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VIS absorption spectrophotometry of disperse dyes

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Abstract

In the investigations of the dyeing processes, the low solubility of disperse dyes in water represents a practical problem for the determination of dye concentration in dyebaths and waste waters. Therefore the use of an organic solvent which, dissolves disperse dyes, is recommended in visible spectrophotometry of disperse dyes. Three organic solvents (ethanol, *N*,*N*-dimethylformamide, acetone) and two disperse dyes, the disazo dye C.I. Disperse Orange 29 and the anthraquinone dye C.I. Disperse Blue 56, were used for spectroscopic analysis in this present work. The absorbance of aqueous dye dispersions and various organic solvent dye solutions was measured to evaluate the effect of the solvent on the shape and intensity of the absorption spectra and on the wavelength shift of maximum absorption. The validity of Beer–Lambert's law in each system was ascertained. A suggestion is made how VIS absorption spectrophotometry can be used to determine the dye concentration in disperse dyebaths. The addition of organic solvent to the dyebath leads to dye dissolution, and the Beer-Lambert's law is then fulfilled. The optimum ratio between the dyebath dispersion and the organic solvents for the dyes investigated is also determined. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: VIS absorption spectrophotometry; Absorption spectra; Disperse dyes; Organic solvents; Dye concentration; Disperse dyebath

1. Introduction

Disperse dyes are non-ionic aromatic compounds, scarcely soluble in water but soluble in organic solvents. The majority of them are azo and anthraquinone dyes. Commercial disperse dyes also contain auxiliaries, especially dispersants.

In the exhaustion dyeing process, disperse dyes are applied from a stable aqueous dispersion which contains an equilibrium distribution of solid dye particles of various sizes [1]. In the presence of dyeing auxiliaries and at higher application temperature, disperse dyes do dissolve sequentially during the dyeing process. Only dyes in the molecular state are initially adsorbed onto the fibre surface and are then transferred into the polyester fibre. Dyeing, therefore, takes place from a saturated dye solution where undissolved particles of dye act as a reservoir, i.e. as dissolved dye is taken up by the fibre, the dyebath is continuously replenished by progressive dissolution of dye particles from the dispersion.

In investigations of the dyeing process, the dye uptake is usually followed by spectrophotometric analyses of the dyebath, and the dye concentration is calculated according to the Beer–Lambert's law. To ensure the validity of this law, the use of organic solvents is recommended to prepare a true solution of the disperse dyes. In the analysis of disperse dyebaths or waste waters containing

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disperse dyes, the presence of water cannot be eliminated, and therefore the choice of a suitable organic solvent to be added, and the determination of an optimum mixture aqueous dispersion/organic solvent is of great importance in the visible spectroscopy of disperse dyes.

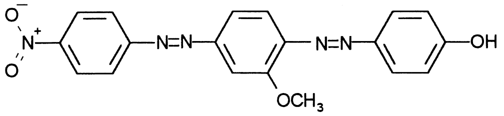
Three organic solvents (ethanol, *N*,*N*-dimethylformamide, acetone) and two disperse dyes (the disazo dye C.I. Disperse Orange 29 and the anthraquinone dye C.I. Disperse Blue 56) were used in order to study the effect of different solvents and water on the shape and intensity of the absorption spectra of the dyes. The changes in the spectra in different solvents are a consequence of the intermolecular solute–solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding, etc.), which tend to alter the energy difference between the ground and the exited states of chromophores [2]. Aqueous dispersions show different type of spectra primarily due to undissolved dye. The validity of Beer–Lambert's law in each system was ascertained.

The addition of an organic solvent to the dyebath dispersion ensures the validity of the Beer–Lambert's law. The optimum ratio between the dyebath dispersion and the organic solvents was also studied.

2. Experimental

2.1. Dyes

Experiments were carried out with two disperse dyes: viz., the disazo dye - C.I. Disperse Orange 29 (**1**) and the anthraquinone dye C.I. Disperse Blue 56 (**II**).



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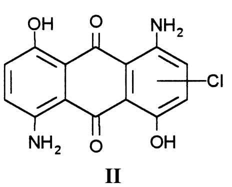

II

2.2. Solvents

The solvents in Table 1, are listed by decreasing polarity values $E_T(30)$, as an empirical solvent polarity parameters were used [2].

Water, ethanol and acetone were used, but in the case of *N*,*N*-dimethyl-formamide, a mixture DMF and water in the ratio of 19:1 was used with 2% addition of acetic acid (99.5%).

2.3. Dyebaths

Dyebaths were made up from:-

- 0.024 g/l of C.I. Disperse Orange 29 and 0.036 g/l of C.I. Disperse Blue 56, respectively;
- 2 g/l anionic dispersing agent;
- 1 g/l anionic levelling agent;
- pH = 4.5–5 (acetic acid).

The concentrations of dyes were chosen regarding to optimum values of absorbance maximum [4].

2.4. Absorbance measurements

A UV/VIS Spectrophotometer (Lambda 2, Perkin–Elmer) was used for the absorbance measurements. The relationship between absorbance and concentration is governed by the Beer–Lambert's law [3,4]:

$$A = \log \frac{P'}{P} = k.c.l$$

A = absorbance
P, P_0 = radiant power
k = absorptivity (l/g-cm)
l = optical length (cm)
c = concentration (g/l)

Table 1
Characteristics of solvents

Solvent	Melting point (°C)	Boiling point (°C)	$\mu.10^{30a}$ (Cm)	$E_T(30)$ (kcal/mol)
Water	0	100	6.07	63.1
Ethanol	−114	78	5.77	51.9
N,*N*-Dimethyl-formamide	−61	152	12.88	43.8
Acetone	−95	56	9.54	42.2

[a] Dipole moment μ in Coulombmeter.

2.5. Preparation of samples for absorbance measurement

Solutions and dispersions of the individual dyes at four different concentrations (0.012, 0.024, 0.036 and 0.048 g/l) with the solvents listed in Table 1 were prepared, and the absorbance measured immediately. These concentrations were chosen because the solutions for testing are best kept within the range 0.2 to 1.5 absorbance units [4].

To the aqueous dyebaths, various amounts of organic solvents were also added (dye concentration remains constant—0.024 g/l of C.I. Disperse Orange 29 and 0.036 g/l of C.I. Disperse Blue 56, respectively). Additions of DMF, ethanol and acetone, respectively were chosen to reach 20, 40, 60 and 80% of organic solvent in the solutions.

3. Results and discussion

3.1. Solvent effect

Figs. 1 and 2 illustrate the effect of solvents on the shape and intensity of the absorption spectra and on the position of the $\lambda_{\max}$ of C.I. Disperse Orange 29 and C.I. Disperse Blue 56, respectively. The $\lambda_{\max}$ shifts and absorption coefficient change with change in solvent and are, for both dyes, presented in Tables 2 and 3.

Each dye shows two different types of absorption spectra; i.e., absorption curves of organic solvent solutions and absorption curves of aqueous dispersions.

For C.I. Disperse Orange 29, the most intense absorption band in organic solvent solutions appears around 420 nm (Table 2). At wavelengths

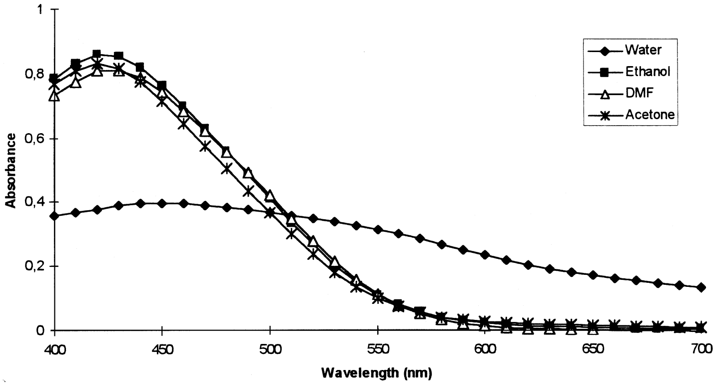

Fig. 1. Absorption spectra of C.I. Disperse Orange 29 in various solvents (dye concentration: 0.024g/l).

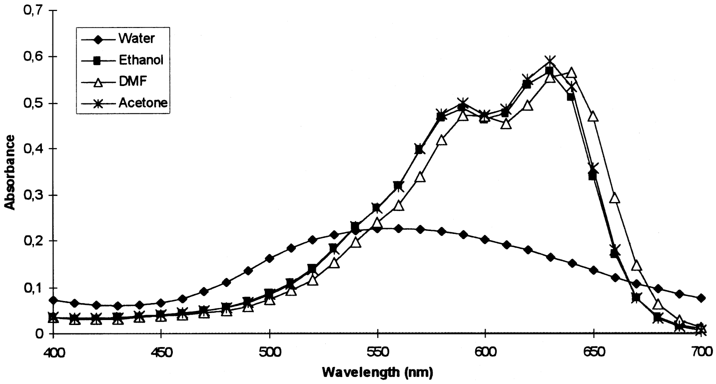

Fig. 2. Absorption spectra of C.I. Disperse Blue 56 in various solvents (4ye concentration: 0.036g/l).

Table 2
Spectral data for C.I. Disperse Orange 29 in the solvents used

c (g/l)	Water	Ethanol	DMF	Acetone
	$\lambda_{\max}$ (nm)			
0.012	451	423	426	419
0.024	451	423	426	419
0.036	451	423	426	419
0.048	451	423	426	419
	k (l/gcm)			
0.012	16.39	36.34	34.02	35.80
0.024	16.50	35.91	33.78	35.51
0.036	16.71	35.32	34.05	35.43
0.048	16.80	35.09	34.05	35.30

Table 3
Spectral data for C.I. Disperse Blue 56 in the solvents used

c (g/l)	Water	Ethanol	DMF	Acetone
	$L_{\max\ (\mathrm{nm})}$			
0.012	557	630	638	631
0.024	557	630	638	631
0.036	557	630	638	631
0.048	557	630	638	631
	k (l/gcm)			
0.012	6.56	16.66	16.89	16.92
0.024	6.58	16.68	16.85	16.70
0.036	6.56	16.56	16.61	16.60
0.048	6.61	15.96	16.61	16.56

above 600 nm, the absorbance is practically zero. By changing the nature of the solvent, the curve is slightly changed. The differences of $\lambda_{\max}$, the absorption intensity and the absorptivity (k) among the organic solvent solutions are very small. The highest absorbance is shown by the solution of dye in ethanol and the smallest in DMF. The differences in k among all the solvent solutions did not exceed 4% and the shift of $\lambda_{\max}$, was less than 10 nm.

The anthraquinone dye C.I. Disperse Blue 56 shows the typical double peak spectra in organic solvent solutions. The most intense band appears around 630 nm, and the use of DMF causes a bathochromic shift (Table 3). The differences in k values within all the organic solvent solutions are small over the chosen range of concentration, which confirms the linear relationship between dye concentrations and absorbance.

The aqueous dispersions of both dyes behave completely different compared to organic solvent solutions. The shape of the spectra indicates that a large proportion of the absorbance can be attributed to light scattering.

The absorbance of C.I. Disperse Orange 29 of an aqueous dispersion in the short wavelength range is higher than in other parts of the visible spectra, but never equals zero. The $\lambda_{\max}$ in water appears at 451 nm (30 nm bathochromic shift) and the absorbance and k are much smaller (less than a half of those in the case of the organic solvent solutions).

The aqueous dispersion of C.I. Disperse Blue 56 showed the most intense absorption in the middle wavelength range, with $\lambda_{\max}$ at 557 nm (80 nm hypsochromic shift). The absorption curve is very broad and does not show the double peaks characteristic of anthraquinone dyes. Absorptivity (k) at $\lambda_{\max}$ of the aqueous dispersion was almost three times smaller than that in organic solvents.

3.2. Effect of organic solvent addition to aqueous dyebaths

The effect of dyeing auxiliaries on the absorption spectra can be seen by comparing the absorption curves of each dye in water and in the dyebath (Figs. 3–8). Levelling and dispersing agents additionally increase light scattering of disperse dyebaths. The addition of organic solvents to the disperse dyebath alter the shape of the absorption curve considerably. Small quantities of organic solvents first dissolve the dyeing auxiliaries and the absorption curves of the dyebaths approach to those of aqueous dye dispersions. Further addition of organic solvents to the dyebaths dissolves the dyes, and the absorptions curves of their mixtures have a similar shape to those of the dyes in pure organic solvents.

The solubility of the used dyes differs in various organic solvents; in both cases, ethanol is a less powerful solvent than DMF or acetone. To obtain accurate measurements of C.I. Disperse Orange 29 at least 40% of DMF or acetone, and at least 60%

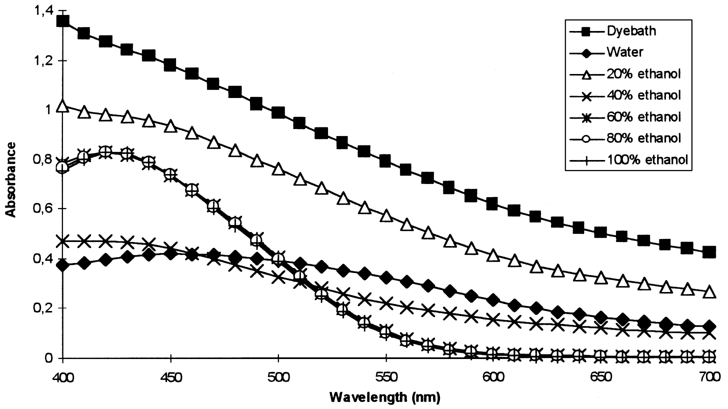

Fig. 3. Absorption curves of aqueous C.I. Disperse Orange 29 dispersion, dyebath, and its mixtures with various ethanol addition (concentration of dye: 0.024 g/l).

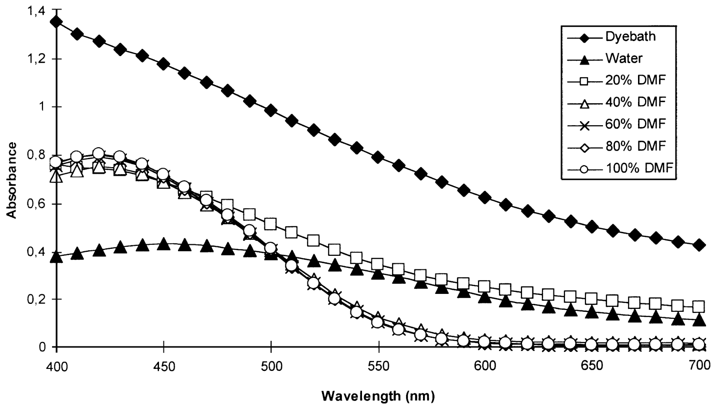

Fig. 4. Absorption curves of aqueous C.I. Disperse Orange 29 dispersion, dyebath, and its mixtures with various DMF addition (concentration of dye: 0.024 g/l).

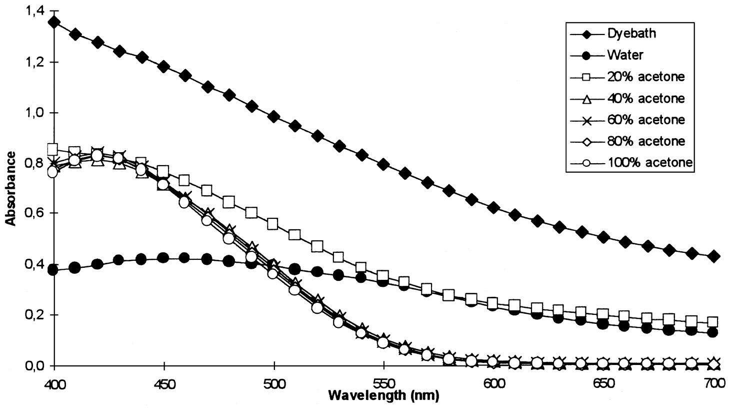

Fig. 5. Absorption curves of aqueous C.I. Disperse Orange 29 dispersion, dyebath, and its mixtures with various acetone addition (concentration of dye: 0.024 g/l).

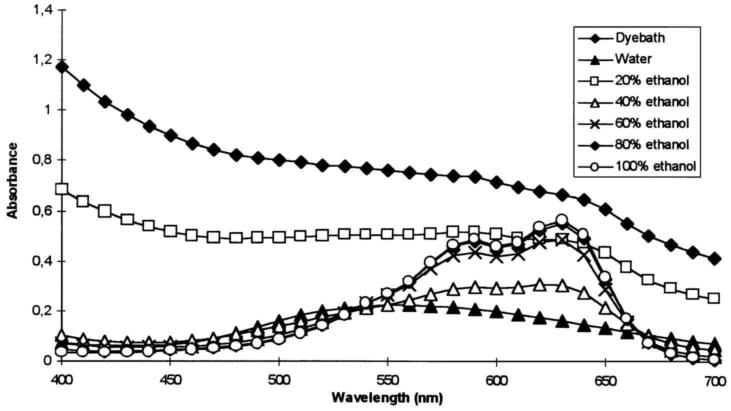

Fig. 6. Absorption curves of aqueous C.I. Disperse Blue 56 dispersion, dyebath, and its mixtures with various ethanol addition (concentration of dye: 0.036 g/l).

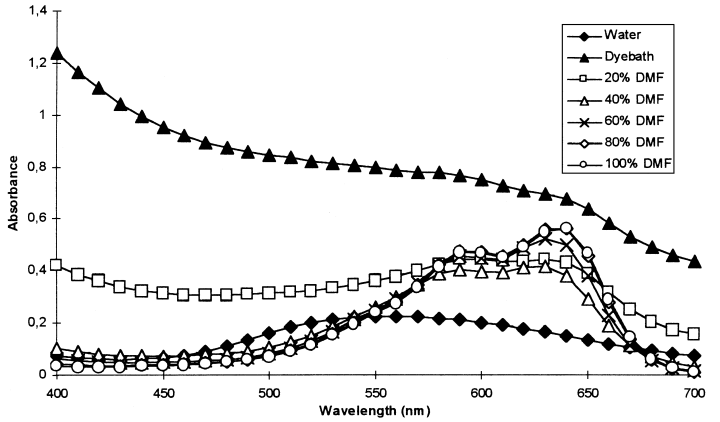

Fig. 7. Absorption curves of aqueous C.I. Disperse Blue 56 dispersion, dyebath, and its mixtures with various DMF addition (concentration of dye: 0.036 g/l).

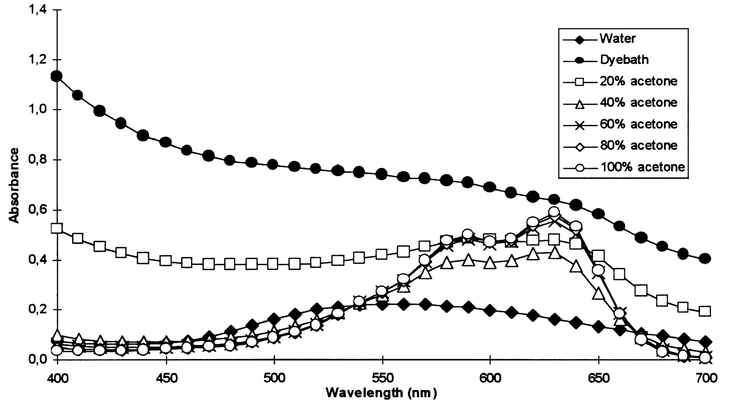

Fig. 8. Absorption curves of aqueous C.I. Disperse Blue 56 dispersion, dyebath, and its mixtures with various acetone addition (concentration of dye: 0.036 g/l).

ethanol, should be added to the aqueous dyebath at the chosen dye concentration (Figs. 3–5). For investigation of C.I. Disperse Blue 56 (Figs. 6–8) the addition of organic solvents needs to be higher, i.e. at least 80%.

4. Conclusions

The nature of organic solvents such as ethanol, *N*,*N*-dimethylformamide and acetone only slightly effects the shape and intensity of the absorption spectra of the disperse dyes investigated. The differences of absorptivities (k) at $\lambda_{\max}$ among various organic solvent solutions over a wide range of dye concentrations were small; therefore all the studied solvents are suitable for the VIS spectrophotometry of disperse dyes. For all systems the Beer–Lambert's law is valid.

The aqueous dispersions of disperse dyes show completely different absorption spectra due to light scattering compared to the absorption spectra of the solvent solutions of the dyes.

Dyeing auxiliaries in the dyebath have an additionally great effect on the absorption curve of the dye. The absorption spectra of dyebaths are not attainable due to scattering and the high absorption of auxiliaries at short wavelengths. The concentration of dyes in the dyebaths by VIS spectrophotometry can be determined by adding organic solvents. The quantities of organic solvent added to the dyebath which are necessary to dissolve the dye and the auxiliaries should be initially determined for a particular dye-solvent system.

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