*Available online at* www.joac.info

ISSN: 2278-1862

**Journal of Applicable Chemistry**

2017, 6 (4): 526-532

(International Peer Reviewed Journal)

# Speciation of Binary Complexes of Cd(II) and Pb(II) with L-Glutamine in Anionic Micellar Medium

**P. Sujatha[1], Y. Vamsi Kumar[1], P. Surya Sunitha[2] and G. Himabindu[1]***

1. Department of Engineering Chemistry, Andhra University, Visakhapatnam-530 003, **INDIA**
2. SKBR College, Amalapuram, East Godavari District-533201, **INDIA**

Email: himabinduauce@gmail.com

Accepted on 17th July 2017, Published online on 27th July 2017

## ABSTRACT

*Speciation of binary complexes of Cd (II) and Pb (II) with L-Glutamine (Gln) in presence of water - anionic surfactant mixtures in the concentration range of 0.0-2.5% w/v SLS have been studied pH-metrically at a temperature of 303 K and at an ionic strength of 0.16mol $L^{-1}$. The stability constants were determined using the computer program MINIQUAD 75. The selection of best fit chemical models is based on statistical parameters and residual analysis using crystallographic R-factor and sum of squares of residuals in all mass-balance equations. The predominant species detected were ML, $ML_2H$ 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. Distribution of the species with pH at different compositions of SLS-water media was also presented.*

**Keywords:** Chemical speciation, L-Glutamine, Anionic surfactant, Stability constants, MINIQUAD 75.

## INTRODUCTION

In human blood plasma Glutamine is the most abundant element at concentrations of0.6 to0.9 mmol $L^{-1}$ [1]. Gln when orally loaded increases plasma hGH levels by stimulating the anterior pituitary gland [2]. It is depleted under stress conditions, such as malignancy [3], and the development of cachexia is accompanied by massive depletion of Gln in skeletal muscle. This results in a negative impact on the function of host tissues that are dependent upon adequate stores of Gln for optimal functioning [4]. Furthermore, the extent of normal tissue damage from chemotherapy as well as radiation may be influenced by the presence of adequate tissue Gln stores [5]. Studies have indicated that Gln supplementation is well tolerated and potentially effective in preventing side effects for patients receiving high-dose chemotherapy and bone marrow transplantation [6].

In all living systems, the biochemical functions of both essential and toxic metals are mediated through specific chemical species or complexes and the concentrations of these particular species are important for the biochemical reactions but not just the total concentration of the metal in the system. Therefore, extensive studies have been carried on chemical speciation of toxic and essential metal ions with α-aminoacids [7, 8].

Cadmium is an abundant nonessential element present in food, water and the environment and it accumulates in human tissues, particularly in the lungs, liver, kidneys, brain, heart and testes [9]. Cd (II) can induce oxidative stress and cause oxidative disorders in both animal cells [10] and plants [11]. Lead is known to have toxic effects on membrane structure and functions [12]. Erythrocytes have high affinity for lead and are more vulnerable to oxidative damage than many other cells [13]. Lead intake by humans can be due to the consumption of crop plants grown on soils with high plant-available metal concentrations [14].

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, speciation studies of Gln with some toxic metal ions, such as Cd and Pb in SLS-water mixtures are reported in this paper.

## MATERIALS AND METHODS

**Materials:** 0.05 mol $dm^{-3}$ aqueous solution of L-Glutamine (GR grade, E-Merck, Germany) was prepared by dissolving sample in water. To increase the solubility of ligand, 0.05 mol $dm^{-3}$ concentration was maintained in the solution.GR samples of sodium lauryl sulphate (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 $dm^{-3}$. Solutions of Cd (II) and Pb (II) 0.1 mol $dm^{-3}$ by dissolving G.R. Grade (E-Merck, Germany) salts in triple distilled water maintaining 0.05 mol $dm^{-3}$ to suppresses the hydrolysis of metal salts. Sodium hydroxide (Qualigens, India) of 0.4 mol $dm^{-3}$. 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 [15]. The strengths of alkali and mineral acid were determined using the Gran plot method [16, 17].

**Procedure:** A Systronics (Model 335, India) digital pH meter of 0.01readability (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 [18] was used to calculate the correction factor. The binary stability constants were calculated from pH-metric titration data using the computer program MINIQUAD75 [19], 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 Glutamine 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.

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

| %w/v SLS | log βmlh (SD) | | | NP | $U_{corr}$ | Skew-ness | $\chi^2$ | R-factor | kurtosis | pH range |
|---|---|---|---|---|---|---|---|---|---|---|
| | 110 | 111 | 120 | | | | | | | |
| | | | | | Cd(II) | | | | | |
| 0.0 | 3.90(12) | 10.59(10) | 6.88(09) | 122 | 17.87 | -.24 | 34.57 | 0.0150 | 3.69 | 2.0-8.9 |
| 0.5 | 3.46(28) | 10.91(32) | 6.76(20) | 68 | 26.76 | -.06 | 52.09 | 0.0240 | 2.95 | 2.6-8.7 |
| 1.0 | 3.22(15) | 10.57(22) | 6.00(11) | 77 | 43.39 | -.02 | 19.54 | 0.0170 | 5.69 | 2.5-9.1 |
| 1.5 | 3.23(24) | 10.90(23) | 6.12(16) | 87 | 13.45 | .20 | 43.70 | 0.0260 | 6.05 | 2.3-9.0 |
| 2.0 | 3.90(19) | 10.47(15) | 7.41(12) | 100 | 24.12 | .43 | 22.07 | 0.0200 | 3.80 | 2.1-8.5 |
| 2.5 | 2.91(37) | *** | 5.75(20) | 101 | 126.0 | .26 | 13.31 | 0.0340 | 4.13 | 2.0-8.4 |
| | | | | | Pb(II) | | | | | |
| 0.0 | 4.50(14) | 10.14(26) | 7.59(19) | 107 | 65.99 | 7.56 | 217.04 | 0.0280 | 110.8 | 1.8-8.7 |
| 0.5 | 4.30(21) | 10.13(35) | 7.70(19) | 100 | 75.69 | 8.00 | 193.0 | 0.0280 | 121.0 | 2.1-8.7 |
| 1.0 | 3.90(24) | 10.41(48) | 6.68(23) | 75 | 49.40 | 0.18 | 24.14 | 0.0320 | 4.17 | 2.1-8.7 |
| 1.5 | 3.64(15) | 10.90(19) | 6.38(14) | 96 | 17.21 | -0.08 | 18.35 | 0.0340 | 4.23 | 2.1-8.7 |
| 2.0 | 3.62(26) | 10.00(61) | 6.16(22) | 87 | 65.09 | 0.01 | 38.25 | 0.0325 | 4.04 | 1.9-8.7 |
| 2.5 | 3.14(74) | 10.12(64) | 6.04(18) | 55 | 80.87 | 0.29 | 48.89 | 0.0330 | 4.32 | 1.9-8.7 |

$U_{corr}$= U/(NP-m)X$10^8$, where m = number of species; NP=Number of experimental points; SD=Standard deviation

**Residual Analysis:** The results of the 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. A very low standard deviation values indicates the precision of these parameters. The small values of $U_{corr}$ (the sum of squares of deviations in concentrations of ingredients at all experimental points) corrected for degrees of freedom, indicate that the model can represent the experimental data. Small values of mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean 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 -0.24 and 8.00. 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:** 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.

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

| Ingredient | % Error | log β (SD) | | |
|---|---|---|---|---|
| | | 110 | 111 | 120 |
| | 0 | 3.91(24) | 10.41(48) | 6.68(23) |
| Alkali | -5 | 3.16(18) | Rejected | Rejected |
| | -2 | 3.36(21) | Rejected | 5.87(16) |
| | +2 | 4.52(28) | 10.96(37) | 7.61(28) |
| | +5 | 5.63(67) | 13.76(25) | 24.93(13) |
| Acid | -5 | 5.39(48) | 11.64(53) | 8.73(49) |
| | -2 | 5.39(48) | 11.63(53) | 8.74(49) |
| | +2 | 3.84(24) | 10.14(69) | 6.70(22) |
| | +5 | 3.20(26) | Rejected | 5.83(17) |
| Ligand | -5 | 3.73(21) | Rejected | 6.79(17) |
| | -2 | 3.76(24) | 9.44(24) | 6.72(21) |
| | +2 | 3.86(24) | 10.21(62) | 6.70(22) |
| | +5 | 3.94(23) | 10.47(43) | 6.69(22) |
| Metal | -5 | 3.89(26) | 10.22(64) | 6.83(23) |
| | -2 | 3.87(25) | 10.21(63) | 6.74(23) |
| | +2 | 3.84(24) | 10.20(61) | 6.64(22) |
| | +5 | 3.82(23) | 10.20(60) | 6.56(21) |

**Effect of Surfactant:** The variations of stability constants (log β) with mole fraction of different micellar media are shown in figure1. The stabilities of binary complexes varied almost linearly with the mole fraction of the surfactant. This linear variation, due to the dielectric constant of the medium, decreases with increasing concentration of the surfactant [20]. The non-linear variation 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. 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)-Gln complexes (Figure 1).

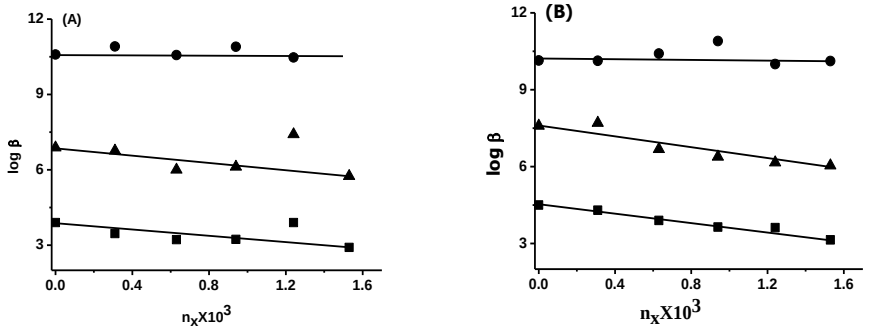


**Figure 1.** Variation of overall stability constant values of metal-Gln complexes with mole fraction ($n_x \times 10^3$) of SLS-water mixtures (**A**) Cd(II) and (**B**) Pb(II), (■) log β110, (●)log β120, (▲)log β111

**Distribution Diagrams:** The distribution plots (Figure 2) of various forms of glutamine 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 proton. In the pH range of study, Gln loses carboxylic and amino protons successively. The binary complexes formed by Gln 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 glutamine. The formation of various binary complex species is shown in the following equilibria.

$$M(II) + LH_2 \rightleftharpoons MLH + H^+ \quad (1)$$

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

$$M(II) + LH \rightleftharpoons ML + H^+ \quad (3)$$

$$MLH \rightleftharpoons ML + H^+ \quad (4)$$

$$ML + LH_2 \rightleftharpoons ML_2 + 2H^+ \quad (5)$$

$$ML + LH \rightleftharpoons ML_2 + H^+ \quad (6)$$

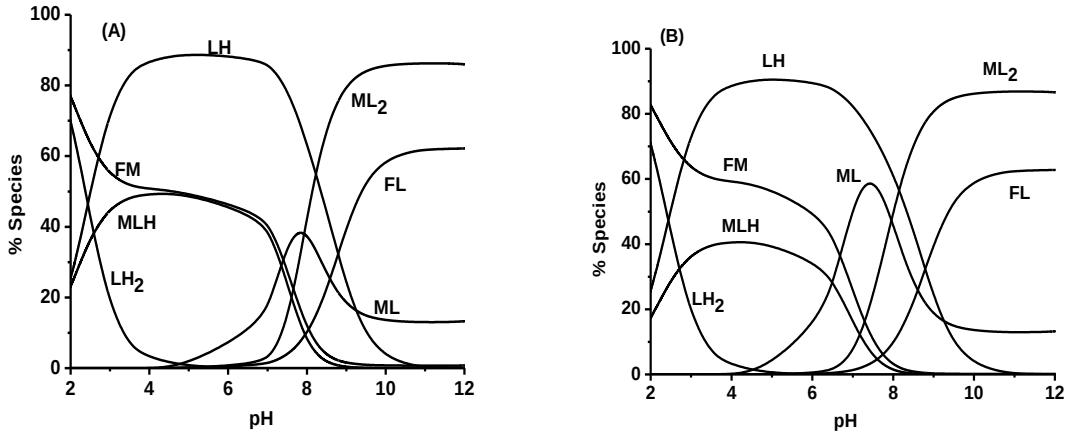


**Figure 2.** Distribution diagrams of Gln complexes in 1.0% w/v SLS-water medium. (A) Cd(II) (B) and (B) Pb(II).

## APPLICATIONS

Speciation determines the behavior of toxic metals in a system, and in the human organism speciation has a great effect on bioavailability, distribution and toxicity. The studies carried out on these systems under the present experimental conditions are useful to understand the role played by the active site cavities in biological molecules. Hence, the speciation studies on the metal-ligand equilibria of L-Gln with Cd and Pb in varying compositions of SLS – water mixtures have been carried out.

## 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 linear or almost linear variation of stability constants as a function of mole fraction of the medium indicates the dominance of electrostatic forces over non-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.

## ACKNOWLEDGEMENTS

The authors (P.Sujatha) thank the University Grants Commission, Government of India, New Delhi, for financial support under Faculty Development Programme.

## REFERENCES

[1] J. Fürst, P. Norée LO, E. Vinnars, Intracellular free amino acid concentration in human muscle tissue. *J Appl Physiol*, **1974,** 36(6), 693–697.
[2] T.C. Welbourne, Increased plasma bicarbonate and growth hormone after an oral glutamine load, *Am. J. Clin. Nutr*, **1995,** 61, 1058– 1061.
[3] J.M. Lacey, D.W. Wilmore, Is glutamine a conditionally essential amino acid? *Nutr. Rev.*, **1990,** 48, 297–309.
[4] D.L. Bartlett, S.Charland, M.H. Torosian, Effect of glutamine on tumor and host growth, *Ann. Surg. Oncol*, **1995,** 2, 71–76.
[5] D.M. Savarese, G. Savy, L. Vahdat, P.E. Wischmeyer, B. Corey, Prevention of chemotherapy and radiation toxicity with glutamine. *Cancer Treat Rev.*, **2003,** 29, 501–513.
[6] T.R. Ziegler, Glutamine supplementation in bone marrow transplantation, *Br.J. Nutr*, **2002** 87(Suppl. 1), S9–S15.
[7] M.P. Latha, V.M. Rao, T.S. Rao, G.N. Rao, Chemical Speciation of Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) binary complexes of L-Methionine 1,2-Propanediol-Water Mixtures, *Bulletin of the Chemical Society of Ethiopia*, **2007,** 21, 363-372.
[8] G. HimaBindu, G. Nageswara Rao, Protonation and complexation equilibria of L-Glutamine in non-ionic micellar medium, *Proceedings of National Academy of Sciences*, **2012,** 82(2), 129-136.
[9] D. Manca, A.C. Richard, B.Trottier, G. Chevlier, studies on lipid peroxidation in rat tissues following administration of cadmium chloride. *Toxicology*, **1991,** 67, 303-323.
[10] *M. Galazyn-Sidorczuk, M.M. Brzoska, M. Jurczuk, J. Moniuszko-Jakoniuk* , Oxidative damage to proteins and DNA in rats exposed to cadmium and/or ethanol. *Chem. Biol. Interact, **2009***, 180, 31–38.
[11] *A.J. Lin, X.H. Zhang, M.M. Chen, Q.Cao,* Oxidative stress and DNA damages induced by cadmium accumulation. *J. Environ. Sci*., ***2007***, 19(5), 596-602
[12] **W. E. Donaldson** and **S. O. Knowles,** Is lead toxicosis a reflection of altered fatty acid composition of membranes? ***Comp. Biochem Physiol****.C,* **1993**, **104, 377-379.**
[13] *R.W. Leggett,* An age-specific kinetic model of lead metabolism in humans. *Environ Health Perspect*, ***1993****;101*(7), *598*-616.
[14] *P. D. Alexander, B. J. Alloway and A. M. Dourado,* Genotypic variations in the accumulation of Cd,Cu,Pb, and Zn exhibited by six commonly grown vegetables. *Environmental Pollution***.** ***2006****, 144, 736*-745.
[15] R.S. Rao, G.N. Rao, Computer Applications in Chemistry, **2005,** Himalaya Publishing House, Mumbai, India.
[16] G. Gran, Determination of the equivalence point in Potentiometric titrations. Part II, *Analyst*, **1952,** 77, 661–671.
[17] G. Gran, Equivalence volumes in potentiometric titrations, *Anal.Chim.Acta*, **1988,** 206, 111–123.

[18] G.N. Rao, Complex equilibria of biological importance in aquo organic media-Computer augmented modeling studies, Ph.D. thesis, **1989,** Andhra University, Visakhapatnam, India.
[19] P. Gans, A. Sabatini, A. Vacca, An improved computer program for the computation of formation constants from potentiometric data, *Inorg. Chim. Acta*, **1976,** 18, 237-239.
[20] A.K. Singh, D. Manjula, A fluorescence study of 1-paminophenyl-4-phenylbuta-1E, 3E-diene in organic solvents, 1,4-dioxane-water binary mixtures and micelles, *J. Indian Chem. Soc*, **2001,** 78, 635-641.

## AUTHORS' ADDRESSES

1. **P. Sujatha**
Lecturer in Chemistry (Faculty Development Programme),
M.R. (A) College, Vizianagaram, AP, India.
E-mail: PeddadaSujatha@gmail.com, Mobile no. 9949407098
2. **Y. Vamsi Kumar**
Lecturer in Chemistry,
M.R. (A) College, Vizianagaram, AP, India.
E-mail:vamsi_yagati@yahoo.com, Mobile no.9849509244
3. **P. Surya Sunitha**
Lecturer in Chemistry (Faculty Development Programme),
SKBR College, Amalapuram, East Godavari district, AP, India
E-mail id: pssskbramp@gmail.com, Mobile no. 9492782348
4. **Dr. G. Himabindu**
Assistant Professor,
Department of Engineering Chemistry
Andhra University,Visakhapatnam.
Email:himabinduauce@gmail.com, Mobile no.9866706605