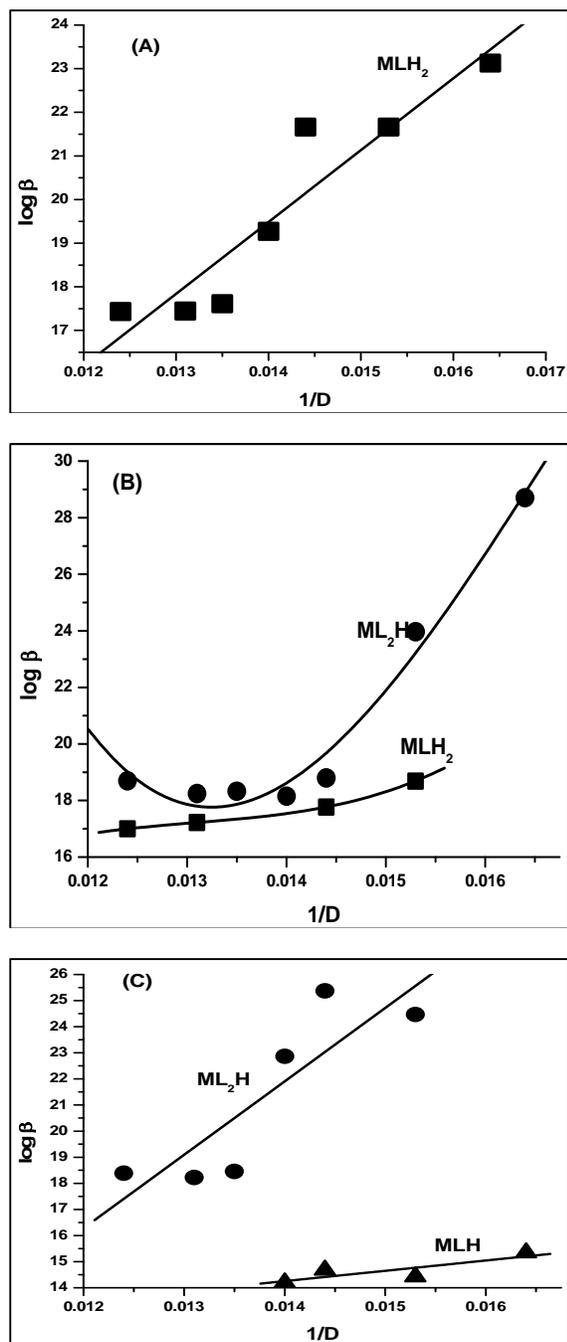


Fig 1: variation of stability constant of the values of (A) Pb(II); (B) Cd (II); Hg(II)-MSA complexes with reciprocal of dielectric constant (1/D) in dmf-water mixtures; (■) $\log \beta_{112}$; (●) $\log \beta_{121}$; (▲) $\log \beta_{111}$.

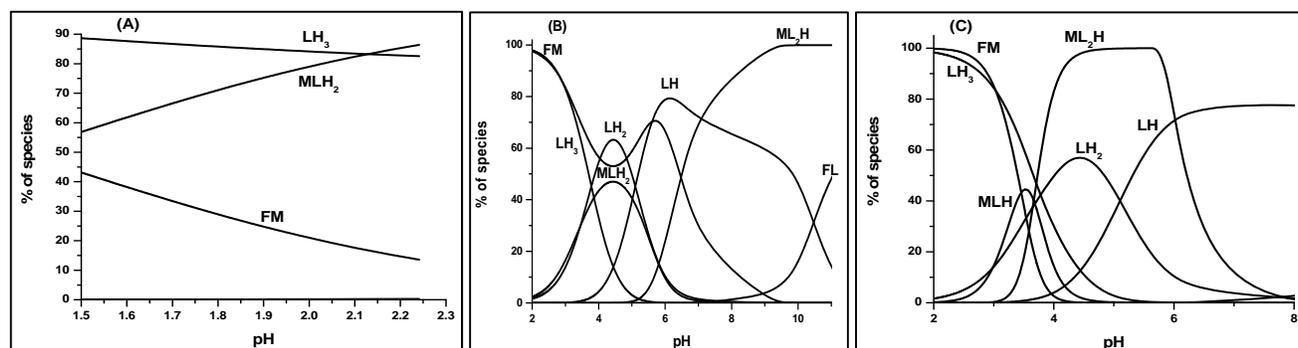
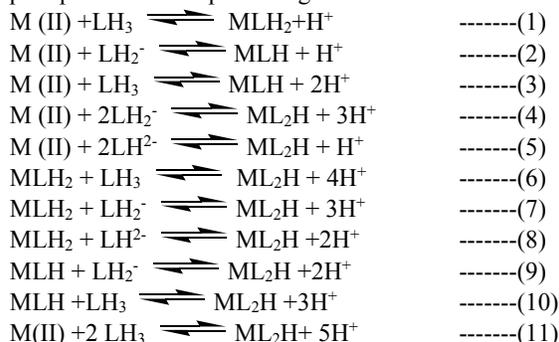


Fig 2: Distribution diagrams of (A) Pb(II); (B) Cd(II); (C) Hg(II)-MSA complexes in 40% of dmf-water mixture

Distribution diagrams

MSA has three dissociable protons. The different forms of MSA are LH_3 , LH_2^- , LH^- , L^{3-} which exist in the pH ranges <5.5, 2-8.5, 2.5-11.5, and <7.0, respectively²². The present study is confined to the pH ranges 1.6-2.5 for Pb(II), 3.5-6.5 for Cd(II), and 4.0-7.0 for Hg(II). In these pH ranges the active forms of the ligand are LH_3 , LH_2^- , LH^- (reference 22). Hence it is possible to predict a large number of binary metal-ligand complexes from these data. The present investigation reveals the existence of only MLH_2 for Pb(II) and MLH_2 and ML_2H for Cd(II) and MLH and ML_2H for Hg(II). The formation of various binary complex species are shown in the following equilibria. The species could not be refined at a higher pH for Pb(II)-MSA systems due to the formation of precipitate at lower pH during the titration.



In the case of Pb(II) and Cd(II) MLH_2 is formed through equilibrium (1), by the interaction of protonated ligand with the metal ion which may be appropriate as LH_3 decreases with increase in pH.

ML_2H species is formed by the interaction of metal and protonated ligand (equilibrium 4,5) and also formed by the interaction of MLH_2 with the protonated ligand (equilibrium 6,7,8) but the equilibria 6 and 7 may be appropriate as the concentration of MLH_2 decreases and also the protonated ligands LH_3 and LH_2^- decreases simultaneously

MLH species is formed by the interaction of metal with the protonated ligand equilibria 3 and 4 as LH_3 species decreases with the increase in pH.

The distribution diagrams are shown in figure 2.

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. Although it is not possible to

elucidate or confirm the structures of complexes pH metrically, they can be proposed based on the literature reports and chemical knowledge^[23].

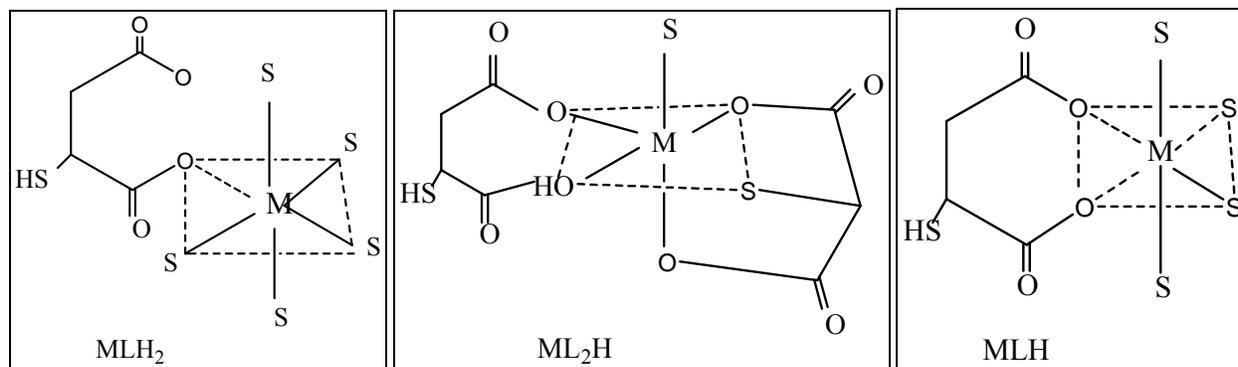


Fig 3: Structures of Metal-MSA complexes where M= Pb, Cd and Hg; L=mercaptosuccinic acid and S is either solvent or water molecule.

Conclusion

The following conclusions have been drawn from the modeling studies of MSA complexes of Pb(II), Cd(II) and Hg(II) in dmf-water mixtures.

1. The present biomimic studies of metal ion complexes with mercaptosuccinic acid in dmf-water mixtures indicated that the complexes were protonated in acidic pH values. The species detected were MLH_2 to Pb(II), MLH_2 and ML_2H to Cd(II) and MLH and ML_2H to Hg(II) ions.
2. The $\log \beta$ values increased linearly with $1/D$ of the medium, indicating the dominance of electrostatic forces over the non electrostatic forces in the case of Pb(II) and Hg(II). In the case of Cd(II) increased non linearly, indicating the dominance of non electrostatic forces over 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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