

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.

Aggregation von Mordant-Schwarz 11 in wäßriger Lösung

Zusammenfassung. Mittels Spektrophotometrie wurde das Aggregationsverhalten von Mordant-Schwarz 11 (MB-11) in wäßriger Lösung untersucht. Die Aggregationszahl und -konstante wurde nach der Maximalanstiegsmethode bestimmt. Die Aggregationscharakteristika wurden mit Ergebnissen aus anderen Methoden verglichen, und die spektroskopischen Veränderungen als Resultat der Dimerisierung von MB-11 wurden im Rahmen des Cluster-Modells und der hydrophoben Wechselwirkung am Farbstoff-Ion diskutiert.

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 obtained 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 $\lambda \approx 550$ nm and a shoulder located at $\lambda \approx 610$ 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

$$K = \frac{\kappa}{nC_0^{n-1}(1-\kappa)^n}, \quad (1)$$

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

The apparent extinction coefficient ε at a definite wavelength can be expressed by means of ε_n and ε_m which are the extinction coefficients of aggregate and monomer at the same wavelength

$$\varepsilon = \frac{1}{n}\kappa\varepsilon_n + (1-\kappa)\varepsilon_m. \quad (2)$$

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

$$\log C_0 \left(1 - \frac{\varepsilon}{\varepsilon_m} \right) = \log (CK) + n \log C_0 \left(\frac{\varepsilon}{\varepsilon_m} - \frac{\varepsilon_n}{n\varepsilon_m} \right), \quad (3)$$

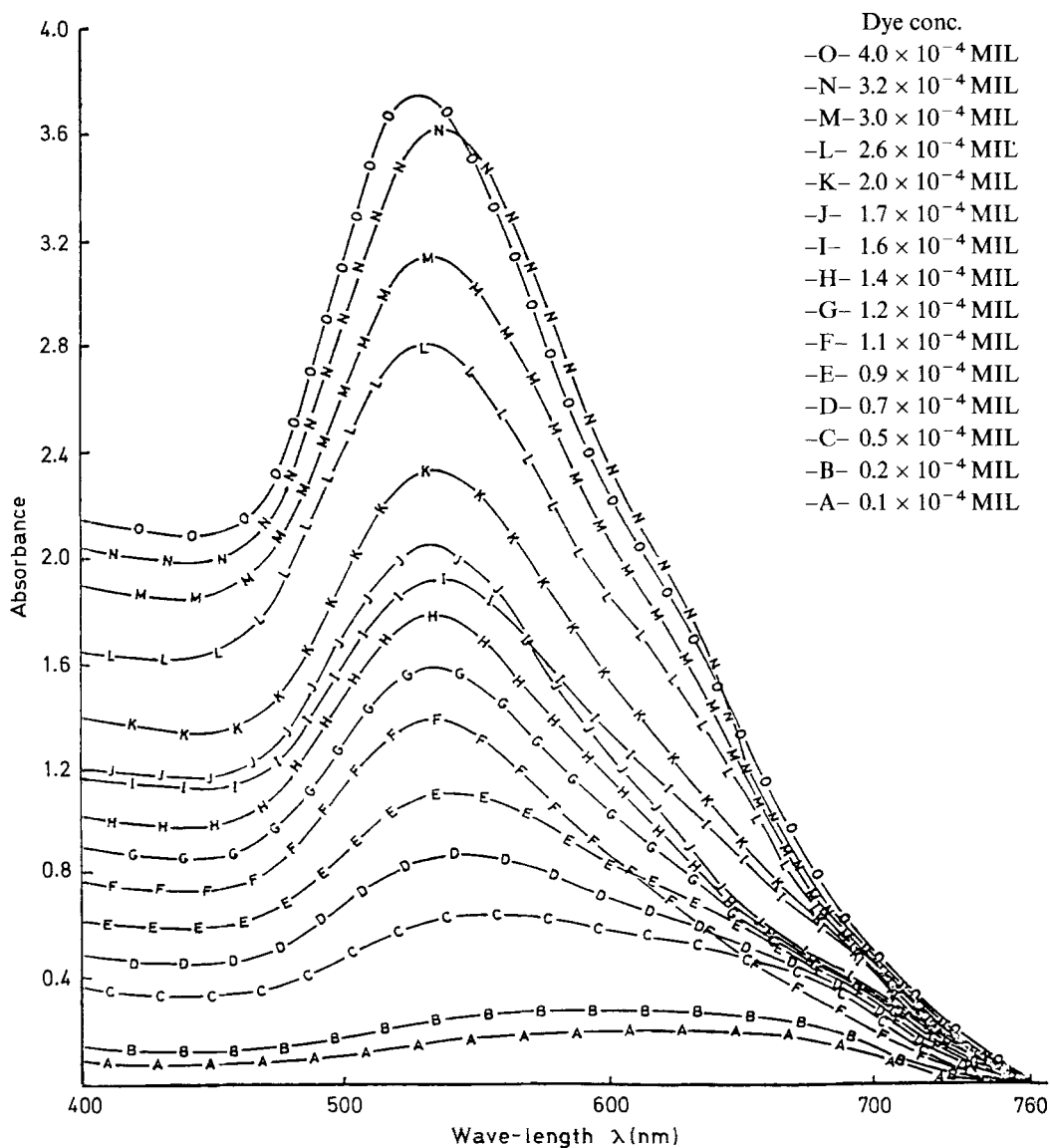


Fig. 1. Absorption spectra of Mordant Black 11 in H₂O

where

$$C = \frac{1}{n^n \left(n - \frac{\epsilon_n}{\epsilon_m} \right)^{n-1}}$$

Zanker [14] and Mataga [15] neglected the value ϵ_n/ϵ_m as compared with ϵ/ϵ_m in Eq. (3), and Eq. (4) was then obtained,

$$\log C_0 \left(1 - \frac{\epsilon}{\epsilon_m} \right) = \log (CK) + n \log C_0 \left(\frac{\epsilon}{\epsilon_m} \right). \quad (4)$$

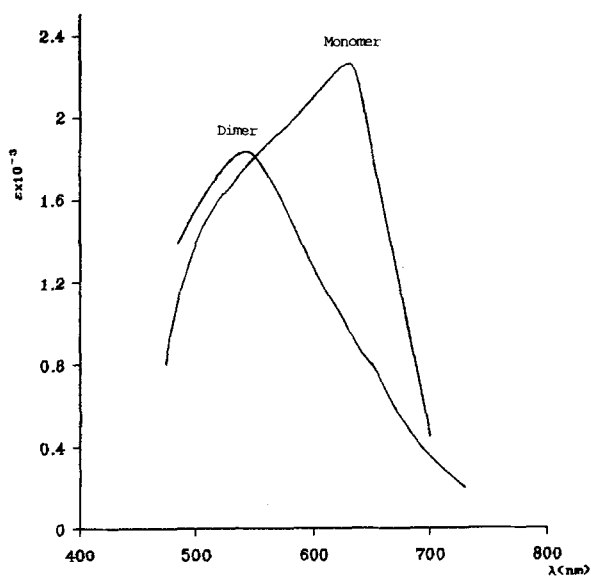


Fig. 2. Resolved monomer and dimer extinction coefficient for aqueous C.I. MB-11

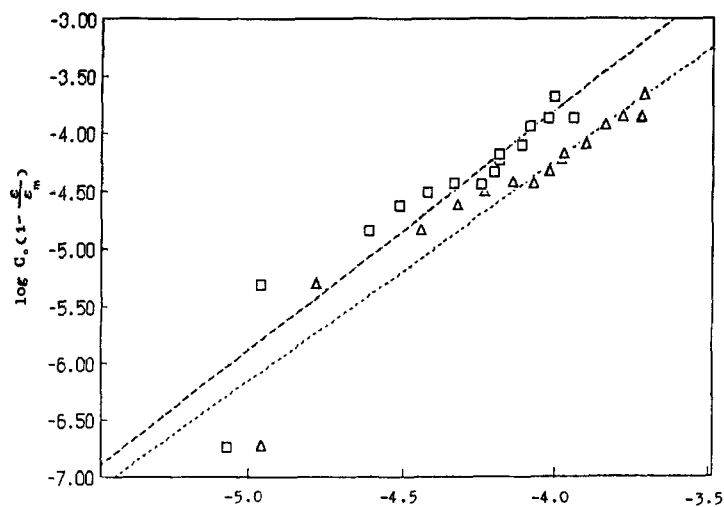


Fig. 3. $\Delta \log C_0 \left(1 - \frac{\epsilon}{\epsilon_m}\right)$ vs. $\log C_0 \left(\frac{\epsilon}{\epsilon_m}\right)$ and $\square \log C_0 \left(1 - \frac{\epsilon}{\epsilon_m}\right)$ vs. $\log C_0 \left(\frac{\epsilon}{\epsilon_m} - \frac{\epsilon_n}{n\epsilon_m}\right)$

By means of Eqs. (4) and (3), the degree of aggregation and the equilibrium constant can be evaluated. ϵ_m and ϵ_n can be estimated by extrapolation of the ϵ vs. $\log C_0$ plot to infinite dilution and to high concentration, respectively.

Figure 3 shows that firstly (n) can be obtained from the slope of a linear plot of Eq. (4). Secondly, (K) can be obtained from the intercept of a linear plot of Eq. (3). The obtained results are collected for comparison in Table 1.

Equation (3) was taken by Hida et al. [11] to get (n) always as integer. This point was difficult to obtain by Zanker and Mataga in most of the cases and (n) was assumed by them to be a weighted mean of some degree of aggregation. Then, the

Table 1. Comparison of the true and obtained values of the aggregation parameters

Aggregation parameters	The maximum slope method	Zanker's method
$\varepsilon_m \times 10^{-3}$	18.5	18.5
$\bar{\varepsilon}_2 \times 10^{-3}$	4.0	0.0
$\bar{\varepsilon}_3 \times 10^{-3}$	2.7	-
$\bar{\varepsilon}_4 \times 10^{-3}$	2.0	-
$(\bar{\varepsilon}_n)_0 \times 10^{-3}$	4.0	-
$\log k$	3.7	4.0
n	2.0	1.89

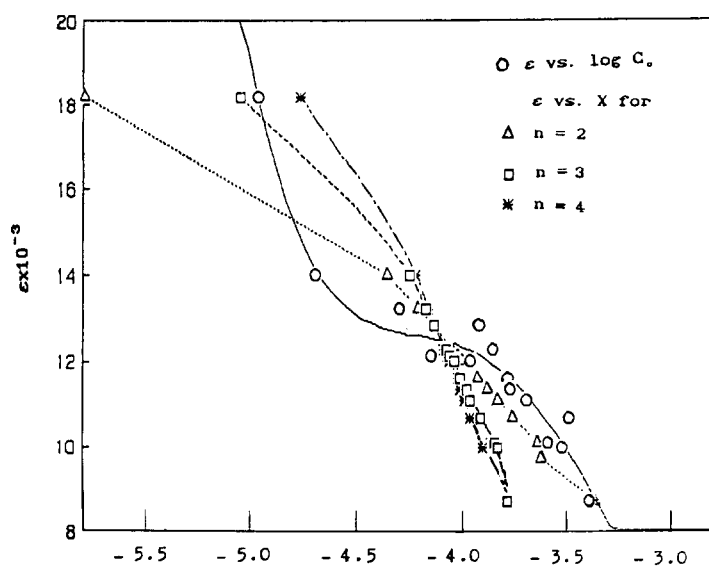


Fig. 4. The experimental and theoretical curves for C.I. MB-11

relationship between ε and $\log C_0$ can be written by Eq. (5),

$$\frac{1}{n-1} \log(\varepsilon_m - \varepsilon) - \frac{n}{(n-1)} \log\left(\varepsilon - \frac{\varepsilon_n}{n}\right) = \log \alpha C_0, \tag{5}$$

where

$$\alpha = (nK)^{1/(n-1)} \left(\varepsilon_m - \frac{\varepsilon_n}{n}\right).$$

Taking $\log \alpha C_0 = X$, Eq. (5) reads:

$$\frac{1}{n-1} \log(\varepsilon_m - \varepsilon) - \frac{n}{n-1} \log\left(\varepsilon - \frac{\varepsilon_n}{n}\right) = X.$$

The integer (n) can be determined with the best fit to the theoretical curve of ε vs. X for different values of $n = 2, 3, 4, \dots$ etc., with the experimental curve ε vs. $\log C_0$.

Figure 4 shows a typical graph of ε vs. $\log C_0$ and ε vs. X for C.I. MB-11 in water. It is obvious from this graph that the best fit between the theoretical and experimental curves is obtained for $n = 2$. The obtained results are calculated by means of linear regression analysis.

The quantitative results obtained by the maximum slope method could explain the change in the spectra due to the stacking of the dye-dye interaction through the π -orbital system of aromatic rings [13]. Also, on the basis of the vital role of water as solvent, the large existence of iceberg structure of water around the polar dye molecule at high concentrations should provide a promotion of dye association strongly [16].

On the other hand, the application of the maximum slope method in calculating both (n) and (K) is superior to Zanker's treatment, since it can confirm whether a simple aggregation model can be assumed or not [17]. Further, the mathematical basis of the maximum slope method cannot neglect $\varepsilon_n/n\varepsilon_m$, especially when the polymer band does not differ very much from the monomer band. The maximum slope method can derive correct values of ε_n/n and K for the dimerization of dye molecule because the value of ε_m and the maximum slope can be determined accurately. Then ε_n/n or $\bar{\varepsilon}_n$ can easily be adjusted to its true value $(\bar{\varepsilon}_n)_0$ by the following equation [11],

$$\frac{m_0}{m} = \frac{\varepsilon_m - (\bar{\varepsilon}_n)_0}{\varepsilon_m - (\bar{\varepsilon}_n)},$$

where m and m_0 are the maximum slopes of the tangents of the experimental and theoretical curves.

It thus seems from the results obtained that the application of the maximum slope method to estimate (n) and (K) give reliable results.

Finally, the values of (n) and (K) obtained by the maximum slope is slightly different from those calculated by Zanker's treatment which could be due to the approximation used by Zanker.

References

- [1] Bishop E. (1972) Indicators. Pergamon Press, Oxford
- [2] Flaschka H. (1952) Mikrochim. Acta **39**: 38
- [3] Biedermann W., Schwarzenbach G. (1948) Chimia (Switz.) **2**: 56
- [4] Diehl H., Lindstrom F. (1959) Anal. Chem. **31**: 414
- [5] Schwarzenbach G., Biedermann W. (1948) Helv. Chim. Acta **31**: 678
- [6] Schwarzenbach G. (1956) Die komplexometrische Titration, 2nd ed. Enke, Stuttgart, pp. 28–30
- [7] Ringbom A. (1963) Complexation in Analytical Chemistry. Interscience, New York
- [8] Coates E. (1969) J. Soc. Dyers. Col. **85**: 355
- [9] Malik W. U., Gupta P. N. (1977) Indian J. Chem. **15A**: 273
- [10] Pugh D., Giles C. H., Duff D. G. (1971) Trans. Faraday Soc. **67**(2): 563
- [11] Hida M., Yabe A., Murayama H., Hayashi M. (1968) Bull. Chem. Soc. Jpn. **41**: 1776

- [12] El-Mariah, Afaf A. R., Kafafi Z. H., Moussa E. A. (1982) *J. Chinese Chem. Soc.* **29**: 279
- [13] Constantino L., Guarino G., Ortona O., Vitaglino V. (1984): *J. Chem. Eng. Data* **29**: 62
- [14] Zanker V. (1952) *Z. Phys. Chem.* **200**: 250
- [15] Mataga N. (1957) *Bull. Chem. Soc. Jpn.* **30**: 375
- [16] Forster Th., König E. (1957) *Electrochem.* **61**: 344
- [17] Hida M. (1981) *Memoris of Faculty of Technology Tokyo Metropolitan University, Tokyo Japan* **31**: 3055

Received November 24, 1991. Accepted November 5, 1992