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The Tautomeric and Acid–Base Equilibria of *p*-Methyl Red in Aqueous Solutions

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ABSTRACT

The UV–visible spectra of p-*methyl red were examined at 25°C in water at various acidities and the variations in the spectra were correlated with the structures of the several forms of the compound. The monoprotonated form gives aggregates at concentrations exceeding* $1{\cdot}50 \times 10^{-5}$ *mol* dm^{-3} p-*methyl red. In* 0·1–1·0 *mol* dm^{-3} *HCl,* p-*methyl red is present as a tautomeric equilibrium mixture with an equilibrium constant of 4·0. The microscopic acid dissociation constants that describe the acid–base equilibria involving the cationic form were calculated. The partition coefficient that describes the distribution of* p-*methyl red between di*-n-*butyl ether and water attains a maximum value of 49·0 at pH 3·5.*

1 INTRODUCTION

There has been an interest in studying the inclusion complexes of cyclodextrins with several azo dyes in both acidic and alkaline aqueous media. Equilibrium studies concerning the inclusion processes of cyclodextrins with the acid forms of methyl orange and methyl yellow,[1–3] methyl orange and *o*-methyl red[4] have been reported. It was also possible to evaluate the stability constants of the inclusion complexes of the individual tautomers of methyl orange and methyl yellow[1] and to estimate the thermodynamic parameters of such inclusion complexes.[3] In this regard *p*-methyl red received less attention compared with structurally-

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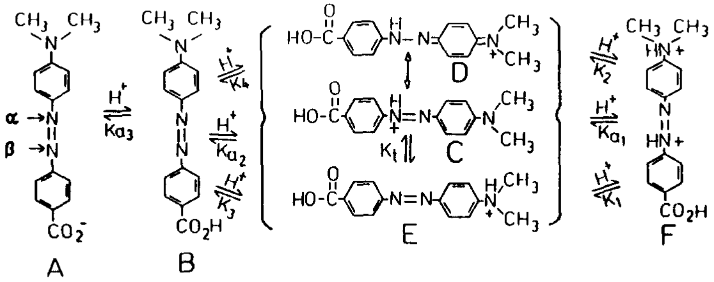


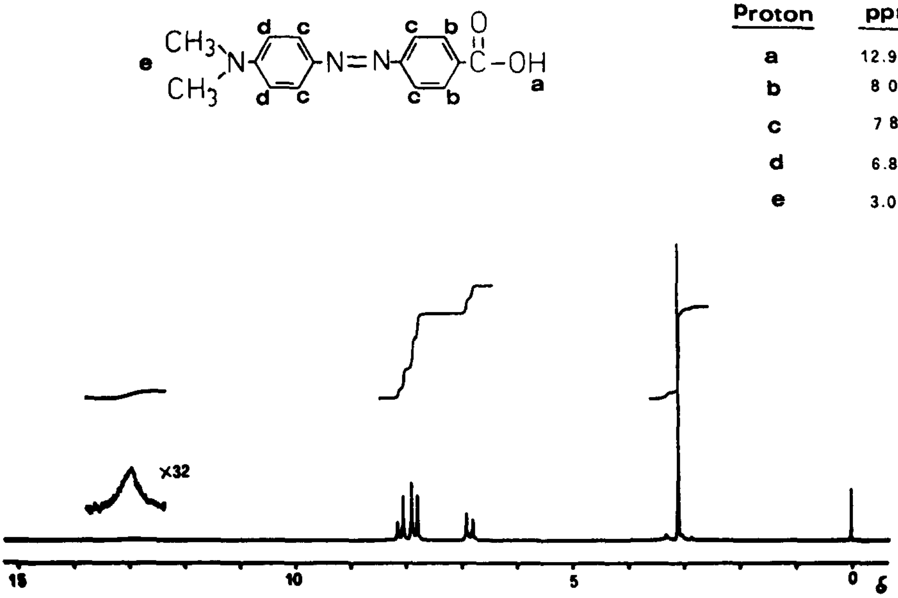
Fig. 1. The tautomeric and acid–base equilibria of *p*-methyl red in aqueous acidic solutions.

related azo dyes such as methyl orange and *o*-methyl red. Recently, *p*-methyl red has been the subject of several studies aimed at its photoisomerization in the host-guest Langmuir–Blodgett films prepared with amphiphilic β-cyclodextrin derivatives.[5-8]

The purpose of the present study is to investigate the tautomerism and the acid–base equilibria of *p*-methyl red spectrophotometrically. The results of such studies are crucial in studying the inclusion processes with cyclodextrins.[1,9] The results of the present study have been exploited for calculating the stability constants of the inclusion complexes of the acidic and alkaline forms of *p*-methyl red with α-, β- and γ-cyclodextrins, and these results will be reported separately. The partition coefficient which describes the distribution of *p*-methyl red between water and di-*n*-butyl ether is also reported at pH values allowing the coexistence of the monoprotonated form (structure B, Fig. 1) and either its conjugate base (structure A, Fig. 1) or its conjugate acid (structure E which is the ammonium tautomer and the resonance hybrid of structures C and D, which is the azonium tautomer, Fig. 1). The values of the microscopic acid dissociation constants K_1, K_2, K_3 and K_4 (as indicated in Fig. 1) were calculated from literature information on Ka_1, and Ka_2, and the value of K_t (the tautomeric equilibrium constant) obtained in the present study. The structures proposed in Fig. 1 are to be considered as the conceivable structures of *p*-methyl red in water, and can be compared with structures proposed for other aminoazobenzene dyes.[10-12] The protonation of the α-nitrogen of the azo linkage was ignored on the basis of the argument given by Yeh & Jaffe.[13]

2 EXPERIMENTAL

The acid form of *p*-methyl red ($C_{15}H_{15}N_3O_2$) was prepared according to a procedure similar to that suggested for the synthesis of *o*-methyl red,[14,15] except that *p*-aminobenzoic acid was used instead of *o*-aminobenzoic acid



Proton	ppm
a	12.97
b	8 09
c	7 83
d	6.85
e	3.08

Fig. 2. ^{1}H-NMR spectrum of *p*-methyl red in DMSO-d_6.

for coupling with dimethylaniline. The details of the preparation procedure are given elsewhere.[16,17] The crude *p*-methyl red was recrystallized four times from dimethyl formamide, giving a product with m.p. 260°C; further purification using toluene Soxhlet extraction[14] afforded a product of melting point 266°C, and which showed a single spot on TLC experiment as described in the literature.[16] The results of the elemental analysis (performed at M.H.W. Laboratories, Phoenix, Arizona, USA) were 67·03% for carbon, 5·54% for hydrogen and 15·75% for nitrogen. $C_{15}H_{15}N_3O_2$ requires 66·90% for carbon, 5·61% for hydrogen and 15·60% for nitrogen. The ^{1}H-NMR spectrum was recorded on a Bruker WP 80-SY in DMSO-d_6 with tetramethyl silane as internal reference; a typical spectrum is shown in Fig. 2.

The test sample was dried at 130°C for 10 h before use. The stock solutions of *p*-methyl red were prepared in the presence of dilute aqueous NaOH. A typical stock solution had a concentration of $3{\cdot}97 \times 10^{-4}$ mol dm^{-3}, an ionic strength of $7{\cdot}1 \times 10^{-4}$ mol dm^{-3} and a pH of 10·5. The pH of a test solution was adjusted by adding an appropriate amount of either NaOH or HCl as an aqueous solution. Concentrated HCl and H_2SO_4 were used for solutions of high acidity. In the distribution experiments, equal volumes (50 cm^3 each) of di-*n*-butyl ether and an aqueous solution of *p*-methyl red were used. The aqueous phase was buffered with monochloroacetic acid–KOH for pH 2·5, formic acid–KOH for pH 3·5 and with acetic acid–potassium acetate buffer for pH 4·5 and 5·3. The ionic strength was 0·01 mol dm^{-3} in the aqueous phase. The UV–visible spectra, as well as the distribution experiments, were carried out at 25°C. Other experimental details and equipment used were the same as reported previously.[9]

3 RESULTS AND DISCUSSION

The UV–visible spectrum of the alkaline form of *p*-methyl red (structure A, Fig. 1) at pH 9·5 shows two main absorption maxima at 273 nm and 464 nm. The maximum at 464 nm is attributed to the π–π^* transition of the azo group since this transition is centered at λ_{max} 320 nm in azobenzene,[11] at 446 nm in methyl yellow,[9] at 466 nm in methyl orange[9] and at 430 nm in *o*-methyl red.[18] The maximum occurring at 273 nm is attributed to the n–π^* transition of the —COO^- group since the alkaline form of *o*-methyl red[18] gives an absorption maximum at 288 nm, while methyl orange and methyl yellow do not absorb appreciably in the 250–300 nm range.[9] No significant changes were detected in the UV–visible spectrum of the alkaline form of *p*-methyl red up to a concentration of $1{\cdot}50 \times 10^{-4}$ mol dm^{-3}. Beer's law was obeyed at 273 and 464 nm and the molar absorptivities of the anion of *p*-methyl red were found to be $2{\cdot}74 \times 10^4$ and $9{\cdot}90 \times 10^3$ cm^{-1} mol^{-1} dm^3 at 464 and 273 nm, respectively. It is concluded that the anion of *p*-methyl red is present in the monomer form under the experimental conditions used in the present study.

Figure 3 shows the effect of pH on the UV–visible spectrum of *p*-methyl red. At pH 4·68 the maximum absorption occurs at 550 nm and a shoulder appears at 510 nm (curve 1, Fig. 3). However, as the pH is lowered the absorption band in the visible region becomes more symmetrical, as indicated by curve 3 in Fig. 3. The absorption in the UV region has its maximum at about 300 nm as given in Fig. 3. This absorption shows a gradual decrease in intensity as the pH is lowered. Another observation to be deduced from Fig. 3 is that *p*-methyl red absorbs appreciably at $\lambda > 600$ nm. Such an absorption was not observed for solutions having pH > 5·6 or HCl concentration >0·2 mol dm^{-3}. The absorption at $\lambda >$ 600 nm is believed to arise from aggregates of the neutral species of *p*-methyl red (structure B, Fig. 1), since *o*-methyl red[18] and methyl orange[9] did not give such an absorption. By considering the literature values of Ka_2 and Ka_3 of *p*-methyl red, which are $8{\cdot}32 \times 10^{-3}$ and $1{\cdot}17 \times 10^{-5}$ mol dm^{-3}, respectively,[19] the percentages of the monoprotonated form are 64·0, 92·7 and 59·6 at pH values 4·68, 3·38 and 2·25, respectively. The absorptions occurring at 550 and 537 nm (curves 1 and 2, Fig. 3) cannot be assigned to the monomer of the monoprotonated form because of the

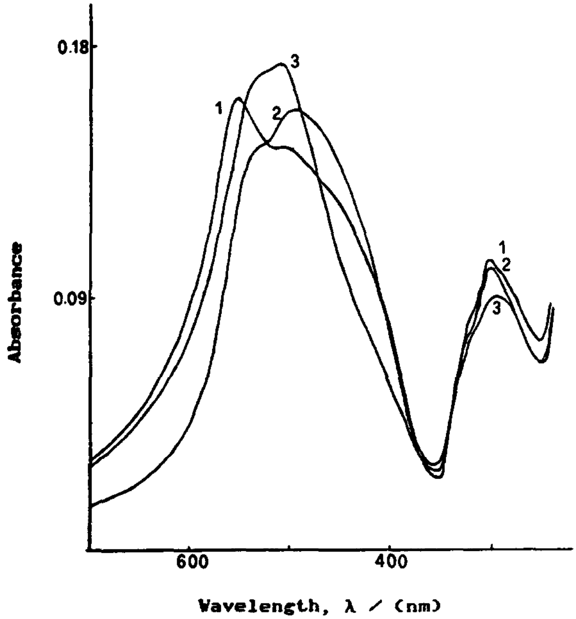


Fig. 3. The UV–visible spectrum of 1·10 × 10^{-5} mol dm^{-3} *p*-methyl red as a function of pH. Curves 1–3 correspond to pH values 4·68, 3·38 and 2·25, respectively.

lack of correlation between the abundance of the monoprotonated form and the intensity of absorption at these two wavelengths. These absorptions are probably due to the presence of an aggregate species arising from the monoprotonated species. Formation of such aggregates is believed to be the cause of the positive deviation from Beer's law which was observed in solutions having the maximum abundance of the monoprotonated species at pH 3·5 for λ = 500 and 300 nm when the total concentration of *p*-methyl red exceeds 1·1 × 10^{-5} mol dm^{-3}. Based on these arguments the absorption at 510 nm (see Fig. 3) is assigned to the diprotonated form of *p*-methyl red. The increase of the absorbance at 510 nm as the pH is lowered is in agreement with this assignment, since the abundance of the diprotonated form is expected to increase with lowering of the pH.

The effect of HCl concentration on the visible spectrum of *p*-methyl red is shown in Fig. 4. A well-defined band appears at HCl concentrations >0·2 mol dm^{-3} with λ_{max} at 510 nm. Figure 5 shows the effect of HCl concentration on the UV absorption of *p*-methyl red. This figure shows a band at λ_{max} 288 nm, which is assigned to the —COOH group, and a shoulder centered at 320 nm. The absorption at this wavelength is usually attributed to the ammonium tautomer, while the absorption at 510 nm is attributed to the azonium tautomer of an azobenzene dye.[12]

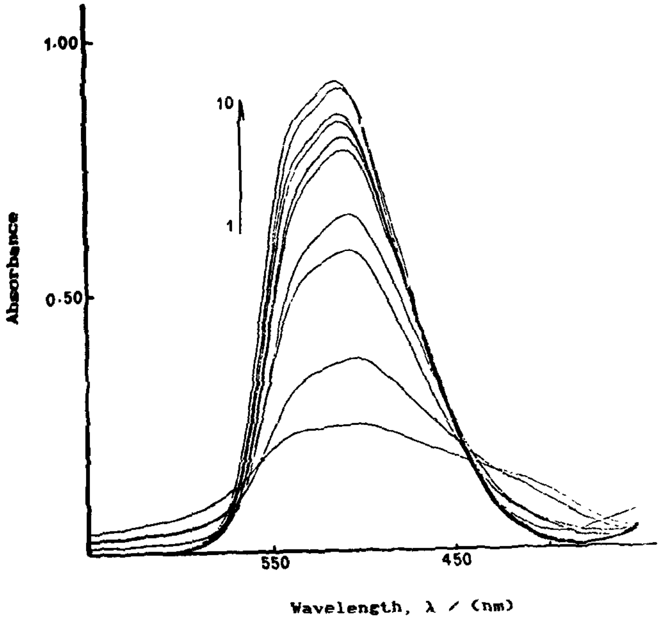


Fig. 4. The effect of HCl on the visible spectrum of 1·586 × 10^{-5} mol dm^{-3} *p*-methyl red. Curves 1–10 correspond to 0·01, 0·05, 0·10, 0·20, 0·50, 1·0, 1·8, 3·0, 7·5 and 10·0 mol dm^{-3} HCl, respectively.

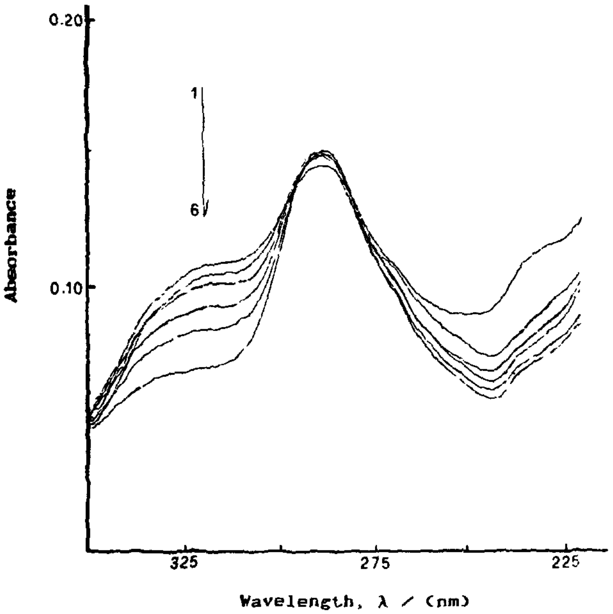


Fig. 5. The effect of HCl on the UV spectrum of 1·586 × 10^{-5} mol dm^{-3} *p*-methyl red. Curves 1–6 correspond to 0·10, 0·20, 0·50, 1·8, 3·0, and 7·5 mol dm^{-3} HCl, respectively.

The absorbance at 320 nm was found to be nearly constant at a value of 0·1 for HCl concentrations in the range 0·1–1·0 mol dm^{-3}. In this concentration range, *p*-methyl red is considered to exist in the cationic form as a tautomeric mixture. The spectra shown in Figs 4 and 5 indicate that the band of the azonium tautomer increases while that of the ammonium tautomer decreases as the HCl cncentration is increased. This pattern is due to a shift in the position of the tautomeric equilibrium of *p*-methyl red as the acidity of the solution is increased, a phenomenon generally observed for the tautomerism of azobenzene dyes.[12] When H_2SO_4 is used to attain higher acidities, the intensities of the absorption bands of both tautomers decrease as the concentration of H_2SO_4 is increased and a new absorption maximum appears at 410 nm as indicated in Fig. 6. The solution becomes yellow in colour in 80% (w/w) aqueous H_2SO_4. This colour is assigned to structure F in Fig. 1.

The distribution of *p*-methyl red between water and di-*n*-butyl ether was studied at a fixed concentration of *p*-methyl red at 1·50 × 10^{-5} mol dm^{-3}. The partition coefficient, K_p, is defined as the ratio $[dye]_o/[dye]_a$, where $[dye]_o$ and $[dye]_a$ are the molar concentrations of *p*-methyl red in the ether and the aqueous layers, respectively. The value of $[dye]_o$ was obtained from a calibration graph at λ_{max} 500 nm in di-*n*-butyl ether. The

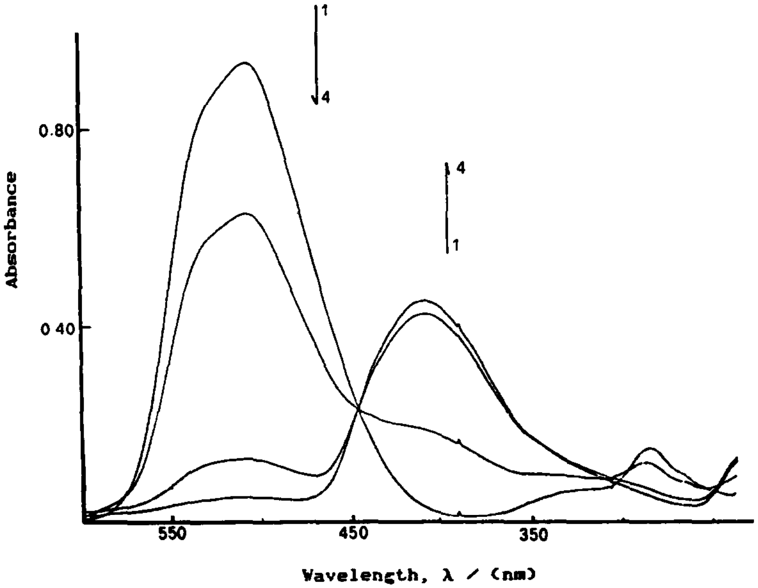


Fig. 6. The effect of H_2SO_4 on the UV–visible spectrum of 1·586 × 10^{-5} mol dm^{-3} *p*-methyl red. Curves 1–4 correspond to 55·1, 73·4, 82·6 and 88·0% (w/w) aqueous H_2SO_4, respectively.

TABLE 1
Effect of pH on the Distribution of 1·50 × 10^{-5} mol dm^{-3} *p*-Methyl Red between di-*n*-Butyl Ether and Water at 25°C

pH	A^a	10^5 *[dye]*$_o$	10^6 *[dye]*$_a$	K_p
5·3	0·308	0·98	5·2	1·88
4·5	0·432	1·38	1·2	11·5
3·5	0·460	1·47	0·3	49·0
2·5	0·340	1·08	4·2	2·57

[a] Absorbance of *p*-methyl red in the di-*n*-butyl ether layer at λ_{max} 500 nm.

value of $[dye]_a$ was obtained by difference. The results of the distribution study are given in Table 1, which shows that the partition coefficient attains its maximum value at pH 3·5. It can be shown that the neutral form of *p*-methyl red attains its maximum abundance at the pH value given by $\frac{1}{2}(pKa_2 + pKa_3)$, which is 3·51 as calculated from the literature values of pKa_2 and pKa_3 of *p*-methyl red. Based on this information and the data of Table 1, it can be concluded that the monoprotonated form of *p*-methyl red or any aggregate derived from it, constitutes the state via which *p*-methyl red migrates to the ether phase. It has been reported that the extraction of *o*-methyl red into CCl_4 is complete in the pH range 1·25–5·6[18] and that of methyl yellow into CCl_4 is complete at acidities ≤0·3 mol dm^{-3} HCl.[9] However, methyl orange was not extractable into CCl_4 at these acidities.[9] These results indicate that the ionic and the zwitterionic species of such azo dyes are not involved directly in the partition process between the aqueous phase and the organic phase.

The following equation describes the tautomeric equilibrium of *p*-methyl red

$$\text{am} \overset{K_t}{\rightleftarrows} \text{az} \tag{1}$$

where am and az represent the ammonium and the azonium tautomers. Since K_t is given by the ratio [az]/[am], a value for K_t can be calculated from the spectrophotometric data by using the following equation

$$K_t = (E - E_{am})/(E_{az} - E) \tag{2}$$

where E is the apparent molar absorptivity of the tautomeric mixture while E_{am} and E_{az} are the molar absorptivities of the ammonium and the azonium tautomers, respectively. E_{am} and E_{az} cannot be measured directly, but can be estimated from the spectra of suitable model compounds. A possible model compound for estimating E_{az} is the first conjugate acid of 4-amino-3,5-di-*tert*-butylazobenzene, which exists solely as the azonium

TABLE 2
Effect of HCl on K_t and the Absorbance Ratio A_{510}/A_{320} of *p*-Methyl Red at 25°C

[HCl](mol dm^{-3})	K_t	A_{510}/A_{320}
0·10	3·76	5·44
0·20	4·02	6·32
0·50	4·24	7·76
1·8	4·93	9·01
3·0	5·94	10·12
7·5	8·50	12·87

species with a molar absorptivity of 2×10^3 cm^{-1} mol^{-1} dm^3 at 320 nm.[13,20] Reeves[20] had considered 4-phenylazo-N,N,N-trimethyl 4'-sulphonato anilium ion as a model compound for the ammonium tautomer of methyl orange with an E_{am} of $2{\cdot}50 \times 10^4$ cm^{-1} mol^{-1} dm^3 in H_2O at 316 nm. By using these values of E_{az} and E_{am}, the tautomeric equilibrium constant of *p*-methyl red was calculated from absorbance data obtained at 320 nm and at several concentrations of HCl. Table 2 shows the results of such calculations at 25°C and a total concentration of $1{\cdot}59 \times 10^{-5}$ mol dm^{-3} for *p*-methyl red. The absorbance ratio at 510 and 320 nm, A_{510}/A_{320}, has been proposed as a rough estimate of the concentration ratio [az]/[am] for azobenzene dyes.[12] Table 2 indicates that both the absorbance ratio and K_t increase as the concentration of HCl is increased and the two parameters are not equal indicating that the absorbance ratio cannot be considered for describing the tautomerism in a quantitative manner.

The microscopic acid dissociation constants K_1, K_2, K_3 and K_4 (as described in Fig. 1) can be related to K_t and the macroscopic acid dissociation constants Ka_1 and Ka_2 by the following equations

$$K_1 = Ka_1/(1 + K_t) \tag{3}$$

$$K_2 = Ka_1K_t/(1 + K_t) \tag{4}$$

$$K_3 = Ka_2(1 + K_t) \tag{5}$$

$$K_4 = Ka_2(1 + K_t)/K_t \tag{6}$$

Although the acid–base equilibria of Fig. 1 are established at different acidities, eqns (3)–(6) 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. Such a value can be obtained at two different acidities (one allowing the establishment of the equilibrium described by Ka_1 and the other allowing the establishment of the equilibrium described by Ka_2) because the tautomeric equilibrium exists only over a certain range of acidity. Since the absorption maximum at 320 nm was nearly constant in the concentration range 0·1–1·0 mol dm^{-3} HCl, an average value of 4·0 was considered for K_t in this acidity range. It is assumed that Ka_1 of *p*-methyl red is the same as Ka_1 for methyl orange with a value of $1 \cdot 22 \times 10^6$ mol dm^{-3} in aqueous solution at 25°C.[9,20] By using the literature values of Ka_1 and Ka_2 and the above value of K_t, the constants K_1, K_2, K_3 and K_4 were calculated as $2 \cdot 44 \times 10^5$, $9 \cdot 76 \times 10^5$, $4 \cdot 16 \times 10^{-2}$ and $1 \cdot 04 \times 10^{-2}$ mol dm^{-3}, respectively. Since $K_1 < K_2$ and $K_4 < K_3$, then the β-nitrogen of the azo linkage is more basic than the amino nitrogen. A similar conclusion was given for methyl orange and methyl yellow.[9]

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