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Computer augumented modelling studies of Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of L-glutamic acid in 1,2-propanediol–water mixtures

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Abstract: Chemical speciation of Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of L-glutamic acid was studied at 303 K in 0–60 vol. % 1,2-propanediol–water mixtures, whereby the ionic strength was maintained at 0.16 mol dm^{-3}. The active forms of the ligand are LH_3^+, LH_2 and LH^-. The predominant detected species were ML, ML_2, MLH, ML_2H and ML_2H_2. The trend of the variation in the stability constants with changing dielectric constant of the medium is explained based on the cation stabilizing nature of the co-solvents, specific solvent–water interactions, charge dispersion and specific interactions of the co-solvent with the solute. The effect of systematic errors in the concentrations of the substances on the stability constants is in the order alkali > > acid > ligand > metal. The bioavailability and transportation of metals are explained based on distribution diagrams and stability constants.

Keywords: chemical speciation; L-glutamic acid; 1,2-propanediol; bioavailability; metals.

INTRODUCTION

Investigations of acido–basic equilibria of amino acids, their interaction with metal ions in media varying ionic strength, temperature and dielectric constant throw light on the mechanism of enzyme-catalyzed reactions. Although it is known that the polarity of the active site cavities in proteins is lower than that of the bulk, a direct measurement of the dielectric constant is not possible. Comparing the formation constants of acido–basic equilibria and/or metal complex equilibria with those at biological centres offers a way to estimate the effective dielectric constant or equivalent solution dielectric constant for the active site cavity.[1] This brought a renaissance in the study of complex equilibria in aqua–organic mixtures apart from its established utility in understanding solute–solvent interactions, increasing sensitivity of reactions of analytical and industrial importance and solubilising ligands or their metal complexes.

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Chemical speciation of metals is important for an understanding of their distribution, mobility, bioavailability, toxicity and for setting environmental quality standards.[2] Bioavailability of a particular metal depends on its complex chemical reactions of dissolution, binding and complexation with the constituents of the environmental aquatic phase.[3] The activities 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.[4] Complexation signifycantly decreases bioavailability.[5]

Due to the multiple biological roles of glutamic acid,[6–9] speciation studies of L-glutamic acid (Glu) with Co(II), Cu(II) and Zn(II) in DMF–water mixtures and Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) in urea–water mixtures were reported earlier.[10,11] Ionic strength dependence of the formation constants of Glu with uranium(VI) and beryllium(II) and pH-metric and spectrophotometric studies of oxovanadium(IV) with Glu, aspartic acid and imidazoles were also reported.[12–14] Herein, the results of chemical speciation of Glu complexes of Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) and Zn(II) in 1,2-propanediol–water mixtures are reported.

EXPERIMENTAL

Chemicals

1,2-Propanediol (propylene glycol, PG), obtained from Merck, Mumbai, was used as received. Aqueous solutions of L-glutamic acid, Pb(II), Cd(II) and Hg(II) nitrates, Co(II), Ni(II), Cu(II) and Zn(II) chlorides, nitric acid, sodium hydroxide and sodium nitrate were prepared by dissolving GR Grade (Merck, Germany) samples in triple distilled water. To increase the solubility of Glu and to suppress the hydrolysis of metal salts, the nitric acid concentration was maintained at 0.050 mol dm^{-3}. All the solutions were standardized by usual standard methods. To assess the errors that might have entered into the determinations of the concentrations, the data were subjected to analysis of variance of one way classification (Anova).[15] The strength of the alkali was determined using the Gran plot method.[16]

Apparatus

The titrimetric data were obtained with a calibrated Elico (Model L1-120) pH meter (readability 0.01), which can monitor changes in the H^+ concentration. The pH meter was calibrated with a 0.050 mol dm^{-3} potassium hydrogen phthalate solution in the acidic region and a 0.010 mol dm^{-3} borax solution in the basic region. The glass electrode was equilibrated in a well-stirred PG–water mixture containing an inert 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 factors.[17,18]

Procedure

The titrations were performed at 303±0.1 K in media containing 0–60 vol. % PG, whereby the ionic strength was maintained constant at 0.16 mol dm^{-3} 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, a strong acid was titrated with an alkali every day until no appreciable differences were observed between the pH values of two titrations at the corresponding volumes of titrant. Under the above conditions, the electrode was assumed to be equilibrated. A calomel electrode was refilled with PG–water mixture of the equivalent composition to that of the titrand. Free acid titrations were performed before the metal–ligand titrations to calculate the correction factor. In each of the titrations, the titrand consisted of a mineral acid of approximately 1 mmol in a total volume of 50 cm^3. Titrations with different ratios (1:2.5, 1:3.5 and 1:5) of metal–ligand were performed with 0.40 mol dm^{-3} sodium hydroxide. Other experimental details are given elsewhere.[19]

Modelling strategy

The approximate complex stability constants of metal–Glu complexes were calculated with the computer program SCPHD.[20] The best fit chemical model for each investigated system was arrived at using Miniquad75.[21]

RESULTS AND DISCUSSION

The results of the best fit models that contain the type of species and overall formation constants along with some of the important statistical parameters are given in Tables I and II. A very low standard deviation in the log β values indi

TABLE I. Parameters of the best fit chemical models of Pb(II), Cd(II) and Hg(II)–glutamic complexes in PG–water mixtures. Temperature 303 K, ionic strength 0.16 mol dm^{-3}

y(PG) vol. %	log β_{mlh}(*SD*)				*NP**	U_{corr}^{**} / 10^{-8}	Skewness	χ^2	*R* factor	Kurtosis	pH Range
	ML	MLH	ML_2	ML_2H_2							
					Pb(II)						
00.00	6.58(14)	–	–	–	15	3.817	–0.57	10.64	0.0137	2.79	3.7–4.7
10.00	6.81(11)	–	–	–	13	1.778	–0.81	9.21	0.0090	3.50	3.7–4.6
20.00	6.54(9)	–	–	–	29	0.448	–0.80	34.47	0.0091	3.73	3.8–4.7
30.00	6.78(8)	–	–	–	36	3.332	–0.68	47.26	0.0135	2.85	3.7–4.9
40.00	6.85(8)	–	–	–	34	3.096	–0.71	31.96	0.0129	3.39	3.8–4.9
50.00	6.70(7)	–	–	–	28	1.267	–0.70	22.86	0.0080	3.52	4.0–4.9
60.00	6.74(8)	–	–	–	29	1.358	–0.84	39.99	0.0082	4.23	4.0–5.0
					Cd(II)						
00.00	3.99(12)	–	7.22(10)	22.38(50)	23	0.892	0.26	4.16	0.0090	3.08	5.0–9.3
10.00	4.14(7)	–	7.46(6)	23.21(10)	55	1.015	0.19	27.44	0.0076	5.46	3.0–9.5
20.00	4.10(8)	–	7.05(8)	22.36(71)	21	0.363	–0.11	3.92	0.0061	4.24	6.0–9.5
30.00	4.33(13)	–	7.69(12)	22.96(54)	22	0.732	0.16	16.42	0.0084	7.41	5.6–9.5
40.00	4.46(13)	–	7.83(12)	23.20(43)	22	0.622	0.16	16.91	0.0078	6.15	5.6–9.5
50.00	4.49(9)	–	7.96(9)	22.72(71)	27	0.526	0.35	6.60	0.0074	4.72	5.5–9.8
60.00	4.48(10)	–	7.95(11)	23.39(33)	34	1.756	0.23	20.20	0.0127	5.14	5.0–10
					Hg(II)						
00.00	10.96(4)	13.41(5)	–	–	82	7.997	1.00	85.84	0.0028	6.66	1.7–2.6
10.00	11.60(4)	14.32(4)	–	–	48	0.365	–0.08	9.78	0.0025	4.75	2.1–2.6
20.00	11.52(8)	14.48(5)	–	–	31	0.206	–0.14	16.68	0.0018	5.36	2.1–2.5
30.00	12.13(2)	14.81(4)	–	–	29	0.059	–0.52	11.30	0.0011	6.14	2.1–2.5
40.00	12.68(3)	15.02(11)	–	–	25	0.416	0.11	2.55	0.0024	3.45	2.1–2.5
50.00	12.71(3)	15.48(4)	–	–	19	0.070	–0.78	7.14	0.0009	7.02	2.1–2.5
60.00	12.24(7)	15.63(3)	–	–	10	0.014	0.18	0.93	0.0004	3.01	2.3–2.5

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

Table II. Parameters of the best fit chemical models of Co(II), Ni(II), Cu(II) and Zn(II)–glutamic acid complexes in PG–water mixtures. Temperature 303 K, ionic strength 0.16/mol dm^{-3}

y(PG) vol. %	Log β_{mlh}(*SD*)					*NP*	U_{corr} / 10^{-8}	Skewness	χ^2	*R*-Factor	Kurtosis	pH-Range
	ML	MLH	ML_2	ML_2H	ML_2H_2							
Co(II)												
00.00	4.58(4)	–	7.75(4)	–	22.94(34)	23	0.939	0.14	6.94	0.0096	6.79	
10.00	4.69(3)	–	8.12(3)	–	23.16(8)	12	0.124	–0.03	3.11	0.0014	5.14	
20.00	4.65(4)	–	7.96(4)	–	22.92(14)	12	0.055	–0.17	10.67	0.0021	2.77	
30.00	4.87(6)	–	8.43(6)	–	22.92(27)	12	0.137	–0.27	10.22	0.0034	2.03	
40.00	4.73(7)	–	8.30(9)	–	22.24(64)	37	1.069	0.06	30.33	0.0080	3.76	
50.00	5.08(4)	–	8.79(6)	–	23.14(10)	38	0.488	–0.28	38.98	0.0054	3.72	
60.00	4.88(22)	–	8.22(7)	–	23.62(81)	16	2.653	0.14	13.00	0.0148	4.16	
Ni(II)												
00.00	5.14(7)	–	9.56(50)	16.47(2)	-	22	6.939	2.23	27.30	0.0288	6.90	
10.00	5.78(3)	–	10.07(5)	–	23.36(5)	29	0.257	–0.02	14.79	0.0042	3.43	
20.00	5.66(3)	–	9.91(6)	–	22.98(6)	31	0.227	–0.05	4.12	0.0039	3.11	
30.00	5.85(3)	–	10.14(5)	–	23.32(4)	33	0.225	–0.12	21.81	0.0038	4.57	
40.00	6.36(2)	–	10.91(3)	–	23.83(3)	34	0.135	0.00	4.98	0.0030	2.89	
50.00	6.31(2)	–	10.85(4)	–	23.79(3)	36	0.205	0.01	8.59	0.0035	2.48	
60.00	6.23(2)	–	10.42(5)	–	24.20(3)	39	0.207	0.15	13.94	0.0034	3.58	
Cu(II)												
00.00	7.99(11)	12.52(2)	14.49(5)	19.50(19)	24.11(7)	38	0.438	–0.08	10.77	0.0055	4.15	
10.00	8.32(11)	12.91(4)	15.29(3)	20.81(5)	24.49(13)	43	0.123	–0.31	12.21	0.0025	4.37	
20.00	8.11(8)	12.62(3)	14.75(3)	20.26(5)	24.32(9)	45	0.110	–1.50	19.73	0.0023	9.34	
30.00	8.42(8)	13.02(2)	15.12(2)	20.69(5)	24.75(9)	45	0.083	–0.37	10.36	0.0020	4.09	
40.00	8.61(9)	13.48(21)	16.44(18)	21.74(18)	26.06(17)	43	4.636	–0.08	75.34	0.0151	1.55	
50.00	8.90(31)	13.84(5)	16.32(5)	21.86(8)	26.14(10)	43	0.312	–0.05	7.62	0.0037	2.24	
60.00	9.12(20)	14.16(3)	15.93(5)	22.21(5)	26.59(9)	47	0.153	–0.69	76.09	0.0026	10.09	
Zn(II)												
00.00	4.90(5)	–	8.88(5)	–	22.94(5)	45	0.418	0.29	17.24	0.0047	5.61	
10.00	4.90(7)	–	8.89(7)	–	23.13(9)	37	0.692	0.08	11.16	0.0063	3.82	
20.00	4.90(2)	–	8.82(20)	–	22.86(82)	15	1.899	0.20	9.93	0.0125	3.55	
30.00	4.89(18)	–	8.87(17)	–	22.80(96)	21	1.515	0.06	4.94	0.0121	3.59	
40.00	5.20(13)	–	9.35(13)	–	23.20(46)	16	0.707	0.22	6.33	0.0079	3.43	
50.00	5.41(5)	–	9.61(6)	–	23.14(18)	19	0.355	0.10	4.89	0.0053	5.47	
60.00	5.05(18)	–	8.77(19)	–	23.51(74)	11	1.158	–0.06	31.73	0.0098	1.83	

cates the precision of these parameters. The small values of U_{corr} (sum of the squares of the deviations in the concentrations of 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 the mean, standard deviation and mean deviation for the systems corroborate that the residuals are around a zero mean with little dispersion. For an ideal normal distribution, the values of the 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 the Tables are between –1.50 and 2.23. These data evince that the residuals form a part of a normal distribution, hence, the least squares method can be applied to the present data. The sufficiency of the model is further evident from the low crystallographic *R*-value recorded. Thus, these statistical parameters show that the best fit models portray the metal–ligand species in PG–water mixtures. The stability constants of the metal–ligand species are compared with literature reported values in Table III.

TABLE III. Comparison of the results of the present study with the binary stability constants of Glu complexes reported in the literature in aqueous medium

Metal ion	Species	Presented values	Literature reported value	Ref.
Co(II)	ML, ML_2	4.58, 7.75	4.56, 7.86	22
Ni(II)	ML, ML_2	5.14, 9.56	5.62, 9.82	22
	ML, ML_2	5.14, 9.56	5.60, 9.76	23
Cu(II)	ML	7.99	7.87	23
	ML, MLH	7.99, 12.52	8.07, 12.39	24
	ML, MLH	7.99, 12.52	8.39, 12.49	25
	ML, MLH, ML_2, ML_2H, ML_2H_2	7.99, 12.52, 14.49, 19.50, 24.11	8.55, 12.73, 15.22, 20.57, 25.18	26
Zn(II)	ML, ML_2	4.90, 8.88	4.69, 8.55	27

Effect of systematic errors on best fit model

Miniquad75 does not provide for a study of the effect of systematic errors in influential parameters, such as the concentrations of the reactants, on the magnitude of the equilibrium constant. In order to rely upon the best chemical model for critical evaluation and application under varied experimental conditions 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 IV). The order of the compounds that influence the magnitudes of the stability constants due to incorporation of errors is alkali > acid > ligand > metal. Some species, such as ML_2 and ML_2H_2, were even rejected when errors were introduced in the concentrations of the components. This shows that any deviation from the experimental concentrations of the components increases the standard deviation in the log β values and results ultimately in the rejection of the species.

This study infers that the experimental concentrations are appropriate and the proposed models are adequate for the experimental data.

TABLE IV. Effect of errors in the influential parameters on the metal–glutamic acid equilibria in a 30 vol. % v/v PG–water mixture

Component	Error, %	Log β(*SD*)		
		ML	ML_2	ML_2H_2
		Cd(II)		
Alkali	0	4.33(13)	7.69(12)	22.96(53)
	–5	2.13(60)	Rejected	Rejected
	–2	3.76(30)	6.15(33)	22.48(256)
	+2	4.73(17)	8.78(14)	Rejected
	+5	6.10(69)	10.97(66)	Rejected
Acid	–5	5.74(36)	10.19(37)	Rejected
	–2	4.97(32)	8.82(31)	23.63(64)
	+2	3.84(29)	6.61(26)	22.16(467)
	+5	3.12(24)	Rejected	Rejected
Ligand	–5	4.44(10)	8.28(9)	Rejected
	–2	4.36(12)	7.92(11)	22.64(84)
	+2	4.29(20)	7.43(19)	23.16(61)
	+5	4.22(33)	6.98(33)	23.34(82)
Metal	–5	4.32(15)	7.81(13)	22.95(59)
	–2	4.33(14)	7.74(13)	22.96(56)
	+2	4.33(13)	7.64(12)	22.97(52)
	+5	4.33(12)	7.56(11)	22.97(50)
		Zn(II)		
Alkali	0	4.89(18)	8.88(16)	22.80(96)
	–5	3.13(42)	Rejected	Rejected
	–2	4.41(39)	7.26(43)	22.53(340)
	+2	5.35(12)	9.96(11)	Rejected
	+5	6.31(52)	11.72(43)	Rejected
Acid	–5	6.06(28)	11.09(26)	Rejected
	–2	5.24(9)	9.69(8)	Rejected
	+2	4.46(16)	7.74(21)	Rejected
	+5	3.83(29)	Rejected	Rejected
Ligand	–5	5.07(8)	9.46(7)	Rejected
	–2	4.94(14)	9.10(12)	22.38(154)
	+2	4.85(25)	8.63(24)	23.03(94)
	+5	4.80(38)	8.20(38)	23.27(105)
Metal	–5	4.85(18)	9.00(16)	22.66(115)
	–2	4.88(18)	8.93(16)	22.75(101)
	+2	4.90(18)	8.82(17)	22.85(91)
	+5	4.92(19)	8.74(18)	22.92(86)

Effect of solvent

The presence of PG in aqueous solutions considerably decreases the dielectric constant of the medium and these solutions are expected to mimic physiological conditions where the concept of equivalent solution dielectric constant for protein cavities is applicable. Hence, PG was selected for the biomimetic study. The dielectric constants of PG at different percentages (0–60 vol. %) of water were taken from literature.[28] PG is an amphiprotic and coordinating solvent. It is a structure former and hence it enhances the structure of water in PG–water mixtures. It also removes water from coordination sphere of metal ions, making them more reactive towards ligands. As a result, the stability of the complexes is expected to increase with increasing concentration of PG. On the other hand, PG is a coordinating solvent and competes with ligands for coordination with the metals. This decreases the stability of the complexes. Hence, variation in the stability of complex with solvent is a result of both the opposing behaviours.

The variation of the values of the overall stability constant or change in free energy with content of co-solvent depends upon two factors, *viz*. electrostatic and non-electrostatic. The Born classical treatment accounts well for the electrostatic contribution to the free energy change.[29] According to this treatment, the energy of electrostatic interaction is related to the dielectric constant. Hence, the log β values should vary linearly with the reciprocal of the dielectric constant of the medium. The plots given in Fig. 1 show that the values of log β increase linearly with decreasing value of the dielectric constant. This trend indicates the dominance of the structure forming nature of PG over its complexing ability. The cation stabilizing nature of co-solvents, specific solvent–water interactions, charge dispersion and specific interactions of the co-solvent with the solute (indicated by the changes in the solubility of different species in aqua–organic mixtures) account for the small deviation from a linear relationship. Since the complex formation can be viewed as the competition between pure and solvated forms of the ligand and metal ion, solute–solvent interactions, relative thermodynamic stabilities, kinetic labilities play an important role.[30,31]

Distribution diagrams

Glu has two dissociable carboxyl protons and an amino group that can associate with a proton. The different forms of Glu that exist in the pH regions 2.0–4.0, 2.0–5.0, 4.0–9.0 and 8.0–10.0 are LH_3^+, LH_2, LH^- and L^{2-}, respectively. Hence, the probable species existing in different systems can be predicted from these data. The species formed in the present study for different metals, as given in Tables I and II, are ML for Pb(II); ML and MLH for Hg(II); ML, ML_2 and ML_2H_2 for Cd(II), Co(II), Ni(II) and Zn(II); ML, MLH, ML_2, ML_2H and ML_2H_2 for Cu(II).

Distribution diagrams were drawn for various complex species using the formation constants of the best fit models as shown in Figs. 2 and 3. These diagrams indicate that the percentage of the ML species of Pb(II) increases with increasing PG content. With increasing percentage of solvent, the percentage of protonated species decreases and the unprotonated species increases for Cd(II). For Hg(II), the

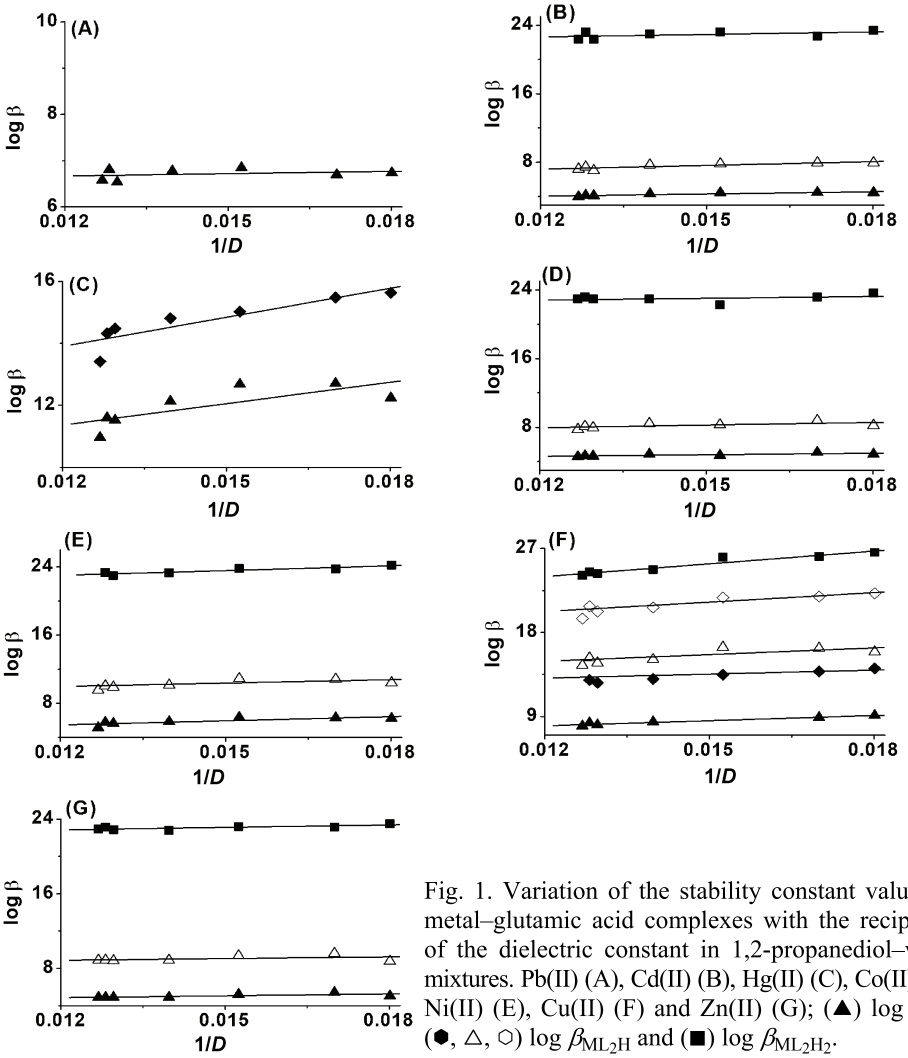

Fig. 1. Variation of the stability constant values of metal–glutamic acid complexes with the reciprocal of the dielectric constant in 1,2-propanediol–water mixtures. Pb(II) (A), Cd(II) (B), Hg(II) (C), Co(II) (D), Ni(II) (E), Cu(II) (F) and Zn(II) (G); (▲) log β_{ML}, (◆, △, ◇) log β_{ML_2H} and (■) log $\beta_{ML_2H_2}$.

species exist at very low and narrow pH region. For Co(II), the percentages of ML, ML_2 are not affected by the solvent. For Ni(II), the distribution of all the species is almost the same in all proportions of the solvent. The percentages of MLH, ML_2H and ML_2 are greater at high solvent concentrations and that of ML_2H_2 is very low in all compositions of the solvent. The percentage of ML_2H_2 is lower when compared to ML and ML_2. The formation of various binary complex species is shown in the following equilibria:

$$M(II) + LH_3^+ \rightleftarrows MLH_2^{2+} + H^+ \quad \text{(minor process)} \tag{1}$$

$$MLH_2^{2+} \rightleftarrows MLH^+ + H^+ \tag{2}$$

$$\mathrm{M(II)} + \mathrm{LH_2} \rightleftarrows \mathrm{MLH^+} + \mathrm{H^+} \tag{3}$$

$$\mathrm{MLH^+} \rightleftarrows \mathrm{ML} + \mathrm{H^+} \tag{4}$$

$$\mathrm{MLH^+} + \mathrm{LH_2} \rightleftarrows \mathrm{ML_2H_2} + \mathrm{H^+} \tag{5}$$

$$\mathrm{M(II)} + 2\mathrm{LH_2} \rightleftarrows \mathrm{ML_2H_2} + 2\mathrm{H^+} \tag{6}$$

$$\mathrm{ML_2H_2} \rightleftarrows \mathrm{ML_2H^-} + \mathrm{H^+} \tag{7}$$

$$\mathrm{M(II)} + \mathrm{LH^-} \rightleftarrows \mathrm{ML} + \mathrm{H^+} \tag{8}$$

$$\mathrm{ML_2H^-} \rightleftarrows \mathrm{ML_2^{2-}} + \mathrm{H^+} \tag{9}$$

$$\mathrm{M(II)} + 2\mathrm{LH^-} \rightleftarrows \mathrm{ML_2^{2-}} + 2\mathrm{H^+} \tag{10}$$

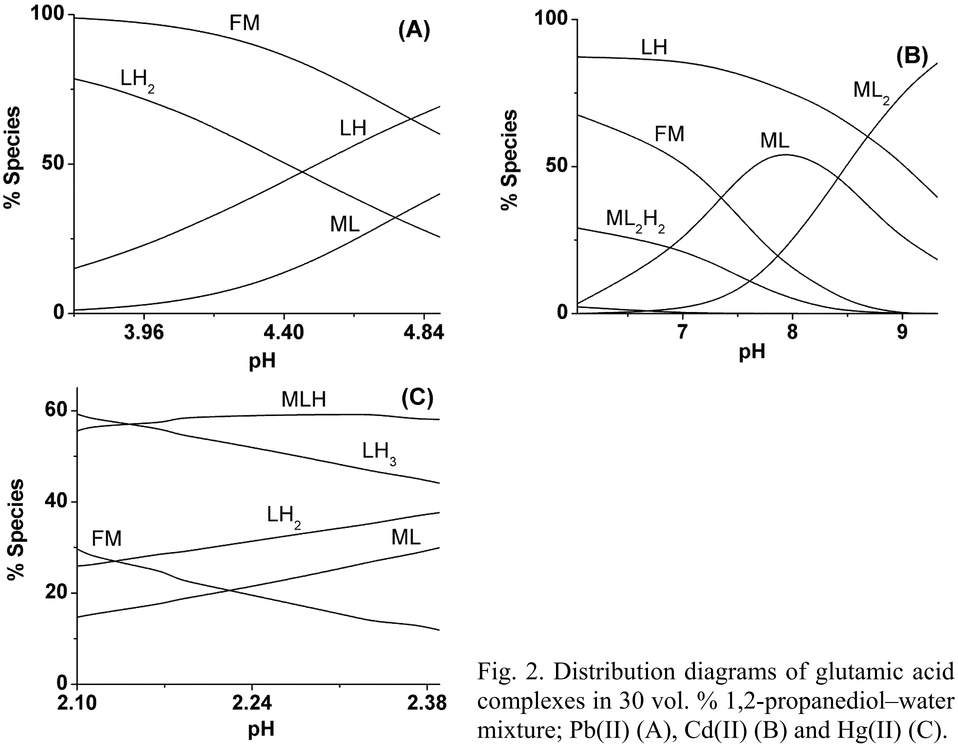

Fig. 2. Distribution diagrams of glutamic acid complexes in 30 vol. % 1,2-propanediol–water mixture; Pb(II) (A), Cd(II) (B) and Hg(II) (C).

The species shown in Equilibrium (1) was not detected, may be because the process is minor or the species is unstable. Soluble metal species are more bioavailable than insoluble ones.[32] Complexation of the metals by natural complexing agents, such as amino acids and humic acids, alter their bioavailability.[5,33] Bioavailability is also affected by pH value, composition of interfering anions and cations, dissolved organic matter, sequestration and binding in plants, species-dependent regulation mechanisms for the uptake, amount of metal and the oxidation state of mineral components.[34,35] Thus, the distribution of the species over the entire pH range is useful to understand the pH where a particular species is likely to form. By using these data, the bioavailability of a metal can be predicted. For example, in Figs. 2 and 3 the concentration of free metal ion (FM) is very high in acidic pH values, more so with the toxic metals. Hence, in these pH ranges the metals are more bioavailable than in higher pH ranges. Hence, the concentrations of the complex chemical species have more significance than the total concentrations for the bioavailability and toxicity of trace metals in soils and water.

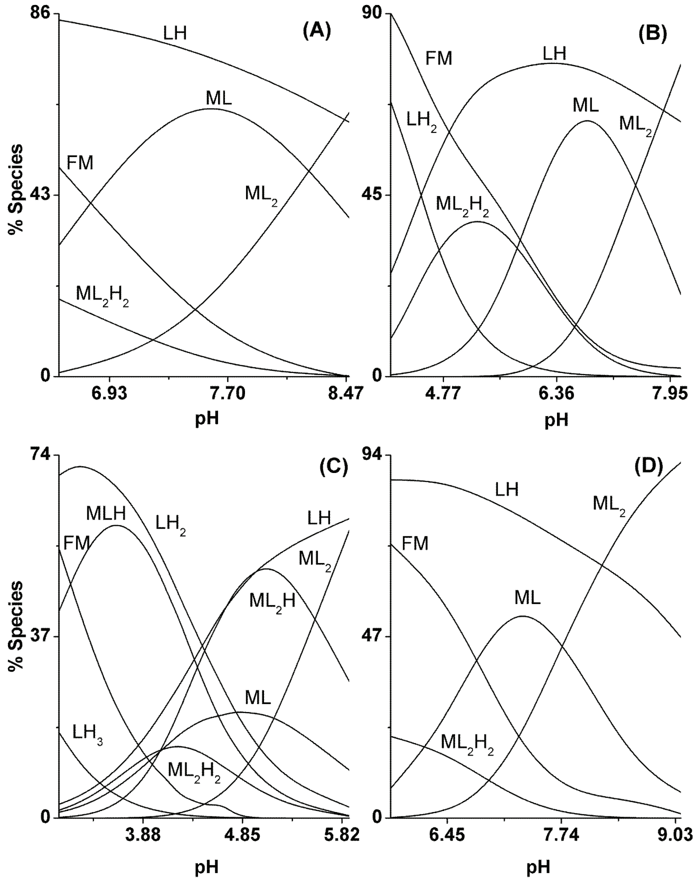

Fig. 3. Distribution diagrams of glutamic acid complexes in 30 vol. % 1,2-propanediol–water mixture; Co(II) (A), Ni(II) (B), Co(II) (C) and Zn(II) (D).

CONCLUSIONS

1. The present biomimetic studies of metal ion complexes with L-glutamic acid in PG–water mixtures indicate that all the complexes were protonated in acidic pH values.

2. The predominant species detected were ML, ML_2, MLH, ML_2H and ML_2H_2.

3. The log β values linearly increased with $1/D$ 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.

ИЗВОД

Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) И Zn(II) КОМПЛЕКСИ СА L-ГЛУТАМИНСКОМ КИСЕЛИНОМ У СМЕШИ 1,2-ПРОПАНДИОЛ–ВОДА ПРОУЧАВАНИ МОДЕЛОВАЊЕМ ПОТПОМОГНУТИМ КОМПЈУТЕРОМ

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Проучавана је хемијска специјација Pb(II), Cd(II), Hg(II), Co(II), Ni(II), Cu(II) и Zn(II) комплекса са L-глутаминском киселином у 0–60 vol. % 1,2-пропанол–вода смешама при јонској јачини од 0,16 mol dm^{-3} на 303 K. Активни облици лиганда су LH_3^+, LH_2, LH^-. Предоминантне детектоване специје су ML, ML_2, MLH, ML_2H and ML_2H_2. Тренд варијације константи стабилности са променом диелектричне константе средине објашњен је на основу природе ко-растварача који стабилизује катјон, специфичних интеракција растварача и воде, дисперзије наелектрисања, специфичних интеракција ко-растварача са растворком. Утицај систематских грешака у концентрацијама састојака на константе стабилности следи редослед алкални метал > киселина > лиганд > метал. Транпорт метала и биолошка доступност објашњени су дистрибуционим дијаграмима и константама стабилности.

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