of Mohair and Cashmere with Sheep's Wool, *Textile Res.* J. 56, 442–446 (1986).

- Wortmann, F.-J., and Arns, W., Untersuchungen zu den Cuticulaschuppenkantenhöhen textilrelevanter Tierhaare, in "Proc. Int. Wool Text. Org. Techn. Cttee.," rep. no. 2, Avignon, France, 1988.
- Wortmann, F.-J., and Phan, K.-H., Cuticle Scale Heights of Wool and Specialty Fibers and Their Changes Due to Textile Processing, *Textile Res. J.* 69, 139-144 (1999).

- Wortmann, F.-J., and Wortmann, G., "Scanning Electron Microscopy as a Tool for the Analysis of Wool/ Speciality Fiber Blends," Comett-Eurotex, Guimares, Portugal, 1991.
- Zielinski, M., A New Approach to Hair Surface Topography: Fourier Transform and Fractal Analysis, J. Soc. Cosmet. Chem. 40, 173-189 (1989).

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Color Change of Disperse Dyes on Nylon 6 Films with Dye Concentration

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ABSTRACT

Spectral changes of disperse dyes on nylon 6 film are investigated with decreasing dye concentration (C_f). The visible absorption maxima (λ_{max}) of most azo disperse dyes shift to longer wavelengths with decreasing C_{ℓ} . The shift is significant for dyes with dipole structures caused by the intramolecular charge transfer. The spectral change is analyzed in detail for CI Disperse Orange 3 and 5, practical disperse dyes, in terms of McRae's equation and a factor analysis. The λ_{max} values for these dyes on film in the range of low C_f are much longer wavelengths than those estimated by McRae's equation and shift to shorter wavelengths with increasing temperature. The results of the factor analysis indicate that the visible absorption spectra of dyed films with decreasing C_f can be described as the sum of two distinct spectra, designated as species I and II. Species I has λ_{max} at longer wavelengths than species II. The ratio of [species I]/[species II] increases with decreasing C_f , causing a red shift of λ_{max} with decreasing C_f . This result is consistent with the sorption behavior of these dyes by nylon 6 film from water, where the dyes are sorbed by the polymer as two distinct species: L-species---dye taken up by the polymer through the Langmuir sorption mechanism, and P-species-dye taken up by Nernst-type partitioning. For both dyes, the relations between C_f and the concentrations of species I and II are very similar to the relations between C_f and the concentrations of the L- and P-species. We estimate that species I and II in this study correspond to L- and P-species in sorption studies, respectively.

The shades of some disperse dyes depend on the polymeric substrates on which they are sorbed, *e.g.*, CI Disperse Orange 3 shows yellowish orange on secondary cellulose acetate and brick red on polyamide [2], and CI Disperse Violet 1 shows red-violet on secondary cellulose acetate and blue-violet on nylon 66 [21].

Irick and Pacifici [5] studied the change in visible absorption maxima (λ_{max}) of dyes [I] with solvents in-

cluding polymeric substances; they found that the λ_{max} shifts to longer wavelengths with increasing polarity of the solvent:



where X and Y denote electron withdrawing and electron donating substituents, respectively. They concluded that the modified McRae's equation [8], Equation 1, and empirical relationships permit prediction of changes in λ_{max} with solvents:

$$\Delta \nu = \nu_s - \nu_g$$

= $(AL_0 + B) \frac{n_D^2 - 1}{2n_D^2 + 1} + C \left[\frac{D - 1}{D + 2} - \frac{n_D^2 - 1}{n_D^2 + 2} \right] ,$
(1)

where Δv is the difference in absorption frequency for λ_{\max} in solution (v_s) and in the gas (v_g) ; $(AL_0 + B)$ and C are constants, which are independent of solvent properties; n_D is the refractive index of the solvent measured at the sodium D-line; and D is the static dielectric constant of the solvent. In Equation 1, the first term on the right-hand side expresses the contribution of the dispersion interaction of the dye with the solvent, and the last term expresses the dipole-dipole interactions.

Recently, we have found, however, that the λ_{max} of azo disperse dyes (4'-nitro, 4-aminoazobenzene derivatives) [II] on nylon 6 film shifts to longer wavelengths with decreasing dye concentration (C_f) in the substrate, as shown in Figure 1. We have observed the appreciable shift for dyes with chlorine atoms at 2'- and 6'-positions, particularly in a very low C_f range.



FIGURE 1. Absorption spectra of CI Disperse Orange 5 in nylon 6 films: a dotted line is passing through the λ_{max} of each spectrum.



Dyes [I] and [II] have a conjugated π -electron system, with both electron withdrawing and releasing substituents at opposite ends of the molecule. Such molecules have a large contribution of dipole structure [III] caused by intramolecular charge transfer (CT) [5]:



The λ_{max} of the CT band shifts to longer wavelengths with increasing polarity of the solvents [13].

Disperse dyes are often applied to polyamide fabrics to produce pale shades because of their excellent ability to cover barré effects [1]. Therefore, changes in color with decreasing C_f will be interesting to both theoretical and practical dyers. The spectral change gives us information about changes in the local polarity around the dye in the polymer with decreasing C_f [19]. The same phenomenon also provides basic data for computer color-matching jobs.

In this study, we clarify the spectral change of disperse dyes on nylon 6 with C_f . Then we analyze the nature of the spectral shift for CI Disperse Orange 3 and 5 (abbreviated as Orange 3 and 5) in detail through various methods, since both dyes are practical azo dyes with simple structures (Orange 3) or with appreciable red shifts in λ_{max} with decreasing C_f in nylon 6 (Orange 5).

Experimental

The dyes were identical to those used in previous studies [15–18], and the solvents were spectrophotomeric grade. Nylon 6 film was biaxially drawn, prepared by Unitika Ltd. The film was treated in water at 95°C for 25 hours before use.

The film was dyed using the same method as that used in measurements of sorption isotherms [15, 17, 18] and the concentration profiles of dyes in the polymer in the diffusion studies [16], where dye concentration (C_f) in the film ranged from saturation C_f to approximately zero. The dye in the dried film (10–20 mg) was extracted with 25% aqueous pyridine solution (4–10 mL) at 80–90°C two or three times. There were no concentrations of the extracts by evaporation. The amount of dye in the extract (10–25 mL) was estimated colorimetrically.

Visible absorption spectra of the dyes in solvents and on the film were measured on a Hitachi U-3300 or U-2000A spectrophotometer at room temperature in the usual way. For spectral measurements of the dyed film at various temperatures, each film specimen $(1 \times 2.5 \text{ cm})$ was sandwiched between two brass blocks (1.25 cm wide \times 0.6 cm thick \times 5.0 cm high) with narrow slits at their centers. The two blocks combined formed a structure the same size as a normal quartz cuvette. The blocks with the sandwiched specimen were placed in the cell holder and thermostatted at a desired temperature for about 20 minutes. After that, the spectrum of the dyed film was measured on a Hitachi U-2000A spectrophotometer.

The film had enough thickness (l = about 0.0027 cm) to avoid the appearance of a sinusoidal curve caused by the interference of incident light into the film over the wavelength measured [7]. Thus, the measured value of λ_{max} for each dye on the film was accurate.

Results and Discussion

Spectral Change of Disperse Dyes on Nylon 6 Film with Decreasing C_f

The results of the measurements are summarized in Table I, and indicate that a red shift in the λ_{max} of azo dyes with decreasing C_f is appreciable for dyes with an electron withdrawing substituent, —NO₂ group, at the X-position. For dyes 1–3 (X = H), there is only a slight red shift with decreasing C_f , while for dyes 4–12, an appreciable red shift occurs, particularly for dyes 10–12, as typified in Figure 1. These dyes have two chlorine atoms acting as electron withdrawing groups at 2' and 6' positions and have a large contribution of dipole structure.

The UV/visible absorption spectrum arises from the electronic transition between molecular orbitals, reflecting the chemical structure of the compound. The position of λ_{max} is related to the difference between the energies at the ground state (E_g) and the exited state (E_e) . Both

 E_g and E_e decrease in polar solvents [13] for molecules with a large contribution of dipole structure caused by an intramolecular charge transfer, such as Orange 3 and 5. But E_e of the polar excited state in polar solvents decreases to a much greater extent. This reduces the difference between E_g and E_e : a pronounced red-shifted λ_{max} would result in increasing polarity of the solvents. Therefore, the significant red shift of λ_{max} with decreasing C_f is a characteristic of a dye with a large contribution of dipole structure [III].

The visible absorption spectrum of a typical anthraquinone disperse dye, CI Disperse Violet 1 (1,4-diaminoanthraquinone), in polar solvents is characterized by a double head peak (peak 1 at shorter and peak 2 at longer wavelengths). The relative strength of two peaks at each λ_{max} , Intensity_{Peak2}/Intensity_{Peak1}, depends on the polarity of the solvent [20]. The ratio increases with the increased dielectric constant (D) of the solvents, as shown in Table II. For the same dye on nylon 6 film, this ratio increases from 1.040 to 1.094 with decreasing C_f , as shown in Table II. This fact also indicates that the character of the medium around the dye changes with C_f .

Spectral Change of Orange 3 and 5 on Nylon 6 Film with Decreasing C_f

The color changes of these dyes have only one intense band in the visible region; therefore, we can assess color change with C_f from the value of λ_{max} in the visible region. Hence, we analyze the spectral shift in detail for these two dyes.

Figure 2 shows the relation between C_f and λ_{max} of the dyes on the film and in the extract (25% aqueous pyri-

$X - \bigvee_{Y_2}^{Y_1} N = N - \bigvee_{R_2}^{R_1} N = N - \bigvee_{R_2}^{R_1} N = N - \bigvee_{R_2}^{R_2} N = \bigvee_{R_2}^{R_2} $									
No.	X	Y ₁	Y ₂	Z	R 1	R ₂	Shift in λ_{max} , nm ^a	Change in C_f , mol/kg	Cl name
1	Н	н	н	н	н	н	$404.0 \rightarrow 407.0$	$2.50 \times 10^{-2} \rightarrow 9.32 \times 10^{-4}$	
2	Н	H	Н	Н	CH ₂ CH ₂ OH	CH,CH,OH	$422.0 \rightarrow 423.5$	$1.81 \times 10^{-2} \rightarrow 3.26 \times 10^{-4}$	
3	Н	Н	H	Н	CH,CH,	CH,CH,CN	$411.5 \rightarrow 412.5$	$2.22 \times 10^{-2} \rightarrow 2.00 \times 10^{-4}$	
4	NO ₂	Н	Н	Н	Н	н	478.0 → 489.0	$1.51 \times 10^{-2} \rightarrow 1.22 \times 10^{-4}$	Disperse Orange 3
5	NO ₂	Н	Н	Н	CH ₂ CH ₃	CH ₂ CH ₂ OH	500.5 → 507.5	$1.82 \times 10^{-2} \rightarrow 5.00 \times 10^{-5}$	Disperse Red 1
6	NO ₂	Н	Н	CH ₃	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	511.5 → 516.0	$2.50 \times 10^{-2} \rightarrow 9.32 \times 10^{-4}$	Disperse Red 17
7	NO ₂	NO_2	Н	Н	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	543.0 → 5 47.0	$1.37 \times 10^{-2} \rightarrow 4.03 \times 10^{-4}$	
8	NO2	Cl	Н	н	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	523.0 → 528.0	$1.69 \times 10^{-2} \rightarrow 1.17 \times 10^{-4}$	
9	NO ₂	Cl	Н	CH ₃	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	533.5 → 537.0	$1.61 \times 10^{-2} \rightarrow 7.60 \times 10^{-4}$	Disperse Red 5
10	NO ₂	Cl	Cl	н	CH ₃	CH ₂ CH ₂ OH	481.5 → 506.5	$2.78 \times 10^{-2} \rightarrow 8.00 \times 10^{-4}$	Disperse Orange 5
11	NO_2	Cl	Cl	н	CH ₂ CH ₂ OH	CH ₂ CH ₂ OH	478.5 → 516.5	$3.17 \times 10^{-2} \rightarrow 5.10 \times 10^{-4}$	• •
12	NO ₂	Cl	Cl	Н	CH ₂ CH ₂ CN	CH ₂ CH ₂ OCOCH ₃	462.0 → 487.0	$1.19 \times 10^{-2} \rightarrow 4.50 \times 10^{-4}$	Disperse Orange 30

TABLE I. Change in absorption maximum of disperse dyes with dye concentration in nylon 6.

* Measured for absorbance below 2.5.

TABLE II. Relation between dielectric constant of solvent and ratio of absorbance at peak 1 and peak 2 of CI Disperse Violet 1 in the solvent.

Solvent	Dª	Intensity _{Peak2} /Intensity _{Peak1}
Benzene	2.275	0.877
Pvridine	12.4 (21°C)	0.978
Methylethylketone	18.51 (20°C)	0.937
Ethanol	24.3	1.030
Methanol	32.6	1.010
Dimethylformamide	36.7	1.004
Dimetylacetamide	37.78	1.017
Dimethyl sulfoxide	46.68	1.040
Water	78.0	1.049
Nylon 6	3.65 (30°C) ^c	1.040 ~ 1.094
		$(C_f \text{ high } \rightarrow \text{ low})$

^a Dielectric constant for the pure liquid at 25°C unless followed by another temperature in parentheses [8]. ^b Measured at room temperature. ^c Values extrapolated at log(frequency) = 1 KHz from the experimental linear relation between log(frequency) and D in reference 2.

dine). The red shift in λ_{max} of Orange 5 with decreasing C_f is much more appreciable than that of Orange 3, particularly in the range of very low C_f . On the other hand, the λ_{max} values in the extracts are almost constant for both dyes, regardless of C_f , indicating that the shift in λ_{max} with C_f shown in Figures 1 and 2 cannot be attributed to dye decomposition during dyeing.



FIGURE 2. Change in λ_{max} with decreasing $C_{j^{+}} \odot =$ Orange 3 in nylon 6, $\Delta =$ Orange 5 in nylon 6, $\Phi =$ Orange 3 in extract (25% pyridine), $\Delta =$ Orange 5 in extract (25% pyridine).

Figure 3 shows the plots of C_f versus the optical density of dyed film per unit thickness of the film (Abs/l) at λ_{max} for Orange 3 and 5, respectively. Each plot shows a straight line meets the origin.

Red shifts in λ_{max} with decreasing dye concentration have been observed for some dyes in water, where the



FIGURE 3. Relation between C_f and the optical density (Abs/l) of the dyed film per unit thickness at λ_{max} for Orange 3 (O) and Orange 5 (Δ).

dyes are liable to associate as the concentration (C_s) of dye in water increases [4]. In this case, the dye dissolved in water as a monomer usually has a λ_{max} at a longer wavelength and a higher molar absorptivity (ϵ) than those of the dye associated in water [4]. This results in a decrease in the apparent ϵ of the dye with increasing C_s . However, as shown in Figure 3, the values of ϵ for both dyes are constant over the whole range of C_f examined, indicating no aggregation of the dyes occurs in the film.

Solvent Effect on Absorption Spectra of Orange 3 and 5 $\,$

Table III shows the values of λ_{max} (in wave number) of Orange 3 and 5 measured in various solvents and the physical constants (n_D, D) of those solvents. The values of ν_{obs} at λ_{max} decrease with an increase in D. We have estimated the values of constants ν_g , $AL_0 + B$, and C in Equation 1 by means of the multiple regression analysis shown in Table IV. Then we have calculated the values of the absorption frequency (ν_{calc}) at λ_{max} using Equation 1. The results of the calculations indicate that the difference in $\Delta \nu$ with solvents arises mainly from the dipole interactions expressed by

$$C\left[\frac{D-1}{D+2} - \frac{n_D^2 - 1}{n_D^2 + 2}\right]$$

rather than the dispersion interaction expressed by

$$(AL_0 + B) \frac{n_D^2 - 1}{2n_D^2 + 1}$$

Figure 4 shows the plot of experimental absorption frequency (ν_{obs}) at λ_{max} versus ν_{calc} . The filled symbols denote ν_{max} values in solvents and the open symbols

TABLE III. Physical constants of solvents used and absorption
maxima of Orange 3 and Orange 5 in the solvents.

			V _{obs} , C	cm ^{-1 c}
Solvent	n _D ª	D ^b	Orange 3	Orange 5
Hexane	1.37226	1.8799	25250	24450
n-Heptane	1.38551	1.924 (20°C)	25140	24380
Cyclohexane	1.42354	2.023 (20°C)	24970	24270
Dioxane	1.42025	2.209	23530	23310
Carbon tetrachloride	1.45739	2.238 (20°C)	24720	23920
Benzene	1.49792	2.275	23980	23280
Toluene	1.49413	2.379	24040	23360
Carbon disulfide	1.62409	2.641 (20°C)	23750	23020
Chloroform	1.44293	4.806 (20°C)	24180	23140
Pyridine	1.50745	12.4 (21°C)	21860	22150
1-Butanol	1.3973	17.51	22370	22650
2-Propanol	1.3752	19.92	22270	22810
Ethanol	1.35941	24.3	22420	22560
Methanol	1.32652	32.6	22810	22830
Dimethylformamide	1.42817	36.7	21600	22220
Acetonitrile	1.34163	37.5 (20°C)	23360	22740
Dimethyl sulfoxide	1.4773	46.68	20990	22080
Nylon 6	1.53 ^d	3.65 ^d	20660	20830
· · · · · · · · · · · · · · · · · · ·		2.00	~20900	~19510

^a Refractive index at the D-line of sodium at 25°C unless followed by another temperature in parentheses [14]. ^b Dielectric constant for the pure liquid at 25°C unless followed by another temperature in parentheses [14]. ^c Measured at room temperature. ^d Values taken from reference 3.

TABLE IV. ν_g , $AL_0 + B$, C determined by the modified McRae's equation.

Dye	ν_g , cm ⁻¹	$AL_0 + B$; С
Orange 3	30207	-26660	-4278
Orange 5	27878	- 19197	-2547

denote ν_{max} in nylon 6 film. The filled symbols are distributed along a theoretical straight line (dotted line) with standard deviations of 507 cm⁻¹ for Orange 3 and 219 cm⁻¹ for Orange 5, respectively. The magnitudes of the deviations from the theoretical line are of the same order as those obtained by Iric and Pacifici [5].

Points 1 and 2 denote ν_{max} values in dioxane. The two points deviate appreciably to longer wavelengths from the theoretical line; these deviations are attributable to the hydrogen bonding that forms between the protondonating group of the dye and proton-acceptor atoms in the solvent. Frequency shifts in some solvents often include the contribution of hydrogen bonding, which is not taken in McRae's equation.

Open symbols in Figure 4 deviate greatly from the theoretical line. Irick and Pacifici [5] pointed out that the λ_{max} of nonionic azo dyes in polymers shifted to longer wavelengths than those predicted by Equation 1. They ascribed this phenomenon to the presence of water in the polymer films. However, the red shift of λ_{max} with decreasing C_f , shown in Figures 1, 2 and 4, cannot be



FIGURE 4. Plots of v_{calc} versus v_{obs} for Orange 3 and Orange 5: $\bigcirc =$ Orange 3 in nylon 6, $\triangle =$ Orange 5 in nylon 6, $\blacksquare =$ Orange 3 in solvents, $\blacktriangle =$ Orange 5 in solvents.

interpreted in terms of hydrogen bonding or the presence of water, but rather to changes in the local polarity around the dyes. Such effects on λ_{max} cannot be explained by macroscopic properties such as n_D or D of polymer.

Factor Analysis of Spectral Changes in Orange 3 and 5 on Nylon 6 Film [6]

The polymer substrate, nylon 6 film, is not a homogeneous solid but a heterogeneous one in which there are various regions with different orders of chain segment alignment, from the ordered nuclei (crystalline region) to the completely disordered domain (amorphous region). The λ_{max} of a dye with a large contribution of dipole structure [III] in nylon 6 shifts to a longer wavelength as the interaction energies of the dye with the polymer become higher.

The interaction energies depend on the space in the polymer in which the dye is sorbed, such as in the amorphous regions or on the surface of the crystalline portions or both [11, 15]. We have found that nonionic azo dyes are sorbed by nylon 6 from water through two different sorption mechanisms, *i.e.*, Nernst-type partitioning and Langmuir sorption mechanisms [15–18]. In our earlier analysis of the sorption isotherm of a nonionic azo dye by nylon 6 from water, the saturation value for Langmuir sorption in dual-mode sorption increased with the crystallinity of nylon 6 [15]. We also found that for the sorption of Langmuir sorption to the total dye uptake was appreciably greater for the fiber with a large 806

crystallite size (010) [9]. These findings suggest that Langmuir sorption in the dual-mode sorption of nonionic dyes by the polymer is associated with the crystalline phase. To calculate the factor analysis, we assume first that the dye exists in the polymer as an assembly of several distinct species with different visible spectra according to the interaction energies of the dye with the substrate. Then the shift in λ_{max} with C_f can be ascribed to the change in the composition of each species in the polymer with C_f .

Factor analysis has been used to separate overlapped spectra [6, 10]. To get the number of species and each spectrum based on the individual species, we have analyzed spectral changes of Orange 3 and 5 on nylon 6 film with C_f by means of a factor analysis.

Spectral changes of dyes on nylon 6 film with C_f are expressed by a data matrix **D**, which is formed of absorption intensities, *e.g.*, Orange 3, of 31 wavelengths and 13 dye concentrations. In the case of this example, the matrix **D** consists of 31 rows and 13 columns. Each column corresponds to the spectrum of each dyed film. On the other hand, a spectrum matrix **R**, where columns consist of individual spectra for each *n* pure species, has dimensions of 31 rows and *n* columns. And a composition matrix **C**, where rows represent the concentration distributions of the pure species at each dyed film, has dimensions of *n* rows and 13 columns. The relation of **R** and **C** with **D** can be expressed by

$$\mathbf{D} = \mathbf{R}\mathbf{C} \quad . \tag{2}$$

A covariance matrix Z is obtained by multiplying the transpose 'D and the original D

$$\mathbf{Z} = {}^{\prime}\mathbf{D}\mathbf{D} \quad . \tag{3}$$

The number of independent species can be obtained as the number of independent base vectors forming the space of the matrix \mathbf{Z} .

We obtain an eigenvalue matrix E and an eigenvector matrix Q for Z using the Jacobi method [12]:

$$\mathbf{Z} = '\mathbf{Q}\mathbf{E}\mathbf{Q} \quad , \tag{4}$$

where E is an eigenvalue matrix having 13 eigenvalues at diagonal elements and Q is a corresponding eigenvector matrix having eigenvectors at columns. The eigenvalues are the relative weights of how important each factor is for reconstructing the spectral data. If the number of active species is n, then n eigenvalues are large and any other values are negligible or small. When the eigenvectors corresponding to the former eigenvalues are extracted, matrix Q' is newly constructed by lining them up in columns. The transpose of the eigenvector matrix Q' has dimensions of n rows and 13 columns similar to matrix C and is the first expression of the composition matrix C. Multiplying D and the transpose C gives the 31 by n matrix, which has the same dimensions as R and is one expression of the spectral matrix R:

$$\mathbf{R} = \mathbf{D}'\mathbf{C} \quad . \tag{5}$$

The number of factors n can be selected as the smallest number, such that $\mathbf{D} = \mathbf{RC}$ within experimental error.

After treatments corresponding to Equations 3-5, we obtained a composition matrix C of two rows and 13 columns and a spectral matrix **R** of 31 rows and 2 columns by taking out the eigenvectors corresponding to



FIGURE 5. (A) Separation of absorption spectrum of Orange 3 on nylon 6 film: — = measured spectrum, $- \Phi_{-} =$ spectrum of species I, $- \Phi_{-} =$ spectrum of species II. (B) Change in the concentration of species I and II with increasing C_{j} : $- \Phi_{-} =$ concentration of species I, $- \Phi_{-} =$ concentration of species I.



FIGURE 6. (A) Separation of absorption spectrum of Orange 5 on nylon 6 film: ——— = measured spectrum, ——— = spectrum of species I, ——— = spectrum of species II. (B) Change in the concentration of species I and II with increasing C_{f} ——— = concentration of species I, ———— = concentration of species II.

the two largest eigenvalues. But these matrices had some negative values, so we had to rotate the base axes of the matrices **R** and **C**. The rotation matrices T^{-1} and **T** $(TT^{-1} = T^{-1}T = I, I$ is the unit matrix) had to be inserted between **R** and **C**

$$\mathbf{D} = \mathbf{R}\mathbf{C} = (\mathbf{R}\mathbf{T}^{-1})(\mathbf{T}\mathbf{C}) = \mathbf{R}'\mathbf{C}' \quad . \tag{6}$$

When we selected the rotation matrices so as to avoid negative absorbances and negative concentrations, we determined \mathbf{R}' and \mathbf{C}' , but not uniquely.

An example of the sets of \mathbf{R}' and \mathbf{C}' obtained for Orange 3 is shown in Figure 5. The spectra of Orange 3 on nylon 6 film can be well described as the sum of two intrinsic spectra (species I and II); the fraction of species I and II changes with C_f . We obtained a similar result for Orange 5 with this method, as shown in Figure 6. It suggests that there are distinct sorption regions in nylon 6 film, and the dyes bind to substrates with different levels of binding energy.

SPECTRAL SHIFT BASED ON THE DUAL-MODE SORPTION MODEL

We have found that the sorption of Orange 3 and 5 by nylon 6 film from water follows Equation 7 [18]:

$$C_f = C_P + C_L = K_P C_s + \frac{SK_L C_s}{1 + K_L C_s}$$
, (7)

where C_f and C_s are the equilibrium dye concentration on polymer and in solution, C_P and C_L are the equilib-



FIGURE 7. Relations between C_f and C_P , C_L estimated from the sorption isotherms for Orange 3 (A) and Orange 5 (B) on nylon 6 film from water at 60°C: \bigcirc = experimental points, $----= C_P$, $----= C_L$.



rium dye concentration on polymer sorbed by Nernsttype partitioning and Langmuir sorption, respectively, S is the saturation value for the Langmuir sorption, K_P is the partition coefficient, and K_L is the Langmuir constant.

According to Equation 7, we have separated the isotherms into Nernst-type partitioning and Langmuir sorption. The dye exists in the polymer as two distinct species: that sorbed by the partitioning mechanism (Pspecies) and that by the Langmuir sorption mechanism (L-species). The amounts of L-species are usually smaller than the P-species. The ratio C_L/C_f increases with decreasing C_f and decreases with rising temperature [15, 18].

Figures 7A and B show the relation between C_f and C_P , C_L at the sorption equilibrium for Orange 3 and 5, respectively. We calculated the values of C_P and C_L from $K_P = 1.06 \times 10^3$ dm³/kg, $K_L = 4.08 \times 10^5$ dm³/mol, $S = 2.46 \times 10^{-3}$ mol/kg for Figure 7A, and $K_P = 2.15 \times 10^3$ dm³/kg, $K_L = 2.60 \times 10^6$ dm³/mol, $S = 6.90 \times 10^{-4}$ mol/kg for Figure 7B [18].

The relations between C_f and the concentration of Land P-species shown in Figure 7 seem to be very similar to the relations between C_f and the concentrations of species I and II shown in Figures 5B and 6B.

Figure 8 shows the spectral shift of Orange 5 on nylon 6 film with rising temperature. The λ_{max} shifts to a shorter wavelength with increasing temperature. This fact indicates that species I decreases with increasing temperature as the concentration of L-species (C_L) decreases with increasing temperature. Figures 7A and B agree with the results of the factor analysis shown qualitatively in Figures 5B and 6B, if we consider the different temperatures at which they were measured.

Conclusions

Shades of disperse dyes on nylon 6 change with C_f , particularly in the range of low C_f for dyes with large contributions of dipole structure. The λ_{max} of the dyes on



FIGURE 8. Spectral change of Orange 5 on nylon 6 film with increasing temperature: $C_f = 9.32 \times 10^{-4}$ mol/kg.

nylon 6 film shifts to a longer wavelength with decreasing C_f . The λ_{max} of the dyes in solvents also shifts to a longer wavelength with increasing polarity of the solvents. These facts suggest that the local polarity around the dye in nylon 6 film increases with decreasing C_f .

Detailed studies of spectral changes of CI Disperse Orange 3 and 5 on nylon 6 film in terms of the factor analysis and for the sorption behavior of the dyes indicate that the visual absorption spectrum of the dyes is expressed as the sum of two distinct spectra, e.g., the spectrum of species I with λ_{max} at a longer wavelength and that of species II with λ_{max} at a shorter wavelength. Spectral changes with C_f are the result of changes in the ratio of [species I]/[species II] in the film. The λ_{max} shifts to shorter wavelengths with decreases in [species I]. The λ_{max} of the dye shifts to a shorter wavelength with increasing temperature. C_L also decreases with increasing temperature. The relations between C_f and [species I], [species II] are very similar to the relation between C_f and [L-species], [P-species] estimated from the experimental sorption isotherms, suggesting species I and II correspond to the L- and P-species, respectively.

Literature Cited

- Aspland, J. R., The Application of Nonionic Dyes to Fibers: Nonionics and Their Sorption by Man-Made Fibers, *Textile Chem. Color.* 24(10), 36-40 (1992).
- Bamford, C. H., Boulton, J., Hanby, W. E., and Ward, J. S., The Dyeing of Synthetic Polypeptides, *Farady Soc. Disc.* 16, 222–229 (1954).
- Brandrup, J., and Immergut, E. H., Eds., "Polymer Handbook," 3rd ed., John Wiley & Sons, NY, 1989, pp. V-109, V-115.
- 4. Coates, E., Aggregation of Dyes in Aqueous Solutions, J. Soc. Dyers Colour. 85, 355-368 (1969).
- 5. Irick, G. Jr., and Pacifici, J. G., Solvent and Substituent on the Ultraviolet-Visible Absorption Spectra of Azo Dyes, *Textile Res. J.* 42, 391-397 (1972).
- 6. Malinowski, E. R., Obtaining the Key Set of Typical Vectors by Factor Analysis and Subsequent Isolation of

Component Spectra, Anal. Chim. Acta 134, 129-137 (1982).

- McDowell, W., and Weingarten, R., New Experimental Evidence about the Dyeing of Polyester Materials with Disperse Dyes, J. Soc. Dyers Colour. 85, 589-597 (1969).
- McRae, E. G., Theory of Solvent Effects on Molecular Electronic Spectra, Frequency Shifts, J. Phys. Chem. 61, 562-572 (1957).
- 9. Nakamura, T., Ohwaki, S., and Shibusawa, T., Dyeing Properties of Polyester Microfibers, *Textile Res. J.* 65, 113-118 (1995).
- Ozeki, T., Morikawa, H., and Kihara, H., Estimation of the Preferential Tautomer Structure of the Phenolphthalein in Solution by a Chemometrical Analysis of Its UV/Visible Absorption Spectra, Bunseki Kagaku 42, 887-894 (1993).
- Peters, R. H., Textile Chemistry, vol. 3, in "Physical Chemistry of Dyeing," Elsevior Scientific Publishing Co., Amsterdam, 1975, p. 70.
- Ralston, A., "A First Course in Numerical Analysis," International Student Edition, Kogakusha Company, Tokyo, 1965, pp. 487-492.
- 13. Reichardt, C., "Solvents and Solvent Effects in Organic Chemistry," 2nd ed., VCH, NY, 1990, p. 296.

- Riddic, J. A., and Bunger, W. B., "Organic Solvents, Physical Properties and Method of Purification," 3rd ed., Wiley-Interscience, NY, 1970.
- Shibusawa, T., and Chigira, Y., Dual-Mode Sorption of Nonionic Azo Dyes by Nylon 6, J. Polym. Sci. Part B Poly. Phys. 30, 563-568 (1992).
- Shibusawa, T., Diffusion of Nonionic Azo Dyes in Nylon 6, J. Polym. Sci. Part B Poly. Phys. 31, 29-31 (1993).
- Shibusawa, T., and Nakamura, T., Multimodal Sorption of Nonionic Dyes with Two Amino Groups by Various Polymers from Water, J. Polym. Sci. Part B Poly. Phys. 33, 159-165 (1995).
- Shibusawa, T., Sorption of Azo Disperse Dyes by Nylon 6 from Water, *Textile Res. J.* 66, 37-44 (1996).
- Strop, P., Mikeš, F., and Kálal, J., On the Microenvironment of Polymers in Solution, I: Properties of Pyridinium Type Polarity Reporters in Synthetic Polymers, J. Phys. Chem. 80, 694-701 (1976).
- Suda, Y., Absorption Spectra of 1.4-Diaminoanthraquinone in Mixed Solvents of Carbon Tetrachloride and Ethyl Alcohol, Bull. Chem. Soc. Jpn. 32, 1384-1385 (1959).
- Wegmann, J., Some Fundamental Aspects in the Dyeing of Synthetic Fibres with Disperse Dyes, *Can. Textile Res. J.* 79, 37-51 (1962).

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