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Coordination studies of Ritodrine Hydrochloride with selected transition Metal ions

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ABSTRACT: The stability constants of binary complexes of metal ions Cu^{2+}, Ni^{2+}, Co^{2+}, Cr^{3+} and Zn^{2+} with Ritodrine Hydrochloride ligand were studied in aqueous media at 28^0 C temperature. The Protonation constant and metal ligand stability constants were determined by Calvin Bjerrum titrations in combination with Microsoft excel software programme. 1 N $NaNO_3$ used to maintain ionic strength. Metal ligand ratio kept was 1: 1. The Protonation constant and metal ligand stability constants calculated by half integral and pointwise method found to be in agreement. Protonation constant obtained were 9.42 and 9.72. The decreasing order of stability of the complexes found to be Zn (II) < Cu(II) < Co(II) < Ni(II) < Cr(III) which is accordance to Irving-Williams order. Application of inexpensively available HNO_3, $NaNO_3$ and natural media are the salient features of the work. The results provide new insights into the complexation of ritodrine and its biological significance.

KEYWORDS: Protonation constant, Ritodrine, Stability constant.

INTRODUCTION

Transition metal complexes play a vital role in several biological processes and industrial applications, depending on pH, type of ligand(s), and the nature of metal ion. The β-adrenergic agonist ritodrine hydrochloride, which is used for the treatment of preterm labour, can form complexes with transition metal. Although its pH-dependent behaviour and stability constants of complexes with Cu^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+} and Cr^{3+} have not been extensively studied. Knowledge of such metal-ligand interactions is necessary for the design of new drugs and important for therapeutic purposes. This work was initiated to fill this void by collecting the pKa parameters and the stability constants of ritodrine–metal ion complexes mentioned above.

MATERIALS AND METHODS

A ligand solution was prepared by dissolving the required amount of ligand in a minimal volume of distilled water, which was subsequently diluted to attain the final volume. The metal ion solution was prepared by dissolving metal nitrate and standardizing it using the EDTA titration. A carbonate-free sodium hydroxide solution was obtained by dissolving pellets in distilled water and standardizing the solution. Subsequently, a solution of nitric acid and sodium nitrate was also prepared.

All measurements were conducted at room temperature using a digital pH meter equipped with a magnetic stirrer and a combined glass electrode assembly was employed for pH determinations. The pH meter was calibrated before each titration using aqueous standard buffer solutions of pH 7.00,4.00 and 10 prepared from buffer tablets. The instrument exhibited a sensitivity of 0.01 pH units and a measurement range of 0.00 to 14.00 pH with a resolution of 0.005 pH units. The pH meter was switched on for at least 30 minutes before measurements to ensure stability. Glass electrodes were stored in appropriate storage solutions when not in use and were rinsed thoroughly with distilled water before each measurement.

PROCEDURE

The experimental procedure involved the titrations of

1. HNO_3 (5ml) + $NaNO_3$(5ml)
2. HNO_3 (5ml) + $NaNO_3$ (5ml) + ligand (10ml)
3. HNO_3 (5ml) + $NaNO_3$ (5ml) + ligand (10ml) + Metal ion(3ml)

A standard sodium hydroxide solution was employed to titrate the sample using the Calvin-Bjerrum pH titration technique. All solutions were prepared using double distilled water and maintained at a constant ionic strength by adding sodium nitrate

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($NaNO_3$). Titrations were conducted in distilled water, with pH readings recorded for every 0.02 ml increment of NaOH added. The resulting pH versus volume of NaOH curves were analyzed using the Irvin-Rossotti[1] method and a computer program to determine the proton-ligand constants.

RESULTS AND DISCUSSION

The observed pH values from above three titrations are then plotted against the volume of alkali added. Three titration curves are obtained, corresponding to the titrations mentioned in the experimental part. The titration curves were separated from each other each taking approximately S shape. The end point for the titration increased in the order I > II > III. The maximum value of *n* did not exceed two for all complexes indicating the formation of 1:1 and 1:2 complexes. Considerable separation of metal complexes curve from reagent curve along volume axis is an evidence for complex formation. The use of very dilute solution ruled out the possibility of formation of polynuclear complexes.

The pH-metric study of ritodrine hydrochloride with transition metals (Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cr^{3+}) confirmed the formation of metal-ligand complexes. Proton-ligand stability constants revealed two dissociable protons from the amino (-NH_2) and hydroxyl (-OH) groups of Ritodrine, with pK_1= 9.42 (for –NH_2) and pK_2= 9.72 (for -OH). $logK_1$ and $logK_2$ stability constants of the binary complexes in accordance with statistical expectation ($logK_1 – logK_2$) values are positive, showing that the coordination of the first ligand molecule with the M^{+2} ion is more favourable than its bonding to the second one because for M^{+2} the coordination sites of the metal ions are more freely available for coordinating as reported by Khaled et al[2]. The decreasing order of stability of the complexes found to be Zn(II) < Cu(II) < Co(II) < Ni(II) < Cr(III) which is accordance to Irving-Williams[3] order.

Mhaske and Patil[4] studied complexes of Paracetamol and determined pKa value 9.67 for –OH group in paracetamol. The formation of 1:1 and 1:2 complexes reported and observed the order of stability for metal chelate as Mn (II) < Co (II) < Ni (II) < Zn (II). P. J. Parmar[5] studied pKa values of pyrazoline (PYZ) and found that mono basic nature of PYZ due to presence of –OH group. He reported pKa values in the range of 8.00- 9.00. Gouda et al[5] reported pK_1 10.36 for phenolic amino derivatives.

Stability constants (Log β) indicated Zn (II) and Cu(II) formed the most stable complexes, with values of 9.1198 and 7.4637, respectively, while Cr(III) had the lowest stability (Log β = 5.6146). Reported high stability of Zn(II) complexes was exceptional. The stability order $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ known as the Irving-Williams order, observed by many workers[7-9]. The higher stability of the copper complex is attributed to its unique electronic configuration, which allows for additional stabilization due to the John-Teller effect.

Table 1*:* Proton-ligand stability and Metal-ligand stability constant values

Proton Ligand Constant	Metal Ligand Stability Constant			
	Metal ion	**Log K_1**	**LogK_2**	**Log β**
Half integral pK_1 = 9.4701 pK_2 = 9.7464	**Zn(II)**	**5.108415**	**4.011426**	**9.119841**
	Cu(II)	**3.988254**	**3.475452**	**7.463706**
Point Wise	**Co(II)**	**3.609682**	**3.423973**	**7.033655**
pK_1 = 9.46383 pK2 = 9.75982	**Ni(II)**	**3.885795**	**3.062453**	**6.948248**
	Cr(III)	**2.9707**	**2.643904**	**5.614604**

Zn(II) < Cu(II) < Co(II) < Ni(II) < Cr(III)

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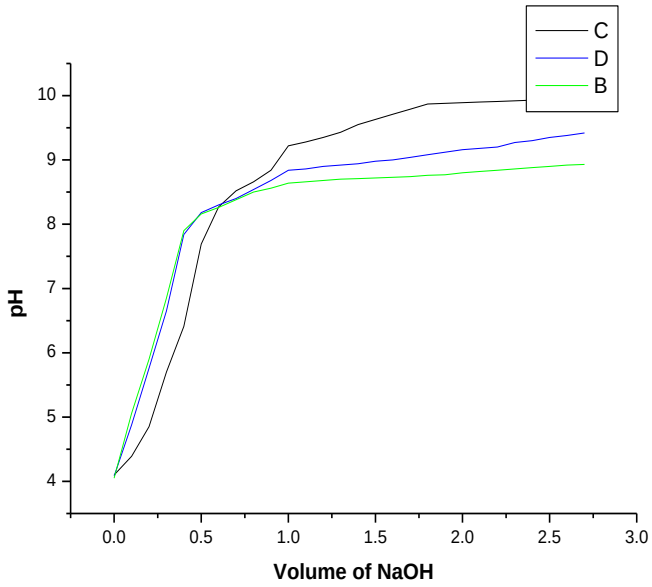

Titration curve

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