A Chemometric Speciation Study of the Binary Ditopic Terephthalic Acid Dihydrazide and Divalent Metal Ion Systems in Aqueous Medium.

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Abstract: *Chemical speciation study of the interaction of Terephthalic acid dihydrazide with H^+, Mn^{2+} and Co^{2+} was carried out using a potentiometric method of data acquisition followed by chemometric modeling methods of analysis. The ligand possesses two hydrazide chelating units and is therefore able to form monometallic and bimetallic species in different protonated, unprotonated and deprotonated forms. Several species of the type $M_mL_lH_h$ (m=1or 2, l=1 or 2 and h varies from 4 to -1 depending on m and l) were observed to be present in solution. Concentration distribution diagrams were generated using the HYSS program.*
Key Words:*Terephthalic acid dihydrazide, ditopic, binuclear, chemical speciation, stability constants*

I. Introduction

Homo and hetero metallic complexesformed by polytopic ligands have been shown to exhibit synergistic catalytic properties[1-5] that cannot be exhibited by monometallic species. The presence of metal ions in adjacent pockets of a molecule leads to interesting magnetic[6], electron transfer and catalytic properties. Some of these ligands and their metal complexes possess useful properties, for instance antimicrobial/ antifungal activity and capacity for DNA binding.The specificity and selectivity achieved by metalloproteins have been recognised,in many instances, as due to the presence of polymetallic cores.   Aliphatic and aromatic polyhydrazides possessing several –CO-NH-NH_2 groups separated by variable hydrocarbon chains are promising candidates for the custom design and synthesis of model compounds to mimic biological compounds[7] for *invitro* studies. The interaction of metal ions with a polytopic ligand may lead to the formation of several mono and polynuclear complexes with different degrees of protonation. To understand the nature and extent of formation of each species under specified experimental conditions, a complete speciation study of the systems of interest in solution phase is mandatory. Therefore, in continuation of our solution phase speciation studies of polytopic ligands[8-12], we report here the results of our study on the chemical speciation ofbinary terephthalic acid dihydrazide (TPDH)–M^{2+} systems (M^{2+}= Mn^{2+}, Co^{2+}) in aqueous medium. TPDH and its derivatives have been widely used for coatings of epoxy resins and in varnishes. They are also used as copper and aluminium corrosion inhibitors in sulphuric acid[13].Hydrazides display antioxidental[14], antimicrobial[15] and antibacterial[16] properties based on their tendency to form metal chelates. Further, they are employed aschain extenders**,** latent hardeners, curing agents, and cross-linkers in many industrial products including semiconductors[17-20].

TPDH is an aromatic ditopic ligand with two coordinating hydrazide groups on either side of the benzene ring.

Figure 1: Terephthalic acid dihydrazide

Each hydrazide group may act as a monodentate or bidentate bonding through carbonyl oxygen and – NH_2 groups to different metal ions. Therefore, there is a chance of formation of mono- and bimetallic species with different degrees of protonation/ deprotonation. Literature reports[21-25] on the solid state physico-chemical studies of the divalent metal ion-TPDH complexesindicate ambidentate nature of the ligand. However, solid

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phase studies cannot predict the behaviour of the ligand in solution phase as there exists a number of overlapping equilibria leading to the formation of different species. Precipitation of a particular species for solid state study may even change its nature including composition. There were no reports on the chemical speciation of TPDH complexes in solution phase.

II. Materials And Methods

Reagents: All the reagents were of analytical grade and obtained from Sigma-Aldrich or MercK. Terephthalic acid dihydrazide, purchased from Tokyo Chemical Industry Co., Ltd. (TCI), Japan, was recrystallised from ethanol before use. Stock solutions of metal chlorides (~0.1 mole dm^{-3}) were prepared in triple distilled water. Overall 0.01 mole dm^{-3} strength of hydrochloricacid was maintained in all the metal ion solutions to repress the hydrolysis[26]. Metal ion solutions were standardized by titrating with EDTA[27]. The ionic product of water, carbonate content of the base (KOH) and pH correction factor for converting hydrogen ion activity to concentration were determined using Gran's method[28,29].

Equipment: A Metrohm-877 Titrino plus auto titrator equipped with 801-stirrer (Switzerland) in conjunction with a combination electrode of type LL-Unitrode (6.0259.100; 0-14pH range) was used inpotentiometric titrations. The readability of the instrument was 0.001 pH unit or 0.1 mV.A double-walled Pyrex glass vessel with a provision for the passage of the nitrogen gas was used to conduct potentiometric titrations. The temperature of the solution was maintained at 30.0 ±0.1 ^{0}C by passing thermostated water through the annular space of the cell.

Data acquisition and analysis: The data acquisition was made using Bjerrum's[30] potentiometric titration technique modified by Calvin and Wilson[31]. This involves the titration ofa mixture of hydrochloric acid (0.02 -0.04 mole dm^{-3}) and TPDH (0.005-0.01 mole dm^{-3}) in the absence and presence of a metal ion (0.005-0.02 mole dm^{-3}) with a standard solution of KOH (~0.2 mole dm^{-3}). Ionic strength was maintained at 0.1 mole dm^{-3} in a solution of total volume 50.0 cm^3. The metal to ligand concentration ratio was varied in different experiments. Purified nitrogen gas was passed through the experimental solution both before and during the titrations to expel carbon dioxide.

In a solution containing a divalent metal ion and a ligand forming 'N' complexes the equilibrium at i^{th} experimental point and the corresponding formation constant of a complex with stoichiometric coefficient m, l and h are represented by equations (1) and (2) respectively.

$$m[M^{2+}]_i + l[L]_i + h[H^+]_i \xrightleftharpoons{\beta_j} [M_mL_lH_h]_i \quad \text{------(1)}$$
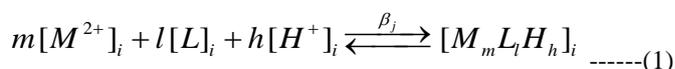
$$\beta_{mlh} = \frac{[M_mL_lH_h]_i}{[M^{2+}]_i^m.[L]_i^l.[H^+]_i^h} \quad \text{------- (2)}$$

Different species in solution possess characteristic values of m, l and h. Negative value of h indicates either deprotonation or hydroxylation of the species. In the case of polytopic and polydentate ligands there is a chance of formation of mono or poly metallic species with different degrees of protonation/ deprotonation in addition to simple complexes. Classical methods of analysis using formation curves[32,33]that are useful only for the determination of formation constants of simple species fail in such a complex system. Therefore, the analysis of acquired data was conducted using the Miniquad-75 computer program which uses bothconstrained least-squares and Marquardt methods for steepest descent of the shift vector leading to better convergence properties. The experimental data acquired for metal ion- TPDH systems of 1:1, 1:2 and 2:1 metal to ligand molar concentration ratios were first subjected to analysis by classical procedures[32,33] to get the formation constants of simple mono-nuclear complexes. The stability constants of the simple complexes thus obtained were used to simulate the primary data using the computer program SOPHD[34] developed in our laboratory. The experimental and simulated titration curves were plotted together to determine whether or not these species alone satisfy the experimental data. The difference between the two curves indicates inadequacy of the proposed model. Keeping in view of the position and extent of deviation between simulated and experimental curves suitable chemically plausible models including protonated and deprotonated species were prepared and subjected to refinement by the Miniquad-75 program[35]. The stability constants obtained from classical procedures were taken as the initial estimates for simple complexes. The formation constant estimates for protonated and deprotonated species were calculated using the stability constants of simple complexes and the experimentally determined protonation/ deprotonation constants of the ligand. As the metal ions are susceptible to hydrolysis, the formation constants of the corresponding hydroxylated species were also included in the models. Initial estimates of the metal ion hydrolysis constants were obtained from the literature reports[36, 37]. The best-fit model that represents the solution equilibria was selected on the basis of statistical parameters. The concentration distribution diagrams of the species were generated using HYSS program[38].

III. Results And Discussion

Acid-base equilibria of TPDH:

In the presence of an acid TPDH (L) may be protonated at the terminal $-NH_2$ groups forming monoprotonated (LH^+) and biprotonated (LH_2^{2+}) cationic species. Hydrazide groups are known to undergo keto-enol tautomerism and therefore, TPDH may also lose enolic protons in basic medium forming (LH_{-1})$^-$ and (LH_{-2})$^{2-}$type of deprotonated species. In literature, there were no reports on the proton-ligand equilibria of TPDH. The potentiometric data for the acid-base equilibria of TPDH was subjected to analysis using the Miniquad-75 program. The best-fit model obtained (Table 1) contained three formation constants β_{011}, β_{012} and β_{01-1} corresponding to the formation of LH, LH_2 and LH_{-1}species(charges are omitted for brevity) respectively (Figure 2).
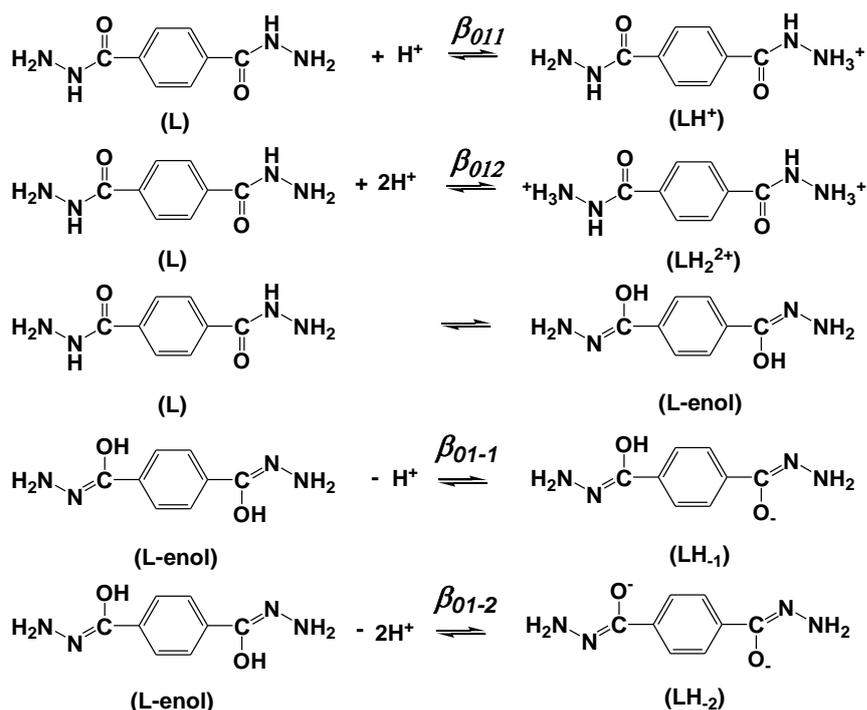

Figure 2: Acid-base equilibria of TPDH

Table no. 1: Best fit chemical model for acid-base equilibria of
Terephthalic acid dihydrazide in aqueous medium.
Temp. = $30.0 \pm 0.1°C$ and ionic strength, $I = 0.1$ mol dm^{-3} (KCl)

Species *mlh*	Log β_{0lh}(SD)	Number of experimental points analyzed	Sum of the squares of residuals, U	χ^2
011	3.12 (0.01)			
012	5.24 (0.01)	130	6.230 e-09	37.72
01-1	-10.85 (0.01)			

The formation constant β_{01-2} corresponding to the species LH_{-2} was not converged as its equilibrium may be out of the reliable pH region of study using the glass electrode.

Metal ion-TPDH systems:

The best-fit models obtained for $Mn^{2+}$and Co^{2+} systems for various metal ion to TPDH concentration ratios were depicted in Table no. 2.

Table no. 2: Best-fit chemical models for metal ion-TPDH equilibria in aqueous medium.
Temp. = $30.0 \pm 0.1°C$ and ionic strength, $I = 0.1$ mol dm^{-3} (KCl)

Molar Ratio (M^{2+}:TPDH)	Species *mlh*	$log_{10}\,\beta_{mlh}(SD)$	
		Mn^{2+}	Co^{2+}
1:1	111	4.91 (0.04)	5.07 (0.02)
	110	2.16 (0.02)	2.47 (0.01)
	11-1	-5.92 (0.03)	-5.54 (0.02)
	U/NP	3.699 e-08	7.006 e-09
	NP	107	105
	χ^2	98.07	77.86
	R	0.01052	0.0046
1:2	122	10.04 0.02	10.42 0.03
	121	7.11 (0.01)	7.87 (0.01)
	120	4.30 (0.01)	4.85 (0.01)
	12-1	-3.76 (0.01)	-3.00 (0.01)
	U/NP	6.360 e-11	9.096 e-10
	NP	56	84
	χ^2	51.05	56.19
	R	0.0006	0.0023
2:1	111	4.91	5.07
	210	4.26 (0.02)	4.59 (0.01)
	21-1	-3.57 (0.04)	-3.40 (0.02)
	U/NP	8.124 e-08	2.077 e-08
	NP	120	115
	χ^2	81.47	88.83
	R	0.0116	0.0063

The species converged for 1:1 metal to ligand mole ratio systems were, MLH, ML and MLH$_{-1}$. In MLH the ligand binds the metal ion at one of the hydrazide moieties, leaving the other protonated and non-bonding. With the increase in pH MLH species lose this proton forming ML type of species. The values of Δ log K (= log β_{111}- log β_{110}) are 2.75 and 2.60 respectively for Mn^{2+} and Co^{2+} systems which are less than 3.12, the protonation constant of the ligand. This indicates that the complex formation at one end of the molecule affects the protonation at the other end. The species ML$_2$H$_2$, ML$_2$H, ML$_2$ and ML$_2$H$_{-1}$ were found to exist in solutions of 1:2 metal to ligand mole ratio. Again the protons associated with the species are due to the protonated –NH$_2$ groups of the non-bonding hydrazide moiety. Homo binuclear species of the type M$_2$L and M$_2$LH$_{-1}$ were observed in 2:1 metal to ligand mole ratio solutions in which the ligand binds two metal ions at the two hydrazide groups. The probable bonding nature in bimetallic species, supported by solid state studies[21-25] was shown in Figure 3.
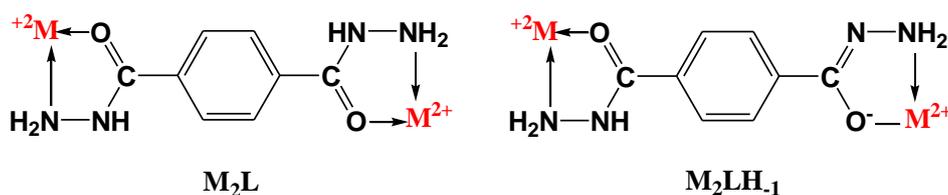

Figure3: Probable bonding nature of TPDH in bimetallic species.

The formation of deprotonated species, MLH$_{-1}$, ML$_2$H$_{-1}$ and M$_2$LH$_{-1}$ may be due to the release of enolic proton at one of the hydrazide groups or hydroxylation of the corresponding species. The concentration distribution diagrams generated using HYSS program[38] for all the systems under study are shown in Figure 4. All the protonated species exist only below a pH of ~4.0. The bimetallic, M$_2$L type of species exists in the pH range 4.0- 7.0 and reaches a maximum of 60% of total metal. With the increase in pH these species lose enolic proton and are converted into M$_2$LH$_{-1}$ species. The stabilities of Mn^{2+} complexes are less than those of Co^{2+} satisfying the Irving & William order[39].
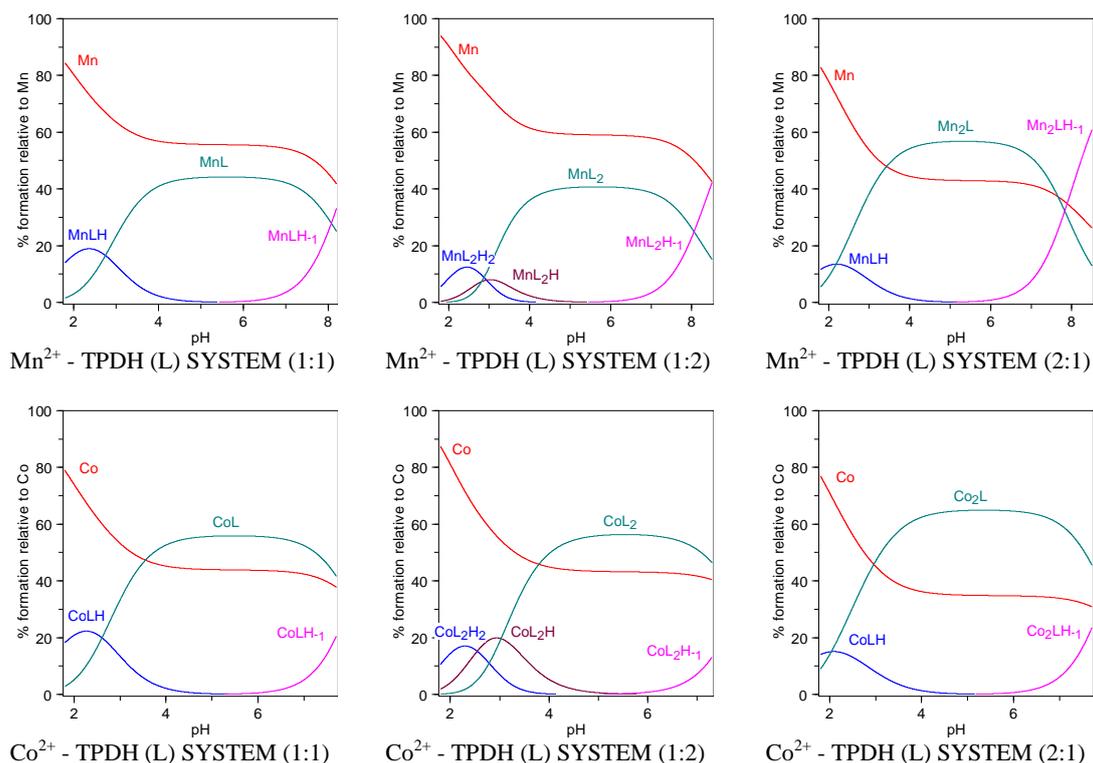
Figure 4: Concentration distribution diagrams of metal ion-TPDH systems

IV. Conclusions

Terephthalic acid dihydrazide is a ditopic ligand that can bind two metal ions at different sites of the same molecule forming bimetallic complexes. Bimetallic species are known to exhibit versatile catalytic and magnetic properties. Therefore, a speciation study using maticulous data acquisition procedure and chemometric method of analysis was carried out on the interaction of H^+, Mn^{2+} and Co^{2+} with TPDH. A study on the acid-base equilibria of TPDH (L) in aqueous solution indicated the formation of mono (LH^+) and biprotonated (LH_2^{2+}) species in an acidic medium and mono deprotonated species (LH_{-1}) in basic medium. The protonation being at the terminal $-NH_2$ groups of the two hydrazide moities and the deprotonation is of the enolic proton. Best-fit models obtained for metal ion-TPDH systems using the Miniquad-75 program showed the presence of mono and bimetallic species with different degrees of protonation/ deprotonation.

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