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Potentiometeric study of protonation and complex formation of some amino acids with Zn (II) , Co(II) and Ni (II) in aqueous solution

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Abstract

The stability constants and complexation reaction between L-glutamine, L-arginine and glycine with Zn (II) , Co (II) and Ni (II) were studied potentiometrically in aqueous solution at 25° C and μ=0.1 M KNO_3. The overall stability constants log β'_s of all species are obtained by computer refinement of pH-volume data using BEST computer program. Several models were tested and the lowest δ_{FIT}, the best one is accepted. The main species in binary complexes MHL, ML, ML_2, MLOH, $ML(OH)_2$ and for ternary complexes are ML_1L_2, ML_1L_2H, ML_1L_2OH, $ML_1L_2(OH)_2$. The order found for the resulting stability constants vary as Co (II) < Ni (II) <Zn (II). The concentration distribution diagram was obtained with the program SPEPLOT.

Keywords: L-glutamine; L-arginine; glycine; BEST; Potentiometrically; Nonaqueous; solvents.

1. Introduction

Formation or stability constants are of interest in chemical analysis whenever a predication is to be made concerning the feasibility of a given separation, masking reaction, titration, or other measurements involving complexation. If the necessary stability constants are not known, it is generally simpler to experimentally evaluate the proposed procedure rather than to measure the constants. Thus, in spite to their usefulness in analytical chemistry, many formation constants have yet to be measured [1-5].

Potentiometry is a widely accepted method providing accurate, reliable results as well as a convenient investigative tool applied to electrolytic systems. It possesses a number of attributes that make it a useful and sensitive tool allowing accurate equilibrium data to be obtained for complexes formed within the system; these data can be provided efficiently [6]. Moreover, it withstands the contemporary demands put on the information gained from analytical procedures: speed, simplicity of operation, reliability, analytical performance and automation. A great informative potential inherent in it should be particularly stressed [7]. Potentiometry is one of the most convenient and successful techniques employd for metal complex equilibrium measurements. While some workers measure metal ion concentration with specific ion electrodes, or with metal electrodes, it is usually sufficient to use the highly accurate glass

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electrode for measuring the hydrogen ion concentration in a procedure termed potentiometric titration, whereby, for example, standard base is added in increments to a well characterized acid solution of the ligand in the absence of and in the presence of known total metal ion concentration. In most typical case, the p[H] is varied between 2.0-12.0 during which time some 50-100 equilibrium readings are obtained constituting the potentiometric equilibrium curve [8-12].

A special attention has been paid to the complexation reaction of the amino acids mainly due to their importance role in biological systems [13-15]. There are several papers on proton and metal complex formation equilibria of the aliphatic amino acids have been reported and discussed. Many different procedures (mainly electrochemical and spectroscopic methods) have been employed to determine the stability constants of the various complexes formed [16-21]. pH-metry has been applied most extensively for determination of the stability constants of the metal complexes of aliphatic amino acid.

In this paper, we applied pH-metry method for determine the protonation constants of L-glutamine, L-arginine, glycine and the stability constants of its complexes in binary and ternary systems with Zn (II), Co (II) and Ni (II) ions in aqueous solution at 25 °C and μ=0.1 M KNO_3 . The analysis is readily performed with the computer program BEST and concentration distribution diagram were obtained with the program SPEPLOT [22].

2. Theory

The basic algorithm in BEST [23-26] can be stated in terms of equation (1):

$$T_i = \sum_{J=1}^{NS} e_{ij} B_j \prod_{K=1}^{i} [C_K]^{e_{ij}} \qquad (1)$$

Which is a statement of the mass balance (at a given titration point) of the i-th component in terms of j-th species summed over all species present or NS, (NS=number of species, T_i=total concentration of i-th component). Each species concentration consists of a product of the overall stability constant and individual component concentration [C_k] raised to the power of the stoichiometric coefficient e_{ij}. The value of [C_k] is special when it represents the calculated concentration of H^+, which then is compared with the measured hydrogen ion concentration. The calculation process is repeated at all measured equilibrium points. In any calculation based on a pH profile there will be some known, previously calculated, β values as well as the unknown values to be determined. The first pass of the calculation procedure uses both the known and the estimated values of the unknown constants.

Thus the use of the algorithm for computing equilibrium constant in BEST involves the following sequence: 1. Start with a set of known and estimated overall stability constants (β'_s) and compute [H^+] at all equilibrium point. 2. Compute the weighted sum of the squares of the deviation in p[H] as in equation (2):

$$U = \sum w(p[H]_{obs} - p[H]_{calcd})^2 \qquad (2)$$

where $W = 1/(p[H]_{i+1} - p[H]_{i-1})$ is a weighting factor which serves to lesson the influence of the less accurate p[H] profile. 3. Adjust the unknown stability constants and repeat the calculation until no further minimization of a U can be obtained.

3. Experimental section

3.1 Potentiometry

The apparatus consisted of a custom-designed, thermostat 80-mL capacity all-glass vessel. It was fitted with a cover having a 50-mm 'O' ring seal, through which was inserted a combined glass electrode, a delivery tube for a Metrohm piston burette, and inlets and outlets for purified nitrogen. Each experiment was preceded by standardization of the pH meter, which was calibrated to display –log $[H^+]$ using buffer solutions. The system was maintained at an ionic strength of μ=0.10 mol L^{-1} with KNO_3 as a supporting electrolyte. In general, an experimental run involves collecting equilibrium data points throughout the entire pH range, between 2.0 and 11.0 as a function of millimoles standard KOH, added using the piston burette through a fine capillary tip immersed in the solution.

In titration, after each addition, the required time was allowed to reach chemical equilibrium. The concentrations of the reactants in the experimental solution were in the order 1.0×0^{-3} mol L^{-1} for each component. The hydrogen concentration was measured using a Metrohm model CH-9101 titroprocessor connected to a confident 286 PC for data transfer and computation. The potentiometric equilibrium measurements of the ligand solution in the absence and presence of metal ions was calculated using the program Best [23-26]. The protonation and formation constants of all species were obtained through the least-squares refinement of its p$[H^+]$ profiles. Throughout this investigation the function minimized was the weighted average of the sums of squares of deviations between calculated and observed p$[H^+]$ value (δ_{FIT}).

3.2. Reagents

The nitrate salts of nickel, cobalt and zinc (all from Merck) were used as supplied and the stock solutions were standardized by EDTA in the presence of suitable indicator. HCl, KOH, KNO_3, L-glutamine, L-arginine and glycine (all from Merck) were used without any further purification. Carbonate free KOH solution was standardized with potassium hydrogen phthalate (KHP). The HCl solution was standardized with KOH. All solutions were prepared in triply distilled deionized water.

4. Results and Discussion

4.1. Protonation constants

The protonation constants of L-glutamine, L-arginine and glycine were calculated under the same conditions of ionic strength and temperature which were applied for the study of binary and mixed systems. The distribution curves of the amino acids are shown in Fig 1. All ligands contain two donor groups (the amino and carboxylate groups), and therefore two hydrogen ions can dissociate from the fully protonated cations of the amino acids. Dissociation of these protons occurs stepwise, but in well-separated process, and aliphatic amino acids can appear in three different forms in different pH ranges. Analogous to glycine, aliphatic amino acids generally act as bidentate ligands, yielding, mono, bis, and tris complexes with most metal ions. In aqueous solution aliphatic amino acids exist as zwitter ions (HL), the amino group being protonate ($-NH_3^+$), while the carboxyl group is deprotonated ($-COO^-$). In the case of the α- amino acids, deprotonation of the ammonium group occurs in slightly basic solution (pH=9.0-10.0) to give the species (L^-).

The carboxylate group undergoes protonation in acidic media (pH=2.0-3.0), and therefore the two dissociation processes of the fully protonated cation form (H_2L^+) are completely separated. The overall protonation constants of ligands studied were calculated from computer refinement of the pH-volume data. The obtained values are shown in Table 1 and are in good

agreement with previously reported data [27]. The small differences between our values and previously reported values are within limits of experimental errors or due difference in experimental conditions (i.e difference in ionic strength and temperature).

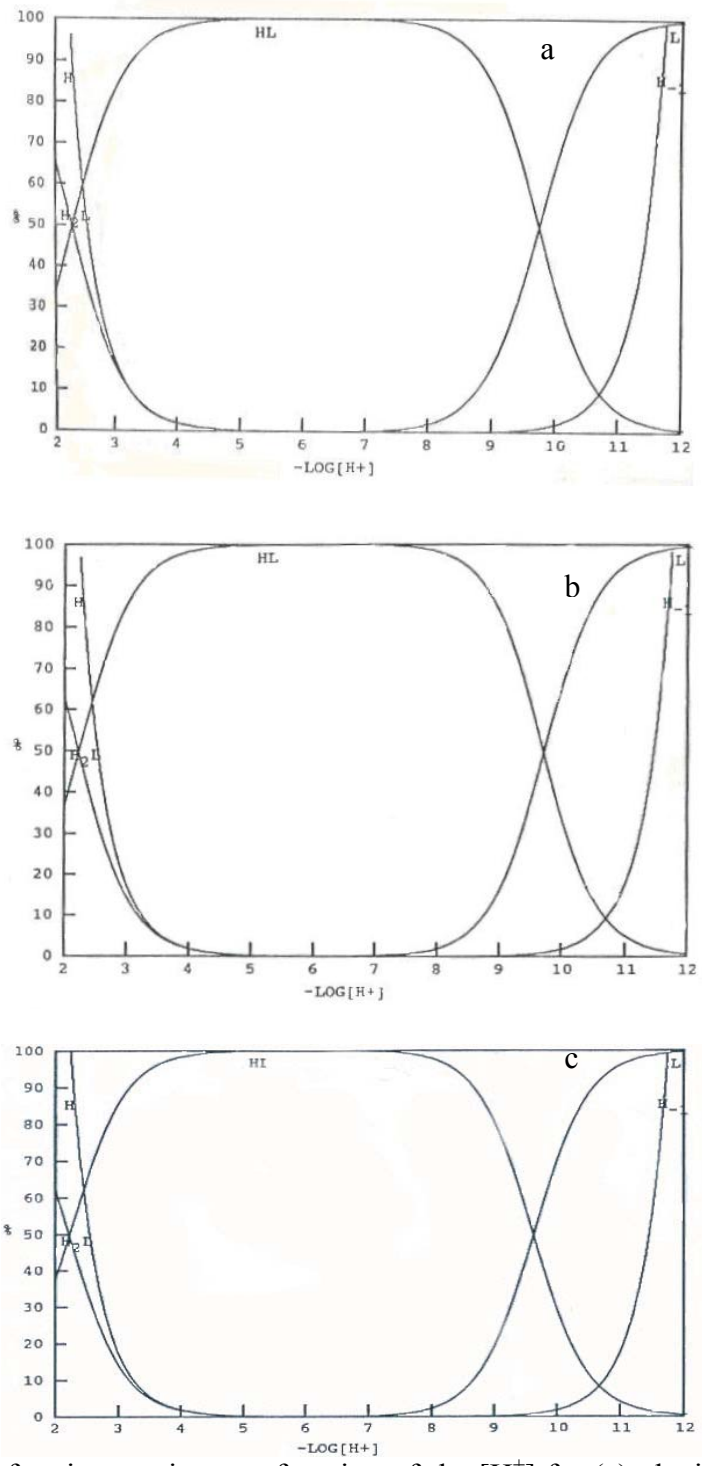

Fig. 1. Distribution of major species as a function of -log[H^+] for (a) glycine, (b)L-arginine, (c) L-glutamine.

4.2. Binary complex formation equilibria

The formation constants of Co^{2+}, Ni^{2+} and Zn^{2+} with L-glutamine, L-arginine and glycine binary complexes were determined under conditions identical to those of ternary system, values are given in Table 2. The experiments were run in 1:3 metal-ligand systems. All of these metal ions were found to combine readily with all amino acids to form ML, MHL, ML_2, MLOH

complex depending on the p[H] of the solution. The sample distribution curve of the amino acid-metal cation species are shown in Fig 2.

Table 1
Protonation constants of various amino acids in aqueous solution (t=25°C, μ=0.1 KNO_3).

Amino acids	Log K_1(-NH_2)	Log K_2(-COOH)
Glycine	9.78	2.35
L-glutamine	9.21	2.25
L-arginine	9.14	2.12

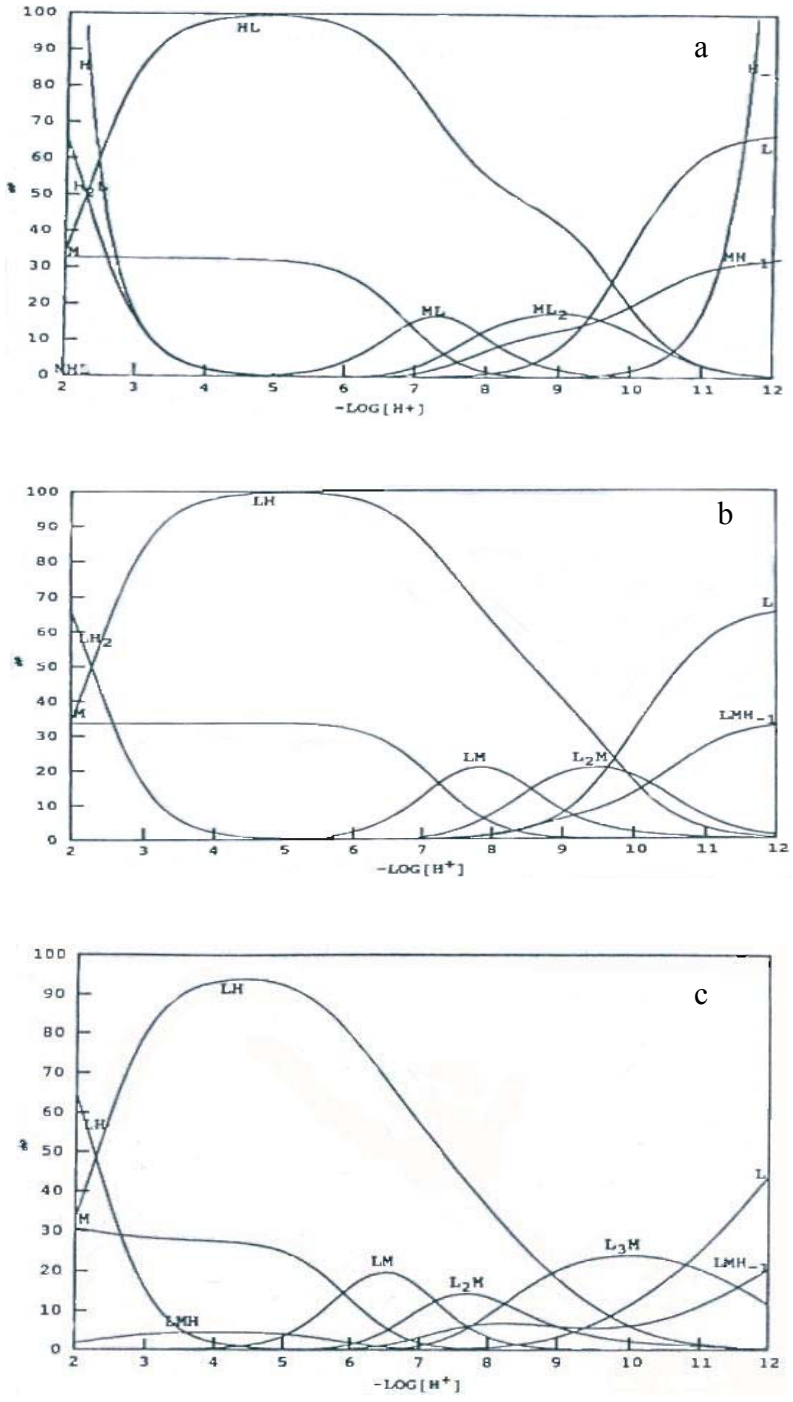

Fig. 2. Distribution of major species as a function of -log[H^+] for 3:1 molar ratio of (a) glycine to Zn^{2+}, (b) glycine to Co^{2+}, (c) glycine to Ni^{2+}.

It is seen from distribution curves for M^{2+}- amino acid system mono-protonated form, MLH forms at wide range of pH (2.0-8.0). The mono-protonated form, MLH, is converted to the deprotonated form ML at around pH 8.5, which in turn is converted at about pH 8.2 to ML_2 form. It is also can be seen from Table 2 and distribution diagrams from Fig 2 that all binary system show that same behavior as explained. The exception of this trend is Ni^{2+} complexes. Ni- amino acid system, from ML_3 species, this is because of coordination geometry of Ni^{2+} complexes [28-31].

It is seem from Table 2 that the glycine complexes have higher stabilities. This is due to absence of alkyl group in glycine. Substitution of the methyl group on the α-carbon atom produces a small decrease in logβ values but further lengthening of the glycine skeleton shows a marked influence on stability. As discussed above and Table 2 that the order of stability for chelates of the divalent transition metal ions is $Co^{2+} < Ni^{2+} < Zn^{2+}$.

Table 2
Stability constants for the Co^{2+}, Ni^{2+}, Zn^{2+} complexes of L-glutamine, L-arginine and glycine in binary system. (t=25°C, μ=0.1 (KNO_3)).

Parameters	Glycine	L-Arginine	L-Glutamine
$\log\beta_{NiAH}$	11.16	12.01	12.19
$\log\beta_{NiAH-1}$	-2.13	-2.68	-4.56
$\log\beta_{NiA}$	6.28	6.05	6.12
$\log\beta_{NiA2}$	11.12	10.75	10.85
$\log\beta_{NiA3}$	16.05	15.41	15.66
$\log\beta_{ZnAH}$	6.33	11.38	11.18
$\log\beta_{ZnAH-1}$	-4.07	-5.63	-7.12
$\log\beta_{ZnA}$	5.21	4.82	4.13
$\log\beta_{ZnA2}$	9.52	8.31	8.35
$\log\beta_{CoAH}$	8.31	11.87	11.24
$\log\beta_{CoAH-1}$	-4.42	-4.45	-4.81
$\log\beta_{CoA}$	4.95	5.12	5.03
$\log\beta_{CoA2}$	8.43	8.05	8.25

4.3. M^{2+}-amino acid-amino acid ternary system

The formation constants for each of three mixed complexes systems (M^{2+}- glycine(A), L-glutamine or L-arginine (B), M^{2+}- L-glutamine (A), L-arginine (B)) were obtained from refinement of pH-titration data, by computer program BEST, and listed in Table 3. In contrast with the stability of the binary complexes, the relative stability of the ternary ones can be expressed in several ways. The most common method is the calculation of Δlog K that is the difference in stabilities for the addition of ligand B to the 1:1 MA complex and to the solvated metal ion as shown by equation (3):

$$\Delta \log K = \log K^{MA}_{MAB} - \log K^{M}_{MA} = \log K^{MB}_{MBA} - \log K^{M}_{MB} \qquad (3)$$

Another parameter generally used for indicating the stabilization of the ternary complexes relative to the binary ones, is the disproportions constant, log X that is shown by equation (4):

$$MA_2 + MB_2 \Leftrightarrow 2MAB \qquad X_{MAB} = \frac{[MAB]^2}{[MA_2][MB_2]}$$

$$\log X_{MAB} = 2\log\beta_{MAB} - (\log\beta_{MA_2} - \log\beta_{MB_2}) \qquad (4)$$

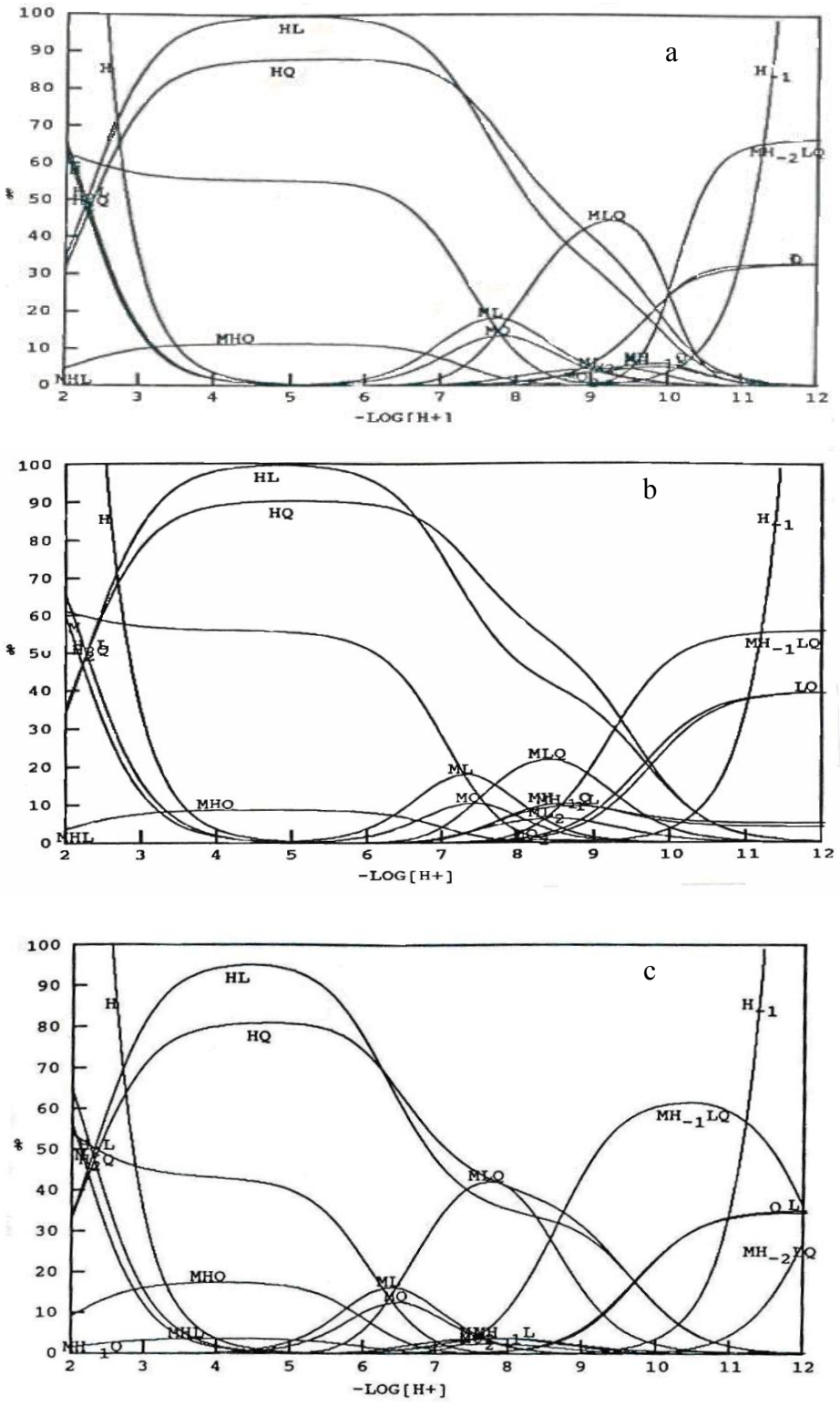

Fig. 3. Distribution of major species as a function of -log[H^+] for 1.5:1.5: 1(L:Q:M molar ratio) of (a)L=glycine, Q= L-arginine, M= Co^{2+} (b) L=glycine, Q= L-arginine, M= Zn^{2+}, (c) L=glycine, Q= L-arginine, M= Ni^{2+}.

On the statistical calculations [32], the positive logX values indicate the remarkable stability of the mixed complexes over the binary complexes. It is interesting to note that, the main species of mixed complexes in all systems is MAB. This is because of little variation in structure of amino acids. In most cases ΔlogK is negative showing that the secondary ligands add on the MA primary ligand binary complex species rather than to the aquatic metal ion. The disproportionation constant values log X in the above systems are also greater than the

statistically expected value of 0.6 indicating that the formation of MAB type of species in all the systems is more favored compared to the formation of MA_2 or MB_2 types of binary complexes. The sample distribution curve of the metal-amino acid- amino acids species are shown in Fig 3.

Table 3
Stability constants of ternary systems for the Co^{2+}, Ni^{2+}, Zn^{2+} complexes in mixed ligand (t=25°C, μ=0.1 (KNO_3)).

	M^{2+}-glycine(A)-B system ligand B		M^{2+}- L-Glutamine (A)- B system ligand B
Parameters	L-Arginine	L-Glutamine	L-Arginine
$\log\beta_{NiABH-1}$	1.95	3.49	2.16
$\log\beta_{NiABH-2}$	-9.61	-8.93	-9.85
$\log\beta_{NiAB}$	7.655	11.97	11.47
$\Delta\log K_{NiAB}$	-0.65	-0.032	-0.56
$\log X_{NiAB}$	1.25	2.15	1.92
$\log\beta_{ZnABH-1}$	0.98	1.21	1.03
$\log\beta_{ZnABH}$	9.96	10.13	9.57
$\Delta\log K_{ZniAB}$	-0.95	-.025	0.26
$\log X_{ZnAB}$	2.04	2.68	1.86
$\log\beta_{CoABH-2}$	-10.67	-9.52	-10.72
$\log\beta_{CoAB}$	9.52	9.81	8.85
$\Delta\log K_{CoAB}$	0.04	0.36	-0.36
$\log X_{CoAB}$	2.63	3.13	2.21

In all the species distributions the concentration of the ternary complexes increasing pH thus making M^{2+} biologically available in the physiological pH range. In all the system reported MAB ternary species occur in greater concentration than MA or MB binary species. This is in accordance with the conclusion arrived from the statistical parameter ΔlogK that ternary complex formation is preferred over that of the binary analogues.

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