Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 4097-4102

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19101

Study of Electronic Absorption Spectra of Thiophene Schiff Bases in Varied pH Buffer Solutions

M. EL-BATOUTI[1,*], E.H. EL-MOSSALAMY[2] and N.F. AL-HARBI[3]

[1]Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt
[2]Chemistry Department, Faculty of Science, Benha University, Benha, Egypt
[3]Chemistry Department, Faculty of Science and Arts, Qassim University, Buraydah 52571, Saudi Arabia

*Corresponding author: E-mail: mervette_b@yahoo.com

Received: 10 February 2015; *Accepted*: 24 April 2015; *Published online*: 16 July 2015; AJC-17411

The absorption spectrum was measured for Schiff bases of thiophene in buffer solution at 25 °C to study medium effect in acidic and basic solutions, to determine pKa values and to identify the sensitivity of these compounds for the ionization movement in the medium. This facilitates the studied process of these compounds and understanding of their behaviour when exposed to electron acceptors. The UV-visible spectra of the Schiff bases were studied in buffer solutions of different pH = (2-12) containing 30 % (v/v) ethanol to affect the solubility of the organic compounds. In the present paper the electronic absorption spectra of some Schiff base compounds derived from thiophene have studied in organic solvents of varying polarity and buffer solutions of different pH.

Keywords: Charge transfer complex, pKa determination, Solvent effects, pH measurements.

INTRODUCTION

The study of the charge-transfer complexes formed by the reaction of aromatic electron acceptors (π-acceptors) with various electron donors have attracted considerable interests and growing importance owing to their significant physical and chemical properties[1-6]. Some of the charge-transfer complexes show interesting applications in the field of analytical chemistry[7,8]. Thiophene charge-transfer complexes are of special interest and importance. This is because some of these complexes have shown interesting properties dealt mainly with the determination of the electron affinities of the acceptors or the ionization potential of the donor molecules[9-12] and the investigation of the charge transfer interaction within the complex molecules[13]. The stoichiometric structure, spectral, thermal and electronic properties of the complexes depend strongly on the type and nature of the donor base as well as the electron acceptors and polarity of the solvents. The properties of multiple molecules compounds were one of the current challenges in the field of physical chemistry to detect the structure of such molecules and test the correlation properties of the chemical and physical nature.

Issa *et al.*[14] studied the electronic absorption spectra of some hydroxyl aryl Schiff bases in organic solvents of different polarity. Also the pK_a values of the investigated compounds were determined from spectral measurements in buffer solutions of varying pH.

The present article deals with a study on the intermolecular charge-transfer complexes of some thiophene with nitrobenzene derivatives. The effect of changing buffer solutions of various pH Schiff bases compounds of thiophene donor was studied to set the values of pK_a. Elucidation of the role of molecular structure of the complexes as well as the nature of the organic solvents and buffer solutions have been studied, the stoichiometry, the apparent formation constant, some physical parameters of charge transfer complexes.

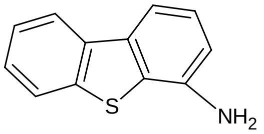
EXPERIMENTAL

To prepare Schiff bases we used compounds consisting of a primary amine: addition 2-amino dibenzothiophene to the three aldehydes are: benzaldehyde, salicylaldehyde and 2,4-dihydroxy benzaldehyde, all from the Laboratory Rasayon (LR).

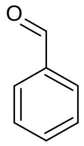
Analysis elements of carbon, hydrogen, nitrogen and sulfur and calculated practical and theoretical percentage and recorded in the Table-1. And comparing these theoretically calculated ratios with those found in practice, was noted that it is close to a large extent. As shown by the elemental analysis of the above-mentioned compounds that Schiff bases were obtained with molecular formulae shown in the Table-2. Results of elemental analysis, melting points in addition to the molecular formula in Table-1 clearly points to match the results of the analysis process with the ratios calculated, as can also be charge transfer complexes by 1:1 and 1:2 donor:acceptor.

TABLE-1
ELEMENTAL ANALYSIS AND MELTING POINT FOR SCHIFF BASE COMPOUNDS AND SOME CHARGE TRANSFER COMPLEXES

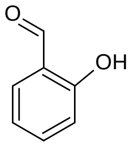
Comp.	C (%)		H (%)		N (%)		S (%)		m.p. (°C)
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
D_1	79.41	79.74	4.56	4.55	4.87	4.34	11.16	11.00	87-90
D_1A_3 (1:1)	58.14	57.98	3.12	3.02	10.85	10.39	6.21	6.01	88-91
D_1A_3 (1:2)	49.94	49.74	2.57	2.46	13.15	12.85	4.30	4.03	75-77
D_2	75.22	75.63	4.32	4.47	4.62	4.51	10.57	10.02	102-103
D_2A_3 (1:1)	56.39	58.41	3.03	3.93	10.52	10.25	6.02	5.81	96-98
D_2A_3 (1:2)	48.89	48.69	2.51	2.54	12.87	12.76	4.21	4.20	102-104
D_3	71.45	70.98	4.10	4.18	4.39	3.66	10.04	10.02	59-60
D_3A_3 (1:1)	54.75	54.93	2.94	2.88	10.21	10.76	5.85	5.65	138-140
D_3A_3 (1:2)	47.88	47.92	2.46	2.37	12.61	12.91	4.12	4.06	54-57



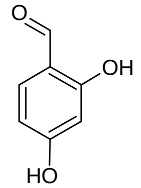
2-Aminodibenzothiophene



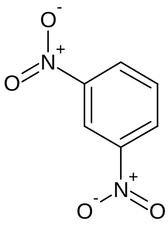
Benzaldehyde



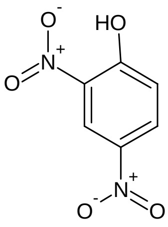
Salicylaldehyde



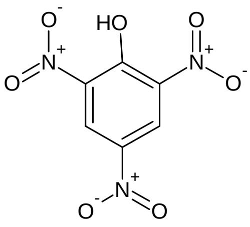
2,4-Dihydroxybenzaldehyde



1,3-Dinitrobenzene (A_1)

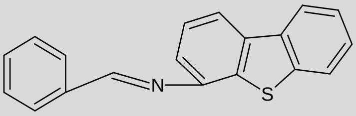
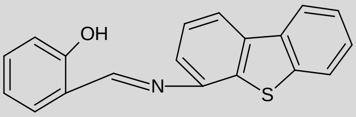
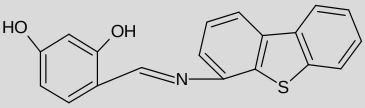


2,4-Dinitrophenol (A_2)



Picric acid (A_3)

TABLE-2
MOLECULAR FORMULA FOR DONOR SCHIFF BASES

Comp. Code	m.f. (m.w.)	Proposed structure
D_1	$C_{19}H_{13}NS$ (287.38)	
D_2	$C_{19}H_{13}NOS$ (303.38)	
D_3	$C_{19}H_{13}NO_2S$ (319.38)	

The impact of the electromagnetic spectrum of chemical compounds is very important to identify the molecular structure of compounds that are prepared and to through light on the structure of Schiff bases and charge transfer complexes prepared of them, it will use the infrared spectrum in addition to the spectrum, nuclear magnetic resonance and UV and visible spectra.

To measure pH, a digital device of the type (Hanna Model 211) with (combined electrode) and sensitivity 0.01 has been used. To calibrate the device buffer solutions of BDH was also used.

RESULTS AND DISCUSSION

Visible and ultraviolet spectra of Schiff bases were measured in aqueous solutions containing 30 % (v/v) ethanol to affect the solubility of the organic compounds. These measurements have applied using universal buffer to control the value of pH in the range between pH = (2-12)[15]. The spectra in buffer solutions of varied pH are also studied and utilized for the determination of the ionization constants (pK_a) of the Schiff bases complexes.

Absorption spectra of Schiff bases are shown in Fig. 1 prepared in concentration solutions 0.5×10^{-4} M of varying pH observed the appearance of many absorption bands at different wavelengths ranging between 200-400 nm. The bands due to localized π-π^* transitions displayed slight changes, while the charge transfer band showed interesting changes with increasing pH.

The spectra of compound D_1, which not containing the phenolic OH group, exhibited changes in the extinction, density and position of the charge transfer band only within the base range of pH. The band absorbance increased and was slightly shifted to red with increasing the pH of the medium. While in acidic solutions characterize the existence of absorption bands at 213, 280.5 nm due to the absorption of the presence of the exposed non ionized in this medium also due to the transitions π-π^* and transitions for charges within the molecule. The band absorbance increased and the band was slightly shifted to red with increasing the pH-absorbance curves. With rise of pH, Fig. 1 showed new band developed at longer wavelength 293 nm due to the ionized while a, clear isosbestic points are observed denoting the existence of an equilibrium of the acid base type[16].

For the two compounds D_2 and D_3, the absorption of the charge transfer band decreased with rise of pH and a new absorption shoulder developed at longer wavelength, while the appearance of isosbestic points are observed denoting the existence of an equilibrium of the acid base type. The absorption band appeared in the two compounds D_2 and D_3 at 214, 275 nm and 219, 281 nm, respectively, the absorption of the charge transfer band decreased with rise of pH. However the absorption of the charge transfer band increases in basic medium with rise of pH as occurred to red shift wavelength

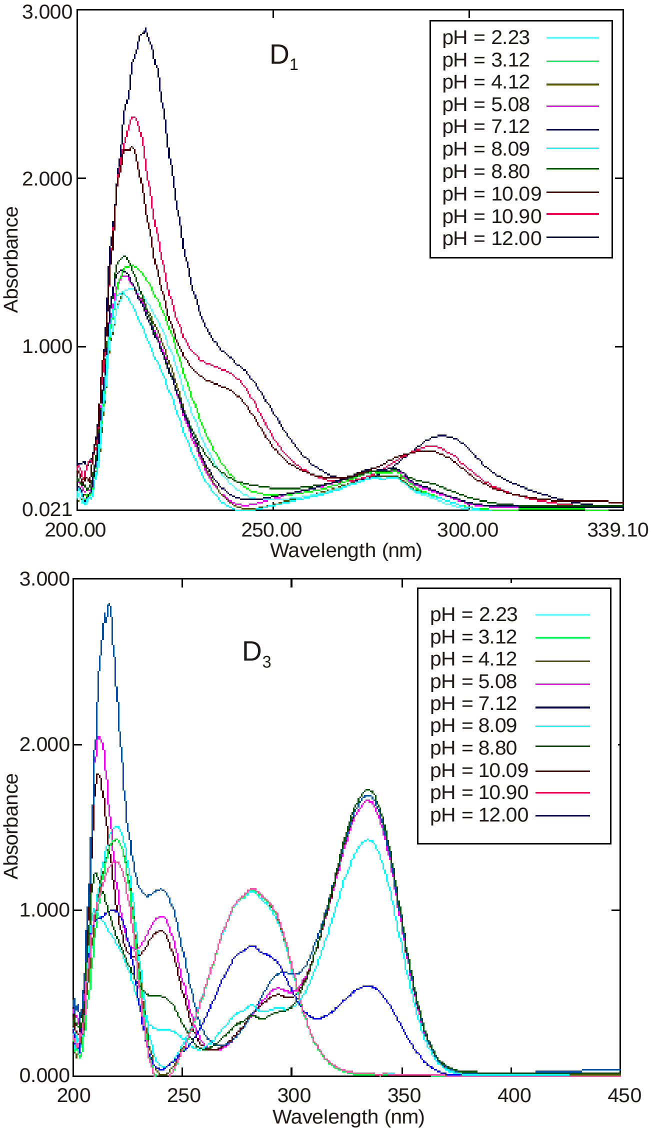
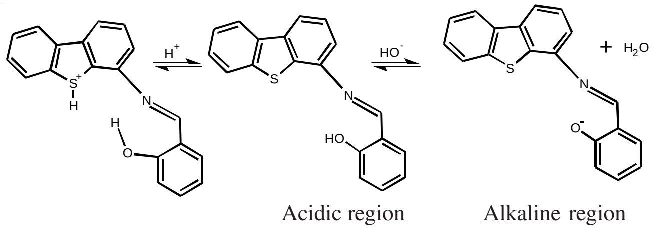


Fig. 1. Absorption spectra of D_1 and D_3 in universal buffer variable pH

longer 290, 334.5 nm in D_2, D_3, respectively. The pH absorbance changes were utilized to calculate the acid dissociation constants of the protonated species and the phenolic OH groups[17]. On considering the behaviour of D_2 and D_3, it can be concluded that the acid base equilibrium on the acid side would involve the dissociation of a proton from the protonated benzene ring. On the alkaline side, the ionization of the phenolic group takes place in compounds D_2 and D_3. These equilibrium can be presented as follows:



It was also noted that the appearance of convergence clear points and indicate the presence of acid - base equilibrium confirms the existence of two points of isosbestic point in both of the two compounds at a wavelength of 260, 277 nm in the compound D_2 and at 256, 303 nm in the case of compound D_3.

Determination of the ionization constants values pK_a of thiophene Schiff bases in buffer solutions of varied pH: The pH absorbance changes were utilized to calculate the acid dissociation constants of the protonated species and the phenolic OH groups. This was achieved by applying the half height, limiting absorbance and modified limiting absorption[18,19].

Half-height methods (HHM)[20]: The method is based on the higher value of the absorption A_{max} represents the transfer of one form of the compound to another and as the pH value equal pK_a when both the two forms are in equal amounts, the pH value which corresponds to half the height of the absorption curves in absorption with pH equal to the value of pK_a. Using the following formula to estimate the values of pK_a:

$$pK_a = pH\ (A1/2) + \log f$$

where f was the efficiency coefficient and reach 0.9 value in case of the following ionization:

$$HR = R- + H+$$

And the value of A1/2 given the following relationship:

$$A1/2 = (A_{max} - A_{min})/2 + A_{min}$$

or

$$A1/2 = (A_{max} + A_{min})/2$$

where A_{min} is the value of less absorption, A_{max} is the value higher absorption and A1/2 the value of Half-height methods in pH curves with absorption.

Limiting absorbance method (LAM)[21]: According to this method and in the dilute solutions:

$$pH = pK_a + \log\ [A/(A_{max} - A)]$$

The relationship between pH and log $[A/(A_{max} - A)]$ get a straight line, the pK_a value can be evaluated which is equal to pH value when the value of the amount log $[A/(A_{max} - A)]$ equal to zero.

Modified limiting absorbance method (MLAM)[22]: Since the specific absorption A_{max} match the total concentration parts present in the solution and the absorption A at a given measuring pH, the value of A changes with pH and at a certain wavelength.

pK_a value is evaluated of the following relationship:

$$pH = pK + \log\ [(A_{max} - A)/(A - A_{min})] + \log f$$

where log f = 0 in very dilute solutions, then the previous equation becomes as follows:

$$pH = pK + \log\ [(A_{max} - A)/(A- A_{min})]$$

The relationship between pH and log $[(A_{max} - A)/(A-A_{min})]$ get a linear relationship of which pK_a can be evaluated when equal pH value where the amount of log $[(A_{max}-A)/(A-A_{min})]$ equal to zero.

Effect of buffer solutions at varying pH on Schiff base compounds was studied to determine peak values and to identify the sensitivity of these compounds for the ionization movement in the medium, thus facilitate the studied process of these compounds and understand their behaviour when exposed to electron acceptors. To study in more than one area of the spectroscopic studies and conductivity.

Figs. 2 and 3 show the relationship diagrams used to calculate the values of the ionization constant for the Schiff bases donor compounds using three methods (half-height methods, limiting absorbance method, modified limiting absorbance method) in universal buffer solutions (Table-3) and the calculated pK_a values that depend on the nature of the compound and the medium study and calculated at different wavelengths of the three above-mentioned methods.

The pK_a values were obtained for each compound in three different ways and it was observed that the values have coincided to some extent with each other. For example, the values pK_a calculated for donor compound D_1 in universal buffer at a wavelength of 293 nm and using the method of half-height methods equal to 9.5 while the value of 8.11 in a method limiting absorbance method while equaled 9.56 method modified limiting absorbance method, while at the wavelength at least 217 nm were values equal to 10.2 by half-height method and 7.19 limiting absorbance method found a way while they are equal to 10.4 when using modified limiting absorbance method for the same compound and with the buffer solution.

The pK_a values calculated for the donor compound D_2 in universal buffer at a wavelength of 291.5 nm and using the method of half-height methods equal to 8.5 while it was 10.2 limiting absorbance method while in a method equaled 10.06 modified limiting absorbance method, while at least 218.5 nm

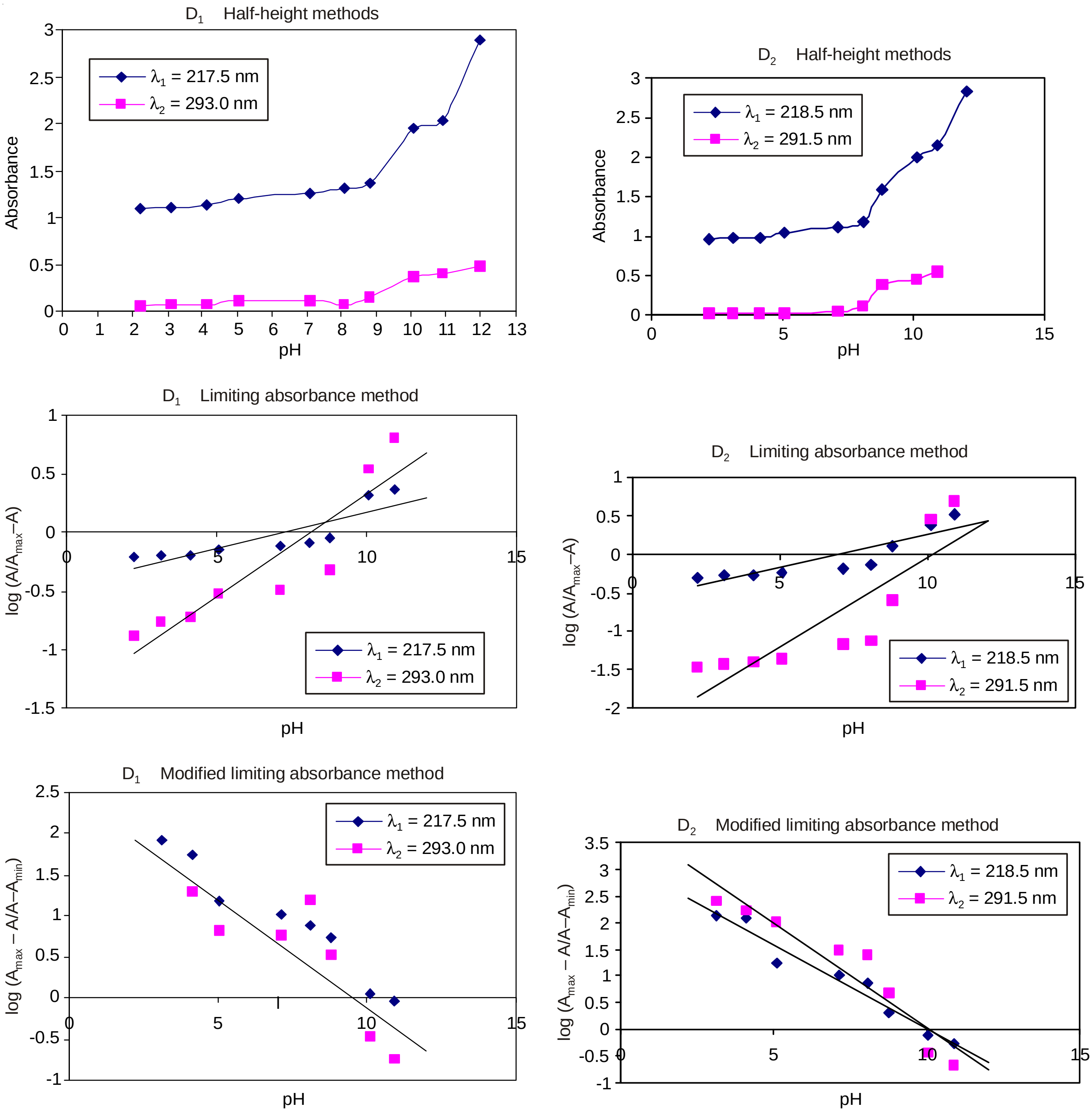


Fig. 2. Relations graphs of three methods (half-height methods, limiting absorbance method, modified limiting absorbance method) used to calculate the pK_a values for donor compounds D_1 and D_2 using universal buffer

TABLE-3
VALUES OF THE IONIZATION CONSTANT pKa CALCULATED AT DIFFERENT WAVELENGTHS OF THE DONOR COMPOUNDS UNDER STUDY WITH UNIVERSAL BUFFER THREE WAYS HALF-HEIGHT METHODS, LIMITING ABSORBANCE METHOD, MODIFIED LIMITING ABSORBANCE METHOD

Compd.	pH	Absorbance		pK_a						Mean
		λ_1 = 293.0	λ_2 = 217.5	Half-height methods		Limiting absorbance method		Modified limiting absorbance method		
				λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	
D_1	2.23	0.054	1.096	9.5	10.2	8.11	7.19	9.56	10.4	9.16
	3.12	0.069	1.117							
	4.12	0.074	1.128							
	5.08	0.109	1.209							
	7.12	0.114	1.251							
	8.09	0.079	1.302							
	8.80	0.150	1.371							
	10.09	0.361	1.952							
	10.90	0.403	2.031							
	12.00	0.465	2.893							
Compd.	pH	Absorbance		pK_a						Mean
		λ_1 = 291.5	λ_2 = 218.5	Half-height methods		Limiting absorbance method		Modified limiting absorbance method		
				λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	
D_2	2.23	0.017	0.954	8.5	9.6	10.2	7.17	10.06	10.07	9.27
	3.12	0.019	0.968							
	4.12	0.02	0.97							
	5.08	0.022	1.053							
	7.12	0.033	1.119							
	8.09	0.037	1.182							
	8.80	0.107	1.591							
	10.09	0.394	2.000							
	10.90	0.444	2.165							
	12.00	0.536	2.836							
Compd.	pH	Absorbance		pK_a						Mean
		λ_1 = 334.5	λ_2 = 281.5	Half-height methods		Limiting absorbance method		Modified limiting absorbance method		
				λ_1	λ_2	λ_1	λ_2	λ_1	λ_2	
D_3	2.23	0.012	1.115	7.7	7.4	7.79	9.4	8.1	7.26	7.94
	3.12	0.009	1.125							
	4.12	0.012	1.129							
	5.08	0.016	1.133							
	7.12	0.542	0.790							
	8.09	1.425	0.428							
	8.80	1.729	0.369							
	10.09	1.694	0.478							
	10.90	1.662	0.380							
	12.00	1.691	0.375							

wavelength values were equal to 9.6 and 7 way half-height methods 0.17 limiting absorbance method way while they found equal to 10.07 when using modified limiting absorbance method.

Curves between pH and absorption in the (half-height methods) method of compound D_3 at different wavelengths Z-shape or S as shown in Fig. 3. This behaviour is used to estimate the pK_a of this compound by the application of the limiting absorbance method and Half-height methods. The calculated values of pK_a of the compound in the donor D_3 Universal buffer at a wavelength of 334.5 nm and using the method of half-height methods equal to 7.7, while their value was 7.79 limiting absorbance method while in a method equaled 8.1 modified limiting absorbance method, while at least 281.5nm wavelength values were equal to 7.4 and 9 half-height methods. 4 limiting absorbance method way while they found equal to 7.26 when using modified limiting absorbance method.

The above study, where Issa was able to calculate the pK_a values for some compounds bisazo-dianils three ways (half-height methods, limiting absorbance method, modified limiting absorbance method) in buffer solution pH value ranging between 4.5-12[23]. Khedr *et al.*[24] also reported the calculation of pK_a values in the buffer solution in which the values of pH ranged between 2.12 and that for some dyes using new methods (half-height methods, limiting absorbance method). On comparing our findings with the findings of the previous methods for the same and it was observed that the values of pK_a be close despite the differences in method of calculation.

Raafat method (half-height methods, limiting absorbance method) in the calculation of pK_a values for five compounds of Schiff bases formed by condensing derivatives aminubensuthiazul

2-aminobenzothiazole with some aldehydes in buffer solutions where the values of pH ranged[25] between 2-12.

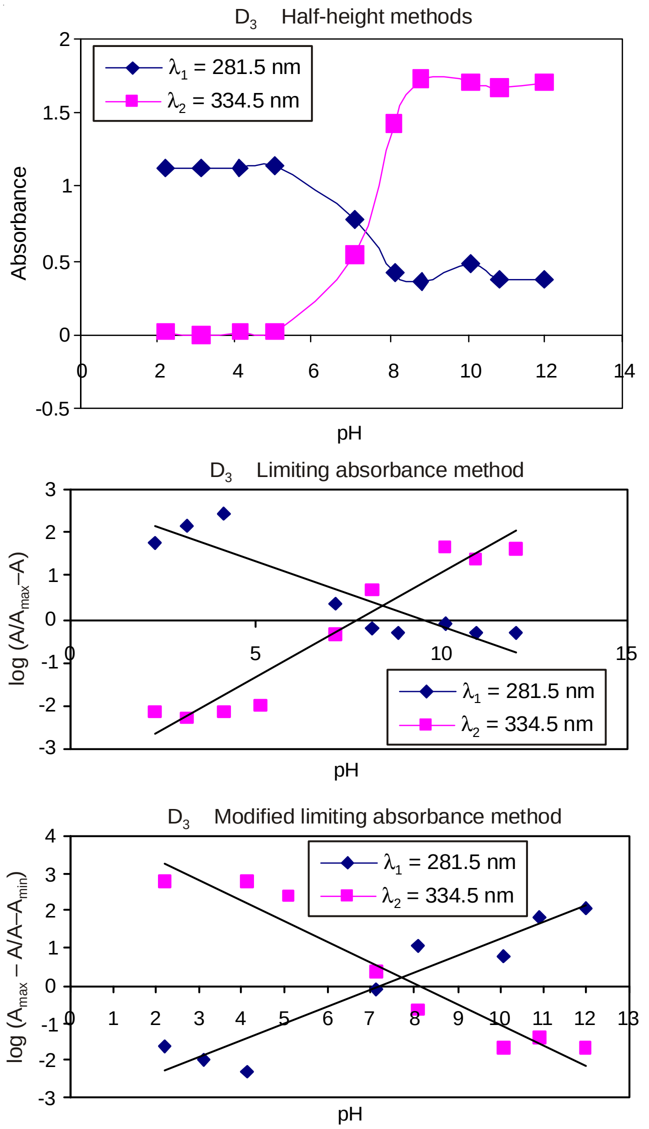


Fig. 3. Relations graphs of three ways (half-height methods, limiting absorbance method, modified limiting absorbance method) used to calculate the values of pK_a of the donor D_3 compounds using Universal buffer

REFERENCES

1. E.M. Nour, S.M. Metwally, M.A.F. El-Mosallamy and Y. Gameel, *Spectrosc. Lett.*, **30**, 1109 (1997).
2. R. Foster, Organic Charge-Transfer Complexes, Academic Press, London and New York (1969).
3. R. Foster and T.J. Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).
4. R.S. Mulliken and W.B. Person, Molecular Complexes, A Lecture and Reprint Volume, Wiley, New York (1969).
5. S.M. Metwally, *Can. J. Appl. Spectrosc.*, **40**, 152 (1995).
6. K.K. Lahiri, K.K. Mazumdar and K. Masumdar, *Spectrochim. Acta A*, **46**, 1137 (1990).
7. L.I. Bebawy, K.E. Kelani, L.A. Fattah and A.K.S. Ahmad, *J. Pharm. Sci.*, **86**, 1030 (1997).
8. M. Luo, *Yaowu Fenxi Zazhi*, **15**, 52 (1995).
9. E.H. El-Mossalamy and K.Y. El-Baradie, *Monatsh. Chem.*, **128**, 255 (1997).
10. J. Czekalla, G. Briegleb and W. Herre, *Ber. Bunsenges. Phys. Chem.*, **63**, 712 (1959).
11. G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).
12. R. Foster, D.L. Hammick and B.N. Parsons, *J. Chem. Soc.*, 555 (1956).
13. Y.M. Issa, A.E. El-kholy, A.M. Hindawy and R.M. Issa, *J. Indian Chem. Soc.*, **57**, 216 (1980).
14. R.M. Issa, A.A. El-Samahy and S.H. Etaiw, *Z. Phys. Chem. (Leipz.)*, **253**, 853 (1974).
15. H.T.S. Britton, Hydrogen Ions, Chapman and Hall, London (1955).
16. S.A. Abdel-Latif, H.B. Hassib and Y.M. Issa, *Spectrochim. Acta A*, **67**, 950 (2007).
17. R.M. Issa, A.A. Hassanein, I.M. El-Mehasseb and R.I.A. El-Wadoud, *Spectrochim. Acta A*, **65**, 206 (2006).
18. T. Sakabe, M. Iizuka, S. Kuniyoshi, K. Kudo and K. Tanaka, *Mol. Cryst. Liq. Cryst.*, **349**, 367 (2000).
19. K. Kudo, M. Iizuka, S. Kuniyoshi and K. Tanaka, *Electr. Eng. Jpn.*, **134**, 10 (2001).
20. R.M. Issa and A.H. Zewail, *Egypt. J. Chem.*, **14**, 461 (1971).
21. I.M. Issa, R.M. Issa, M.S. El-Ezaby and Y.Z. Ahmed, *Z. Phys. Chem. (Leipzig)*, **242**, 169 (1969).
22. A. Harvey and D. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).
23. R.M. Issa, K.Y. El-baradie and N.A. El-Wakiel, *Spectrochim. Acta A*, **60**, 2883 (2004).
24. A.M. Khedr, M. Gaber, R.M. Issa and H. Erten, *Dyes Pigments*, **67**, 117 (2005).
25. R.M. Issa, A.M. Khedr and H. Rizk, *J. Chil. Chem. Soc.*, **55**, 875 (2008).