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pH-metric Investigation on Binary Complexes of Ca (II), Mg (II) and Zn (II) with Glycylglycine in TX100 -Water Mixtures

Pondala Seetharam¹, Malla Ramanaiah² and B. B. V. Sailaja*¹

¹Department of Inorganic & Analytical Chemistry, Andhra University, Visakhapatnam-530 003, India

²Department of Chemistry, Aditya Institute of Technology and Management, Tekkali-532201, India

ABSTRACT

The formation constants of binary complexes of Ca(II), Mg(II) and Zn(II) with glycylglycine in (0.0-2.5% v/v) TX100-water mixture were determined pH metrically at 303.0 K and an ionic strength of 0.16 mol L⁻¹. The existence of various binary complexes was established from modeling studies using the computer program MINQUAD75. The best fit chemical models were arrived at based on the statistical parameters like crystallographic R factor and sum of squares of residuals in mass-balance equations. The trend in the variation of stabilities of binary complexes with change in the mole fraction of the medium was explained based on electrostatic and non-electrostatic forces. The distribution diagrams of the complex species are also presented.

Keywords: Formation constants, Binary Complexes, Glycylglycine, TX100, pH.

INTRODUCTION

The chemical speciation of elements in aquatic environments is one of the most important topics in the fields of analytical chemistry, geochemistry, toxicology, and environmental chemistry. Chemical speciation is essential for discussing the chemical reactivity of trace constituents in the environment, such as biological availability and toxicity, and the geochemical behavior of chemical species. The term “chemical speciation” has been defined in IUPAC Recommendations 2000[1]. In this recommendation, the term “chemical species” is utilized as a specific form of an element: isotopic composition, electronic or oxidation state, and complex or molecular structure. “Speciation analysis” is an analytical process for identifying and/or measuring the quantities of one or more individual chemical species in a sample, and “speciation of an element” implies to know the distribution of an element amongst defined chemical species in a system.

The purpose of this study is to confirm the species formed under the present experimental conditions and to validate the models by statistical treatment of the data. The effect of medium on the chemical speciation of the complexes and the influence of errors in ingredients the magnitudes of stability constants are also studied. Hence, the stability constants of the binary complexes of glycylglycine with Ca (II), Mg (II) and Zn (II) have been determined using pH metry. These values are potentially useful to environmental and biological problems [2-4].

MATERIALS AND METHODS

Chemicals and Standard Solutions

Glycylglycine (GG) (E-Merck, Germany) solution (0.05 mol L^{-1}) was prepared in triple-distilled deionised water by maintaining 0.05 mol L^{-1} hydrochloric acid concentration to increase the solubility. TX100 (Merck, India) was used as received. 2 mol L^{-1} sodium chloride (Qualigens, India) was prepared to maintain the ionic strength in the titrand. 0.1 mol L^{-1} aqueous solutions of Ca (II), Mg (II) and Zn (II) chlorides were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple-distilled water maintaining 0.05 mol L^{-1} hydrochloric 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 [5-10]. The strengths of alkali and mineral acid were determined using the Gran plot method [11, 12].

Instrumentation

The titrimetric data were obtained using Metrohm (Model 905) Auto titrator (readability 0.001), 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 TX100-water mixture containing the inert electrolyte. All the titrations were carried out in the medium containing varying concentrations of TX100-water mixtures (0.0-2.5% v/v) by maintaining an ionic strength of 0.16 mol L^{-1} with sodium chloride at $303.0 \pm 0.1 \text{ K}$. 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 [13, 14].

Analytical Procedures

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 TX100-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 metal to ligand ratios (1:2.5, 1:3.75, 1:5) were carried out with 0.40 mol L^{-1} sodium hydroxide. The analytical concentrations of the ingredients are given in Table 1. Other experimental details are given elsewhere [15].

Modeling Strategy

The computer program SCPHD [16-18] was used to calculate the correction factor. By using the pH-metric titration data, the binary stability constants were calculated with the computer program MINIQUAD75 [19], which exploit the advantage of the constrained least-squares method in the initial refinement and reliable convergence of Marquardt algorithm. During the refinement of binary systems, the correction factor and the protonation constants of glycylglycine were fixed. The variation of stability constants with the mole fraction of the medium was analyzed on electrostatic grounds on the basis of 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 2. Very low-standard deviation in overall stability constants ($\log \beta$) 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 [20-22].

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 TX100-water mixtures, as discussed below.

In the present study, the χ^2 values are less than the table values, and so the models are accepted. The kurtosis values in this study indicate that the residuals form leptokurtic pattern. The values of skewness recorded in Table 2 are between 0.10 and 1.64 for Ca (II), -2.51 and 0.89 for Mg (II) and -0.12 to 0.85 for Zn (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 TX100 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, metal, log F and volume (Table 3). The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > metal > ligand > volume > log F . 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 ingredients) and choice of the best-fit models.

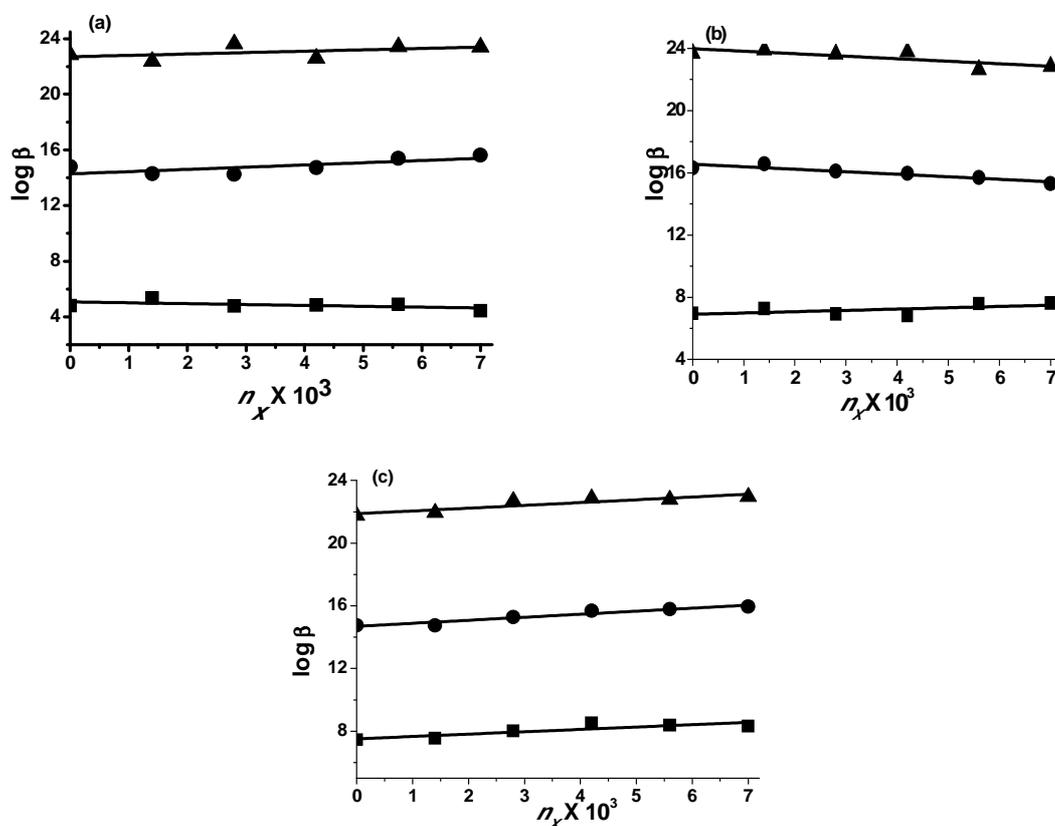


Figure 1: Variation of overall stability constant values of metal-glycylglycine complexes with mole fraction ($n_x \times 10^3$) of TX100-water mixtures (a) Ca (II); (b) Mg(II); (c) Zn(II); (■) $\log \beta_{ML2}$; (●) $\log \beta_{ML2H}$ (▲) $\log \beta_{ML2H2}$

Effect of Solvent

Many workers were opinion that both electrostatic and non-electrostatic effects should be considered even in the case of simple acido-basic equilibria; one dominates the other, depending upon the nature of solute and solvent [23-25]. The effect of surfactant on complex equilibria and apparent shift in the magnitude of stability constants in micellar media can be attributed [26] to the creation of a concentration gradient of proton between the interface and the bulk solution. The number of micelles increases with the concentration of surfactant, and oppositely charged ions are concentrated in the Stern layer [27]. The dielectric constant of the medium has a direct influence on the protonation-deprotonation equilibria [28, 29]. According to Born equation, the energy to electrostatic interaction is

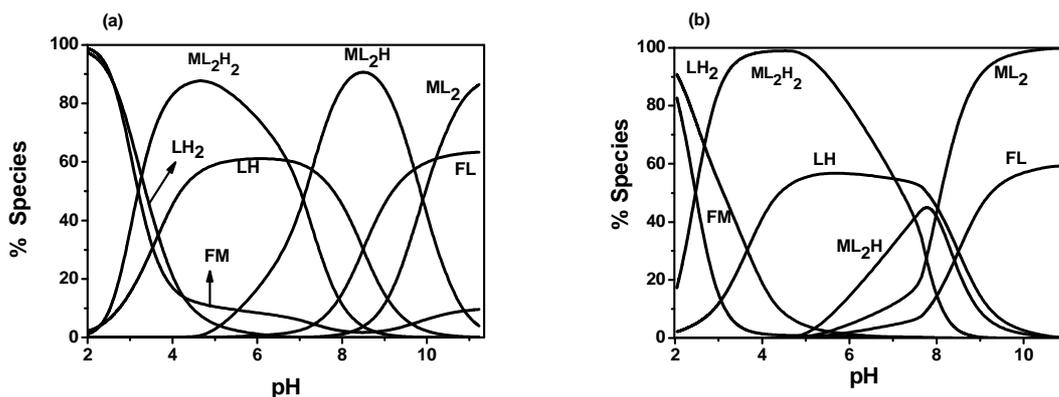
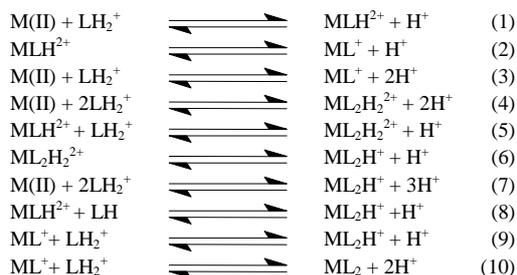
related to dielectric constant of medium [30]. The variations in log βs of complexes of glycylglycine with mole fraction of TX100-water mixtures are given in Figure.1. The linear trend indicates that long range interaction between metal ion and ligand is electrostatic in nature. The deviation from linearity may be due to some contributions from non-electrostatic forces.

Distribution Diagrams

Glycylglycine contains one dissociable (carboxylate) and one associable (amino) proton. The different forms of glycylglycine are LH₂⁺, LH, and L⁻ in the pH ranges viz., below 5.0, 3.0–9.0 and above 7.0, respectively. Hence, the plausible binary metal-ligand species in different systems can be predicted from these data and confirmed by MINIQUAD75. The present investigation reveals the existence of ML₂H₂, ML₂H and ML₂ for Ca (II), Mg (II) and Zn (II).

The formation of ML₂H₂ by Ca (II), Mg (II) and Zn (II) probably indicates that the side chain amino group is still protonated in the presence of Ca (II), Mg (II) and Zn (II). The ML₂ species is the predominant species at higher pH and ML₂H₂ 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 glycylglycine. The formation of various binary complex species is shown in the following equilibria. Some typical distribution diagrams of TX 100-water media are shown in Figure. 2. The present investigation reveals the existence of ML₂H₂, ML₂H and ML₂ for Ca (II), Mg (II) and Zn(II).

In case of ML₂H₂ is formed as the concentration of free metal ion and LH₂⁺ decreased as seen in Equilibrium (4). Equilibria (7) and (8) are proposed for formation of ML₂H but the latter is more probable than the earlier because is ML₂H formed with decreasing concentration of MLH. In the case of, Equilibria (9) is the possible ways for the formation of ML₂H but (10) is more appropriate because during its formation there is a decrease in ML concentration and the percentage of ML₂ is increased as the concentration of ML and ML₂H are decreased at the same pH range which is described by Equilibria (5) and (6).



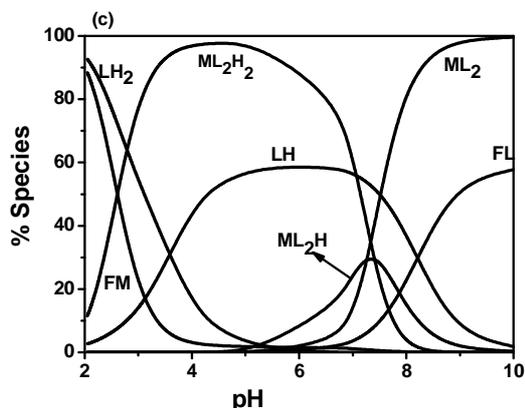


Figure 2: Distribution diagrams of binary complexes of glycylglycine in 1.0% v/v TX100-water mixture: (a) Ca (II), (b) Mg (II) and (c) Zn (II)

Structures of Complexes

It is not possible to elucidate or confirm the structures of the complex species pH metrically but they can be proposed based on literature reports and chemical knowledge. Taking this into consideration, both *mono*- and *bis*-glycylglycine complexes have been identified for M (II)-glycylglycine system of the Ca, Mg and Zn metals. The first donor is the oxygen of carboxyl group and the second donor site is amine nitrogen atom of glycylglycine. The oxygen or nitrogen in the amide group could also act as third donor site of glycylglycine. This additional chelation results in a five-membered ring. In view of the principle of soft and hard acid and bases (SHAB), the very soft character of Ca (II), Mg (II) and Zn (II) prefers amine nitrogen site over to harder carboxylate or amide oxygen. Probst and Rode [31] observed that below pH 8.0, the terminal carboxyl group and terminal amino group are simultaneously coordinated to cadmium ion and the amide might also be simultaneously coordinated through carbonyl oxygen atom resulting in a five-membered chelate ring, which is proved from the X-ray diffraction analysis of glycylglycine complexes of cadmium ion [32] and mercury ion [33].

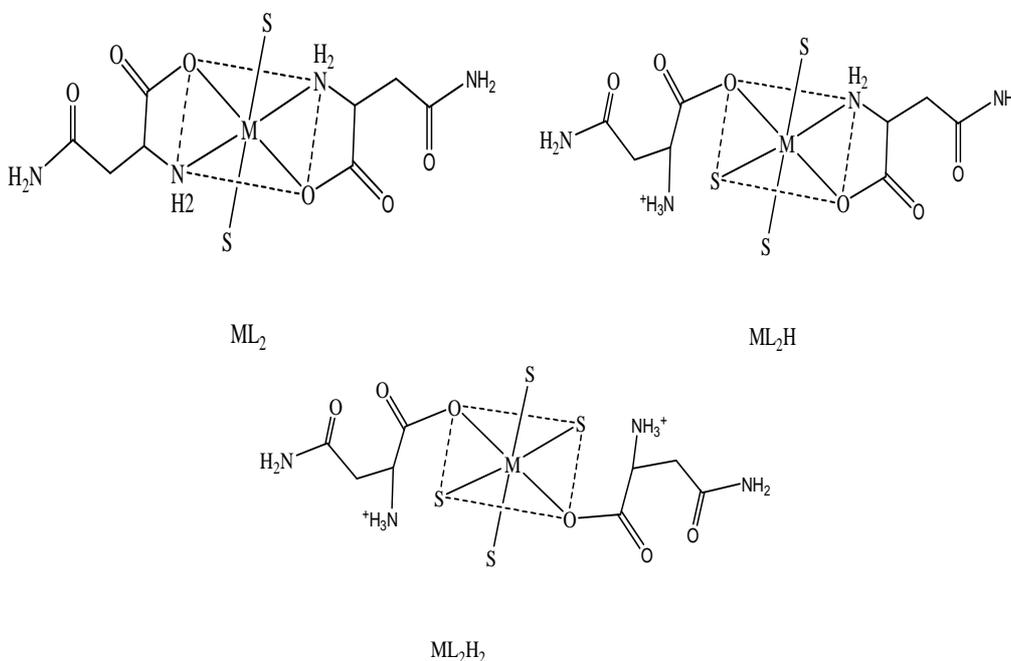


Figure 3: Structure of glycylglycine complexes (S is either solvent or water molecules)

Octahedral structures are proposed to the complexes of Ca (II), Mg (II) and Zn (II). Amine nitrogen atoms can associate with hydrogen ions in the lower 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 equilibria producing protonated and unprotonated complexes. The possible structures for the species of M (II)- glycyglycine complexes are given in Figure.3.

Table 1: Total initial concentrations of ingredients (in mmol) of titrands in TX100-water mixtures [NaOH] = 0.4 mol L⁻¹; V₀=50.0 cm³; temp=303 K; ionic strength= 0.16 mol L⁻¹; mineral acid= 1mmol

% v/v TX100	TM0				TL0(GG)	TL0:TM0
	Ca(II)	Cd(II)	Mg(II)	Zn(II)		
0.0	0.10031	0.10019		0.10012	0.2488	2.50
					0.3767	3.75
					0.4990	5.00
0.5	0.10031	0.10019		0.10012	0.2483	2.50
					0.3749	3.75
					0.4996	5.00
1.0	0.10031	0.10019		0.10012	0.2493	2.50
					0.3744	3.75
					0.4986	5.00
1.5	0.10031	0.10019		0.10012	0.2494	2.50
					0.3771	3.75
					0.4968	5.00
2.0	0.10031	0.10019		0.10012	0.2498	2.50
					0.3762	3.75
					0.4986	5.00
2.5	0.10031	0.10019		0.10012	0.2498	2.50
					0.3737	3.75
					0.4966	5.00

Table 2: Parameters of best fit chemical models of Ca (II), Mg (II) and Zn (II) - glycyglycine complexes in TX100-water mixtures

TX100% v/v	log β _{min} (SD)			pH-Range	NP	U _{corr}	χ ²	Skew-ness	Kurt-osis	R-factor
	ML ₂	ML ₂ H	ML ₂ H ₂							
Ca(II)										
0.0	4.80(38)	14.80(22)	22.85(27)	3.0-10.1	28	16.76	0.80	0.16	3.32	0.0280
0.5	5.35(36)	14.28(26)	22.37(39)	3.0-10.1	25	5.13	53.3	0.10	5.02	0.0318
1.0	4.78 (39)	14.25(21)	23.63(28)	3.0-10.8	26	16.08	46.92	0.52	3.39	0.0238
1.5	4.84(24)	14.71(29)	22.59(32)	2.3-10.9	36	10.57	18.37	1.64	6.93	0.0206
2.0	4.91(26)	15.38(36)	23.43(39)	2.8-10.9	37	22.88	87.41	0.25	5.51	0.0256
2.5	4.44(46)	15.61(34)	23.40(32)	2.8-10.8	28	10.32	58.48	0.27	3.73	0.0372
Mg(II)										
0.0	6.97(28)	16.32(25)	23.68(19)	2.2-10.3	73	21.14	56.98	0.14	4.37	0.0343
0.5	7.27(26)	16.58(28)	23.91(17)	2.2-10.3	67	41.09	16.11	0.89	4.13	0.0442
1.0	6.92(20)	16.11(25)	23.65(19)	2.5-10.3	54	16.52	6.49	-0.71	3.86	0.0331
1.5	6.82(29)	15.96(30)	23.78(22)	2.5-10.5	47	19.5	25.75	-2.51	13.5	0.0370
2.0	7.59(37)	15.70(41)	22.64(47)	3.8-10.5	39	11.36	25.02	-1.29	5.96	0.0328
2.5	7.62(52)	15.30(12)	22.84(25)	3.9-10.0	39	12.77	34.25	0.37	4.29	0.0390
Zn(II)										
0.0	7.46(30)	14.76(35)	21.76(40)	2.5-8.1	56	13.94	32.67	0.33	4.55	0.0305
0.5	7.55 (40)	14.75(47)	21.94(43)	2.7-8.3	57	10.12	5.05	0.85	5.75	0.0259
1.0	8.02(32)	15.29(37)	22.69(32)	2.4-8.3	66	11.47	33.19	0.39	4.05	0.0254
1.5	8.54(26)	15.68(33)	22.86(21)	2.8-8.1	49	18.76	9.24	0.12	2.32	0.0370
2.0	8.39(28)	15.79(51)	22.77(13)	2.8-8.1	45	20.40	11.79	0.62	3.65	0.0297
2.5	8.33(44)	15.95(59)	22.97(45)	2.8-7.5	32	15.58	10.83	0.12	3.44	0.0459

$$U_{corr} = U / (NP - m) \times 10^8; NP = \text{Number of points}; m = \text{number of protonation constants}; SD = \text{Standard deviation}$$

Table 3: Effect of errors in influential parameters on Zn(II)-glycylglycine complex stability constants in 1.5% v/v TX100-water mixture

Ingredient	% Error	Log $\beta_{\text{ml}}(\text{SD})$		
		120	121	122
Acid	0	8.54(26)	15.68(33)	22.86(21)
	-5	10.78(65)	17.75(70)	24.20(61)
	-2	9.35(31)	16.61(37)	23.46(26)
	+2	7.83(24)	15.42(35)	22.70(20)
	+5	6.82(21)	14.51(50)	22.14(24)
Alkali	-5	6.82(27)	14.71(44)	22.35(23)
	-2	7.83(24)	15.49(33)	22.77(20)
	+2	9.28(30)	16.48(37)	23.36(24)
	+5	10.52(49)	17.34(58)	23.89(43)
Ligand	-5	8.42(23)	15.77(33)	22.87(19)
	-2	8.49(25)	15.89(33)	22.98(20)
	+2	8.59(27)	16.06(34)	23.13(22)
	+5	8.68(29)	16.19(35)	23.25(24)
Metal	-5	8.70(28)	16.04(37)	23.14(23)
	-2	8.61(22)	16.01(35)	23.09(27)
	+2	8.49(25)	15.96(32)	23.03(20)
	+5	8.40(24)	15.92(30)	22.99(19)
Volume	-5	8.49(25)	15.92(33)	23.00(20)
	-2	8.52(25)	15.96(33)	23.03(21)
	+2	8.56(26)	15.99(33)	23.06(21)
	+5	8.58(26)	16.02(33)	23.09(21)
Log F	-5	8.55(26)	15.98(33)	23.06(21)
	-2	8.55(26)	15.98(33)	23.06(21)
	+2	8.54(26)	15.98(33)	23.06(21)
	+5	8.54(26)	15.98(33)	23.06(21)

CONCLUSION

The following conclusions have been drawn from the modeling studies of the speciation of binary complexes of Ca (II), Mg (II) and Zn (II) with glycylglycine in TX100-water mixture.

1. Glycylglycine forms both protonated and unprotonated complexes under a pH range of 2.0-10.0
2. The binary species formed due to the interaction of glycylglycine with metals are CaL_2H_2 , CaL_2H , CaL_2 , MgL_2H_2 , MgL_2H , MgL_2 , ZnL_2H_2 , ZnL_2 and ZnL_2H . These models are validated by statistical treatment of data.
3. The linear variation of stability constants as a function of dielectric constant of the medium indicates the dominance of electrostatic forces over non-electrostatic forces. Some species are stabilized due to electrostatic interactions and some are destabilized due to the decreased dielectric constant.
4. The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal > total volume > Log F.

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