The effect of different concentrations of DMF-H2O on the proton ligand dissociation constant and the stability constant of Mn-Acetyl Salicylic acid complex

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Abstract: — The stepwise stability constant values of Acetyl Salicylic acid with Mn(II) have been studied using pH measurements in 70% DMF- 30% water and 50% DMF- 50% water medium. The values of proton-ligand dissociation constants and metal – ligand stability constants were calculated. The Irving- Rossotti titration technique was employed. The values were found to be comparable with the literature values.

I. INTRODUCTION

Acetyl Salicylic acid, also known as Aspirin is often used as an analgesic, antipyretic and anti inflammatory medication [1]. Low doses of Aspirin may be given immediately after a heart attack to reduce the risk of another heart attack [2], [3]. It is also known to prevent certain types of cancer [4], [5], [6]. Researchers are studying the stability of the metal-Acetyl Salicylic acid complex in order to expand its usage. The stability constant is a measure of the strength of the interaction between the reagents that come together to form the complex. This helps in the pharmaceutical applications of the complex. This work is an endeavor to achieve that and this work emphasizes the effect of different concentrations of the binary solvent on the stability constant. Previously scientists have studied this in aqueous media and other media [7], [8], [9].

II. MATERIALS AND METHODS

All the chemicals used in this work were of Analar grade. The metal ion solution, acid solution, KNO_3 solution and NaOH solution were prepared in double distilled water. NaOH was standardized with standard oxalic acid solution and it was used for further potentiometric titration. Systronics pH meter with a combined glass electrode were used for the pH measurements.

The experimental procedure for binary metal complexes involves the following titrations.

1. Free HNO_3

2. Free HNO_3 + Acetyl Salicylic acid

3. Free HNO_3 + Acetyl Salicylic acid + Metal ion

The above mentioned solutions are titrated against standardized 0.1M NaOH in 0.2 ml aliquots, under an inert atmosphere of nitrogen. The ionic strength of the solutions was maintained at 0.1M by addition of calculated amounts of 1M KNO_3. The concentration of Acetyl Salicylic acid and metal ions were 20×10^{-4}M and 4×10^{-4}M respectively.

III. RESULTS AND DISCUSSION

The proton-ligand stability constant and the metal ligand stability constants are fund for Mn(II) with Acetyl Salicylic acid in 70%-30% DMF-water and 50%-50% DMF-water. Irving Rossotti expression was used to calculate the proton ligand formation number n_A. Bjerrum proposed the half integral method in 1957 by which we calculated the pK values at n_A=0.5 (Figure-1). The pointwise calculations were also done and the results were similar to the half integral method (Table 1). The n_A values were calculated by using the following equation

$$n_A = \gamma - \frac{(E^\circ + N) \times (V_2 - V_1)}{(V^\circ + V_1) \times T^\circ_L} \quad (1)$$

where γ is the replaceable H^+ ions, E° is the concentration of acid, N is the normality of the base, T°_L is the concentration of ligand, V° is the total volume and V_2-V_1 is the horizontal difference in the volume at the given pH.

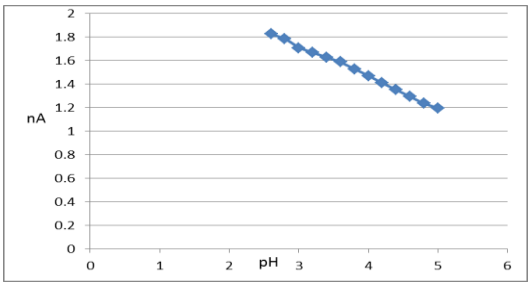

Figure-1 Half integral method for determining pK (70%DMF-30% water)

Table-1Pointwise method for calculation of pK(70%DMF-30% water)

pH	n_A
2.6	1.8255
2.8	1.7857
3	1.7063
3.2	1.6669
3.4	1.6274
3.6	1.5888
3.8	1.5290
4	1.4700
4.2	1.4111
4.4	1.3523
4.6	1.2934
4.8	1.2347
5.0	1.1955

The metal-ligand stability constants were calculated by the half integral method by plotting n vs pL. The n values were obtained by using the equation.

$$n = \frac{(E°+ N) X (V_3 - V_2)}{(V°+ V_2) x T°_m} \quad (2)$$

Where E° is the concentration of acid, N is the normality of the base, $T°_m$ is the concentration of metal, V° is the total volume and V_3-V_2 is the horizontal difference in the volume at the given pH.

The proton-ligand stability constant and the metal ligand stability constants for Mn(II) with Acetyl Salicylic acid in 50%-50% DMF-water can be found by the half integral method (Figure-2) and point wise calculation method (Table -2).

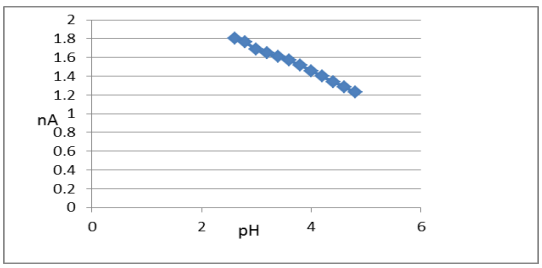

Figure- 2 Half integral method for determining pK (50% DMF-50% water)

Table-2 Point wise method for calculation of pK (50%DMF-50% water)

pH	n_A
2.6	1.8
2.8	1.7623
3	1.6858
3.2	1.6475
3.4	1.6092
3.6	1.5709
3.8	1.5136
4	1.4564
4.2	1.3992
4.4	1.342
4.6	1.2849
4.8	1.2279

The pK values and the metal ligand stability constants are summarized in Table-3 and Table-4.

Table -3 pK values at different solvent concentrations

Ratio of DMF-water	pK (Half integral method)	pK_1 (point wise calculation)
70%-30%	3.70	3.90
50%-50%	3.60	3.80

Table -4 Stability constant values at different solvent concentrations

Ratio of DMF-water	Log K_1	Log K_2
70%-30%	3.29	2.81
50%-50%	3.19	2.72

This shows that the stability of the Mn(II)-Acetyl Salicylic acid complex is slightly more in DMF-water concentration of 70%-30%.

The present study has great importance in the development of co-ordination chemistry. The deviation of metal titration curves from ligand curve indicates the formation of binary complex.

IV. CONCLUSION

- This is a rapid method of determination of stability of a complex.
- The method can be extended to real life samples where the stability of metal-Acetyl Salicylic acid complex can be studied.
- This method helps in studying the stability of pharmaceutically important samples so that its behavior can be studied.

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