

Solvatochromism and Preferential Solvation of Methyl Orange and Methylene Blue within Water + Ethanol Mixture

Abhra Sarkar

Assistant Professor, Department of Chemistry
Gurudas College, University of Calcutta
1/1, Suren Sarkar Road, Narikeldanga,
Kolkata-700054, India

ABSTRACT

The importance of the solvent medium in any type of chemical reaction is beyond any question. The rate, equilibrium of a chemical reaction as well as the position, intensity of absorption band in UV-Vis and other similar spectroscopies are significantly dependent on the solvents. The drawbacks or limitations of any lone solvent is sometimes complemented by another solvent(s); mixture of the two or more solvents enhances or enriches some of the physicochemical properties substantially. Significant changes in position, intensity and shape of the absorption bands obtained from any solute (probes) with the solvent polarity are termed as solvatochromic shifts and the property is called 'Solvatochromism'. These solvatochromic probes are quite useful in investigating the solvation behaviour of an analyte or studying physicochemical properties in the cybotactic region that is first solvation shell of any compound. Our present work is focused on the solvatochromic behaviour of dyes like methyl orange (MO) and methylene blue (MB) within water and ethanol mixture as well as their preferential solvation property to find any environmental difference between bulk of the solvent with the solvation sphere of the probe. For both the probes we found significant positive solvatochromism and preferential solvation of the probes by polar water rather than less polar ethanol.

KEYWORDS: Solvatochromism, Solvent mixture, Preferential solvation, Methyl orange, Methylene blue.

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I. INTRODUCTION

The medium surrounding chemical compounds may bring about changes in their UV-Visible or near IR absorption or fluorescence spectrum. These alterations can be in different forms like change in position, intensity and shape of the absorption bands and are termed as solvatochromic shifts and the property is referred to as 'Solvatochromism' by Hantzsch [1]. The genesis of solvatochromism is supposed to be due to variations of chemical structures and physical properties of the solvent molecules and the chromophore. Nonetheless, this results through various intermolecular solute-solvent interactions in equilibrium ground and Frank-Condon excited state [2]. These solvatochromic probes are quite useful for investigating the solvation behaviour of an analyte or studying physicochemical properties in the cybotactic region that is first solvation shell of any compound. Significant solvatochromic shifts arise since solute-solvent interaction cause changes in solvation energy of the ground and the excited states. Often, these sensitive probes are the sole medium of studying the structure binding sites and dynamics of lipid layers, carrier proteins, and other naturally occurring bio-membranes on a molecular microscopic level. Thus, these probes afford us invaluable information regarding solvation within any solvent or solvent mixture. Our present work is focused on the solvatochromic behaviour of dyes like methyl orange and methylene blue within water and ethanol mixture which will be helpful in predicting the nature of solvation of several solutes within the above-mentioned solvent mixture.

Dyes are organic substances which are used to impart colour of a substance. They have been used in several sectors like industrial, scientific and technological to show their excellent applicability as colourant of substances like textiles, plastics, cosmetics, photonics, for DNA protein recognition and nonlinear optical devices etc. [3-9]. Among the dyes most frequently used are azo dyes having $R_1-N=N-R_2$ functional group which frequently absorbs visible light due to its conjugated system. A good example is Methyl Orange (MO).

In order to study different modes of interactions between organic anions with proteins, synthetic polymers, polyelectrolytes and surfactants in aqueous solution, Methyl orange (MO) has been used as a probe frequently [10-12]. These interactions obviously are accompanied by spectral changes which indicates the

solvatochromic behaviour of methyl orange. The findings that some hydrophobic dyes undergo specific solvation changes in mixed aqueous solvents that are related to changes in solvent structure was the key feature for making the detailed spectral analysis of MO in pure hydrogen bond donating solvents like ethanol-water.

Methylene Blue (MB) is another important dye used widely in textile, pharmaceutical, medical or surgical etc. purposes [13-15]. Though they have some detrimental effects on human body, their superior mode of activities made them inevitable for different applications mentioned earlier. Since aggregation and temperature have a significant effect on the visible spectra of methylene blue in aqueous solution, here we will consider that the dye remains in monomer state and the temperature will have a little effect on the spectroscopic behaviour of the dye [16]. Since water-ethanol based mixed solvent system has been very widely explored and used by scientists specifically chemists and biologists because of its application covered several areas such as biofuels, protein aggregation and pharmaceutical industry, we have chosen this solvent mixture as our subject of investigation [17-18].

II. MATERIALS AND METHOD

All the reagents used were of analytical grade, purchased from Merck (Methyl Orange: Sodium 4-[[4-(dimethylamino)phenyl]diazinyl]benzene-1-sulfonate; 99.9 % pure), Qualigen Fine Chemicals (Methylene Blue: [7-(dimethylamino)phenothiazin-3-ylidene]-dimethylazaniumchloridetrihydrate, 99.9 % pure) and Changshu Hangsheng Fine Chemical (Ethanol, 99.9 % pure). Double distilled deionized water was used in all experiments. All glass wares used were of Borosil. The UV-Vis double beam spectrophotometer with variable bandwidth (Systronics, Model No.-AU-2702) was used to measure the molecular spectral response using quartz cells.

The probe methyl orange stock solution of 1×10^{-5} M was prepared in ethanol taking appropriate amount of the solid probe by weight with the aid of a Sartorius (Model No-BS 224 S) electronic balance with a precision of ± 0.1 mg and stored at 4 ± 1 °C in a suitable 40 mL amber-coloured vial. Required amount of stock was taken in the 1 cm² path length quartz cuvette and the ethanol was evaporated by passing dry air. Then the required solutions with different proportions were prepared by taking appropriate volume (by weight) of water and ethanol to produce requisite mole fraction of ethanol in water or vice versa. Similar procedure was followed for methylene blue. For all the spectral responses appropriate blanks were subtracted before data analysis. All measurements were taken thrice and averaged. All data were analysed and plotted with MS Excel software.

III. RESULT AND DISCUSSION

3.1. Behavior of Methyl Orange dye. The absorption spectra within the range 300-650 nm at ambient condition (~ 25 °C) with an optimized concentration of the dye $\sim 10^{-5}$ M in the aqueous solution or ethanolic solution were measured. Spectral response up to 1.0 mole fraction of ethanol (i.e., pure ethanol) in water starting from 0.0 mole fraction of ethanol in water (i.e., pure water) were recorded. By virtue, the longest wavelength UV-Vis absorption bands are shifted to the largest extent with solvent polarity. Here the most prominent peak of the MO dye was found to be at the region near 420-470 nm. The spectral response λ_{\max} of MO in neat water was recorded at 464 nm. This agrees well with some earlier works [19-21]. It was observed that the dye showed a very significant solvatochromic behavior within 0.0 to 1.0 mole fraction of ethanol in water exhibiting a hypsochromic shift of the λ_{\max} from 464 nm to 420 nm respectively indicating the effect of hydrogen bond donating (HBD) acidity of the solvent; hydrogen-bond donating solvents stabilize the ground state more compared to the excited state. Interestingly, it was seen that, mixing of 0.1 mole fraction of ethanol in water there was a bathochromic shift by almost 3 nm. This might be caused by the formation of H-bonding between the water with the N-atom of azo group [22]. After the initial red shift, a regular hypsochromic shift was seen and ultimately at 1.0 mole fraction of ethanol in water i.e., in neat ethanol it showed λ_{\max} at 420 nm. The shift in λ_{\max} is due to difference in stabilization of ground and excited states with the variation of polarity of the solvent medium and thus causes alteration in energy gaps between these electronic states. Primary reason behind the bathochromic shift may be out-of-plane twisting of the dye structure in solvent. The spectral response (i.e., λ_{\max}) might be conformed with two overlapping bands and the low-frequency bands arose from a solvate comprising an intermolecular H-bonding between water and the N- of azo-group of the dye. To add to our exquisite observation, there was a steeper shift in the λ_{\max} values near the ethanol-rich region. The straight line joining the two terminal points represents the mole-fraction weighted response predicted from simple mixing considerations.

On the other way round, we may say that by addition of only 0.1 or 0.2 mole fraction of water to pure ethanol in the bulk of the solution we may achieve a huge bathochromic shift in MO spectral response indicating a vast drop in the transition energy. This drop is very significant as transition energy is inversely proportional to the polarity and HBD acidity of the solvent milieu in the cybotactic region (microenvironment of the probe molecules) here. Therefore, obviously it appears that, with addition of minimum amount of water to ethanol we may achieve a dramatic enhancement of polarity as well as HBD acidity in the cybotactic region. This result is very inspiring as far as enhancing solubilizing ability of various solutes in the solvent mixture is concerned and

notably, this is a strong indicator of the solute-solvent interaction rather than mere solvent-solvent interaction. Here it is to be mentioned that most of the spectroscopic probe techniques neglect solvent-solvent interactions.

The polarity of the bulk solvent is inversely proportional to the molar transition energy (E_T) in Kcal mole⁻¹ which is calculated by the following relation (equation 1):

$$E_T = \frac{hcN_A}{\lambda} \quad (1)$$

Where h is Plank's constant, c is the speed of light and N_A is Avogadro's number. Putting all the known constant values the equation becomes:

$$E_T = \frac{28591.5}{\lambda} \quad (2)$$

After calculating all the values of E_T , we plotted E_T vs. mole fraction of water in ethanol and arrived to the observation that, with decrease in bulk solvent polarity the E_T values increased or vice versa (**Fig. 1**). It is much easier to conceive this plot rather than the wavelength plot. From the plot it is observed that with increase in $x_{\text{etoh, bulk}}$ in water the E_T values increases indicating the decrease in polarity in the cybotactic region of MO with decrease in dielectric of the solvent milieu. There is a sharp increase in E_T value at $x_{\text{etoh, bulk}} \sim 0.8$ to 1.0. From this observation we may conclude that the probe MO is being preferentially solvated by the more polar water rather than less polar ethanol (discussed later). Again, since MO is showing a hypsochromic shift with decreasing polarity of the solvent milieu, MO appears to be a positive solvatochromic dye by virtue of its structure and properties. In general, dye molecules show solvatochromism when there is a significant change in their permanent dipole moment upon excitation. If in the excited state the dipole moment of the dye becomes larger than in its ground state ($\mu_g < \mu_e$) then, it is quite natural that we should observe positive solvatochromism [23].

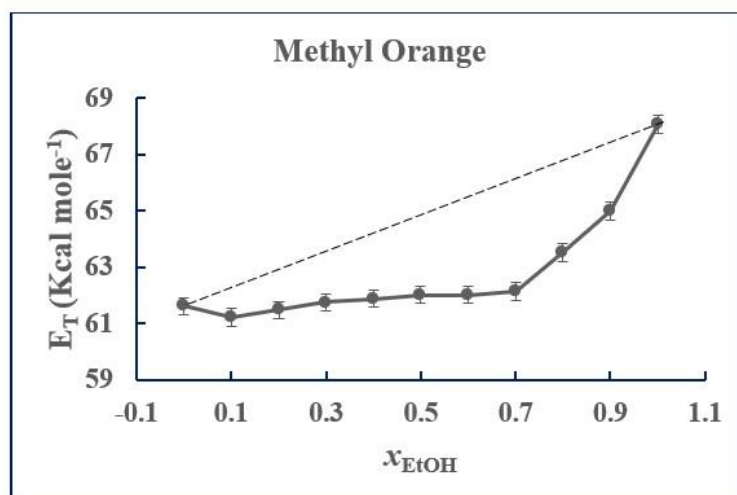


Figure 1: Variation in E_T obtained from spectral response of MO with the mole fraction of ethanol in water; dashed line is the ideally predicted E_T values which would have obtained upon addition of ethanol to water.

It is always a matter of difficulty as well as challenging to study about the solute-solvent dependent physicochemical properties of a mixed solvent system than a pure solvent alone [24]. The main reason behind this tough task being the probability of occurrence of simultaneous solute-solvent as well as solvent-solvent interaction along with preferential solvation of the solute in any of the solvents. When there is a difference between the bulk mole fraction solvent composition and the solvation microsphere (or, cybotactic region) solvent composition, we arrive at a unique relationship between solute and solvent, i.e., preferential solvation of the solute in any one of the solvents. The spectral response of the probes is reliant on the composition of the solvation microsphere which provides convenient ways to measure the extent of preferential solvation. The measured spectral response, R , in a binary solvent mixture is given by [24,25]:

$$R = Y_A R_A^0 + (1 - Y_A) R_B^0 \quad (3)$$

which is a weighted local mole fraction of the probe's spectral response in the two pure solvents, R_A^0 and R_B^0 . Here, Y_A and $(1 - Y_A)$ refer to the solvation sphere composition. In case of preferential solvation, the solvation microsphere composition may be quite different from the overall bulk liquid-phase composition. If we consider the spectral response to be E_T , we find that at all the compositions the $x_{\text{etoh, calculated}} < x_{\text{etoh, bulk}}$ indicating a substantial preferential solvation of MO in water rather than in ethanol.

3.2. Behavior of Methylene Blue dye. Spectral response up to 1.0 mole fraction of ethanol (i.e., pure ethanol) in water starting from 0.0 mole fraction of ethanol in water (i.e., pure water) were recorded from the absorption spectra within the range 400-750 nm at ambient condition ($\sim 25^\circ\text{C}$) with an optimized concentration of the dye $\sim 10^{-5}$ M in the aqueous solution or ethanolic solution. Solvatochromic effect of the dye in the solvent mixture including the pure ones were observed within the range 650-670 nm as most prominent peaks were identified there. The highest λ_{max} of MO in neat water was found to be at 664 nm. Some of the earlier studies agree well with our results [26,27]. The dye exhibited a very significant solvatochromic behavior within 0.0 to 1.0 mole fraction of ethanol in water exhibiting a hypsochromic shift of the λ_{max} from 664 nm (in neat water) to 653 (in neat ethanol) nm respectively indicating the effect of hydrogen bond donating (HBD) acidity of the solvent; hydrogen-bond donating solvents stabilize the ground state more compared to the excited state. Throughout the mole fraction range from neat water to neat ethanol, the hypsochromic shift was seen to be commensurating almost with the mole fraction weighted expected spectral response which has been shown by a straight dotted line joining the two terminals with neat water and ethanol respectively. The shift in λ_{max} may be due to difference in stabilization of ground and excited states with the alteration of polarity of the solvent medium and thus causes alteration in energy gaps between these electronic states.

Next, we calculated all the values of E_T following equation (2) and plotted E_T vs. mole fraction of water in ethanol. We got to observe that, with increase in solvent polarity the E_T values increased or vice versa (**Fig. 2**). From the plot it is observed that with increase in $x_{\text{etoh, bulk}}$ in water the E_T values increase indicating the decrease in polarity of the solvent milieu in the cybotactic region of MB. Nonetheless, since MB is showing a hypsochromic shift with decreasing dipolarity of the solvent milieu, MB appears to be a positive solvatochromic dye by virtue of its structure and properties. From the equation (3) considering E_T as the spectral response and calculating $x_{\text{etoh, calculated}}$, we see that they are lesser than $x_{\text{etoh, bulk}}$ at all compositions. Hence it could be said that the solvatochromic dye MB appears to be preferentially solvated in polar water than less polar ethanol though the difference is very meagre here compared to the other dye MO.

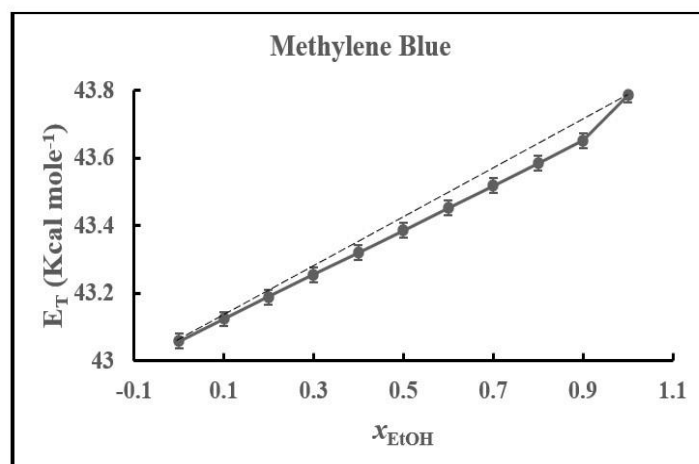


Figure 2: Variation in E_T obtained from spectral response of MB with the mole fraction of ethanol in water; dashed line is the ideally predicted E_T values which would have obtained upon addition of ethanol to water.

IV. CONCLUSION

As scientist Menshutkin said that “a chemical reaction cannot be separated from the medium in which it is performed” [28], it is well-perceived that if we improve the multi-functionality of a solvent, the pathway for chemical reactions therein would automatically be very easily-conceivable. Thus, exploring solvation capacity of varied number of solutes in wide range of solvents would obviously be very prolific as far as improvement of reaction environment is concerned. In this regard, our work on examining the solvation capability of solute type like MO and MB in neat and mixture of solvents like water and ethanol is very significant. It is universally accepted that water is a green solvent in which several important reactions can take place and since we are using water as a major solvent component here the overall system of the solvent mixture became ‘greener’. Our experiments exhibited a unique phenomenon of the above-mentioned dyes called ‘solvatochromism’ and showed that solute-solvent interaction is very important in bulk as well as in the microenvironment of the solute in terms of ‘preferential solvation’ and may show pathways to many more similar solutes to explore their solubilities in similar neat solvent or solvent mixture. In both the cases we arrived at results which are undoubtedly inspiring for further expansion and may open newer avenue in the field of solution chemistry. Especially in the case of MO, on addition of slight amount of water to ethanol, we obtained a significant change in E_T value which, definitely made the scope of solubilization to a greater extent and, side by side, the entire system more environmentally

benign. Therefore, finally we can say that, this work may help in studying the scope of growth for the utilization of these dyes and some other related compounds in neat and aqueous ethanol in several academic and industrial sectors which were explored never before.

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CONFLICT OF INTEREST

The author doesn't have any Conflict of Interest.

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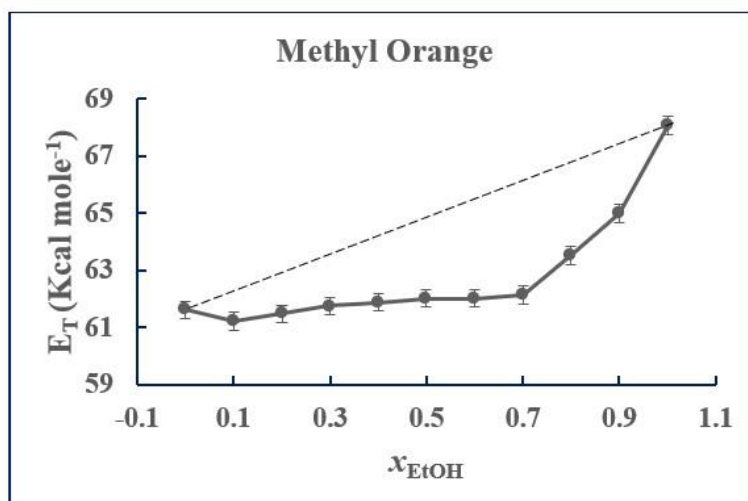
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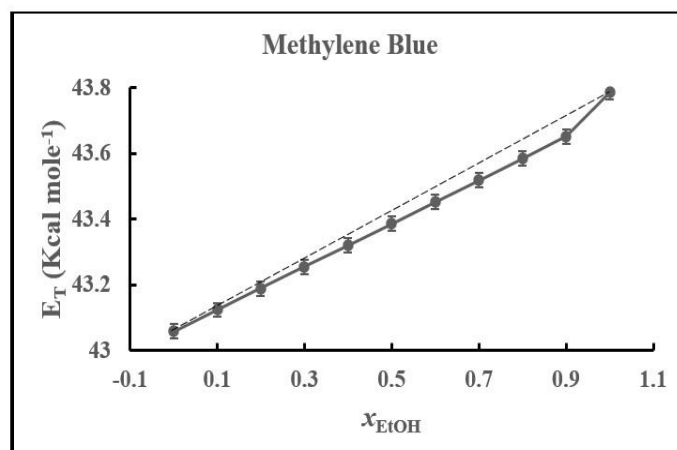
FIGURES AND SCHEMES

Figure 1:



II **Figure 1:** Variation in E_T obtained from spectral response of MO with the mole fraction of ethanol in water; dashed line is the ideally predicted E_T values which would have obtained upon addition of ethanol to water II

Figure 2:



II **Figure 2:** Variation in E_T obtained from spectral response of MB with the mole fraction of ethanol in water; dashed line is the ideally predicted E_T values which would have obtained upon addition of ethanol to water II