

العدد السابع والعشرون - 02 / سبتمبر ( 2017 )

## Spectral Parameters of Methyl Orange Interacted with Ethanol-Water Mixtures

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### Abstract

The UV-visible absorption spectra of 4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt, also known as methyl orange (MO), were taken in binary solvent mixture consisted of different gradients from ethanol and water, with different polarity and solvation size, in order to examine the binary solvent-MO interaction. The measured parameters were found to strongly depend on the clustering of ethanol-water molecules.

**Keywords:** UV-visible spectroscopy, Water-ethanol mixture, Spectral parameters, Methyl orange

### المعاملات الطيفية لصبغة الميثيل البرتقالية المذابة في خليط من الكحول الايثيلي والماء

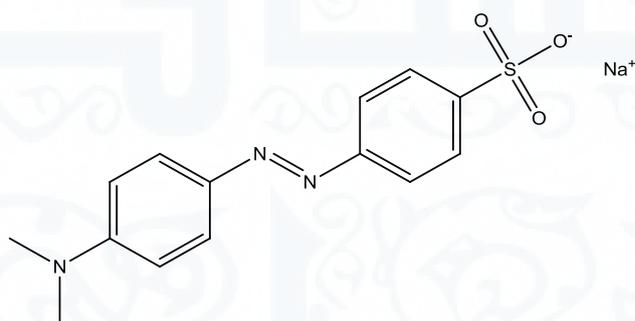
#### الملخص:

الأطياف فوق بنفسجية والمرئية لمح 4-ثنائي ميثيل أمينو أزو بنزين-4-ملح الصوديوم لحمض السلفونيك، والمعروفة كذلك باسم صبغة الميثيل البرتقالية، تم أخذها في مذيب مختلط يحتوي على نسب مختلفة من الايثانول والماء، حيث كانت كل من قطبية المذيب المختلط وحجم الاحاطة مختلفتين لغرض اختبار تأثيرهما على ارتباط الصبغة مع المذيب. وجد أن المعاملات المقاسة تعتمد بدرجة كبيرة على تجمع جزيئات الايثانول والماء.

**الكلمات المفتاحية:** مطياف الأشعة فوق بنفسجية والمرئية، مخلوط الكحول الايثيلي والماء، المعاملات الطيفية، الميثيل البرتقالي.

## Introduction

Ethanol-water mixtures have been widely examined by chemists and biologists because of its application in several areas such as biofuels, protein aggregation, and pharmaceutical industry (Kurihara-Bergstrom, Knutson, DeNoble, & Goates, 1990; Dixit, Crain, Poon, Finney, & Soper, 2002; Hoogenboom, Thijs, Wouters, Hoepfener, & Schubert, 2008; Ghoraiishi, Hawk, Phani, Khan, & Thundat, 2016). Ethanol-water mixtures enhance the solubility of hydrophobics in aqueous system and accordingly, these mixtures play an important role in the investigation of stability hydrophobic solution and protein folding (Pratt & Chandler, 1980; Dixit, Soper, Finney, & Crain, 2002; Ghoraiishi, Hawk, Phani, Khan, & Thundat, 2016), where solute-solute, solvent-solvent and solvent-solute interactions govern such study. The polarity effect of solvent on the absorption spectra of the methyl orange (MO) and similarly structured compounds have been studied by UV spectroscopy (Masoud & Hammud, 2001). In this work, we examine the effect of ethanol-water composition on the spectral parameters of MO dye in the ultraviolet and visible regions where this compound absorbs light because of extensive conjugation of the azo moiety with the aromatic rings. The electronic spectra of MO in different composition of ethanol-water solvents have been analyzed using UV-visible spectroscopy technique. The structure of the MO is depicted below:



**Figure 1. Methyl Orange, 4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt.**

UV-visible spectroscopy is a simple technique that can be used to investigate dye-solvent interaction. Spectroscopic analysis of dye-solvent system has been the area of much interest (Mahmood, Hussain, & Aminuddin, 2001). Methyl orange dye is the topic of discussion in this paper, this study is important in understanding of the removal of methyl orange dye from aqueous solution (Haldorai & Shim, 2014). Since the UV-visible spectroscopic data can be related to the dye solubility in different environments, additionally could be also useful in probing dye-solvent size via investigating molar absorptivity. The molar absorptivity is controlled by the size of solvated dye (Mahmood, Hussain, & Aminuddin, 2001).

The mathematical expression,  $\log I_0/I_t = \epsilon bC$  is well known as Beer-Lambert law, where  $I_0$  is the intensity of incident light,  $I_t$  is the intensity of transmitted light,  $\epsilon$  is the molar absorptivity,  $b$  is the length of sample cell (cm), and  $C$  is the molar solubility of dye (Mahmood, Hussain, & Aminuddin, 2001).

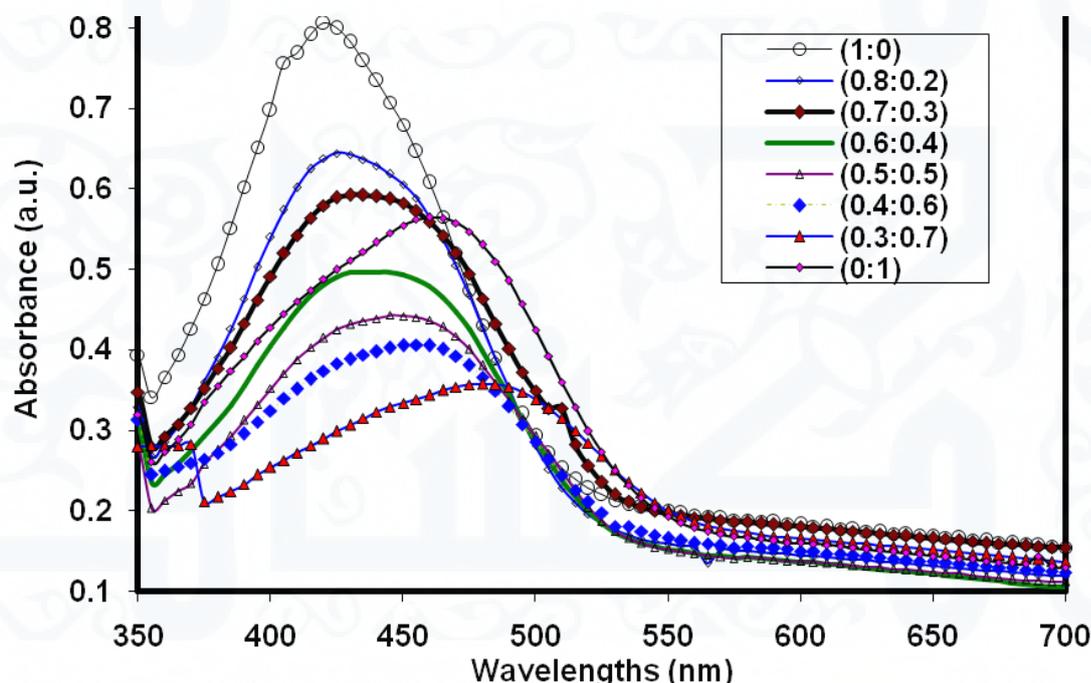
In this work, we aim to re-examine the effect of ethanol-water mixtures on the spectral behaviour of methyl orange dye.

## Experimental

Methyl Orange (MO), 4-dimethylaminoazobenzene-4'-sulfonic acid sodium salt was obtained from BDH Chemical LTD Poole England, as sodium salt. A stock aqueous solution  $1 \times 10^{-5} \text{M}$  of the Methyl Orange was prepared in ethanol. Then series of Methyl Orange solutions were prepared by adding doubly distilled water in these ratios (Ethanol: Water, 1:0, 0.8:0.2, 0.7:0.3, 0.6:0.4, 0.5:0.5, 0.4:0.6, 0.3:0.7, 0.2:0.8, 0:1). MO and ethanol were in analytical grade. The spectroscopy measurement was carried out by measuring the absorbance at maximum wavelength after scanning in the range of 350 to 700 nm.

## Results and discussion

The absorption spectrum of methyl orange shows a typical MO band peaked at 425 nm in ethanol solvent (Figure 2). This band is assigned to the individual monomeric dye species in the studied concentration. It can be noted that the band shifted to longer wavelengths with increasing the amount of water in ethanol-water mixture. The large shift in band to longer wavelengths for MO could be because of an increase in mixture polarity. The polarity increase lead to further stabilization of the excited state than that of the ground state (Lakowicz, 2006). This proposes that the absorption peaks obtained are owing to  $\pi-\pi^*$  electronic transition (Masoud&Hammud, 2001).



**Figure 2. Absorbance of MO as a function of wavelengths at different ethanol fractions in aqueous solution.**

The wavelength of maximum absorbance ( $\lambda_{\text{max}}$ ) picked up from MO spectra in Figure 2, is displayed as a function of ethanol-water fractions (Figure 3). A marked decline in  $\lambda_{\text{max}}$  values (from 465 nm to 420 nm) was observed when the fraction of ethanol increased up to 1, this decrease in  $\lambda_{\text{max}}$  might be as a result of a decrease in ethanol-water mixture polarity, since ethanol is much less polar than water. The polarity decrease, because of adding more ethanol

العدد السابع والعشرون - 02 / سبتمبر ( 2017 )

in the binary solvent, caused stabilization of the excited state than that of the ground state. This suggests that the absorption peaks obtained will be shifted to shorter wavelengths.

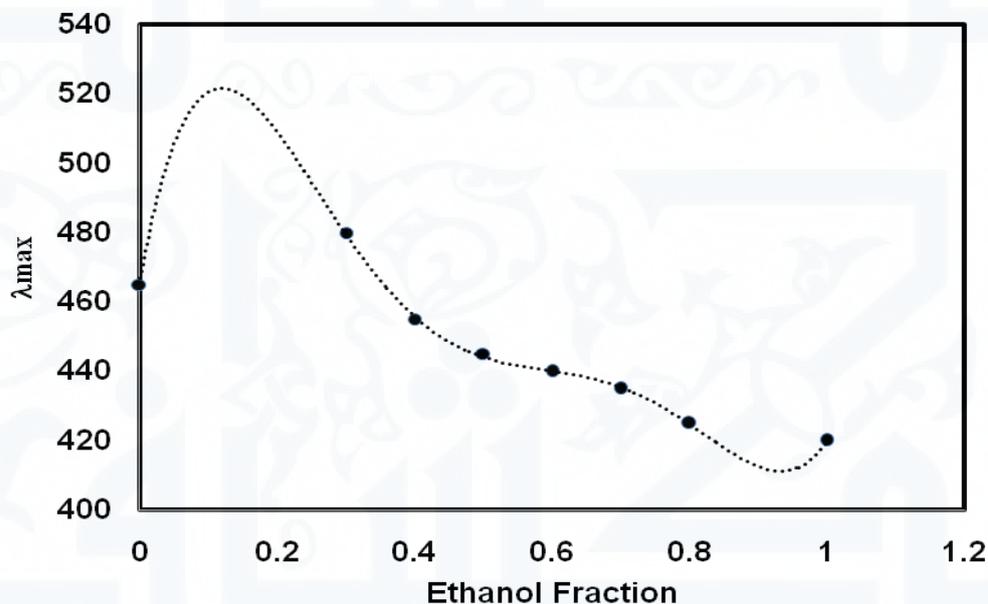


Figure 3. Wavelengths maxima of MO at different ethanol fractions in aqueous solution.

Figure 4 represents the relationship between the absorbance and ethanol fraction in binary solvent, as it can be observed adding extra ethanol in the mixture was a combined with a gradual increase in the MO absorbance. This could be attributed to the fact that the methyl orange salt is highly soluble in organic solvents but relatively insoluble in water (Brodie, Udenfriend, Dill, 1947).

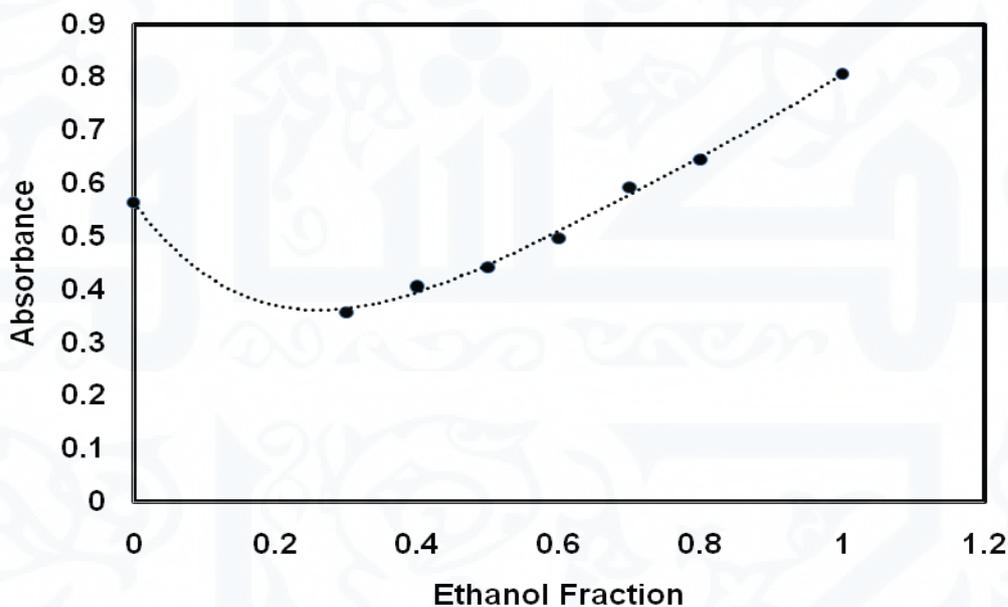
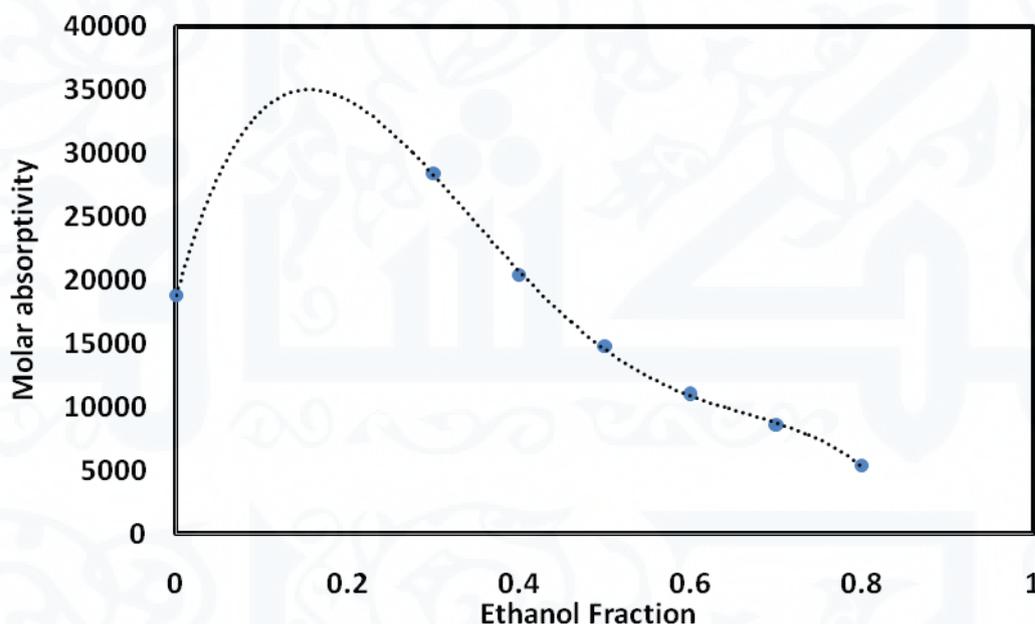


Figure 4. Absorbance of MO at different ethanol fractions in aqueous solution.

### العدد السابع والعشرون - 02 / سبتمبر ( 2017 )

The dependence of molar absorptivity on the fraction of ethanol is displayed in Figure 5. Increase ethanol fraction caused in decrease in molar absorptivity values. This decline in molar absorptivity could be credited to the fact that molar absorptivity is controlled by the solvation size of dye, as it was explained in above section the MO is more solvated in ethanol than water, this means that the hydrodynamic size of MO surrounded by ethanol is bigger than that bounded by water molecules, as a result decrease in molar absorptivity is recorded when MO-solvated becoming bigger in size.



**Figure 5. Molar absorptivity of MO at different ethanol fractions in aqueous solution.**

### Conclusion

We have investigated the effect of ethanol-water mixtures on the spectral parameters of MO by using UV-vis spectroscopy. This technique offers a means to study and understand polarity and solvation size dependences on molecular absorbance and its related parameters. It was found that the  $\lambda_{\max}$  shifted to longer wavelengths with increasing the fraction of water in ethanol-water mixture. This shift was attributed the increase in mixture polarity. While adding extra ethanol was followed by an increase in the MO absorbance, which was ascribed to increase MO solubility in ethanol. The increase of solubility lead to increase in solvation size as a result decrease in molar absorptivity.

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