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Diffuse Reflection Spectra of Filter Papers Dyed with 1-Arylazo-2-naphthols

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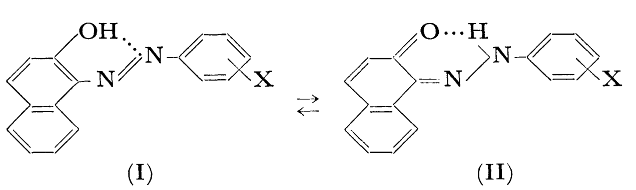
The diffuse reflection spectra of filter papers dyed with sixteen 1-arylazo-2-naphthols were examined in the range from 350 to 700 mμ. The absorption bands due to both the azo and hydrazone tautomers were observed in this state. Appreciable changes in the hue of the dyed papers caused by moisture were attributed to the deviation from the Kubelka-Munk theory due to the increased regular reflection; however, the movement of the tautomeric equilibrium caused by moisture was also clearly demonstrated in many cases. The direction was found to depend upon the kind and position of the substituents, *e.g.*, towards the azo tautomer in the case of the *p*-Cl and *o*-NO_2 derivatives and towards the hydrazone tautomer in the case of the *m*-Cl and *o*-MeO derivatives.

Spectroscopic studies of 1-arylazo-2-naphthols have indicated that these compounds exist in solution and also in the solid state as mixtures of the azo and hydrazone tautomers, I and II.[1-5]



(I) (II)

In a previous paper, we demonstrated that diffuse reflection spectra of 1-phenylazo-2-naphthol and its fifteen derivatives diluted with sodium chloride consist of absorption bands which can be assigned to both the azo and hydrazone tautomers.[6] In addition, we disclosed that the equilibrium moves by dilution towards the hydrazone tautomer, regardless of the kind and position of the substituents. As the compounds are prototypes of azo dyestuffs, it seemed that it would be interesting to examine the possible tautomerism in the compounds deposited on various substrates, *e.g.*, cotton, silk, wool *etc.*, by the same technique. We wish to report in this paper, the first of our attempts along this line, the results of our spectral measurements of filter papers dyed with 1-arylazo-2-naphthols. As we noticed that the hue of the dyed papers is sensitive to moisture, the effects of this on the spectra were also studied.

Experimental

Materials. The samples of 1-arylazo-2-naphthols were the same as those used in our previous work.[6] The derivatives carried one of the following substituents in the *o*-, *m*-, and *p*-positions on the phenyl ring: methyl, chloro, hydroxy, methoxy, and nitro.

Measurements. Toyo filter papers, No. 2, 5.5 cm in diameter, were wetted as uniformly as possible with an acetone solution of one of the 1-arylazo-2-naphthols, dropped from a 1-m*l* pipette with graduations. The concentration and volume were adjusted to achieve 3—6 μg of the dye per cm^2 of the paper. After the solvent had been evaporated at room temperature, the papers were dried at 100°C for 10 min and then cooled in a desiccator over silica gel. The difference in reflectance between the filter paper and the dyed paper, which is generally in the range from 0 to 60%, was recorded in the visible region by means of a Beckman DK 2A spectroreflectometer. When this measurement was finished, both the dyed paper and the reference were left overnight in a desiccator containing distilled water; then the difference in reflectance was measured in order to obtain the spectrum affected by moisture. To check the reproducibility, the papers were dried again and the measurements were repeated. The spectra were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. The absorption spectra of the 1-arylazo-2-naphthols dissolved in *n*-hexane, ethanol, and chloroform were measured by means of a Beckman DK 2A spectrophotometer. The concentrations were in the order of 10^{-5} mol/*l*. In all the figures in this paper, the reflection and absorption spectra are plotted taking the maxima arbitrarily as 1.00.

Results and Discussion

1-Phenylazo-2-naphthol (Figs. 1 and 2). As is shown in Fig. 1, the spectrum of the dried dyed paper consists of a broad band located in the region between 350 and 440 mμ and a sharp strong band with a maximum at 490 mμ. This spectrum closely resembles that measured in the chloroform solution (see curve *c* in Fig. 2). The former band, which dominates in the spectrum observed in a hexane solution, has been assigned to the azo tautomer, and the latter, to the hydrazone tautomer.[1] When the dyed paper is moistened, the relative intensity in the region from 350 to 440 mμ is much increased. However, the correlation between the spectral change and the movement of the equilibrium is not straightforward. Examining the solution spectra presented in Fig. 2, we reach the conclusion that the movement of the equilibrium towards the azo tautomer is probably not accompanied by an increase in the relative intensity in the region above 500 mμ. This is in serious disagreement with the finding in Fig. 1. The apparent change of the spectrum by moisture may be mostly caused by the deviation from the Kubelka-Munk theory due to the increased regular reflection. In accordance with this view, the absolute intensity at the absorption maximum

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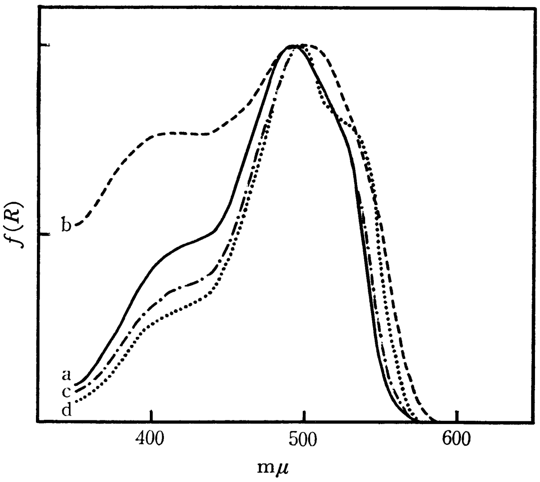

Fig. 1. Spectra of filter papers dyed with 1-phenylazo-2-naphthol; (a) dried and (b) moistened, and with 1-(*o*-tolylazo)-2-naphthol; (c) dried and (d) moistened.

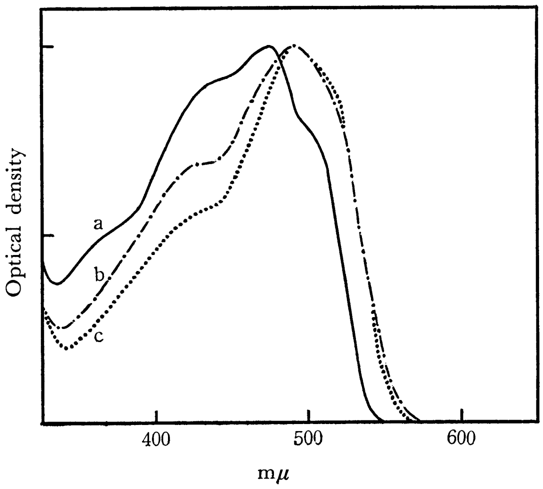

Fig. 2. Spectra of 1-phenylazo-2-naphthol dissolved in (a) *n*-hexane, (b) ethanol, and (c) chloroform.

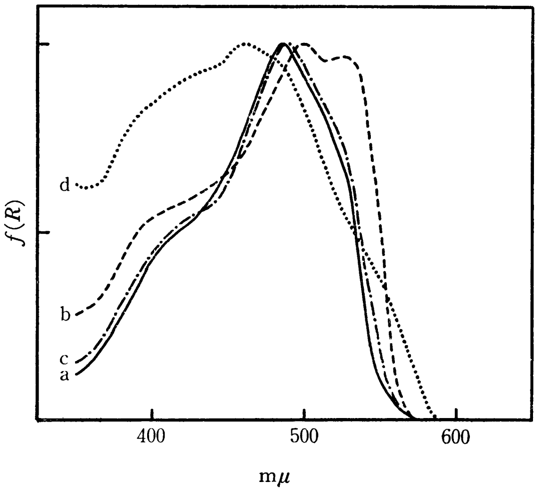

Fig. 3. Spectra of filter papers dyed with 1-(*m*-chlorophenylazo)-2-naphthol; (a) dried and (b) moistened, and with 1-(*p*-chlorophenylazo)-2-naphthol; (c) dried and (d) moistened.

observed with the moist dyed paper is only one eighth of that observed with the dried paper.

1-Tolylazo-2-naphthols (Fig. 1). When the papers are dried, all the Me derivatives show essentially the same spectrum. In the case of the *o*-Me derivative shown in Fig. 1, the spectrum is only slightly flattened by moisture (see Table 1). It is easy to see that the relative intensity decreases in the region from 350 to 490 mμ and increases in the region from 520 to 580 mμ upon this treatment. A shoulder due to the hydrazone tautomer can be clearly seen around 530 mμ. As the azo tautomer has an absorption maximum around 430 mμ, the whole change may be considered as an indication of a slight movement of the equilibrium towards the hydrazone tautomer. In the other two derivatives, marked decreases in the absolute intensity were observed upon moistening; however, no movement of the equilibrium could be detected. The relative intensity in the region from 350 to 450 mμ, which has been considered a measure of the amount of the azo tautomer by Burawoy and also by Bansho, increases in the order of substituents: *o*-Me$<$*m*-Me$\lesssim$H$\lesssim$*p*-Me. This is in accordance with the order found in an ethanolic solution by Burawoy *et al.*

1-Chlorophenylazo-2-naphthols (Fig. 3). The spectra of the dried papers dyed with these derivatives are very close to each other; however, large differences can be found when they are moistened. The spectrum of the *o*-Cl derivative is least affected by moisture. A relatively slight flattening and the appearance of a shoulder around 525 mμ can be noted. The spectrum of the moistened paper dyed with the *m*-Cl derivative presented in Fig. 3 has a well-resolved doublet, located at 500 and 525 mμ, indicating the movement of the equilibrium towards the hydrazone tautomer. This spectrum is similar to that of the same compound highly diluted with sodium chloride.⁶⁾ Not only a flattening by a factor of ten by moisture, but also a drastic change in the spectrum, was observed in the case of the *p*-Cl derivative. The relative intensity is very much increased in the region from 350 to 480 mμ and is decreased in the region from 490 to 540 mμ. This change may be attributed to the movement of the equilibrium towards the azo tautomer. It may be pointed out that the spectrum thus obtained looks like the spectrum of the same compound diluted with sodium chloride at a concentration of 1%.⁶⁾ As may be noticed in Fig. 3, the relative intensities in the region from 350 to 450 mμ are little different from each other in the dry state.

1-Hydroxyphenylazo-2-naphthols (Figs. 4 and 5). When the dyed papers are dry, the *o*-OH and *m*-OH derivatives exhibit spectra similar to that of 1-phenylazo-2-naphthol. Upon moistening, the spectrum of the *o*-OH derivative shows a decrease in its relative intensity in the region between 500 and 550 mμ. As a result, a shoulder appears around 550 mμ. The equilibrium seems to move a little towards the azo tautomer upon the addition of moisture. As is shown in Fig. 4, the effect of moisture on the spectrum of the *m*-OH derivative is somewhat strange. The whole spectrum seems to be simply shifted to wavelengths shorter by 30 mμ. However, from a comparison with the spectra measured in various solvents shown in Fig. 5, we may conclude that the observed change arises from

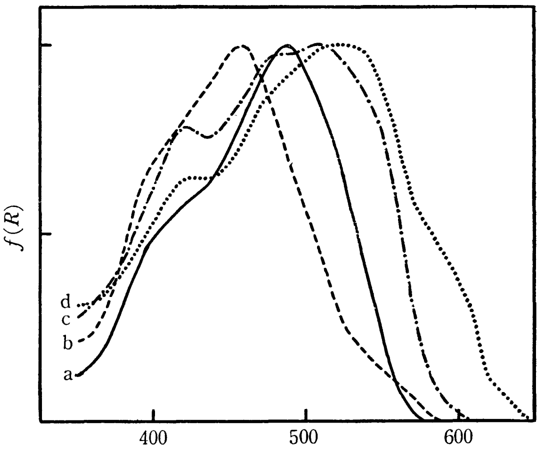

Fig. 4. Spectra of filter papers dyed with 1-(*m*-hydroxyphenylazo)-2-naphthol; (a) dried and (b) moistened, and with 1-(*p*-hydroxyphenylazo)-2-naphthol; (c) dried and (d) moistened.

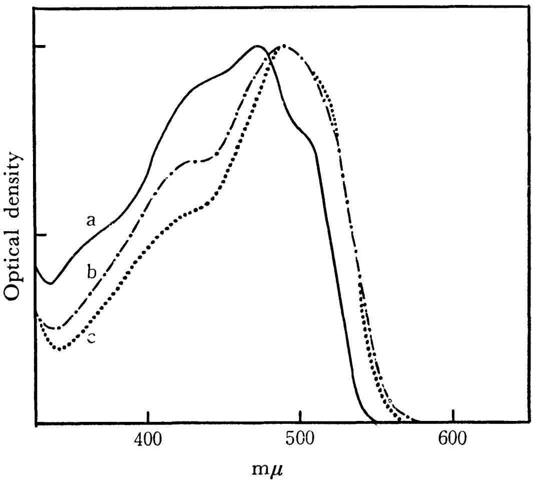

Fig. 5. Spectra of 1-(*m*-hydroxyphenylazo)-2-naphthol dissolved in (a) *n*-hexane, (b) ethanol, and (c) chloroform.

the movement of the equilibrium towards the azo tautomer. The *p*-OH derivative shows a spectrum very different from those of the other two, even in the dry state. The high relative intensity of the absorption around 420 mμ indicates that a fairly large amount of the azo tautomer is present. The spectral change caused by moisture may be attributed to an increase in the amount of the hydrazone tautomer.

1-Anisylazo-2-naphthols (Fig. 6). The spectra of the *o*-MeO and *m*-MeO derivatives are of the same kind. The only difference is in the relative intensity in the region from 350 to 450 mμ; it is much higher in the *m*-MeO derivative than in the *o*-MeO derivative. The same tendency is also observed in various solvents. Both of them are flattened by moisture. The doublet appearing at 525 and 560 mμ and assignable to the hydrazone tautomer can be distinctly seen in the case of the *o*-MeO derivative. The spectral change caused by moisture found in the case of the *m*-MeO derivative is less pronounced here. Nevertheless, the appearance of a shoulder at 525 mμ is undoubtedly a sign of the movement of the equilibrium towards the hydrazone tautomer. The spectrum of the *p*-MeO derivative is rather similar to that of the *p*-OH derivative. For these two compounds, the equilibria in solution very much favor the azo tautomer. The presence of strong maxima at 420 and 480 mμ to be assigned to the azo and hydrazone tautomers respectively indicates that the amounts of the two are comparable in the dry state. When the dyed paper is moistened, the above-mentioned maxima are replaced by those at 500 and 550 mμ assignable to the hydrazone tautomer. The former maximum apparently corresponds to the one at 480 mμ in the dry state. The relative intensities in the region from 350 to 450 mμ are in the order: *o*-MeO<*m*-MeO<H<*p*-MeO; this order is in good agreement with the order found in ethanolic solutions.[1]

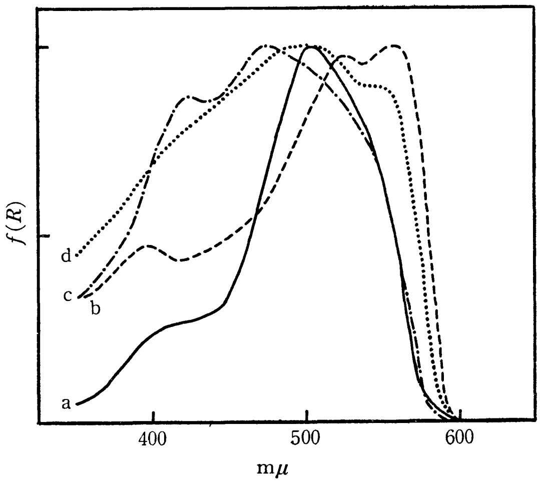

Fig. 6. Spectra of filter papers dyed with 1-(*o*-anisylazo)-2-naphthol; (a) dried and (b) moistened, and with 1-(*p*-anisylazo)-2-naphthol; (c) dried and (d) moistened.

1-Nitrophenylazo-2-naphthols (Figs. 7 and 8). Although the spectra of these derivatives look alike in the dry state, the effects of moisture are not the same. In the case of the *o*-NO_2 derivative, the sharp peak at 490 mμ disappears and a broad band with a maximum at 440 mμ becomes dominant. The tautomeric

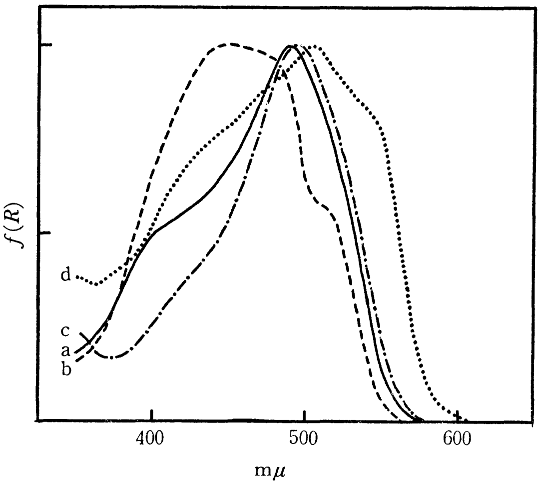

Fig. 7. Spectra of filter papers dyed with 1-(*o*-nitrophenylazo)-2-naphthol; (a) dried and (b) moistened, and with 1-(*p*-nitrophenylazo)-2-naphthol; (c) dried and (d) moistened.

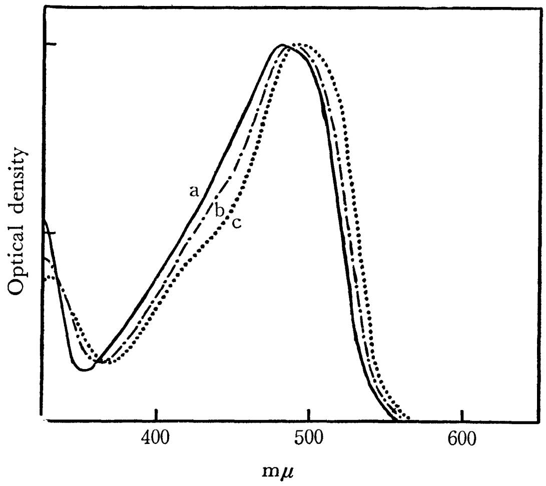

Fig. 8. Spectra of 1-(*p*-nitrophenylazo)-2-naphthol dissolved in (a) *n*-hexane, (b) ethanol, and (c) chloroform.

equilibrium moves drastically towards the azo tautomer. The spectrum of the *m*-NO_2 derivative is most flattened by moistening; nonetheless, the movement of the equilibrium is clear. The sharp peak at 480 mμ observed in the dry state is replaced by a broad one at 510 mμ on moistening. It must be added that these absorption bands are shifted to wavelengths longer by 50 mμ compared to those observed in solution.

Although the spectrum of the *p*-NO_2 derivative looks similar to those of the other two, comparison with the spectra observed in the solid, two-component system with sodium chloride suggests that the peak located at 495 mμ is due to the azo tautomer. The shoulder appearing at 540 mμ on moistening is to be assigned to the hydrazone tautomer. These assignments are supported by our measurements of the absorption spectra. This compound has been considered to exist nearly exclusively as a hydrazone tautomer in solution; however, a close examination of the spectra presented in Fig. 8 shows that the two tautomers exhibit absorption maxima only 40—50 mμ apart. Compared to these spectra, the bands in the spectrum of the dyed paper appear to be shifted by as much as 70 mμ.

TABLE 1. THE INTENSITY RATIO OF THE ABSORPTION MAXIMUM IN THE SPECTRUM OF MOISTENED DYED PAPER TO THAT IN THE SPECTRUM OF THE CORRESPONDING DRIED PAPER AND THE DIRECTION OF THE MOVEMENT OF THE EQUILIBRIUM BY MOISTURE; TOWARDS THE AZO TAUTOMER (+) OR THE HYDRAZONE TAUTOMER (−)

Substituent	Position		
	ortho	*meta*	*para*
None		0.12 (±)	
Methyl	0.8 (−)	0.1 (±)	0.2 (±)
Chloro	0.45 (−)	0.3 (− −)	0.1 (+ +)
Hydroxy	0.3 (+)	0.5 (+)	0.5 (−)
Methoxy	0.25 (− −)	0.35 (−)	0.2 (−)
Nitro	0.4 (+ +)	0.2 (−)	0.3 (−)

General Remarks. On the basis of the spectrum, we may conclude that 1-arylazo-2-naphthol exists, in general, as a mixture of the azo and hydrazone tautomers when deposited on filter paper. As is summarized in Table 1, the spectrum plotted using the Kubelka-Munk function is flattened by moisture, mostly by a factor between two and ten. This phenomenon, attributed to the deviation from the theory due to the increased regular reflection, suggests a drastic change in the state of the dispersion of the dye molecules caused by moisture. As cellulose, the substrate in the present work, is a kind of polyhydric alcohol, and as the dyestuff is less soluble in water than in alcohol, it is very likely that the molecules of the dyestuff deposited on filter paper are segregated on moistening. Of course, the extent of the segregation may depend upon the strength of the interaction between the dye molecule and the substrate, which, in turn, depends upon the nature of the substituent carried on the dye molecule.

It has been noted by Burawoy *et al.* that the relative stabilities of the hydrazone tautomer increase in this order of the solvents: hexane<alcohol<chloroform<water.[1] Therefore, the movement of the equilibrium of the dyestuff deposited on filter paper towards the hydrazone tautomer on moistening is reasonable if we consider the chemical constitution of cellulose. However, our observations, summarized in Table 1, indicate that this is not necessarily the case. Such a disagreement may be accounted for if we take into consideration the effect of moisture on the state of dispersion. In our previous work on the dyestuff-sodium chloride system, the spectral changes by dilution were attributed, at least in part, to the movement of the equilibrium towards the hydrazone tautomer.[6] The segregation of dye molecules deposited on filter paper by moisture must, therefore, favor the azo tautomer. These two effects of moisture oppose each other, but their magnitudes appear to be comparable. As is observed in our present study, the total effects depend on the kind and position of the substituent carried on the phenyl ring. As a matter of fact, the *o*-NO_2 derivative, which exhibits an exceptionally pronounced spectral change caused by moisture, is known to be one of those compounds which have solid-state spectra dominated by the absorption which is to be assigned to the azo tautomer.[6] In conclusion, the whole phenomenon is determined not only by the nature of the dyestuff itself, but also by the interaction between the dye molecule and the substrate. The results of the spectral measurements of the same compounds deposited on various fabrics made of both natural and synthetic fibers are in good accordance with this conclusion; the semeasurements will be the subject of forthcoming papers.