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Speciation of binary complexes of Co(II), Ni(II), and Cu(II) with L-phenylalanine in anionic micellar medium

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ABSTRACT

Speciation of binary complexes of Co(II), Ni(II), and Cu(II) with L-phenylalanine (Phe) in the presence of water–anionic surfactant mixtures in the concentration range of 0.0–2.5% w/v SLS has been studied pH-metrically at a temperature of 303 K and at an ionic strength of 0.16 mol L^{-1}. The selection of best fit chemical models is based on statistical parameters and residual analysis. The predominant species detected were ML, ML_2, and ML_2H_2 for Co(II), Ni(II), and Cu(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.

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Chemical speciation; L-phenylalanine; anionic surfactant; SLS; stability constants

Introduction

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. Hence, extensive attention has been paid in recent years to the study of the chemical speciation of ligands with metal ions.[1–4] Phe is an essential α-amino acid. It is classified as non-polar because of the hydrophobic nature of the benzyl side chain. Phe is an electrically neutral amino acid, one of the twenty common amino acids used to biochemically form proteins, coded for by DNA. It is used in the manufacture of food and drink products and sold as a nutritional supplement for its reputed analgesic and antidepressant effects. A non-food source of phenylalanine is the artificial sweetener aspartame. Phe is the starting compound used in the flavonoid biosynthesis.

Cobalt is a central component of the vitamin, cobalamin (vitamin B_{12}). Cobalt in the form of cyanocobalamin is most efficiently stored in kidneys and liver. Cobalt is essential for the production of red blood cells. It acts as coenzyme in several biochemical processes. Nickel is associated with several enzymes,[5,6] and any variation in its concentration leads to metabolic disorders. Nickel is present in enzymes like urease, present in a wide range of plant species. The signs of nickel deprivation include depressed growth, reproductive performance, and plasma glucose. It also affects distribution and proper functioning of other nutrients including calcium, iron, zinc, and vitamin B_{12}. Copper is an essential element for life on earth. The biological functions include electron transfer, dioxygen transportation, oxygenation, oxidation, reduction, and disproportionation.[7,8] The melanin pigment of the skin is also a copper containing protein.

Sodium lauryl sulphate (SLS) or sodium dodecyl sulphate is an anionic surfactant used in many cleaning and hygiene products, food, pharmaceuticals, and cosmetics. Micellar–water mixtures are chosen in these studies to maintain the dielectric constants of the medium comparable to those of the physiological fluids since the polarity of the active site cavities should generally be applicable, to compare ligand binding to the metal ion in protein and mixed solvent environments. 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, speciation studies of phenylalanine with some essential metal ions such as Co, Ni, and Cu in SLS–water mixtures are reported in this article.

Experimental

Materials

0.05 mol dm^{-3} aqueous solution of L-phenylalanine (GR grade, E-Merck, Germany) was prepared by dissolving sample in water. To increase the solubility of ligand,

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Table 1. Stoichiometric protonation constants of L-phenylalanine SLS–water mixtures. Temp = 303 K, ionic strength = 0.16 mol dm^{-3}.

	L-phenylalanine	
% w/v SLS	log K_1	log K_2
0.0	2.16	9.13
0.5	3.52	9.09
1.0	3.5	9.34
1.5	3.6	9.33
2.0	3.79	9.40
2.5	3.99	9.47

0.05 mol dm^{-3} hydrochloric acid 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} at 303 K. Solutions of Co(II), Ni(II), and Cu(II) chlorides (0.1 mol dm^{-3}) were prepared by dissolving G.R. Grade (E-Merck, Germany) salts in triple-distilled water maintaining 0.05 mol dm^{-3}acid (HCl) to suppress the hydrolysis of metal salts. Sodium hydroxide (Qualigens, India) of 0.4 mol dm^{-}3 was prepared. All the solutions were standardized by standard methods. Cobalt, Nickel, and Copper [9] chlorides were standardized using EDTA. 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.[10] The strengths of alkali and mineral acid were determined using the Gran plot method.[11,12]

Procedure

An ELICO (Model Li 120, India) pH meter of 0.01 readability (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/w) maintaining an ionic strength of 0.16 mol dm^{-3} with sodium chloride. In each of the titrations, the titrand consisted of approximately 1 m mol mineral acid in a total volume of 50 cm^3. Titrations with different metal-to-ligand ratios (1:2.5, 1:3.75, and 1:5) were carried out with 0.4 mol dm^{-3} sodium hydroxide.

Modeling strategy

The computer program SCPHD [13] was used to calculate the correction factor. The binary stability constants were calculated from with the pH-metric titration data using the computer program MINIQUAD75 [14] 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 phenylalanine were fixed. The stoichiometric protonation constants of L-phenylalanine determined in various SLS–water mixtures are listed in Table 1. The variation of stability constants with the mole fraction of the medium was analyzed on electrostatic grounds based on solute–solute and solute–solvent interactions.

Results and discussion

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 2.

A very low standard deviation in log β 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).[15,16] 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 −1.64 and 0.78. 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 under taken by introducing pessimistic errors in the influential parameters like concentrations of alkali, mineral acid, ligand, and metal (Table 3). 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. Parameters of best fit chemical models of M(II)–L-phenylalanine complexes in SLS–water medium.

% w/v	log β_{mlh} (SD)									
SLS	ML	ML_2	ML_2H_2	NP	$U_{corr} \times 10^8$	Skewness	χ^2	*R*-factor	Kurtosis	pH-range
Co(II)										
0.0	5.58(09)	9.41(07)	23.84(03)	66	0.78	0.14	15.01	0.0044	5.08	1.8–8.5
0.5	5.69(11)	9.60(11)	24.34(06)	30	1.32	−0.18	5.47	0.0108	4.11	2.5–8.5
1.0	6.59(11)	10.82(10)	25.21(05)	29	0.98	0.09	7.62	0.0094	3.51	2.5–8.5
1.5	6.50(13)	10.79(10)	24.79(05)	37	1.47	0.70	4.68	0.0085	4.33	2.5–8.5
2.0	5.42(09)	9.38(08)	24.21(05)	31	0.81	0.77	15.30	0.0075	4.02	2.5–8.5
2.5	5.80(13)	9.91(10)	24.85(06)	57	0.23	0.10	18.05	0.0100	4.69	2.5–8.5
Ni(II)										
0.0	8.55(10)	13.33(14)	23.50{04)	81	2.70	0.78	62.28	0.0073	7.34	1.7–8.5
0.5	7.32(14)	12.18(12)	25.00(03)	122	2.91	0.63	31.73	0.0078	4.49	1.7–8.5
1.0	8.72(19)	13.82(18)	25.94(09)	51	4.19	0.01	3.08	0.0150	2.68	2.3–7.5
1.5	7.71(14)	12.79(13)	24.99(05)	41	1.94	0.10	12.87	0.0089	3.12	2.3–7.5
2.0	7.40(17)	12.30(17)	24.83(07)	53	3.88	−0.01	4.97	0.0132	2.67	2.3–7.5
2.5	6.45(17)	10.98(18)	24.71(08)	52	3.78	0.21	5.13	0.0125	3.20	2.3–7.5
Cu(II)										
0.0	9.15(05)	16.51(09)	23.65(07)	70	1.62	0.19	45.85	0.0084	4.71	2.0–8.0
0.5	9.67(05)	16.52(08)	24.47(05)	56	0.84	0.00	11.24	0.0050	2.89	2.0–8.0
1.0	10.88(18)	18.72(18)	25.93(34)	73	7.54	−0.01	4.89	0.0175	2.91	2.0–8.0
1.5	8.83(06)	15.86(11)	23.85(21)	32	1.61	0.37	3.33	0.0117	2.14	2.6–8.0
2.0	9.25(05)	16.39(09)	24.45(20)	16	0.39	−1.33	8.67	0.0057	9.00	2.3–8.0
2.5	9.72(58)	17.05(60)	25.58(62)	68	38.78	−1.64	72.63	0.0295	5.4	1.6–8.0

$U_{corr} = U/(NP - m) \times 10^8$, where *m* = number of species; NP = number of experimental points; SD = standard deviation.

Table 3. Effect of errors in influential parameters on the stability constants of Co(II)–Phe complexes in 2.0% w/v SLS–water medium.

		log β (SD)		
Ingredient	% Error	ML	ML_2	ML_2H_2
Alkali	0	5.42(09)	9.38(08)	24.21(05)
	−5	3.79(21)	Rejected	Rejected
	−2	4.65(15)	8.24(14)	23.58(13)
	+2	6.73(20)	10.89(20)	24.66(07)
	+5	8.90(16)	13.76(25)	24.93(13)
Acid	−5	9.12(15)	13.88(23)	25.20(11)
	−2	6.85(19)	10.97(19)	24.77(07)
	+2	4.57(18)	8.23(16)	23.44(16)
	+5	3.89(23)	Rejected	Rejected
Ligand	−5	5.24(12)	9.26(11)	24.00(08)
	−2	5.34(10)	9.33(09)	24.13(06)
	+2	5.51(08)	9.44(07)	24.30(04)
	+5	5.63(08)	9.53(07)	24.42(04)
Metal	−5	5.46(10)	9.52(08)	24.45(05)
	−2	5.44(10)	9.44(08)	24.23(05)
	+2	5.41(10)	9.33(08)	24.20(05)
	+5	5.38(09)	9.24(08)	24.18(05)

Effect of surfactant

The variations of stability constants (log β) with mole fraction of different micellar media are shown in Figure 1. 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.[17,18] 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 formed by the metals are either positive charged or neutral. 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. 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 stabilities of these species in SLS–water medium do not show a particular trend. One of the reasons for such behavior is the accumulation of metal ions and ligands on the surface of micelles with an increased concentration of surfactant, and species with lower charge or high hydrophobicity are stabilized in the micellar pseudophase. The second reason that the species with lower charge or high

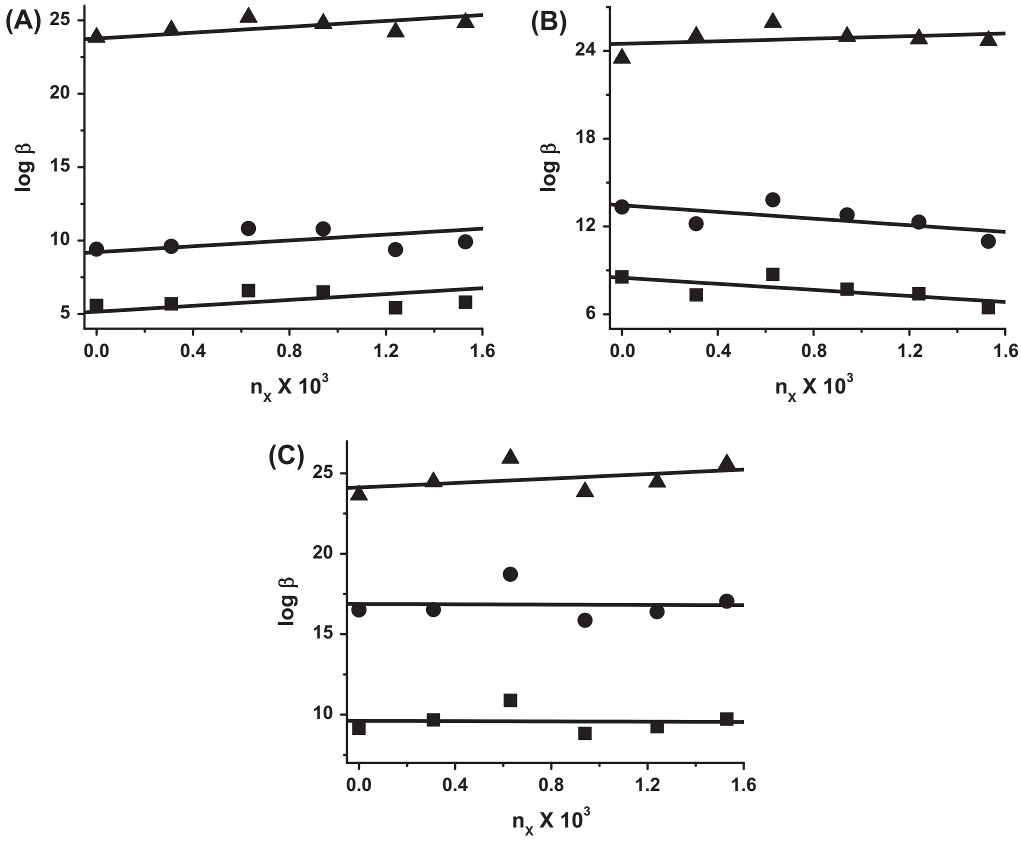

Figure 1. Variation of overall stability constant values of metal–Phe complexes with mole fraction ($nx \times 10^3$) of SLS–water mixtures (A) Co(II), (B) Ni(II), and (C) Cu(II), (■) log β_{ML}, (●) log β_{ML_2}, (▲) log $\beta_{ML_2H_2}$.

hydrophobicity are stabilized in the micellar pseudophase. So metal ligand combinations resulting in neutral complexes will be favoured. Highly hydrophobic ligands are expected to partition significantly between the surface of the micelle and its interior, which would lead to the reduction in log β. On the other hand, more hydrophobic ligands will distribute between micelle surface and bulk water leaving less of the ligand available in the surface region of the micelle for reaction. Thus in either case, the log β may decrease. Amino acids exist either as charged species or as zwitter ions, and so the probability of inserting them into the inner core is minimal. Since there is alkyl chain between the polar groups of Phe may not completely go into bulk water. Thus depending on the charge on amino acids and nature of the complex species, the stability varies. This trend reflects in all M(II)–Phe complexes (Figure 1).

Distribution diagrams

Some typical distribution diagrams of M(II)–Phe in SLS–water medium are shown in the Figure 2. The different forms of Phe are LH_2^+, LH, and L^- in the pH range of 3.0–5.0, 3.0–10.0, and 8.0–10.0, respectively. The plausible binary metal–ligand species in different systems can be predicted from these data. The present investigation reveals the existence of ML^+, ML_2, and $ML_2H_2^{2+}$ for Co(II), Ni(II), and Cu(II). The ML_2 species is the predominant species (Figure 2) at higher pH, and $ML_2H_2^{2+}$ 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 Phe. The formation of various binary complex species is shown in the following equilibria. Some typical distribution diagrams of SLS–water media are shown in Figure 2. Equilibria (1)–(3) represent the formation of complexes from metal ion and the ligand. In alkalimetric titrations, protons are removed successively from the complexes by the addition of aliquots of the alkali. Equilibrium (4) represents the successive deprotonation of the complexes with increasing pH of the solution during alkalimetric titrations. Formation of ML_2 through the equilibria (4)–(6) is proved by the increase in concentration of ML_2 by the decrease in concentration of ML^+ and $ML_2H_2^{2+}$. The formation of various binary complex species is shown in the following equilibria.

$$\mathrm{M(II)} + LH_2^+ \rightleftharpoons ML^+ + 2H^+ \tag{1}$$

$$\mathrm{M(II)} + LH \rightleftharpoons ML^+ + H^+ \tag{2}$$

$$\mathrm{M(II)} + 2LH_2^+ \rightleftharpoons ML_2H_2^{2+} + 2H^+ \tag{3}$$

$$ML_2H_2^{2+} \rightleftharpoons ML_2 + 2H^+ \tag{4}$$

$$ML^+ + LH_2^+ \rightleftharpoons ML_2 + 2H^+ \tag{5}$$

$$ML^+ + LH \rightleftharpoons ML_2 + H^+ \tag{6}$$

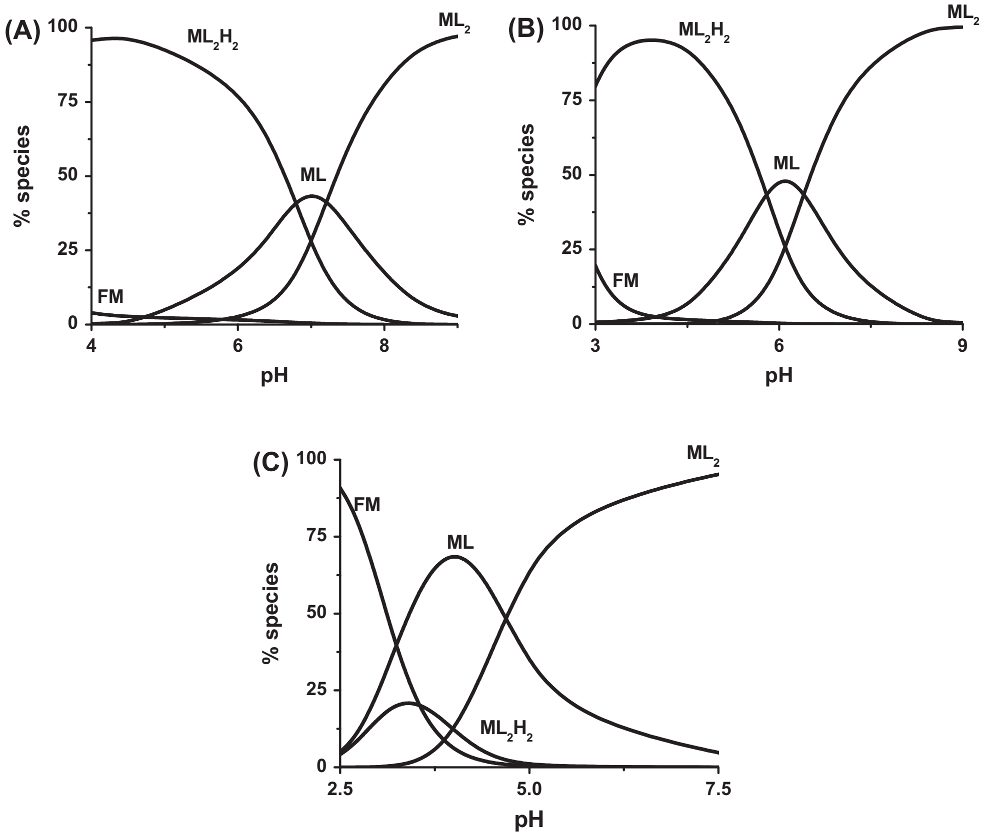

Figure 2. Distribution diagrams of Phe complexes in 1.5% w/v SLS–water medium. (A) Co(II) (B) Ni(II), and (C) Cu(II).

Conclusions

(1) The binary species detected are CoL^+, CoL_2, $CoL_2H_2^{2+}$, NiL^+, NiL_2, $NiL_2H_2^{2+}$, CuL^+, CuL_2, and $CuL_2H_2^{2+}$. These models are validated by statistical treatment of data.

(2) The non-linear variation of stability constants as a function of mole fraction of the medium indicates the dominance of non-electrostatic forces over 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 is influencing the magnitudes of stability constants due to incorporation of errors in their concentrations is alkali > acid > ligand > metal.

Notes on contributors

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Disclosure statement

No potential conflict of interest was reported by the authors.

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