Available Online at

http://www.ijcpa.in

IJCPA, 2014; 1(3): 89-92

International Journal of CHEMICAL AND PHARMACEUTICAL ANALYSIS

ISSN: 2348-0726

Research Article

# Thermodynamic Ionisation Constant of 5- Nitro-Salicyloylhydrazide in Aqueous Solution

**Sangeeta Rajput*[1], Amrata Pawaiya[2], R.K. Bhatnagar[3] and M.C. Agrawal[4]**

Research Scholars, Chemical laborateries, SMS Govt. Science College, Gwalior (M.P.), India

Received: 1 June 2014 / Revised: 19 June 2014 / Accepted: 20 June 2014 / Online publication: 01 July 2014

**ABSTRACT**

*5-Nitro salicyloylhydrazide was prepared by reaction of 5-Nitro-Methyl salicylate and Hydrazine Hydrate. The present investigation involves determination of thermodynamic ionisation constant of 5-Nitro salicyloylhydrazide in aqueous solution on which no data exist in the literature. The measurements are performed at room temperature, and at ionic strength of 0.1, 0.25 and 0.5mol. The absorption spectra of each sample were measured at different wavelengths. The results showed that the numerically calculated pKc values are identical to those graphically obtained.*

**Keywords:** *5-nitro salicyloylhydrazide, pH-Meter, thermodynamic ionisation Constant, Spectrophotometer.*

## 1. INTRODUCTION

Some hydrazide acts as reagents. Hydrazide are previously used in the identification of aldehyde and ketones by condensation[1]. Hydrazide and its derivatives have been recognized for therapeutic importance since the initial epoch-making discovery[2]. Measurement of the extent of ionisation were previously made by the method of visual colorimetry[3] and also applied to spectrophotometry in the ultraviolet region for cases where there was no visible change in colour[4].

The antitubercular properties of hydrazine and hydrazides have been frequently investigated and research in this field recently culminated in the discovery of drugs effective in tuberculosis notably is nicotinic acid hydrazide[5]. 5-Nitrosalicloylhydrazide is also found pharmacologically and microbiologically effective[6].

5-nitro-salicyloylhydrazide readily gives coloured soluble and insoluble complexes with certain bivalent cations and thus it is a useful reagent for colorimetric and gravimetric determination of the metal ions. The present investigation deals with the determination of thermodynamic ionisation constant pKa[7].The data is of primary importance in various analytical procedures and in the elucidation of the structure of metal complexes.

*Corresponding Author

Email: rajputsangeeta2013@gmail.com

## 2. MATERIAL AND METHODS

All the other reagents used were of analytical grade and Solutions were prepared in Double distilled conductivity water.

### 2.1. Method for preparation of 5-nitro-salicyloylhydrazide

It has been prepared in two stages as described below:

#### 2.1.1. Preparation of 5-Nitro-Methyl Salicylate

Methyl salicylate (10 g) was dissolved in acetic anhydride (10 mL) and solution was cooled to $0^0$C an ice cold mixture of conc.$HNO_3$ (4.3 mL) and acetic anhydride (30 mL) was gradually added in portion of (5 mL) each. In addition there was rise in temperature which is no care was allowed to go beyond $10^0$ C. A thick paste was formed. After one hour, mixture was warmed on water both until it became brown. It was cooled in ice and powered into excess of ice and $H_2O$ (1000 mL ) which stirring. After standing for sometimes, the separation of yellowish solid was complete. It was filtered at the pump, washed with excess of $H_2O$ and dried on a porous plate. The dried mass extracted with Petroleum ether (b.p. 40 – $60^0$C, 300 mL) 5- nitro methyl salicylate being in soluble in petroleum ether was thus separated by filtering. It was crystallized from methyl alcohol

giving light yellow solid whose melting point is found to be $99^0$C.

**2.1.2. Preparation of 5- Nitro – salicyloylhydrazide**

5- Nitro methyl salicylate (2 g) was dissolved in methanol (40 mL) by gentle warning. It was allowed to cool and 60% hydrazine hydrate (5 mL ) was added slowly with shaking . Heat was evolved and yellow solid separated. The reaction mixture was refluxed on water bath for 15 min. To complete the reaction and allowed to cool. When a yellow crystalline mass deposited at the bottom of flame filtered at the pump washed with small quality of methyl alcohol and dried (1.5 g). It was crystallized from methyl alcohol giving yellow solid whose melting point is found to be $154^0$C.

**3. RESULTS AND DISCUSSION**

Optical measurements were made on DU-Z Beckman Spectrophotometer (Model 109200). 1 cm long cuvettes were used to take spectra. pH measurements were made on ELICO pH meter. The sample for the absorption measurements were prepared by diluting a liquid volume of a stock solution of the hydrazide in water. The ionic strength was adjusted at 0.05 to 0.20 M by mixing 1 M solution of sodium perchlorate. The spectrum of each sample was measured from 280 to 380 nm.

The absorbance spectrum of 5-nitro-slicyloylhydrazide was determined in (a) 0.01 HCl (b) a buffer solution containing sodium acetate and acetic acid of pH 4.40, 4.45 and 4.50 and (c) 0.01 NaOH. The data obtained in pH 4.45 is given in Fig. 1. The experimental results at constant ionic strength (0.01 M) are given in table No.1.

**Table 1:** Ionic strength of 5-nitro-slicyloylhydrazide

| S. No. | pH | Absorbance | | | pKc |
|---|---|---|---|---|---|
| | | Acid | Base | Buffer | |
| Set I (350 nm) | 4.40 | 0.155 | 0.430 | 0.215 | 4.94 |
| | 4.45 | 0.175 | 0.250 | 0.200 | 4.75 |
| | 4.50 | 0.160 | 0.420 | 0.235 | 4.88 |
| Set II (355 nm) | 4.40 | 0.145 | 0.460 | 0.220 | 4.84 |
| | 4.45 | 0.160 | 0.275 | 0.195 | 4.81 |
| | 4.50 | 0.145 | 0.450 | 0.240 | 4.87 |
| Set III (360 nm) | 4.40 | 0.130 | 0.490 | 0.230 | 4.81 |
| | 4.45 | 0.120 | 0.310 | 0.200 | 4.75 |
| | 4.50 | 0.130 | 0.480 | 0.245 | 4.80 |
| Set IV (365 nm) | 4.40 | 0.125 | 0.520 | 0.240 | 4.76 |
| | 4.45 | 0.110 | 0.340 | 0.200 | 4.75 |
| | 4.50 | 0.125 | 0.510 | 0.250 | 4.81 |
| Set V (370 nm) | 4.40 | 0.110 | 0.550 | 0.200 | 4.72 |
| | 4.45 | 0.125 | 0.370 | 0.255 | 4.81 |
| | 4.50 | 0.115 | 0.530 | 0.255 | 4.79 |
| Set VI (375 nm) | 4.40 | 0.100 | 0.570 | 0.205 | 4.70 |
| | 4.45 | 0.115 | 0.395 | 0.260 | 4.77 |
| | 4.50 | 0.105 | 0.560 | 0.260 | 4.79 |
| Set VII (380 nm) | 4.40 | 0.095 | 0.580 | 0.260 | 4.70 |
| | 4.45 | 0.110 | 0.410 | 0.205 | 4.79 |
| | 4.50 | 0.110 | 0.570 | 0.260 | |
| *Average : 4.78 ± 0.1* | | | | | |

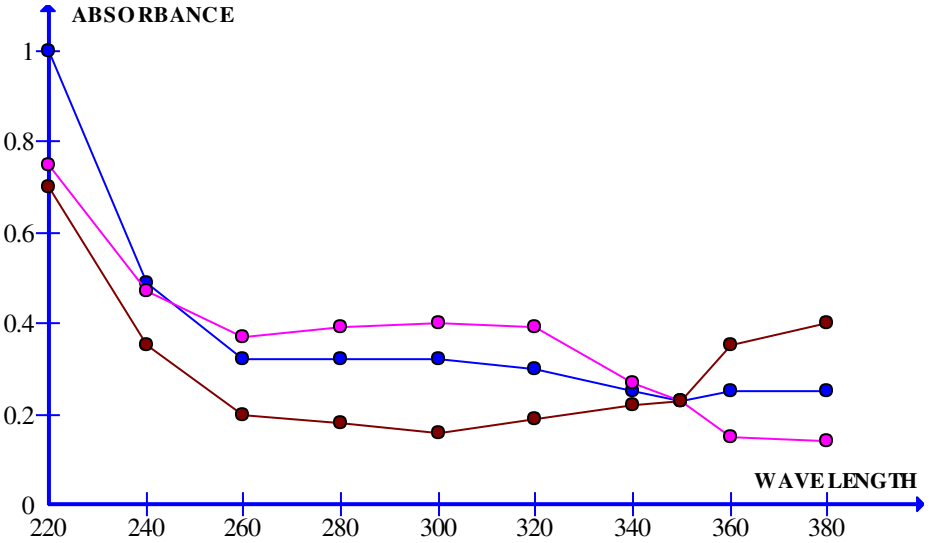


**Fig.1:** Absorption spectra of 5- Nitro-salicylolylhydrazide (2 x $10^{-3}$ M) in aqueous medium at pH 4.45 (a) 0.01 M HCl (b) Sodium acetate acetic acid (c) 0.01 M NaOH

The average values of pKc for different ionic strength viz. 0.05M, 0.10M, 0.15M and 0.20 M come out to be 4.86, 4.77, 4.58 and 4.52 respectively. After extraplotation to zero ionic strength, the value of pKc comes out to be 4.98(Fig. 2).

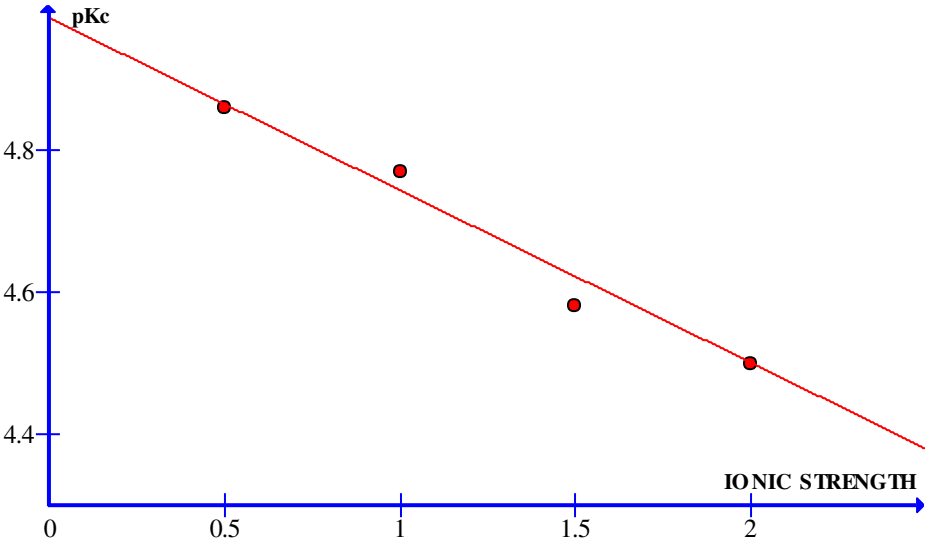


**Fig. 2:** Extraplotation of pKc to zero ionic concentration

The ionization constants at different ionic strengths, pKc were calculated from the equation

$$pKc = pH + \frac{\log b - e}{e - a} \quad \text{.....(1)}$$

Where the pH is that of the buffer solution having absorbance "e" ,while "a" and "b" are the values of absorbance of the same concentration of acid in 0.01 HCl and 0.01 NaoH respectively. The value of thermodynamic constant pKa has been calculated from the equation.

$$pKa = pKc\ I^{1/2}/1+I^{1/2} \quad \text{.....(2)}$$

Where I is the ionic strength of the buffer solution. The average value of pka has been calculated to be 5.01 +0.1 at $20^0$C from the spectra omitting those in the neighborhood of the isobestic point (in the region of wavelength 280 to 345 nm).

Further, the value of -ΔF as calculated from the above value of thermodynamic ionisation constant according to Vant Hoff's isotherm at $20^0$C is 0.932 K cal/mole.

## 4. CONCLUSION

This study is carried out in order to determine the pKc values and absorption spectra of 5-Nitro–Salicoylhydrazide**.** For that purpose, the pH metric method and spectrophotometric method is applied. The absorption spectra of the investigated 5-Nitro –Salicoylhydrazide is followed in acidic media *i.e.* in pH

region 4.40, 4.45 and 4.50. The changes in the absorbance *vs.* pH are used for determination of thermodynamic ionisation constants at ionic strength of 0.0, 0.5, 1.0, 1.5 and 2.0 mol $dm^{-3}$. From these values the thermodynamic dissociation constants of 5-Nitro–Salicoylhydrazide**.**

**5. ACKNOWLEDGMENTS**

The authors would like to express gratitude to the S.M.S. Govt. Model Science College for the facilities to carry out the research work. Authors are also thankful to supervisor and co-supervisor for their guidance in research work.

**REFERENCES**

1. Th.Curtius, O.Trachamann, H.H.Strain, J.Prakt.Chem, 51,168(1895).
2. Fox, H.H.; Takata, Y.; Yamamoto Takata, K.; J. Pharm. and Chem., Japan, (1954) 26,702- 704.
3. Hammett LP, Dingwill A. . J. Amer. Chem. Soc 1932; 54: 2721-56.
4. Flexser LA, Hammett LP, Dingwall A. The Determination of Ionization by Ultraviolet Spectrophotometry: Its Validity and its Application to the Measurement of the Strength of Very Weak Bases 1. J. Am. Chem. Soc 1935;57(11):2103-2115. Available from: http://pubs.acs.org/doi/abs/10.1021/ja01314a020 doi: 10.1021/ja01314a020.
5. Buu. Hoing, Phyuogen, J. Chem. Soc.; (1958) 1358.
6. Baker,W.; Haksar, C.N. and McOmie, J. F. N., (1950) J. chem. Soc. 170-172.
7. Phillips, (1954) J. Chem. Education., (1954), 31, 82.