

## SPECTROSCOPIC STUDY OF SOLUBILIZATION OF A DISPERSE AZO-DYE IN THE MICELLE OF A NONIONIC SURFACE-ACTIVE SUBSTANCE

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The electronic absorption spectra of two disperse azo-dyes were measured in light petroleum, benzene, ethanol, and in aqueous solutions of ethylene-oxidized nonylphenols. The dyes investigated exhibit phototropic properties in nonpolar solvents, but not in polar solvent; phototropy was not found in aqueous solutions of surface-active substances either. Spectra in polar solvents have a less pronounced fine structure and the absorption maxima are shifted to lower wave-numbers, as compared with nonpolar solvents.

It is well-known<sup>1-3</sup> that in aqueous solutions of surface-active substances (tensides) — to the nonionic type of which also ethylene-oxidized nonylphenols belong — organic substances low-soluble in water are solubilized. Solubilization occurs in solutions with concentrations higher than the critical micelle concentration of the tenside, and the solubilized substance — according to its nature — can be dissolved in the hydrocarbon core of the micelle, penetrate deeply or superficially into its pallisade layer, or can be adsorbed on its surface<sup>3</sup>. The micelle of the nonionic tenside with ethylene oxide groups can be considered to be composed of an inner hydrocarbon core and an outer shell of hydrated polyoxyethylene. The solubilized molecule with affinity to the ethyleneoxide groups may be incorporated into this outer area<sup>1</sup>. It was established<sup>4</sup> that the disperse dyes *I* and *II* (*I* methyl ester, *II* octyl ester of anthranilic acid, in both cases copulated to 2-naphthol) are also solubilized in aqueous solutions of ethylene-oxidized nonylphenols above their critical micelle concentration.

The light absorption and thus the shape of the absorption spectra of organic compounds in solutions are influenced by the solvents. Therefore the comparison of the spectra of some aromatic compounds<sup>1</sup> and anthraquinone dyes<sup>5</sup> solubilized by nonionic as well as ionic tensides with the spectra of the same substances in solvents of different polarities was used for the determination of the position of the solubilized molecule in the micelle. Some disperse dyes, derivatives of azobenzene and azonaphthalene, are phototropic<sup>6-8</sup>. The irradiation by light, especially by light of the wavelength corresponding to the maximum absorption, causes a transition of the *trans* form of the molecule to the *cis* form, which has a lower absorption in the wavelength region of the main band of the *trans* form. A decrease of the absorption intensity in this region occurs in solutions<sup>9,10</sup>, or even on textile materials<sup>11-13</sup>. The isomerism is reversible and the original equilibrium with the predominance of the *trans* form is re-established after a resting period in darkness<sup>9</sup>. Intense phototropy appears in nonpolar organic solvents and it is strongly suppressed by ethanol.

In this paper the optical absorption spectra of dyes *I* and *II* solubilized in aqueous solutions of ethylene-oxidized nonylphenols with nine (in further text "909"), twenty ("920") and forty ("940") ethylene oxide groups are being compared with spectra in solvents of different polarity — light petroleum, benzene and ethanol, *i.e.* with substances, which are designed to simulate the possible parts of the micelle of selected tensides. By this it was followed whether the dye is phototropic or not in each medium.

## EXPERIMENTAL

**Chemicals.** The dyes used were prepared in the laboratories of VÚOS Pardubice-Rybitví and dried at 60°C before use. The dyes contain 1–2% unreacted semiproducts, otherwise they are chromatographically pure<sup>14</sup>. The tensides used were produced in the research laboratory of the W. Pieck Chemical Works, Nováky. These are polydisperse substances; the analytical results were given previously<sup>4,15,16</sup>. Light petroleum was pure grade, benzene analytically pure grade, ethanol denatured with 1% gasoline.

**Preparation of solutions.** The solutions in organic solvents were prepared in the colorimetrically suitable concentrations 0.0025 g.l<sup>-1</sup> (dye *I*) and 0.00625 g.l<sup>-1</sup> (*II*). With the preparation of solutions by solubilization, 0.005 g dye was always flushed into 250 ml of aqueous solution of the tenside of the concentration of 0.01 mol.l<sup>-1</sup> (this concentration lies safely above the critical micelle concentration<sup>1,4</sup>). After shaking for 8 h the solutions were left at the room temperature for 30 days. The solutions cannot be considered as saturated to equilibrium (the concentration of the solubilized dye can be influenced by the amount of the excess dye in the solution as well as by the accidental effects with the preparation of the solution), their concentrations were, however, high enough for measuring the spectra. The solutions were always left without access of light for a longer period before the measurements.

**Spectra.** The spectra were measured on the Specord UV VIS spectrophotometer (Zeiss, Jena), cell thickness 3 cm, always against the corresponding solvent (hence also against the 0.01M tenside solutions). The procedure was always the same: at first the spectrum of the solution which had been kept in darkness (*1*) was measured, then the cell containing the solution was exposed to light of a 250 W bulb for 15 s from a 5 cm distance; the light source was separated by a cell with distilled water to reduce heating up. Spectrum 2 was measured immediately, spectrum 3 and 4 after further illumination for 30 and 120 s, resp. After the apparatus had been switched off, the cell was left in its dark cell compartment for 10 min and then the last spectrum 5 was measured. The spectra were recorded using the scanning speed 2.2 or 4.4 min on a 275 mm chart.

## RESULTS AND DISCUSSION

The spectra of the dye *I* are shown in Fig. 1. The spectra of the dye *II* are similar, the results are given in Table I. The spectra in nonpolar solvents exhibit a somewhat more pronounced structure than those in ethanol and in aqueous solutions of tensides. The spectra of solutions in light petroleum and benzene kept in the dark resemble the spectrum in ethanol, the absorption in the long-wavelength range of the spectrum decreases on illumination (these changes are shown in Table I for two more pronounced absorption maxima). The two dyes, the absorption maxima of which are equal, display distinctly phototropic properties in nonpolar solvents — light petroleum and

benzene, but not in the polar solvent — ethanol — or in the solubilized state. Phototropic changes appear also in the UV spectral region. The changes are reversible (the curves 5 exhibit a considerable increase of absorption after a 10 min resting period in the dark, the spectra measured after a resting period of 60 minutes in the dark resemble closely curve 1). The spectral patterns depend also on the scanning speed (obviously various stages of the *cis-trans* conversion are recorded), therefore the highest scanning speed was chosen for the media, where phototropy occurs.

Phototropy of the dyes *I* and *II* found in hydrocarbon solvents and suppressed in ethanol proves the results obtained by Brode and coworkers<sup>9,10</sup>, according to which phototropy did not appear in ethanol with the majority of the dyes tested. These authors, however, state further that for *o*-hydroxyazobenzene and its deriva-

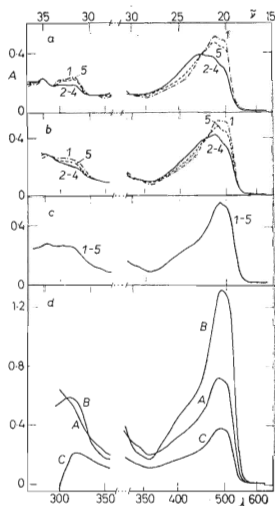


FIG. 1

#### Spectrum of Dye *I* in Organic Solvents and in the Solubilized State

*a* Light petroleum, *b* benzene, *c* ethanol, *d* aqueous solutions of ethylene-oxidized nonylphenols (A — 909, B — 920, C — 940). Curve 1 after a longer resting period in darkness, 2 after exposing to light for 15 s, 3 after illumination for further 30 s, 4 after illumination for further 120 s, 5 after resting in darkness for 10 min. In the Fig. *d* all five curves coincide. Time of the spectrum scanning 2.2 min for *a* and *b*, 4.4 min for *c* and *d*.  $\bar{\nu}$  in  $10^3 \text{ cm}^{-1}$ ,  $\lambda$  in nm.

TABLE I

Absorption Maxima, Molar Absorptivities and Relative Decrease of Absorbance on the Illumination of Dyes *I* and *II* in Solutions

$\tilde{\nu}$  Wavenumbers of the pronounced absorption maxima in  $10^3 \text{ cm}^{-1}$ ,  $\epsilon$  molar absorptivity in the absorption maximum,  $n$  ratio of absorptivities at the wavenumber of the given maximum after exposing to light and after a long resting period in darkness. Time of scanning the spectra 2.2 min.

Solvent	Dye <i>I</i>			Dye <i>II</i>		
	$\tilde{\nu}$	$\epsilon \cdot 10^3$	$n$	$\tilde{\nu}$	$\epsilon \cdot 10^3$	$n$
Light petroleum	21.20	20.4	0.72	21.20	14.2	0.77
	20.15	19.6	0.60	20.15	13.5	0.67
Benzene	20.90	20.4	0.82	20.90	15.1	0.83
	19.95	20.2	0.67	19.95	14.7	0.71
Ethanol	20.70	21.6	1.00 <sup>a</sup>	20.70	16.3	1.00
	0.01M-909	20.80	—	—	—	—
0.01M-920	20.60	—	1.00 <sup>a</sup>	20.75	—	1.00
0.01M-940	20.60	—	1.00 <sup>a</sup>	20.75	—	1.00

<sup>a</sup> Time of scanning the spectra 4.4 min.

tives (for substances similar to the dyes *I* and *II*) the *trans* form is stabilized by the hydrogen bond, so that phototropy either does not occur or is very weak. *E.g.* *o*-hydroxyazobenzene does not change its spectrum in benzene ( $n = 1.00$ ), small changes occur in isooctane ( $n = 0.96$ ), slight changes are found in methyl ethyl ketone ( $n = 0.98$ )<sup>10</sup>. The higher phototropy of the dyes *I* and *II* in comparison with the results cited can be apparently attributed to the effect of the ester group.

The results for the dyes *I* and *II* show that the character of the spectra of the dye solubilized by any ethylene-oxidized nonylphenol fits best the spectrum in ethanol. The five curves measured coincide, hence phototropy does not occur; also the structure of the spectrum corresponds to the solution in ethanol. From this it can be deduced the two solubilized dyes tested are bound in the ethylene oxide hydrophilic and hydrated shell of the micelle. From the results it may be also deduced that with the dyes displaying phototropy, this quality can serve better for the determination of the localization of the solubilized dye in the micelle, than the comparison of the wavelength of the spectral absorption maximum alone.

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