Journal of Natural Sciences,
Life and Applied Sciences
Issue (1), Volume (2)
March 2018
ISSN: 2522-3356

المجلة العربية للعلوم و نشر الأبحاث
Arab Journal of Sciences & Research Publishing
AJSRP

BEHAVIOURE STUDY OF THE ASSOCIATION BETWEEN ACID-BASE INDICATORS IN ACIDIC MEDIUM BY USING SPECTROSCOPY TECHNIQUE

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Abstract: The association behavior between Acid-Base indicators in buffered aqueous solution (pH = 4) has been studied by UV–Vis spectroscopy technique at room temperature. The spectroscopic results show that association are formed evidenced by highly red shift to λ_{max} = 485nm and large hypo-chromic shift in absorbance signal upon addition of ago dye. The electronic absorption spectra represented by broadening bands and lack of isosbestic point that indicate of formation of higher order dye aggregates from the type J-aggregate as results as change of the pH of the medium were discussed according to exciton kasha theory.

Keyword: Acid-Base Indicators; Electronic Absorption Spectrum; Buffer Solution; Lack of Isosbestic Point; Higher Aggregates.

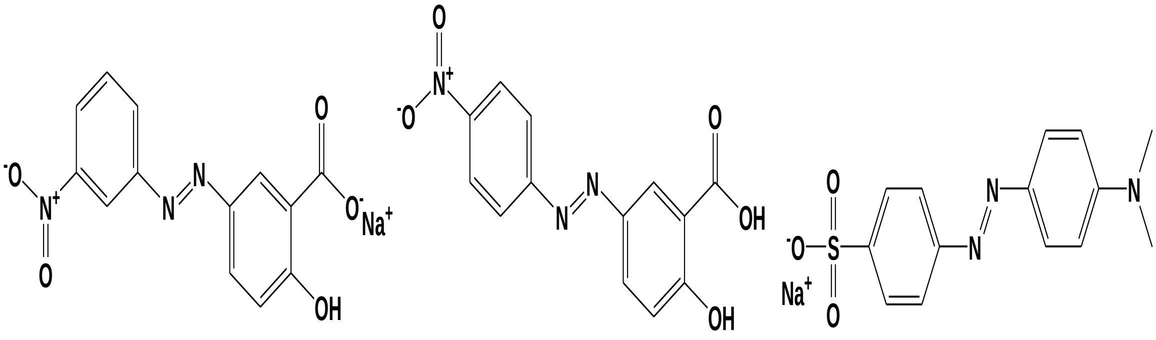
INTROUDUCTION

UV–Vis absorption spectra of dyes may be influenced by the surrounding medium such as ionic strength, temperature, pH and solvents can bring about changes in the position, intensity and shape of absorption bands that accompanied by the presence of donor and acceptor substituent's in the conjugated systems of dyes as result as formation specific or non-specific interactions (1-3). In addition, the effects of addition Co-solvent by different ratios as mole fraction from 0.1-0.9 to dye aqueous solution have the same changes in electronic absorption properties as result as change of the polarity of solution (4). The aggregation of dyes is accompanied by the changes in the absorption or fluorescence spectrum compared to the individual monomeric molecules. According to Kasha, exciton theory (5). J- or H-aggregates can be formed depending on the angle (α) between the transition dipoles and the molecular axis of the aggregate. J-aggregates of dyes are very important for photo-physical and nonlinear optical applications, which are characterized by an intense red shifted absorption band compared to the monomers. The coupled monomers of J-aggregates would yield a side-by-side or a slipped face-to-face stacking geometry. In contrast, the absorption spectra of H-aggregates are hypso-chemically shifted and usually broad, where the aggregated molecules are arranged in a parallel fashion (6,7). The charge transfer interactions within a molecular complex consisting of an electron donor (ED) and an electron acceptor (EA) involved a resonance with a transfer of charge from ED to EA (8). The aggregation of dyes in aqueous solution is of extreme importance in biological, colloid, photographic and analytical chemistry (9,10).

Azo dyes as well known to form dimmers or higher order aggregates in aqueous solution depending on the dye structure and media properties (11). General trends in the development of investigations of ion associates, involving an ion of an organic dye, in aqueous solutions are considered. The contributions of different kinds of intermolecular interactions (Coulomb, Vander Waals, hydrophobic, etc.) that cause the association of ions were analyzed. The interrelationship between the characteristics of dyes (charge, structure, hydrophobic behavior, etc.) and the properties of ion associates (strength, geometry) is discussed (12). The spectrophotometric determination of some selected drugs with bromophenol blue (**BPB**) and Methyl Orange (**MO**) through formation of ion-pair association complex in buffered aqueous solution (13-15)**.** Interaction of Methyl Orange with different surfactants at different conditions was studies by spectrophotometric technique (16-18). Interaction between of Methyl orange (electron acceptor) with Alizarin Yellow **GG** and Alizarin Yellow **G** (electron donors) in a neutral medium at different properties of media was studies by Uv-Visible spectroscopy technique. The results showed that association between acid–base indicators disaggregated with an increasing of ionic strength and decreasing of dielectric constant for the Co-solvent and decreasing the concentration of Methyl Orange (19).

THE AIM OF THE STUDY:

The aim of this study was to investigate of the acidic medium influence on the UV–Vis absorption spectra of association between acid- base indicators, See (Fig.1)., The spectral characteristics of the studied acid-base indicator molecules in buffered solution at room temperature were discussed according to exciton Kasha theory.



AYGG AYG MO

Figure (1): Molecular Structure of Ligands (19-20)

METHODS

The UV-Visible spectrum measurements were performed at room temperature by using CECIL – CE 7400(S.n.146368, England) UV-Visible Spectrophotometer with a 1-cm path length quartz cell was used for UV–Vis spectra acquisition at room temperature ~ 20 oC. The pH value for potassium phthalate buffer solution was checked by using MARTINI instrument pH-benchmeter that was previously calibrated with a standard buffer solution of pH's 4.00, 7.00 and 9.00.

Chemical and Reagents:

Methyl Orange (MO, 4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt), Alizarin yellow G it is commonly known as (alizarin yellow R, 5-(4-nitrophenylazo) salicylic acid (III), chrome orange, mordant orange1) and Alizarin yellow GG it is commonly known as (AYGG, [5-(3-nitrophenylazo)-2-hydroxybenzoic acid sodium salt]), In Fig.(1). Were obtained from BDH Chemical LTD Poole England and sigma companies. These reagents used without further purification.

Preparation of Standard Solutions:

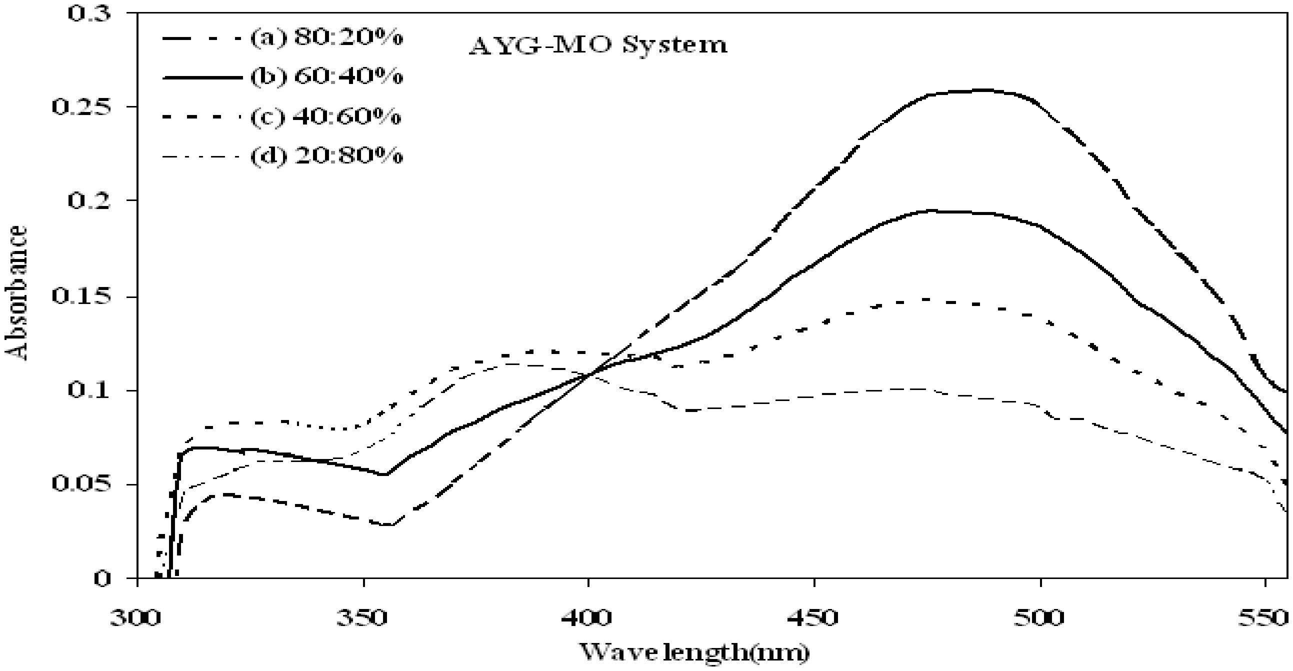
Standard stock aqueous solution 1×10^{-3}M from these dyes was prepared in de-ionized and CO_2-free water by dissolving proper amount from these compounds and working solutions 1×10^{-4}M. Then prepared series between methyl orange and another azo dye mixtures in these ratio (MO:Azo dye , 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8.) . In measuring flask 10 ml, take 1ml from mixture and 1ml of buffer then complete to mark by distilled water. All solutions for spectroscopic studies was analytical grade in the range (250 nm to 600nm) in acidic medium were recorded.

Preparation of Buffer:

In measuring flask 250ml, take one ply from Potassium Phthalate placed in beaker dissolved by distilled water then travel the mixture to measuring flask 250ml and complete to mark by distilled water.

RESULTS AND DISCUSSION

MO, **AYG** and **AYGG** are all unsaturated substitution derivates. Their molecular to structures contain **σ**-bond, **π**-bond and **n**-bond electrons. The electronic transitions (**σ⟶σ***) and (**n⟶σ***) need high energy, so, the absorption spectra are located at the ultraviolet-visible zone. The experiments showed that the **MO**, **AYGG** and **AYG** are conjugated systems almost had strong absorption band at λ_{max} 465 nm (21), 350 nm (20) and 375(20) nm in pure water in Ultraviolet –Visible zone, respectively. Although the Coulomb interactions of two oppositely charged particles are of fundamental importance, apart from electrostatic forces one should expect enhancement of the association at the expense of nonspecific and unsaturable Vander Waals interactions. In some cases, also, at the expense of saturable forces (hydrogen bonds, charge transfer) and capable of leading to the formation of stoichiometric compounds. Although some dyes can spontaneously aggregate in aqueous solution, the acid-base indicators we used in present study obey Beer's law in the employed concentration ranges.



Figure(2): Electronic Absorption Spectra for AYG- Methyl Orange System.

The acidity of solution pH is one of the most important parameters affected on the association between acid-base indicators. In **Figs. (2,3)**, shows the absorption spectra of Methyl Orange (electron acceptor) with different contents of 0.2 ,0.4,0.6 and 0.8 from another dyes (electron donor) in potassium phthalate buffer solutions. As a consequence of successive introduction of dye solution into the Methyl Orange solution, all the absorption maxima undergo hypochromicity and bathochromic shift to longer wavelength, λ_{max}, 485 nm.

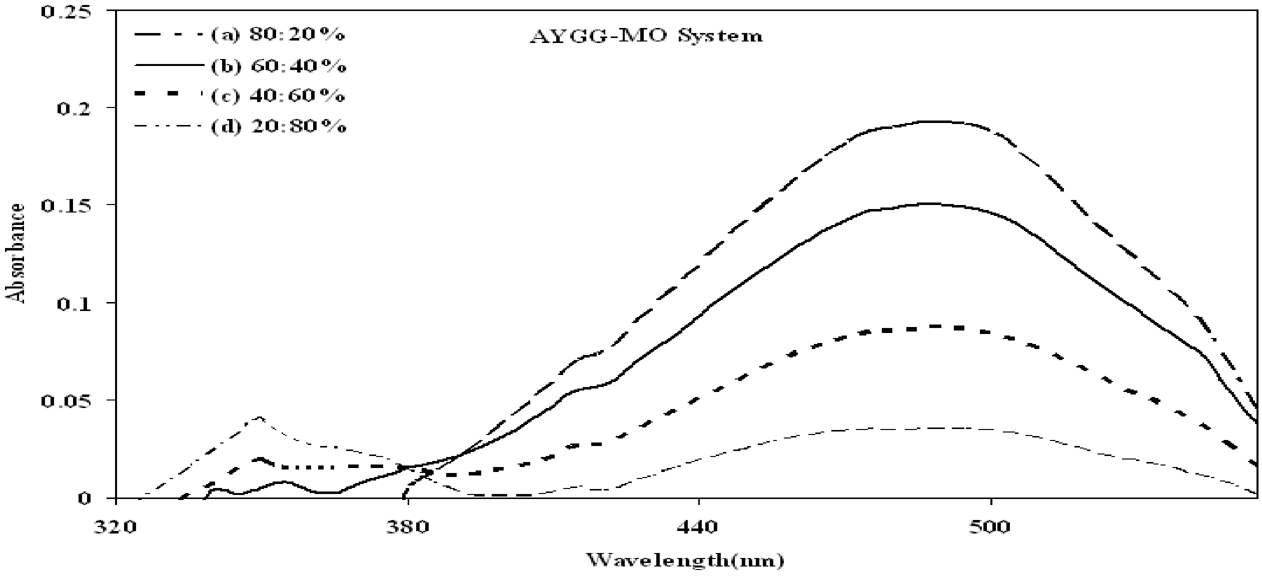


Figure (3): Electronic Absorption Spectra for AYGG- Methyl Orange System.

The spectra broadening compared to that of monomeric dye in pure water. According to the Kasha exciton theory, **J**-aggregates of azo dye - Methyl Orange molecules were formed, yielding a side-by-side or a slipped face-to-face stacking structure, **Fig.(4)**. The lack of isosbestic point, which may point to the presence in the system of associates with a different relationship between the stoichiometric coefficients (12), this supported by spectrum broadening indicate the formation of higher order dye aggregates and there is no simple monomer–dimer equilibrium, in addition to formation of hydrogen bonding between Methyl Orange and another dye. The aggregates might consist of the mixture of dimmers, trimmers or more higher aggregates instead of one single species. In addition, the bands at 350 and 380 nm disappeared this opposite to association between acid-base indicators in neutral medium (19) in previous study.

CONCULUSION

In this paper, the association behavior between Acid-Base indicators in buffered aqueous solution has been studied by **UV–Vis** spectroscopy at room temperature. The spectroscopic results show that association is formed evidenced by highly red shift and large hypo-chromic shift in absorbance signal upon addition of azo dye. The electronic absorption spectra represented by broadening bands and lack of isosbestic point that indicate of formation of higher order dye aggregates from the type **J**-aggregate.

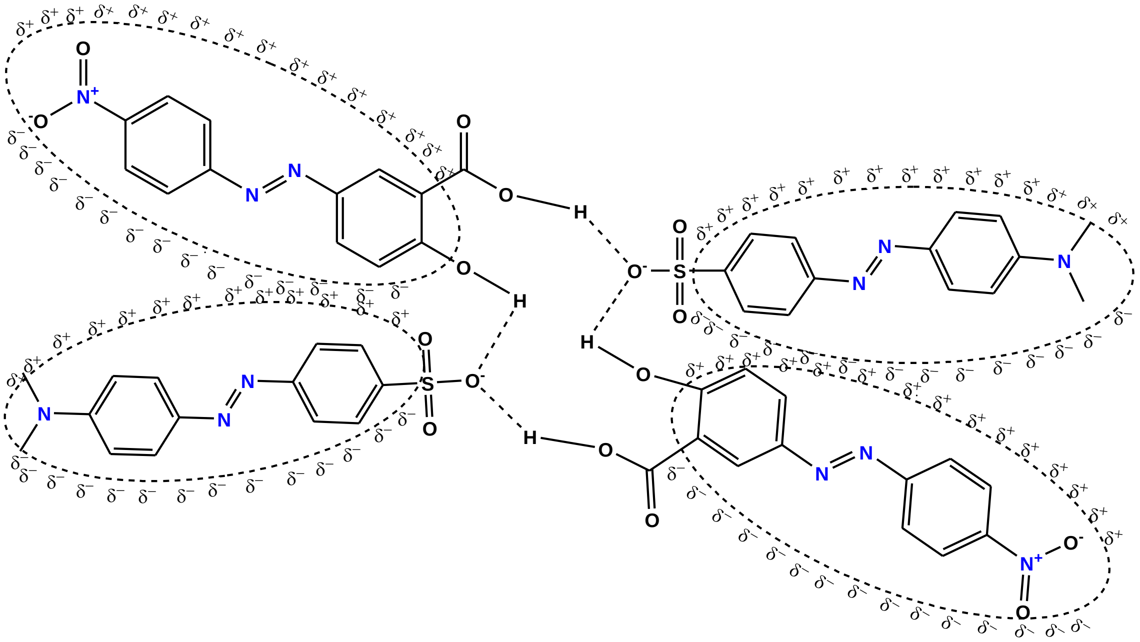


Figure (4): Mixture of dimmer exhibit an association between acid-base indicators face-to-face and side-by-side

RECOMMENDATIONS

The study recommends by the following: studying effect of solvent on the association constant between acid-base indicators by applied different techniques.

REFERENCE

1. Sun, W.; Han, J.; Li, Q. & Jiao, K.; *S. Afr. J. Chem.*, 60(2007)42–46.
2. Al Jebaly, A.; Hemdan, S. & Ali, F.; *J. Natu. Sci., Life & Appl. Sci.,* 1(4)(2017) 33-50.
3. Al Jebaly, A.; Hemdan, S. & Ali, F.; *J. Human. Sci.*, 39(2017) 1-14.
4. Eltaboni, F.; Hemdan, S. & Ali. F.; *Glob. Libyan J.,* 27(2017) 1-7.
5. Hestand, N. & Spano, F.; *Acc. Chem. Res.,* 50(2)(2017)341-350.
6. Bian, S.; He, J.; Li, L.; Kumar, J. & Tripathy, S.; *Adv. Mater.*, 12(2000) 1202–1205.
7. Eisfeld, A. & Briggs, J.; *Chem. Phys.,* 324(2006)376-384.
8. Refat, M.; El-Sayed, M.; Adam, A.; Saad, H. & Eldaroti, H.; *Inter. J. Electrochem. Sci.,* 8(3) (2013)4234–4259.
9. Zollinger, H.; *Color Chemistry, VCH, Weinheim*, (1991).
10. Chowdhury, A.; Wachsmann-Hogiu, S.; Bangal, P.; Raheem, I. & Peteanu, L; *J. Phys. Chem. B*, , *105* (48) (2001)12196–12201.
11. Murakami, K.*; Dyes Pigm.*, 53 (2002) 31–43.
12. Ishchenko, A. & Shapovalov, S.; *J. Appli. Spectrosc.*, 71(5) (2004) 605-629.
13. Mostafa, S.; El-Sadek, M. & Alla, E.; *J. Pharm. & Biomed. Anal.,* 28 (2002) 173–180.
14. El-Didamony, A.; *Spectrochim. Acta Part A,* 69 (2008) 770–775.
15. Sawunyama, P.; Jackson, M.; & Bailey*z*, G.; *J. Colloid & Interface Sci.*, 237 (2001) 153–157.
16. Safavi, A.; Abdollahi, H.; Maleki, N. & Zeinali, S.; *J. Colloid & Interface Sci.*, 322 (2008) 274–280.
17. Gehlen, M.; Ferreira, M. & Neumann, M.; *J. Photochem. & Photobio. A: Chem.,* 87 (1995) 55-60.
18. Karukstis, K.; Savin, D.; Loftus, C. & D'Angel, N.; *J. colloid & Interface Sci.,* 203 (1998) 157–163.
19. Hemdan, S.; Al Jebaly, A. & Ali, F.; *J. Human. Sci.*, 35 (2017) 1-10.
20. Masoud, M.; Elsamra R. & Hemdan, S.; *J. Serb. Chem. Soc.,* 82 (7-8) (2017) 1–14.
21. Masoud, M. & Hammud, H.; *Spectrochim. Acta Part A,* 57 (2001) 977–984.

دراسة سلوك الترابط بين أدلة الحامض والقاعدة في وسط حامضي باستخدام تقنية الأشعة المرئية

الملخص: دراسة سلوك الترابط بين أدلة الحامض والقاعدة في وجود وسط حامضي عند درجة حرارة الغرفة باستخدام تقنية التحليل الطيفي. النتائج أظهرت أن الترابط المتكون أثبت بوجود انحدار كبير إلى أطول طول موجى وانخفاض كبير وتدريجي في الامتصاص عند إضافة الصبغة الأخرى. الأطياف المرئية تميزت بانبساط القمم و غياب نقطة التقاطع لأطياف يدل على وجود ترابط بين أدلة الحامض والقاعدة من درجات الأعلى .

الكلمات المفتاحية: أدلة الحامض- القاعدة ، أطياف مرئية، محلول منظم ،غياب نقطة التقاطع، ترابط عالي.
