Research Article

CHEMICAL MODELING STUDIES OF THE SPECIATION OF Co^{2+}, Cu^{2+} AND Zn^{2+} COMPLEXES OF AZELAIC ACID DIHYDRAZIDE IN AQUEOUS MEDIUM

Nirmala Devi Danabala., Shyamala Pulipaka and Satyanarayana Atreyapurapu*

Department of Physical & Nuclear Chemistry and Chemical Oceanography, School of Chemistry, Andhra University, Visakhapatnam- 530003, Andhra Pradesh, India

A R T I C L E I N F O	A B S T R A C T
	A potentiometric chemical speciation study was carried out on Azelaic acid dihydrazide (L)-divalent metal ion systems in aqueous medium. In solution the ligand was found to exist in neutral (L), mono protonated (LH$^+$) and biprotonated (LH$_2$$^{2+}$) forms. The best-fit models obtained for metal ion-dihydrazide systems using the Miniquad-75 program indicated the formation of mono and bimetallic species with different degrees of protonation and deprotonation. The formation of bimetallic species reflects the ditopic nature of the ligand. Species concentration distribution diagrams against pH of the solution were generated using the HYSS program.

INTRODUCTION

Azelaic or nonanedioic acid dihydrazide (AZDH) is an aliphatic ditopic ligand with two hydrazide groups separated by seven –CH$_2$- units. Linear aliphatic dicarboxylic acid dihydrazides are used to produce linear polymers that are used in the fabrication of heat and flame resistant fibres, films and coatings (De Witt *et al*., 1964). They are also used as photographic film stabilizers (Swan *et al*., 1943), acid corrosion inhibitors of mild steel (Al-Amiery *et al*., 2016) and in de-bonding of polyurethane adhesives (Burckhardt and Kramer, 2009). Dihydrazides are capable of forming mono-metallic and homo/ hetero bimetallic complexes with metal ions possessing specific catalytic (Shibasaki *et al*., 2004, Jonasse *et al*., 1959, Steinhagen *et al*., 1996, McKenzie *et al*, 1988) and biological properties (Carraher *et al*., 1990). The presence of two metal ions in adjacent pockets leads to a tailored creation of supra molecular structures that are used to mimic metalloproteins to understand *in vitro* structure-activity relationship (Thomas, 1999). Tsitsishvili *et al*. (Tsitsishvili *et al*., 1978, 1982) and Gogorishvili *et al*. (Gogorishvili *et al*., 1976, 1977) synthesized and characterized Co^{2+}, Ni^{2+} and Cu^{2+} complexes of azelaic acid dihydrazide in which the ligand acts as a monodentate or bidentate in neutral or deprotonated anionic form. There were no literature reports on the solution phase metal complex equilibria of AZDH. In continuation of our previous studies on the chemical speciation of dicarboxylic

---

Corresponding author: **SatyanarayanaAtreyapurapu**
Department of Physical & Nuclear Chemistry and Chemical Oceanography, School of Chemistry, Andhra University, Visakhapatnam- 530003, Andhra Pradesh, India

acid dihydrazide metal ion complexes (Satyanarayana *et al*., 2013; Dunkana *et al*., 2014, 2015; Uma Rani *et al*., 2015, 2016) we report here a chemical speciation study on the interaction of AZDH with Co^{2+}, Cu^{2+} and Zn^{2+}.

Reagents

Azelaic acid dihydrazide obtained from Tokyo Chemical Industry Co., Ltd. (TCI), Japan was recrystallised from ethanol. All the other chemicals used were of analytical grade. Solutions were prepared in double distilled and deionized water. An overall ~0.01 mole dm^{-3} concentration of hydrochloric acid was maintained in the stock solutions of metal chlorides to repress the hydrolysis (Baes *et al*., 1976). Metal ion solutions were standardized using standard procedures (Schwarzenbach, 1957). Carbonate content of potassium hydroxide solution, the ionic product of water and pH correction factor for converting hydrogen ion activity to concentration were calculated using Gran's method (Gran, 1950, 1952).

Equipment

The potentiometric titrations were carried out in a jacketed Pyrex glass cell, probing the hydrogen activity with a combination glass electrode of type LL-Unitrode (6.0259.100; 0-14 pH range) attached to a Metrohm-877 Titrino plus auto-titrator. The readability of the instrument was 0.001 pH unit or 0.1 mV. Purified nitrogen gas was passed through the experimental solution both before and during the data acquisition to expel any carbon dioxide present. Thermostated water was passed through the outer jacket of the cell to maintain the temperature at 30.0 ±0.1 ^{0}C.

Data acquisition and analysis

Speciation is generally determined through analytical data acquisition methods that measure free metal ion and/ or free ligand and/or free hydrogen ion concentration(s) in conjunction with thermodynamically feasible and chemically plausible predicted models. Robust mathematical algorithms are used to refine the predicted models to get the best-fit out of them that accounts for all the species in solution, satisfying the probed data and all the mass balance equations. Species concentration distribution against pH of the solution is then generated using the formation constants in the best-fit model. Bjerrum's (Bjerrum, 1957) potentiometric titration method modified by Calvin and Wilson (Calvin and Wilson, 1945) was used for data acquisition. A mixture of hydrochloric acid (0.02-0.05 mole dm^{-3}) and AZDH (0.005-0.015 mole dm^{-3}) was titrated with a standard solution of KOH in the absence and presence of a metal ion (0.01-0.02 mole dm^{-3}) in a total volume of 50.0 cm^3. The ionic strength of the solution was adjusted to 0.1 mole dm^{-3} using a solution of KCl. 1:1, 1:2 and 2:1 metal to ligand molar concentration ratios were maintained in different experiments. Ditopic ligands are prone to form mono- and bi- metallic species with different degrees of protonation and deprotonation. Classical methods of analysis using formation curves (Irving, Rossotti, 1953, 1954) fail in such cases as several overlapping equilibria coexist in solution. Therefore, the acquired data was analysed using the Miniquad-75 program (Gans *et al*., 1976) to get best-fit model of the formation constants that represents the system under study. The initial estimates of the formation constants of the simple complexes were obtained using classical methods and of the other plausible protonated/ deprotonated species were calculated using the acid-base equilibrium constants of AZDH. As the metal ions are susceptible to hydrolysis, the initial estimates of their hydrolysis constants required for inclusion in the models were taken from the literature reports (Barnum, 1983 and Paul L. Brown *et al*., 2016). The best-fit model contains the log β_{mlh} values of all the converged species along with statistical parameters, standard deviations (SD), U/NP (some of the squares of the residuals in mass balance equations/ number of experimental points) and χ^2. The *m, l* and *h* values of the generalised species $M_mL_lH_h$ are the stoichiometric coefficients of the metal ion, ligand and proton respectively in the corresponding equilibrium. Different species in solution possess characteristic values of *m, l* and *h*. A negative value of *h* indicates either deprotonation or hydroxylation of the species. The concentration distribution diagrams of the species in best-fit models were generated using the HYSS program (Alderighi *et al*., 1999)

RESULTS AND DISCUSSION

Proton-AZDH system

As a prelude to the determination of formation constants of binary systems containing a metal ion and dihydrazide, the author has taken up a study on the proton-ligand equilibria of AZDH under similar experimental conditions. This is an essential prerequisite as the formation of a metal complex is also an acid-base equilibrium, where, there is a competition between the metal ion and proton for the binding site(s) of the ligand. This leads to the pH dependence of the formation of metal ligand species that can be monitored using a glass electrode. AZDH belongs to a group of nitrogenous organic

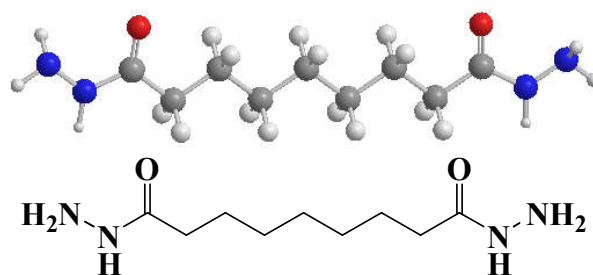compounds with general formula, R $(-CO-NH-NH_2)_2$ as shown in Fig 1. In the case of AZDH, R= $(CH_2)_7$

Fig 1 Azelaic or nonanedioic acid dihydrazide

In the presence of an acid the neutral form of the ligand (L) may be protonated at the terminal $-NH_2$ groups forming mono-protonated (LH^+) and biprotonated (LH_2^{2+}) species. Hydrazides are also known to undergo keto-enol tautomerism and may also lose enolic protons in basic medium, leading to the formation of LH_{-1} and LH_{-2} type of deprotonated species. In literature, there were no reports on the proton-ligand equilibria of AZDH. The pH metric titration data for AZDH in aqueous medium is shown graphically in Figs 2a. Curve 1 represents titration of hydrochloric acid in the absence of ligand, while curve 2 represents the titration of acid + ligand with potassium hydroxide. The titration curve of AZDH (curve 2 in Figs 2a) is above that of free acid below a pH of ~5.0. This difference between the free acid and ligand curves in the lower pH region indicates the presence of proton associable centres in the ligand.
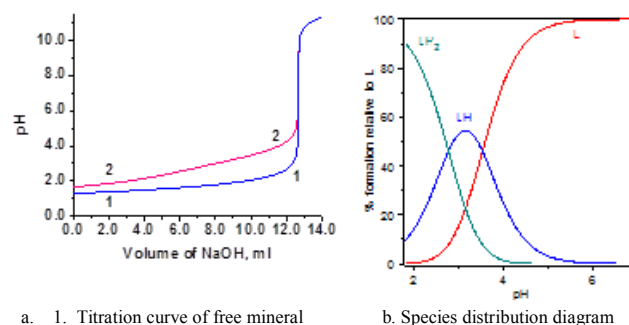

a.   1. Titration curve of free mineral acid   b. Species distribution diagram
2. Titration curve for acid + AZDH

[AZDH] = 0.0150 mol dm^{-3} [HCl] = 0.05034 mol dm^{-3} [KOH]= 0.1989 moldm^{-3}

Temp.: 30.0 ±0.1^{0}C   Total volume= 50.0 cm^3 I = 0.1 mol dm^{-3} KCl

Fig 2 Proton-Ligand System of Azdh

On the basic side there is no significant lowering of the ligand titration curve relative to the free acid indicating the deprotonation of the enolic protons is not taking place in the pH region of study. The best-fit model obtained using the Miniquad-75 program (Table 1) contained two formation constants β_{011} and β_{012} corresponding to the formation of LH^+ and LH_2^{2+} species respectively.

Table 1 Best fit chemical model for acid-base equilibria of Azelaic acid dihydrazide in aqueous medium. Temp. = 30.0 ± 0.1°C and ionic strength, I = 0.1 mol dm^{-3} (KCl)

Species *mlh*	Log β_{0lh} (SD)	Number of experimental points analysed (NP)	Sum of the squares of residuals, U/NP	χ^2
011 012	3.53 (0.01) 6.30 (0.01)	190	3.601 e-10	21.14

The species distribution diagram of AZDH (Fig 2b) indicates that the LH_2^{2+} form exists only below a pH of 4.0. The extent of its formation is ~90% at ~1.8 pH. The species LH^+ which attains a maximum of 55% formation around a pH of 3.1 ceases to exist above ~6.0 pH.

Metal ion-AZDH systems

The best-fit models obtained for all the M^{2+}-AZDH ($M^{2+}=$ Co^{2+}, Cu^{2+} and Zn^{2+}) systems are tabulated in Table 2. The table contains the composition and formation constants of all the species converged along with their standard deviations and other statistical parameters. Inclusion of metal hydroxide species in the models resulted in a final rejection, suggesting their absence or existence at undetectable low concentrations in the pH region of analysis. Only ligand containing deprotonated or hydroxylated species were found to be present in the best-fit models.

group of the free hydrazide moiety on the other side of the molecule. In other words LH form of AZDH is involved in bonding. The formation of MLH_{-1} species may be due to the loss of enolic proton or hydroxylation of the species. The species concentration distribution diagrams generated using the HYSS program[31] are shown in Fig.3. The formation of ML is more than 78% of the total metal in all the cases.

The best-fit models for 1:2 metal ion to ligand molar concentration ratio for all the metal ion-AZDH systems indicate the formation of ML_2H_2, ML_2H, ML_2 and ML_2H_{-1} species. The $\Delta \log K$ values (= $\log \beta_{122}$ - $\log \beta_{121}$ or = $\log \beta_{121}$ - $\log \beta_{120}$) of protonation of the species range from 2.42 to 3.39. This indicates that in all the protonated species the associated proton is probably due to the LH form of the ligand. The species distribution diagrams show that the extent of formation of ML_2 varies from 74 to 80% for different metal ions.
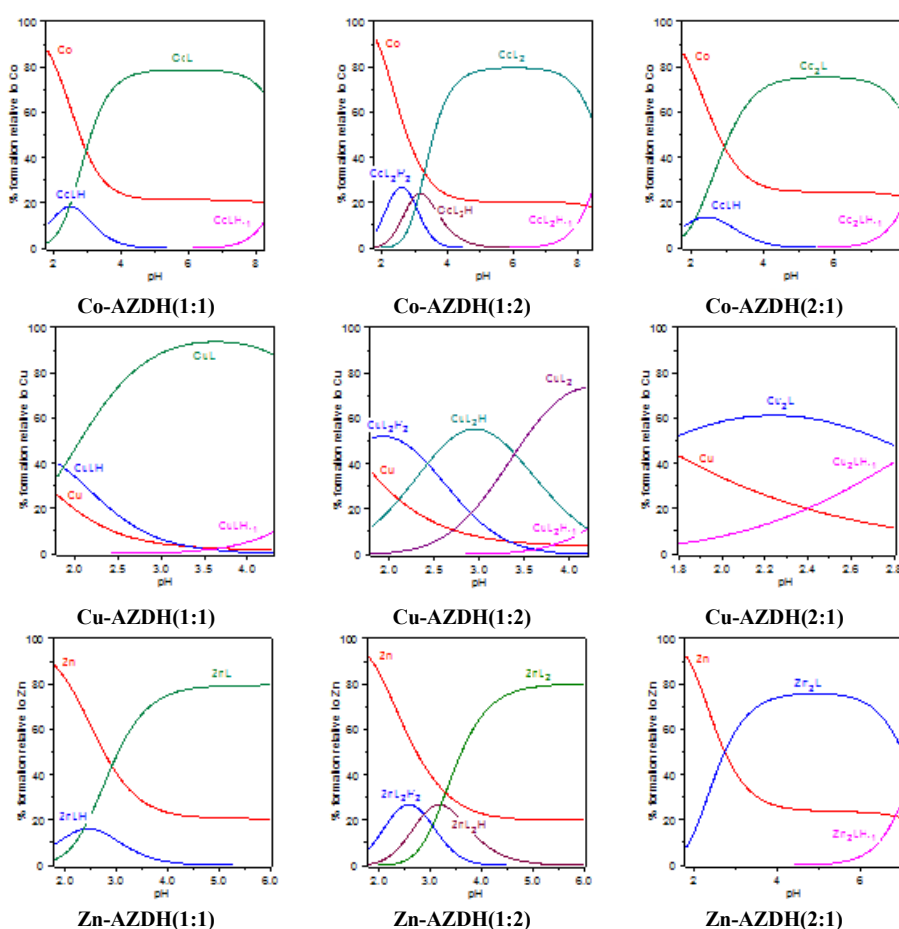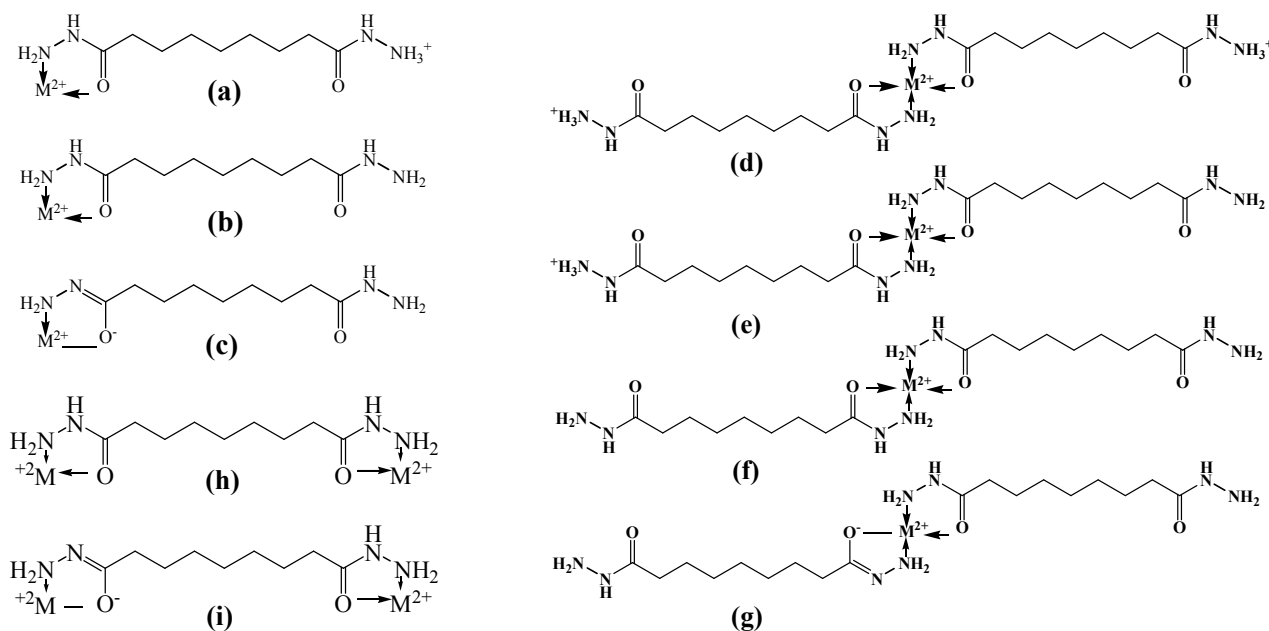

Fig 3 Species concentration distribution diagrams of M^{2+}- AZDH systems
([AZDH] = 0.0100 mol.dm^{-3} and [M^{2+}] = 0.0100, 0.0050 and 0.0200 mol.dm^{-3}
for 1:1, 1:2 and 2:1 metal to ligand mole ratio systems)

The species converged for 1:1 (mole ratio) metal ion-AZDH (L) systems were MLH, ML and MLH_{-1} (M= Co^{2+}, Cu^{2+} and Zn^{2+}). The formation of MLH species indicates that one of the hydrazide groups of AZDH is bonded to the metal ion while the other is free and protonated. With an increase in the pH of the solution, MLH species loses its proton on the non-bonding side leading to the formation of ML. The $\Delta \log K$ (= $\log \beta_{111}$ - $\log \beta_{110}$) values for the formation of ML from MLH are 2.45, 1.87 and 2.36 respectively for Co^{2+}, Cu^{2+} and Zn^{2+} systems, which are less than 3.53, the protonation constant of free ligand. This clearly indicates that the associated proton in the MLH type of species is due to the protonation of the $-NH_2$

Bimetallic species of the type M_2L and M_2LH_{-1} were found to exist in 2:1 (M: L mole ratio) solution for all the metal ion systems under study. In homo-binuclear type of species (M_2L), AZDH acts as a ditopic ligand probably bonding through amino and carbonyl groups on both the sides. These species are predominant in 2:1 systems and represent 61 to 75% of the total metal concentration. With an increase in the pH, M_2L species are converted to M_2LH_{-1} by hydroxylation or losing an enolic proton. Further deprotonation or hydroxylation could not be observed due to the appearance of turbidity leading to precipitation.

Table 2 Best-fit models for AZDH- metal ion systems (Temp. =30.0 ± 0.1°C and ionic strength, I = 0.1 mol dm^{-3})

Initial concn. ratio (M:L)	Species $M_mL_lH_h$	Log β_{mlh} (SD)		
		Co^{2+}	Cu^{2+}	Zn^{2+}
1:1	MLH	5.69 (0.01)	7.32 (0.01)	5.63 (0.01)
	ML	3.24 (0.01)	5.45 (0.01)	3.27 (0.01)
	MLH$_{-1}$	-5.74 (0.02)	0.20 (0.02)	-
	NP	204	185	187
	U/NP	5.552e-09	9.396e-10	8.340e-10
	χ^2	39.92	24.36	44.39
1:2	ML$_2$H$_2$	12.05 (0.01)	14.11 (0.01)	12.08 (0.01)
	ML$_2$H	9.12(0.01)	11.69 (0.01)	9.21 (0.01)
	ML$_2$	5.98 (0.01)	8.30 (0.01)	6.00 (0.01)
	ML$_2$H$_{-1}$	-2.80 (0.02)	3.29 (0.02)	-
	NP	134	199	151
	U/NP	2.742e-09	1.547e-09	6.141e-09
	χ^2	21.36	21.71	20.38
2:1	MLH	5.69	-	
	M$_2$L	5.11 (0.01)	6.95 (0.01)	5.15 (0.01)
	M$_2$LH$_{-1}$	-3.29 (0,02)	4.08 (0.01)	-2.12 (0.02)
	NP	73	100	205
	U/NP	8.315e-09	7.203e-09	4.296e-08
	χ^2	5.03	24.80	28.42

acquisition method followed by analysis using the Miniquad-75 program. In solution depending on the pH, AZDH exists in neutral (L), mono protonated (LH$^+$) and biprotonated (LH$_2^{2+}$) forms. Several mononuclear and binuclear species with different degrees of protonation/ deprotonation were found to be present in solution. The formation constants were calculated and the species concentration distribution diagrams were generated using the HYSS program. The formation of bimetallic species indicates the ditopic nature of AZDH.

Acknowledgements

Fig 4 Probable bonding nature of AZDH in mononuclear and binuclear species
(a) MLH (b) ML (c) MLH$_{-1}$ (d) ML$_2$H$_2$ (e) ML$_2$H
(f) ML$_2$ (g) ML$_2$H$_{-1}$ (h) M$_2$L and (i) M$_2$LH$_{-1}$

The formation constants are in the order Co^{2+}<Cu^{2+}>Zn^{2+} satisfying Irving & William's order (Irving and William, 1953).

Bakir Jeragh *et al.*(Bakir Jeragh *et al.*, 2014) in their studies on solid state metal complexes of dihydrazides reported that these ligands in neutral or anionic form act as bidentates in mononuclear complexes and bis bidentates in binuclear species. This supports our speciation results of the identification of mono and binuclear species in protonated, unprotonated and deprotonated forms in the solution. The probable bonding nature of AZDH in the observed species based on our results and supported by literature reports on solid state structural elucidation studies is shown in Fig. 4.

CONCLUSIONS

Interaction of Azelaic acid dihydrazide with the metal ions Co^{2+}, Cu^{2+} and Zn^{2+} was investigated using potentiometric data

References

1. Al-Amiery A.A., Binti Kassim F.A., Kadhum A.A.H. and Mohamad A.B. (2016). Synthesis and characterization of a novel eco-friendly corrosion inhibition for mild steel in 1 M hydrochloric acid. Scientific Reports, 6:19890.
2. Alderighi L., Gans P., Ienco A., Peters D., Sabatini A. and Vacca A. (1999). Hyperquad simulation and speciation (HySS): A utility program for the investigation of equilibria involving soluble and partially soluble species. *Coord. Chem. Rev.*, 184: 311–318.
3. Baes C.F. and Mesmer R.E. (1976). The Hydrolysis of Cations. John Weily & Sons: New York.
4. Bakir Jeragh, and Ahmed A. El-Asmy. (2014). Structure and spectroscopic studies of homo- and heterometallic complexes of adipic acid dihydrazide. *Spectrochimica*

Acta Part A: Molecular and Biomolecular Spectroscopy, 125: 25-35.

5. Barnum D.W. (1983). Hydrolysis of cations. Formation constants and standard free energies of formation of hydroxo complexes. *Inorg. Chem.*, 22:2297-2305.

6. Bjerrum J. (1957) Metal ammine formation in aqueous solution: theory of the reversible step reactions. P. Haase and Son, Copenhagen.

7. Brown Paul L. and Christian Ekberg. (2016). Hydrolysis of metal ions. Wiley-VCH Verlag GmbH & Co, Germany. 1:742.

8. Burckhardt U. and Kramer A. (2009). Use of carboxylic acid hydrazide for de-bonding polyurethane adhesives. Patent Application No. US 20100323202A1.

9. Calvin M. and Wilson K.W. (1945). Stability of chelate compounds. *J. Am. Chem. Soc.*, 67:2003-2007.

10. Carraher C.E., Chen W., Hess G.G. and Giron D.J. (1990). Biological Characterization of Selected Palladium (II) Poly(amides), Poly(thioamides) and Poly(hydrazides). In: Gebelein C.G., Dunn R.L. (eds). Progress in Biomedical Polymers, Springer, Boston, MA, :363-370.

11. De Witt and D. Hobson D. (1964). Polyhydrazides containing phosphorous. Patent No. US 3124560.

12. Dunkana N.K., Satyanarayana A. and Shyamala P. (2015). Chemical Speciation Study of ternary complexes of Cu(II) with succinic acid dihydrazide and some amino acids in aqueous solution. *Chemistry and Materials Research*. 7(4): 93-102.

13. Dunkana N.K., Shyamala P., Satyanarayana A. and Krishna Prasad K.M.M. (2014). Chemical speciation studies on the complexation of ditopic ligands: Interaction of malonic acid dihydrazide with some divalent transition metal ions in aqueous medium. *J. Indian Chem. Soc.*, 91:729-737.

14. Gans P., Sabatini A. and Vacca A. (1976). An improved computer program for the computation of formation constants from potentiometric data. *Inorg. Chim. Acta.*, 18: 237.

15. Gogorishvili P.V., Machkhoshvili R.I., Tsitsishvili L.D., Shvelashvili A.E., Kharitonov Yu.Ya. and Tsutsunava T.I. (1976). Complex compounds of cobalt thiocyanate with some acid dihydrazides. *Koordinatsionnaya Khimiya*, 2(7):958-964.

16. Gogorishvili P.V., Tsitsishvili L.D, Tsutsunava T.I., Kharitonov Yu.Ya. and Machkhoshvili R.I. (1977). New complexes of metals with dihydrazides of glutaric and azelaic acids. *Koordinatsionnaya Khimiya*, 3(9):1438.

17. Gran G. (1950). Determination of the equivalence point in potentiometric titrations- Part I. *Acta. Chem. Scand.* 4:559.

18. Gran G. (1952). Determination of the equivalence point in potentiometric titrations-Part II. Analyst. 77:661.

19. Irving H.M. and Rossotti H.S. (1953). Methods for Computing Successive Stability Constants from Experimental Formation Curves. *J. Chem. Soc*. :3397-3405.

20. Irving H.M. and Rossotti H.S. (1954). The Calculation of Formation Curves of Metal Complexes from pH-Titration Curves in Mixed Solvents. *J. Chem. Soc.*: 2904-2910.

21. Irving H.M. and Williams R.J.P. (1953). The stability of transition-metal complexes. *J. Chem. Soc*. 167:3192-3210.

22. Jonasse H.B and Ramanujam V.V. (1959). Binuclear complexes as catalysts. *J. Phys. Chem.*, 63 (3):411-415.

23. McKenzie C.J. and Robson R. (1988). High turnover catalysis at bimetallic sites of the hydration of nitriles to carboxamides co-catalyzed by acid. *Chem. Commun.*:112-113.

24. Satyanarayana A., Dunkana N.K. and Shyamala P. (2013). Speciation study on the interaction of some divalent transition metal ions with succinic acid dihydrazide in aqueous medium. *Acta Chim. Slov.*, 60:807–812.

25. Schwarzenbach G. (1957). Complexometric titrations. Methuen & Co. Ltd.: London.

26. Shibasaki M. and Yamamoto Y. (2004) Multimetallic Catalysts in Organic Synthesis. Wiley-VCH: Weinheim, Germany.

27. Steinhagen H. and Helmchen G. (1996). Asymmetric two-center catalysis: Learning from Nature. *Angew. Chem. Int. Ed.*, 35:2339-2342.

28. Swan D.R. and Calhoun J.M. (1943). Photographic film comprising nitrocellulose film base stabilized by a dihydrazide of an aliphatic dicarboxylic acid. Patent No.US 2311098.

29. Thomas A.K. (1999). Dinuclear metal complexes of bis-macrocycles", *Coord. Chem. Rev.*, 190-192:371-389.

30. Tsitsishvili L.D., Tsutsunava T.I. and Kharitonov Yu. Ya, (1982). Complexes of cobalt with deprotonated dihydrazides. *Koordinatsionnaya Khimiya*, 8(5):674-679.

31. Tsitsishvili L.D., Tsutsunava T.I., Gogorishvili P.V. and Kharitonov Yu. Ya, (1978). Cobalt, nickel, and copper complexes with azelaic acid dihydrazide. *Redkikh Metallov*, 3:23-31.

32. Uma Rani B., Shyamala P. and Satyanarayana A. (2015). Chemical speciation studies on complexation of ditopic ligands: Interaction of adipic acid dihydrazide with Mg(II) and Ca(II) in aqueous medium. *IOSR Journal of Applied Chemistry (IOSR-JAC)*. 8(12):52-58.

33. Uma Rani B., Shyamala P. and Satyanarayana A. (2016). Chemical speciation studies on complexation of ditopic ligands: Interaction of adipic acid dihydrazide with Pb^{2+}, Hg^{2+} and Cd^{2+} metal ions in aqueous medium. *International Research Journal of Pure & Applied Chemistry*. 11(2):1-10.

****