

Stability Constant Determination of Complexes of Taurine with Mn(II), Cu(II) and Zn(II) in DMF-Water Mixture pH-Metrically

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Abstract: The stepwise stability constant values of Taurine with Mn(II), Cu(II) and Zn(II) have been studied using pH measurements in 70%DMF- 30%Water and 50%DMF- 50% Water media. The values of proton-ligand stability constants and metal – ligand stability constants are calculated. The metal- ligand stability constant of binary complex iscalculated using Irving- Rossotti titration technique.

Keywords: stability constant, taurine, DMF-Water mixture, pH-metric method

1. Introduction

Taurine(2-aminoethane sulphonic acid)analogue of β -alanine is a biologically active compound, occurs in all vital organs of human body.Number of researchers classifies taurine as vitamin-like substances due to its diverse biological activities [1]. Taurine has many physiological functions as an antioxidant, neurotransmitter and toxicicide and in conjugation of bile acids, modulation of the levels of intracellular ions(e.g calcium, potassium and sulphur), membrane stabilization and osmosis [2-4]. Changes in taurine levels in physiological fluids and tissues occur in various diseases or pathological conditions such as psychosis, inflammation, sepsis and cancer [5]. Taurine plays an important role in prenatal development, especially in neural development as an inhibitory and neuroprotective, neurotransmitter and neuromodulator [6].

To date, various methods have been developed for the determination of taurine. These methods include gas chromatography [7], high-performance liquid chromatography with amperometric detection [8], HPLC with electrospray ionization, mass spectrometry [9-10] and capillary electrophoresis [11-12]. However, the complexation properties of taurine have not been described much in the literature. Singh studied the stability of taurine complexes with heavy-metal ions by paper electrophoresis which is not strictly quantitative; hence the results cannot be considered to be adequately reliable [13].pH-metric method is regarded for the study of solution equilibria because of its accuracy, reliability, experienced data analysis and relatively cheap instrumentation [14-15]. In this study, taurine refers to a class of compounds for its stability used for various analytical and biological applications. A good knowledge of its ionization in Dimethyl formamide- Water media is highly desirable. For this reason, knowledge of constants for taurine is expedient for gaining an understanding of their mechanism of action in both chemical and biological processes.So, the stability constants of taurine were determined with various metal complexes by pH-metrically in DMF- Water mixtures of different proportions.

2. Materials and Experimental Methods

The 2-Aminoethanesulfonic acid (Taurine) used in this study is a commercially available chemical (Sigma) products and used without further purification; all the other chemicals used in this work were of Analar grade.Dimethyl formamide is purchased from Merck and used without further purification. The metal ion solution, acid solution, KNO_3 solution and NaOH solution were prepared in double distilled water. NaOH was standardized potentiometrically with standard oxalic acid solutionand it was used for further potentiometric titration. The nitric acid and potassium nitrate were purchased from Merck p.a.The concentrations of taurine and metal ions are $20 \times 10^{-4}\text{M}$ and $4 \times 10^{-4}\text{M}$. The ionic strength of the solutions was maintained at 0.1M by addition of calculated amounts of 1M KNO_3 . The carbonate free sodium hydroxide solution (0.1 M).

3. Apparatus and Procedure

All pH-metric titration were carried out at 27°C in an inert atmosphere by bubbling oxygen free nitrogen gas through an assembly containing the electrodes in order to prevent atmospheric oxidation using carbonate free NaOH. The pH of the solution measured using with Systronics pH meter (QJ-666B) with a combinedglass electrode. This pH meter has built in internal electronic voltage supply with temperature compensator covering the range $0\text{-}100^\circ\text{C}$. The pH meter was switched on half an hour before starting the titration for the initial warm up of the instruments. Before taking any reading, the electrodes are washed with distilled water and dried with filter paper. The readings were recorded only when the instrument registered a steady value for atleast one minute. The pH meter as standardized before each titration with a buffer solution of pH 4.00, 7.00 and 9.20, prepared from a Qualigens buffer tablets.

The following three solutions were titrated separately against standard carbonate free NaOH(total volume 25 ml). a) Free HNO_3 (2.5 ml) + KNO_3 (2.5 ml), b) Solution a + ligand solution (5 ml) and c) Solution b + metal solution (1 ml). The ligand is acidified with HNO_3 in a 50%DMF-water

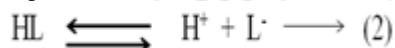
medium and 70%DMF-water medium and the ionic strength was kept constant by added the KNO₃. The ligand was titrated against standard NaOH (carbonate free) using Calvin-Bjerrum and Calvin-Wilson pH titration methods [16-17]. The pH meter readings were taken after fixed interval until stable reading was obtained and the curves of pH values obtained from the titration using the Irving-Rossotti method [18].

4. Results and Discussion

The proton-ligand stability constant and metal-ligand stability constants (Log K) of taurine and their complexes with Mn(II), Cu(II) and Zn(II) metal ions determined in 50% DMF-Water mixture and 70% DMF-Water mixture at ±27°C. The extent of deviation observed may be due to the dissociation of OH group completely (Fig.1). The proton-ligand formation number n_A was calculated by the Irving-Rossotti expression. The pK values of the ligand and formation constants of the complexes were calculated by the algebraic method point wise calculation and also estimated from formation curves n_A Vs pH (half integral method) by noted pH at which n_A = 0.5 (Bjerrum 1957). The accurate values of pK were determined at different solvent media by point wise calculations which are represented in Table- 1& 2. The n_A values were calculated by using the equation.

$$n_A = \frac{\gamma - (E^0 + N)X(V_2 - V_1)}{(V^0 + V_1) \times T_m^0} \longrightarrow (1)$$

Where γ denote the replaceable H⁺ ion, T_L⁰ is concentration of ligand, E⁰ is concentration of acid, N is normality of alkali, and V⁰ is the total volume of the mixture. The data of n_A obtained at various pH values along with horizontal difference (V₂ - V₁) for representative systems. The dissociation equilibrium can be shown as



The formation curves are constructed by plotting the values of n_A against pH of the solution. The dissociation constant pK of ligand is calculated from the formation curves. The values of pK obtained are given in Table- 3. The accurate pK values of ligand are calculated by pointwise calculation method is in good concordance with those obtained by the half integral method (Fig. 2& 3). The increase in pK in binary solvent medium than pure water shows that DMF plays a major role to enhance the basicity. It is well known that the addition of DMF to pure water breaks the three dimensional network of water and it forms the H-bonded complexes between DMF-nH₂O [5]. These H bonded complexes are presumably more basic than pure water by considering the +I effect of the methyl group which tends to increase the mesomeric shift of the lone pair of electrons on Nitrogen to the more electronegative Oxygen of DMF. It is further enhanced when a molecule capable of delocalizing this excess charge on Oxygen of DMF is present. Since water molecules are capable of forming H-bonds with such sites the excess negative charge on Oxygen of DMF (arising due to mesomeric shift) is now partially transferred on to the Oxygen of water. Hence, the co-operative nature of H-bonding in all DMF-nH₂O molecule complexes is expected to be more basic than the water molecule in pure solvent and thereby reduces its protonation constant. In addition, dielectric constant also plays a major role in dissociation

constant. The solvent which has low dielectric constant increases the electrostatic forces between the ions and facilitates the formation of molecular species. Therefore, while increasing the DMF concentration, the dielectric constant of solvent decreases resulting in the increase in pK values.

The metal-ligand stability constants were calculated by the half integral method by plotting n Vs pH. The n values are determined by using the equation.

$$n = \frac{(E^0 + N)X(V_3 - V_2)}{(V^0 + V_2) \times T_m^0} \longrightarrow (3)$$

Where N, E⁰, V⁰ and V₂ have the same significance as in Equation (1). V₃ is the volume of alkali added in the metal titration to attain the given pH reading, and T_m⁰ is the concentration of the metal ion in the reaction mixture. The stability constants of complexes have been calculated from n values (Fig.4) and are represented in Table-4. This shows that the stability of the Metal- Taurine complex is slightly more in DMF-water concentration of 70%DMF-30%Water mixture.

The present study has great importance in the development of co-ordination chemistry metal-ligand stability constant of Mn(II) is given in the table. The deviation of metal titration curves from ligand curve indicates the formation of binary complex. The binding of metal ions used in the cancer treatment is suggested by Furst [22]. The difference between LogK₁ and LogK₂ are smaller. It seems, therefore, that both the 1:1 and 1:2 complexes are formed simultaneously and not in a stepwise process. The ligand used was found to be weak complexing agent. The change in the colour (without precipitation) with respect to pH value of solution and deviation of ligand curve from metal ion curve also shows the commencement of complex formation.

The value of stability constants are found to be higher in 70% DMF-30% water than 50% DMF-50% water because the dielectric constant value of DMF is lower than water which is responsible for the less solvation of metal ion in DMF, which in turn, makes the approach of the ligand to occupy a coordination site in the coordination sphere of metal ion easier and hence greater the stability of the complex in higher solvent (DMF) composition.

5. Conclusion

There are only quite a few data in the literature regarding stability constants of transition metal complexes with taurine. Most of the studies show that taurine can able to form 1:1 complexes with metal ions. Owing to the second step formation constant, Log K₂ could not be studied due to the occurrence of precipitation and turbidity of weak complexes. Even though, the basicity of taurine is comparatively less than its analogue because of its weak sulfo group, the role of solvent DMF in this work compensates the basicity and forms moderately stable complexes. The stability of taurine complexes with the metal-taurine ratio 1:2, transition metal ions can be arranged in the following order Mn < Cu > Zn, which is in conformity with the Irving-William order of stabilities. Henceforth, the

role of taurine which binds with metal ions plays a major role in biological applications under physiological conditions.

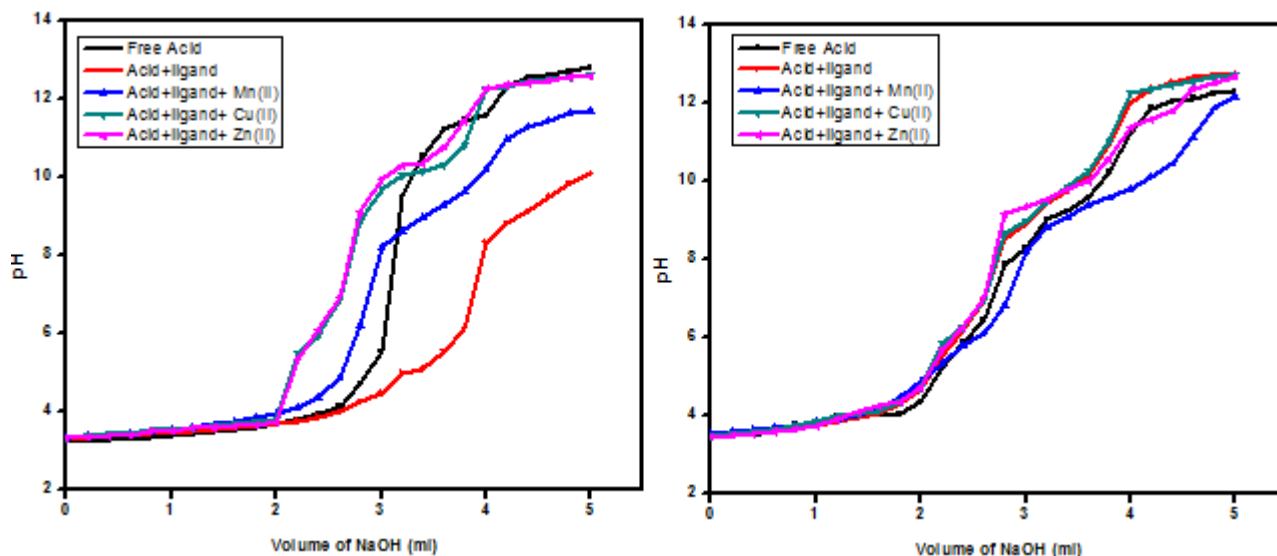


Figure 1: pH-metric titration curves of Free acid+Ligand +metal ions Mn(II),Cu(II),Zn(II) a) 50%DMF-50%Water system b) 70%DMF-30%Water system

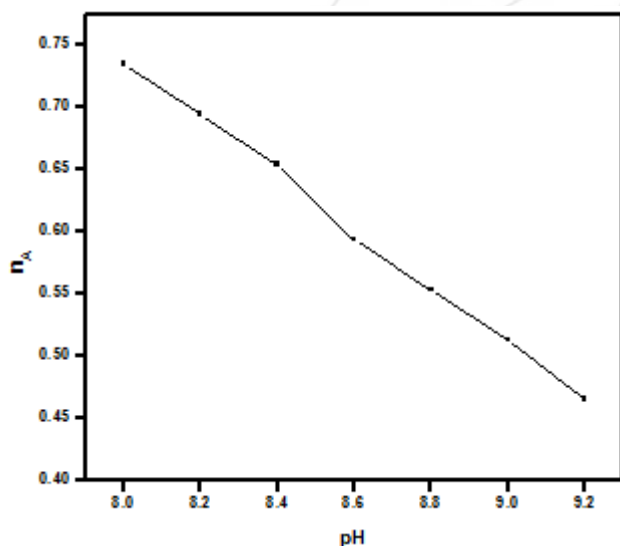


Figure 2: Half integral method for determining pK of taurine at 70% DMF-30% Water mixture

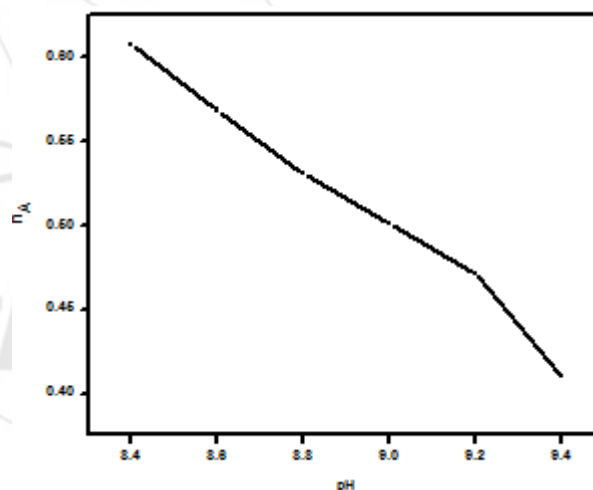
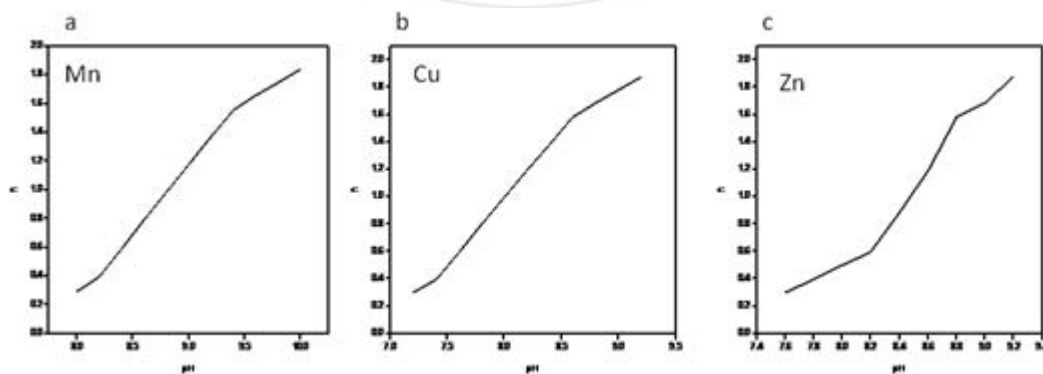


Figure 3: Half integral method for determining pK of taurine at 50% DMF-50% Water mixture



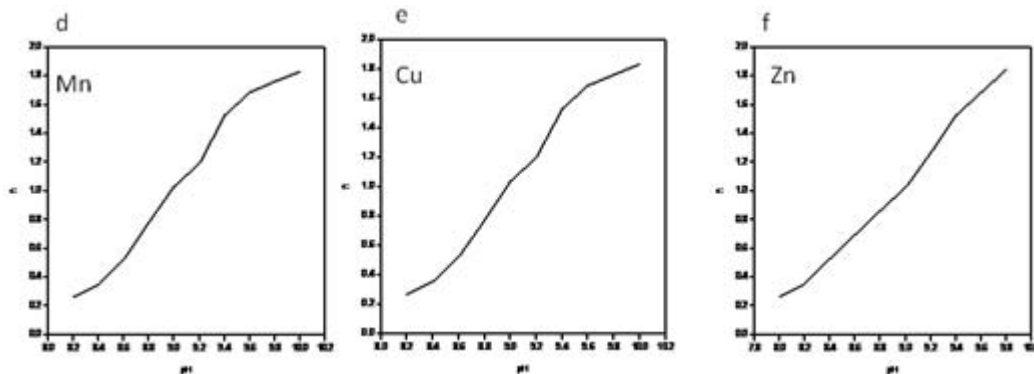


Figure 4: Plot of n Vs pH of ligand taurine-with metal ions Mn(II), Cu(II), Zn(II) a-c) 50% DMF-50% Water mixture d-e) 70% DMF-30% Water mixture

Table 1: Pointwise method for calculation of pK in 70%DMF-30% water

Proton-ligand dissociation constant of taurine at $27^{\circ}C \pm 0.1$ K and at ionic strength $I = 0.1 \text{ mol.dm}^{-3} \text{ KNO}_3$ in 70% DMF-30%Water medium

pH	V_1	V_2	$\Delta V = V_2 - V_1$	n_A
8.4	3.07	3.24	0.17	0.654
8.6	3.12	3.32	0.20	0.594
8.8	3.16	3.38	0.22	0.554
9.0	3.18	3.42	0.24	0.513
9.2	3.21	3.51	0.26	0.466
9.4	3.25	3.54	0.29	0.406

Table 2: Point wise method for calculation of pK in 50%DMF-50% water

Proton-ligand dissociation constant of taurine at $27^{\circ}C \pm 0.1$ K and at ionic strength $I = 0.1 \text{ mol.dm}^{-3} \text{ KNO}_3$ in 50% DMF-50%Water medium

pH	V_1	V_2	$\Delta V = V_2 - V_1$	n_A
8.4	3.0	3.20	0.20	0.607
8.6	3.02	3.24	0.22	0.568
8.8	3.04	3.27	0.23	0.531
9.0	3.06	3.30	0.24	0.501
9.2	3.08	3.33	0.26	0.471
9.4	3.10	3.35	0.29	0.410

Table 3: pK values at different solvent concentrations

Ratio of DMF-water mixture	pK (Half integral method)	pK (Pointwise calculation)	pK value in water (literature)
70% DMF-30% Water	9.03	8.96	8.90 [19]
50%DMF-50% Water	9.00	8.93	9.01 [20] 8.95 [21]

Table 4: Stability constant of Taurine with Mn(II), Cu(II) and Zn(II) ions in different solvent concentrations

Ratio of DMF-Water mixture	Taurine-Metal ion(complex)	$\text{Log } K_1$	$\text{Log } K_2$
70% DMF-30% Water	Mn(II)	3.29	2.62
	Cu(II)	3.99	3.11
	Zn(II)	3.29	2.71
50% DMF-50% Water	Mn(II)	3.19	2.81
	Cu(II)	2.99	2.52
	Zn(II)	2.90	2.43

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