INTERACTION OF METHYL ORANGE WITH CATIONIC, ANIONIC AND NONIONIC SURFACTANTS IN BUFFERED SOLUTIONS

A THESIS

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TO MY DEAR FAMILY

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ABSTRACT

The interaction of methyl orange, an anionic dye, with various surfactants, viz. Anionic (sodium dodecyl sulfate, SDS), nonionic (tritonX-100, TX-100), and cationic (cetyltrimethylammonium bromide, CTAB), has been investigated spectrophotometrically in the submicellar and micellar concentration range. The apparent dissociation constant of the dye, and the apparent thermodynamic parameters, and the association constants of the two forms of the dye were evaluated in presence of different surfactant concentrations.

The results indicates that the $pK^{\backslash}_{a}$ of methyl orange decrease from 3.67 to 3.32, and 0.70 above CMC values of TX-100 and CTAB respectively. On the other hand, it increases to 3.94 above CMC value of SDS.

The effect of CTAB and TX-100 concentration on MO indicates that when the concentration of CTAB or TX-100 increased in the submicellar concentration it results in decreasing the enthalpy of ionization, entropy of ionization and Gibbs free enegy of ionization untill they reach a constant value when the concentration of these surfactants reaches their CMC value. In the case of TX-100 thethermodynamic parameters of ionization of the dye, $\Delta H^{\backslash}_{In}$, $\Delta S^{\backslash}_{In}$ and $\Delta G^{\backslash}_{In}$ values decreases from 21.15 kJ/mol, 1.87J/mol.K, and 20.95kJ/mol in aqueous media to 0.00 kJ/mol, -63.57J/mol.K, and 18.95 kJ/mol in the presence of micelles, respectively. In the case of CTAB $\Delta H^{\backslash}_{In}$, $\Delta S^{\backslash}_{In}$ and $\Delta G^{\backslash}_{In}$ decreases from 21.15 kJ/mol, 1.87J/mol.K, and 20.95kJ/mol in aqueous media to –53.30 kJ/mol, -200.00J/mol.K , and 4.00kJ/mol in the presence of micelles, respectively. And in the case of SDS $\Delta H^{\backslash}_{In}$, $\Delta S^{\backslash}_{In}$ and $\Delta G^{\backslash}_{In}$ increases from 21.15 kJ/mol, 1.87J/mol.K, and 20.95kJ/mol in aqueous media to 32.76 kJ/mol, 34.44J/mol.K, and 22.49kJ/mol in the presence of micelles, respectively.

The effect of SDS concentration on $\Delta H^{\backslash}_{In}$ of methyl orange indicates that when the concentration of SDS is increased it hampers the ionization

process and hence increases its $\Delta H^{\backslash}_{In}$ from 21.15 kJ/mol in aqueous media to 32.76 kJ/mol above the CMC value of SDS. The entropy of ionization for this system increase from 1.87J/mol.K in aqueous media to 34.44 J/mol.K above the CMC value. However the increase in $\Delta H^{\backslash}_{In}$ is larger than the increase in $\Delta S^{\backslash}_{In}$ leading to a net increase of $\Delta G^{\backslash}_{In}$ which make this process less thermodynamically favorable.

The association constant of the two forms of the dye, $K^{\backslash}_{o}$ values, to all micelle types were calculated. The results indicated that the association constants of the acidic form of the dye in presence of TX-100 , CTAB and SDS were $2.50\text{x}10^{4}$, $2.00\text{x}10^{4}$, and $2.00\text{x}10^{4}$liter/mol, respectively. While the association constant of the basic form of the dye in the presence of TX-100, CTAB, and SDS were $2.50\text{x}10^{4}$, $2.50\text{x}10^{4}$, and $1.67\text{x}10^{4}$liter/mol, respectively.

The results are discussed in light of the stabilization of the two forms of the dye in the micellar core of the different surfactant employed in this work and their effect on properties of the bulk solution phase.

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LIST OF ABBREVIATIONS

$\Delta H'_{In}$: Apparent enthalpy of ionization of the indicator.

$\Delta H'_{B}$: Apparent enthalpy of ionization of the buffer.

$\Delta G'_{In}$: Apparent Gibbs free energy of ionization of the indicator.

$\Delta S'_{In}$: Apparent entropy of ionization of the indicator.

K'_{a} : Apparent dissociation constant of the indicator.

K'_{c}: Apparent association constant

R : Gas constant (8.314 KJ/mol).

A: Absorbance value at a specified wavelength.

A_a: Absorbance value at a specified wavelength of the acidic form of MO.

A_b: Absorbance value at a specified wavelength of the basic form of MO.

A_m^{∞} : Absorbance at the saturation limit (i.e. at high surfactant concentration)

A_a : Absorbance at the lowest surfactant concentration.

η: Absorbance Ratio (A_m^{∞} -A_a/A-A_a)

μ : Ionic strength of the solution.

CMC: Critical micelle concentration.

[M]: Micelle concentration (surfactant molar concentration divided by the aggregation number of the surfactant).

CTAB: Cetyltrimethyl ammonium bromide.

TX-100: Triton X-100.

SDS: Sodium dodecyl sulfonate.

MO: Methyl orange.

C_p : Heat capacity.

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CHAPTER I

INTRODUCTION

I.1: THEORY OF COLORS

Colors are a human observation of the inverse of a visible absorption spectrum. It is created by the absorption of electromagnetic radiation of wavelength between 400 and 700nm. The energy of the light absorbed by the molecule promotes an electron to a higher energy level. This energy difference corresponds to 170-300kJ/mol for visible light and 300-12000kJ/mol for ultraviolet light(1).

According to the Einstein-Bohr frequency condition (eq.1), the energy difference between the ground and excited states, ΔE, is directly proportional to the observed frequency (υ) and so inversely proportional to the wavelength of light (λ)(2,4).

$$\Delta E = h\upsilon = \frac{hc}{\lambda} \cdots\cdots\cdots\cdots (1)$$

In the wave-mechanical model for the three-dimensional distributions of an electron, the electron orbits in the original Bohr atomic model are replaced by orbital, i.e. the distribution function of single electrons. The Shrodinger equation (2) describes the motion of an electron of mass *m* under a potential energy *U* as a function of the three Cartesian coordinates *x*, *y* and *z*. *E* and ψ the total energy and the eigenfunction of the electron in different states respectively.

$$\frac{\vartheta^2\psi}{\vartheta x^2} + \frac{\vartheta^2\psi}{\vartheta y^2} + \frac{\vartheta^2\psi}{\vartheta z^2} + \frac{8\pi^2 m}{h^2}[E - U(x,y,z)]\psi = 0 \cdots\cdots\cdots (2)$$

An exact solution for this equation is possible only for extremely simple systems. Multi-electron systems, however, are solved by appropriate approximation methods such as the *valance bond theory* (VB) and molecular orbital theory. The valence bond theory was first applied to the hydrogen molecule. The wave mechanical computation showed that this process corresponds to a stabilization of H_2 relative to 2 H. Extreme distributions of electrons in VB representations are called limiting structures. In the *molecular orbital theory* (MO), the molecular wave functions are formed by a linear