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Decoding the Behavior of Bio-Relevant Metal Ions in Water Using Chemometric Speciation Modeling

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Abstract

Chemometric speciation studies on transition metal ions lead to the improvement of biologically active compounds for good health, the binding of toxic organic chemicals in aquatic systems, and the development of effective green catalysts in the context of sustainable development goals. In the present study, the solution equilibria of ternary complexes such as metal-azelaic acid dihydrazide-L-proline were investigated using pH-metric titrations. In these complexes, azelaic acid dihydrazide (AZDH) serves as the primary interacting ligand (L) and L-proline acts as the secondary interacting ligand (X). Hereafter, these complexes are represented as MLX, where M is nickel (II) or copper (II). At the temperature of 303 ± 0.1 K and 0.1 M ionic strength, potentiometric titrations were conducted for different metal-to-ligand ratios (M: L:X). Binary and ternary complexes formation constants were analysed by the MINIQUAD-75 programme, employing a chemometric method. To establish the best-fit chemical model, statistical parameters such as the chi-square test, residual analysis and standard deviation were applied.

Titration curves and species distribution figures were produced by the SOPHD program and HySS software respectively. The results suggested the formation of stable ternary metal-ligand complexed (M-L-X) over a wide pH range. By $\Delta \log K$ calculations, the authors assessed the relative stability for ternary and binary complexes, thereby providing insight into bond strength and cooperative interactions in ternary complexes.

The work contributes to Sustainable Development Goals (SDGs) 3, 6, 9, and 12 promoting good health, clean water through the removal of toxic substances, and green catalytic activity in the chemical industry for sustainable growth.

Keywords: Chemical speciation; Ternary metal complexes; L-Proline; Chemometric modelling; Sustainable chemistry

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1. Introduction

In biological and environmental chemistry, speciation studies [1, 2] play a crucial function in estimating bioavailability, and bio accumulation. Nickel and copper ions were chosen for this study due to their accumulation in biological systems, which leads to adverse effect [3,4]. The non-essential amino acid L-proline, a bidentate ligand was selected for investigation, and it is nonpolar in nature. The chelate rings in five-membered are connected through the oxygen in carboxylate group and nitrogen atoms present in ring.

Metal Dihydrazide complexes exhibit the properties catalytically [5-7] and biologically [8,9]. The existence of these metal ions is available in neighbouring groups metalloproteins [10] are formed. when these metal ions is present in adjacent groups. These complexes have been proven to be non-genotoxic substances and FDA has approved these [11] for packaging in food materials. Azelaic acid dihydrazide (AZDH) was chosen for the present study. The chemical formula is $(-\text{CO}-\text{NH}-\text{NH}_2)-(\text{CH}_2)_7-(\text{CO}-\text{NH}-\text{NH}_2)$. Most of the research pointed on Identification of structures and Chemical synthesis using various physicochemical techniques in the literature [12-16]. Table 1 represents the unique bond formation patterns observed in dihydrazides, which depend upon the interaction of the two functional groups. The determination of probable species of dihydrazides in solution phase was reported by the research group of authors [17-24].

Here, the speciation experiment results present a study of the stability of nickel and copper ions under experimental conditions, namely an inert N_2 atmosphere at a temperature of 303 K and of 0.01 M ionic strength in aqueous medium. Understanding the solution-phase speciation of transition metal ions is crucial in predicting their bioavailability, mobility, and potential toxicity in biological and environmental systems. Nickel (II) and

copper (II), though essential trace elements, are known to cause adverse health effects when present in excess making their chemical speciation in aqueous media particularly relevant to human health and environmental safety. In this context, the present study subsidizes to United Nations Sustainable Development Goals, particularly Sustainable Development Goal 3 and Sustainable Development Goal 6, which focus on ensuring good health and access to clean water, respectively, by understanding metal ligand interactions in biological environments as well as in aqueous media.

2. Experimental Procedure

2.1 Solutions:

AZDH (TCI, Japan), L-proline (Merck, Pro analysis) were dried in a vacuum oven. Before being used in pH-metric titrations, fresh solutions of 0.05 M AZDH in 0.1 M of HCl and 0.1 M of proline solutions were made ready for use. Analytical grade chemicals from Sigma Aldrich included potassium hydroxide, metal chlorides, HCl and potassium chloride. Water that had been de-ionized and double-distilled was used to prepare each solution. To control hydrolysis, the metal chloride solutions were prepared in approximately 0.01 M hydrochloric acid. For standardizing the metal solutions, volumetric and complexometric [25] methods were employed. Determined the carbonate concentration in the KOH (potassium hydroxide) solution; the correction factor of pH and the ionic product (K_w) of water were followed by the Gran method [26,27] for a better result before performing each pH-metric titration.

An 801 stirrer (Switzerland) equipped with an 877 Titrino Plus autotitrator was used for all pH titrations. It was combined with a pH electrode model LL-Unitrode type 6.0259.100 with a pH range from 0 to 14. A 303 K temperature was maintained by a thermostat for experimental solutions. Nitrogen gas was continuously supplied to remove any traces of carbon dioxide.

The experimental investigations were carried out entirely in an aqueous medium under controlled conditions to avoid the usage of harmful organic solvents. The practice aligns with the principles of green chemistry by supporting Sustainable Development Goal

12 (SDG12). The safe use of chemicals in consumption and the effective utilization of chemical resources.

3. Results

3.1. Data sampling and interpretation

To determine the (LH, XH): ligand proton, (ML, MX); binary metal-ligand, and ternary (MLX): metal-ligand mixed equilibria, an updated Calvin-Wilson titration [28-30] method was used. Data acquisition was performed under experimental conditions namely a nitrogen gas atmosphere, 303 ± 0.1 K temperatures, and 0.1 M of ionic strength. Titrations were continued until precipitation occurred due to pH shift. The software MQDP (MINIQUAD-75) program is used for data analysis [31]. The investigation examined ternary systems with different mole ratios of metal ions (Ni^{2+} and Cu^{2+}), the primary ligand (AZDH), and the secondary ligand (L-Proline). Specific M: L:X ratios considered were 1:1:1, 1:1:2, 2:1:1, and 2:1:2. In such ternary systems, the formation of a species linking a metal ion (M) and dual ligands (L and X) can be described by a over-all equilibrium expression (1).

$$m.M + l.L + x.X + h.H \rightleftharpoons M_m L_l X_x H_h \dots\dots\dots (1)$$

The generalized equation (2) represents the formation constants.

$$\beta_{m l x h} = \frac{[M_m L_l X_x H_h]}{[M]^m [L]^l [X]^x [H]^h} \dots\dots\dots (2)$$

The symbols m, l, x, and h denote the number of moles of M, L, X, and H, respectively. The parameter h takes a positive value for protonated species and is zero for unprotonated species.

The variables m, l, x, and h denote the number of moles of M, L, X, and H respectively. The value of h is +ve for protonated species and zero (0) for unprotonated species. The value is -ve for deprotonated or hydroxylated species. Assuming the formation of binary L-proline and AZDH species, Computed titration data were generated by SOPHD program [32]. To select the best-fit models, statistical criteria such as the chi-square test, standard deviations of the polished formation constants, and the sum of residuals squares (U) were applied. Species concentration distribution diagrams were produced by with software of HySS [33].

The implementation of chemometric modeling tools such as MINQUAD-75, SOPHD, and HySS for evaluating formation constants and species distribution diagrams demonstrates the role of advanced computational approaches in coordination chemistry. This methodological framework supports Sustainable Development Goal 9 (SDG 9) for innovation by advancing innovative analytical techniques for understanding complex metal-ligand equilibria in solution.

3.2 Interpretation of Acido-basic equilibria of proton (H)-AZDH and L-Proline systems

AZDH is a species consisting two protons at lower pH values due to two amino groups and protonation occurs. In a basic medium, AZDH can undergo deprotonation through keto-enol tautomerism. The formation of mono-protonated and bi-protonated species, were specified by $\log \beta$ values of 3.53 and 6.30 (Fig. 1a) correspondingly. β_{011} and β_{012} values are the two formation constants with the proton-ligand equilibria [20] of AZDH. The constants β_{011} and β_{012} correspond to the two formation constants associated with the proton–ligand equilibria [20] of AZDH. AZDH interacts with metal ions in various forms, such as LH_2^{2+} , LH^+ , and L , depending on the pH.

The IUPAC name of L-proline is pyrrolidine-2-carboxylic acid. It is an amino acid with a ring structure that imparts specific properties to proteins. This substance consists of donor groups such as carboxylate and amino groups will associate with protons. L-proline, a cyclic α - amino acid and is unique because of its ring structure, which provides unique physical properties to proteins. Ultimately, the fully protonated form (XH_2^+) donates two hydrogen atoms. Proline exists in three protonation states in solution: positively charged (XH_2^+), neutral or zwitterionic ($XH^\pm$), and negatively charged (X^0), as illustrated in Fig 1b. The stepwise dissociation of these protons occurs in distinct pH ranges.

3.3. AZDH (L)/L-proline (XH)-Metal ion (M^{2+}) Binary Systems

From the chemical speciation studies, the binary complexed of AZDH with Ni^{2+} and Cu^{2+} , are formed as various species due to the coordination with the carbonyl or enolic oxygen groups and terminal nitrogen groups, depending upon the metal-to-ligand ratio.

AZDH is a bidentate or bis-dentate ligand through coordination. Depending on the composition, MLH_n , ML_2H_n , and M_2LH_n species are formed [20].

Proline, like glycine forms mono-, bis-, and tris-complexes with various metal ions. These complexes feature five-membered chelate rings resulting from coordination between the carboxylate oxygen and amino nitrogen donor atoms. MX and MXH species were observed in 1:1 composition of metal-to-ligand systems, while MX_2H_2 , MX_2H , and MX_2 species were present in 1:2 models.

3.4 L-Proline-AZDH - $Ni^{2+}/Cu^{2+}(M^{2+})$ Ternary Model

To investigate complexes formed under specific pH conditions, virtual titration curves were produced, assuming that only binary species were formed. Ternary systems of M^{2+} , L and XH with different molar compositions (1:1:1, 1:1:2, 2:1:1, and 2:1:2) were represented in these curves (Fig. 2). There is inconsistency among the theoretical and experimental titration curves due to the formation of mixed-ligand species.

With the support of the formation constants and ligand protonation constants of the binary species, the formation constants of the ternary complexes were obtained. The data were evaluated using the MINQUAD-75 (MQDP) software. The optimized representations for each system are presented in Table 2.

$MLXH_2$, $MLXH$, and MLX species were formed in the 1:1:1 M: L: X configuration. In $MLXH_2$, L coordinates in its protonated LH form. Here, one bidentate unit is coordinated to the metal ion, while the other unit remains protonated. The protonated unit is non-coordinated. XH binds as a monodentate ligand through the carboxylate oxygen in its zwitterionic arrangement, though the α -amino group remains protonated and non-coordinated.

The deprotonation constants of $MLXH_2$, whose values are lower than the protonation constant of AZDH (3.53) for the metal ions suggested the strong bonds in complexes as shown in Table 3. The species distribution graphs (Fig. 3) indicate that $MLXH_2$ reaches an extreme concentration of 30-40% at $pH < 3.0$ for the metal ions. As the pH increases, $MLXH_2$ is deprotonated to $MLXH$ and MLX . The α -amino group of proline

deprotonates upon binding to the metal ion. Due to this, deprotonation of MLXH occurs, leading to the formation of MLX. The deprotonation constant value is lower than the protonation constant of proline (10.39), as shown in Table 3, indicating a preference for deprotonation and the formation of MLX.

For the pH choice 3.0-7.0, 80-85% of the MLXH species is formed for the given metal ions. For the Ni^{+2} system, the deprotonated species MLXH_{-1} forms up to 30%, reaching a maximum in the pH range 8-10.0.

MLX_2H_3 , MLX_2H_2 , MLX_2H , and MLX_2 type ternary species were formed on In 1:1:2 (M:L:X) systems. For the metal ions, the dissociation constant of MLX_2H_2 is lower than the protonation constant of AZDH (3.53) showing that one proton in MLX_2H_3 , is associated with the dihydrazide, and the added two protons originate from the proline zwitterionic form, which acts as a monodentate ligand and binds with the carboxylate groups. Furthermore, AZDH contains one hydrazide group that is kept free and protonated, despite the fact the other hydrazide group is in coordination.

Along with the pH rises, MLX_2H_3 loses a proton, and the MLX_2H_2 species is formed. The α -amino groups of the L-proline molecules in these species remain protonated, resulting in the proline molecules existing in the zwitterionic form.

The AZDH molecule coordinates through one hydrazide group, while the other group remains protonated and free. Upon the rise in pH, MLX_2H_3 loses a proton forming MLX_2H_2 . The α - amino fragments of proline in MLX_2H_2 retain both protons. The protonation constants demonstrate that either complexation or the absence of proline liberates the $-\text{NH}_3^+$ proton. It is challenging to ascertain the $-\text{NH}_3^+$ group's involvement in bonding based just on solution investigations, even though its role may change based on the coordination number and metal ion-specific factors. Figure 3 displays the species concentration dispersal as a function of pH. (Fig. 3).

Aimed at the 2:1:1 systems, four binuclear mixed-ligand species were observed, namely M_2LXH , M_2LX , $\text{M}_2\text{LXH}_{-1}$, and $\text{M}_2\text{LXH}_{-2}$. In M_2LXH , proline binds monodentately to the metal via its carboxylate oxygen. In M_2LX , proline binds bidentately through the α -

amino nitrogen and carboxylate oxygen, whereas AZDH acts as a bis-bidentate ligand, producing five-membered rings on both sides upon coordination with the metal ions through the amino nitrogen and carbonyl oxygen atoms.

The formation constants for M_2LX indicate that the H^+ in M_2LXH initiates from the α -ammonium fragment of proline. This proton is lost upon complex formation, resulting in M_2LX . The formation of M_2LXH_{-1} and M_2LXH_{-2} species associated with either hydroxylation or deprotonation of the hydrogen atoms form the enolic forms. According to the distribution graphs, M_2LXH makes up almost 90% of all species in the four systems and is the most common species below pH 6.

$M_2LX_2H_2$, M_2LX_2H , and M_2LX_2 species, as well as their deprotonated forms, contribute to the development of ternary complexes in 2:1:2 systems. The AZDH ligand functions as a bis-bidentate ligand in the symmetric form of $M_2LX_2H_2$, producing a bridge structure by bonding to two metal ions via its terminal amine and carbonyl groups. By creating two monodentate bonds with their carboxylate groups, the proline molecules participate in complexation, keeping the other α -amino groups protonated and uncoordinated.

Upon the rise in pH, they undergo deprotonation of the ammonium protons, resulting in the formation of M_2LX_2H and M_2LX_2 species. The $\log K_1$ and $\log K_2$ protonation constants correspond to $M_2LX_2H_2$ form M_2LX_2H and M_2LX_2H from M_2LX_2 respectively.

Like the bonding approach, the deprotonation mechanism and the pH range of the species can remain estimated. From figure 4 (Fig. 4), the distribution diagrams indicate that $M_2LX_2H_2$ is the prime species at $pH < 6.0$, indexing that 50-90% of the total metal ion concentration for all the metal ions studied. Above pH 6, M_2LX_2H , M_2LX_2 , and $M_2LX_2H_{-1}$, coexist in solution.

The development of $M_2LX_2H_{-1}$ and $M_2LX_2H_{-2}$ species can be marked to hydroxylation or deprotonation of the enolic form of AZDH. Interestingly, the formation constants for all compositions follow the Irving-Williams sequence, with $Ni^{2+} < Cu^{2+}$ [34].

4. Discussion

The existence of metal-ligand-amino acid complexes in biological systems is common. Here, several complexes with species are can coexist. It is a procedure plays an important role in several actions are available within the metal's coordination sphere. A relationship provided by equation 3 between the ternary complexes stability and respective binary complexes yielding valuable information regarding these interactions about thermodynamics.

$$\Delta \log K = \log \beta_{ML_1X_x} - (\log \beta_{ML_1} + \log \beta_{MX_x}) \quad \text{..... Eq (3)}$$

In this case, X is the amino acid's deprotonated state and L, the neutral dihydrazide ligand. The reaction stability between ligand X and ML is compared to that between ligand X and the metal aqua ion using the $\Delta \log K$ values. Owing to the fact that more the metal aqua ion has more coordination sites than ML, and the statistical likelihood of the reaction between ML and X is lower than that of the reaction between M and X. As seen for the MLX species in Table 4, this outcome is $-\Delta \log K$ values. These negative values, however, just show reduced stability in comparison to the statistical prediction; they do not stop the emergence of ternary species.

In an octahedra complex, there are 12 available edges. As the L and X approach, the numerical factor for L is 5/12 resulting in $\Delta \log K_{oh} = -0.4$ [35]. For complex in planar structure $\Delta \log K_{pl} = -0.6$. In the case of distorted octahedral complexes such as Cu^{2+} , the $\Delta \log K$ value exists in the range of -0.9 to -0.3 [36]. If the statistical values less than experimental values, this shows a maximum probability of mixed ligand complex forming.

Meanwhile electrostatic components are cancelled when a ligand becomes neutral, the positive $\Delta \log K$ observed for M_2LX and M_2LX_2 , as presented in Table 4, indicates the conditions suitable for bonding. From a sustainability perspective, the stability constants and speciation profiles obtained in this study provide valuable information for predicting the behaviour of metal ions in biological and aqueous systems. These insights are essential for evaluating metal binding and accumulation, thereby contributing to good health (SDG

3) and water quality (SDG 6). Furthermore, complexed formation in an aqueous medium supports sustainable chemical practices.

The schematic diagram (Fig. 5) visually summarizes the molecular-level speciation. The conclusion clearly illustrates the speciation of $\text{Ni}^{2+}/\text{Cu}^{2+}$ - AZDH – proline system and highlights its relevance to associated Sustainable Development Goals.

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4.2. Conclusions

Speciation studies of metal ions with ditopic ligands have attracted increasing attention due to their ability to form extended coordination structures and exhibit synergistic effects that mimic metalloprotein environments. In the present study, the binding efficiency of AZDH with proline and Ni and Cu ions was systematically investigated in an aqueous medium using pH-metric titrations. The results demonstrate that AZDH exhibits high affinity toward both metal ions, with an enhanced capability to bind two metal centres under suitable compositional conditions.

The ternary species were observed strongly individual on the metal ion and metal-ligand composition. MLXH species were predominant in the nickel (II) system, where MLX species predominated in the copper (II) system. At higher ligand-to-metal ratios, MLX_2H_2 , and M_2LXH species were observed as the major complexes in 1:1:2 and 2:1:1 compositions, respectively. The evaluated stability constants follow the Irving-Williams order, with $\text{Ni}^{2+} < \text{Cu}^{2+}$, confirming the greater complex-forming tendency of copper (II).

Comparative analysis using $\Delta \log K$ values, further indicates that these ternary complexes exhibit solid bonding interactions compared to corresponding binary species, as reflected by the $\Delta \log K$ values. Beyond this fundamental understanding of coordination and solution chemistry, these findings are relevant to sustainability. The elucidation of aqueous speciation and stability of biologically important metal ions contributes to improved assessment of metal bioavailability and non-genotoxicity, thereby aligning with SDG3 and SDG6. The application of chemometric modelling and computational analysis

represents methodological innovation aligned with SDG 9, while the exclusive use of aqueous solutions and environmentally benign experimental conditions supports SDG12.

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[Table 1 Some literature reports on the bonding behaviour of dihydrazides in metal complexes

S.No	Dihydrazide(s) (L)	Metal ion(s) (M)	Species	Methods	Nature of Bonding	Ref. no.
1.	Dicarboxylic (oxalic, succinic, malonic, adipic, phthalic and terephthalic) acid dihydrazide complexes of Cu (II) tetrafluoro borate.	Cu(II)	[Cu (L) _x]. (BF ₄) ₂ x=3/2, 2 & 3	Physico-chemical methods.	Distorted octahedral geometry around the metal ion	12
2.	Dicarboxylic (oxalic, succinic, malonic, adipic Phthalic and Terephthalic) acid dihydrazide complexes of metal (II) tetrafluoro borates.	Mg(II), Zn(II), Mn(II), Cd(II), Ni(II), Co(II). Hg(II)	(ML _n)(BF ₄) ₂ n=1, 1.5, 2 or 3	Electronic and IR spectral study	Through any two of the carbonyl, amino and amide groups.	13
3.	Malonic acid dihydrazide	Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Ag(I), Cd(II), Pb(II).		IR, Visible and U.V. spectral studies	Through secondary amide nitrogen atoms	14
4.	Succinic and malonic acid dihydrazides	Co(II), Ni(II), Cu(II), Pd(II).		Electronic spectra	Through secondary amide nitrogen atoms	15
5.	Malonic acid and phthalic acid dihydrazides	Fe(II)	ML ₂	Magnetic suscept, IR, electronic and Mossbauer spectral studies	Fe (II) is coordinated octahedrally in the complexes.	16

Table 2 Best-Fit chemical models of M²⁺- AZDH- Proline ternary systems in the aqueous medium at 303± 0.1K and ionic strength, I = 0.1 mol. dm⁻³

Initial concentration of M:L:X	Species (MmLIXxHh)	logβ _{mlh} (SD)	
		Ni ²⁺	Cu ²⁺

1:1:1	1112	19.35 (0.01)	20.11(0.01)
	1111	16.72 (0.01)	18.20(0.01)
	1110	10.23(0.01)	13.51(0.01)
	111-1	0.071(0.02)	-
	U/NP	1.237×10^{-8}	1.795×10^{-8}
	χ^2	46.61	72.16
1:1:2	1123	31.51 (0.02)	32.29(0.01)
	1122	29.75(0.01)	30.11(0.01)
	1121	22.74(0.02)	25.36(0.01)
	1120	14.81(0.02)	19.04(0.01)
	U/NP	5.74×10^{-8}	3.161×10^{-8}
	χ^2	106.45	32.21
2:1:1	2111	19.90 (0.01)	20.74 (0.01)
	2110	13.33(0.02)	16.32 (0.01)
	211-1	4.57 (0.03)	11.69 (0.02)
	211-2	-	6.20 (0.01)
	U/NP	7.990×10^{-8}	2.387×10^{-8}
	χ^2	229.03	130.01
2:1:2	2122	32.27 (0.01)	32.66 (0.01)
	2121	26.35 (0.01)	29.62 (0.01)
	2120	19.31 (0.01)	25.12 (0.01)
	212-1	10.80 (0.01)	19.15 (0.01)
	212-2	-	12.59 (0.01)
	U/NP	5.434×10^{-9}	8.804×10^{-9}
	χ^2	55.71	35.0

Table 3 Stepwise protonation constants of MLX, ML₂X, M₂LX and M₂LX₂ type of species of M²⁺- AZDH-Proline systems (from Table 2)

	Ni²⁺	Cu²⁺
MLX	log K = 2.63 (logβ ₁₁₁₂ –logβ ₁₁₁₁)	log K = 1.91 (logβ ₁₁₁₂ –logβ ₁₁₁₁)
	log K = 6.49 (logβ ₁₁₁₁ –logβ ₁₁₁₀)	log K = 4.69 (logβ ₁₁₁₁ –logβ ₁₁₁₀)
ML₂X	log K = 1.76 (logβ ₁₁₂₃ –logβ ₁₁₂₂)	log K = 2.18 (logβ ₁₁₂₃ –logβ ₁₁₂₂)
	log K = 7.01 (logβ ₁₁₂₂ –logβ ₁₁₂₁)	log K = 4.75 (logβ ₁₁₂₂ –logβ ₁₁₂₁)
	log K = 7.93 (logβ ₁₁₂₁ –logβ ₁₁₂₀)	log K = 6.32 (logβ ₁₁₂₁ –logβ ₁₁₂₀)
M₂LX	log K = 6.57 (logβ ₂₁₁₁ –logβ ₂₁₁₀)	log K = 4.42 (logβ ₂₁₁₁ –logβ ₂₁₁₀)
	log K = 8.76 (logβ ₂₁₁₀ –logβ ₂₁₁₋₁)	log K = 4.63 (logβ ₂₁₁₀ –logβ ₂₁₁₋₁)
M₂LX₂	log K = 5.92 (logβ ₂₁₂₂ –logβ ₂₁₂₁)	log K = 3.04 (logβ ₂₁₂₂ –logβ ₂₁₂₁)
	log K = 7.04 (logβ ₂₁₂₁ –logβ ₂₁₂₀)	log K = 4.50 (logβ ₂₁₂₁ –logβ ₂₁₂₀)
	log K = 8.51 (logβ ₂₁₂₀ –logβ ₂₁₂₋₁)	log K = 5.9 (logβ ₂₁₂₀ –logβ ₂₁₂₋₁)

Table 4 $\Delta\text{Log K}$ values for the formation of MLX type of species

Species	Metal Ion	(A)	(B)	C=A+B	(D)	$\Delta\text{log K} = \text{D}-\text{C}$
MLX	Ni^{2+}	4.65	5.99	10.64	10.23	-0.41
	Cu^{2+}	5.45	8.90	14.35	13.51	-0.84
M₂LX	Ni^{2+}	6.77	5.99	12.76	13.33	0.57
	Cu^{2+}	6.95	8.90	15.85	16.32	0.47
M₂LX₂	Ni^{2+}	6.77	11.98	18.75	19.31	0.56
	Cu^{2+}	6.95	17.80	24.75	25.12	0.37

For MLX, $\Delta\text{log K} = \text{D}-(\text{A}+\text{B}) = [\text{log } \beta_{1110}-(\text{log}\beta_{1100}+\text{log}\beta_{1010})]$

For ML₂X, $\Delta\text{log K} = \text{D}-(\text{A}+\text{B}) = [\text{log } \beta_{2110}-(\text{log}\beta_{2100}+\text{log}\beta_{1010})]$

For ML₂X₂, $\Delta\text{log K} = \text{D}-(\text{A}+\text{B}) = [\text{log } \beta_{2120}-(\text{log}\beta_{2100}+2 \times \text{log}\beta_{1010})]$

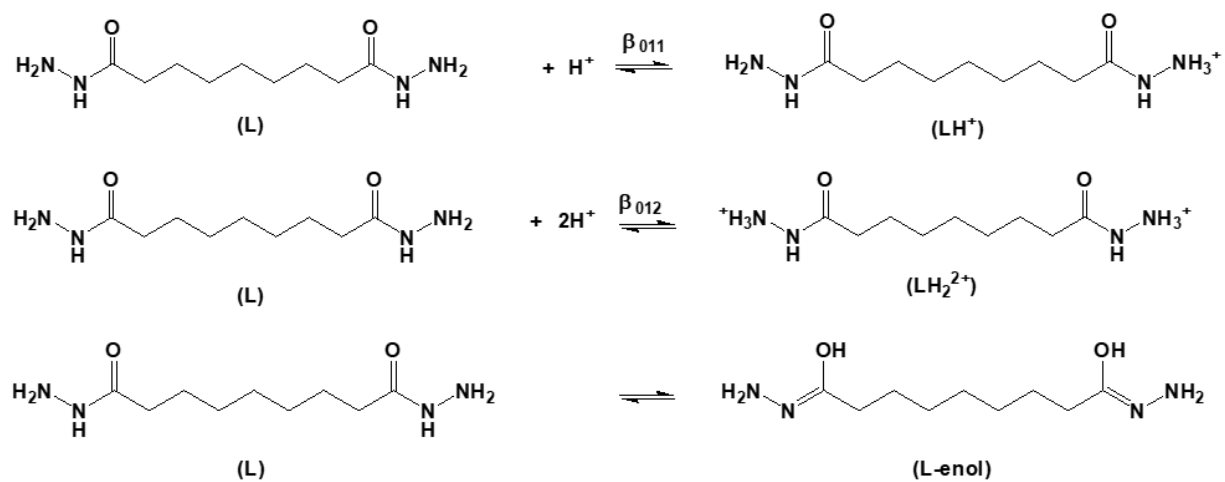


Figure 1a

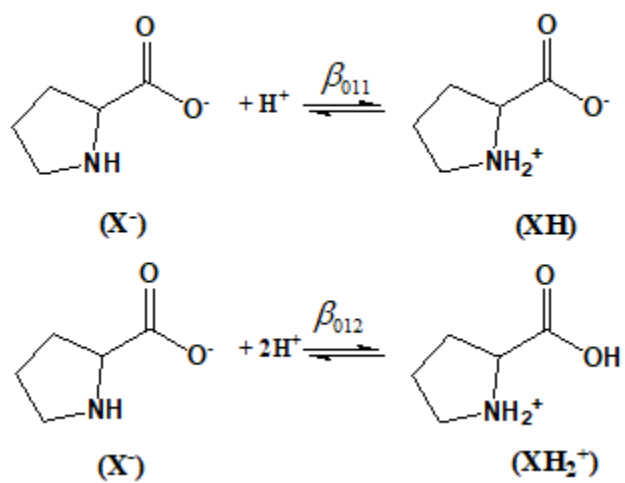
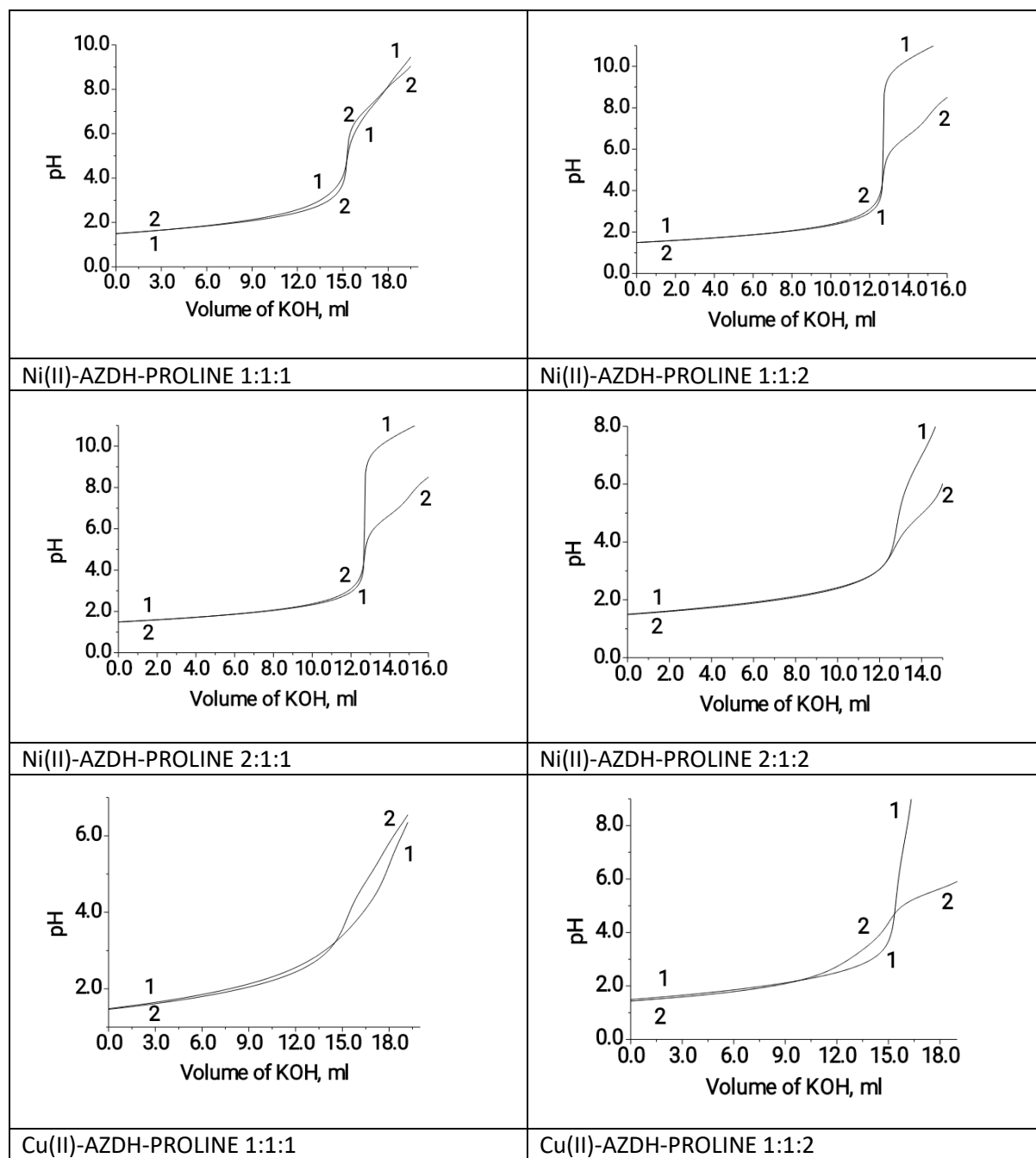


Figure 1b



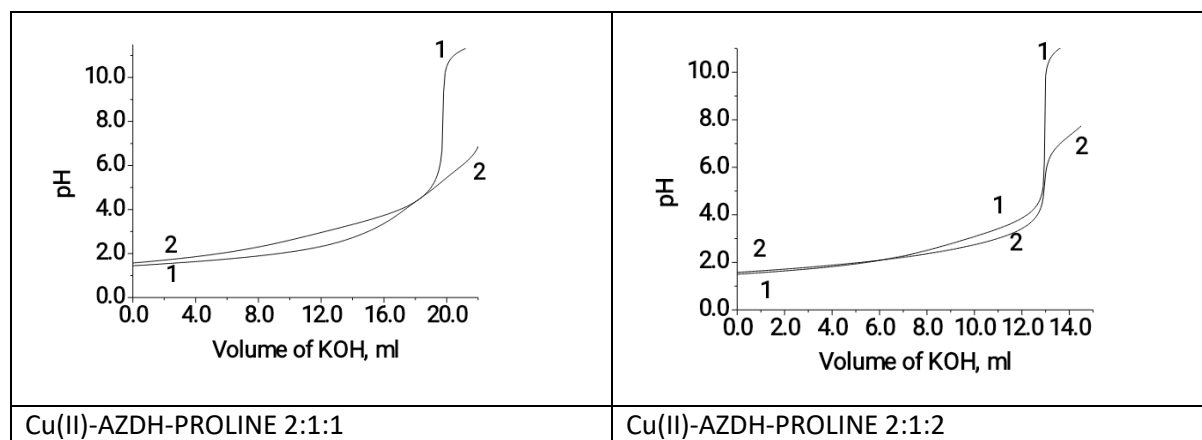


Figure2

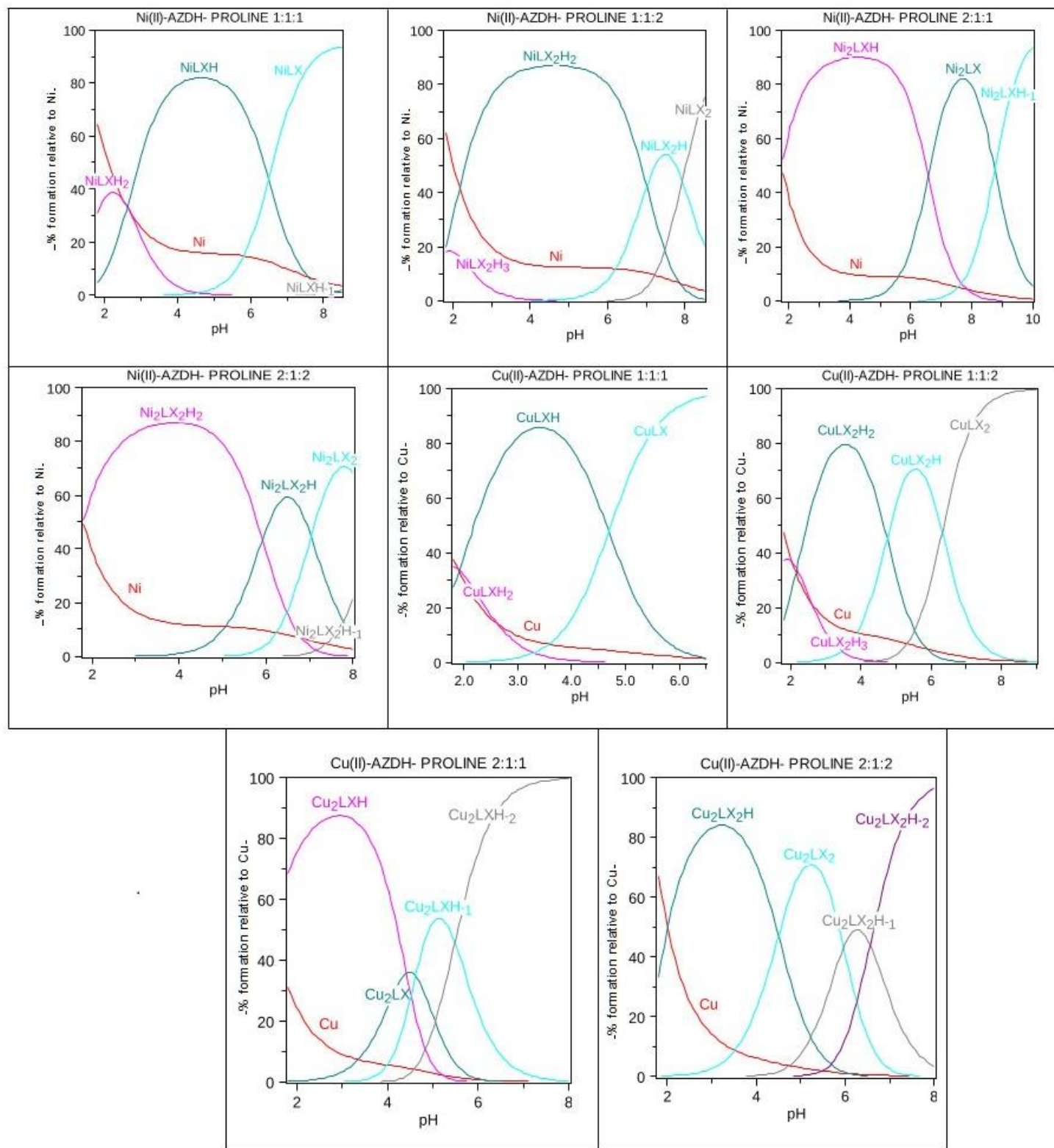


Figure3

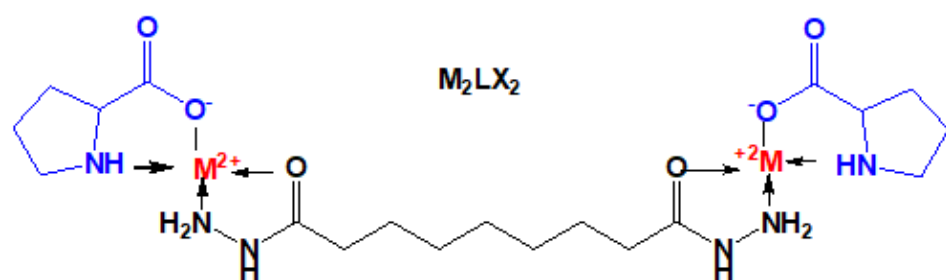


Figure 4

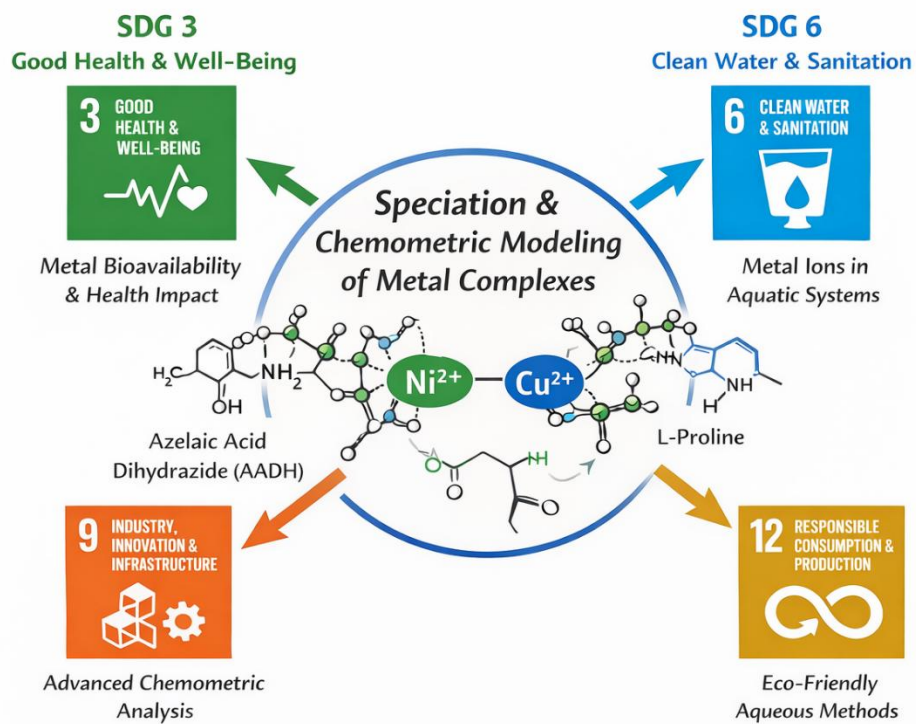


Figure 5