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THERMODYNAMIC STUDY ON MOLECULAR ASSOCIATION OF SOME ORGANIC DYESTUFFS IN AQUEOUS SOLUTION

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ABSTRACT

The temperature effects on the absorption spectra of acridine orange and methylene blue in aqueous solution at various concentrations have been observed, and it was found that the increase in temperature has an effect on the spectra similar to that of the dilution. The heats of dimerization of the dyestuffs in aqueous solution have been measured directly by the calorimetric titration method, and ΔH_d for acridine orange and methylene blue were found to be -49.6 and -83.3 kJ mol^{-1}, respectively. The entropy of dimerization values were also calculated to be $\Delta S_d = -54.9$ and -211.6 J K^{-1} mol^{-1} for acridine orange and methylene blue, respectively. It has been concluded that the stacking interactions are primarily responsible for the self-association of the dye molecules.

INTRODUCTION

The metachromatic behavior of some organic dye molecules has been extensively studied through various kinds of spectroscopic methods [1–5] for a number of years. The spectral change found in aqueous solutions of dyestuffs with the concentration change has been generally attributed to the aggregation of the dye molecules as the concentration increased [2–7]. There have also been a number of structural studies [3–7] of the dimer formed in aqueous solutions of planar dye molecules and a sandwich stacking structure of the dimer was suggested.

Recently, kinetic and thermodynamic studies on the dimerization of the dye molecules, which elucidate the mechanism of metachromasy, have been reported [11–14]. Since Rabinowitch and Epstein [1] reported the thermodynamic data for dimerization, a number of groups [14–16] have attempted to evaluate thermodynamic parameters for metachromasy to elucidate the

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bonding nature of the dimers. However, those thermodynamic data were estimated through the temperature dependences of the equilibrium constants which were determined by spectrophotometric [1,14–16] and isoextraction [15] methods.

In this study, the thermodynamic parameters for the dimerization equilibria of methylene blue and acridine orange have been measured directly in aqueous solutions by the titration calorimetric method. The temperature effects on the absorption spectra of the systems were also studied.

EXPERIMENTAL

Reagents

Acridine orange and methylene blue (BDH, microscopical stain) were purified before use. The procedures for the purification of the dyestuffs have been described elsewhere [4]. The working solutions were buffered to pH 4–5 with 0.01 M acetate buffer. Deionized water was used for all experimental procedures.

Spectrum measurement

The absorption spectra were measured using a Pye Unicam SP 1800 spectrophotometer with a matched silica cell of 1–400-mm pathlength. The cell temperature was controlled by the circulation of water which was preset to the desired temperature in a constant temperature bath, through the cell compartment. The temperature discrepancy between the cell and water bath was corrected for by calibration.

Calorimetric titrations

The calorimetric titration was performed using a Tronac calorimeter (Model 450). The titration procedures are similar to those described in the literature [18].

RESULTS AND DISCUSSION

Temperature effect on the absorption spectrum

Figure 1 shows the variation of the absorption spectrum of acridine orange solution with varying temperature for three different concentrations. The temperature dependence of the spectrum seems to decreases with decreasing dye solution concentration. For cases (I) and (II), whose concentrations are relatively higher than that of case (III), the temperature effect on the spectrum is conspicuous. However, for case (III), whose concentration is 9×10^{-6} M, the effect is very weak; the difference is undetectable at 50 and 70 °C. This would mean that the concentration of the monomer increases, by the dissociation of the dimer species, with increasing temperature. Similar results were also obtained for the methylene blue solutions, which are shown in Fig. 2.

Thermodynamic parameters

The heat of titration (Q) was obtained by adding 2 ml of the titrant to 50 ml of water solvent. The concentrations of the titrants are 1.04×10^{-2} M for methylene blue and 9.32×10^{-3} M for acridine orange. The entropy of the dimerization (ΔH_d) was calculated from the equation, $\Delta H_\mathrm{d} = Q/\Delta[D]$, assuming that the heat produced during the titration process is due mainly to the dissociation of the dimeric species. The concentration change of the dimer during the dilution, $\Delta[D]$, is calculated from the known values of the dimerization constants. The dimerization constants (K_d) are reported [4] to be 2.24×10^4 and 6.46×10^3 l mol^{-1} at 20 °C for acridine orange and methylene blue, respectively. The entropy of dimerization is determined by the simple thermodynamic relationship, $\Delta G_\mathrm{d} = \Delta H_\mathrm{d} - T\Delta S_\mathrm{d}$.

The heats of dimerization obtained by the calorimetric titration are listed

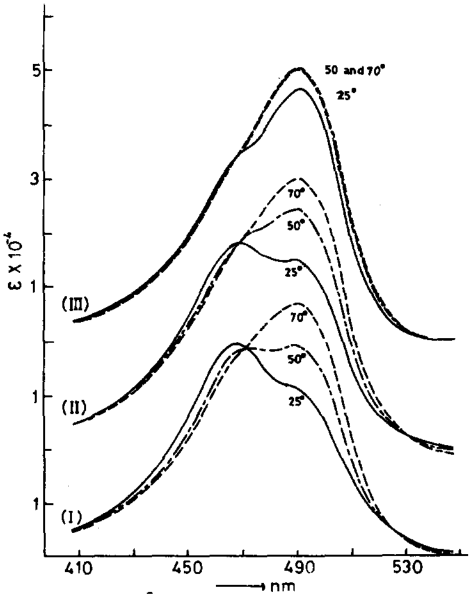

Fig. 1. The effect of temperature on the spectra of acridine orange for three different concentrations: (I) 1.8×10^{-4} M; (II) 9.0×10^{-5} M; and (III) 9.0×10^{-6} M. pH = 4.65, temperatures in °C.

TABLE 1

Enthalpy of dimerization measured by calorimetric titration at 20 °C

No.	Acridine orange ($C_i = 1.04 \times 10^{-2}$ M)		Methylene blue ($C_i = 9.32 \times 10^{-3}$ M)	
	Q (mJ)	$-\Delta H_d$ (kJ mol^{-1})	Q (mJ)	$-\Delta H_d$ (kJ mol^{-1})
1	166.9	43.7	165.7	81.7
2	207.5	54.4	184.1	80.8
3	192.9	50.5	164.9	81.3
4	183.7	48.1	170.3	83.9
5	196.2	51.4	164.0	80.9
Av.	189.1	49.6 ± 3.9	169.9	83.3 ± 4.1

in Table 1. The thermodynamic parameters for the dimerizations of some organic dyestuffs are summarized in Table 2 with previously reported results for comparison.

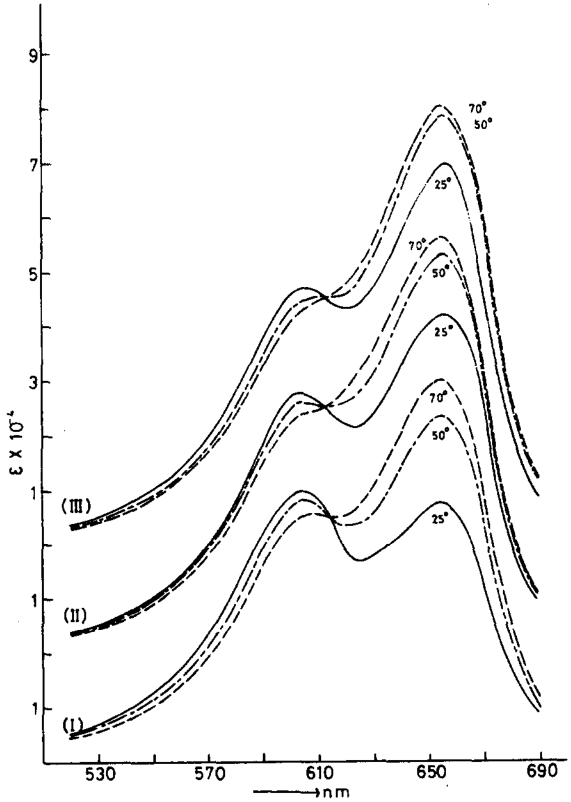

Fig. 2. The effect of temperature on the spectra of methylene blue for three different concentrations: (I) 2.0×10^{-4} M; (II) 1.0×10^{-4} M; and (III) = 5.0×10^{-5} M. pH = 4.65, temperatures in °C.

There are quite large discrepancies in the thermodynamic parameters of dimerization (ΔH_d and ΔS_d) of methylene blue between present data and those obtained by the isoextraction method [17]. However, it is noted that the values of ΔH_d and ΔS_d measured directly by the calorimetric method are in fairly good agreement with those determined by the *T*-jump method by other workers [11,13].

It has been suggested [4] that the geometry of the dimer is that of a sandwich dimer formed via the approach of two monomers in opposite directions. The dimerization process of the dyestuffs in aqueous solutions would cause a negative enthalpy change by the attractive interactions between the two monomers, through dispersive forces and hydrophobic interactions, and a positive entropy change by the disruption of the solvated solvent molecules. However, a negative entropy change on the formation of one mole of the dimer with two moles of the monomer is also expected. From the values of ΔH_d and ΔS_d, the driving force for the dimerization is the enthalpy effect. The larger negative enthalpy of the dimerization of methylene blue compared to acridine orange would be attributed to the more attractive interaction between positively charged sulfur and the electron-rich region of the nitrogen in methylene blue. It has already been suggested [19] that the negative enthalpy and entropy changes indicate that the dispersive interactions are the major contribution to the stability of the dimer.

The negative entropy of dimerization would suggest that the disruption of the solvation sphere by molecular aggregation is not strong enough to overcome the positive entropy change by dimerization. Water molecules may exist in the space between two monomers of the dimer. Ballard and Park [4] calculated an intermolecular separation of ca. 7.5 Å in the dimer. The diameter of a water molecule is generally known to be < 5 Å.

TABLE 2

Thermodynamic parameters for the dimerization of some organic dyestuffs in aqueous solution

$-\Delta G_d$ (kJ mol^{-1})	$-\Delta H_d$ (kJ mol^{-1})	$-\Delta S_d$ (J K^{-1} mol^{-1})	Temp. (°C)	Ref.
Methylene blue				
19.2	24.7	18.8	25	9
20.2	83.3	253.9	20	12
21.7	83.7	211.6	20	This work
Acridine orange				
23.8	38.0	48.1	20	11
24.8	49.6	54.9	20	This work
Thionine				
17.1	28.5	38.1	26	3

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