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The Diffuse Reflection Spectra of 1-Arylazo-2-naphthols Deposited on Various Synthetic Fibers

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The diffuse reflection spectra of sixteen 1-arylazo-2-naphthols deposited on polypropylene, polyacrylonitrile, polyethylene terephthalate, and Nylon-6,6 were recorded in the range from 350 to 700 nm. The spectra indicate the coexistence of the azo and hydrazone tautomers in these systems. By a comparison with the absorption spectra of the compounds dissolved in *n*-hexane, acetonitrile, methyl benzoate, and formamide, it was concluded that the nature of the fibers is the major factor determining the tautomeric equilibria. The effect of moisture on the spectra was found to be rather small except in the cases of the *p*-OH and *p*-MeO derivatives deposited on polyacrylonitrile.

In earlier work, evidence from diffuse reflection spectra was presented for the existence of an azo-hydrazone tautomerism of 1-arylazo-2-naphthols[1] diluted with sodium chloride.[2] The spectra were found, in many cases, to be temperature-dependent. The direction of the change is governed by the kind and position of the substituents; *e.g.*, the change is towards the hydrazone tautomer when the temperature is elevated in the cases of the *p*-Cl and *o*-NO_2 derivatives. Furthermore, the equilibrium was found to move by dilution towards the hydrazone tautomer in all cases. As more and more molecules of the compound are dispersed by dilution, the trend observed was attributed to the stabilization of the hydrazone tautomer by the highly polar surface of the alkali halide. This conclusion has been confirmed by recent measurements of the fluorescence of the same samples.[3] On the other hand, the equilibrium in solution was well established by Burawoy *et al.* about twenty years ago.[4] The relative stability of the hydrazone tautomer was reported to increase in this order of solvents: *n*-hexane$<$ethanol$<$chloroform$<$water. On the basis of these observations, we would expect the tautomeric composition of the azo dyestuff to be much affected by the nature of the substrate on which the compound is deposited.

Our previous work on the diffuse reflection spectra of filter papers dyed with 1-arylazo-2-naphthols revealed that the two tautomeric forms coexist in this state.[5]

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[1] This designation is used throughout this paper for convenience; it is not intended to define the structure of the compounds.

[2] C. Dehari, Y. Matsunaga, and K. Tani, This Bulletin, **43**, 3404 (1970).

[3] Y. Matsunaga and M. Shimane, *ibid.*, **45**, 295 (1972).

[4] A. Burawoy, A. G. Salem, and A. R. Thompson, *J. Chem. Soc.*, **1952**, 4793.

[5] Y. Matsunaga and N. Miyajima, This Bulletin, **44**, 361 (1971).

In addition, the appreciable changes in the hue of the dyed papers caused by moisture could be explained by the deviation from the Kubelka-Munk theory due to the increased regular reflection and, in many cases, by the movement of the equilibrium. In order to demonstrate clearly the effect of substrates on the equilibrium, it would seem to be convenient to employ substrates less hygroscopic than cellulose. Therefore, we selected for this study four synthetic fibers—namely, polypropylene, polyacrylonitrile, polyethylene terephthalate, and Nylon-6,6. To check whether or not the equilibria are essentially determined by the interaction with the substrate, the absorption spectra of 1-arylazo-2-naphthols dissolved in the following solvents were also examined: *n*-hexane, acetonitrile, methyl benzoate, and formamide. These solvents will be considered as model compounds of the synthetic fibers employed.

Experimental

Materials. The samples of 1-arylazo-2-naphthols were the same as those used in our previous work.[5] The derivatives carried one of the following substituents in the *o*-, *m*-, and *p*-positions on the phenyl rings: methyl, chloro, hydroxyl, methoxy, or nitro group.

Fabrics made of polypropylene, polyacrylonitrile, polyethylene terephthalate, and Nylon-6,6 were kindly provided by the Japan Exlan Co. and the Toyo Spinning Co.

Measurements. Fabrics cut into squares, 5 cm × 5 cm, 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 amount of the compound was then adjusted to about 6 μg per cm^2. The procedure in the diffuse-reflectance measurements was similar to that described in our previous paper.[5] The spectra were plotted using the Kubelka-Munk function, $f(R)=(1-R)^2/2R$, where R is the reflectance. Both the reflection and absorption spectra are presented by taking the maxima arbitrarily as 1.00 in all the figures.

Results and Discussion

1-Phenylazo-2-naphthol (Figs. 1 and 2). The absorption spectra in the four solvents are shown in Fig. 1. For example, the spectrum in *n*-hexane shows two strong bands at about 420 and 460 nm, and a weak one around 500 nm, whereas in formamide the intensity of the first band is relatively reduced and those of the second and third are considerably increased. The band at 420 nm is known to be due to the azo tautomer, and the rest, to the hydrazone tautomer. A comparison of the spectra in Fig. 1 and those recorded in our related works indicates that the concentration of the azo tautomer of 1-phenylazo-2-naphthol decreases in this order of solvents: *n*-hexane (1.890)>acetonitrile (37.5)>ethanol (24.30)>methyl benzoate (6.59)>chloroform (4.806)>formamide (109.5)>50% ethanol. The numbers in parentheses are the dielectric constants of the respective solvents.[6] Burawoy and Thompson noted that the order of solvents obtained by them is approximately in line with the increasing dielectric constant.[7] However, the above-mentioned order, where acetonitrile, methyl benzoate, and formamide were newly added, does not support their suggestion.

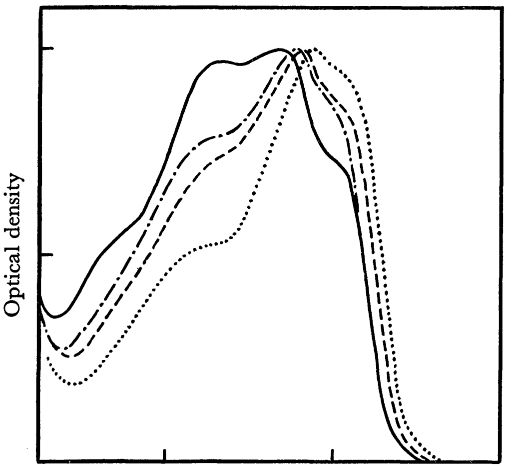

Fig. 1. Absorption spectra of 1-phenylazo-2-naphthol dissolved in *n*-hexane (——), acetonitrile (-·-·), methyl benzoate (----), and formamide (······).

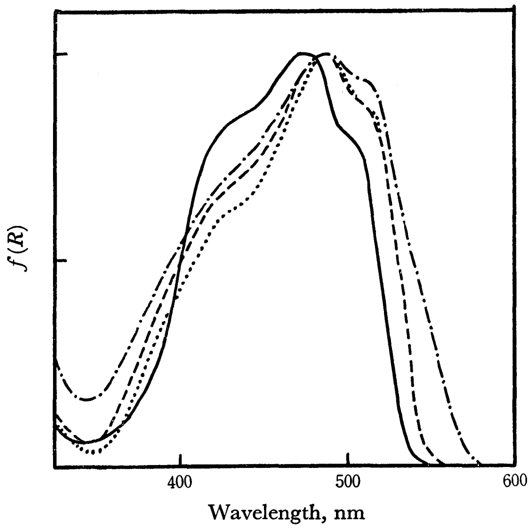

Fig. 2. Reflection spectra of 1-phenylazo-2-naphthol deposited on polypropylene (——), polyacrylonitrile (-·-·), polyethylene terephthalate (----), and Nylon-6,6 (······).

Figure 2 presents the diffuse reflection spectra of the 1-phenylazo-2-naphthol deposited on the four synthetic fibers. The relative intensity of the 420 nm band due to the azo tautomer decreases in this order of substrates: polypropylene>polyacrylonitrile>polyethylene terephthalate>Nylon-6,6, an order which corresponds well to the order of solvents. Therefore, it seems to be certain that the nature of the fibers is the major factor determining the equilibrium. Unfortunately, the relative intensity of the band appearing around 500 nm and assignable to the hydrazone tautomer is not quite consistent with that of the band at 420 nm. As will be mentioned, the disagreement seems to arise from the anomalous behavior of the compound deposited on polyacrylonitrile.

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[6] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," Wiley-Interscience, New York (1955).

[7] A. Burawoy and A. R. Thompson, *J. Chem. Soc.*, **1953**, 1443.

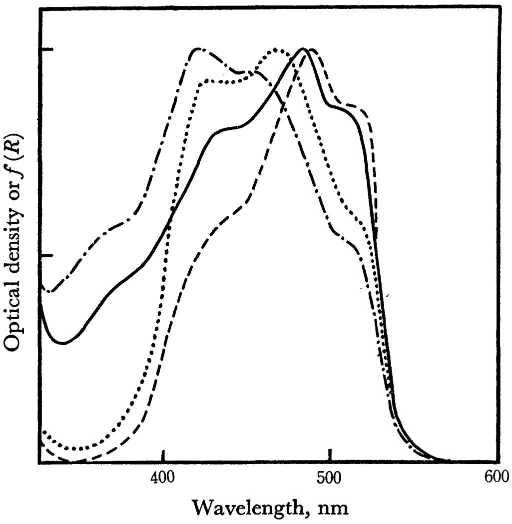

Fig. 3. Absorption spectra of 1-(*o*-tolylazo)-2-naphthol (——) and 1-(*p*-tolylazo)-2-naphthol (-·-·) dissolved in *n*-hexane and reflection spectra of the former compound (----) and the latter (······) deposited on polypropylene.

1-Tolylazo-2-naphthols (Fig. 3). Burawoy *et al.* reported that the intensity of the absorption band due to the azo tautomer in an ethanolic solution increases in this order of substituents: *o*-Me$<$*m*-Me$\sim$H$<$*p*-Me.[4] As an example, the absorption spectra of the *o*- and *p*-Me derivatives in *n*-hexane are compared with the reflection spectra of the same compounds deposited on polypropylene in Fig. 3. In accordance with the order of substituents reported by Burawoy *et al.*, the concentration of the azo tautomer in *n*-hexane appears to be higher in the *p*-Me derivative than in the *o*-Me derivative. The same tendency is also found in the reflection spectra. However, it may be noted that the hydrazone tautomer is a little more stabilized by polypropylene than by *n*-hexane. The spectrum of the *p*-Me derivative is the most markedly dependent on not only the solvent, but also on the substrate, among the 1-tolylazo-2-naphthols. The relative intensity of the band due to the azo tautomer around 420 nm was found to decrease in this order: polyacrylonitrile$>$ polypropylene$>$polyethylene terephthalate$>$Nylon-6,6. Here again, polyacrylonitrile is not located in the expected position. On the other hand, the intensity of the band due to the hydrazone tautomer at about 520 nm increases in the order to be expected from the nature of the substrates.

1-Chlorophenylazo-2-naphthols (Fig. 4). The relative intensity of the band due to the azo tautomer in solution increases in the following order: *o*-Cl$<$*m*-Cl$<$ *p*-Cl, as has been reported by Burawoy *et al.*[4] The solution spectra of the last derivative are nearly the same as those of 1-phenylazo-2-naphthol. In the other two cases, the hydrazone tautomers are so favored that their spectra are rather insensitive to the change in solvents. In accordance with this observation, their reflection spectra are not much modified by the substrates. In Fig. 4, the absorption spectra of the *o*- and *p*-Cl derivatives in acetonitrile are compared with the reflection spectra of the compounds deposited on polyacrylonitrile. The structures observed in the former spectra are not detectable in the latter; however, it is not difficult to see that the reflection spectrum bears a similarity to the respective absorption spectrum.

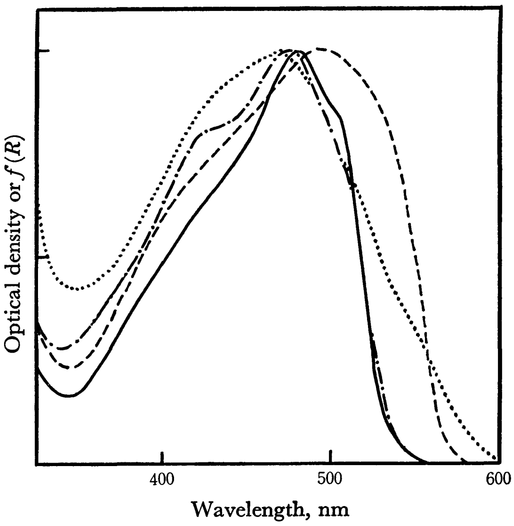

Fig. 4. Absorption spectra of 1-(*o*-chlorophenylazo)-2-naphthol (——) and 1-(*p*-chlorophenylazo)-2-naphthol (-·-·) dissolved in acetonitrile and reflection spectra of the former compound (----) and the latter (······) deposited on polyacrylonitrile.

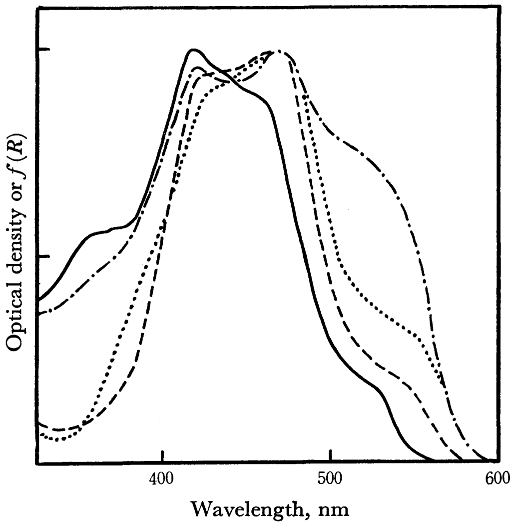

Fig. 5. Absorption spectra of 1-(*p*-hydroxyphenylazo)-2-naphthol dissolved in *n*-hexane (——) and formamide (-·-·) and reflection spectra of the same compound deposited on polypropylene (----) and Nylon-6,6 (······).

1-Hydroxyphenylazo-2-naphthols (Fig. 5). On the basis of the relative intensity of the band at 420 nm, the concentration of the azo tautomer may be concluded to increase in this order of substituents: *o*-OH$<$ *m*-OH$<$H$<$*p*-OH. Consequently, the most pronounced solvent effect on the spectrum can be observed with the *p*-OH derivative. The two extremes of the spectra, that is, those in *n*-hexane and formamide, are shown in Fig. 5. In the former solution, the band at 420 nm, assignable to the azo tautomer, is the strongest. On the other hand, the band due to the hydrazone tautomer located at 470 nm is much intensified in the latter solution. In addition, it must be noted that the shoulder around 525 nm is appreciably enhanced. The solvent effect on the tautomeric equilibrium is not exactly the same as that found for 1-phenylazo-2-naphthol, suggesting the presence of some specific interaction between the solute and solvents. In the order of solvents for the *p*-OH derivative, methyl benzoate comes before ethanol. As is represented by the spectra of the *p*-OH derivative deposited on polypropylene and Nylon, the effect of substrates on the reflection spectra is much less than that of solvents on the absorption spectra. The tautomeric equilibrium is shifted more towards the hydrazone tautomer compared with that in the model-compound solution. Nevertheless, the spectral change by the substrates is in the expected direction. In the other two derivatives, the effects of the solvents and also of the substrates are generally not appreciable. The only exception is the combination of the *m*-OH derivative and polyacrylonitrile, where a blue shift as much as 25 nm is found.

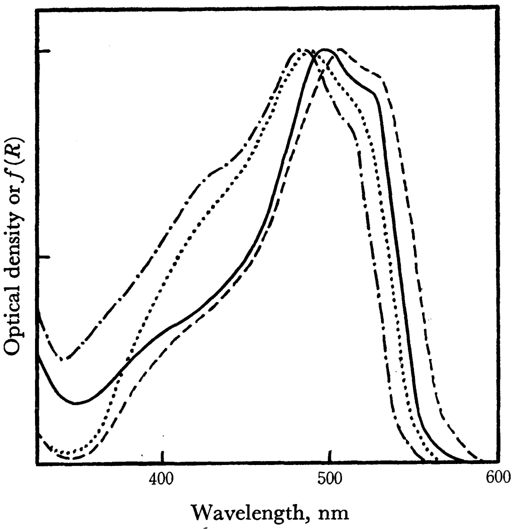

Fig. 6. Absorption spectra of 1-(*o*-anisylazo)-2-naphthol (——) and 1-(*m*-anisylazo)-2-naphthol (–·–·) dissolved in methyl benzoate and reflection spectra of the former compound (– – –) and the latter (······) deposited on polyethylene terephthalate.

1-Anisylazo-2-naphthols (Fig. 6). The solution spectra are similar to those of the corresponding hydroxy derivatives. However, the solvent effect on the former spectra is a little more pronounced than that on the latter. In the cases of the *o*- and *m*-MeO derivatives, the order of solvents is modified in the same way as is found with the *p*-OH derivative. In Fig. 6, the absorption spectra of the *o*- and *m*-MeO derivatives in methyl benzoate are compared with the reflection spectra on polyethylene terephthalate. The excellent correspondence between the absorption and reflection spectra supports the hypothesis that the interaction between the compound and the substrate is responsible for the determination of the tautomeric compositions on polyethylene terephthalate. The order of the relative intensities of the band due to the azo tautomer is quite normal in the reflection spectra of the *m*-MeO derivative. However, some anomalies are observed with the other two derivatives deposited on polyacrylonitrile; that is, a red shift of the whole spectrum as much as 30 nm was observed with the *o*-MeO derivative, and an intensification of the bands above 500 nm was noted in both the derivatives.

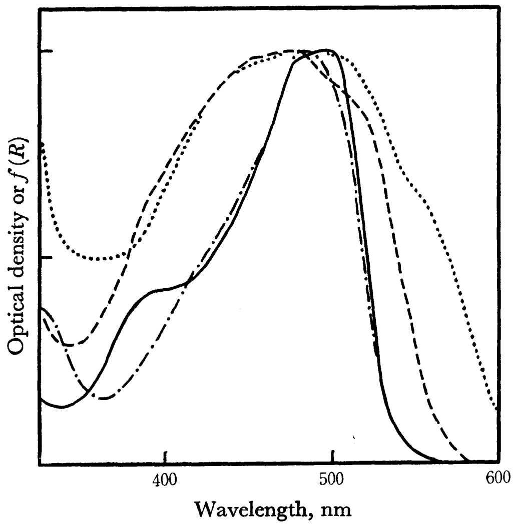

Fig. 7. Absorption spectra of 1-(*o*-nitrophenylazo)-2-naphthol (——) and 1-(*p*-nitrophenylazo)-2-naphthol (–·–·) dissolved in acetonitrile and reflection spectra of the former compound (– – –) and the latter (······) deposited on polyacrylonitrile.

1-Nitrophenylazo-2-naphthols (Fig. 7). Except in the case of the *m*-NO_2 derivative, the band to be assigned to the azo tautomer is hardly observable in the solution spectra. As may be expected from this observation, no clear solvent effect is found in these cases. Nonetheless, the reflection spectra of the *o*- and *p*-NO_2 derivatives on polyacrylonitrile were found to be very different from the absorption spectra measured in acetonitrile (see Fig. 7). The reflection spectra are much broader than the absorption spectra and resemble the solid-state spectra reported in our previous works.[2,3] These two compounds appear not to be well dispersed on polyacrylonitrile. As a result, the tautomeric equilibria are shifted to the azo tautomer. It must be added that a similar situation has previously been found in the moistened filter papers dyed with these nitro derivatives.[5]

The moisture regains of the synthetic fibers are known to be as follows: polypropylene, 0%; polyacrylonitrile, 1.3%; polyethylene terephthalate, 0.4%; and Nylon-6,6, 4.5%.[8] In accordance with the low values for polypropylene and polyethylene terephthalate, the reflection spectra do not respond to the addition of moisture. The only exceptions are the *m*-OH and *o*-MeO derivatives deposited on polyethylene terephthalate. In the former case, a blue shift of the absorption maximum by 10 nm is observed. The spectrum of the latter derivative is dominated by the bands located at 505 and 530 nm. The intensity ratio

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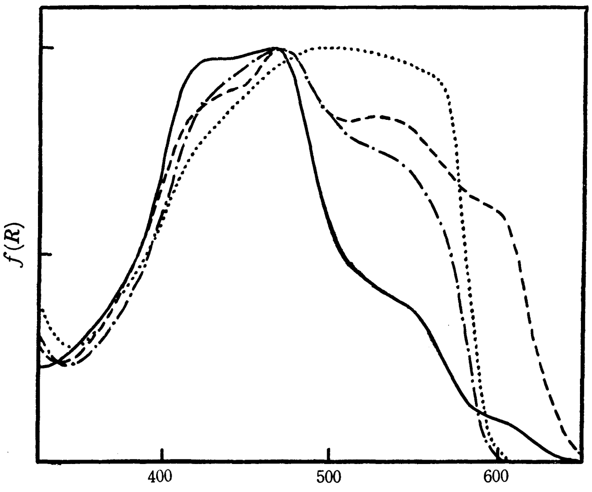
[8] H. Sofue, "Gosei-sen'i (Synthetic Fibers)," Dai-nippon Tosho, Tokyo (1968), p. 167.



Wavelength, nm

Fig. 8. Reflection spectra of 1-(*p*-hydroxyphenylazo)-2-naphthol deposited on polyacrylonitrile; dried (——) and moistened (----), and those of 1-(*p*-anisylazo)-2-naphthol deposited on the same substrate; dried (-·-·) and moistened (······).

of these two bands is 1.00: 0.95 when dried, but 0.99: 1.00 when moistened, indicating a slight movement of the tautomeric equilibrium towards the hydrazone tautomer on moistening.

The spectra of the *p*-OH and *p*-MeO derivatives deposited on polyacrylonitrile were found to be drastically modified by moistening (see Fig. 8). By a comparison with the spectra recorded in *n*-hexane and formamide (shown in Fig. 5), the change in the spectrum of the *p*-OH derivative can be attributed to the movement of the equilibrium towards the hydrazone tautomer. The spectral change exhibited by the *p*-MeO derivative can also be explained by the movement in the same direction. The latter spectrum after moistening is rather similar to that recorded with a solid sample diluted with sodium chloride.[2] However, the coincidence cannot be considered as an indication that the dye molecules are segregated upon moistening, because the movement is not in the direction to be expected in such a case. In addition, it must be noted that no marked decrease in the absorption intensity due to the segregation is observed here. Therefore, the movement of the tautomeric equilibrium appears to be caused solely by the change in the medium. A less pronounced but definite change in the spectrum was observed with some other derivatives. The results are summarized in Table 1. The intensity ratio of the absorption maximum in the spectrum of a moistened sample to that in the spectrum of the corresponding dried sample is also presented in this table. The latter is the average of the measurements made before moistening and after drying again. The flattening of the spectrum by moisture observed with polyacrylonitrile is found to be rather small if compared with the flattening observed with filter paper.

Table 1. The intensity ratio of the absorption maximum in the spectrum of 1-arylazo-2-naphthol deposited on moistened polyacrylonitrile to that deposited on the dried substrate and the direction of the movement of the equilibrium by moisture; towards the azo tautomer (+) or the hydrazone tautomer (−)

Substituent	Positon		
	ortho	*meta*	*para*
None		0.5 (−)	
Methyl	0.6 (±)	0.9 (−)	0.5 (−)
Chloro	0.9 (±)	1.1 (−)	0.8 (±)
Hydroxy	0.5 (+)	0.7 (±)	0.3 (--)
Methoxy	1.0 (±)	0.8 (−)	0.8 (--)
Nitro	0.8 (±)	0.8 (−)	1.0 (±)

Although the highest moisture regain is shown by Nylon, the effect on the spectra is not very appreciable. The equilibrium was found to move, if at all observable, slightly towards the hydrazone form. As has been mentioned earlier, formamide, the model compound of this substrate, is located next to 50% ethanol in the order of solvents. Therefore, it is not surprising to see that the tautomeric composition in 1-arylazo-2-naphthols deposited on Nylon is not much affected by moisture.