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# Quantitative Analysis of Tautomeric Equilibrium in 1-Phenylazo-4-naphthols—A New Approach

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## *ABSTRACT*

*A new quantitative approach, based on the analysis of overlapping bands, in determining the tautomeric equilibrium constant and the individual spectral curves of the pure tautomeric forms of 1-phenylazo-4-naphthol and its derivatives is applied. The influence of some important factors affecting the tautomeric equilibrium, such as solvent polarity, substituents in the phenyl ring, etc., is evaluated.*

## 1 INTRODUCTION

Statistical evaluation of the commercially disclosed structures[1] of azo dyes in the Colour Index shows that 92% of them have a potentially tautomeric structure and that about 50% of all azo dyes contain an isomeric naphthol ring. The position of the tautomeric equilibrium determines their colour, dyeing behaviour, photochemical properties, etc., and investigation of factors influencing it are therefore of both theoretical and technological importance. Since it is impossible to determine directly from the UV-Vis absorption spectra the molar absorptivities of pure tautomeric forms, semiquantitative approaches are usually used in determining the tautomeric equilibrium constant $K_T$.[2-8] In our preview study,[9] an approach for the quantitative analysis of the azo (A)-quinonehydrazone (H) tautomeric equilibrium in 1-phenylazo-4-naphthol and its derivatives (Fig. 1) was proposed.

In spite of the advantages of this method, there are two factors restricting its application to other potentially tautomeric systems such as isomeric 1-phenylazo-2-naphthols, viz.

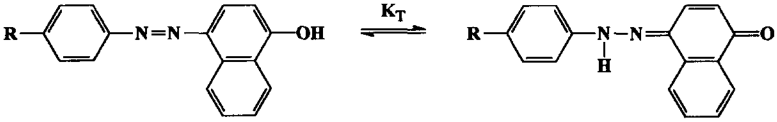

**Fig. 1.** Azo-quinonehydrazone tautomerism of 1-phenylazo-4-naphthols.

—both tautomeric forms have to possess individual areas of absorption, which is not fulfilled in the case of 1-phenylazo-2-naphthols;
—the individual spectral characteristics of the tautomeric forms should not depend on the solvent polarity in changing the volume ratio of the solvent used.

On the other hand, the resolution of overlapping bands in the UV-Vis absorption spectra provides important information about the energies and probabilities of the electronic transitions involved[10,11] and the values of the basic parameters characterizing any individual absorption band could be used to assign each band to a specific tautomeric form.[12]

The object of this study is to apply a new quantitative approach, based on the analysis of overlapping bands, in determining the tautomeric equilibrium constant $K_T$ and the individual spectral curves of the pure tautomeric **A** and **H** forms of 1-phenylazo-4-naphthol and its derivatives.

## 2 MATERIALS AND METHOD

The compounds used in this study were 1-phenylazo-4-naphthols in which R=H (I); R=$CH_3$ (II); R=$OCH_3$ (III); R=Cl (IV); R=$COCH_3$ (V) and R=$NO_2$ (VI). They were prepared by conventional methods of diazotization and coupling, carefully purified free from the *o*-isomer and their purity confirmed by TLC and m.p. Absorption spectra were recorded on a Perkin-Elmer Lambda 17 UV-Vis spectrophotometer using spectral grade solvents. The calculations were performed on a PC/AT computer with original programs for the analysis of overlapping bands and tautomeric equilibria developed previously.[10-12]

The following procedures characterize the proposed approach for the quantitative analysis of the tautomeric equilibria:[12]

1. A change of external factors (solvent polarity, T, pH, UV-irradiation, etc.) is applied in order to shift as much as possible the position of the tautomeric equilibrium.
2. The absorption spectra of a number of isomolar solutions are measured and stored in digitized spectrum files;

3. A computer analysis of experimental spectra is made including:
   - resolution of each absorption spectrum into individual bands and determination of their integral intensities;[10]
   - each individual band is assigned to one tautomeric form according to the principle: '*The increase in the content of a particular tautomeric form leads to an increase in the integral intensities of the individual bands composing its absorption spectrum, and vice versa*';
   - the values of individual areas $I_A^0$ and $I_H^0$ of pure **A** and **H** tautomeric forms are determined using the eqn (1):

$$\frac{I_A^i}{I_A^0} + \frac{I_H^i}{I_H^0} = 1 \tag{1}$$

     where $I_A^i$ and $I_H^i$ are the corresponding areas of the *i*th spectrum within the chosen spectral range;[12]
   - the values of the molar parts $X_A^i$, $X_H^i$ and $K_T^i$ are determined using eqns (2)–(4):

$$X_A^i = \frac{I_A^i}{I_A^0} \tag{2}$$

$$X_H^i = \frac{I_H^i}{I_H^0} \tag{3}$$

$$K_T^i = \frac{X_H^i}{X_A^i} \tag{4}$$

   - the individual absorption spectra of the tautomeric forms in any solution are constructed easily from the determined spectral parameters of the individual absorption bands forming the spectral envelope.[12]

## 3 RESULTS AND DISCUSSION

The absorption spectra of a number of isomolar solutions of I in ethanol/water are presented in Fig. 2(a) and the second derivative ($d^2A/d\nu^2$) spectra of the initial and final isomolar solutions are depicted in Fig. 2(b). According to our approach, each absorption spectrum is resolved into individual bands[10,11] and each band is assigned to a particular tautomeric form.[12] It should be noted that assignment is much easier in the visible region where the spectral differences between the **A** and **H** tautomeric forms are more pronounced (Fig. 2).

The absorption spectra of I in ethanol and ethanol/water = 20%/80%,

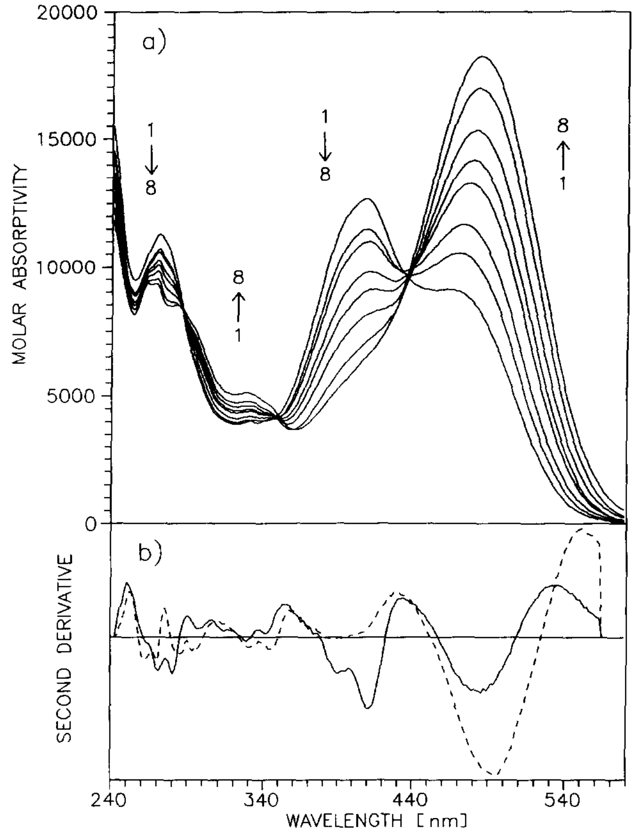

**Fig. 2.** (a) Absorption spectra of I in different volume ratios of ethanol/water. The percentage of water for the curves 1–8 are given in Table 1; (b) second derivative ($d^2A/d\nu^2$) spectra of 1 (———) and 8 (- - - -).

**TABLE 1**
Values of $X_A$, $X_H$ and $K_T$ for Each Isomolar Solution of I in Ethanol/Water

| *No.* | *Water (%)* | *$X_A$ (%)* | *$X_H$ (%)* | *Std. dev. of $X_H$ (%)* | *$K_T$* |
|---|---|---|---|---|---|
| 1 | 0 | 80·6 | 19·4 | 0·06 | 0·240 |
| 2 | 10 | 74·7 | 25·3 | 0·10 | 0·338 |
| 3 | 20 | 70·4 | 29·6 | 0·50 | 0·420 |
| 4 | 40 | 63·0 | 37·0 | 1·00 | 0·587 |
| 5 | 50 | 60·4 | 39·6 | 1·10 | 0·655 |
| 6 | 60 | 55·5 | 44·5 | 0·90 | 0·801 |
| 7 | 70 | 47·5 | 52·5 | 1·00 | 1·105 |
| 8 | 80 | 42·7 | 57·3 | 1·00 | 1·341 |

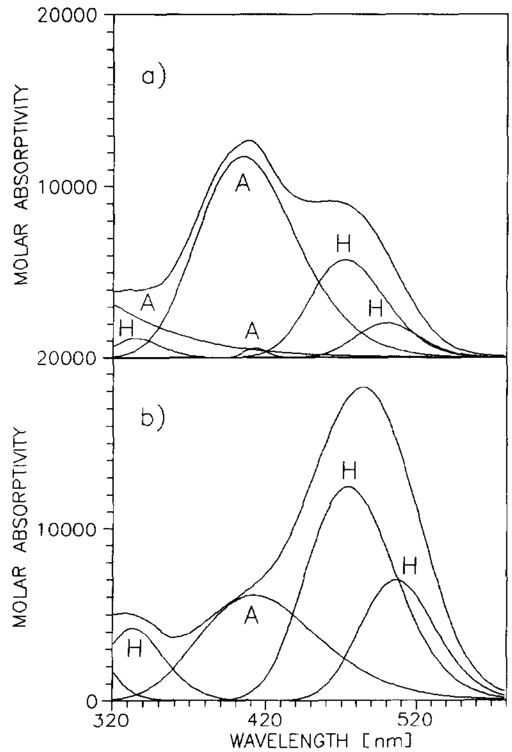

**Fig. 3.** (a) Absorption spectrum of I in ethanol with resolved individual bands; (b) absorption spectrum of I in ethanol/water = 20%/80% with resolved individual bands.

together with their assigned composing individual bands, are shown in Figs 3(a) and 3(b). The calculated values of $X_A^i$, $X_H^i$ and $K_T^i$ are presented in Table 1.

Analysis of the spectral data in Fig. 2 reveals that the absorption bands at ~400 nm and ~500 nm, assigned[2-5,13] to the **A** and **H** forms respectively, are bathochromically shifted with increase in water content. Since each individual spectrum in any solution could be readily constructed, the influence of the solvent polarity could be evaluated using the present approach. The individual spectra of the **A** and **H** forms in ethanol and ethanol/water = 20%/80% are depicted in Fig. 4. Evidently the long wavelength maxima of both tautomeric forms are shifted bathochromically and this effect is more pronounced in the more polar **H** form.

Using the same approach and the same solvent, the tautomeric equilibrium of II–VI was also investigated and the values of $X_H^i$ for the compounds I–VI and also the corresponding literature are presented in Table 2. In most cases the values of $X_H$, calculated by using eqns (5) and

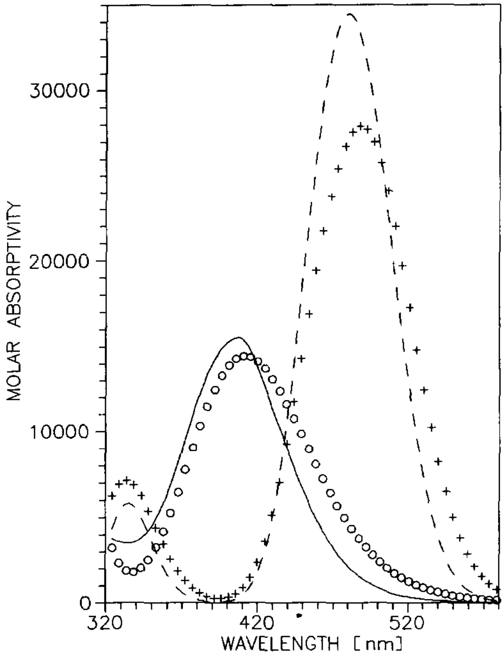

**Fig. 4.** Individual absorption curves of both tautomeric forms of I: **A** in ethanol (———); **H** in ethanol (- - - -); **A** in ethanol/water = 20%/80% (ooooooo); **H** in ethanol/water = 20%/80% (++++++).

(6) derived by Ospenson[2] and Sawicki,[3,4] are higher than those obtained by us:

$$X_{\mathrm{H}} \approx \frac{\varepsilon_{\mathrm{obs}}(\lambda_{\mathrm{H}})}{\varepsilon_{\mathrm{obs}}(\lambda_{\mathrm{A}}) + \varepsilon_{\mathrm{obs}}(\lambda_{\mathrm{H}})} \tag{5}$$

$$X_{\mathrm{H}} \approx \frac{A_i(\lambda_{\mathrm{H}})}{A_i(\lambda_{\mathrm{A}})} \tag{6}$$

where $\varepsilon_{\mathrm{obs}}(\lambda_{\mathrm{H}})$ and $\varepsilon_{\mathrm{obs}}(\lambda_{\mathrm{A}})$ are the observed molar absorptivities of the tautomeric compounds at the absorption maxima of the **A** and **H** forms respectively, while $A_i(\lambda_{\mathrm{H}})$ and $A_i(\lambda_{\mathrm{A}})$ are the corresponding absorbances.

It has been noted[9] that eqns (5) and (6) are valid only if:

(a) $\varepsilon_{\mathrm{A}}(\lambda_{\mathrm{H}}) = 0$ and $\varepsilon_{\mathrm{H}}(\lambda_{\mathrm{A}}) = 0$, i.e. the **A** form has no absorption at the absorption maximum of the **H** form and vice versa;

(b) $\varepsilon_{\mathrm{A}}(\lambda_{\mathrm{A}}) = \varepsilon_{\mathrm{H}}(\lambda_{\mathrm{H}})$, i.e. the molar absorptivities of tautomeric forms are equal.

The calculated spectral characteristics of the pure tautomeric forms of I–VI in ethanol and 50% ethanol/water are given in Table 3. From the data in

TABLE 2

Literature Values of $X_H$ [%] for Compounds I–VI in Comparison with those Determined in this Investigation[a]

| *Solvent* | *R=H* | *R=CH$_3$* | *R=OCH$_3$* | *R=Cl* | *R=COCH$_3$* | *R=NO$_2$* |
|---|---|---|---|---|---|---|
| Ethanol | 43·0 [3, 4] | 31·0 [3, 4] | 18·0 [8] | 35·0 [8] | 80·0 [8] | 100·0 [7] |
| | 42·0 [14] | 28·0 [8] | 10·9[a] | 29·0 [7] | 48·2[a] | 93·0 [8] |
| | 35·0 [8] | 12·0 [7] | 6·5 [9] | 16·9[a] | 25·1 [21] | 77·7 [21] |
| | 31·0 [7] | 13·9[a] | 0·0 [7] | 7·5 [9] | | 60·0[a] |
| | 30·0 [19] | 8·7 [9] | | | | |
| | 29·1 [20] | | | | | |
| | 19·4[a] | | | | | |
| | 9·3 [9] | | | | | |
| 50% | 62·0 [6] | 47·3 [6] | 37·0 [6] | 69·4 [6] | 86·2 [6] | 100·0 [6] |
| Ethanol/water | 52·4 [20] | 29·7[a] | 16·5 [9] | 41·9[a] | 67·8[a] | 82·0 [21] |
| | 39·6[a] | 25·0 [9] | 14·8[a] | 36·8 [9] | 53·5 [21] | 76·6[a] |
| | 34·2 [9] | | | | | |

Fig. 4 and Table 3, it is evident that both conditions (a) and (b) are not fulfilled, and in most cases the calculated ratio $\varepsilon_A(\lambda_A)/\varepsilon_H(\lambda_H)$ is between 1·6 and 2·2, leading to overestimated values of $X_H$ if eqns (5) and (6) are used. The values of $\varepsilon_H$ and $\varepsilon_A$ of the model compounds with fixed **A** and **H** forms, used[7,8] in order to 'improve' eqns (5), may lead to significant uncertainties due to the possible noncoplanarity of the model **H** form[14]

TABLE 3

Spectral Characteristics Calculated for Pure Tautomeric Forms of I–VI

| *Compound* | *Forms* | *Ethanol* | | | *50% ethanol/water* | | |
|---|---|---|---|---|---|---|---|
| | | $\lambda_{max}$ | $\varepsilon_{max}$ | $\varepsilon^H_{max}/\varepsilon^A_{max}$ | $\lambda_{max}$ | $\varepsilon_{max}$ | $\varepsilon^H_{max}/\varepsilon^A_{max}$ |
| R=H | **A** | 407·2 | 15 560 | 2·21 | 408·8 | 15 110 | 1·95 |
| | **H** | 479·2 | 34 430 | | 485·6 | 29 470 | |
| R=CH$_3$ | **A** | 405·6 | 20 570 | 1·92 | 404·0 | 19 830 | 1·82 |
| | **H** | 484·0 | 39 510 | | 492·0 | 36 030 | |
| R=OCH$_3$ | **A** | 407·2 | 20 960 | 1·73 | 404·8 | 20 030 | 1·83 |
| | **H** | 455·2 | 36 180 | | 464·8 | 36 590 | |
| R=Cl | **A** | 417·2 | 21 560 | 1·75 | 415·6 | 20 740 | 1·70 |
| | **H** | 482·8 | 38 150 | | 482·2 | 35 280 | |
| R=COCH$_3$ | **A** | 436·0 | 23 810 | 2·10 | 434·4 | 27 500 | 1·75 |
| | **H** | 472·8 | 50 000 | | 477·6 | 48 220 | |
| R=NO$_2$ | **A** | 444·0 | 8 120 | 4·43 | 458·4 | 9 080 | 3·74 |
| | **H** | 496·8 | 35 950 | | 501·6 | 33 990 | |

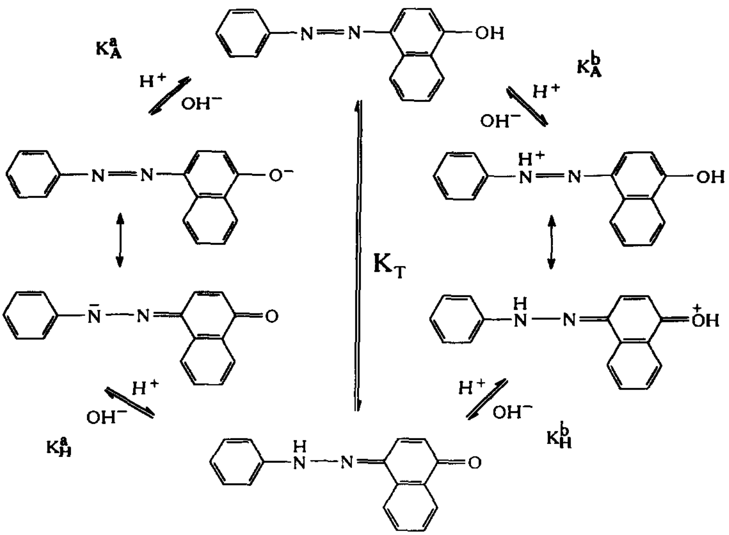

**Fig. 5.** Possible equilibrium processes of I in alkaline medium.

and the significant decrease in the model $\varepsilon_H$ values[7,15,16] in comparison with the corresponding values in Table 3. On the other hand, there is a good conformity between the calculated values of $\lambda_{max}^A$ and $\varepsilon_{max}^A$ (Table 3) and the corresponding values for the model A form,[7,15,16] since in this case there is no steric hindrance and the influence of the OH— and $H_3CO$— groups on their absorption properties is similar.

It should be noted that the values of $X_H^i$ and $K_T^i$, obtained with the current approach, are slightly higher than those calculated[9] and that these differences decrease with increase in the solvent polarity. The influence of solvent polarity on the position of the corresponding bands, which is not taken into account in Ref. 9, is the main reason for these differences.

The possible equilibria processes of I–VI in alkaline medium are schematically presented in Fig. 5. Using eqns (4), (7) and (8), which are valid for any two component tautomeric system,[17] along with the values of $pK_a^{obs}$ in 50% ethanol/water,[18] it is possible to calculate the values of $K_A$ and $K_H$ as $pK_a^A$ and $pK_a^H$ respectively (Table 4).

$$K_A = K_a^{obs}(1 + K_T) \tag{7}$$

$$K_H = K_a^{obs}(1 + 1/K_T) \tag{8}$$

Taking into account eqn (9), it is possible to evaluate the influence of the substituents R in the phenyl ring on the tautomeric equilibrium:

$$K_T = \frac{K_A}{K_H} \tag{9}$$

TABLE 4
Observed and Calculated Equilibrium Constants for I and its Derivatives in 50% Ethanol/Water

| $R$ | $K_T$ | $pK_a^{obs}$ | $pK_a^A$ | $pK_a^H$ | $\sigma_0$ |
|---|---|---|---|---|---|
| $R{=}OCH_3$ | 0·173 | 9·15 | 9·08 | 8·32 | −0·12 |
| $R{=}CH_3$ | 0·422 | 9·14 | 8·99 | 8·61 | −0·07 |
| R=H | 0·655 | 9·18 | 8·96 | 8·77 | 0·00 |
| R=Cl | 0·721 | 8·89 | 8·65 | 8·51 | 0·25 |
| $R{=}COCH_3$ | 2·106 | 9·05 | 8·56 | 8·88 | 0·46 |
| $R{=}NO_2$ | 3·273 | 8·91 | 8·28 | 8·79 | 0·82 |

In accordance with previous data[9] and conclusions[2–7] the presence of an electron donor substituent leads to an increase in $K_H$ and a decrease in $K_A$ (Table 4). The total effect is evidently a decrease in the $K_T$ value or a shift of tautomeric equilibrium towards the **A** forms. An opposite effect results from the introduction of an electron acceptor substituent, shifting the equilibrium towards the **H** form.

The application of the present quantitative approach to the isomeric 1-phenylazo-2-naphthols is also promising and further results will be reported later.

## 4 CONCLUSIONS

A new approach for the quantitative analysis of tautomeric equilibria is developed and its reliability demonstrated using the azo-quinonehydrazone tautomerism of I–VI. The individual spectra of both tautomeric forms, taking into account solvent polarity, are calculated. The influence of substituents in the phenyl ring is evaluated.

## ACKNOWLEDGEMENTS

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