Research Article

EFFECT OF ANIONIC SURFACTANT ON BINARY COMPLEXES OF L-ARGININE WITH Cd(II) AND Pb(II)

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ARTICLE INFO	ABSTRACT
	Chemical speciation of binary complexes of L-Arginine (Arg) with Cd(II) and Pb(II) in presence of water - anionic surfactant mixtures in the concentration range of 0.0-2.5% w/v sodium lauryl sulphate (SLS) was investigated pH-metrically at a temperature of 303 K and at an ionic strength of 0.16 mol L^{-1}. The stability constants were determined using the computer program MINIQUAD 75. The number of species in the models is chosen based on exhaustive modeling. The appropriateness of experimental conditions is verified by introducing errors intentionally in the concentrations of ingredients. The predominant species detected were ML and ML$_2$ for both Cd(II) and Pb(II). The trend in the variation of stability constants with the mole fraction of SLS was explained on the basis of electrostatic and non-electrostatic forces. The species distribution and the plausible equilibria for the formation of the species are also presented.

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 behaviour of protein residues with the metal ion. Therefore, extensive studies have been carried on chemical speciation of toxic and essential metal ions with α-amino acids [Ananda Kumar et al., 2011; Himabindu et al., 2012]. The species refined and their relative concentrations under the experimental conditions represent the possible forms of amino acids in bio fluid.

L-arginine is an important amino acid found in the protein food. It is α-amino acid that is used in biosynthesis of proteins. Arg may be a useful drug in treatment under lead intoxication. Arg participates in many important and diverse biochemical reactions associated with normal physiology of an organism [Halyna tkachenko et al., 2007].

Cadmium is a known carcinogen to mammals [Bertin et al, 2006]. Cadmium, a potentially toxic metal, has been shown to accumulate in plants, where it is detoxified by binding to phytochelatins [Wagner, 1984; Steffens, 1990; Cobbett et al., 1999; Rauser, 1990], a family of thiol-rich peptides [Galazyn-Sidorczuk et al, 2009]. Lead is known to have toxic effects on membrane structure and functions [Lin et al, 2007]. Erythrocytes have high affinity for lead and are more vulnerable to oxidative damage than many other cells

[Donaldson et al, 1993]. Lead intake by humans can be due to the consumption of crop plants grown on soils with high plant-available metal concentrations [Gran, 1952].

Sodium Lauryl Sulphate (SLS) or sodium dodecyl sulphate (SDS) is an anionic surfactant used in many cleaning and hygiene products, food, pharmaceuticals and cosmetics. Hence, chemical speciation of Arg with some toxic metal ions, such as Cd and Pb in SLS-water mixtures are reported in this paper.

Experimental Procedure

MATERIALS

Solutions of Cd(II) and Pb(II) nitrates (0.1 mol dm^{-3}) were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple distilled water maintaining 0.05 mol dm^{-3}acid (HNO$_3$) to suppresses the hydrolysis of metal salts. 0.05 mol dm^{-3} aqueous solution of L-Arganine (GR grade, E-Merck, Germany) was prepared by dissolving in triple distilled water. To increase the solubility of ligand, 0.05 mol dm^{-3} nitric acid was maintained in the solution. GR sample of sodium lauryl sulfate (SLS, Qualigens, India) was used as such and its purity was checked by determining critical micellar concentration (CMC) conductometrically. The CMC value of SLS was 0.0081 mol dm^{-3} at 303K. Sodium hydroxide (Qualigens, India) of 0.4 mol dm^{-3} was prepared. All the solutions were standardized by standard methods. The strengths of alkali and mineral acid were determined using the Gran plot method [Gran, 1988]. To assess the errors that might have crept into the determination of the concentrations, the data were

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subjected to analysis of variance of one way ANOVA [Rao *et al.*, 2005].

Procedure

A Systronics (Model 335, India) digital pH meter of 0.01 readability (0-14 pH) in conjunction with a glass combination pH electrode was used to monitor changes in hydrogen ion concentration. The glass electrode was equilibrated in a well-stirred micellar solution containing an inert electrolyte. All the titrations were performed at 303.0 ± 0.1 K in a medium containing varying concentrations of SLS (0.5-2.5% w/v) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium nitrate. In each of the titrations, the titrand consisted of approximately 1m mol mineral acid in a total volume of 50 cm^3. Titrations with different metal-to-ligand ratios (1:2.5, 1:3.5 and 1:5) were carried out with 0.4 mol dm^{-3} sodium hydroxide.

Modelling Strategy

The computer program SCPHD [Rao, 1989] was used to calculate the correction factor. The binary stability constants were calculated from pH-metric titration data using the computer program MINIQUAD75 [Gans, 1976], which exploit 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 Arg were fixed. The variation of stability constants with the mole fraction of the medium was analysed 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.

with little dispersion. Kurtosis is a measure of the peakedness of the error distribution near a model value. For an ideal normal distribution kurtosis value should be three (mesokurtic). If the 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 and very few form mesokurtic patterns. The values of skewness recorded in Table are between -0.99 and -0.02. These data suggest that the residuals form a part of normal distribution. Hence, least-squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic R-values. These statistical parameters thus show that the best fit models portray the metal–ligand species in micellar media.

Effect of Systematic Errors on Best Fit Model

MINIQUAD75 does not have an inbuilt provision to study the effect of systematic errors in the concentrations of the ingredients and electrode calibration, on the magnitude of equilibrium constants. In order to obtain the best 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 > ligand > metal. Some species were even rejected when errors are 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 ingredients) and choice of the best fit models.

Effect of Surfactant

The variations of stability constants (log β) with mole fraction of different micellar media are shown in Figure1. The non-linear variation in the stabilities of binary complexes with the mole fraction of surfactant depends upon the polarity of the medium, charge on the micellar surface and on the non-electrostatic forces/hydrophobic interactions operating between the complex species and micellar surface.

Table 1 Parameters of best fit chemical models of M(II) – L-Arginine complexes in SLS-water medium

% w/v SLS	Log β_{mlh} (SD)			NP	U_{corr}	Skew-ness	χ^2	R-factor	kurtosis	pH range
	110	111	120							
					Cd(II)					
0.0	15.70(32)	19.68(10)	21.75(45)	45	11.50	-.21	2.55	0.0523	2.55	3.7-8.7
0.5	17.01(17)	21.25(90)	23.29(11)	44	23.07	-.81	4.16	0.0733	4.16	3.7-8.7
1.0	17.37(21)	22.00(49)	23.34(12)	44	19.12	-.64	3.18	0.0648	3.18	3.7-8.7
1.5	17.88(16)	22.68(20)	24.74(29)	32	30.92	-.36	2.37	0.0758	2.37	3.7-8.7
2.0	16.79(19)	20.00(36)	23.11(16)	44	24.14	-.02	4.72	0.0712	4.72	3.7-8.7
2.5	16.43(24)	20.13(26)	23.12(12)	42	24.31	-.11	5.54	0.0729	5.54	3.7-8.7
					Pb(II)					
0.0	15.05(17)	19.70(38)	21. 42(20)	45	96.00	-.05	5.15	0.0477	3.07	3.7-8.7
0.5	15.20(05)	****	22.02 (05)	55	17.79	-.20	32.88	0.0531	5.17	3.7-8.7
1.0	17.69(08)	22.53(14)	23.76(13)	44	23.83	-.99	6.69	0.0734	4.33	3.7-8.7
1.5	18.16(22)	23.48(17)	23.98(17)	43	23.37	-.71	4.64	0.0701	4.45	3.7-8.7
2.0	17.29(14)	22.79(21)	23.00(23)	40	21.08	-.68	7.47	0.0645	3.70	3.7-8.7
2.5	16.27(17)	20.22(30)	22.030(16)	30	25.70	-.30	6.60	0.0762	3.41	3.8-8.7

U_{corr}= U/(NP-m)X10^8, where m = number of species; NP=Number of experimental points; SD=Standard deviation

Residual Analysis

Small values of mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean

The species should be stabilized in the micellar medium with opposite charges due to electrostatic interactions but these charged species should be destabilized due to the decreased

dielectric constant of the medium. This trend reflects in all M(II)-Arg complexes (Figure 1).

Table 2 Effect of errors in influential parameters on the stability constants of Pb(II)-Arg complexes in 1.0% w/v SLS-water medium.

| Ingredient	% Error	log β (SD)		
		110	111	120
	0	17.69(08)	22.53(14)	23.76(13)
	-5	Rejected	Rejected	22.90(81)
Alkali	-2	17.32(08)	21.98(16)	23.24(16)
	+2	17.81(26)	Rejected	23.93(10)
	+5	17.90(48)	23.15(16)	Rejected
	-5	18.11(05)	22.84(10)	Rejected
Acid	-2	16.18(10)	Rejected	23.00(13)
	+2	15.91(20)	21.37(27)	21.39(27)
	+5	16.92(56)	22.01(20)	22.67(19)
	-5	17.86(07)	22.50(13)	24.08(10)
Ligand	-2	17.18(06)	21.12(24)	23.59(09)
	+2	17.49(07)	21.19(33)	23.87(10)
	+5	15.51(24)	Rejected	24.15(14)
	-5	17.19(08)	22.07(15)	23.24(14)
Metal	-2	17.18(06)	21.79(13)	23.25(11)
	+2	17.68(07)	22.44(14)	23.77(12)
	+5	17.87(07)	22.62(14)	23.98(12)
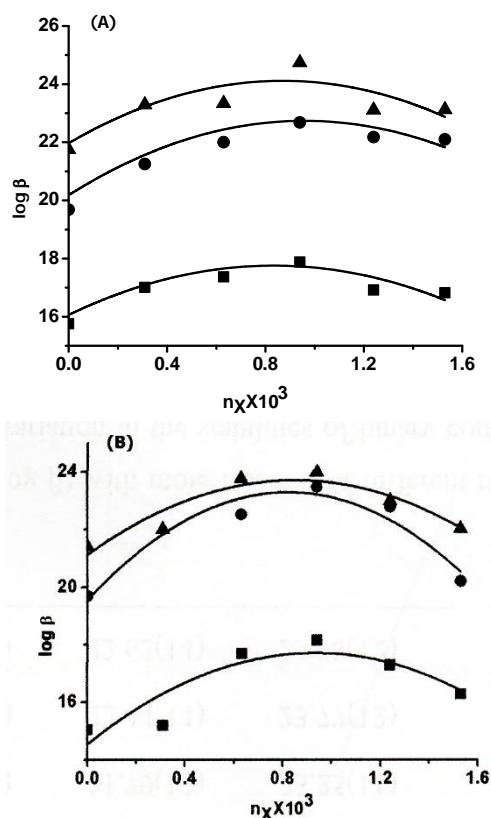
Figure 1 Variation of overall stability constant values of metal-Arg complexes with mole fraction ($n_x \times 10^3$) of SLS-water mixtures (**A**) Cd(II) and (**B**) Pb(II), (■) log β_{110}, (●)log β_{111},(▲)log β_{120}.

Distribution Diagrams

The distribution plots (Figure 2) of various forms of Arg exhibit the existence of LH_2^+, LH and L^- in different pH ranges. As the alkali is added to the titrand containing the ligands, the protonated forms of the ligands lose their protons. In the pH range of study, Arg loses carboxylic and amino protons successively. The binary complexes formed by Arg with Cd(II) and Pb(II) in the present study are MLH, ML, and ML_2. The ML_2 species is the predominant species (Figure 2) among all the binary complexes. Low concentration of free

metal ion (FM) indicates the strong complexing nature of arginine. The formation of various binary complex species is shown in the following equilibria.
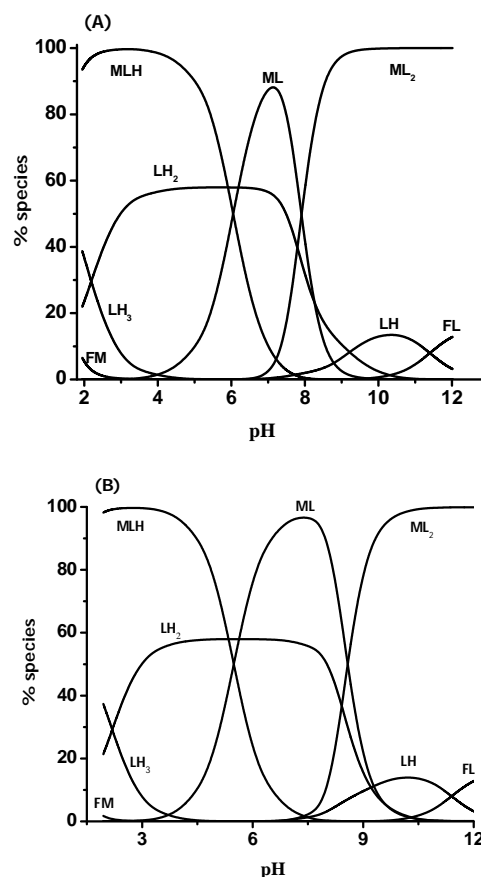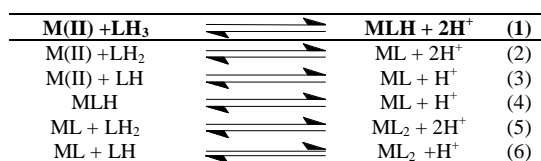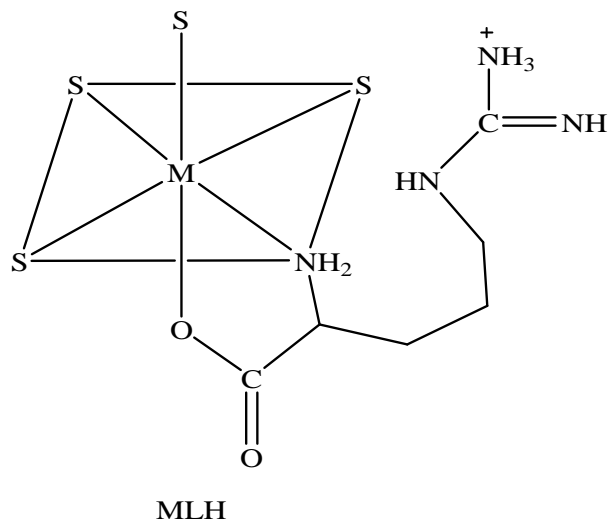
$M(II) + LH_3$	⇌	$MLH + 2H^+$	(1)
$M(II) + LH_2$	⇌	$ML + 2H^+$	(2)
$M(II) + LH$	⇌	$ML + H^+$	(3)
MLH	⇌	$ML + H^+$	(4)
$ML + LH_2$	⇌	$ML_2 + 2H^+$	(5)
$ML + LH$	⇌	$ML_2 + H^+$	(6)

Figure 2 Distribution diagrams of Arg complexes in 2.0% w/v SLS-water medium. (A) Cd(II) and (B) Pb(II).

Structures of complexes

In aqueous solutions metal ions are coordinated by six water molecules.

MLH

Amino acids replace water molecules and form metal-amino acid complexes. Depending upon the nature of the ligands and metal ions and based on the basic chemical knowledge tentative structures of the complexes are proposed as shown in Figure 3. Carboxyl oxygen and amino nitrogen of Arg are bonded to the metal ions. Amino nitrogen can associate with hydrogen ions in physiological pH ranges. Hence there is often significant competition between hydrogen and metal ion for this donor site and it results in the formation of protonated species. Hence protonated complex species are detected in the present study.
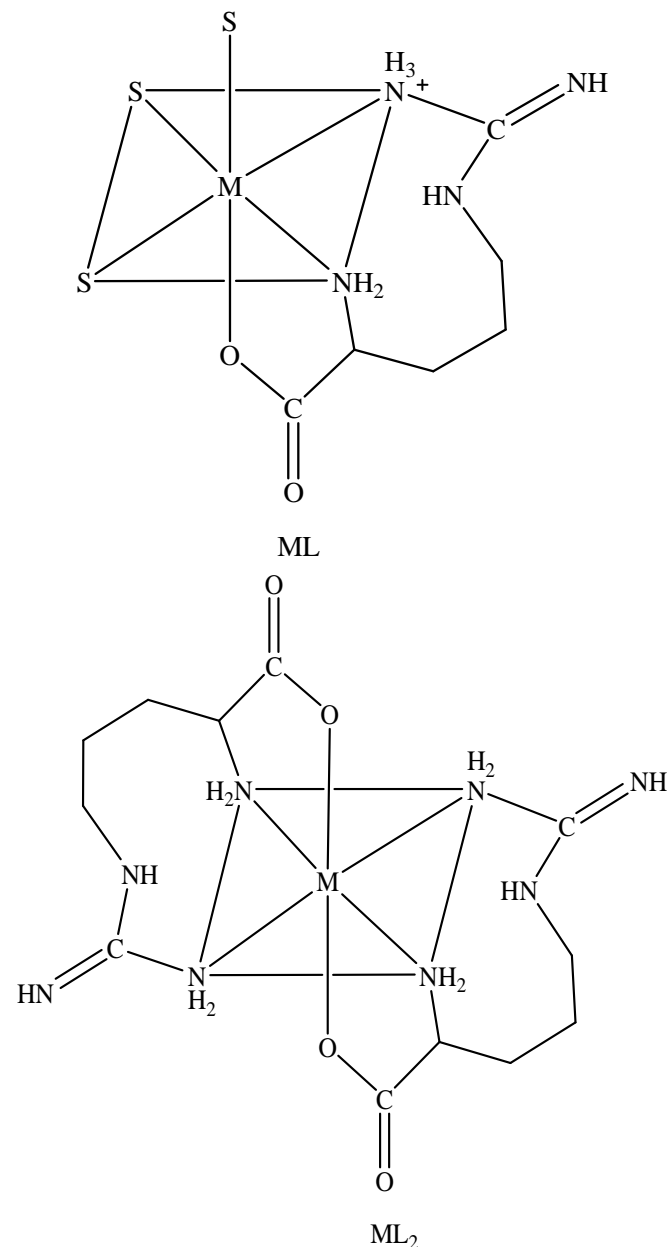
CONCLUSIONS

1. The binary species detected are CdL, CdL_2, CdLH, PbL, PbL_2, PbLH. These models are validated by statistical treatment of data.
2. The non-linear variation of stability constants as a function of mole fraction of the medium indicates the dominance of non-electrostatic forces over electrostatic forces.
3. Some species are stabilized due to electrostatic interactions and some are destabilized due to the decreased dielectric constant.
4. The order of ingredients in influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal.

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Figure 3 Structures of of metal-Arg complexes, where S is either solvent or water molecule.

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