International Journal of Chemical Studies

P-ISSN: 2349–8528
E-ISSN: 2321–4902
IJCS 2017; 5(4): 970-974

Received: 12-05-2017
Accepted: 14-06-2017

Prasanthi J
School of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India

Aditya Deepthi D
School of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India

Nageswara Rao G
School of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India

Correspondence
Nageswara Rao G
School of Chemistry, Andhra University, Visakhapatnam, Andhra Pradesh, India

Speciation study of binary complexes of pb (ii), cd (ii) and hg (ii) with 1, 10-phenanthroline in acetonitrile-water mixtures

Prasanthi J, Aditya Deepthi D and Nageswara Rao G

Abstract
Speciation of Pb(II), Cd(II) and Hg(II) complexes of 1,10-phenanthroline has been studied pH metrically in acetonitrile –water mixtures (0.0-60.0 % v/v) at 303 K and an ionic strength of 0.16M. The predominant species detected are ML and ML_3 for Pb(II); ML_2, ML_3 for Cd(II) and Hg(II). The trend in the variation of stability constants of these species with decreasing dielectric constants of the medium is attributed to the electrostatic forces and the complexing ability of the co-solvent. The species distribution and the feasible equilibria for the formation of the species are also presented.

Keywords: Acetonitrile, Phenanthroline, Speciation, Toxic metals

Introduction
The human body needs some heavy metals in trace amounts which are essential to mentain the metabolism. Usally, to a small extent they enter our bodies, via food, water and air. However, at high concentrations they lead to poisoning of humans, plants and microorganism [1-6]. Toxic effects of heavy metal ions such as Pb (II), Cd (II) and Hg (II) may be the result of their strong bonding with reactive groups of enzymes. Long term (chronic) over exposure to lead may result in severe damage to the blood forming, nervous, urinary and reproductive systems. High concentration of Cd inhibit plant growth, causes cellular damage [7] and reduces tissue water content [8]. Various forms of mercury also exhibit toxic effects in a number of organs, especially in the kidneys [9].
Acetonitrile (AN) is a colourless polar aprotic solvent [10]. It behaves as a weaker base [11] and as a much weaker acid [12] than water. It has a dielectric constant of 36 and auto protolysis constant of 33.6. AN also acts as a strongly differentiating solvent with a modest solvating power for many polar ionic solutes [13]. Speciation profoundly influences both the toxicity and bioavailability of an element. The speciation studies of toxic metal ion complexes are useful for behavior of protein residues with the metal ions and helpful to understand the interaction with other ligands commonly exist in biological fluids. 1, 10-phenanthroline (phen) and its derived complexes containing phen and 2, 2-bipyridene were reported [15]. Phen is a neutral base and found to form extremely stable complexes with Bp (II), Cd (II) and Hg (II). Which are more favored in biological environments of lower dielectrical constants. This communication describes the pH metric study of Pb (II), Cd (II) and Hg (II) with phen in AN-water mixtures.

Experimental Technique
Materials and Method
All the reagents were of analytical grade solutions of Pb (II), Cd (II) and Hg (II) nitrates were prepred in trople distilled water. An aqueous solution of phen was prepared. To increase the solubility of the phen and to suppress the hydrolysis of metal salts, nitric acid concentration was maintained at 0.05M. AN was used as it was supplied. Sodium nitrate was prepared to mentain the ionic strength in the titrand. Sodium hydroxide of 0.4M and nitric acid of 0.2M were prepared. Gran plot method [16] was employed to determine the strengths of alkali and mineral acid. To assess the errors that might have crept into the determination of concentrations, the data were subjected to ANOVA [17] Alkalimetric titration assembly with different ratios (1:2.5, 1:3.75, 1:5) for Pb(II) and Cd(II), (1:5, 1:7.5, 1:10) for Hg(II) of metal to ligand were carried out in the medium containing varying concentrations (0.0-60.0 % v/v) of

AN in water at an ionic strength of 0.16M with sodium nitrate at 303 K using a ELICO LI 120 pH meter. The glass electrode was equilibriated in AN-water mixture containing inert electrolyte. The details of experimental procedure and titration assembly were given elsewere [18]. Modelling strategy the correction factor (log F), to correct the pH meter dial reading, was determined using the computer program SCPHD [19]. By following some heuristics in the refinement of the stability constants, the best-fit chemical model for each system was arrived at using the computer program MINIQUAD75 [20]. The variation og step-wise protonation constant was analyzed on electrostatic grounds on the basis of solute-solute and solute-solvent interactions.

Results and Discussion

The results of the best-fit models that contain the type of spices and overall formation constants along with some of important statistical parameters are given in Table 1

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

%v/v AN	Logβmlh(SD)			NP	U_{corr}	Skewness	Kurtosis	χ^2	R-Factor	pH range
	1 1 0	1 2 0	1 30							
Pb(II)										
0	3.69(12)			26	7	-0.06	2.68	6.10	0.0316	2.5-5.0
10	5.89(29)		13.23(33)	44	5.42	1.31	7.49	17.09	0.0213	2.2-5.0
20	5.00(05)		11.80(09)	41	3	-0.18	3.04	1.68	0.0151	2.2-4.8
30	5.10(11)		11.11(17)	37	8.31	-0.52	3.34	3.81	0.0257	2.2-5.0
40	5.39(05)		11.82(15)	92	10.14	-0.11	2.54	6.61	0.0177	1.7-4.8
50	5.36(07)		11.89(13)	52	5.78	-0.10	2.77	5.23	0.0188	2.0-4.8
60	5.37(10)		11.93(17)	55	11.5	-0.23	2.36	5.13	0.0267	2.0-4.8
Cd(II)										
0		11.73(28)	15.72(40)	33	1.69	4.92	32.99	46.86	0.0164	2.0-6.0
10		10.68(39)	15.47(24)	30	14.82	1.54	6.46	9.02	0.0407	2.5-5.0
20		10.77(09)	14.27(24)	53	3.31	-0.48	2.79	6.28	0.0146	2.0-5.0
30		10.79(03)	14.10(30)	102	6.82	-0.52	4.08	15.57	0.0138	1.6-4.5
40		10.65(08)	15.72(06)	81	4.46	-0.39	8.66	36.93	0.0143	1.8-9.0
50		10.93(43)	15.67(54)	34	75.62	0.80	2.74	11.78	0.0652	2.0-5.0
60		11.11(05)	15.56(09)	54	2.61	0.04	3.98	3.04	0.0133	2.0-5.0
Hg(II)										
0		9.23(28)		14	40.6	-0.28	2.65	8.29	0.0828	2.5-5.0
10		11.28(18)	15.77(16)	22	0.13	-0.21	3.97	2.61	0.0032	2.25-3.26
20		10.93(21)	15.26(17)	26	0.43	-0.31	4.63	7.33	0.0058	2.3-4.0
30		11.18(37)	14.03(48)	35	2.70	-0.43	3.28	4.03	0.014	2.2-5.0
40		11.20(42)	14.53(52)	34	3.34	-1.10	4.18	6.55	0.0155	2.2-4.6
50		10.65(18)	15.06(16)	38	1.86	2.25	9.05	34.77	0.0124	2.2-5.0
60		15.20(24)	18.39(31)	34	9.12	0.04	2.58	20.98	0.0281	2.2-5.0

The low standard deviation in log β values indicates the adequacy of the models. The small value of U_{corr} (sum of squares of the deviations in the concentrations of metal, ligand and hydrogen ions at all experimental points corrected for degrees of freedom) indicate that the experimental data can be represented by the model. Small values of mean, standard deviation for the systems corroborate that residuals are around zero mean with little dispersion. For an ideal normal distribution, the values of kurtosis and skewness should be three and zero, respectively. The kurtosis values in the present study indicate that the residuals form a leptokurtic pattern and a few form a platykurtic pattern. The values of the skewness given in Table 1 are between -0.06 and 4.92. These data evince 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-value [21] recorded. Thus these statistical parameters support the best fit models which portray the metal-ligand species in AN-water mixtures.

Effect of Systamatic Errors on Best Fit Model

In order to rely upon best chemical model for critical evaluation and appliacation under varied experimental condition with different accuracies of data acquisition, an investigation was made by introducing pessimistic errors in the concentrations of alkali, mineral acid, ligand and metal (Table 2)

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

Ingradient	% of error	ML	ML_3
Acid	-2	6.06(38)	12.62(41)
	+2	4.35(10)	9.75(21)
	-5	Rejected	Rejected
	+5	3.26(14)	7.79(40)
	0	5.10(11)	11.11(17)
Alkali	-2	4.60(11)	10.06(22)
	+2	5.60(17)	12.07(22)
	-5	3.68(13)	8.16(49)
	+5	Rejected	Rejected
Ligand	-2	4.91(10)	10.81(17)
	+2	5.27(13)	11.39(19)
	-5	4.62(09)	10.36(17)
	+5	5.54(20)	11.74(28)
Metal	-2	5.14(12)	11.19(18)
	+2	5.07(11)	11.04(17)
	-5	5.19(12)	11.32(18)
	+5	5.02(10)	10.93(17)

Errors were introduced in the concentrations of the ingradients intentionally to find their effect on the perturbation of stability constants. If the concentrations determined and the experimental conditions maintained by the research were appropriate, any variations in the concentrations of the ingradients will affect the magnitudes and statistical parameters of the stability constants.

Sometimes even the species shall be rejected. Hence, we have studied the effect of errors in the concentrations of ingradients on the stability constants is alkali>acid>ligand>metal. Some species, were even rejected when errors were introduced in the concentrations of the components. This shows that any deviation from the experimentsl concentrations of the components increases the standard deviation in the stability constants (log β) and also results in the rejection of the species.

Effect of Solvent

AN is a polar aprotic solvent. The dielectric constant of AN-water mixture decrease with increasing concentration of AN and these solutions are expected to mimic physiological conditions where the concept of equivalent solution dielectric constant for protein cavities is applicable [22]. The dielectric constants of AN at different percentages (0.0-60.0 vol%) of water were taken from literature [23]. The linear variation (Figure 1) of stability constants of phen complexes of Pb(II), Cd(II) and Hg(II) in AN-water mixtures with 1/D (where D is dielectric constant of the medium) indicates that electrostatic forces dominate the equilibrium process under the present experimental conditions.

Distribution Diagrams

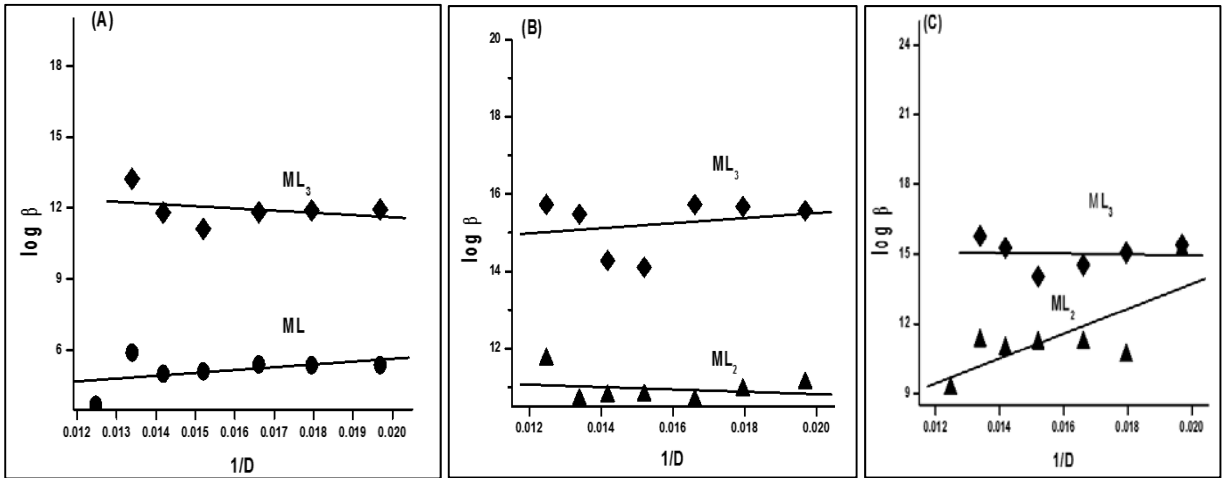

Fig 1: Variation of stability constant values of (A) Pb(II); (B) Cd(II); (C) Hg(II)-phen complexes with reciprocal of dielectric constant (1/D) IN AN-water mixtures; (●) log β_{110}, (▲) log β_{120}; (♦) log β_{130}.

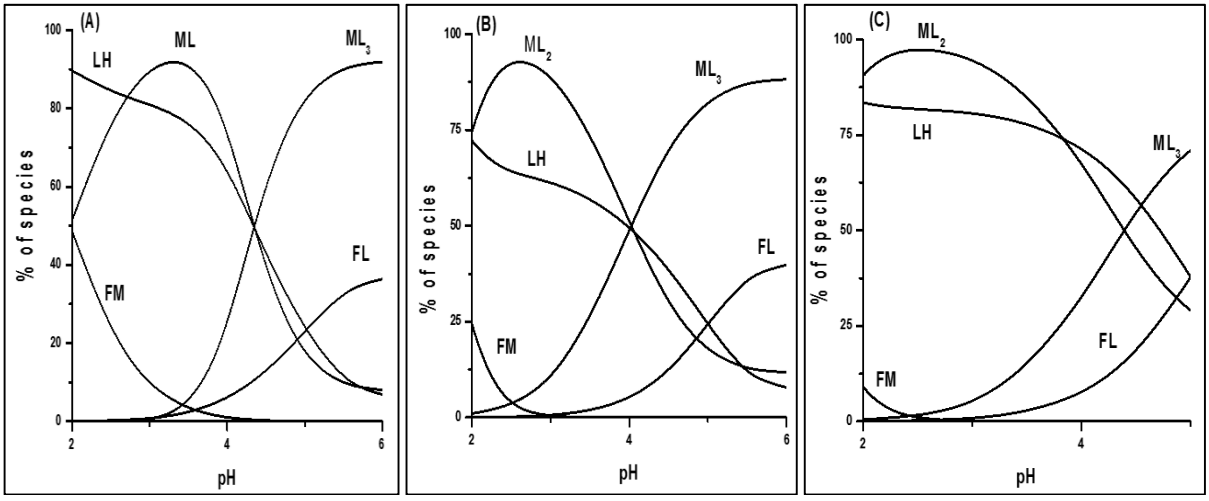

Fig 2: Distribution diagrams of phen complexes in 30% v/v AN-water mixture. (A) Pb(II) (B) Cd(II) and (C) Hg(II).

Phen, a neutral base, has only one protn attached to the nitrogen atom under the present experimental conditions. The form of phen that exist in the pH region of 3.0-6.0 is LH^+. Hence, there is no possibility for the existence of protonated species [24]. The possible species are ML, ML_2 and ML_3, as the two imine nitrogen atoms of phen are the potential sites for coordination of metal ligands. The species formed in the present study for different metals, as given in Table 1 are ML and ML_3 for Pb(II); ML_2, ML_3 for Cd(II) and Hg(II). The formation equilibria based on the distribution of species with pH are represented below.

$M(II)+LH \rightleftharpoons ML+H^+$ ……(1)
$ML+LH \rightleftharpoons ML_2+H^+$ ……... (2)
$M(II)+2LH \rightleftharpoons ML_2+2H^+$ …… (3)
$ML_2+LH \rightleftharpoons ML_3+H^+$……... (4)
$ML+2LH \rightleftharpoons ML_3+2H^+$ …… (5)

Distribution diagram were drawn for various complex species using the formation constants of the bes-fit models as shown in Figure 2. These diagrams indicate that the percentage of ML species of Pb(II) and then decreases with increase of pH. The percentage of ML_3 species increase with increase of pHin case of Pb(II), where as in case of Cd(II) and Hg(II) the

percentage of ML_3 species increases. In both cases of Cd(II) and Hg(II) the percentage species of ML_3 in the present experimental conditions. Depending on the active sites in ligand and the nature of the metal ions, the structures were proposed for the species detected as shown in Figure 3.

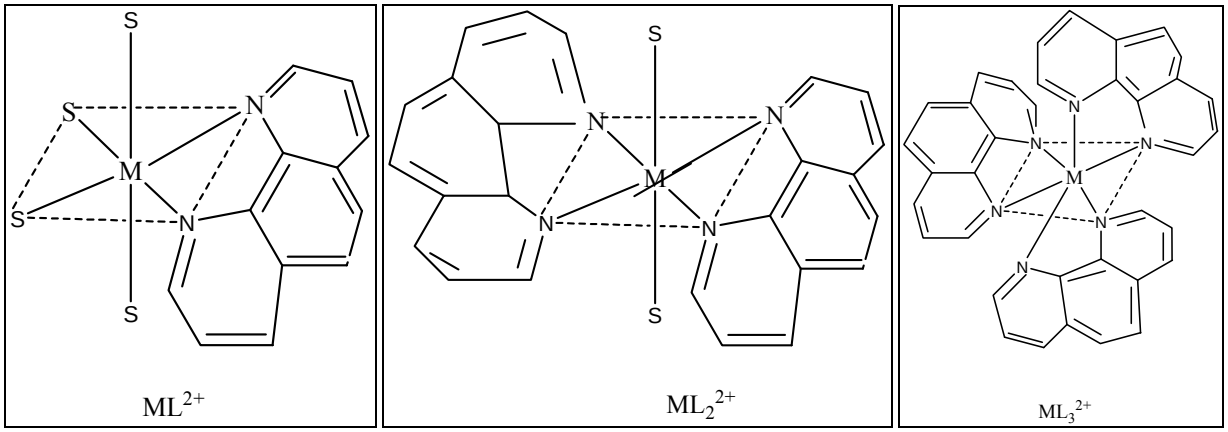

Fig 3: Structures of Metal-phen complexes where M=Pb, Cd or Hg; L=phen; S is either solvent or water molecule

Conclusions

1. The common species formed due to interaction of phen with the toxic metal ions are ML, ML_2 and ML_3.
2. The linear variation of stability constants of phen complexes with the reciprocal of dielectric constant of AN-water mixtures indicates the dominance of electrostatic forces over non-electrostatic forces. A linear increasing trend with AN over its complexing ability.
3. The order of ingradients in influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali>acid>ligand>metal.
4. At higher pHvalues, the high concentrations of chemical species indicate that the metals are more amenable for transportation at higher pH values. Pb(II) and Cd(II) are more bioavailable at lower pHvalues.

References

1. Nodelkoska TV, Doran PM Interactive effects of tempareture and metal stress on the growth and some biochemical compounds in wheat seedling. Environment pollut, 2000; 107:315-320.
2. Donderski W, Brzezinska MS The influence of heavy metals on activity of chitinases produced byplanktonic, benthic and epiphytic bacteria. Pol J environ Stud 2005; 14:851-859.
3. Tkaczuk C. The effect of selective metal ions on the growth and conidial germination of the arhid pathogenic fungus Pandora neoaphidis Humber. Pol J E nviron Stud 2005; 14:897-902.
4. Topolska K, Sawicka-Kapusta K, Cieslik E, The effect of contamination of the KraKow Region on heavy metals content in the organs of Bank Voles. Pol J Environ Stud 2004; 13:103-109.
5. Nasiadek M, Krawczwk T, Sapota A. Tissue levels of cadmium and trace elements in Patients with myoma and uterine cancer. Hum Exp Toxicol, 2005; 12:623-630.
6. Rydzewska A. A comparsion of concentrations of selected heavy metals in neoplastic and peri-neoplastic lung tissues ij inhabitants from Wiekopolska and upper Silesian industrial district in Poland. Pol J Ennviron Stud 2001; 4:289-292.
7. Schutzen Duel A, Polle A Plant responses to abiotic stresses: heavy metal-induced oxidative stress and protection by mycorrhization. J Exp Bot, 2002; 53:1351-1365.
8. Barcelo I, Poschenrieder Ch Plant water relations as affected by heavy metal stress: a review. J Plant Nutr 1990; 13:1-37.
9. Zalups RK Molecular interactions with mercury in kidney. Pharmacol Rev, 2000; 52:113-143.
10. Ludon, Mark G. Organic Chemistry, 4th ed., Oxford University Press, New York, 2002; 317.
11. Laubengayer AW, Sears DS. Donor acceptor bonding, III. Methyl cyanide addition compounds of boron trifluoride. J. Am Chem. Soc., 1945; 67:164-167.
12. Aktas AH, Sanli N, Pekcan G. Spectromettric determination of pKa values for some phenolic compounds in acetonitrile-water mixture. Acta Chim. Slov. 2006; 53:214-218.
13. Bapna MS, Mukherjee S, Myrphy R. Thenantimicrobial effect of an iron binding agent on spectrococcus mutans. J Oral Rehabit, 2007; 19:111-113.
14. Agwara MO, Ndifon PT, Ndosiri NB, Paboudam AG, Yufany DM, Mohamadou A *et al.* Synthesis, characterization and antimicrobial activities of cobalt(II), copper(II) and zinc(II) mixed ligand complexes containing 1,10 phenanthroline and 2,2`-bipyridine. Bull Chem Soc Ethiop, 2010; 24:383-389.
15. Gran G. Equivalence volumes in potentiometric titrations. Anal Chim Acta. 1998; 206:111-123.
16. Rao RS, Rao GN. Computer applications in chemistry. Himalaya Publishing House, Mumbai, 2005, 302.
17. Latha MP, Rao VM, Rao TS, Rao GN. Chemical speciation of Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) binary complexes of L-methionine in 1,2-propanediol-water Mixtures. Bull Chem Soc Ethiop 2007; 21:363-372.
18. Rao GN Ph.D Thesis, Andhra University, Visakhapatnam, India, 1989.
19. Grans P, Sabatini A, Vacca A. An improved computer program for the computation of Formation constants from potentiometric data. Inorg Chim Acta 18:237-23921.
20. Hmilton WC. Significance tests on the crystallographic R factor. Acta Chim Slov. 1965; 54:160-165.
21. Latha MP, Rao VM, Rao TS, Rao GN Determination of protonation constants of L- glutamic acid and L-

methionine in 1,2-propanediol-water mixtures. Acta Chim Slov, 2007; 54:160-165.
22. Akhadov YY, Dielectric properties of binary solutions. Pergamon Press, Oxford, 1980.
23. Akhadov N, Babu MS, Rao GN, Rao RS, Ramana KV. Effect of urea on the speciation of 1,10-phenanthroline complexes of toxic metal ions: computer augmented modeling studies. Polyhedron. 1990; 9:2497-2506.