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Chemical Speciation of Divalent Metal complexes of L-Aspartic Acid in Propylene Glycol-Water Mixtures

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ABSTRACT

Chemical speciation of some essential metal complexes of L-aspartic acid in 0.0-60.0% v/v propylene glycol-water mixtures has been studied pH metrically at an ionic strength of 0.16 mol L^{-1} and 303 K. The active forms of the ligand are LH_3^+, LH_2, LH^- and L^{2-}. The predominant species detected are ML, ML_2H_2, ML_2H_3, and ML_2H_4. Models containing different numbers of species were refined by using the computer program MINIQUAD75. The best-fit chemical models were arrived at based on statistical parameters. The trend in variation of complex stability constants with change in the dielectric constant of the medium is explained on the basis of electrostatic and non-electrostatic forces.

1. Introduction

Metals play a vital role in all living systems. Any malfunctioning of these metals can initiate a number of physiological abnormalities and symptoms of clinical disorders. Divalent metal ions are responsible for proper functioning of different enzymes. The metals are generally found either bound directly to proteins or in cofactors such as porphyrins or cobalamins, or in clusters that are in turn bound by the protein. Proteins associated with divalent metal ions most commonly catalyze the intramolecular or intermolecular rearrangement of electrons.

Calcium is an important component of a healthy diet and a mineral necessary for life and plays an important role in human body in building stronger, denser bones early in life and keeping bones strong and healthy later in life [1]. Its deficiency leads to rickets and poor blood clotting. Magnesium plays a role in the stability of all polyphosphate compounds in the cells in every organism in different concentrations [2, 3]. Magnesium deficiency in the body leads to asthma, diabetes and osteoporosis [4]. Zinc is a versatile ion as it can bind to different combinations of ligand types resulting in a broad range of stability, reactivity and functions [5].

L-aspartic acid (Asp) is a non-essential amino acid found copious in plant proteins. It maintains the solubility and ionic character of proteins as well as in removing excess ammonia and other toxins from the blood stream and in the functioning of RNA and DNA [6]. Asp is popular as a drug for chronic fatigue as it plays crucial role in generating cellular energy [7]. Hence, speciation studies of Asp with Ca, Mg and Zn in PG-water mixtures are reported in the present communication.

2. Experimental Methods

2.1 Materials

Exactly 0.05 mol L^{-1} solution of L-aspartic acid (Merck, India) was prepared in triple distilled deionized water by maintaining 0.05 mol L^{-1} hydrochloric acid concentration to increase the solubility. 1,2-Propylene glycol (Merck, India) was used as received. 0.2 mol L^{-1} Hydrochloric acid (Qualigens, India) and 0.4 mol L^{-1} sodium hydroxide (Qualigens, India) were prepared. The 2 mol L^{-1} sodium chloride (Qualigens, India) was prepared to maintain the ionic strength in the titrand. The 0.05 mol L^{-1} solutions of Ca(II), Mg(II) and Zn(II) chlorides were prepared by dissolving GR grade (Merck, India) salts in triple distilled water maintaining 0.05 mol L^{-1} acid to suppress the hydrolysis of metal salts. 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.[8] The strengths of alkali and mineral acid were determined using the Gran plot method [9, 10].

2.2 Procedure

The titrimetric data was obtained using ELICO (Model LI-120) pH meter (readability, 0.01). The glass electrode was equilibrated in a well stirred PG-water mixtures containing inert electrolyte for several days. The effects of variations in asymmetry, liquid junction potential, activity coefficient, sodium ion error and dissolved carbon dioxide on the response of glass electrode were accounted for in the form of correction factor. For the determination of stability constants of binary species, initially strong acid was titrated with alkali at regular intervals to check the complete equilibration of the glass electrode. Then, the calomel electrode was refilled with PG-water mixture of same composition as that of the titrand. All the titrations were performed in medium containing varying concentrations of PG-water mixtures (0-60% v/v) pH metrically at 303.0 ± 0.1 K. In each of the titrations, the titrand consisted of approximately 1mmol mineral acid in a total volume of 50 cm^3. Titrations with different ratios (1:2.5, 1:3.75 and 1:5) of metal-to-ligand were carried with 0.4 mol L^{-1} sodium hydroxide [11, 12].

2.3 Modeling Strategy

The computer program SCPHD [13] was used to calculate the correction factor. The binary stability constants were calculated from the pH metric titration data using the computer program MINIQUAD75 [14]. The correction factor and protonation constants of Asp were fixed during the refinement of binary systems [15]. The variation of stability constants with the dielectric constant of the medium was analyzed on the basis of electrostatic/non-electrostatic, solute-solute and solute-solvent interactions.

3. Results and Discussion

Results of exhaustive modeling for the Mg-Asp in 10% PG-water mixture are given in Table 1. The models indicate better statistics as the number of species was increased, confirming better fit. There was no further improvement in the fit on inclusion of some more species. This indicates that the exhaustive model appropriately fits the experimental

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data. Such exhaustive modeling was performed for all the systems. The results of the best fit models that contain the stoichiometric coefficients 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 deviations in overall stability constants (log β) and small values of U_{corr} (sum of squares of deviations in concentrations of ingredients at all experimental points corrected for degrees of freedom) for the systems signify the precision of the constants. The models are further validated by the residual analysis.

Table 1 Exhaustive modeling study performed on Mg(II)-L-aspartic acid system in 10% v/v PG-Water mixture, pH range =2.0-9.0 and NP=77

Model no	log βmlh (SD)				U_{corr} x10^8	χ^2	Skewness	Kurtosis	R –factor
	ML	ML_2H_2	ML_2H_3	ML_2H_4					
1	2.73(19)	-----	----	-----	4.11	137.94	-1.64	4.73	0.0098
2	----	22.74(127)	----	-----	4.59	132.60	-1.35	4.56	0.0103
3	-----	-----	28.37(12)	-----	3.63	100.39	-1.28	5.24	0.0092
4	-----	-----	-----	31.67(12)	3.51	87.03	-1.10	5.27	0.0090
5	2.83(20)	23.27(44)	-----	-----	4.07	118.40	-1.62	4.81	0.0097
6	2.73(17)	-----	28.37(12)	-----	3.15	81.00	-1.64	5.46	0.0085
7	2.73(17)	-----	-----	31.67(11)	3.03	75.67	-1.43	5.46	0.0084
8	-----	23.53(39)	28.42(13)	-----	3.58	90.14	-1.18	5.65	0.0091
9	----	24.27(13)	----	32.02(10)	2.74	105.45	-0.42	8.00	0.0079
10	----	----	28.51(11)	31.82(10)	2.36	102.82	-0.78	7.00	0.0074
11	2.97(17)	23.77(25)	28.46(11)	----	2.96	58.97	-1.54	5.46	0.0083
12	2.73(13)	----	28.51(10)	31.82(9)	1.88	83.77	-1.22	6.85	0.0066
13	3.23(12)	24.35(11)	----	32.05(9)	1.99	94.51	-0.70	5.85	0.0068
14	----	24.30(12)	28.62(10)	32.04(8)	1.74	118.61	0.02	14.13	0.0064
15	3.25(9)	24.38(8)	28.64(8)	32.07(6)	0.99	67.84	-0.24	5.31	0.0048

Table 2 Parameters of best fit chemical models of Aspartic acid complexes of Ca, Mg and Zn in PG-water mixtures

% v/v PG	log β_{mlh} (SD)				pH-range	NP	U_{corr} x10^8	χ^2	Skew-ness	Kurt-osis	R-factor
	110	122	123	124							
Ca(II)											
00.0	3.56(61)	25.14(67)	29.11(68)	32.43(72)	3.0-9.5	35	4.06	16.98	-0.15	3.18	0.0144
10.0	3.41(13)	24.52(11)	28.74(11)	32.17(9)	2.0-9.0	75	2.03	31.68	-0.57	4.78	0.0066
20.0	3.25(39)	24.70(62)	29.81(45)	33.15(51)	2.8-11.2	71	6.55	92.77	2.55	14.05	0.0205
30.0	4.11(31)	26.24(10)	30.52(11)	34.17(9)	2.0-9.0	78	2.49	43.81	-0.79	7.30	0.0075
40.0	3.19(11)	24.33(10)	28.63(12)	31.86(21)	2.0-9.0	84	0.69	116.25	-1.33	8.77	0.0039
50.0	3.13(8)	24.13(12)	28.54(16)	32.72(6)	2.0-10.0	100	1.55	110.13	-0.99	9.57	0.0063
60.0	4.22(14)	25.39(12)	29.36(27)	33.70(9)	2.0-9.6	95	3.88	73.04	-0.97	8.90	0.0101
Mg(II)											
00.0	2.88(20)	24.23(21)	28.33(18)	31.71(18)	2.0-9.2	71	3.54	98.47	-0.15	6.71	0.0095
10.0	3.25(9)	24.38(8)	28.64(7)	32.07(6)	2.0-9.0	77	0.98	67.84	-0.24	5.31	0.0047
20.0	4.53(15)	24.95(9)	28.61(19)	32.15(13)	2.0-8.5	46	0.80	50.64	-0.15	4.52	0.0052
30.0	5.70(14)	26.48(10)	30.63(10)	34.30(8)	2.0-8.8	79	2.37	51.57	-0.34	5.57	0.0075
40.0	5.03(14)	25.98(10)	30.11(12)	33.92(9)	2.0-9.0	82	2.96	37.45	-0.09	5.87	0.0085
50.0	5.20(17)	25.77(18)	30.10(17)	33.64(20)	2.5-9.0	55	1.16	100.84	-0.33	11.74	0.0068
60.0	6.01(18)	26.34(11)	30.28(17)	34.32(10)	2.0-9.0	88	4.48	40.79	-0.03	5.60	0.0105
Zn(II)											
00.0	6.22(32)	23.84(92)	27.77(94)	31.51(80)	2.7-8.0	44	3.15	24.00	0.72	7.17	0.0122
10.0	5.94(15)	23.92(30)	28.74(17)	32.46(8)	1.7-7.0	114	3.85	165.42	-2.03	10.54	0.0076
20.0	7.42 (15)	25.08(15)	28.71(27)	32.07(24)	2.0-8.0	84	4.22	134.22	0.83	15.08	0.0110
30.0	6.23(25)	24.65(67)	29.61(42)	33.52(44)	3.0-7.0	40	2.64	37.87	0.76	8.03	0.0114
40.0	7.78(26)	26.14(18)	30.31(21)	34.18(16)	2.0-6.0	75	5.65	71.21	0.75	7.68	0.0115
50.0	7.70(20)	25.45(23)	29.76(21)	33.41(25)	2.7-6.5	48	0.92	25.11	-0.24	3.40	0.0061
60.0	7.47(10)	25.22(12)	29.40(13)	32.70(30)	2.7-6.0	50	1.59	32.29	0.11	4.12	0.0078

U_{corr} = U/ (NP-m); NP = Number of points, m = number of stability constants; SD = Standard deviation

3.1 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 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 following normal distribution in the least squares analysis, 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 PG-water mixtures, as discussed below.

3.1.1 χ^2 Test

χ^2 is a special case of gamma distribution whose probability density function is an asymmetrical function. This distribution measures the probability of residuals forming a part of standard normal distribution with zero mean and unit standard deviation. If the χ^2 calculated is less than the table value, the model is accepted.

3.1.2 Crystallographic R-test

Hamilton's R-factor ratio test [16] is applied in complex equilibria to decide whether inclusion of more species in the model is necessary or not. In pH-metric method, the readability of pH meter is taken as the R_{limit} which represents the upper boundary of R beyond which the model bears no significance. When these are different numbers of species the models whose values are greater than R-table are rejected. The low crystallographic R-values given in Table 2 indicate the sufficiency of the model.

3.1.3 Skewness

It is a dimensionless quantity indicating the shape of the error distribution profile. A value of zero for skewness indicates that the underlying distribution is symmetrical. If the skewness is greater than zero, the peak of the error distribution curve is to the left of the mean and the peak is to the right of the mean if skewness is less than zero. The values of skewness recorded in Table 2 are between -1.33 and 2.55 for Ca, -0.03

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and -0.34 for Mg and -2.03and 0.83 for Zn. These data evince that the residuals form a part of normal distribution; hence, least-squares method can be applied to the present data.

3.1.4 Kurtosis

It is a measure of the peakedness of the error distribution near a modal value. For an ideal normal distribution kurtosis value should be three (mesokurtic). If the calculated 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 pattern.

3.1.5 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 made by introducing pessimistic errors in the influential parameters like concentrations of alkali, mineral acid, ligand, metal and log F (Table 3). The order of the ingredients that influence the magnitudes of stability constants due to incorporation of errors is alkali > acid > ligand > metal > 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 appropriateness of the experimental conditions and choice of the best fit models.

Table 3 Effect of errors in influential parameters on Mg-Asp complex stability constants in 30% v/v PG-water mixture.

Ingredient	% error	log β_{mlh}(SD)			
		110	122	123	124
	0%	5.07(14)	26.48(9)	30.63(10)	34.30(8)
Alkali	-5	Rejected	Rejected	29.15(55)	33.68(17)
	-2	2.72(93)	25.02(21)	30.01(14)	33.82(10)
	2	6.87(15)	27.59(12)	31.30(12)	34.86(12)
	5	11.70(25)	29.10(26)	32.65(22)	35.75(25)
Acid	-5	12.81(26)	30.50(24)	34.21(23)	37.14(24)
	-2	6.98(17)	27.87(14)	31.68(14)	35.20(14)
	2	3.25(33)	25.01(18)	29.80(`14)	33.61(9)
	5	Rejected	Rejected	28.55(84)	33.06(18)
Ligand	-5	5.43(12)	26.49(8)	30.33(12)	34.13(8)
	-2	5.22(13)	26.49(9)	30.51(10)	34.23(8)
	2	4.91(15)	26.47(10)	30.74(10)	34.37(9)
	5	4.60(20)	26.44(11)	30.90(11)	34.49(10)
Metal	-5	5.21(14)	26.58(10)	30.72(11)	34.38(9)
	-2	5.12(14)	26.52(9)	30.66(10)	34.33(9)
	2	5.02(14)	26.44(9)	30.59(10)	34.27(8)
	5	4.95(13)	26.39(9)	30.55(10)	34.22(8)
Log F	-5	5.12(14)	26.53(9)	30.67(10)	34.34(9)
	-2	5.09(14)	26.50(9)	30.65(10)	34.32(8)
	2	5.05(14)	26.45(9)	30.60(10)	34.27(8)
	5	5.02(14)	26.43(9)	30.58(10)	34.25(8)

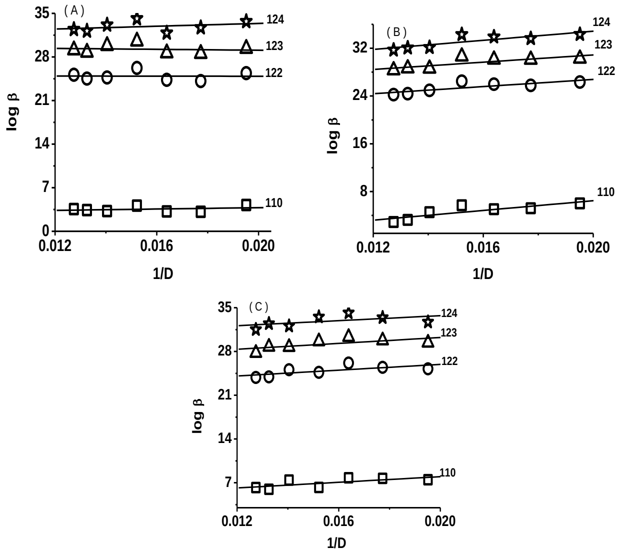

Fig. 1 Variation of stability constants of Metal-Asp complexes with reciprocal of dielectric constant (1/D) of PG - water mixtures: a) Ca, b) Mg and c) Zn (□) log β_{ML}, (○) log β_{ML2H2}, (Δ) log β_{ML2H3} and (☆) log β_{ML2H4}

3.2 Effect of Solvent

PG is an amphiprotic structure forming solvent. At the same time it competes with the ligand to coordinate to the metal ion. Born's classical treatment [17] accounts for the electrostatic contribution to the free energy change. According to this treatment, the energy of electrostatic interaction is related to dielectric constants. The trends of log β values of complexes of Asp with Ca(II), Mg(II) and Zn(II) with the variation of 1/D (D is the dielectric constant of the medium) of PG-water mixtures are shown in Fig. 1. The linear variation indicates that the dielectric constant or long range interactions are responsible for the trend in stability. This linear increase also indicates the dominance of the structure-forming nature of PG over its complexing ability.

3.3 Distribution Diagrams

Asp has two dissociable protons and one amino group which can associate with a proton. It exists as LH_3^+, LH_2, LH^- and L^{2-} in the pH ranges <2.0, 2.0-6.0, 3.0-11.0 and >7.0, respectively. Hence, the plausible binary metal-ligand complexes can be predicted from these data. The present study reveals the existence of ML, ML_2H_2, ML_2H_3 and ML_2H_4 for Ca(II), Mg(II) and Zn(II) and their formation is shown in the following equilibria.

$$M(II) + 2LH_3^+ \rightleftharpoons ML_2H_4^{2+} + 2H^+ \qquad (1)$$

$$M(II) + 2LH_3^+ \rightleftharpoons ML_2H_3^+ + 3H^+ \qquad (2)$$

$$M(II) + 2LH_3 \rightleftharpoons ML_2H_2 + 4H^+ \qquad (3)$$

$$ML_2H_4^{2+} \rightleftharpoons ML_2H_3^+ + H^+ \qquad (4)$$

$$ML_2H_4 \rightleftharpoons ML_2H_2 + 2H^+ \qquad (5)$$

$$ML_2H_3^+ \rightleftharpoons ML_2H_2 + H^+ \qquad (6)$$

$$M(II) + 2LH_2 \rightleftharpoons ML_2H_2 + 2H^+ \qquad (7)$$

$$M(II)+LH_2 \rightleftharpoons ML+2H^+ \qquad (8)$$

$$M(II)+LH \rightleftharpoons ML+H^+ \qquad (9)$$

Some typical distribution diagrams in PG-water mixtures are shown in Fig. 2, which represents the formation of binary complexes of Ca, Mg and Zn with Asp. The percentage species of the metal complexes are calculated with respect to the metal. Hence the total metal percent shall be 100 at any pH. But the content of ligand is superimposed only to show the possible forms of ligand at different pH values. The species ML, ML_2H_2, ML_2H_3 and ML_2H_4 are formed in the pH range 2.0-11.0. The ML_2H_4 is formed from free metal and LH_3^+ form of the ligand (Equilibrium 1) below a pH of 2.0. The species ML_2H_3 is formed either from free metal and LH_3^+ (Equilibrium 2) or by the deprotonation of ML_2H_4 (Equilibrium 4) below a pH of 4.0. Similarly ML_2H_2 can be formed through Equilibria 3 and 7 beyond 2.0 pH. From Fig. 2, the formation of ML_2H_2 from M(II) and LH_3^+ is ruled out since the concentration of LH_3^+ is negligible in the pH range of formation of ML_2H_2. The species ML is formed either from LH_2 (Equilibrium 8) or from LH^- form of the ligand (Equilibrium 9) above a pH of 5.0.

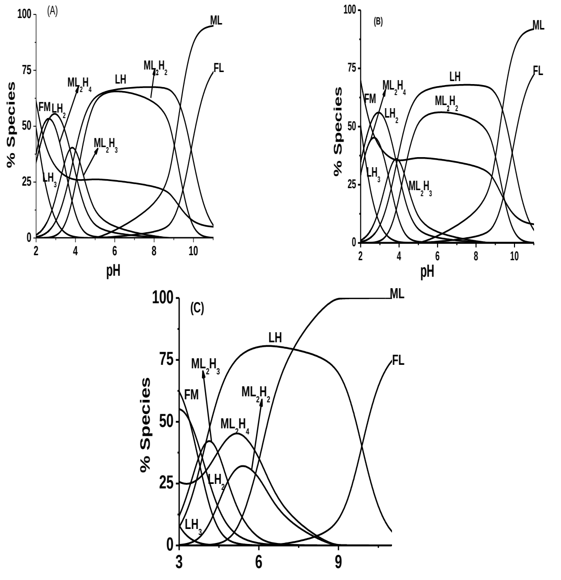

Fig. 2 Distribution diagrams of binary complexes of Asp in 10% v/v PG-water mixture. a) Ca, b) Mg and c) Zn

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Table 4 Total initial concentrations of ingredients (in mmol) for binary metal-ligand titrations in PG-Water medium. [NaOH] =0.4 mol L^{-1}; V_0 = 50 cm^3; Temperature = 303.0 K; Mineral acid = 1 mmol; μ=0.16 mol L^{-1}; TM0 = Number of mmols of ligand; TL0 = Number of mmols of ligand.

% v/v	TM0	TL0	TM0	TL0	TM0	TL0	TL0/TM0
G	Ca(II)	Asp	Mg(II)	Asp	Zn(II)	Asp	
00.00	0.1058	0.250	0.1204	0.251	0.09882	0.251	2.50
		0.375		0.375		0.375	3.75
		0.500		0.511		0.511	5.00
10.00	0.1058	0.251	0.1204	0.251	0.09882	0.251	2.50
		0.375		0.375		0.375	3.75
		0.511		0.511		0.511	5.00
20.00	0.1058	0.251	0.1204	0.240	0.09882	0.239	2.50
		0.375		0.359		0.359	3.75
		0.511		0.478		0.478	5.00
30.00	0.1058	0.251	0.1204	0.251	0.09882	0.239	2.50
		0.374		0.374		0.359	3.75
		0.499		0.499		0.478	5.00
40.00	0.1058	0.251	0.1204	0.251	0.09882	0.251	2.50
		0.375		0.375		0.375	3.75
		0.511		0.511		0.511	5.00
50.00	0.1058	0.251	0.1204	0.251	0.09882	0.250	2.50
		0.375		0.375		0.375	3.75
		0.511		0.511		0.500	5.00
60.00	0.1058	0.250	0.1005	0.250	0.09882	0.250	2.50
		0.375		0.375		0.375	3.75
		0.500		0.500		0.500	5.00

4. Conclusion

The following conclusions have been drawn from the modeling studies of the speciation of binary complexes of Ca, Mg and Zn with Asp in PG-water mixture. L-aspartic acid formed both protonated and unprotonated complexes ML, ML_2H_2, ML_2H_3 and ML_2H_4 for Ca, Mg and Zn in the pH range 2.0-11.0. 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. 3. The order of ingredients influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal > log F. The distribution diagrams infer that the protonated and unprotonated complexes are formed successively and simultaneously from higher protonated species on deprotonation and from free metal and ligand.

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