

## Chemical speciation study of Ditopic Azelaic acid dihydrazide with Manganese(II) and Nickel(II) in aqueous medium

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A chemical speciation study was carried out potentiometrically with Metrohm-877 titrimplus auto titrator for the interaction of a ditopic aliphatic ligand, Azelaic acid dihydrazide (AZDH) with first row transition metal ions Mn<sup>II</sup> and Ni<sup>II</sup> in aqueous medium at 30.0±0.1°C temperature and ionic strength, *I* = 0.1 mol dm<sup>-3</sup> (KCl). The chelating nature exists at both sides of the ligand symmetrically, and there is a possibility of various monometallic and bimetallic species with different states of protonation in the solution. The plausible species existing in the solution were determined by Bjerrum, Calvin-Wilson potentiometric method of data acquisition followed by chemometric methods of analysis for different metal-ligand ratios such as 1:1, 1:2 and 2:1 in different titrations. The distribution of concentration of all species existing in the solution as a function of pH were studied by the species distribution diagrams obtained using HYSS program. Existence of each species in one particular pH range was compared with SOPHD program. The stability constants of all plausible species were determined using Miniquad-75 program. Obtained stability constant values are more significant in giving the probable structures of existing species in the solution.

Keywords: Azelaic acid dihydrazide, ditopic ligand, stability constants, Miniquad-75, HYSS, SOPHD.

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### Introduction

The field of ditopic ligands and their complexes is a developing part of coordination chemistry promising various biological and industrial applications<sup>1</sup>. Biochemically, there is a need of non-toxic ditopic ligands that are efficient at sequestering metal ions with high atom efficiency. Dihydrazides belong to a group of nitrogenous organic compounds that find extensive application in chemotherapy, synthetic chemistry, agriculture and chemical analysis. These compounds are useful curing agents for epoxy resins, chain extenders for polyurethanes, and excellent crosslinking agents for acrylic. The growing commercial and biological applications increased the importance of this class of compounds. These ligands can accommodate metal ions in different coordination pockets leading to the formation of binuclear complexes in addition to the mono nuclear complexes and involves several interesting and important applications. The presence of two metal ions in the same species separated by a flexible

part of the molecule leads to form supramolecular like structures to mimic metallo proteins<sup>2</sup> and to understand their structure-reactivity relationship, DNA binding, specific and selective catalysis. *In vitro* and *in vivo* tests proved dihydrazides to be non-genotoxic. Food and Drug Administration (FDA) approved<sup>3,4</sup> the use of dihydrazides as cross linkers for coatings<sup>5</sup> on plastics used for food package that is not in direct food contact.

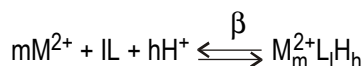
Linear aliphatic dicarboxylic acid dihydrazides such as AZDH are used to produce linear polymers that are used in the fabrication of heat and flame resistant fibres, films and coatings. They are also used as photographic film stabilizers, acid corrosion inhibitors of mild steel<sup>6</sup> and in de-bonding of polyurethane adhesives. Several literature reports<sup>7-16</sup> were found on the metal complexes of dihydrazides that involve synthesis and structural elucidation of complexes by elemental analyses, magnetic moments, molar conductance, ESR, IR, electronic and X-ray diffraction studies. No reports were

found on complexation of AZDH towards  $Mn^{II}$  and  $Ni^{II}$ , therefore in continuation of our previous speciation study and ligational behavior of dihydrazides<sup>17-21</sup> we report here the chemical speciation study and solution equilibria of AZDH with  $Mn^{II}$  and  $Ni^{II}$  in aqueous medium.

## Results and discussion

### Data acquisition and analysis:

The primary aim of the chemical speciation study is to calculate the concentrations of all the species present in the solution including the free metal ion and free ligand at any given experimental point or pH under the specified experimental conditions. Consider a system containing metal ion ( $M^{2+}$ ), and a ligand (L) involved in the formation of a generalized species represented by the equilibrium,



And the overall formation constant is given by the equation

$$\beta_{mlh} = \frac{[M_m^{2+}L_lH_h]_i}{[M^{2+}]_i^m [L]_i^l [H^+]_i^h}$$

Stoichiometric coefficients  $m$ ,  $l$ , and  $h$  specify the composition of the formed species. Positive, zero and negative values of  $h$  indicate, the formation of protonated, unprotonated and deprotonated (or hydroxyated) species respectively.  $[M]$ ,  $[L]$ , and  $[H]$ , represent the free concentrations of the metal ion, ligand and proton respectively.

Data acquisition<sup>22</sup> involves the titrations of solutions (total volume, 50.0 cm<sup>3</sup>) containing a mixture of hydrochloric acid ( $5.0 \times 10^{-2}$  mol dm<sup>-3</sup>), AZDH ( $0.015$  mol dm<sup>-3</sup> with carbonate free potassium hydroxide ( $\sim 0.2$  mol dm<sup>-3</sup>)). The ionic strength was maintained at  $0.1$  mol dm<sup>-3</sup> with potassium chloride as the background electrolyte. The  $C_M:C_L$  molar concentration ratio in different experiments was maintained at 1:1, 1:2 and 2:1. Titrations were conducted until the appearance of turbidity due to precipitation leading to a downward drift in the pH of the solution. The data from different experiments with different metal to ligand ratios were analysed using the Miniquad-75 program<sup>23</sup>, and species distribution diagrams were generated using Hyss program<sup>24</sup>. The best fit models were selected on the basis of  $U$  (sum of the squares of the residuals in mass balance equations), standard devia-

tions in formation constants and statistics like  $\chi^2$  test which tests the distribution of errors against a normal one.

### Acid-base equilibria of proton-AZDH system:

Azelaic acid dihydrazide (AZDH) is a symmetrical molecule with a C7 backbone between two  $-\text{CONHNH}_2$  complexing groups (Fig. 1) on either side of the molecule. It offers amino and carbonyl groups at both the ends which makes it a ditopic ligand and excellent cross linking agent for water based emulsions. In solution at low pH, AZDH (L) exists as a biprotonated species, the protonation being at the

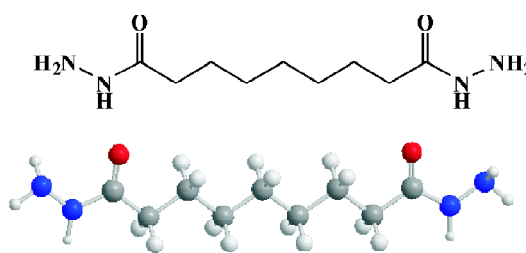


Fig. 1. Structure of Azelaic acid dihydrazide (AZDH).

two amino groups. Hydrazides are prone to lose enolic protons in basic medium by keto-enol tautomerism. As reported elsewhere<sup>18</sup>, the best-fit model obtained by the Miniquad-75 program, for the proton-ligand equilibria of AZDH contains two formation constants,  $\beta_{011}$ , and  $\beta_{012}$  with  $\log \beta$  values 3.53, and 6.30 respectively, corresponding to the formation of mono-protonated, and biprotonated forms of AZDH. The formation constant,  $\beta_{01-1}$ ,  $\beta_{01-2}$  corresponding to the formation of  $LH_{-1}$  and  $LH_{-2}$  in which AZDH loses both the enolic protons were not converged as its equilibrium may not be accessible pH metrically. But in the presence of a metal ion this dissociation may take place leading to the formation of  $MLH_{-1}$  type of species. Therefore, depending on the pH, AZDH exists in solution as  $LH_2^{2+}$ ,  $LH^+$ , and  $L$  (Fig. 2) may interact with a metal ion.

### Metal ion ( $M^{II}$ )-AZDH systems:

In the case of binary metal-AZDH systems, the acquired data for different concentration ratios was first subjected to analysis by classical procedures<sup>22</sup> to get the formation constants of simple mono-nuclear complexes. Simulated titration curves were then generated using a computer program SOPHD<sup>25</sup> developed in our laboratory to see whether these species satisfy the experimental data. The simulated titra-

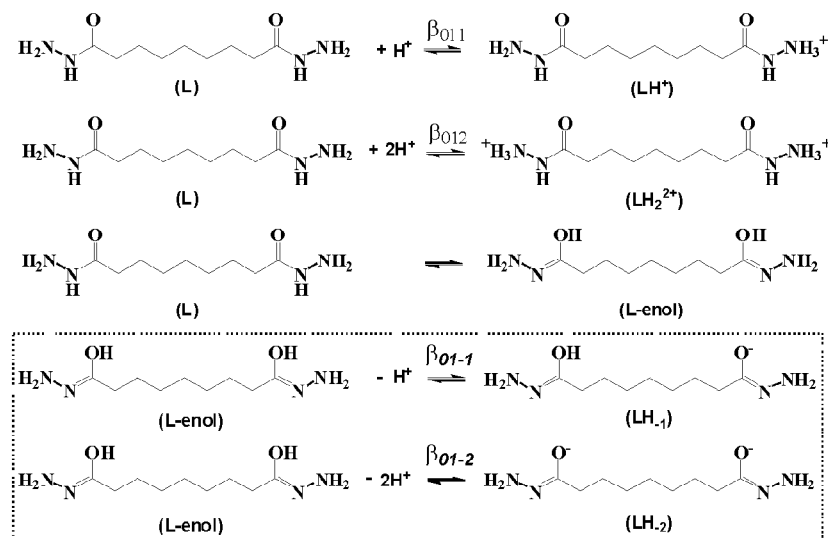


Fig. 2. Protonation and deprotonation equilibria of AZDH.

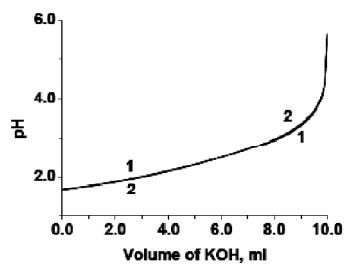
tion curves thus obtained were plotted together with the experimental ones to identify the regions of pH where they differ. Titration curves for metal ion-AZDH systems for all the compositions are shown in Figs. 3 and 4. Differences between the simulated and experimental curves reveal the presence of other major species in addition to simple mononuclear complexes. Different chemical models containing chemically plausible species, based on the nature of the ligand, metal and the pH region of difference in the curves were tested using the Miniquad-75 program. The required initial estimates of the formation constants were calculated basing on the formation constants of simple complexes and protonation/deprotonation constants of the ligand. The best-fit models along with the statistical parameters are depicted in Table 1.

The species converged for 1:1 ( $C_M:C_L$ ) metal ion-AZDH systems were MLH, ML and  $MLH_{-1}$  ( $M = Ni^{2+}$ , and  $Cu^{2+}$ ). 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<sup>26</sup>. 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 formation of  $MLH_{-1}$  species may be due to the loss of enolic proton or hydroxylation. The species distribution diagrams generated using HYSS program are shown in Fig. 5. The extent of formation of MLH species varies between 10 to 15% of total metal ion with a maximum around ~4.5 pH. The formation of ML is above 70% of the total metal in both the cases.

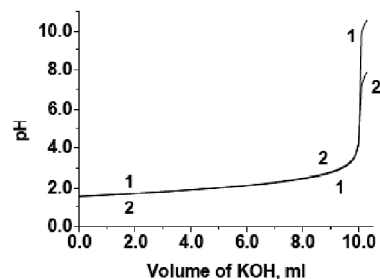
Table 1. Best-fit chemical models of azelaic acid dihydrazide-metal ion systems in the aqueous medium at  $30.0 \pm 0.1^\circ\text{C}$  and ionic strength,  $I = 0.1 \text{ mol dm}^{-3}$  (SD = Standard Deviation)

Initial concentration of M:L	Species ( $M_mL_lH_h$ )	$\log \beta_{mlh}$ (SD)	
		Mn <sup>II</sup>	Ni <sup>II</sup>
1:1	111	5.36 (0.01)	6.21 (0.01)
	110	3.15 (0.01)	4.65 (0.01)
	11-1	–	–4.17 (0.01)
	U/NP	9.505e-10	6.834e-10
	$\chi^2$	25.67	45.33
1:2	122	11.01 (0.01)	13.47 (0.01)
	121	7.48 (0.01)	11.48 (0.01)
	120	4.22 (0.01)	8.21 (0.01)
	12-1	–	–0.98 (0.02)
	U/NP	4.160e-10	4.638e-09
2:1	$\chi^2$	76.89	53.47
	111	5.36	–
	110	–	4.65
	210	4.13 (0.02)	6.77 (0.01)
	21-1	–4.67 (0.03)	–1.34 (0.01)
U/NP	8.443e-08	1.859e-09	
$\chi^2$	51.97	89.07	

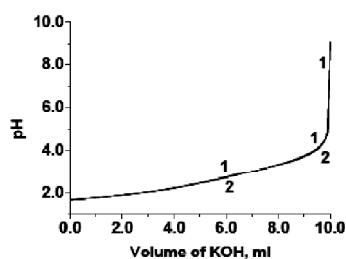
The best-fit model for 1:2 metal to ligand molar concentration ratio indicates the formation of  $ML_2H_2$ ,  $ML_2H$ ,  $ML_2$  and  $ML_2H_{-1}$  species. In all these species probably, only one of the hydrazide groups of the ligand is attached to the metal ion. Bimetallic species of the type  $M_2L$  and  $M_2LH_{-1}$  were



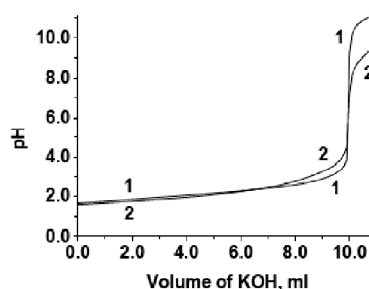
1:1 (M:L)  
 $[Mn^{II}] = 0.01010 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01001 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04008 \text{ mol dm}^{-3}$   
 Total Volume = 50.0 ml



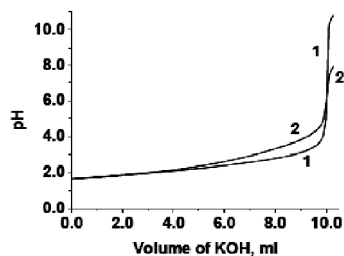
1:1 (M:L)  
 $[Ni^{II}] = 0.01018 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01008 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04022 \text{ mol dm}^{-3}$   
 Total Volume = 50.0 ml



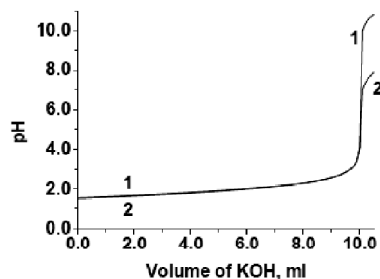
1:2 (M:L)  
 $[Mn^{II}] = 0.00502 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01008 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04003 \text{ mol dm}^{-3}$   
 $[KOH] = 0.2003 \text{ mol dm}^{-3}$



1:2 (M:L)  
 $[Ni^{II}] = 0.00506 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01008 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04002 \text{ mol dm}^{-3}$   
 $[KOH] = 0.2003 \text{ mol dm}^{-3}$



2:1 (M:L)  
 $[Mn^{II}] = 0.02002 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01008 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04011 \text{ mol dm}^{-3}$   
 $I = 0.1 \text{ mol dm}^{-3} \text{ KCl}$



2:1 (M:L)  
 $[Ni^{II}] = 0.02024 \text{ mol dm}^{-3}$   
 $[AZDH] = 0.01008 \text{ mol dm}^{-3}$   
 $[HCl] = 0.04017 \text{ mol dm}^{-3}$   
 $I = 0.1 \text{ mol dm}^{-3} \text{ KCl}$

Fig. 3. Simulated (1) and experimental (2) titration curves of  $Mn^{II}$ -AZDH systems.

found to exist in 2:1 ( $C_M : C_L$ ) solution for both the metal ions under study. In homo-binuclear type of species ( $M_2L$ ), AZDH acts as a ditopic ligand bonding through amino and carbonyl groups on both the sides. These species are predominant in 2:1 systems and represent 40 to 75% of the total metal concentration. With an increase in the pH,  $M_2L$  species are converted to  $M_2LH_{-1}$  by losing an enolic proton. Further

Fig. 4. Simulated (1) and experimental (2) titration curves of  $Ni^{II}$ -AZDH systems.

deprotonation or hydroxylation could not be observed due to precipitation. The studies<sup>12</sup> on solid state metal complexes of AZDH with various metal ions, reported the behaviour of the ligand as a neutral bidentate in mononuclear complexes

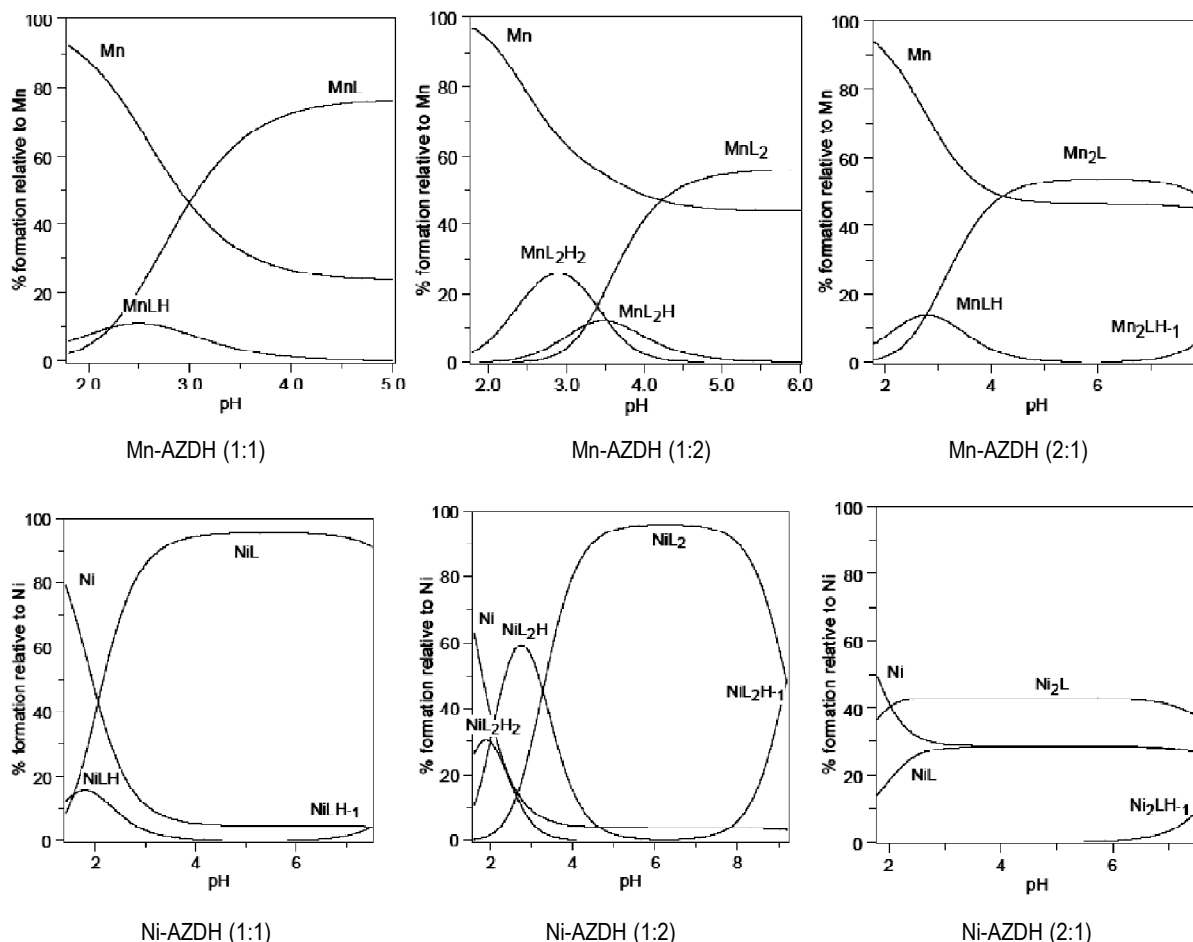


Fig. 5. Species distribution diagrams of  $M^{II}$ -AZDH systems.

([AZDH] = 0.0100 mol dm<sup>-3</sup>, [M] = 0.0100 mol dm<sup>-3</sup>, 0.0050 mol dm<sup>-3</sup>, 0.0200 mol dm<sup>-3</sup> for 1:1, 1:2 and 2:1).

and neutral or binegative tetradentate in binuclear species. In neutral state the ligand bonds through carbonyl oxygen and amino group nitrogen of one (bidentate) or both (tetradentate) of the hydrazide moieties. In binegative tetradentate state the ligand bonds through enolic oxygen and amino groups of both the hydrazide moieties. This sup-

ports our speciation results of identification of mono- and binuclear species in protonated, unprotonated and deprotonated forms in solution. The probable bonding nature of AZDH in the observed species supported by solid state structural elucidation<sup>17-21</sup> is shown in Fig. 6 to 8 of AZDH in mononuclear and binuclear complexes.

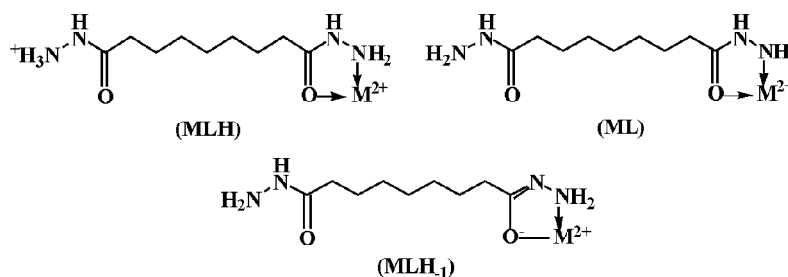


Fig. 6. Probable bonding nature of AZDH in MLH, ML and MLH<sub>1</sub> type of species.

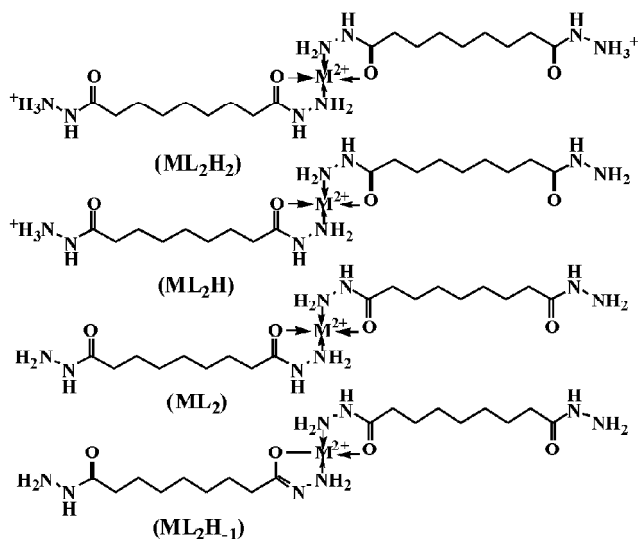


Fig. 7. Probable bonding nature of AZDH in  $ML_2H_2$ ,  $ML_2H$ ,  $ML_2$  and  $ML_2H_{-1}$  type of species.

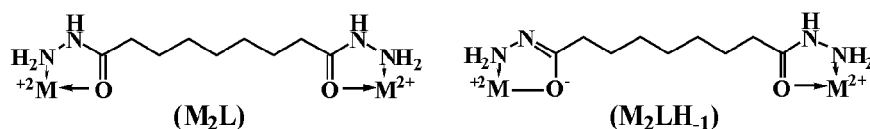


Fig. 8. Probable bonding nature of AZDH in bimetallic complexes.

The ligand acts as a bis-bidentate, coordinating through terminal  $-NH_2$  groups and carbonyl or enolic oxygen forming five-membered rings on both the sides. The coordination of a metal ion at one unit of a ditopic ligand may affect the coordination at the other unit. In the symmetric  $M_2L$  type of complexes, as the second metal ion coordinates to a different hydrazide unit of the same ligand which is away from the first unit, it is expected that the formation constant of  $M_2L$  must be nearly twice that of  $ML$ . For both the metal ion systems, values of  $\log \beta_{210}$  were found to be less than twice of  $\log \beta_{110}$ . This clearly indicates that the bonding at one unit affected the bond strength at the other unit, despite the fact that, they are widely separated. The formation constants of the metal complexes are in the order  $Mn^{II} < Ni^{II}$  and satisfying Irving and William's order<sup>27</sup>.

## Experimental

### Reagents and solutions:

AZDH purchased from Tokyo Chemical Industry Co., Ltd. (TCI), Japan, were recrystallized from ethanol before use.

Solution of  $\sim 0.05 \text{ mol dm}^{-3}$  of AZDH was prepared freshly in  $\sim 0.1 \text{ mol dm}^{-3}$  hydrochloric acid just before use. All the other chemicals such as metal chlorides, hydrochloric acid, potassium chloride and potassium hydroxide were of analytical grade. All solutions were prepared using double distilled and deionized water. Hydrochloric acid of  $\sim 0.01 \text{ mol dm}^{-3}$  was maintained in metal chloride solutions to prevent the hydrolysis. Metal ion solutions were standardized using standard EDTA solution with volumetric and complexometric<sup>28</sup> procedures. Ionic product of water, carbonate content present in the potassium hydroxide solution, pH correction factor were determined using Gran method<sup>29,30</sup> before carrying out each and every potentiometric titration.

### Equipment:

Metrohm-877 titrinoplus auto titrator equipped with 801-stirrer (Switzerland) which is attached with a combined glass electrode of LL-Unitrode type (6.0259.100; 0-14 pH range)

is used for all the potentiometric titrations. This instrument has readability and accuracy up to 0.001 pH or 0.1 mV. The experimental solution is kept under thermostated water bath to maintain the temperature of  $30.0 \pm 0.1^\circ\text{C}$  and nitrogen gas is expelled continuously through it to prevent carbon dioxide content in the experimental solution.

## Conclusions

Azelaic acid dihydrazide is a ditopic ligand with two hydrazide groups on either side of the molecule. Solid state studies<sup>17-21</sup> indicate that the ligand is capable of bonding to the metal ions as a (i) neutral bidentate (ON donor) bonding through carbonyl oxygen and  $-NH_2$  group, (ii) neutral tetradentate (ditopic) bonding through two carbonyl and two  $-NH_2$  groups and (iii) mono or binegative tetradentate bonding in enolic form. The ligational behaviour of the ligand in aqueous solution, towards transition metal ions,  $Mn^{2+}$  and  $Ni^{2+}$  examined using pH-potentiometric technique. The data were analyzed using the Miniquad-75 program. Several species depending on the metal to ligand concentration ratio

were found to exist in solution with overlapping equilibria. The best-fit models obtained were found to include both mono and symmetric binuclear species in protonated, unprotonated and deprotonated forms. The relative order of stability of various species was found to be  $Mn^{II} < Ni^{II}$  satisfying Irving and William's order.

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