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UV-VIS Absorption Spectral Studies of N, N′-Bis(salicylidene)ethylenediamine (Salen) in Different Solvents

Khaled Muftah Elsherif[1*], Ahmed Zubi[2], Hana Shawish[2], Eman Almelah[2], Salima Abajja[2]

[1]Chemistry Department, Faculty of Science, University of Benghazi, Benghazi-Libya
[2]Chemistry Department, Faculty of Science, Misurata University, Misurata-Libya

Abstract

In the present study, the influence of various solvents on UV-VIS absorption spectra of N,N-Bis(salicylidene)ethylenediamine (Salen) has been investigated. Salen ligand has two absorption maxima (around 260 and 320 nm). To explain the obtained spectra, the frequencies and molar absorptivity values were combined with solvent properties using a total solvatochromic equation suggested by the Kamlet and Taft. The multiparametric examination denotes that non-specific dipolar interactions of the solvents (π^*) with the solute play a significant role in absorption maxima in pure solvents. The ionization constant (pK_a) of salen in methanol has been determined by spectrophotometric measurements. Two graphical methods have been applied to evaluate the ionization constant with resulting average value of 8.61.

Keywords: Schiff base, Salen, Solvent Effect, Copper.

دراسة طيف الامتصاص في المنطقة المرئية و فوق البنفسجية للمركب N ، N´– بيس (ساليسيليدين) إيثيلين ثنائي الأمين (سالين) في مذيبات مختلفة

خالد مفتاح الشريف[1]*، أحمد زوبي[2]، هناء الشاوش[2] ، إيمان الملح[2] ، سليمة عبجة[2]

[1]قسم الكيمياء، كلية العلوم، جامعة بنغازي، بنغازي، ليبيا
[2]قسم الكيمياء، كلية العلوم، جامعة مصراتة، مصراتة، ليبيا

الخلاصة

تم في هذا البحث دراسة تأثير بعض المذيبات على طيف الامتصاص في المنطقة المرئية و فوق البنفسجية لمركب N،N– بيس (ساليسيليدين) إيثيلين ثنائي الأمين (السالين). يمتلك مركب السالين قمتي امتصاص في حدود 260 و 320 نانومتر. و من أجل تفسير الأطياف التي تم الحصول عليها، تم الربط بين قيم التردد و قيم الامتصاصية المولارية للمركب مع خواص المذيبات باستخدام معادلة التذاوب الكلية المقترحة من قبل كاملت و ناتف. و أوضح التحليل متعدد العوامل أن التداخلات القطبية غير النوعية للمذيب مع المذاب تلعب الدور الأهم في قمة الامتصاص في المذيبات النقية. و تم تقدير ثابت التأين **pK_a** لمركب السالين في الميثانول باستخدام القياسات الطيفية. وقد تم استخدام طريقتين بيانيتين لإستخراج قيم ثابت التأين و كان معدل قيمته 8.61.

Introduction

Schiff bases prepared from the reaction of primary amines with salicylaldehyde (called salen type Schiff base) exemplify a multilateral series of ligand. In consideration regarding significance of these ligands numerous literatures have been published in this area [1-3]. The Schiff bases are excessively

*Email: elsherif27@yahoo.com

utilized as intermediates in organic synthesis, catalysts, polymer stabilizers, pigments, and dyes. [4]. They also offer a broad chain of biological activity, comprising antiparasitic, antifungal, antiviral, antipyretic, anti-inflammatory [5,6]. Four-coordinated chelates can be formed between the tetradentate salen ligand and most of transition metals [7,8]. These chelates have the wide implementations extending from industrial materials such as catalysts to pharmaceuticals [9,10]. Studying features dealing with these chelates have been focused mostly on their synthesis, electronic characteristics and structural identification. However, studies covering solution investigation are rare [11]. The scarcity of thermodynamic information on the formation of these chelates can be ascribed to their insolubility in water. Various experimental techniques are available for studying of complex formation and stability in solutions such as spectrophotometry, fluorescence spectroscopy, conductometry, potentiometry, polarography, nuclear magnetic resonance spectroscopy, and kinetic measurements [12].

The solvent influences various features of solute involving thermodynamic and kinetic properties. The investigation of solvent impacts on solute properties is of too significant for the development of solution chemistry [13,14]. Spectroscopic properties, such as the intensities and energies of transitions in UV-VIS, fluorescence, and IR spectroscopies are influenced by solvents as well [15]. The most significant tool for studying the interactions between solvent and solute is the UV-VIS absorption spectroscopy [16-18].

In the present work, UV-VIS absorption spectra of N,N′-Bis(salicylidene)ethylenediamine (Salen) in different solvent have been studied. The effect of pH on the absorption spectrum of salen in methanol was studied and the ionization constant was determined.

Materials and methods

Reagents

The solvents in the present study were HPLC or spectroscopic grade. It used without further purification. The solvents were ethanol (99.9%), 2-propanol (99.9%), tetrahydrofuran (99.9%), chloroform (99.9%), and acetonitrile (99.9%). N,N′-Bis(salicylidene)ethylenediamine ligand (shown in Figure-1) (98%) was obtained from SIGMA-ALDRICH. All chemicals (copper chloride, sodium hydroxide, and 37% hydrochloric acid) were ACS reagent grade and obtained from MERCK. The stock of $1.00x10^{-3}$ M solutions of salen in five solvents was prepared. The stock of $1.00x10^{-3}$ M solutions of Cu(II) in deionized water and methanol were also prepared. The Milli-Q water was used in this study.

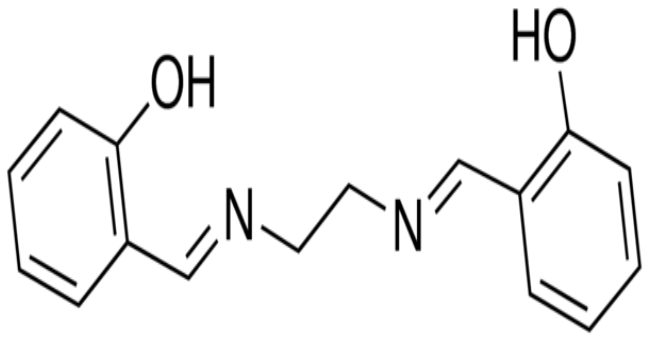

Figure 1- N,N′- Bis (salicylidene) ethylenediamine (salen)

Spectrophotometric Analysis

The UV-VIS absorption spectra were recorded utilizing the Agilent Cary 60 UV-Vis spectrophotometer in the range of 200 to 450 nm. Spectra were recorded at 25°C. To study the effect of solvent on absorption spectrum of salen, a series of diluted solutions ($1.00x10^{-4}$ – $1.00x10^{-5}$ M) in each solvent were used.

The Effect of pH

The pH measurements were performed utilizing a Jenway 3505 pH meter. The pH values were altered using 0.10 M NaOH and 0.10 M HCl solutions. Absorption spectra of salen in methanol were recorded at varied pH values in the range of 1.50 to 11.50.

Results and Discussion

Absorption Spectra of Salen in Different Solvents

The spectra of salen in various solvents are shown in Figure-2. From the figure below, salen exhibits two absorption maxima, the first is sharper and more intense than the second and it is around 260 nm. This absorption maximum could be attributed to π→π* transitions. The second is a broad band and less intense than the first and it locates at about 320 nm (depending on the solvent). The transitions responsible for this absorption should be π→π* and n→π*. Both of the wave length and intensity of these transitions were affected by solvents as shown in Figure-2. The values of λ_{max} and molar absorptivity ε at each solvent were determined and given in Table-1. Comparison for data given in Table-1 indicates that the λ_{max} of salen vary in the order of: chloroform > tetrahydrofuran > acetonitrile > 2-propanol > methanol. The absorption maximum is blue shifted as the polarity of the solvent increased. However, the intensities for this maximum were taken different order: chloroform > 2-propanol > acetonitrile > methanol > tetrahydrofuran. Both the polarity and hydrogen bond ability of the solvent may affect the intensity of the absorption (molar absorptivity). However, the molar absorptivity depends on the probability of the transition; as the probability increases the molar absorptivity also increases. The hydrogen bond between solvent and solute will decrease the interaction between n and π electrons (n-π conjugation) and accordingly the contribution of n electrons in the second absorption maximum will decrease. This means the transition has more π → π* character and therefore the probability of this transition will increase [19].

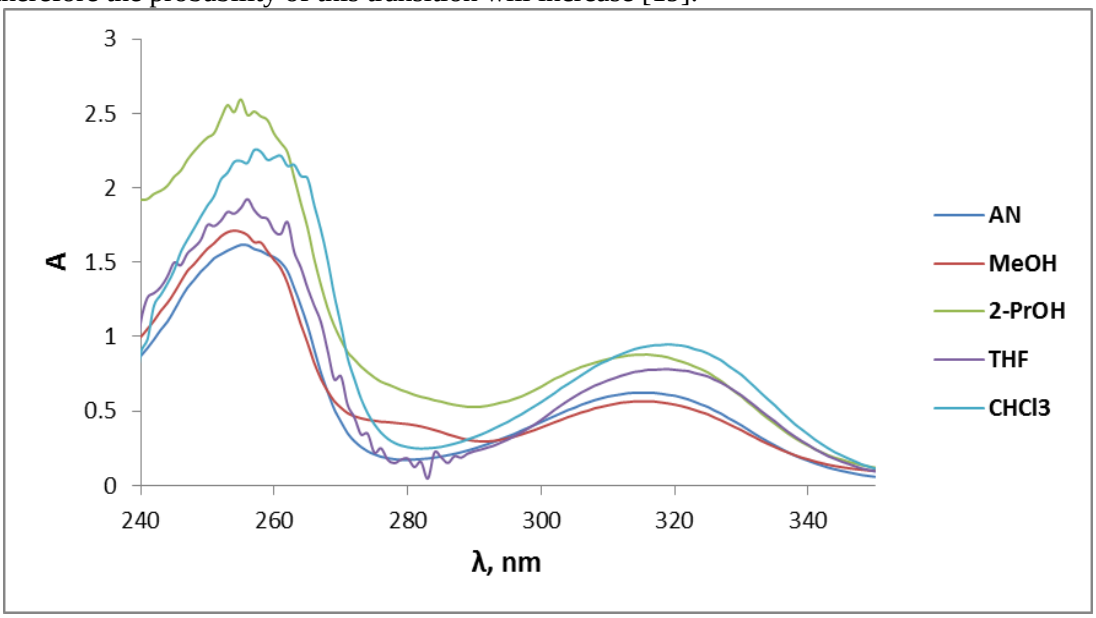

Figure 2- Absorption spectra of salen in different solvents.

Table 1- Values of λ_{max} and ε for salen with each solvent

Solvent	λ_{max} (nm)	ε (L. mol^{-1}. cm^{-1})	R^2
Methanol (MeOH)	314.5	6034	0.9997
2-Propanol (2-PrOH)	315.0	7042	0.9991
Acetonitrile (AN)	315.5	6683	0.9999
Tetrahydrofuran (THF)	318.6	3812	0.9988
Chloroform ($CHCl_3$)	319.0	9240	0.9961

The absorption spectra of salen were affected by polarity and hydrogen bonding ability of the solvent and this could be well evaluated using of the linear solvation energy relationship (LSER) concept suggested by Kamlet and Taft [20], using a general solvatochromic equation (1), of the form:

$$\bar{\nu}_{max} = \bar{\nu}_0 + s\,\pi^* + a\,\alpha + b\,\beta \quad (1)$$

Where s, a, and b are solvatochromic coefficients and α, β, π* are solvatochromic parameters, where: π* is an index of solvent polarity, α represents the hydrogen bond donor ability (HBD-acidity), and β is the hydrogen bond acceptor ability (HBA-basicity). $\bar{\nu}_{max}$ (1/λmax, cm^{-1}) is the absorption wave number for examined compound and $\bar{\nu}_0$ is the absorption wave number in gas phase (without any solvent effect, where: α = β = π* = 0.00). In Table-2 the relevant solvents parameters (α, β, π*) are given.

Table 2- The wave number ($\acute{\upsilon}_{max}$) and solvent parameters [20]

Solvent	$\bar{\nu}_{max}$ (cm^{-1})	π*	α	B
Methanol (MeOH)	31796.5	0.60	0.98	0.66
2-Propanol (2-PrOH)	31746.0	0.48	0.76	0.84
Acetonitrile (AN)	31695.7	0.75	0.19	0.40
Tetrahydrofuran (THF)	31387.3	0.58	0.00	0.55
Chloroform ($CHCl_3$)	31348.0	0.58	0.44	0.00

Electronic spectral data ($\acute{\upsilon}_{max}$) and the solvatochromic parameters α, β, π* for tested solvents were correlated by the multiple linear regression equation (equation 2) correlates, using the LSER (equation 1):

$$\bar{\nu}_{max} = 30417 + 1330\,\pi^* + 346\,\alpha + 446\,\beta \quad (2)$$

$R^2 = 0.950$, n = 5, SE = 95.3, F = 0.3

It can be concluded that the most effective parameter on the absorption maximum is the solvatochromic parameter π* (solvent dipolarity) which had a relative contribution of 63 % (compared to α (16%) and β (21%)). As the polarity increases, the absorption maximum for n→π* will undergo a blue shift, because for this transition, the polar solvents stabilize the ground state (n) more than the excited state π*, leading to a blue shift. The reverse is for π→π* transitions, the polar solvents stabilize the excited state (π*) more than the ground state π (red shift) [19, 21].

Effect of pH on absorption spectrum of salen

Spectrophotometric measurements were performed to investigate the effect of pH on absorption spectrum of salen. The spectra at various pH were used to determine the pK_a of salen in methanol using two graphical methods. The results obtained using the different methods were compared. Plots of absorbance against *λ* for salen at different pH values are given in Figure-3.

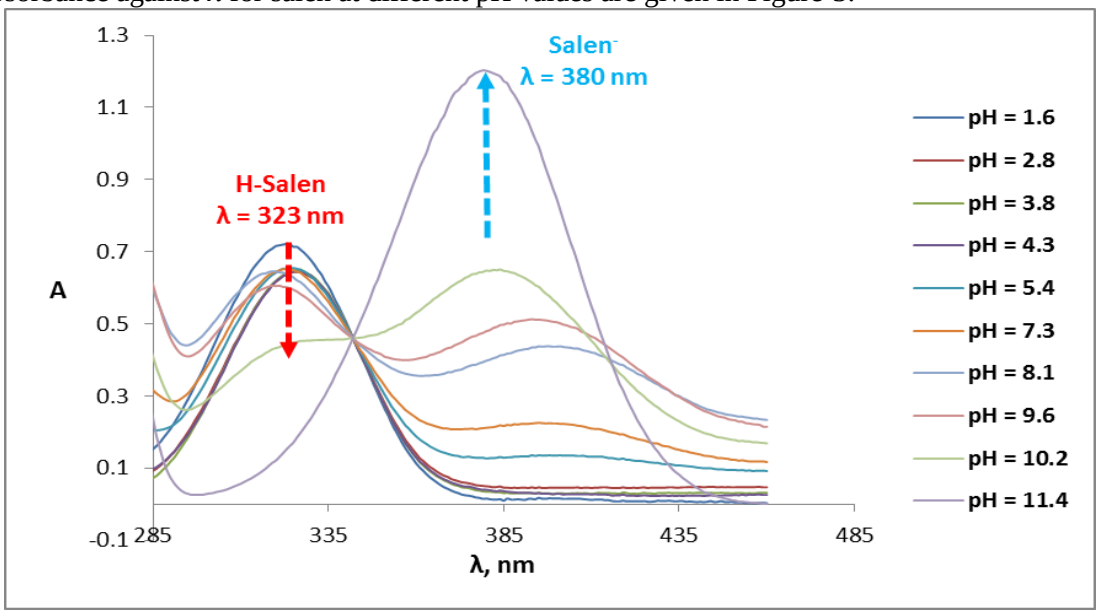

Figure 3- Absorption spectra of salen in methanol at different pH values**.**

As the pH increased the maximum absorption around 320 nm is diminished and a second one (around 380 nm) is raised.

When an acid form of salen (H-salen) is dissolved, the following equilibrium is established:

$$\text{H-salen} \rightarrow \text{salen}^- + H^+ \quad (3)$$

The acid dissociation constant K_a for H-salen can be expressed as follows:

$$K_a = \frac{[\text{salen}^-][H^+]}{[\text{H-salen}]} \quad (4)$$

The dissociation constant K_a is defined in terms of the concentration ratio [salen$^-$]/ [H-salen] which can be determined spectrophotometrically [22].

In very acidic solution all salen exists as H-salen and in very basic solution all salen exists as salen$^-$, and at intermediate pH the two forms will exist. However, at definite pH value the two concentrations of the forms will be equal, and therefore:

$$K_a = [H^+] \quad (5)$$

The absorbance of each form versus pH is shown in Figure-4. At intersection point, [H-salen] = [salen], and from which the dissociation constant can be determined. The value of K_a just determined is given in Table-3.

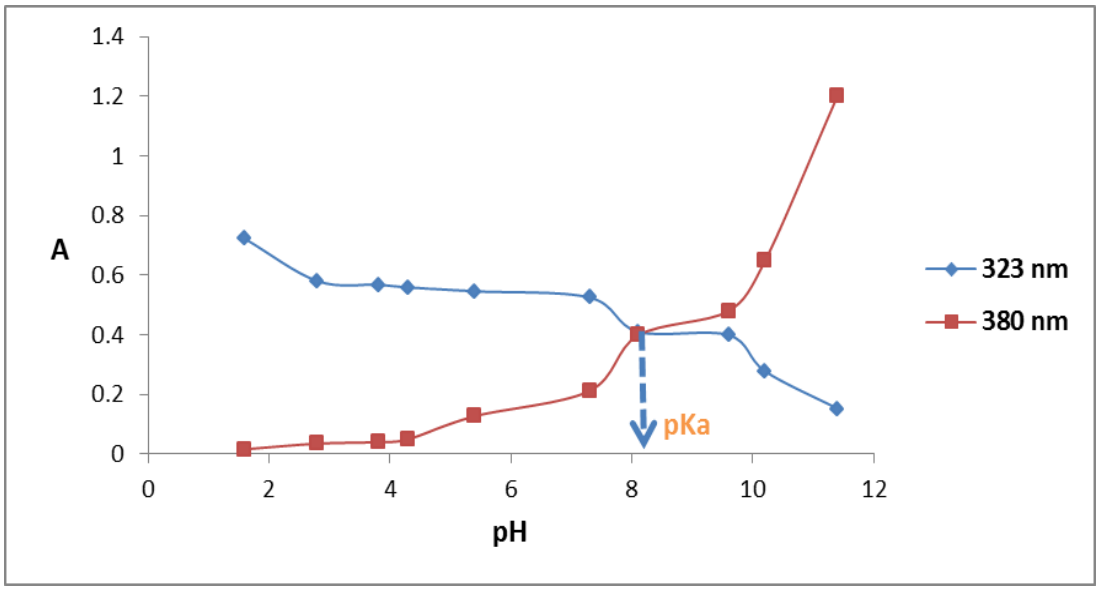

Figure 4- Plot of absorbance at λ = 323 nm and λ = 380 nm vs pH.

The dissociation constant can also be determined using second graphical method [23]. At very acidic solution, the absorbance of the solution at a given wavelength *λ* is given by:

$$A_{H-salen} = \varepsilon_{H-salen}\, b\, C_T \quad (6)$$

Where: $\varepsilon_{H-salen}$ is the molar absorptivity of H-salen at λ = 323 nm, C_T is the total concentration, and b is the width of the cell containing the solution.

In the too basic solution the same concentration is converted into salen$^-$ and the absorbance of salen$^-$ is given by:

$$A_{salen^-} = \varepsilon_{salen^-}\, b\, C_T \quad (7)$$

Where: ε_{salen^-} is the molar absorptivity of salen$^-$ at λ = 380 nm.

At an intermediate pH, the absorbance is given by:

$$A_{salen} = \varepsilon_{H-salen}\, b\, C_T + \varepsilon_{salen^-}\, b\, C_T \quad (8)$$

Where the total concentration of salen is defined as:

$$C_T = C_{H-salen} + C_{salen^-} \quad (9)$$

Equations 6-9 can be combined to obtain:

$$\frac{[\text{salen}^-]}{[\text{H-salen}]} = \frac{C_{salen^-}}{C_{H-salen}} = \frac{A - A_{H-salen}}{A_{salen^-} - A} \quad (10)$$

This relationship must be studied at multiple wavelengths, including one where H-salen absorbs appreciably but salen$^-$ does not, other where salen$^-$ is much more absorbent than H-salen. The pH of the solutions must be in the transition range of the acid so that both H-salen and salen$^-$ are presented in

appreciable concentrations. K_a can be evaluated graphically by converting Equation (4) to logarithmic form:

$$pK_a = pH + \log\frac{[sale^-]}{[H-salen]} \quad (11)$$

The combination of Equation (10) and (11) gives:

$$\log\frac{[A-A_{H-salen}]}{[A_{salen^--}-A]} + pK_a = pH \quad (12)$$

A graph of $\log[(A-A_{H\text{-}salen})/(A_{salen^-} - A)]$ vs pH gives a straight line with an intercept equal to K_a. The value just determined is given in Table-3.

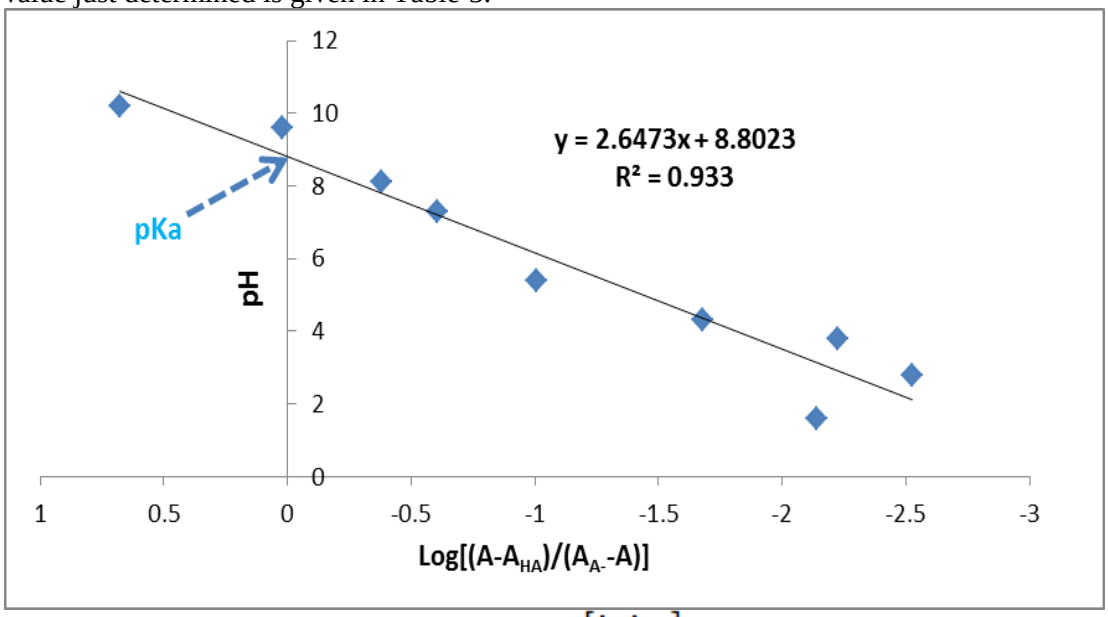

Figure 5- Plot of pH vs **Log** $\left[\frac{A-A_{HA}}{A_{A^--}-A}\right]$ for salen ligand

Table 3- pK_a values of salen in methanol using two methods

	pK_a	R^2
Method I	8.42	-
Method II	8.80	0.933
Average	8.61	-

Conclusion

The UV-VIS absorption spectra of salen (ν_{max}) were related with solvatochromic parameters π*, α, and β of various solvents. The absorption frequencies are affected mainly by dipolarity parameter π* of the solvent with relative contribution of 63 %.

The utilization of spectrophotometric measurements allowed the acid dissociation constant K_a of salen was calculated. Two methods of analysis were utilized and gave results with good similarity.

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