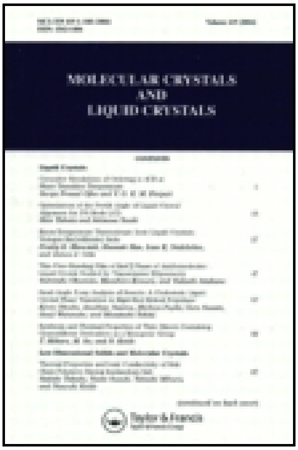

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Investigation of the Solubility of Pleochroic Dyes in Liquid Crystals

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Investigation of the Solubility of Pleochroic Dyes in Liquid Crystals

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A precise, inexpensive and relatively fast method for determining the solubility of pleochroic dyes in liquid cyrstals is described. The method has been used to investigate the solubility of two anthraquinone dyes in liquid crystals of different molecular structure. The solubility of the dye is found to be strongly dependent on the molecular structure of the dye and that of the host liquid crystal. Also the temperature dependence of the solubility in the nematic phase has been found to be different from that in the isotropic phase of the liquid crystals. At the nematic isotropic phase transition temperature a discontinuity in the solubility curve has been observed.

1. INTRODUCTION

The main advantages[1,2] of a guest-host liquid crystal display with pleochroic dyes over widely used twisted-nematic display are: a polariser is not required and the contrast is almost independent of the viewing angle. However, one of the main difficulties for the application of the guest-host display is the very limited solubility of the dye in liquid crystals. Also, if the application of the display for outdoor situations is to be considered e.g. in a car, the temperature dependence of the solubility of the dye in the liquid crystal matrix plays a very important role.

Up till now, only a few data on the solubility of the dye in liquid crystals and its temperature dependence can be found in the literature.[3–7] Normal measurement technique reported in the literature for determining the solubility of the dye in liquid crystal depends on the following steps: An adequate amount of the dye and liquid crystal is intermixed for a few days, the solution is filtered, a fraction of the filterate is dissolved in a known amount of chloroform and the absorbance is measured spectroscopically. The solubility is then determined by comparing this absorbance with that of the solution of known concentration.

The advantage of this method is that the spectroscopic measurements are performed in an isotropic solution (chloroform). However, the method has also some disadvantages. One disadvantage of the method is that the absorbance is measured in chloroform, not directly in the liquid crystal. Further, the value so obtained may be too high, because the microscopic particle of the undissolved dye can pass through the filter during the filteration process and dissolve in chloroform later. It must be kept in mind that chloroform is a very good solvent for dyes. Another disadvantage of this method is that it is very time consuming, particularly if the liquid crystal is very viscous. Also, relatively large quantities of liquid crystal are required and this can be very expensive.

We have, therefore, developed a new technique which is described in the following sections, and used the technique to investigate the solubility of pleochroic dyes in different liquid crystals.

2. THEORETICAL APPROACH

In the present method of determining the solubility of a pleochroic dye in a liquid crystal, in the first step an unsatured solution of known concentration of the dye in the liquid crystal is prepared at a fixed temperature T, and the absorption coefficient, ϵ, of the dye in the liquid crystal is determined according to the expression:

$$\epsilon = \frac{A_{\parallel} + 2A_{\perp}}{3\,cd} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of light polarised parallel and perpendicular to the director of parallel, homogeneously aligned films respectively at the temperature T; d is the thickness of the film and c is the concentration of the dye in the film.

In the second step, a supersaturated solution of the dye in the liquid crystal is prepared at T, then separated by centrifuging at the same temperature and the solubility is determined according to the relation which is obtained by rewriting the expression (1):

$$c = \frac{A_{\parallel} + 2A_{\perp}}{3\,\epsilon\, d} \tag{2}$$

whereby, we take the value of ϵ measured in the first step, assuming that it does not depend on the concentration at the given temperature T.

The advantages of this method are: (1) the solubility is determined directly in the liquid crystal and is therefore precise, (2) only a small quantity of the liquid crystal is required due to the use of a centrifuge in the separation process (3). Centrifugation as the separation method eliminates the possibility of loss of dye from solution by adsorption on the filtering medium or passage of dye in microcrystals through the filter, and (4) the method is comparatively fast. The disadvantage of the method is that it requires polarized absorption measurements, which may be sometimes time consuming especially when the solubility is extremely low in which case the measurement cell needs to have an adequate thickness to obtain the desired accuracy.

3. EXPERIMENTAL

The measurements were made as follows. 1–4 mg of the dye was weighed in about 0.4 g of liquid crystal thermostatically maintained at a fixed temperature in an Eppendorf reacti-vial 'E' (volume 1 cm^3) containing a Teflon® coated stirring bar 'B' (2 × 5 mm). The Eppendorf reacti-vial 'E' was screwed tightly into the cover 'C' of a Plexiglas® vessel 'V' (Figure 1), through which circulated a 1:1 mixture of water and ethylenglycole held thermostatically at the fixed temperature. The solution was stirred by means of a magnetic stirrer 'S'. It was also vigorously shaken from time to time. After a few hours, depending on the temperature at which the measurement of solubility was desired, the Eppendorf vial complete with solution was transferred to a centrifuge held at the desired temperature. When no sediment was observed in the Eppendorf vial and the dye solution showed no light scattering, it was assumed to be a real homogenous solution of the dye in the liquid crystal. In this case a homogenous planar cell of known thickness was filled with the solution and the absorption spectra, A_{II} and A_{I}, measured at the fixed temperature in a variable temperature cell developed in our laboratory. From these measurements the absorption coefficient of the dye in the liquid crystal was calculated using expression (1). Extra dye was added to the solution remaining in the Eppendorf vial, so that after mixing for a few days followed by centrifuging a small amount of the dye was observed at the bottom of the Eppendorf vial. If this saturated solution showed no light scattering, the absorption spectra were meas-

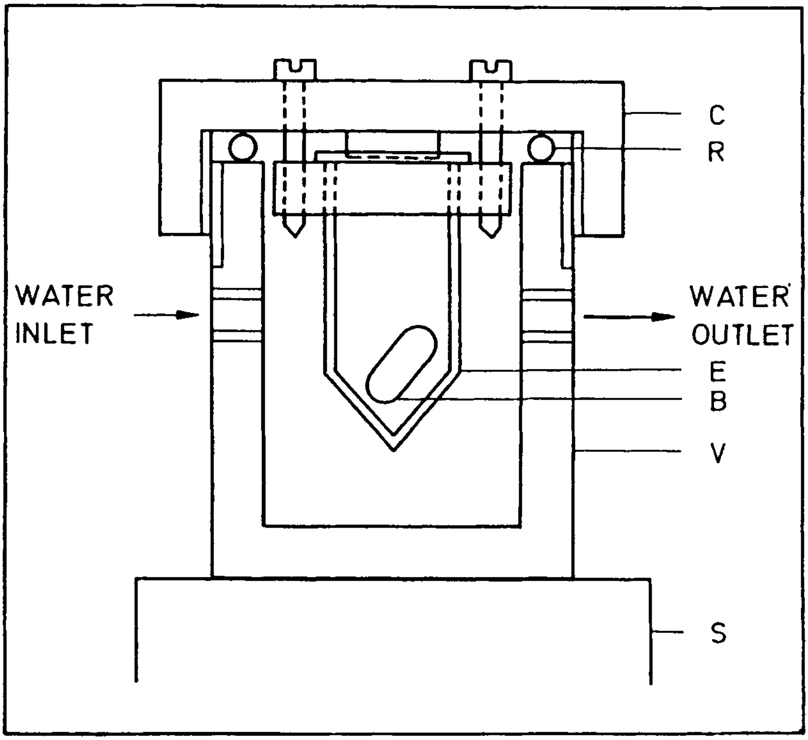

FIGURE 1 Experimental arrangement for dissolving dye in liquid crystal at a particular temperature. B: Stirring bar; C: Cover; E: Eppendorf reacti-vial; R: O-Ring; V: Plexiglas vessel; S: Magnetic Stirrer

ured again in a homogenous planar cell of known thickness at desired temperature. The samples were free from disclination defects during the measurement. To check if equilibrium had been attained during dissolution process, the contents of the Eppendorf vial were further stirred for a few hours, the solution centrifuged and the measurements repeated. The solubility was then calculated using relation (2).

The spectroscopic measurements were performed using a Perkin-Elmer 330 spectrophotometer. The centrifuge used for separating the dye solution from undissolved dye particles was a Kontron ZK 400.

4. RESULTS AND DISCUSSION

In this paper we report results of the investigation of the solubility of two dyes which belong to the same class, namely anthraquinone dyes. The only difference in their molecular structures was that one has an alkyl group attached to it at one end of its long molecular axis (further referred as the dye A-R), whereas the other has an alkyloxy group (further referred as the dye A-OR).

The liquid crystals used in this investigation were of two classes. Those of class I were of three different mocular structures with polar cyano terminal groups in all cases, the difference being in the variation of the ring system. The molecular dimensions remained the same in all cases. The liquid crystals of this class were cyanobiphenyl (CB), cyanophenylcyclohexane (PCH) and cyanobicyclohexyl (CCH).

The liquid crystals of class II were ester liquid crystals, NP 1008 and NP 1052. They have alkyloxy and alkanoyloxy terminal groups and have, additionally, carboxyl group between the two phenyl rings.

The molecular structures of the dyes and that of the liquid crystals are given in Figure 2.

In order to compare the solubilities of the dyes over a wide temperature range of the nematic phase of the liquid crystals, binary mixtures of two homologues were used. To find out the degree of dye/dye interactions and the dependence of the absorption coefficient on concentration at a particular temperature, the dye/liquid crystal system A-R / ZLI 1840 was chosen. Results given in Table I show that the deviation is within the experimental error.

Further, the influence of the molecular structure and that of the temperature are discussed separately.

4.1 Influence of molecular structure

Table II lists the solubilities of the two dyes mentioned above in different liquid crystals at 20°C. Such a comparison is useful for prac-

TABLE I

Concentration dependence of the absorption coefficient of the dye A-R in ZLI 1840 at 18°C.

Concentration of the dye [%-wt.]	0,32	0,85
Absorption coeffizient [cm^{-1}]	299	294

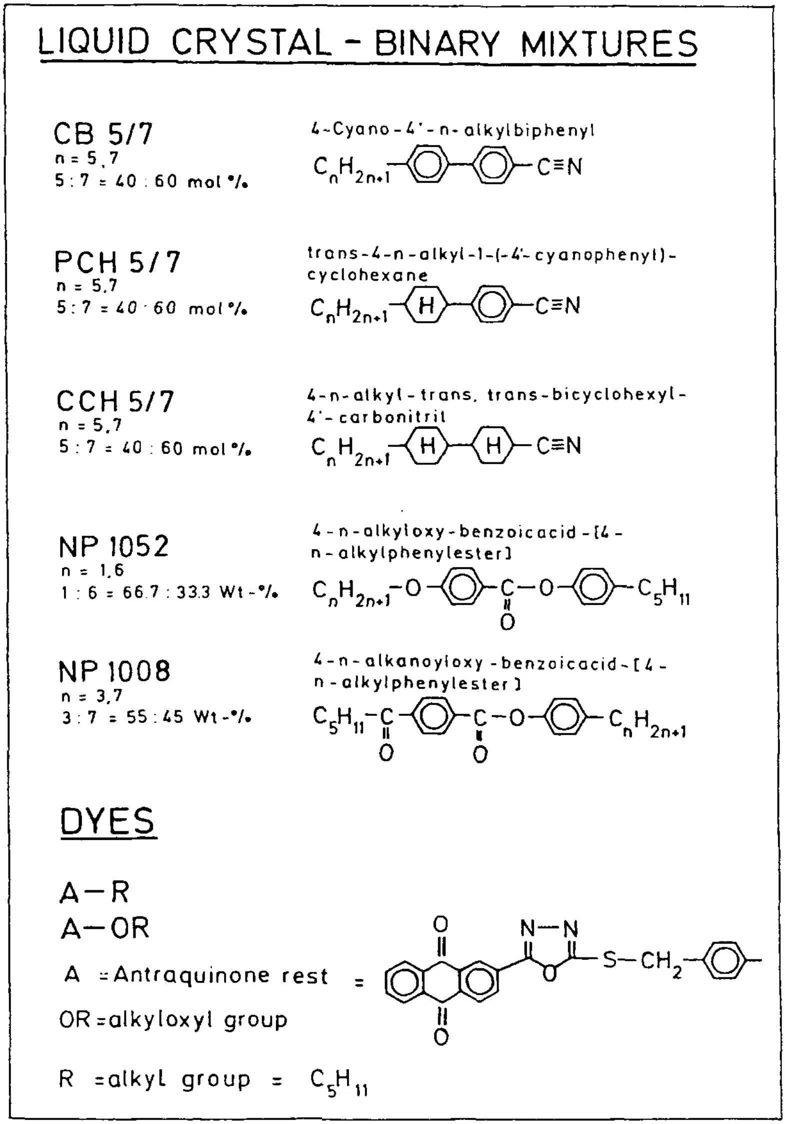

FIGURE 2 Molecular structures of liquid crystals and of dyes investigated in this work.

tical applications. We observe that the solubility of the anthraquinone dye having terminal alkyl group (A-R) is higher, in all the liquid crystals investigated, than that of the anthraquinone dye containing alkyloxyl terminal group (A-OR). We observe further that the sol-

TABLE II

Solubilities of the dyes A-R and A-OR in different liquid crystals at 20°C.

liquid crystal / solubility of	CB 5/7	PCH 5/7	CB 5	CB 7	NP 1052	NP 1008	ZLI 1840
A - R [%-wt.]	1.6	1.4	1.1	2.1	0.48	0.28	1.45
A - OR [%-wt.]	0.05	0.19	-	-	0.13	0.09	0.20

ubility of the dye A-R is higher in CB 5/7 than in ester liquid crystals 1008 and 1052, whereas in the case of the dye A-OR the opposite is true. It is also interesting to note the effect of the variation of the ring system of the liquid crystal solvent on the solubility of the solute dye. As we can see in the Table II, the solubility of the dye A-OR becomes higher when one of the two phenyl rings of the liquid crystal is substituted for a cyclohexyl ring, whereas that of the dye A-R remains almost unchanged. This effect is so large that the ratio of the solubility of the dye A-R to that of the dye A-OR which is 32 in CB 5/7 at 20°C, is reduced to about 8 in PCH 5/7 at the same temperature.

In the case of ester liquid crystals, 1052 and 1008, substitution of the terminal alkyloxyl group of 1052 with alkanoyloxyl group which results in 1008, causes a slight increase in the solubilities of both dyes. However, the ratio of the solubilities of these dyes changes very little.

In Table III we find that the solubility of the dye A-R is additive in the binary mixture CB 5/7. That is to say,

$$c_{CB5/7} = x_{CB5}(c_{CB5}) + x_{CB7}(c_{CB7})$$

TABLE III

Additivity of the solubility of A-R in CB's at $T_r = 0.92$.

liquid crystal / solubility	CB 5	CB 7	CB 5/7	
			calculated: $c=x_1c_1+x_2c_2$	experimental
[%-wt.]	0.60	1.82		
[mole fraction]	0.003	0.010	0.007	0.007

where $c_{CB\,5/7}$, $c_{CB\,5}$, $c_{CB\,7}$ are the solubilities in CB 5/7, CB 5 and CB 7 respectively; x_{CB5} and $x_{CB\,7}$ are the mole fractions of CB 5 and CB 7 in the binary mixture CB 5/7. Whether this relationship holds in general is not at present clear.

4.2 Influence of temperature

For the interpretation of the results of the temperature dependence of solubility, we used the relation:

$$\ln c = -\Delta H/RT + \ln c_0 \qquad (3)$$

where c is the solubility of the dye in mole fraction, ΔH the enthalpy of the solution, R the universal gas constant, T the absolute temperature, and c_0 the solubility in the limit when $T >> \Delta H/R$.

Figures 3, 4 and 5 show the temperature dependence of the solubility of the two dyes mentioned above as ln c vs. $1/T$. Of particular importance is the different temperature dependence of solubility in different liquid crystals. Both anthraquinone dyes dissolved in CCH 5/7 have the strongest temperature dependence of all liquid crystal binary mixtures investigated in this work. In the commercial mixture ZLI 1840 we measured the solubility of the dye A-R to as low as −10°C which is illustrated in Figure 4. However, we did not observe any

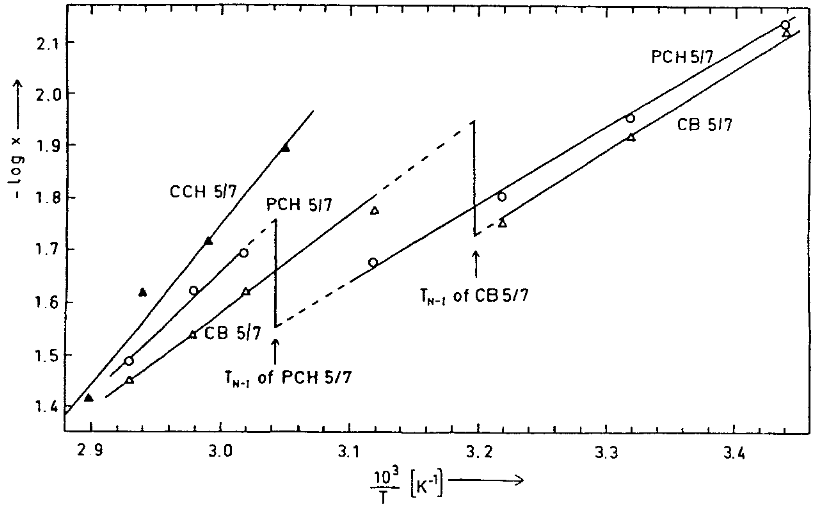

FIGURE 3 Dependence of the logarithm of the solubility (expressed in mole fraction) of the dye A-R in different liquid crystals on reciprocal absolute temperature (continued in Figure 4).

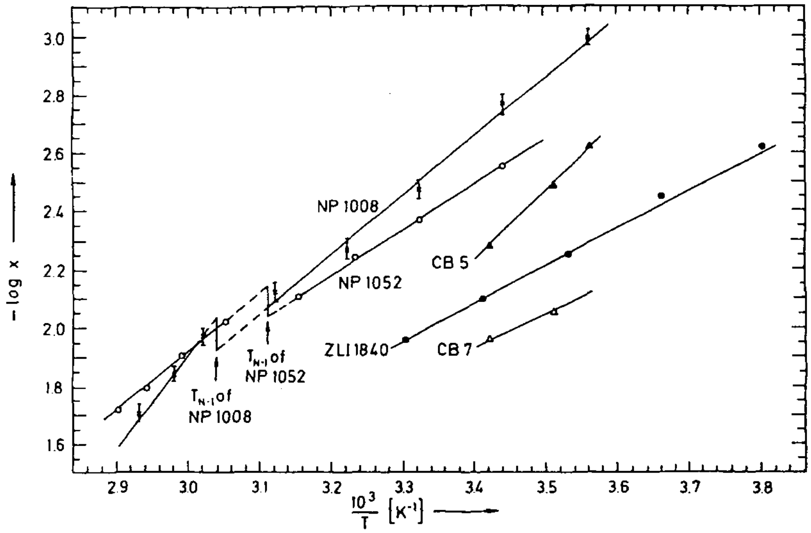

FIGURE 4 Dependence of the logarithm of the solubility of the dye A-R in different liquid crystals on reciprocal absolute temperature.

deviation from the theoretical relation (3) as was observed by two reporters[7] for some anthraquinone dyes in ZLI 1565.

In Figure 3 we observe further that in all cases the temperature dependence of the solubility has a discontinuity at the nematic to isotropic phase transition temperature, T_{N-I}. At T_{N-I} there is a sudden increase in solubility in going from the higher to the lower temperature. Beyond T_{N-I}, in the nematic phase, the temperature dependence is smaller than that in the isotropic phase of the liquid crystal. The higher solubility caused by the nematic order could be due to the greater free volume in the nematic phase than in the isotropic phase. The enthalpy of solution, ΔH, which is the slope of the temperature dependence curves according to the relation (3), assuming that it does not depend on the temperature, is given in Table IV. We observe that in the binary mixtures CB 5/7 and PCH 5/7 the dye A-R has almost the same enthalpy of solution, whereas in CCH 5/7, where both phenyl rings of CB 5/7 are substituted with cyclohexyl rings, the dye has much higher enthalpy of solution. The enthalpy of solution of the dye A-OR is higher in PCH 5/7 than that in CB 5/7 and is again much higher in CCH 5/7 than in PCH 5/7. Because of the relatively low enthalpy of solution one can expect the dye to be readily soluble in PCH 5/7 and CB 5/7 even at low temperatures,

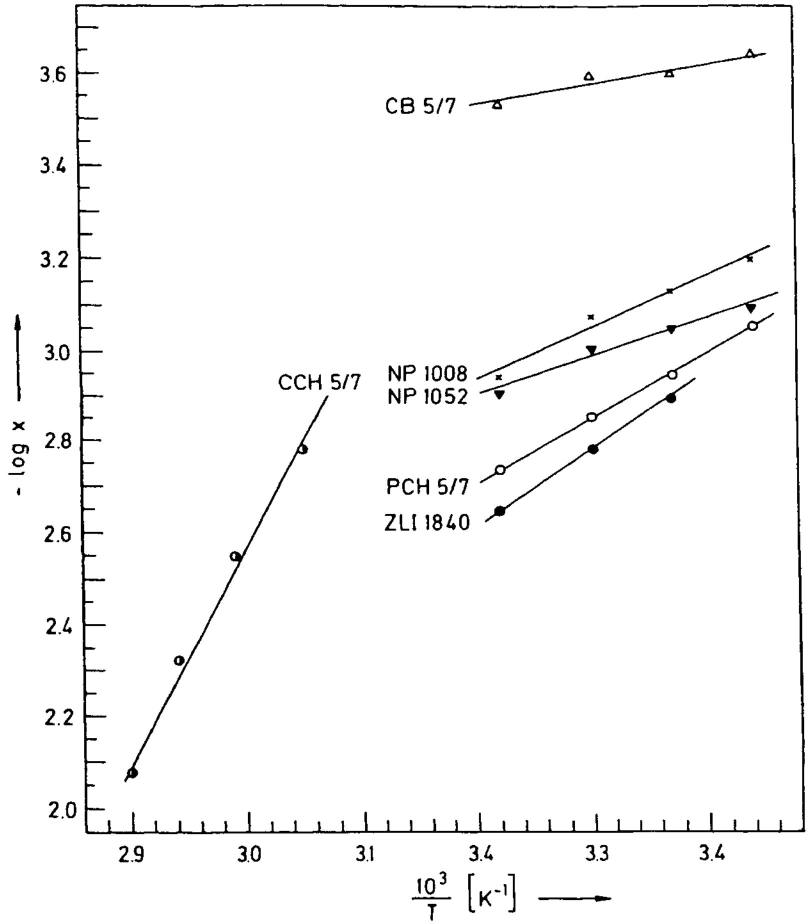

FIGURE 5 Temperature dependence of the solubility (expressed in mole fraction) of the dye A-OR in different liquid crystals.

which is not the case for CCH 5/7. In fact the nematic phase range of CCH 5/7 is at a very high temperature, between 39.7°C and 83.8°C, the lower temperature limit being at the same time the melting point of CCH 5/7.

We observe further in Table IV, that the enthalpy of solution of both anthraquinone dyes is raised by substituting the alkanoyloxyl terminal group of 1008 with alkyloxyl. It is also interesting to note that in the multicomponent commercial mixture, ZLI 1840, the enthalpy of solution was found to be lower than that in any binary mixture investigated in this work.

TABLE IV

Enthalpies, ΔH, of A-R and A-OR in nematic and isotropic phases of different liquid crystals.

liquid crystal / dye	NP 1008		NP 1052		CB 5/7		PCH 5/7		CCH 5/7	ZLI 1840
	nem.	isot.	nem.	isot.	nem.	isot.	nem.	isot.	nem.	nem.
A - OR [kcal/deg.mol.]	5.280		3.872		1.760		6.600		21.874	8.008
A - R [kcal/deg.mol.]	9.309	14.415	7.008	9.026	7.267	8.580	6.793	10.525	13.957	5.799

If we compare the enthalpy of solution in the single component liquid crystals, CB 5 and CB 7, we find that in CB 5, the enthalpy of solution of the dye A-R is much higher than that in CB 7. The additivity law of the binary mixture mentioned in the case of solubility in the previous section holds also in the case of the enthalpy of solution, as is shown in Table V. It means that

$$\Delta H_{\text{mix}} = x_1 \Delta H_1 + x_2 \Delta H_2$$

where ΔH_{mix}, ΔH_1 and ΔH_2 are the enthalpies in CB 5/7, CB 5 and CB 7 respectively, and x_1 and x_2 are the mole fractions of CB 5 and CB 7 in the binary mixture CB 5/7.

5. CONCLUSIONS

It has been shown that only a slight change in the molecular structure of the dye can have a large influence on its solubility in a liquid crystal. Thus when an alkyloxyl terminal group of an anthraquinone dye was substituted with an alkyl group, the solubility exhibited a

TABLE V

Additivity of the Enthalpy of the dye A-R in CB's.

liquid crystal	CB 5	CB 7	CB 5/7	
			calculated: $\Delta H = x_1 \Delta H_1 + x_2 \Delta H_2$	experimental
enthalpy [kcal/deg.mol.]	11.011	5.435	7.6	7.3

very large increase in all liquid crystals investigated in this work. Also the temperature dependence of the solubility of these dyes has a different behaviour in different liquid crystals; although their molecular dimensions were the same.

In the isotropic phase as well as in the nematic phase of a liquid crystal the logarithm of the solubility expressed in mole fraction is a linear function of the reciprocal absolute temperature over a wide temperature range. In the isotropic phase the temperature dependence is steeper than that in the nematic phase. At T_{N-I} there is a discontinuity in the curve. In the nematic phase, i.e. at temperatures below T_{N-I}, the dye has a solubility that is higher than the value one would obtain by extrapolating the solubility curve of the isotropic phase towards lower temperature.

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