*Dyes and Pigments* **16** (1991) 241–251

# A Spectrophotometric Study of the Tautomeric and Acid-Base Equilibria of Methyl Orange and Methyl Yellow in Aqueous Acidic Solutions

Khalid M. Tawarah & Hakam M. Abu-Shamleh

Department of Chemistry, Yarmouk University, Irbid, Jordan

(Received 6 November 1990; accepted 20 December 1990)

*ABSTRACT*

*The UV–visible spectra of methyl orange and methyl yellow were examined in alkaline, acidic and strongly acidic aqueous solutions at 25°C. In the alkaline medium, methyl orange is present in the monomer form for concentrations* $\leq 1{\cdot}2 \times 10^{-4}$ *mol dm*$^{-3}$*, while methyl yellow shows significant deviations from Beer's law in the alkaline medium, and time has a drastic effect on the spectra. In 0·032–0·46 mol dm*$^{-3}$ *HCl, both azo dyes are present as a tautomeric mixture. The position of the tautomeric equilibrium shifts to the side of the azonium tautomer for acidities* $>0{\cdot}5$ *mol dm*$^{-3}$ *HCl. The tautomeric equilibrium constant* ($K_t$) *is calculated at several HCl concentrations. The* $pK_{a_2}$ *values for methyl orange and methyl yellow are* $3{\cdot}37 \pm 0{\cdot}01$ *and* $3{\cdot}01 \pm 0{\cdot}01$*, respectively. The microscopic acid dissociation constants of both azo dyes were calculated. Methyl orange was not extractable into* $CCl_4$ *at any acidity, while methyl yellow was completely extractable into* $CCl_4$ *at acidities* $\leq 0{\cdot}3$ *mol dm*$^{-3}$ *HCl.*

## 1 INTRODUCTION

There has been an interest in studying the inclusion complexes of cyclodextrins with several azo dyes as guest molecules.[1–3] Relatively speaking, methyl orange has been extensively studied in connection with its inclusion complexes with α-, β- and γ-cyclodextrins,[1,4–7] without the full recognition of the tautomerism of methyl orange. The tautomerism of the amino azobenzene salt cations has been the subject of several reports.[8–12]



*Dyes and Pigments* 0143-7208/91/$03·50 

The structure of the first conjugate acid of methyl yellow and the estimation of its tautomeric equilibrium constant were reported by Yeh and Jaffe.[11] Reeves[12] has also reported values for the tautomeric equilibrium constant of methyl orange.

The purpose of the present study is to present data on the spectral behaviour of methyl orange and methyl yellow in acidic aqueous solutions. Based on such data, the microscopic acid dissociation constants of methyl orange are recalculated and those of methyl yellow are reported. A qualitative study concerning the distribution of methyl orange and methyl yellow between $CCl_4$ and $H_2O$ at different acidities is reported. The information obtained from the present work is believed to be a useful guideline for designing experiments concerning the inclusion complexes of azo dyes with cyclodextrins. Such information has been exploited for calculating the individual formation constants of the inclusion complexes of the tautomers of methyl orange and methyl yellow with cyclodextrins, and the results will be reported separately.

## 2 EXPERIMENTAL

The sodium salt of methyl orange ($C_{14}H_{14}N_3SO_3Na$) and the base form of methyl yellow ($C_{14}H_{15}N_3$) were purchased from Sigma (St. Louis, Missouri, USA). The samples were dried at 90°C for 16 h before use. Other chemicals used in this study, such as $CCl_4$, potassium hydrogen phthalate and other buffer materials, were reagent grade chemicals. HCl was used to enhance the solubility of methyl yellow in water. A typical stock solution of methyl yellow had a concentration of $1{\cdot}87 \times 10^{-4}$ mol dm$^{-3}$, an ionic strength of 0·01 mol dm$^{-3}$ and a pH of 2; a typical stock solution of methyl orange had a concentration of $1{\cdot}86 \times 10^{-4}$ mol dm$^{-3}$, an ionic strength of $1{\cdot}86 \times 10^{-4}$ mol dm$^{-3}$ and a pH of 10. The pH of a test solution was adjusted by adding an appropriate amount of either NaOH or HCl aqueous solutions. In the distribution experiments, equal volumes (20 cm$^3$ each) of $CCl_4$ and an aqueous solution of an azo dye were used. After the attainment of equilibrium at the ambient temperature (about 18°C), the colour of each phase was noted. In most cases, the volume measurements were carried out by using a 10-ml microburette. The UV–visible spectra of the azo dyes were recorded at 25·0°C by using a double-beam spectrophotometer (DMS 100, Varian). Stoppered quartz cells with optical path length of 1·00 cm were used. The pH measurements were carried out by using an Orion Research Digital Ionalizer. The meter was calibrated by using phthalate, phosphate and borax buffer solutions as suggested by Albert and Serjeant.[13]

## 3 RESULTS AND DISCUSSION

The effect of pH on the UV–visible spectrum of methyl orange is shown in Fig. 1. Curve 1 in this figure represents the absorption spectrum of the alkaline form (structure A in Fig. 2), which has an absorption maximum at 466 nm and a molar absorptivity of $2{\cdot}45 \times 10^4$ cm$^{-1}$ mol$^{-1}$ dm$^3$. The corresponding literature values are $2{\cdot}44 \times 10^4$, $2{\cdot}72 \times 10^4$ and $2{\cdot}19 \times 10^4$ cm$^{-1}$ mol$^{-1}$ dm$^3$ at 460 nm,[14] 462 nm[15] and 463 nm,[12] respectively. The absorbance of the alkaline form of methyl orange was recorded at 500, 490, 485, 480, 475, 460, and 450 nm for nine solutions covering the range of $1{\cdot}85 \times 10^{-6}$ to $1{\cdot}20 \times 10^{-4}$ mol dm$^{-3}$. Beer's law was obeyed at these wave lengths with correlation coefficients of 0·999. The adherence of the data to Beer's law indicates that the anion of methyl orange is present in solution as a monomer and no aggregation was detected in the concentration range used. This result is in agreement with the work of Kendrick and Gilkerson,[15] who showed that significant dimerisation of the anion of methyl orange occurs above $2 \times 10^{-4}$ mol dm$^{-3}$.

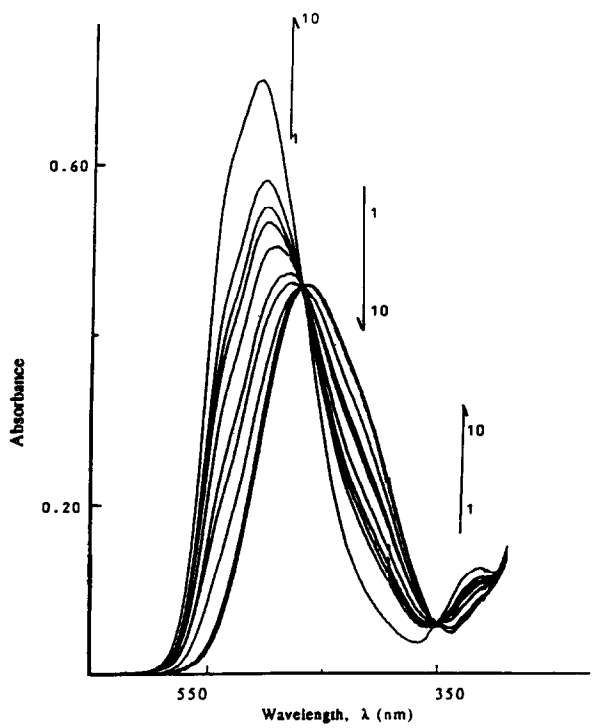


**Fig. 1.** The UV–visible spectrum of $1{\cdot}857 \times 10^{-5}$ mol dm$^{-3}$ methyl orange as a function of pH. Curves 1–10 correspond to pH values 11·0, 5·58, 4·20, 3·90, 3·70, 3·52, 3·39, 3·32, 3·23 and 2·78, respectively.

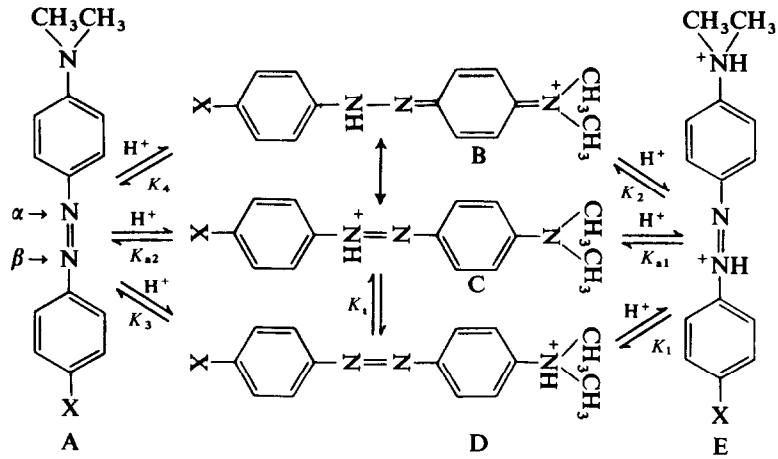


**Fig. 2.** The tautomeric and acid-base equilibria of methyl orange ($X = SO_3^-$) and methyl yellow ($X = H$) in aqueous acidic solutions.

The UV–visible spectrum of $1{\cdot}87 \times 10^{-5}$ mol dm$^{-3}$ of the base form of methyl yellow (structure A in Fig. 2) has its maximum absorption at 446 nm. The intensity of this maximum was found to decrease with time (colour changes from intense yellow to pale yellow) and assumed a constant value (20% of its initial value) after the elapse of about 45 min from the addition of NaOH to the stock solution. Before attaining a constant value, the absorption maximum becomes broader and the sample appreciably absorbs

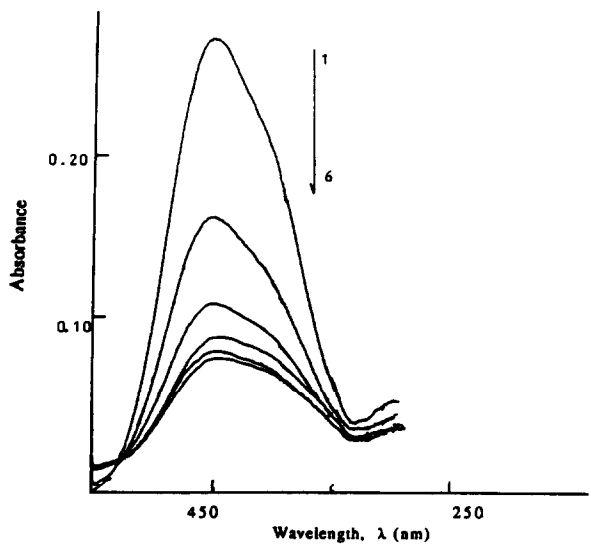


**Fig. 3.** Time dependence of the absorption spectrum of $1{\cdot}873 \times 10^{-5}$ mol dm$^{-3}$ of the base form of methyl yellow. Curves 1–6 correspond to the elapse of 1·0, 4·3, 7·7, 11·0, 14·3 and 45·0 min, respectively.

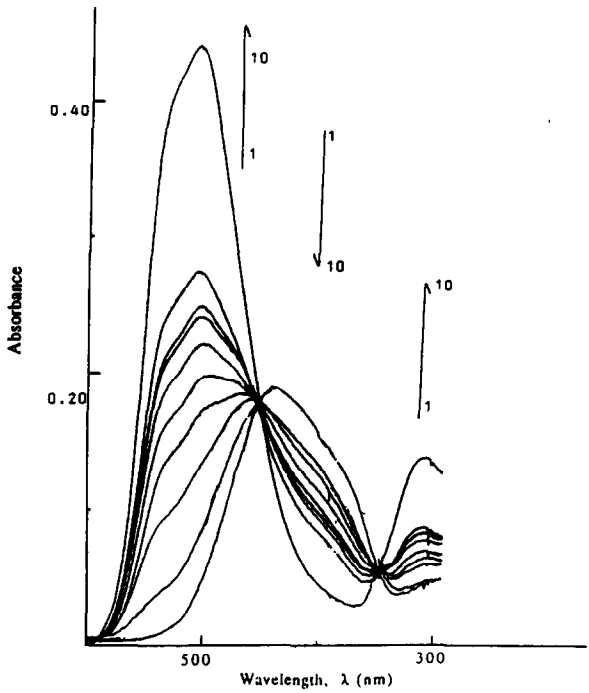


**Fig. 4.** The UV–visible spectrum of $1{\cdot}873 \times 10^{-5}$ mol dm$^{-3}$ methyl yellow as a function of pH. Curves 1–10 correspond to pH values 9·50, 4·22, 3·72, 3·48, 3·37, 3·26, 3·20, 3·18, 3·08 and 2·43, respectively.

at $\lambda > 550$ nm. This behaviour is illustrated in Fig. 3. Several repeated experiments with variable concentrations of methyl yellow in the range of $3{\cdot}75 \times 10^{-6}$ to $3{\cdot}75 \times 10^{-5}$ mol dm$^{-3}$ gave the same behaviour as shown in Fig. 3. However, the absorbances recorded after the attainment of a stable spectrum did not obey Beer's law. Based on these observations, it is concluded that the alkaline form of methyl yellow gives rise to an aggregation process. The details of such process were not pursued in this work. By maintaining the same preparation time, the UV–visible spectra shown in Fig. 4 were obtained for methyl yellow at several pH values.

Figures 1 and 4 indicate that, as the pH is lowered, the absorption maximum shifts to longer wavelength giving a red-coloured solution, which is attributed to the existence of the monoprotonated form of each azo dye. This colour was attributed to the azonium tautomer (az),[10] which is a resonance hybrid of structures B and C in Fig. 2. The maximum absorption bands are at 508 and 518 nm for methyl orange and methyl yellow, respectively. The lowering of the pH is also accompanied by the appearance of an absorption band in the UV region with maximum absorption at 316 nm for both azo dyes. This band was attributed to the ammonium tautomer (am),[10] which is shown as structure D in Fig. 2. Protonation of the

α-nitrogen of the azo linkage was neglected on the basis of the argument of Yeh and Jaffe.[11] The isosbestic point at 470 nm (see Fig. 1) is considered to represent an acid-base equilibrium with an apparent dissociation constant $K_{a_2}$, while the isosbestic point at 344 nm is considered to represent a tautomeric equilibrium with a tautomeric equilibrium constant ($K_t$). The same reasoning can be applied for methyl yellow, which has two isosbestic points at 460 and 344 nm, as shown in Fig. 4. Another observation to be deduced from Figs 1 and 4 is that the intensities of the absorption maxima of a tautomeric mixture increase with increasing acidity of the solution. However, it has been found that the spectra of both methyl orange and methyl yellow were invariant with respect to HCl concentration in the range of 0·032 to 0·46 mol $dm^{-3}$. This observation might indicate that both azo dyes were converted into the monoprotonated form (the azonium–ammonium tautomeric mixture). HCl concentrations higher than 0·46 mol $dm^{-3}$ resulted in an increase in the intensity of the azonium band and a decrease in the intensity of the ammonium band for both methyl orange and methyl yellow. On further acidification, mainly with $H_2SO_4$, the intensities of the absorption bands of the two tautomers started to decrease, and new bands at about 410 and 420 nm were observed for methyl orange and methyl yellow, respectively. A yellow-coloured solution was obtained at about 85 and 73% (w/w) aqueous $H_2SO_4$ for methyl orange and methyl yellow, respectively. In the case of methyl yellow, the yellow colour can be considered to be due to structure E in Fig. 2. However, for methyl orange, the yellow colour might be due to a diprotonated form, as in the case of methyl yellow (structure E in Fig. 2), or to a triprotonated form with the third proton attached to the $SO_3^-$ group. Spectra recorded at lower acidities of

**TABLE 1**

Effect of pH and HCl Concentration on the Distribution of Methyl Orange and Methyl Yellow between $CCl_4$ and $H_2O$ at About 18°C

| *pH or [HCl]* | *Methyl orange* | | *Methyl yellow* | |
|---|---|---|---|---|
| | *$CCl_4$ extraction* | *Colour in $H_2O$ layer* | *$CCl_4$ extraction* | *Colour in $H_2O$ layer* |
| pH > 7 | Nil | Yellow | Complete | Colourless |
| pH 6–7 | Nil | Yellow | Complete | Colourless |
| pH 5·7–6 | Nil | Yellow | Complete | Colourless |
| pH 0·5–5·7 | Nil | Red | Complete | Colourless |
| pH 0·2–0·5 | Nil | Red | Very high | Light red |
| [HCl] 1–2M | Nil | Red | Trace | Red |
| [HCl] 2–3M | Nil | Red | Nil | Red |
| [HCl] > 3M | Nil | Red | Nil | Red |

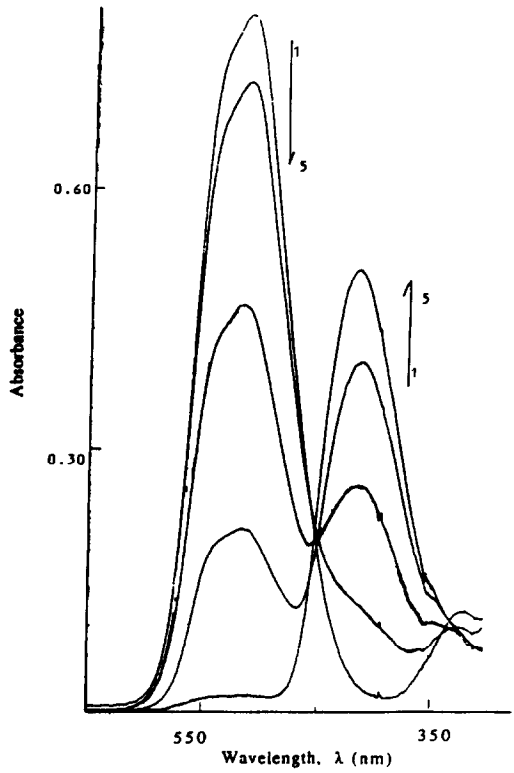


**Fig. 5.** The effect of $H_2SO_4$ on the UV–visible spectrum of $1{\cdot}873 \times 10^{-5}$ mol dm$^{-3}$ methyl yellow. Curves 1–5 correspond to 46·0, 55·1, 64·8, 68·4 and 73·4% (w/w) aqueous $H_2SO_4$, respectively.

$H_2SO_4$ did not yield well-defined isosbestic points, which is probably due to a medium effect. This is evident in Fig. 5, which shows the effect of $H_2SO_4$ on the UV–visible spectrum of methyl yellow. In 0·08 mol dm$^{-3}$ aqueous HCl, the monoprotonated forms of both azo dyes were found to obey Beer's law in the concentration range of $1{\cdot}85 \times 10^{-6}$ to $6{\cdot}50 \times 10^{-5}$ mol dm$^{-3}$. This result indicates that the monoprotonated forms of both azo dyes, as used in this study, exist in the monomer form.

The results of the extraction experiments at about 18°C are summarized in Table 1, which shows the distribution of methyl orange and methyl yellow between $CCl_4$ and the aqueous layer, whose pH or HCl concentration is changing. Methyl orange was not extractable at all acidities indicated in the table. This observation might suggest that the $SO_3^-$ group was probably not protonated and, therefore, that neutral species other than the zwitterions of the azonium and ammonium tautomers were not present. The zwitterions seem not to be extractable by $CCl_4$. On the other hand, Table 1 shows that methyl yellow is completely extractable into $CCl_4$ when the acidity of the

aqueous layer is up to 0·3 mol $dm^{-3}$ HCl (pH = 0·5). No extraction into the $CCl_4$ layer was observed when the acidity of the aqueous phase is higher than 2 mol $dm^{-3}$ HCl. For HCl concentrations in the range of 0·3 to 2 mol $dm^{-3}$, the extraction of methyl yellow into the $CCl_4$ layer depends on the concentration of HCl. These observations suggest that the neutral species of methyl yellow (structure A in Fig. 2) can exist in the aqueous solutions of methyl yellow of acidities up to 2 mol $dm^{-3}$ and such species represent the state via which methyl yellow enters the $CCl_4$ layer. The data of Table 1 are in agreement with the results of an ether-extraction study reported by Williams.[16]

Equation (1) represents a macroscopic acid-base equilibrium of methyl orange or methyl yellow.

$$HB^+ \overset{Ka_2}{\rightleftharpoons} B + H^+ \tag{1}$$

where $HB^+$ (red in colour) represents the monoprotonated form (a cation for methyl yellow and a zwitterion for methyl orange), and B (yellow in colour) is a neutral species for methyl yellow and an anion for methyl orange. The thermodynamic dissociation constant ($Ka_2$) can be obtained from eqn (2):

$$pH = pK_{a_2} + \log[(A - A_a)/(A_b - A)] + \log(\gamma_B/\gamma_{HB^+}) \tag{2}$$

where $A$ is the absorbance of a test solution which contains the forms $HB^+$ and B; $A_a$ or $A_b$ is the absorbance of a solution that contains either $HB^+$ or B, which is isomolar with the test solution; $\gamma_i$ is the molar activity coefficient of either species B or $HB^+$; and the term pH is the reading of the pH meter, which is related to the activity of the $H^+$ species. The effect of the ionic strength ($I$) on the activity coefficients can be calculated according to eqn (3):

$$\log \gamma_i = -0{\cdot}512(I)^{1/2}/[1 + (I)^{1/2}] + bI \tag{3}$$

which is the Guggenheim extension of the Debye–Hückel equation for a singly charged ion in water at 25°C.[17] A value of 0·2 $mol^{-1}$ $dm^3$ was considered for the constant $b$ in eqn (3) for ions of large organic molecules in water at 25°C.[17] In this study, the range of $I$ is $8{\cdot}2 \times 10^{-5}$ to $3{\cdot}1 \times 10^{-3}$ mol $dm^{-3}$ for methyl orange and $8{\cdot}6 \times 10^{-3}$ to $9{\cdot}1 \times 10^{-3}$ mol $dm^{-3}$ for methyl yellow. Under these conditions, it has been assumed that the activity coefficient of the monoprotonated form of methyl orange and the neutral form of methyl yellow are unity. In order to apply eqn (2) the absorbance of a test solution ($A$) was recorded at 500, 505 and 520 nm for methyl orange solutions in the pH range 2·5–4·0 and at 518, 530 and 540 nm for methyl yellow solutions in the pH range 3·0–3·7. The value of $A_a$ was recorded at pH = 1·3 for methyl orange and at pH = 1·0 for methyl yellow, while the value of $A_b$ was recorded at pH = 9 for both azo dyes.

A linear least-squares analysis was applied to the data of methyl orange

and methyl yellow as suggested by eqn (2). The data were in accord with eqn (2) with correlation coefficients of 0·999. The values of $pK_{a_2}$ obtained at 25·0°C are 3·37 ± 0·01 for methyl orange and 3·01 ± 0·01 for methyl yellow. The uncertainties represent standard deviations. The literature values for $pK_{a_2}$ of methyl orange are 3·40,[18] 3·49[12] and 3·35.[14] The literature values for $pK_{a_2}$ of methyl yellow are 3·31[18] and 3·5.[19] These literature values were not specified as thermodynamic ones.

The ammonium–azonium tautomerism of methyl orange or methyl yellow is represented by eqn (4):

$$\mathrm{am} \overset{K_t}{\rightleftharpoons} \mathrm{az} \tag{4}$$

The tautomeric equilibrium constant ($K_t$) is given by eqn (5):

$$K_t = [\mathrm{az}]/[\mathrm{am}] = (E - E_{\mathrm{am}})/(E_{\mathrm{az}} - E) \tag{5}$$

where $E$ is the apparent molar absorptivity of the tautomeric mixture and $E_{\mathrm{am}}$ and $E_{\mathrm{az}}$ stand for the molar absorptivities of the ammonium and azonium tautomers, respectively. $E_{\mathrm{am}}$ and $E_{\mathrm{az}}$ cannot be measured directly, but can be estimated from the spectra of suitable model compounds. Some authors[11,12] have used the approximation $E_{\mathrm{az}} = 2 \times 10^3\ \mathrm{cm^{-1}\ mol^{-1}\ dm^3}$, a value obtained at 320 nm by Wepster[20] for the first conjugate acid of 4-amino-3,5-di-tert-butylazobenzene, which exists solely as the azonium species. This approximation has been used as a value for $E_{\mathrm{az}}$ of both methyl orange and methyl yellow at 316 nm. Yeh and Jaffe[11] have assumed that the molar absorptivity of the 4-phenylazo-*N,N,N*-trimethyl anilium ion, $C_6H_5 . N{=}N . C_6H_4 . N^+(CH_3)_3$, is the same as $E_{\mathrm{am}}$ for the ammonium tautomer of methyl yellow at 316 nm. The value of $E_{\mathrm{am}}$ is $2{\cdot}00 \times 10^4\ \mathrm{cm^{-1}\ mol^{-1}\ dm^3}$ at 316 nm.[11] Likewise, Reeves[12] had considered 4-phenylazo-*N,N,N*-trimethyl 4′-sulfonato anilium ion, $SO_3^- . C_6H_4 . N{=}N . C_6H_4 . N^+(CH_3)_3$, as a model compound for the ammonium tautomer of methyl orange with $E_{\mathrm{am}} = 2{\cdot}50 \times 10^4\ \mathrm{cm^{-1}\ mol^{-1}\ dm^3}$ in $H_2O$ at 316 nm.

It has been found that, for HCl concentrations in the range of 0·5 to 6 mol $\mathrm{dm^{-3}}$, the position of the equilibrium of eqn (4) shifts to the side of the azonium tautomer. By using the literature values given above for the model compounds, together with our experimental values for the apparent molar absorptivities at 316 nm ($6{\cdot}84 \times 10^3\ \mathrm{cm^{-1}\ mol^{-1}\ dm^3}$ for methyl orange and $9{\cdot}24 \times 10^3\ \mathrm{cm^{-1}\ mol^{-1}\ dm^3}$ for methyl yellow), eqn (5) was used to calculate $K_t$ at several HCl concentrations. The results are given in Table 2. Literature values for $K_t$ of methyl yellow are in the range 1·4–2·8 in 6·6–24·2% (w/w) aqueous $H_2SO_4$.[11] Reeves[12] reported a value of 4·7 for $K_t$ of methyl orange in 0·1N aqueous $H_2SO_4$.

The microscopic acid dissociation constants $K_1$, $K_2$, $K_3$ and $K_4$ (as

**TABLE 2**
The Effect of HCl Concentration on the Value of the Tautomeric Equilibrium Constant ($K_t$) of Methyl Orange (MO) and Methyl Yellow (MY) at 25·0°C

| [*HCl*] (*M*) | $K_t$ | |
|---|---|---|
| | *MO* | *MY* |
| 0·46 | 3·75 | 1·49 |
| 1·03 | 4·03 | 1·62 |
| 2·25 | 4·94 | 2·50 |
| 5·75 | 13·3 | 3·85 |

indicated in Fig. 2) can be related to $K_t$ and the macroscopic acid dissociation constants $K_{a_1}$ and $K_{a_2}$ by the following equations:

$$K_1 = K_{a_1}/(1 + K_t) \quad (6)$$

$$K_2 = K_{a_1} \times K_t/(1 + K_t) \quad (7)$$

$$K_3 = K_{a_2}(1 + K_t) \quad (8)$$

$$K_4 = K_{a_2}(1 + K_t)/K_t \quad (9)$$

A value for $K_{a_1}$ was not determined in this study. However, the value $1{\cdot}22 \times 10^6$ mol dm$^{-3}$ was estimated from the data of Reeves[12] for $K_{a_1}$ of methyl orange in $H_2O$ at 25°C. The corresponding literature value for methyl yellow is $2{\cdot}51 \times 10^4$ mol dm$^{-3}$.[19] Although the acid-base equilibria of Fig. 2 are established at different acidities, eqns (6)–(9) require that only one particular value of $K_t$ is to be used in solving for $K_1$, $K_2$, $K_3$ and $K_4$ for methyl orange or methyl yellow. Such a value can be obtained at two different acidities (one allowing the establishment of the equilibrium described by $K_{a_1}$, and the other allowing the establishment of the equilibrium described by $K_{a_2}$), because the tautomeric equilibrium exists only over a certain range of acidity. Since $K_t$ was found to be constant in the acidity range of 0·03 to 0·46 mol dm$^{-3}$ HCl, then this value of $K_t$ is the one used for solving eqns (6)–(9). For methyl orange, $K_t$ was taken as 3·75, and for methyl yellow, $K_t$ was taken as 1·49. The results of the calculations are given in Table 3, together with the literature values of methyl orange. The data of Table 3 indicate that $K_2 > K_1$ and $K_3 > K_4$ for both methyl orange and methyl yellow. Therefore, the $\beta$-nitrogen of the azo linkage is more basic than the amino nitrogen in both compounds. This conclusion is in agreement with the data of Table 2 and with the observation that the intensity of the maximum absorption in the visible region (mainly caused by the azonium tautomer)

**TABLE 3**
The Estimated Values of the Microscopic Acid Dissociation Constants of Methyl Yellow and Methyl Orange in $H_2O$ at 25·0°C

| $K_i$ (*mol dm*$^{-3}$) | *Methyl yellow* | *Methyl orange* | |
|---|---|---|---|
| | | *Literature values*[a] | *Our data* |
| $K_1/10^4$ | 1·0 | 21 | 26 |
| $K_2/10^4$ | 1·5 | 110 | 96 |
| $K_3/10^{-3}$ | 2·4 | 1·9 | 2·0 |
| $K_4/10^{-4}$ | 16 | 4·0 | 5·4 |

[a]Ref. 12.

increases, while that in the UV region (mainly caused by the ammonium tautomer) decreases in the acidity range 0·5–6 mol dm$^{-3}$ HCl.

## ACKNOWLEDGEMENT

This work was supported by Yarmouk University (project 75/84).

## REFERENCES

1. Hersey, A. & Robinson, B., *J. Chem. Soc. (Faraday Trans. I)*, **80** (1984) 2039.
2. Rohrbach, R. P. & Wojcik, J. F., *Carbohydr. Res.*, **92** (1981) 177.
3. Yoshida, N., Seiyama, A. & Fujimoto, M., *J. Inclu. Phenom.*, **2** (1984) 573.
4. Buvari, A. & Barcza, L., *J. Inclu. Phenom.*, **7** (1989) 313.
5. Matsui, Y. & Mochida, K., *Bull. Chem. Soc. Jpn*, **51** (1978) 673.
6. Hirai, H., Toshima, N. & Uenoyama, S., *Bull. Chem. Soc. Jpn*, **58** (1985) 1156.
7. Clarke, R. J., Coates, J. H. & Lincoln, S. F., *Carbohydr. Res.*, **127** (1984) 181.
8. Sawicki, E., *J. Org. Chem.*, **21** (1956) 605.
9. Sawicki, E., *J. Org. Chem.*, **22** (1957) 365.
10. Sawicki, E., *J. Org. Chem.*, **22** (1957) 621.
11. Yeh, S. J. & Jaffe, H. H., *J. Amer. Chem. Soc.*, **81** (1959) 3283.
12. Reeves, R. L., *J. Amer. Chem. Soc.*, **88** (1966) 2240.
13. Albert, A. & Serjeant, E. P., *The Determination of Ionization Constants.* Chapman & Hall, London, UK, 1984, p. 17.
14. Meloun, M., *Iraq. J. Sci.*, **22** (1981) 163.
15. Kendrick, K. L. & Gilkerson, W. R., *J. Solution Chem.*, **16** (1987) 257.
16. Williams, I. W., *Sch. Sci. Rev.*, **49** (1968) 410.
17. Rochester, C. H., *Acidity Functions.* Academic Press, London, UK, 1970, p. 7.
18. Thiel, A. & Petter, O., *Z. Anorg. Chem.*, **137** (1928) 169.
19. Koltz, I. M., Fiess, H. A., Chen Ho, J. Y. & Mellody, M., *J. Amer. Chem. Soc.*, **76** (1954) 5136.
20. Wepster, B. M., A private communication referred to in Ref. 11.