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Chemical Speciation of Cd(II) and Pb(II) Binary Complexes of L-Asparagine in Acetonitrile-Water Mixture

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ABSTRACT

The speciation of L-Asparagine complexes of Cd(II) and Pb(II) has been investigated pH-metrically in Acetonitrile-water mixtures (0-50% v/v) at 303K and 0.16 mol L^{-1} ionic strength. The predominant species detected for Cd (II) and Pb(II) are ML_2, ML_2H, ML_2H_2. The appropriateness of experimental conditions is verified by introducing errors intentionally in the concentrations of reactants. The 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 stability constants of the complexes with dielectric constant of the medium is attributed to the electrostatic and non-electrostatic forces. The species distribution and the plausible equilibria for the formation of the species are also presented.

Keywords: Chemical speciation, L-Asparagine, Acetonitrile, Metals, stability constants.

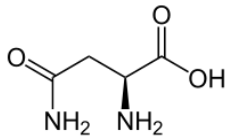
INTRODUCTION

Chemical speciation of metals is important for an understanding of their distribution, mobility, bioavailability, toxicity and for setting environmental quality standards [1]. Bioavailability of a particular metal depends on its complex chemical reactions of dissolution, binding and complexation with the constituents of the environmental aquatic phase [2]. The activity of bacteria increase the concentration of dissolved organic carbon and decreases the pH value of water. This causes an increase in the complexation and mobility of a metal [3]. Complexation significantly decreases bioavailability. Acetonitrile (AN) is a weak base [4] and a much weaker acid [5] than water. It is a photophobic dipolar aprotic solvent and it does not form any hydrogen bond with solute species. The photophobic character of AN may arise from the possible formation of dimers which are shown to exist from IR studies. Very few studies have been reported in the literature [6] hence the authors are reporting the protonation constants of maleic acid and L-asparagine in AN-water mixture.

Heavy metals such as cadmium and lead are toxic substances which exert adverse effects on neurological, reproductive, renal and hematological systems in humans and animals. Cadmium and lead can cause significant reduction in gonadotropin binding, which alters the steroidogenic enzyme activity of granulose cells and dysfunctions the production of hormones, leading to infertility [7].

Cadmium is highly toxic and one of the most important environmental pollutants in industrialised countries. It accumulates in the human body and can induce renal dysfunction [8]. Cadmium can also enter the environment through natural causes, such as volcanic activity and forest fires [9]. Cadmium affects many different kinds of organisms, ranging from microbes to humans. Human exposure to cadmium mainly occurs through cigarette smoking, but exposure can also occur through contaminated food, water or air [10]. Cadmium is a known carcinogen to mammals [11]. Lead affects the bones and teeth, the kidneys, the nervous, cardiovascular, immune and reproductive systems [12]. Lead is also harmful to the immune system, causing production of excessive inflammatory proteins [13]. Lead is known to have toxic effects on membrane structure and functions [14]. Erythrocytes have high affinity for lead and are more vulnerable to oxidative damage than many other cells [15].

L-asparagine is the non essential amino acid. L-asparagine has no known toxicity. It is used for biochemical research and preparation of culture media. It is biodegradable, unlikely to accumulate in the food chain. It participates in the function of the brain and nervous system. It is required by the nervous system to maintain equilibrium and is also required for amino acid transformation from one form to the other in the liver. The structure of the L-Asparagine is given below.



Most of the speciation studies are based on the amino acids. There are no good number of reviews with L-Asparagine. So we have chosen the biologically importance of Cd (II), Pb (II) and L-Asparagine, and also studied the formation of complexes at 303.0 K±0.1 K. In order to study the variation of stability constants with dielectric constantans of the AN, I have choose AN-Water mixtures.

MATERIALS AND METHODS

Materials: L-Asparagine (Qualigens, India) solution (0.05mol L^{-1}) was prepared in triple-distilled water by maintaining 0.05 mol L^{-1} nitric acid concentration to increase the solubility. Acetonitrile (Merck, India) was used as received. 2 mol L^{-1} sodium nitrate (Qualigens, India) was prepared to maintain the ionic strength in the titrand. 0.05 mol L^{-1} aqueous solutions of Cd(II) and Pb(II) nitrates were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple-distilled water maintaining 0.05 mol L^{-1} nitric acid to suppress the hydrolysis of metal salts. All the solutions were standardized by standard methods. To assess the errors that might have crept into the determination of the concentrations, the data were subjected to analysis of variance of one way classification [16]. The strengths of alkali and mineral acid were determined using the Gran plot method [17, 18].

Apparatus: The titrimetric data were obtained using ELICO (Model LI-120) pH meter (readability 0.01), which was calibrated with 0.05 mol L^{-1} potassium hydrogen phthalate in acidic region and 0.01 mol L^{-1} borax solution in basic region. The glass electrode was equilibrated in a well stirred Acetonitrile-water mixture containing the inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of Acetonitrile-water mixtures (0-50% v/v) by maintaining an ionic strength of 0.16 mol L^{-1} with sodium nitrate at 303.0 ± 0.1 K. The effect of variation in asymmetry potential, liquid junction potential, activity coefficient, sodium ion error, and dissolved carbon dioxide on the response of glass electrode was accounted for in the form of correction factor [19, 20].

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 Acetonitrile-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 Cd (II) and Pb(II) of metal-to-ligand were carried out with 0.4 mol L^{-1} sodium hydroxide. Other experimental details are given elsewhere [21].

Modeling Strategy: The computer program SCPHD [22, 23] was used to calculate the correction factor. The binary stability constants were calculated with the pH-metric titration data using the computer program MINIQUAD75 [24, 25], which exploits the advantage of a constrained least-squares method in the initial refinement and reliable convergence of the Marquardt algorithm. During the refinement of the binary systems, the correction factor and the protonation constants of L-Asparagine were fixed. The variation of stability constants with the dielectric constants of the medium was analyzed on electrostatic grounds based on solute-solute and solute-solvent interactions.

RESULTS AND DISCUSSION

The results of the final best-fit models that contain the stoichiometry of the complex species and their overall formation constants along with some of the important statistical parameters are given in table 1. Very low-standard deviation in overall stability constants (log β) signifies the precision of these constants. The small values of U_{corr} (sum of squares of deviations in concentrations of ingredients at all experimental points) corrected for degrees of freedom, small values of mean, standard deviation and mean deviation for the systems are validated by the residual analysis [26].

Table 1: Parameters of best fit chemical models of Cd (II) and Pb (II) – L-Asparagine complexes in Acetonitrile-water mixtures.

% v/v AN	log β_{mlh} (SD)			pH-Range	NP	U_{corr}	χ^2	Skewness	Kurtosis	R-factor
	ML_2	ML_2H	ML_2H_2							
Cd(II)										
0	8.33(14)	16.35(16)	23.37(18)	2.0-9.0	75	4.82	16.10	0.14	3.93	0.0153
10	8.62(33)	16.83(34)	23.97(27)	2.0-9.0	69	17.9	19.84	0.21	3.23	0.0300
20	9.39(26)	17.04(26)	23.59(21)	2.0-9.0	70	82.3	9.35	-0.08	3.59	0.0208
30	9.86(28)	17.40(28)	23.77(20)	2.0-9.0	73	105.3	15.19	0.18	3.94	0.0225
40	10.22(17)	17.53(18)	23.79(67)	2.0-9.0	76	52.1	15.65	-0.17	4.29	0.0150
50	10.73(29)	17.88(29)	23.83(11)	2.0-9.0	79	13.9	2.83	0.14	3.17	0.0250
Pb (II)										
0	9.56(31)	15.90(60)	22.41(6)	2.0-6.5	62	2.55	23.55	-0.07	3.29	0.0097
10	9.63(55)	17.22(24)	23.00(9)	2.0-7.0	39	4.23	15.17	-0.04	3.17	0.0146
20	10.50(64)	17.74(30)	22.06(24)	2.2-6.8	44	11.8	15.52	-0.19	3.17	0.0250
30	9.98(96)	17.05(42)	22.85(16)	2.0-7.0	38	12.0	12.74	-0.07	2.63	0.0212
40	10.44(21)	17.67(12)	22.64(5)	2.0-8.0	26	0.80	19.23	-0.33	3.14	0.0044
50	10.92(95)	18.21(44)	22.76(25)	2.0-7.0	72	38.3	81.63	0.61	4.47	0.0370

Ucorr = U/ (NP − m) X 10^8; m = number of species; NP = number of experimental points; SD = standard devastation

Residual Analysis: In data analysis with least squares methods, the residuals (the differences between the experimental data and the data simulated based on model parameters) are assumed to follow Gaussian or normal distribution. When the data are fit into the models, the residuals should ideally be equal to zero. If statistical measures of the residuals and the errors assumed in the models are not significantly different from each other, the model is said to be adequate. Further, a model is considered adequate only if the residuals do not show any trend. Respecting the hypothesis that the errors are random, the residuals are

tested for normal distribution. Such tests are χ^2, Skewness, Kurtosis and R-factor. These statistical parameters show that the best-fit models portray the metal-ligand species in Acetonitrile-water mixtures, as discussed below. In the present study, the kurtosis values indicate that the residuals form leptokurtic pattern. The values of skewness recorded in Table 1 are between -0.17 and 0.21 for Cd (II), -0.33 and 0.61 for Pb(II). These data evince that the residuals form part of a normal distribution. Hence, least square method can be applied to the present data. The sufficiency of the model is further evident from crystallographic R-values. These statistical parameters thus show that the best-fit models portray the metal-ligand species in Acetonitrile media.

Effect of Systematic Errors on Best Fit Model: 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, an investigation was undertaken by introducing pessimistic errors in the influential parameters 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 > metal > ligand. Some species were even rejected when errors were introduced in the concentrations. The rejection of some species and increased standard deviations in the stability constants on introduction of errors confirm the suitability of the experimental conditions (concentrations of reactants) and choice of the best-fit models.

Table 2: Effect of errors in influential parameters on Pb(II)-Asparagine complex stability constants in 10% v/v Acetontrile-water mixture.

Ingredient	% Error	Log β_{mlh}(SD)		
		120	121	122
Acid	0	9.63(55)	17.22(24)	23.00(9)
	-5	15.08(27)	21.84(24)	25.50(26)
	-2	11.64(37)	19.07(17)	23.91(9)
	+2	9.23(52)	16.60(33)	22.56(13)
	+5	8.47(29)	13.14(378)	Rejected
Alkali	-5	7.64(105)	Rejected	Rejected
	-2	8.77(62)	15.92(59)	23.14(21)
	+2	11.35(31)	18.77(14)	23.57(7)
	+5	14.50(13)	20.97(8)	24.36(9)
Ligand	-5	9.64(43)	17.10(24)	22.80(9)
	-2	9.64(49)	17.17(23)	22.93(9)
	+2	9.63(60)	17.27(23)	23.08(9)
	+5	9.64(70)	17.35(23)	23.19(9)
Metal	-5	9.80(48)	17.30(24)	23.06(9)
	-2	9.69(52)	17.25(24)	23.02(9)
	+2	9.58(57)	17.20(23)	22.98(9)
	+5	9.49(63)	17.15(23)	22.95(9)

Effect of Solvent: The variation of protonation constant or change in free energy with co-solvent content depends upon two factors, viz., electrostatic and non-electrostatic. Born's classical treatment holds good in accounting for the electrostatic contribution to the free energy change [27]. According to this treatment, the energy of electrostatic interaction is related to dielectric constant. Hence, the logarithm of overall stability constant (log β) should vary linearly as a function of the reciprocal of the dielectric constant (1/D) of the medium. These plots (Figure 1) in AN-water mixtures show that the log β values are linearly increasing with decreasing dielectric constant values.

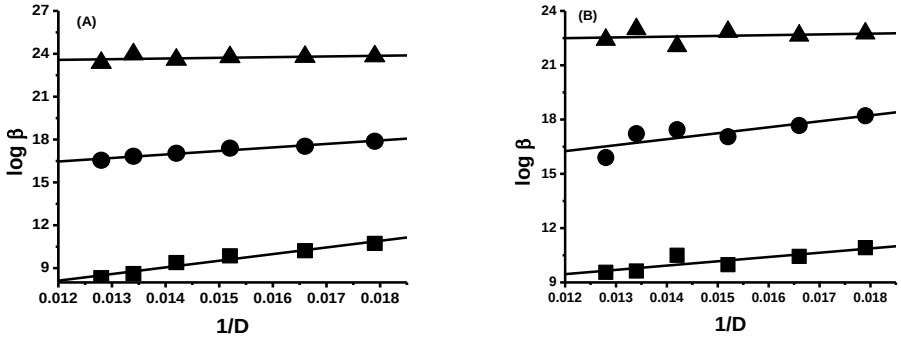


Figure 1: Variation of overall stability constant values of metal- L-Asparagine complexes with Acetonitrile-water mixtures (A) Cd(II) and (B) Pb(II); (■)log β_{ML2}; (●)log β_{ML2H}; (▲)log β_{ML2H2}.

Distribution Diagrams: L-Asparagine is a bidentate ligand that has one dissociable (carboxyl group) and one associable (amino) protons. The different forms of L-Asparagine are LH_2^+, LH, and L^- in the pH range 1.5-5.0, 1.5-11.0, and 5.0-11.0, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present investigation reveals the existence of ML_2, ML_2H, ML_2H_2 for Cd(II) and Pb(II). The ML_2 species is the predominant species (Figure 2) at higher pH and ML_2H_2 is the predominant species at lower pH among all the binary complexes. Low concentration of free metal ion (FM) indicates the strong complexing nature of L-Asparagine. The formation of various binary complex species is shown in the following equilibria. Some typical distribution diagrams of Acetonitrile-water media are shown in Figure 2. The species ML_2H_2, ML_2H, ML_2 are formed in the pH range of 3.0-8.5. ML_2H_2 is formed at lower pH. ML_2H and ML_2 formed with the increasing pH. ML_2H and ML_2 species percentage successively increases with increasing pH. Successive deprotonation of ML_2H_2 forms ML_2H beyond a pH 8.5 [Equilibria (6) and (7)]. ML_2 formed at higher pH with high percentage [Equilibria (9), (10), (19) and (22). The percentage of the ML_2 species increases successively with increase in pH up to 8.5. The concentration of ML_2H_2 species decreased, while the concentration of ML_2H and ML_2 increased in the pH range 6.0-8.5.

$M(II) + LH_2^+ \rightleftharpoons MLH^{2+} + H^+$ (1)

$MLH^{2+} \rightleftharpoons ML^+ + H^+$ (2)

$M(II) + LH_2^+ \rightleftharpoons ML^+ + 2H^+$ (3)

$M(II) + 2LH_2^+ \rightleftharpoons ML_2H_2^{2+} + 2H^+$ (4)

$MLH^{2+} + LH_2^+ \rightleftharpoons ML_2H_2^{2+} + H^+$ (5)

$ML_2H_2^{2+} \rightleftharpoons ML_2H^+ + H^+$ (6)

$MLH^{2+} + LH \rightleftharpoons ML_2H^+ + H^+$ (7)

$ML^+ + LH_2^+ \rightleftharpoons ML_2H^+ + H^+$ (8)

$ML_2H^+ \rightleftharpoons ML_2 + H^+$ (9)

$ML^+ + LH \rightleftharpoons ML_2 + H^+$ (10)

$ML_2 + LH \rightleftharpoons ML_3^- + H^+$ (11)

$M(II) + 3LH_2^+ \rightleftharpoons ML_3H_3^{2+} + 3H^+$ (12)

$MLH^{2+} + 2LH_2^+ \rightleftharpoons ML_3H_3^{2+} + 2H^+$ (13)

$ML_3H_3^{2+} \rightleftharpoons ML_3H_2^+ + H^+$ (14)

$ML^+ + 2LH_2^+ \rightleftharpoons ML_3H_2^+ + 2H^+$ (15)

$ML_3H_2^+ \rightleftharpoons ML_3H^- + H^+$ (16)

$ML_3H^- \rightleftharpoons ML_3^{2-} + H^+$ (17)

$M(II) + 2LH_2^+ \rightleftharpoons ML_2H^+ + 3H^+$ (18)

$M(II) + 2LH_2^+ \rightleftharpoons ML_2 + 4H^+$ (19)

$M(II) + 3LH_2^+ \rightleftharpoons ML_3H_2^+ + 4H^+$ (20)

$M(II) + 3LH_2^+ \rightleftharpoons ML_3H + 5H^+$ (21)

$M(II) + 3LH_2^+ \rightleftharpoons ML_3^- + 6H^+$ (22)

$ML_2H_2 \rightleftharpoons ML_2^{2-} + 2H^+$ (23)

$ML_3H_3 \rightleftharpoons ML_3H^{2-} + 2H^+$ (24)

$ML_3H_3 \rightleftharpoons ML_3^{3-} + 3H^+$ (25)

Structures of complexes: In Acetonitrile-water mixtures, Cd and Pb -L-Asparagine system assumes various coordination modes depending on the pH value. When the second donor site of L-Aspragine is a nitrogen atom, marked bidentate behavior is frequently found, more so when the additional chelation results in a five membered ring (Figure 3). Octahedral structures are proposed to the complexes of all the metal ions. The VSEPR theory suggests that Cd(II) and Pb(II) complexes shall be octahedral because there are six outer electron pairs.

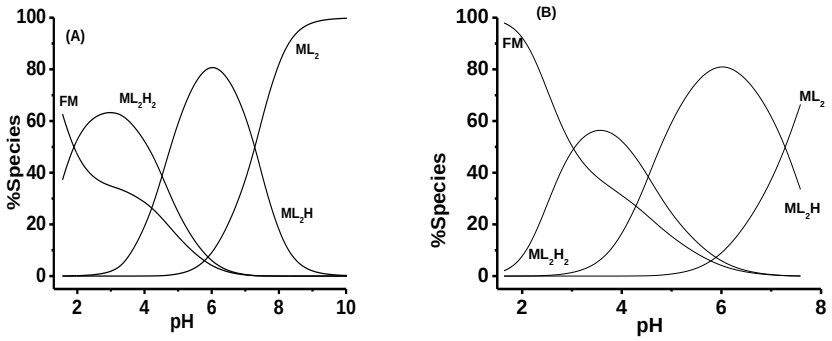


Figure 2: Distribution diagrams of binary complexes of L-Asparagine in 50% v/v Acetonitrile -water mixture: (A) Cd(II) and (B) Pb(II).

Amino nitrogen atoms can associate with hydrogen ions in physiological pH ranges. Hence, there is often significant competition between hydrogen and metal ion for this second donor site. This situation results in the simultaneous existence of a number of equilibria producing an array of successively protonated complexes. Hence, protonated complex species are detected in the present study. Amino nitrogen and carboxyl oxygen of L-Asparagine participate in bonding with metal ions. This argument supports the structures of complexes proposed in figure 3.

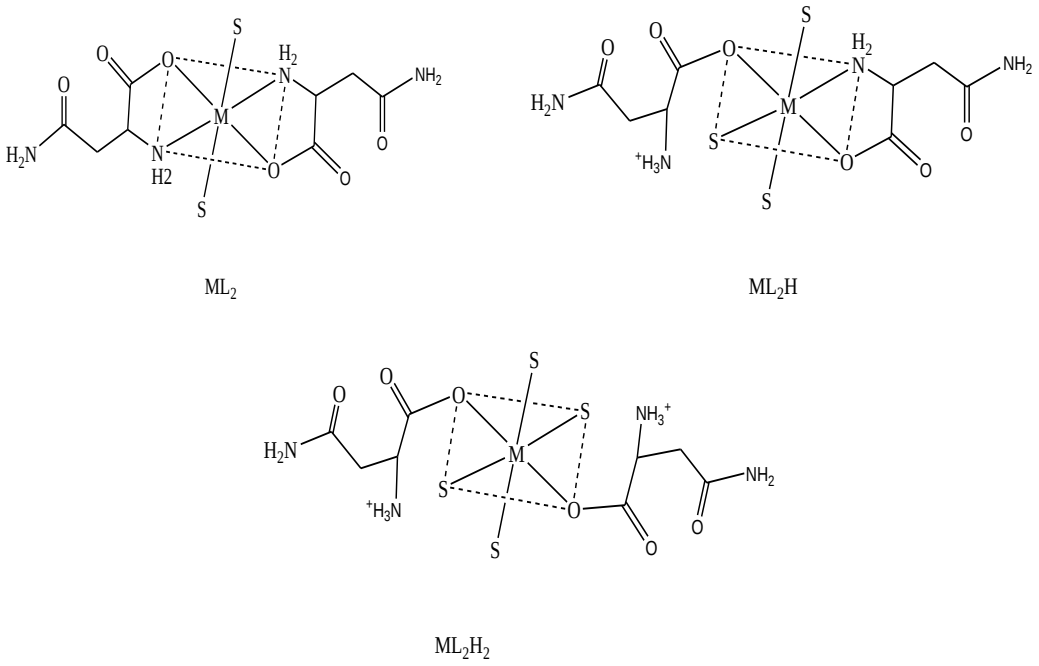


Figure 3: Structures of binary complexes of L-Asparagine with M (II).
Where S is either solvent or water molecule

CONCLUSIONS

1. The present biomimetic studies of metal ion complexes with L-Asparagine in Acetonitrile -water mixtures indicate that all the complexes were protonated in acidic pH values.
2. The predominant species detected were ML_2, ML_2H, and ML_2H_2.
3. The log β values linearly vary with reciprocal of dielectric constant values of the medium, indicating the dominance of electrostatic forces over non-electrostatic forces.
4. The order of the compounds influencing the magnitudes of the stability constants due to the incorporation of errors was alkali > acid > ligand > metal.
5. The higher concentration of free metal in low pH values make the metal more bioavailable, more so in the case of toxic metals. At higher pH values, the higher concentrations of complex chemical species indicate that the metals are more amenable for transportation at higher pH values.

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