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Stability Constants of Metal (II) Complexes with some Derivatives of Malonic Acid in Different Percentage of Dioxane Water Mixture

U.E. CHAUDHARI

Department of Chemistry, Mahatma Fule Arts, Commerce and Sitramji Chaudhari
Science College, Warud, Distt. Amravati (India).

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ABSTRACT

The stability constants of Mn(II), Fe(II) and Zn (II) with p-Chloro Malonic acid (PCMA), p-Amino Malonic Acid (PAMA), p-Nitro Malonic Acid (PNMA) different percentage of dioxane water has been determined potentiometrically by Calvin-Bjerrum titrations. The titrations were carried out at constant ionic strength (0.1 M) and constant temperature i.e. $27 \pm 0.1^\circ\text{C}$. The data obtained can be used to study the values of porton-ligand and metal ligand stability constants for 1:1 and 1:2 complexes.

Key words: Ligands metal (II) ions, Stability Constant, Water-dioxane mixture.

INTRODUCTION

Complexation studies are very important from the point of view of analytical and biochemical researches. This study has received the attention of many researchers. Salicylic acid derivatives, amino acid derivatives and sulphonic and derivatives have considerable interest. However, little information is available on stability constant of these ligands with transition metal ions in dioxane-water mixture. The survey of literature reveals that metal-ligand stability constant of amino acid, adipic and itaconic acid have been studied¹. Narwade *et al.*,² have investigated the stability constants of lanthanide ions with some substituted acids spectrophotometrically. Keeping the importance of

substituted malonic acid in mind; in the present investigation, an effort has been made to study the stability constant of Mn(II), Fe(II) and Zn (II) with p-Chloro Malonic acid (PCMA), p-Amino Malonic Acid (PAMA), p-Nitro Malonic Acid (PNMA) in different percentages of dioxane-water mixture (10%, 20%, 30% and 50%). The titrations were carried out using Calvin-Bjerrum³ titrations technique at $27 \pm 0.1^\circ\text{C}$ temperature and confirmed spectrophotometrically by isobestic point method.

EXPERIMENTAL

All the chemical used in present investigation were of analytical grade. Carbonate free NaOH solution was prepared and standardized

by potassium hydrogen phthalate. The solution of ligand was prepared in different percentage of dioxane-water mixture by dissolving requisite amount of p-Chloro Malonamic acid (PCMA), p-Amino Malonamic Acid (PAMA), p-Nitro Malonamic Acid (PNMA). A digital potentiometer Model Systronics-105 was used for titrations. These titrations were carried out by keeping the ionic strength of medium constant ($m=0.1$ M) by adding appropriate amount of 1M KNO_3 solutions. pH-values were calculated by Van-Unitert and Hass⁴ equation. The stability constant of these of these ligands were determined by Irving and Rossotti (5-6) technique.

RESULTS AND DISCUSSION

Proton ligand stability constant

The value of proton-ligand stability constant (pK-values) were calculated from the formation curves between pH and proton-ligand formation number \bar{n}_A . The proton-ligand formation number (\bar{n}_A) were calculated using Irving and Rossotti equation⁵⁻⁶. The formations curves were constructed by plotting the values \bar{n}_A against pH of solution in all the % of dioxane-water mixture the pK values were estimated by noting the pH at which $\bar{n}_A=0.5$ and accurate values were determined by pointwise calculation method, which are presented in Table 1.

It is clear from table that pK-values with increasing the percentage of dioxane in dioxane-water mixtures⁷⁻⁶. Sondawale and Narwade⁹ have observed the same phenomenon in different percentage of ethanol/acetone-water mixtures. Chachere et al.,¹⁰ have also observed the increase

in pK-values with increasing percentage of dioxane in dioxane-water mixture for amino acids.

The stability of the different 1:1 binary M (II)-ligand complexes increases according to the order-



This can be interpreted in terms of the effect of basicity of these compounds. Besides this, the size of the Metal Ion and charges/size ratios are two other factor in deciding the value of formation constants.

The stability of the 1:1 and 1:2 complex containing Malonamic acid is largely dependent on the (basicities of the ligand) nature of the electron withdrawing group. Generally, the complexes containing the NO_2 , Cl and NH_2 . The order of electron withdrawing tendency is in the order as NO_2, Cl and NH_2 , the order of electron withdrawing tendency is in the order $\text{NO}_2 > \text{Cl} > \text{NH}_2$. Hence, PAMA form more stable complex than the PCMA in turn than PNMA.

The dependence of stability of the complexes studied on the nature of metal ion and is found to follow the trend: $\text{Mn (II)} < \text{Fe(II)} < \text{Zn(II)}$. This is conformity with the Irving-Williams order. The additional high stability of the Zn(II) complex is attributed to the stable electronic configuration ($3d^{10}$) of Zn (II) ion, which is capable of additional stabilization due to John-teller distortion.

Metal-ligand stability constant

The comparison between acid and the metal titration curves indicates that the metal curves

Table 1: pK values

% of Dioxane	Mn (II)			Fe (II)			Zn (II)		
	PNMA	PCMA	PAMA	PNMA	PCMA	PAMA	PNMA	PCMA	PAMA
10%	2.82	3.91	4.02	4.90	5.22	5.36	5.52	6.32	7.57
20%	3.62	4.72	4.49	5.80	5.86	5.96	5.64	6.31	7.65
30%	4.75	5.30	5.65	6.20	6.80	6.97	6.42	7.72	7.98
40%	5.31	5.85	6.82	6.60	7.83	8.12	7.07	8.58	9.72

are well separated from ligand curves. This suggests the formation of metal-ligand complex in the solution. The metal-ligand formation constant n and P_L values were calculated using two different methods i.e.

- Hall integral method i.e. form graph of n vs. P_L at $\bar{x}_A = 0.05$ and $\bar{x}_A = 1.5$
- Pointwise calculation method i.e. as suggested by Irving and Rossotti.

The value of \bar{x}_A at various pH have been calculated from free acid and ligand titration curves. The following equation is used to calculate the values \bar{x}_A , which has been employed by Irving and Rossotti.

$$\bar{x}_A = V \cdot \frac{(E^\circ + N)(V_2 - V_1)}{(V^\circ + V_1)T_L^0}$$

Where V° is the initial volume of solution, V_1 and V_2 denote the volumes of alkali needed to reach the same value of pH in the titration of acid and ligand, respective. T_L^0 is the total concentration of ligand. N is the normality of alkali solution. E° is the initial concentration of free acid. From the values of so obtained, P_L was calculated using the equation.

$$P_L = \text{Log}_{10} \left[\frac{1 + [H^+]}{K} \times \frac{(V^\circ + V_3)}{V^\circ} \right] \frac{1}{[T_L - T_m]^{x/n}}$$

Where K and $[H^+]$ are the stability constant and hydrogen ion concentration for pH values, respectively. The values of n varies between $0.2 <$

$n < 4.5$, which indicates that there is formation of 1:1 and 1:2 complexes in the solution.

It was found that $\text{Log } K_1$ and $\text{Log } K_2$ values increased with increasing percentage of dioxane in dioxane-water mixture. The change in colour during the titration showed the commencement of complex formation. The increase in pK and $\text{log } K$ values may be due to the effect of bulk solvent. The data obtained in present investigations were found to be in good agreement with the values obtained by Yasuda¹¹. Narware and Jahagirdar¹².

Isobestic point method (spectrophotometrically)

The spectrophotometric study was carried out for confirmation of complex formation between metal ion and ligands by isobestic method.

The equimolar solution of Mn(II) , Fe(II) and Zn(II) in (10^{-2} M) and *p*-Chloro Malonic acid (PCMA), *p*-Amino Malonic Acid (PAMA), *p*-Nitro Malonic Acid (PNMA) (10^{-2} M) were mixed in 1:20 ratio. The pH of the solution was varied from 2.5 to 5.5.

It has been observed that all the curves were passing through one point at different wavelengths for different metal (II) ions with different ligands. (Isobestic point). This confirms the formation 1:1 and 1:2 complexes. These complexes were also studied pH-metrically.

Thus, from the results, we conclude that certain metal-ligand complexes are not stable in water or stability of complexes is enhanced as the percentage of dioxane was increased in the mixture.

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