

# Water Complexities Due Potential of Hydrogen (pH) in Lake Waters of Kashmir Valley

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**Abstract**—Stabilities of the heavy metal complexes cannot be accounted by a single factor, each is considered separately in terms of ligands or vice-versa reveals that the stability constants show a large variation in values. The stability constants of heavy metal complexes in solution phase are generally considered as being stable or unstable, depending on the strength of bond between heavy metal ion and the ligands. Stability of a complex is very often expressed in terms of stability constant, which is used to describe the equilibrium behavior of metal complexes. This investigation was carried out to study the interacting behavior of prototype heavy metal ions and ligands as found in the water bodies of our concern in lake waters of Kashmir valley.

**Keywords:** Kashmir water lakes, ligends, metal ions, pH-metric studies, Glycine and Cysteine etc.

## 1. INTRODUCTION

In universe water is not only life sustaining natural resource on earth but all socio-economic developments and human welfare depends on it. Hence the availability of this valuable resource in pure and usable forms is crucial. In spite of its vital importance, it is invariably polluted by both natural and anthropogenic sources. Amongst various polluting species in natural water bodies, the most dreaded and ever increasing are the heavy metals, which are more dangerous than other toxicants because of the fact that they are native to human body due to which they bioaccumulate over time, whenever they are taken up and get stored faster than they are metabolized or excreted. Both the water bodies of Kashmir valley are polluted in terms of majority of the water chemistry parameters studied, ranging from high values of total alkalinity, conductivity, chloride content, nitrate content, ammonia content, total dissolved solids, orthophosphate and total phosphate contents to low levels of water transparency and dissolved oxygen contents. Moderate to large quantities of water flows into these two lakes from northern side and equally good amounts are discharged through the lake exists, leading to low water retention and dilution factor enhancement which does not actually happen due to complex water flow pattern that takes narrow routes, leaving large areas of stagnant waters usually with increased levels of pollutants.

From an environmental stand point, dissolved organic matter and other potential ligands in aquatic systems are known to influence the distribution of heavy metals by complexation. The pH of the water body has an effect on complexation, besides other factors. The complexation reduces the toxicity of a heavy metal to aquatic life. In order to access the extent of complexation viz-a-viz. the stability of the concerned heavy metals as found in the water bodies of our concern with the potential ligands as are available in these water bodies, two types of physicochemical studies were carried out viz.

1. Electrometric studies/pH-metric studies.
2. Comparative avidity studies of the concerned heavy metals and ligands.

The complexing ability viz-a-viz. the stability order of the pollutant heavy metals with the ligands available is of importance in determining the fate of these pollutants in the aquatic environment.

## 2. REVIEW OF LITERATURE

Water temperature influences the uptake of heavy metals by submerged plants in water bodies and increasing temperature increases the heavy metal uptake by them (Fritioff et al. 2005). The lake waters remain well mixed throughout the year without depicting either summer or winter stratification. According to Crumrine and Beeton (1975), for developing summer stratification, the depth of lakes should usually exceed 8 meters. In the present investigation the depth of lakes does not exceed 4.5 metres. Lack of thermal stratification and non-development of thermo cline may be either due to larger area of the lakes (Ruttner 1953) or due to shallow depth (Crumrine and Beeton). Other factors may also be responsible for the absence of thermal structure (Zutshi and Vass 1978). The water temperature in general ranged from 3.3 to 33.4°C during the entire course of study.

### 3. METHODOLOGY

The interacting behaviors of prototype heavy metal ions and ligands was studied by carrying out pH-metric studies in accordance with the requirements by a Micro-processor controlled pH-Analyzer (Model 7B454, make Lab. India Instruments Pvt. Ltd.) in conjugation with an Orion Gel-filled combined electrode (Model-9-06).

The heavy metal salts and ligands used during the studies were all analytical reagent grade chemicals of high purity supplied by standard agencies and suppliers of E-Merck India / Germany and some from Hi Media labs., and Qualigens Fine-Chemicals, India. The aqueous solutions of these chemical species were prepared by dissolving their required amounts in freshly prepared doubly/triple distilled water. The required concentrations of the solutions were maintained in accordance with the requirements. The volume of the alkali (0.1 M KOH) used for each titrations was 10ml. The strength of CO<sub>2</sub> free KOH was checked by titrating it with standard oxalic acid before employing it as the titrant.

### 4. RESULTS AND DISCUSSION

This investigation was carried out to study the interacting behavior of prototype heavy metal ions and ligands as found in the water bodies of our concern. Our main focus has been to calculate the stability constants and examine the formation curves by applying Bjerrum's pH – metric titration method as modified by Albert. All structures contained a 1:2 stoichiometric ratio and the measured stability constants values and thermodynamic data are summarized in Table-4. The complexation process is also evident from the comparative avidity studies of the concerned heavy metal ions and ligands as mentioned in the study.

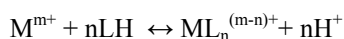
The pH records and computed values along with the pH plots/formation curves of heavy metal-ligand systems selected for present studies are given in Table-4.1.

**Table 4: Thermodynamic stability constant values of heavy metal ligand complexes.**

Ligands	Heavy Metals					
	Fe <sup>2+</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Cd <sup>2+</sup>	Pb <sup>2+</sup>
Glycine	5.2	1.88	2.02	7.24	7.78	5.36
Cysteine	12.34	3.78	11.36	9.98	12.9	13.22
Histidine	9.4	11.42	2.68	6.72	7.18	7.64
Phosphate	10.51	6.43	7.69	14.4	14.72	14.71

### pH-metric Studies

In this electro analytical method, the pH of the solution is determined in a competitive reaction of the type:



**Table 4.1: pH records and computed values of various parameters along with**

V	pH recorded			$\bar{n}$	-log [Sc]	log k <sub>1</sub>	log k <sub>2</sub>
	pH(A)	pH(B)	pH(C)				
0	2.32	4.2	3.38	--	8.19		
0.5	2.37	7.05	3.47	0.1	8.12		
1	2.42	7.53	3.58	0.2	8.05		
1.5	2.48	7.96	4.32	0.29	7.32		
2	2.55	8.23	4.75	0.38	6.91		
2.5	2.63	8.46	4.97	0.48	6.73		
3	2.73	8.73	5.83	0.57	5.19		
3.5	2.83	8.93	6.85	0.65	4.98	5.17	
4	2.89	9.17	7.42	0.74	4.35	4.81	
4.5	2.92	9.47	8.28	0.83	3.52	4.2	
5	2.97	9.8	8.66	0.91	3.17		
5.5	3.01	10.2	9.12	0.99	2.75		
6	3.85	10.38	9.3	1.07	2.6		
6.5	10.11	10.48	9.81	1.15	2.13		
7	11.25	10.75	10.02	1.23	1.68		
7.5	11.52	10.84	10.3	1.3	1.38		
8	11.66	10.96	10.65	1.38	1.18		
8.5	11.88	11.23	10.9	1.45	0.9		
9	12.23	11.45	11.23	1.53	0.7		0.75
9.5	12.4	11.78	11.49	1.6	0.5		0.67
10	12.65	11.97	11.76	1.67	0.45		0.55
Mean	Mean						
log k <sub>1</sub> = 4.72	log k <sub>2</sub> = .72	log K <sub>s</sub> = 5.54 (Calculated)		log K <sub>s</sub> = 5.20 (Graphical)			
V= Val of KOH added in ml							

Since ligands are either weak acids or weak bases, there is competition between hydrogen ions and metal ions for grabbing these ligands, which can be used as a basis for the determination of formation constants. Hence the release of hydrogen ions in this coordination reaction can be correlated with the concentration of uncomplexed ligands and thus, the pH measurement, serves as a suitable method for studying the complex formation phenomena.

Appreciable shifts in pH plots indicated stepwise association of ligands with metal ions. Metal - ligand system may be explained by considering the stepwise formation of complex species of different composition in aqueous solution (ML, ML<sub>2</sub>, ML<sub>3</sub>-----ML<sub>n</sub>) where L stands for ligand and M stands for heavy metal ion and n for number of ligands molecules bound by each heavy metal ion.

In general, at equilibrium the concentration of each species is related to that of each of the other complex species by a series of stepwise formation constant expressions such as;

$$k_1 = [ML] / [M][L]$$

$$k_2 = [ML_2] / [ML][L]$$

$$k_3 = [\text{ML}_3] / [\text{ML}_2][\text{L}]$$

$$k_n = [\text{ML}_n] / [\text{ML}_{n-1}][\text{L}]$$

$K_s$ , the overall stability constant is related to the stepwise formation constants  $k_1, k_2, \dots, k_n$  as:  $K_s = k_1 k_2 k_3 \dots k_n$

For a divalent metal ion

$$K_s = [\text{ML}_2] / [\text{M}^{2+}][\text{L}]^2$$

and a monovalent metal ion

$$K_s = [\text{ML}] / [\text{M}^+][\text{L}]$$

$$\text{Also } \log K_s = \log k_1 + \log k_2$$

When the complex formation starts,  $\text{H}^+$  ions are released and the measurement of the concentration of these ions provides a way to determine the extent of complexation of metal ions with a ligand in aqueous phase. The values of stepwise equilibrium constants are given by the following expression

$$\log k_1 = \log \bar{n} - \log (1 - \bar{n}) - \log [\text{Sc}]$$

$$\log k_2 = \log (\bar{n} - 1) - \log (2 - \bar{n}) - \log [\text{Sc}]$$

Here  $\bar{n}$  ( $n$  bar) is the average number of molecules of complex forming agent attached to one ion of the metal ions and  $[\text{Sc}]$  is the concentration of the coordinating species and its values may be calculated from the equation given below

$$\log [\text{Sc}] = (\text{pH} - \text{pKa}) + \log \{[\text{HSc}]^0 - [\text{KOH}]\}$$

Where  $[\text{HSc}]^0$  is the concentration of the ligand before addition of the metal and  $[\text{KOH}]$  is that concentration of alkali (KOH) which would be present if the complex forming agent and the metal ions were both absent i.e.; the initial concentration of KOH.

The relationship between  $\bar{n}$  and  $[\text{KOH}]$  is given by the expression:

$$\bar{n} = 2[\text{KOH}] / [\text{HSc}]^0$$

The values of all these parameters have been computed.

For calculation of  $\log k_1$  and  $\log k_2$ , the most reliable values of  $[\text{Sc}]$  are found from  $\bar{n} = 0.10$  to  $0.70$  and from  $1.30$  to  $1.70$  respectively as when  $\bar{n}$  lies between  $0.70$  and  $1.30$ , some molecules of  $(\text{MA})^+$  start to take on another molecules of  $(\text{A})$  before all the ligand molecules have interacted with the metallic ions in 1:1 ratio.

Further where  $\bar{n}$  is only a small fraction of  $(1 - \bar{n})$ , knife-edge conditions prevail. Finally when  $\bar{n}$  is approaching 2, the conditions are often such that some of the molecules of the complex  $\text{MA}_2$  form a weak association with an extra molecule of the ligand. With the help of following relation which is

valid only when  $\bar{n} = 1$ , the most reliable value of  $K_s$  are obtained from the formation curves.

$$K_s = 1 / [\text{Sc}]^2$$

$$\text{Or } \log K_s = -2 \log [\text{Sc}]$$

By titrating each ligand in the presence of various metal ions, pH-values were obtained for each addition of alkali and from these readings values. With the help of formation curves, the correct values of  $[\text{Sc}]$  corresponding to  $\bar{n} = 1$  are also found.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. However, exceptions and deviations cannot be ruled out.

## 5. CONCLUSION

As a general rule the greater is stability of the resulting complexes, the higher will be the value of equilibrium constants. In principle, stability constants are determined by studying the concentrations of the various species present in a wide range of equilibrium mixture containing the metal ion and the ligands in different proportions. The disappearance of usual chemical properties of the metal ion in a complex is an important parameter for establishing the possibility and extent of formation of a metal-ligand complex. If a metal-ligand system does not show the usual chemical properties of the metal ion, it is authentic evidence that the free metal ion is either absent or present in an extremely low concentration and most of it has complexed with the ligands.

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