

## Determination of acid dissociation constants of some hydroxy schiff bases by pH-metric titration. application of the Hammett equation

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**Abstract.** Ten compounds hydroxybases Schiff were synthesized from salicylaldehyde and the substituted aniline in the ortho, meta and para methyl groups, chloro and nitro. To study the effect of substituents on their acidities, the acid dissociation constants(  $K_a$ ) of salicylideneaniline and some of their derivatives were determined by pH-metric titration. All Schiff bases were titrated with NaOH in mixtures of 60% dioxane-water and 60% ethanol-water at a constant ionic strength and a temperature of 25 °C. The calculated acidity constants, pKa values were evaluated in protonation –deprotonation mechanisms. The Hammett relationship linear type was applied to quantify the effects of substituents on the acidity of hydroxybases Schiff, and therefore a reaction constant,  $\rho$  is calculated.

### 1 Introduction

The acidity concept has been used in various areas of research and they can give us some useful information about the molecular structure of Schiff bases. Following our work on the synthesis of some hydroxyl Schiff bases we now are reporting on the acid dissociation constants of them to elucidate structure-acidity relation-ship of these novel compounds.

We undertook this work in the study of acid-base behavior of some Schiff bases in two solvent systems; they can give us some useful information can be used to predict the effect of solvent and substituent on the acidity of this compounds. All Schiff bases were titrated by pH-metric titration method with NaOH in 60% mixtures of dioxane-water and 60% ethanol-water at a constant ionic strength and temperature of 25 °C.

### 2 Experimental

#### 2.1 Synthesis of hydroxy schiff bases

All Schiff's bases were prepared by condensing salicylaldehyde with aniline and substituted aniline and they were purified by recrystallisation from ethanol. The derivatives obtained are poorly soluble and precipitate in the form of crystals of colors ranging from pale yellow to orange (Figure 1).

The present work therefore reports to the synthesis of salicylideneaniline (Schiff base taken as the standard HSA), salicylidene-2-methylaniline(o-CH<sub>3</sub>SA), salicylidene-3-methylaniline(m-CH<sub>3</sub>SA), salicylidene-4-methylaniline(p-CH<sub>3</sub>SA), salicylidene-2-chloroaniline(o-CISA), salicylidene-3-chloroaniline(m-CISA), salicylidene-4-chloroaniline(p-CISA),

nitroaniline(o-NO<sub>2</sub>SA), salicylidene-3-nitroaniline(m-NO<sub>2</sub>SA) and salicylidene-4-nitroaniline(p-NO<sub>2</sub>SA).

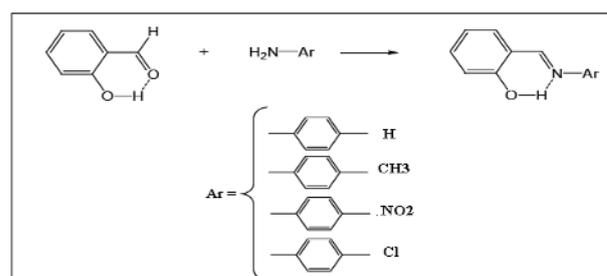


Figure 1. Synthesis of hydroxy Schiff bases.

#### 2.2 Acidity of hydroxy Schiff bases differently substituted

The acidity of hydroxy Schiff bases has been studied by pH-metric titration method. To investigate quantitatively the effect of substituents on the acidity of the azomethine nitrogen of some substituted salicylideneaniline in both solvent systems studied, a correlation of Hammett linear were proposed according to the following equation:

$$pK_0 - pK_a = \sigma\rho \quad (1)$$

### 3 Modeling

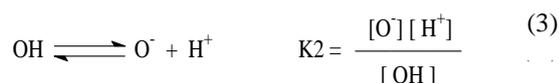
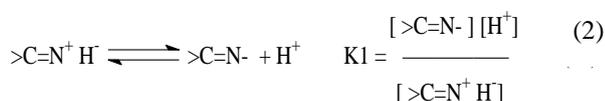
In a first step, the electrode calibration was performed daily before titration using a glass electrode. pH values of the standard buffer solutions were 4, 7 and 10 they were used in the calibration of the Orion pH metre. In a thermostated glass cell at 25 °C, 20 ml of an aqueous solution of perchloric acid (2. 10<sup>-2</sup> M) at constant ionic strength of (1M) NaClO<sub>4</sub> is mixed with 30 ml of an ethanol solution or with a solution of 1,4 Dioxane of Schiff base of 2.10<sup>-2</sup> M. The mixture is left under magnetic stirring about 30 minutes, so that these

compounds are fully protonated. The mixtures were then titrated with an aqueous solution of sodium hydroxide (0.1 M) of the same ionic strength, the volumes paid will be chosen to obtain the best possible accuracy in the region of the equivalence point.

It is recommended to pay by volume fractions of 0.5 mL in remote areas of the equivalence point and fractions of 0.25 ml around the equivalence point.

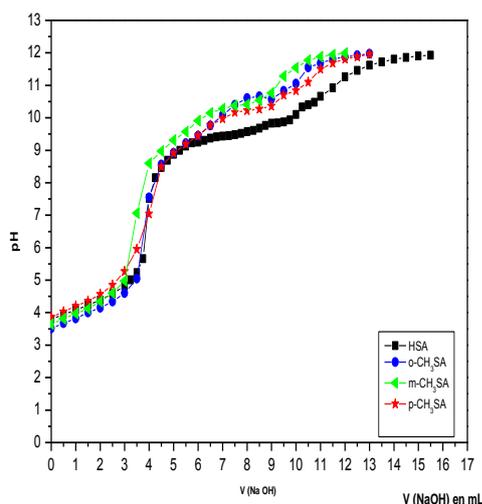
## 4 Results

Calculating the acidity constants of salicylideneaniline and differently substituted salicylideneaniline, was carried out by analyzing the titration data by using a direct method (half neutralisation). The protonation constants listed in Tables 1 are the mean values of at least four results. These constants are defined by equations 2 and 3:

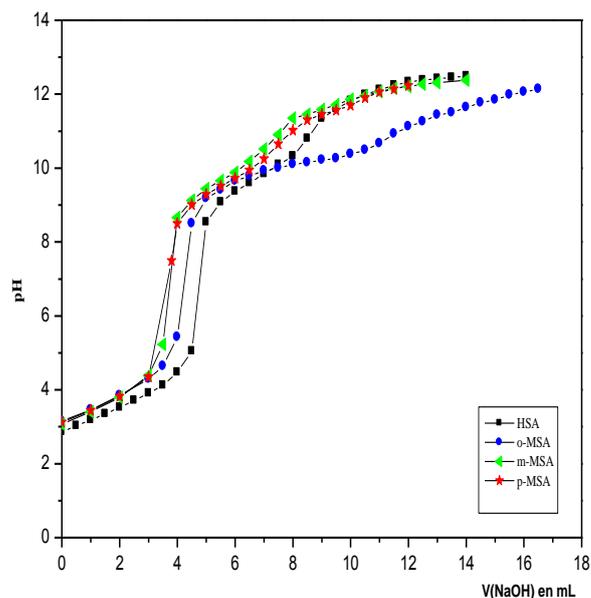


where  $K_1$  values correspond to the deprotonation of imine nitrogen atom and  $K_2$  to the deprotonation of phenolate.

Figures 2 and 3 show an example of a titration curve for the methyl group in the ortho, meta and para in two different mixtures of solvent. The numerical  $\text{p}K_1$  and  $\text{p}K_2$  values of ten Schiff bases determined in ethanol-water and dioxane-water mixtures are given in Table 1.

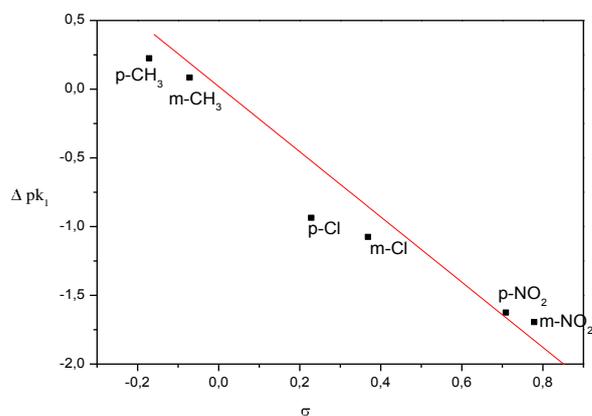


**Figure 2.** Titration curve of  $\text{CH}_3\text{SA}$  ( $2.10^{-2}$  M) in 60% ethanol-water.



**Figure 3.** Titration curve of  $\text{CH}_3\text{SA}$  ( $2.10^{-2}$  M) in 60% dioxane-water.

By using the data on Table 1. Hammett relations, ( $\sigma \sim \Delta \text{p}K_1$ ) of substituted salicylideneaniline in 60% ethanol-water and 60% dioxane-water mixtures are given in Figure 4 and 5 respectively.

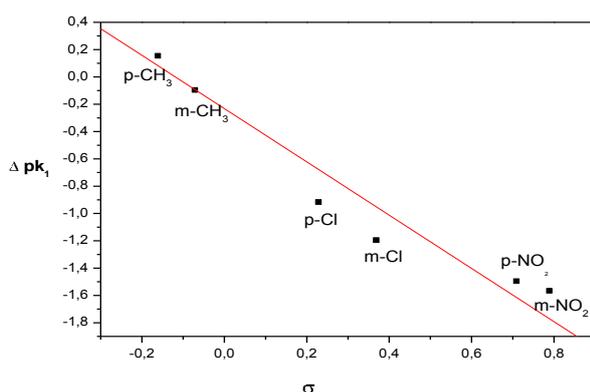


**Figure 4.** Plot of the  $\Delta \text{p}K_a$  of substituted salicylideneaniline against the Hammett substituted constants ( $\sigma$ ) in ethanol solvent.

As shown in Figures 4 and 5, excellent linear correlations govern the influence of the substituent X on the acid dissociation constants of the azomethine nitrogen.

**Table 1.** The acid dissociation constants of substituted salicylideneaniline at 25.0 ± 0.1°C for two different solvent mixtures and the Hammett constants ( $\sigma$ ) [1].

	60% ethanol + 40% water				60% dioxane + 40% water		
	$\sigma$	pK <sub>1</sub>	$\Delta$ pK <sub>1</sub>	pK <sub>2</sub>	pK <sub>1</sub>	$\Delta$ pK <sub>1</sub>	pK <sub>2</sub>
HSA	-	4.33	-	9.55	3.89	-	9.90
o-CH <sub>3</sub> SA	-	4.25	-	9.13	3.76	-	9.73
m-CH <sub>3</sub> SA	-0.07	4.41	0.08	9.35	3.79	-0.1	9.73
p-CH <sub>3</sub> SA	-0.16	4.55	0.22	9.20	4.04	0.15	9.76
o-NO <sub>2</sub> SA	-	2.60	-	9.18	2.25	-	9.51
m-NO <sub>2</sub> SA	0.71	2.63	-1.7	9.28	2.32	-1.57	9.61
p-NO <sub>2</sub> SA	0.79	2.70	-1.63	9.24	2.39	-1.5	9.62
o-CISA	-	2.73	-	9.13	2.42	-	9.64
m-CISA	0.37	3.25	-1.08	9.35	2.69	-1.2	9.65
p-CISA	0.23	3.39	-0.94	9.20	2.97	-0.92	9.63

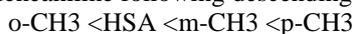
**Figure 5.** Plot of the  $\Delta$ pKa of substituted salicylideneaniline against the Hammett substituted constants ( $\sigma$ ) in dioxane solvent.

## 5 Conclusion

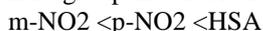
We note that the values of pK<sub>1</sub> for protonated Schiff bases bearing the substituents X from para to ortho, follow an order of increasing acidity.

The order of acidity salicylideneaniline derivatives compared to the reference molecule HAS (salicylideneaniline) is as follows:

The methyl group with an inductive effect donor leads to pK<sub>1</sub> whose values relative to the salicylideneaniline following descending order of acidity:

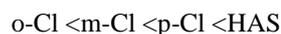


if X is a nitro group the order of the acidity is as follows:



Similarly, we also note that the salicylidene-3-nitroaniline has a pK<sub>1</sub> lower than in the para.

As in the case of the methyl group and nitro, order of acidity for the chloro substituent group is as follows:



For this substituent is observed that the acidity is high when the substituent is in the ortho position.

We note that, during the transition from ortho to para to the chloro pK<sub>1</sub> values increased significantly compared with nitro. This is probably due to the inductive effect attractor that strongly attracts the electron density at the nitrogen when the substituent is in the ortho position, that is to say, a high acidity.

As to the variation of the pK<sub>2</sub> values of these compounds we have not observed any regularity between these values and the type or position of the substituents. This lack of regularity can be probably be attributed to the fact that the substituents are far from the OH group [2, 3].

It is now that the  $\rho$  is a measure of the sensitivity of the reaction of equilibrium to electronic substituent effects. The magnitude of  $\rho$  gives a measure of the degree to which the reaction responds to substituents [4]. For this work, the values of  $\rho$  are negative and lie between (-1.86 for water-dioxane mixture and -2.02 for water-ethanol mixture).

We note that the value of  $\rho$  in the system (water - dioxane) is greater than that determined in the system (water - ethanol). This difference is due to the solvent polarity. This implies that as the solvent polarity decreases, the role of the substituent increases and  $\rho$  values increase, and this is consistent with Tokura's results [5].

## References

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