



Time, Concentration, Ionic Strength and Solvents affects on Electronic Absorption Spectra of Association between Acid-Base Indicators

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تأثير الزمن التركيز القوى الأيونية والمذيب على الاطياف المرئية لترباط بين دلائل الحامض والقاعدة

المخلص:

تمت دراسة الترابط بين أدلة الحامض والقاعدة باستخدام التحليل الطيفي. أظهرت النتائج وجود ترابط بين الدلائل في حجم عالي من الميثيل البرتقالي وهذا يتوافق مع ازاحة إلى طول موجي طويل 470 nm بالإضافة إلى وجود انخفاض كبير وتدرجي في الامتصاص عند إضافة الصبغة الأخرى مع ظهور قمم جديدة يعزز هذا الترابط. وجود قمم منبسطة ونقطة تقاطع يدل على وجود حالة اتزان بين أحادية-ثنائية الترابط في وسط متعادل. درجة الترابط تعتمد على تركيز الميثيل البرتقالي والمذيبات والقوى الأيونية للوسط.

الكلمات المفتاحية: أدلة الحامض والقاعدة، جهاز التحليل الطيفي، مذيبات عضوية، كلوريد صوديوم.

ABSTRACT

The association behavior between Acid-Base indicators in aqueous solution has been studied by UV-vis spectroscopy. The spectroscopic results show that association are formed evidenced by slightly red shift to $\lambda_{max} = 470\text{nm}$ and large hypo-chromic shift in absorbance signal upon addition of azo dye with creating new bands. Present of broad bands and isobestic point that indicate formation of simple dyes aggregate monomer-dimer equilibria in neutral media. The degree of association depends on the concentration of methyl orange, Co-solvents, and ionic strength of the medium.

Key Words: Organic Dyes (Acid-Base Indicators), Spectrophotometer, Miscible Organic Solvents, NaCl.



INTROUDUCTION

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⁽¹⁾ 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^(2,3). The aggregation of dyes in aqueous solution is of extreme importance in biological, colloid, photographic and analytical chemistry^(4,5).

Azo dyes as well known to form dimmers or higher order aggregates in aqueous solution depending on the dye structure and media properties⁽⁶⁾, the aggregation behavior of azo dye Orange I by the addition of polyethylene glycol (PEG) in aqueous solution has been studied by means of UV–vis spectroscopy. The spectroscopic results show that J-aggregates of Orange I are formed in presence of high volume fraction of PEG with low molecular weight (200, 400 and 600), evidenced by large red shifts of the absorption band. The degree of aggregation strongly depends on the PEG molecular weight and concentration, as well as the ionic strength of the solutions⁽⁷⁾.

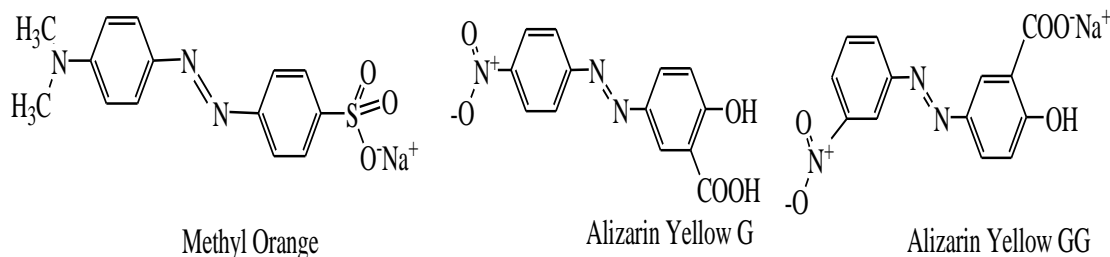
General trends in the development of investigations of ion associates, involving an ion of an organic dye, in aqueous solutions are considered. The contributions of different kinds of intermolecular interactions (Coulomb, Vander Waals, hydrophobic, etc.) that cause the association of ions were analyzed. The interrelationship between the characteristics of dyes (charge, structure, hydrophobic behavior, etc.) and the properties of ion associates (strength, geometry) is discussed⁽⁸⁾.

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⁽⁹⁻¹¹⁾. Interaction of Methyl Orange with different surfactants at different conditions was studied by spectrophotometric technique⁽¹²⁻¹⁴⁾.

EXPERIMENTAL

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]) see scheme(I). Were obtained from BDH Chemical LTD Poole England and sigma companies. These reagents used without further purification. Standard stock aqueous solution $1 \times 10^{-3} \text{M}$ from these dyes was prepared in de-ionized and CO_2 -free water and working solutions $1 \times 10^{-4} \text{M}$. 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.). All solution for spectroscopic studies was analytical grade in the range (250 nm to 600nm) in neutral medium were recorded by 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 °C. Effect of time, ionic strength, solvent, and change concentration of Methyl Orange on the interaction between dyes was studies.



Scheme (I): Molecular Structure of Ligands

RESULTS AND DISCUSSION

MO, AYG and AYG are all unsaturated substitution derivatives. Their molecular structures contain σ -bond, π -bond and n-bond electrons. The electronic transitions ($\sigma \rightarrow \sigma^*$) and ($n \rightarrow \sigma^*$) need high energy, so, the absorption spectra are located at the ultraviolet-visible zone. The experiments showed that the MO, AYG and AYG are conjugated systems almost had strong absorption band at λ_{max} 465 nm⁽¹⁵⁾, 350 nm and 375 nm in 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.

In Figs.(1,2), When the two dyes (electron donor) fading to Methyl Orange (electron acceptor) showed slightly red shift in position of the electronic absorption band at $\lambda_{max} = 465$ nm to longer wavelength $\lambda_{max} = 470$ nm, it seen for a mixture (a) 80% of Methyl Orange it is observed has high absorbance value. It is obvious that association of azo dye molecules occur with increase in concentration. This phenomena can increase the solubility of Methyl Orange - azo dye aggregate. However, it is found hypo-chromic shift observed gradual decrease in intensity of charge transfer band. With creating of new absorption peaks at (295, 365 nm), (290, 380 nm) of MO-AYGG and of MO-AYG, which were attributed to formation of MO-Azo dye association (ion-pair complex) as final product. The absorption peak of the complex formed was apparently different from that of Methyl Orange because the wavelengths corresponding to both absorbance maxima were different. Assumption charge transfer complex is bonded by producing forces from nonbonding resonance causes transfer of electrons from type to another type.

A well-defined one-isobestic point is formed at ~ 380 nm and ~ 400 nm for two systems, this indicates on the present monomer-dimer association equilibria state.

Further, the increase of absorbance signals at λ_{max} 365nm and λ_{max} 380nm were support the azo dyes association of the type heterogeneous association are based on different signs and different structure, the stoichiometry of associations based on this principle is 1:1⁽⁸⁾. The broad band exhibited at λ_{max} = 470 nm for 20%MO:80% azo dye mixture this generalization of broaden the notions on an electrostatic interaction in solutions, so, strong hydrogen bonding^(2, 3). In Fig (2), the mixture b gave very broad band at λ = 395nm because strong charge transfer based on nature type and position of substituent. This behavior is attributed to the position of the (-NO₂) group at the aryl ring, so, present of p-NO₂ group facilities the C.T rather than that of m-NO₂. The association constant K_{ass} , at λ_{max} = 470 nm for two systems MO-AYGG and MO-AYG are $(1.65 \pm 0.15) \times 10^3$ l/mol , $(1.27 \pm 0.2) \times 10^3$ l/mol However, the presence of electron withdrawing group (-NO₂) in para position will weak the bonding O-H in phenolic group lead to the lower k_{ass} value of MO-AYG system.

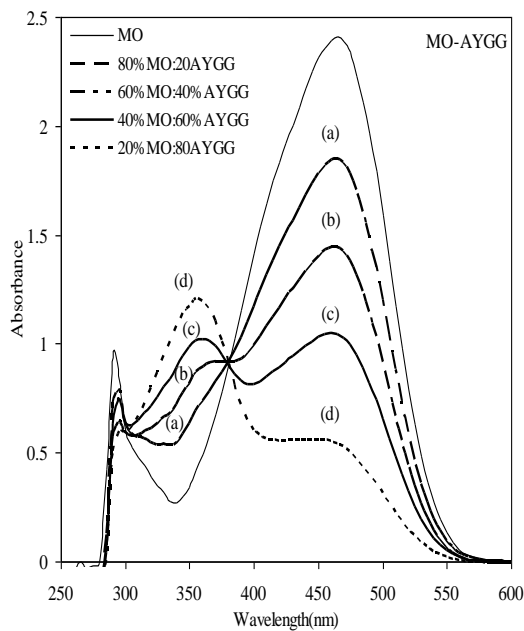


Fig.1. Electronic absorption spectra of interaction between Methyl Orange & Alizarine Yellow GG

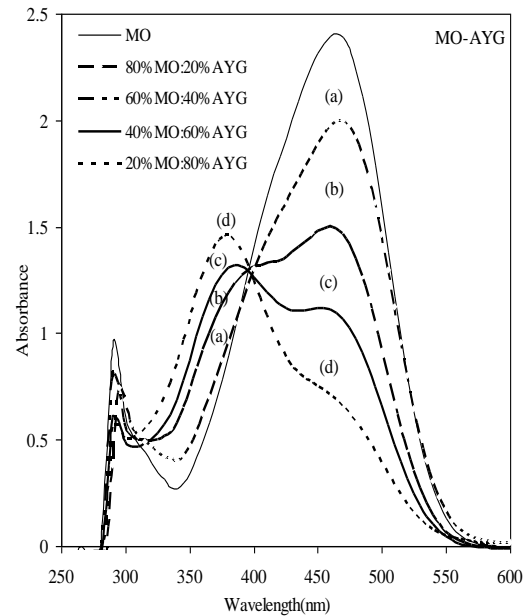


Fig.2. Electronic absorption spectra of interaction between Methyl Orange & Alizarine Yellow G

Calibration Curve for Two Azo Dye

At the optimum conditions, a calibration curve was obtained at $\lambda_{max} = 470\text{nm}$, the increasing of ratio of Methyl Orange for two systems causes increasing of the intensity of absorbance, as the results show the best correlation between concentration of azo dye as mole fraction in two systems and absorbance linear relationship with ($n = 4$) was found. The results obey Beer's Law, show in figs (3, 4). Regression equation, slope, intercept and correlation coefficient determined for each system and detection limits (3 δ) obtained for the absorbance were found to be (1.608, 1.601), respectively. The correlation coefficients were 0.9972, 0.9965 indicating the good linearity.

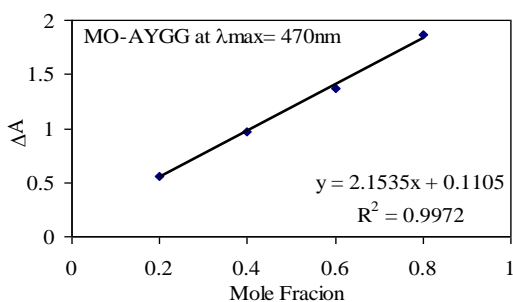


Fig3. Relation between conc. of AYGG & Abs.

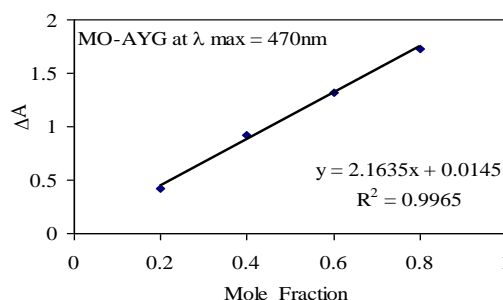


Fig4. Relation between conc. of AYG & Abs

Effect of Concentration of Methyl Orange

The effect of the Methyl Orange (electron acceptor) concentration on the intensity of the color developed at the selected wavelength $\lambda_{max} = 470\text{nm}$ and constant electron donor reagent concentration was tested using different volumes of methyl orange (0.2–0.8ml). It was observed that 0.8ml of ($0.3 \times 10^{-4} \sim 1 \times 10^{-4}\text{M}$) MO was necessary for maximum color development of the interaction, which indicated that the binding reaction had reached its equilibrium. Further, the degree of association: favors concentrated solution, while dilution obstructs it, not only in water but also in non-aqueous media. After this volume, the absorbance decreased gradually by increasing the volume of the reagent. Therefore, a concentration of $1 \times 10^{-4}\text{M}$ of Methyl Orange was recommended for use in this paper.

Effect of Time and Stability:

Under room temperature all the solutions preparation was equilibrated for 24 h, 48 h and 72h in dark before measurements of spectra. After period time don't occur red shift or blue shift in the position of λ_{max} , So, it is found some very little change in intensity of absorbance is below ≤ 0.096 this indicative on the more stability of interaction between MO-Azo dye for longer time >72 hours. Moreover, the electronic absorption spectra it is obtained after 72 h, show in Figs (1,2). The relationship between effect of time and percent of intensity of absorbance, in Figs (5,6).

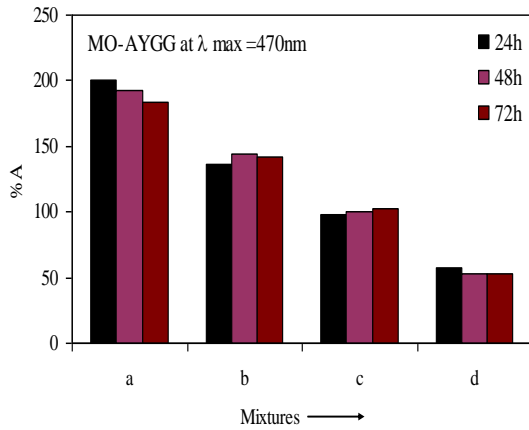


Fig.5. Effect of time on MO-AYGG system

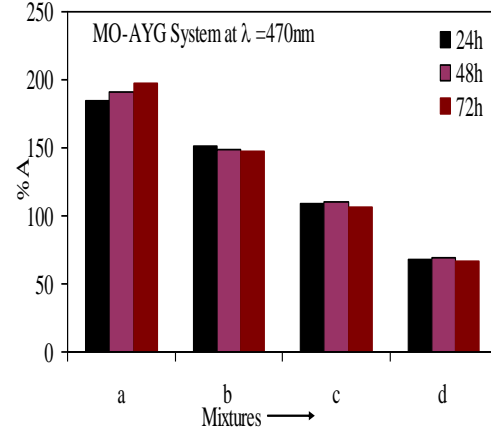


Fig.6. Effect of time on MO-AYG system

Effect of Ionic Strength:

At the optimum concentration, the effect of ionic strength on the intensity of UV-Visible spectra for two systems was investigated with NaCl in a range of 0.025 to 0.22 mol/l. The results demonstrate that the increasing of concentration of NaCl ΔA is decrease gradually, which indicated that the interaction of methyl orange with azo dye was mainly caused by electrostatic attraction⁽¹⁶⁾. The increase of Na^+ concentration caused an increasing electrostatic shielding effect and thereby decreased the formation of MO-AYGG or AYG complex resulting in the decrease of the absorbance signal. Moreover, For MO-AYGG and MO-AYG, systems it found slightly blue shifted to shorter wavelength about $\sim 5\text{nm}$, $\sim 10\text{nm}$, respectively. In addition, hypo chromic shift in absorption maxima peak upon addition of a salt indicating the disaggregation of the dyes. We can see that λ_{max} is both dependent on the azo dye volume fractions and ionic strength, the degree of association is decreased as well as the ionic strength increasing and was in agreement with the Debye-Hückel equation. Therefore, the association reaction should be under a low concentration of ionic strength condition. See Figs (7, 8).

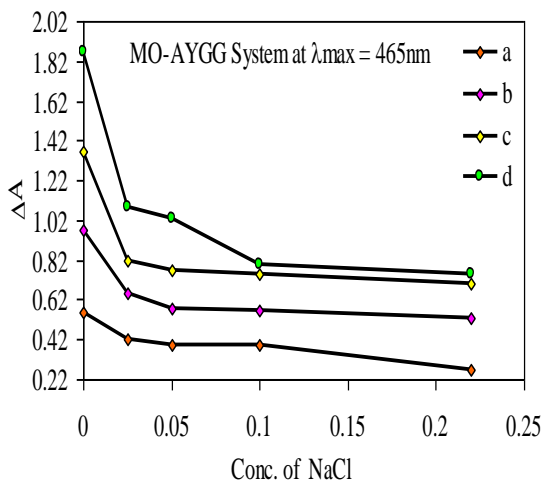


Fig7. Effect of ionic strength on MO-AYGG system.

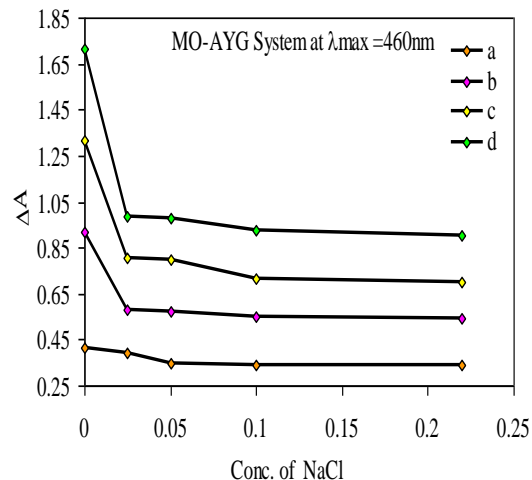


Fig8. Effect of ionic strength on MO-AYG system.

Effect of Solvents

The UV–vis absorption spectra of dyes may be influenced by the surrounding medium and that solvents can bring about changes in the position, intensity and shape of absorption bands ⁽¹⁷⁾. The corresponding bathochromic (or red) shift, with increasing solvent polarity, is termed “solvatochromism” ⁽¹⁸⁾. For the $\pi \rightarrow \pi^*$ transition, the λ_{max} shifts to shorter wavelength when the polarity of solvent is decreased.

The importance of hydrophobic interactions is supported by the fact that addition of organic solvent to water reduces the dye association. The long-range electrical forces as well as short range attractive forces are responsible for dye association forms ⁽¹⁹⁾. Association reaction is dependent on the dielectric constant of the solvent, so, decreasing of dielectric constant of different aqua-organic solvent causes to reduce the stability of association reaction. Some properties of solvent are given in, table (1).

The effectiveness of association depends on the nature of a solvent. However, in a polar solvent the intensity of such an association is smaller than in water. For heterogeneous associates, thus, additions of polar organic solvent to an aqueous solution containing the associate, lead to decrease the interaction

To probe the solvent effect on the electronic absorption spectra of MO-AYGG and MO-AYG systems are dilute to 50 % (v/v) by using different miscible organic solvents (Co-solvent). As for example MO with AYG of composition has some general trends; upon the addition of miscible organic solvent with different polarity and structure 1, 4-Dioxane, Propanol, Ethanol and Methanol.

- The intensity of absorbance is decreased gradually by addition of organic solvent for each mixture in the order $d < c < b < a$ cause a decrease in the strength of association.
- It is found hypso-chromic (or blue) shift about $\Delta\lambda = 95\text{nm}$ to shorter wavelength the colour changed from orange to deep yellow, as result increase in order of



(organic solvent - water) Methanol-Water < Ethanol-Water < Propanol-Water < 1, 4-Dioxane-Water, this order in accordance with decreasing of dielectric constant of organic solvent. In addition, the polarity of solution decreased with decreasing of polarity of solvent compared with pure water, the results appear in the table (2).

- An increasing of no. of -CH₂- group in Co-solvent relative to increase of hydrophobic interaction and stronger charge density, as well as causes shift maximum absorption band to shorter wavelength, as result the association of dyes is reduced. See figs (9, 10) MO-AYG in Ethanol and Propanol as for example.

CONCLUSION

In this paper, we report that the association between Methyl Orange can be induced by addition of volume from another azo dye in aqueous solutions; the association is reflected by strong hypo chromic shift of the maximum absorption band and slightly red shift to 470nm. The association of the azo day is strongly affected by the concentration of Methyl Orange, ionic strength and Co- solvent the results show interaction is dependent on the polarity and dielectric constant of medium in this order Methanol-Water < Ethanol-Water < Propanol-Water < 1,4-Dioxane-Water.

Table (1): Properties of Selected Solvents.

<u>Solvent</u>	<u>n</u>	<u>D</u>	<u>δ</u>	<u>α</u>	<u>β</u>	<u>π*</u>
H ₂ O	1.333	78.5	23.4	1.17	0.47	1.09
Methanol	1.329	32.6	14.5	0.93	0.62	0.6
Ethanol	1.361	24.3	12.7	0.83	0.77	0.54
Propanol	1.385	20.1	11.9	0.78	0.85	0.52
1,4-Dioxane	1.375	1.9	10.1	0.00	0.37	0.55

Table (2): Result of effects of organic solvents on interaction of MO-AYGG system.

<u>Solvents</u>	<u>λ_{max}(nm)</u>	<u>Absorbance</u>			
		<u>(a)</u>	<u>(b)</u>	<u>(c)</u>	<u>(d)</u>
Methanol	455	0.956	0.713	0.606	0.315
Ethanol	450	0.988	0.787	0.657	0.308
Propanol	430	1.032	0.858	0.597	0.433
1,4-Dioxane	440-370	1.066	0.830	0.576	0.671

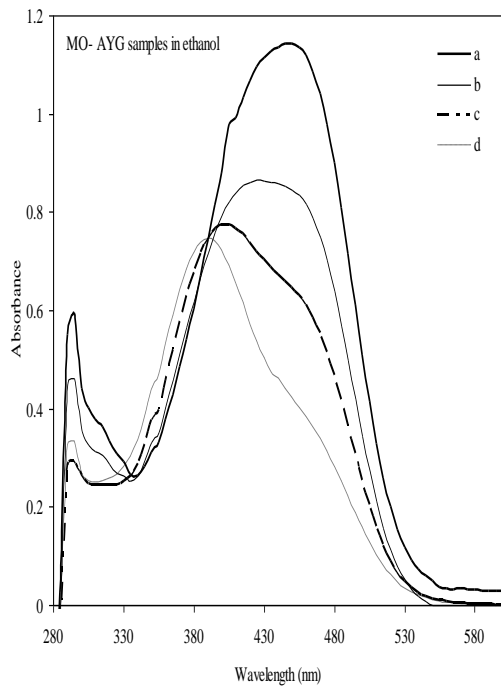


Fig (9) Effect of Ethanol on the electronic Absorption spectra of MO-AYG system

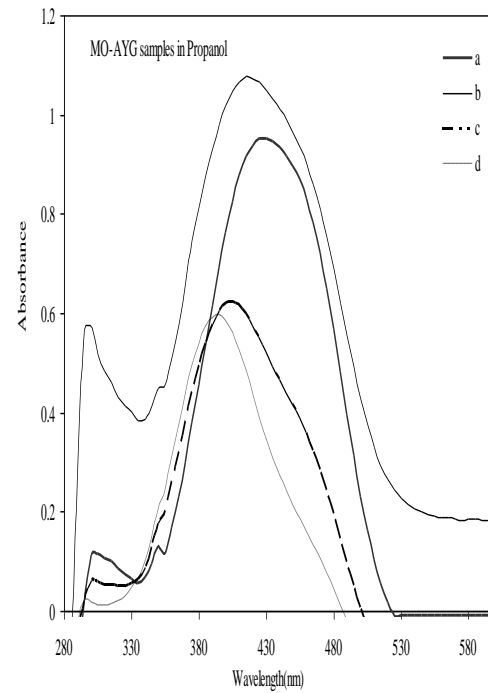


Fig (10) Effect of Propanol on the electronic Absorption spectra of MO-AYG system7



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