Aggregation of Mordant Black 11 in Aqueous Solution

M. M. El-Fass

Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt

Summary. Spectrophotometry was employed to study the aggregation of Mordant Black 11 (MB-11) in aqueous solution. The aggregation number and constant were determined using the maximum slope method. The aggregation characteristics obtained by this method were then compared with other methods. In addition, the spectral change as a result of dimerization of MB-11 was interpreted in terms of the usual cluster model of water exerting hydrophobic interaction around the dye ions.

Keywords. Aggregation; Mordant dye; Spectrophotometrical analysis; Dimerization.

Introduction

Some solochrome dyes have been used for a long time as indicators [1]. The great utility of Eriochrome Black T (MB-11) as indicator in chelatometric titration of metal ions, such as magnesium(II) [2] and zinc(II) [3] with ethylenediaminetetraacetic acid (EDTA) has been a subject of interest for many years [4–7]. The importance of this o,o'-dihydroxyazo dye (MB-11) as acid-base indicator has led to studies concerning the spectral changes when the concentration of this dye increases in aqueous medium.

Coates [8] has investigated qualitatively similar dyes in order to explain the behaviour of these dyes in solution. Also, Malik and Gupta [9] tried to calculate the aggregation number and constant for some solochrome dyes using Pugh's method [10]. The authors attributed the spectral change of the dye to the formation of aggregate molecules. Of the various physico-chemical methods available to study this phenomenon quantitatively, the spectrophotometric methods have been employed widely [11].
The maximum slope method [11, 12] proved to be satisfactory using different types of dyes. In the present paper the maximum slope method was chosen to calculate the aggregation number and constant for MB-11 and the results are discussed and compared with other methods.

**Experimental Part**

Analytical grade C.I. Mordant Black 11 was used in this study. It has been obtain from BDH (Chemicals Ltd. Poole England).

The absorption spectra of the dyestuff were recorded on a Varian Superscan double beam spectrophotometer (UV-VIS) in the region of 400–800 nm at 25 °C using 1 cm silica cell.

The solutions for spectral measurements were prepared using bidistilled water. The dye concentrations range from 0.1 to 4.0 × 10⁻⁴ mol dm⁻³. Solutions were kept in the dark for 24 h before taking the measurements.

**Results and Discussion**

The electronic absorption spectra of various concentrations of the monosulphonic mordant dye C.I. MB-11 in water are given in Fig. 1. At low concentrations there is a broad band whose λ_max occurs at 610 nm. This longer-wavelength band could be for the monomeric dye molecule [8]. As the dye concentration increases, the apparent molar extinction coefficient decreases with the appearance of the shorter-wavelength band at λ ≈ 550 nm and a shoulder located at λ ≈ 610 nm. The shorter wavelength band is about 60 nm shorter than the monomer band. This is assigned to the dimer dye molecule in solution [13]. The resolved monomer and dimer spectra of aqueous MB-11 solution are presented in Fig. 2.

This relation gives a qualitative measure for the state of the dye in aqueous media. To obtain a quantitative information, the maximum slope method was used to calculate both the aggregation number and the aggregation constant using different dye concentrations.

The suggested method by Zanker [14] has ascribed these spectral change as a result of the presence of only two molecular species in equilibrium, monomer and aggregate. The apparent equilibrium constant of association was expressed as

\[ K = \frac{\varepsilon}{nC_0^{n-1}(1 - \varepsilon)^n}, \]  

where \((1 - \varepsilon)\) is the fraction of monomer, \(C_0\) is the total concentration of dye and \(n\) is the degree of aggregation.

The apparent extinction coefficient \(\varepsilon\) at a definite wavelength can be expressed by means of \(\varepsilon_n\) and \(\varepsilon_m\) which are the extinction coefficients of aggregate and monomer at the same wavelength

\[ \varepsilon = \frac{1}{n}\varepsilon_n + (1 - \varepsilon)\varepsilon_m. \]  

From (1) and (2), the following equation was obtained,

\[ \log C_0 \left(1 - \frac{\varepsilon}{\varepsilon_m}\right) = \log (CK) + n \log C_0 \left(\frac{\varepsilon}{\varepsilon_m} - \frac{\varepsilon_n}{n\varepsilon_m}\right), \]