دراسة مشتقة طيف الإشعة فوق البنفسجية لعدد من قواعد شيف في الأيثانول المطلق

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المخلص
نظر و للاهمية البابولوجية والصناعية لمركبات قواعد شيف فقد تم تطبيق طريقة طيفية جديدة لدراسة توزيع مركبات من قواعد شيف متكونة من التفاعل بين مركبات الأنفادة والباراتولون سلفوناميد بالاعتماد على أطياف هذه المركبات عند المرتبة صفر والمشتقة الرابعة حيث سجلت أطياف قواعد شيف التالية:

[نيلازيلدين للمركب I] و (3, 4 - ثنائي ميثوكسي بنزازيلودي للمركب II) و (2, 6 - ثنائي كلورو بنزازيلودي ] مع الباراتولون سلفوناميد في الأيثانول المطلق وكذلك التقدير الكمي لهذا القواعد من خلال رسم المنحنى القياسية لكل منها وابعاد حدود التقدير العليا وال الدنيا والتي تتبع قانون بير- لامبرت وأيضاً اختبار مدى تطبيقية الطريقة للتقدير الكمي لهذه المركبات وحساب قيم معامل الارتباط R^2 والسنة المنوية للأخراف القياسية R.S.D والتي اظهرت ان هذه الطرق ذات حساسية ودقة عالية.

الكلمات المفتاحية:
fourth order , Schiff base , p-toluenesulphonamid
Derivative UV-Spectroscopic Studies of some Schiff Bases in Absolute Ethanol

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ABSTRACT
According to the biological and industrial importance of Schiff bases compounds, a new simple and accurate UV spectrophotometric method was established for the studied and determination of the Schiff bases compounds formed from the reaction between aromatic aldehydes compounds and P-toluenesulphonamide, depending on the zero and fourth derivative mode techniques. The zeroth and fourth order derivative spectra of the Schiff bases: [benzylidine (compound I), 3, 4 – dimethoxybenzylidine (compound II) and 2,6 – dichlorobenzylidine (compound III)] p-toluenesulphonamid, were recorded in absolute ethanol for series of different concentration solutions. The calibration curves were plotted which result in a straight line obeying Beers–Lambert law with $R^2$ values and R.S.D for compound I, II and III. These values indicate that these techniques having good sensitivity and precision for the quantification of these Schiff bases.

Keywords: fourth order, Schiff base, p-toluenesulphonamid

INTRODUCTION
The Schiff bases are very important organic compound, they have different biological activities [1] also they are known to exhibit a wide variety of pharmacological properties, antibacterial, antifungal and anticancer [2] and they are widely used for industrial purposes beside the biological activities [3]. A large number of research works have been reported about study of Schiff bases compounds like: synthesis, spectroscopic studies depending on IR, UV–Visible spectroscopy, H-NMR, C-NMR and mass spectra of new azo ligands Schiff base and amines derived of 5-phenylazo-2- hydroxy bezaldehyde [4]. And about spectrophotometric determination of these compound such as spectrophotometric determination and spectroscopic studies on Schiff base[5]. Derivative UV-spectroscopy has been widely used as a tool for quantitative analysis, characterization and quality control in the agricultural, Pharmaceutical and biomedical fields [6]. So that many researches have been carried out in the field of UV-derivative. For example: second, third and fourth order derivative UV-spectrophotometric methods have been developed and validated for the estimation of abacavir sulphate in bulk and it's tablet formulations, the bulk drug and Pharmaceutical formulations of abacavir sulphate is easily accessed by this method [7]. Sensitive spectrophotometric method has been developed for the
quantitative estimation of famotidine (FAM) and ibuprofen (IBU) individually as well as combined dosage form. First order derivative spectrophotometric method involves the measurement of absorbance of one drug at zero crossing point of other drug. 249nm and 263.6 nm was selected for the estimation of IBU and FAM respectively. linear range was found 4-20µg/ml and 20-60µg/ml with \(R^2 = 0.9987, \% cv=0.32\) to 1.49 and \(R^2 = 0.9930, \% cv = 0.71\) to 1.50) for FAM and IBU respectively. LOD for FAM and IBU were found to be 0.252 µg/ml and 10µg/ml respectively. The proposed validated method was successfully used for the quantitative analysis of synthetic mixture [8]. Also derivative spectrophotometric technique become very useful in the field of kinetic studies[9]. U.V. Derivative spectra studies of some Schiff's bases of amino acids complexes were recorded by first and second order derivative for the complexes of Schiff bases derived from leucine amino acid with sodium -3- acetylpyridine (NaI1) and sodium acetoacetanilide (NaHl2) with Co and Ni and their direct determination [10]. In this work and for the first time the fourth order derivative were studies for the compound of Schiff bases , benzyldiene p-toluensulphonamid (I) , 3,4 – dimethoxybenzylidine p-toluensulphonamid (II) and 2,6 –dichlorobenzylidine p- toluenesulphonamid (III) and their direct quantification by UV derivative spectroscopic technique.
Derivative UV-Spectroscopic Studies of some Schiff Bases

EXPERIMENTAL

Synthesis of compound (I-III): [11]

Materials:

All aldehydes [benzaldehyde, 2, 6 dichlorobenzaldehyde and 3,4 dimethoxybenzaldehyde] are of pure type and were used as freshly distilled for liquid phase, p-toluenesulphonamide obtained from fluka absolute methanol obtained from hopkin and williams.
Preparation of the Schiff base compound (I-III)

To a solution of aromatic aldehyde (0.02 mole) in (30 ml) of methanol (99.5 %). p-toluensulphonamide (0.02 mole) was added, the reaction mixture was refluxed for 24 hours, the solvent was then evaporate under vacuum and the solids was collected and recrystallized from xylend.

Instrumentation

All the U.V.spectra were recorded using UV-visible spectrophotometer shimadzu UV-1650 PC using 1×1×3 Cm matched quartz cells, for UV-spectra measurement (25) ml (10^{-2} M) solution in ethanol were prepared by dissolving (0.0647gm), (0.0797gm) and (0.0820gm) from compound I, II and III respectively and by appropriate dilution the solutions 10^{-3} M, 10^{-4} M and 10^{-5} M in ethanol were prepared.

RESULTS AND DISCUSSION

The zero order UV.spectra of the Schiff bases (I,II and III) were recorded in absolute ethanol solvent shows an absorption maxima and their molar extention coefficient calculated as shown in Fig (1), Table (1). And the UV absorption spectrum of the (blank) absolute ethanol show as:

From the above spectrum it is clear that there is no effect of the UV.spectra of the blank for the compounds under study.
Fig (I) : The UV absorption spectrum of \((4 \times 10^{-5} \text{ M})\) of compound (I,II and III) In absolute ethanol (zero - order).
Table(1): The UV absorption for solution (6×10⁻⁵ M) for the compound I & II and (8×10⁻⁵ M) for compound III.

| compound | Wavelength of absorption (nm) | ε_{max} Lit.mole⁻¹.cm⁻¹ |
|----------|-------------------------------|--------------------------|
| I        | 226                           | 15550                    |
| II       | 226                           | 16150                    |
| III      | 220                           | 21800                    |

For the quantification of these Schiff bases, according to the zero-order absorption spectra were accomplished bases on the measured absorbances at (226nm) for compound I & II and at (220nm) for compound III, the measured absorbances were plotted versus the molar concentration and the result shows a straight line obeying Beers-Lambert law as shown in Fig(2) within a concentration ranges and relative standard deviation, R² as shown in Table(2).
Fig(2): The relationship between the values of absorbance and molar concentration in absolute ethanol of compound I, II and III.
From these relationship, it’s clear that the straight line abeying Beer’s Lambert law within the range of \((3 \times 10^{-6} – 1 \times 10^{-4} \text{ M})\) for compound I, \((2 \times 10^{-6} – 1.5 \times 10^{-4})\) for compound II and \((1 \times 10^{-6} – 4 \times 10^{-4} \text{ M})\) for compound III.

**Table(2):** The values of lower and upper determination limits, \(R^2\) and R.S.D for the compounds of Schiff bases I, II and III.

| compound | Lower determination limit \(\mu g / ml\) | Upper determination limit \(\mu g / ml\) | \(R^2\)  | R.S.D % |
|----------|----------------------------------------|----------------------------------------|----------|---------|
| I        | 0.77                                   | 25.9                                   | 0.9938   | 1.8     |
| II       | 0.63                                   | 47.8                                   | 0.9941   | 3.8     |
| III      | 0.32                                   | 131.2                                  | 0.9987   | 0.6     |

The fourth order derivatives spectra of compounds I, II and III were recorded and show absorption maxima at \((226 \text{ nm})\) for compounds I & II and \((220 \text{ nm})\) for compound III. Compounds I & II show main positive peak at \((226 \text{ nm})\) and two satellites at each side for these peaks, for compound III the main positive peak is at \((220 \text{ nm})\) and two satellites at each side of these peak fig(3).

The presence of substituent in compound II and III effect the values of the determination limits due to their behavior electronically as shown in table(2).
Fig (3) : UV : absorption spectra of fourth order derivatives for compounds I,II and III in absolute ethanol
The quantification of these compounds according to the measured absorbance at these maxima was done and the result in straight line relation within a concentration range, $R^2$ and R.S.D as shown in Fig (4), Table (3).

Fig (4): the fourth order derivatives calibration curve of the compounds of Schiff bases I, II and III at different concentration.
From the calibration curves for the compounds in Fig (4), we can conclude that the straight light obeying Beer's lambert within the range of \((9 \times 10^{-7} - 1 \times 10^{-1} \text{ M})\) for compound (I), \((2 \times 10^{-6} - 1.3 \times 10^{-4} \text{ M})\) for compound (II) and \((7 \times 10^{-7} - 2.7 \times 10^{-4} \text{ M})\) for compound (III).

**Table (3):** the value of lower and upper determination limits, \(R^2\) and R.S.D for the fourth order derivative spectra for compound I, II and III in absolute ethanol.

| Compound | Lower determination limit µg / ml | Upper determination limit µg / ml | \(R^2\) | R.S.D% |
|----------|---------------------------------|---------------------------------|--------|-------|
| I        | 0.23                            | 25.9                            | 0.9960 | 0.9   |
| II       | 0.63                            | 41.47                           | 0.9945 | 0.1   |
| III      | 0.22                            | 88.56                           | 0.9990 | 0.2   |

From Table (2) and (3) it's clear that the fourth order derivative technique is more reliable for the quantification of compound I and III specially the lower determination limit, while the zero order derivative technique is preferable for compound II due to the wider range of determination.

The accuracy and precision of the method were detected through the preparation of three different concentration solutions (each five times) and the measurement of their absorbance’s by the zero and fourth order derivative for the three compounds the results are shown in Table [4,5,6].

**Table (4):** Accuracy and precision of the study the compound (I) in absolute ethanol (zero and fourth order).

|                   | Zero-order |                    | Fourth-order |                    |
|-------------------|------------|--------------------|--------------|--------------------|
|                   | Taken µg / ml | Found µg / ml | Recovery % | Error | Taken µg / ml | Found µg / ml | Recovery % | Error |
|                   | 3.36       | 3.62               | 107.9       | 7.9   | 3.10       | 3.36               | 108.3       | 8.3   |
|                   | 10.61      | 11.13              | 104.9       | 4.9   | 10.36      | 10.61              | 102.4       | 2.4   |
|                   | 24.08      | 23.54              | 97.7        | -2.3  | 23.31      | 23.56              | 101.0       | 1.0   |
Table (5) : Accuracy and precision of the study the compound (II) in absolute ethanol (zero and fourth order).

|         | Taken µg/ml | Found µg/ml | Recovery % | Error |
|---------|-------------|-------------|------------|-------|
| Zero-order |             |             |            |       |
| 3.19     | 2.87        | 89.8        | -10.2      |       |
| 15.63    | 13.71       | 87.8        | -12.2      |       |
| 41.47    | 41.47       | 100         | 0          |       |

|         | Taken µg/ml | Found µg/ml | Recovery % | Error |
|---------|-------------|-------------|------------|-------|
| Fourth-order |          |             |            |       |
| 3.12     | 3.12        | 100         | 0          |       |
| 15.31    | 14.99       | 97.9        | -2.1       |       |
| 41.15    | 39.55       | 96.1        | -3.9       |       |

Table (6) : Accuracy and precision of the study the compound (III) in absolute ethanol (zero and fourth order).

|         | Taken µg/ml | Found µg/ml | Recovery % | Error |
|---------|-------------|-------------|------------|-------|
| Zero-order |             |             |            |       |
| 2.03     | 2.03        | 100         | 0          |       |
| 15.08    | 14.76       | 97.8        | -2.2       |       |
| 54.77    | 49.2        | 89.2        | -10.8      |       |

|         | Taken µg/ml | Found µg/ml | Recovery % | Error |
|---------|-------------|-------------|------------|-------|
| Fourth-order |          |             |            |       |
| 2.14     | 2.14        | 100         | 0          |       |
| 15.08    | 16.07       | 106.5       | 6.5        |       |
| 56.08    | 56.41       | 100.5       | 0.5        |       |

The result indicate that both methods (zero and fourth order) could be applicable for the quantification of these compound with a good recovery and precision.
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