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The Solubilities of the Components of Two Binary Dye Mixtures in a Nematic Host

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The solubilities of the components of two binary dye mixtures in ZLI-1565 were determined at 25°C and 50°C. The mixtures consist of two anthraquinone dyes and one anthraquinone and one azo dye, respectively. The results are compared with those obtained for the pure dyes. The two dye mixtures significantly differ in their behaviour, *i.e.* in the influence of the first dye in solution on the solubility of the second.

Keywords: dye mixtures, guest-host displays

INTRODUCTION

For a pleochroic dye to be used in a guest-host device it must be sufficiently soluble in a liquid crystalline phase. Over the last few years data have become available concerning the solubilities of single dyes in different host phases.[1-8] However, owing to the limited band width of the absorption bands of the compounds a mixture of at least three dyes is necessary for a black-and-white display. Until now it has not been clear whether the solubility of a dye is influenced by the presence of other dyes in solution. Therefore Λ solutions with two dyes were examined.

EXPERIMENTAL

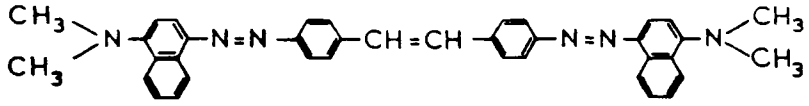
The dye mixtures used for this investigation are listed in Table I. The dye D-16, with its high solubility, was chosen for mixture A in order

TABLE I

Dye mixtures

Mixture	Dyes	λ_{max}(nm) (in $CHCl_3$)	$\epsilon(10^4$ l/mol·cm) (in $CHCl_3$)	
A	D-16	589	1.22	
	azostilbene	487	5.81	(a)
B	D-27	595	1.03	
	D-43	543	1.45	

(a) 4,4'-Bis (4-N,N-dimethylaminonaphthylazo)stilbene



to compensate for the effect of the high extinction coefficient of the azostilbene. The anthraquinone dyes were obtained from BDH Chemicals Ltd., Poole, UK and were used without further purification. The azostilbene was synthesized by tetrazotising 4,4'-diaminostilbene dihydrochloride and coupling it with 1-N,N-dimethylaminonaphthalene. The compound was purified by column chromatography and characterized by VIS, NMR, and mass spectroscopy. The structure was confirmed by an X-ray structure determination which will be reported elsewhere.[9] As host phase, the broad range mixture ZLI-1565 was chosen.

The concentrations of the dyes in the saturated solutions were determined using the VIS-spectra in chloroform. The details of the procedure have been reported elsewhere.[10] For the dye mixtures, the absorption curves were fitted with the curves of the pure dyes in solution.

RESULTS AND DISCUSSION

The results for mixture A are shown in Table II.

At 25°C the solubilities of both dyes are virtually unchanged by the presence of the other. From the additivity of the solubilities one can conclude that the second dye in solution does not influence the dye I/liquid crystal system as a dissolving medium i.e. there is no effect analogous to a 'salting out' process. We are therefore dealing with a situation where the thermodynamic properties of the solvent are scarcely changed by the second dye. In contrast, the data for 50°C

TABLE II

Solubilities of D-16 and the azostilbene in ZLI-1565 (mmol/l)

T (°C)	Binary mixture		Pure dyes	
	D-16	azo-stilbene	D-16	azo-stilbene
25	76.0 ± 1.7	6.7 ± 0.1	75.4 ± 1.1	7.0 ± 0.2
50	258 ± 3	12.0 ± 0.2	270 ± 3	12.2 ± 0.2

TABLE III

Solubilities of D-27 and D-43 in ZLI-1565 (mmol/l)

T (°C)	Binary mixture		Pure dyes	
	D-27	D-43	D-27	D-43
25	3.9 ± 0.3	4.2 ± 0.2	3.3 ± 0.1	5.3 ± 0.2
50	9.5 ± 0.6	15.3 ± 0.2	8.9 ± 0.2	19.5 ± 0.4

point to a partially substitutive behaviour. Owing to the margin of error in the values for D-16, we cannot decide whether the solubility of pure D-16 is the sum of the solubilities of the two compounds in the mixture. The sum could be smaller or greater than the value for the pure D-16.

More pronounced substitutive behaviour was observed for the mixture of the two anthraquinone dyes. The data are shown in Table III. At 25°C the total dye concentration in the mixture is appreciably less than the sum of the two separate solubilities and at 50°C, the difference is even more noticeable.

The transition from additive to substitutive behaviour takes place at much lower concentrations when the two dyes are chemically similar. In all cases of (partially) substitutive behaviour, only the solubility of the more soluble dye is decreased. That of the less soluble dye is unchanged in mixture A and is slightly increased in mixture B.

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