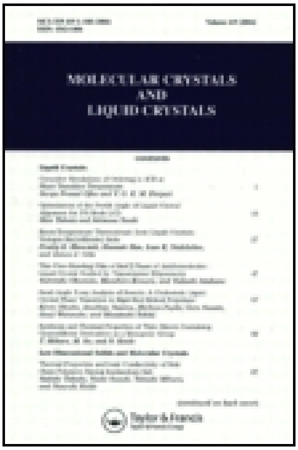

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Properties of Guest-Host Systems with Higher Concentrations of Pleochroic Dyes†

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In this paper we report on the influence of dissolved pleochroic dyes as well on the dye order parameter as on the clearing and melting point of liquid crystalline host as a function of concentration. The investigations of two different anthraquinone dyes in commonly used host systems (Biphenyls, PCHs and CCHs) show, that the order parameter S decreases with increasing dye-concentration comparable for all systems. The influence on the clearing point is different. An increase of the clearing point as well as a decrease has been observed, depending on the used host system. The melting point is influenced in the expected manner (freezing-point depression).

Keywords: guest-host system, anthraquinones, pleochroic dyes, order parameters, thermodynamic data

INTRODUCTION

Some important aspects concerning guest-host systems like the synthesis of pleochroic dyes with high absorption coefficients and high order parameters S,[1–5] the influence of the dye structure on S,[6–10,18] and the solubilities of the dyes in liquid crystalline phases[11–14] had been part of several investigations. For the determination of the order parameters of guest molecules in liquid crystalline hosts in most cases a concentration of the solute of $\approx 0.5 - 1.0\%$ by weight is used. The influence of the solute on the clearing point of the host phase[15] is usually neglected, also as far as the calculation of the reduced temperature is concerned.

For the determination of the order parameter normally only one concentration of the dye is selected. Therefore the dependence of

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the order parameter of the dye on its amount in solution is not investigated, despite to the fact that higher dye concentrations could be necessary for display applications.

So only little data[7,15,18] is available about the following points of interest: the dependence of the order parameters of the dyes on their concentrations and the influence of the dissolved dyes on the phase behaviour of the mixture.

EXPERIMENTAL

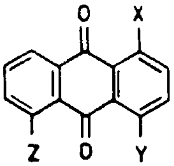
The dyes used for the investigations were anthraquinone derivatives. They are listed in Table I. D-16 and D-35 were obtained from BDH Chemical Ltd., Poole, UK, and dye A from Aldrich-Chemie, Steinheim, FRG. All dyes were used without further purification. D-16 and D-35 were chosen because of the fact that they show rather high solubilities in liquid crystalline hosts and relatively high order parameters.[4,13] The liquid crystals used which were a gift from E. Merck, Darmstadt, FRG, are shown in Table II.

The melting and clearing points of pure hosts as well as of the mixtures which were also determined to get the reduced temperatures, were determined by use of a DSC equipment (DuPont Thermal Analyzer 990) and a polarizing microscope (Leitz Orthoplan-Pol) in conjunction with a Mettler hot-stage FP-52. The melting points could be determined with an accuracy of ±0.5°C with the DSC, using standards in the range of interest. The error at the clearing point, determined with the polarizing microscope, was ±0.1°C.

The order parameters were obtained from the extinctions of the

TABLE I

Pleochroic dyes



dye	X	Y	Z
D-16	NH-(p-OC_9H_{19})C_6H_4	OH	H
D-35	NH-(p-C_2H_5)C_6H_4	H	NH-(p-C_2H_5)C_6H_4
A	NH_2	OH	H

TABLE II

Liquid crystals

host	T_m(°C)	T_c(°C)
PCH-7	30.0	57.8
K-15	24.0	35.0
CCH-357[a]	7.0	84.0

[a] Ternary eutectic mixture of CCH-3, CCH-5, and CCH-7, that additionally shows a smectic B-phase between 7.0°C and 30.0°C.

polarized spectra at the absorption maximum of the dye with a Cary-17 spectrophotometer (Varian).

The dichroic ratio R is given by equation (1):

$$R = A_{\parallel}/A_{\perp} \tag{1}$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances with the incident light polarized parallely and perpendicularly to the director of the nematic host, respectively. From this value R we obtained the order parameter S using equation (2):

$$S = (R-1)/(R+2) \tag{2}$$

The maximum experimental error in S, observed with the equipment used, was 0.02.

Owing to the facts that the dyes under investigation have rather high absorption coefficients ($0.98 \cdot 10^4$ l/mole·cm for A, $1.53 \cdot 10^4$ l/mole·cm for D-35) and the cell thickness of 7.5 μm could not be further reduced with the equipment used, the range of the spectrometer had to be enlarged for the higher concentrated solutions. This was achieved by using also dye solutions in the reference beam. This allowed us to determine absorption values up to 4.0. The modified equipment was checked with the help of test systems. The observed values as well as their reproducibility confirmed, that the modifications in question do not lead to an excess of the experimental error mentioned above. For the systems under investigation this absorbance limit was quite sufficient also for the investigation of dye solutions that were saturated at room temperature. The method we used for the preparation of the mixtures and determination of the concentration of the dyes is described elsewhere.[16]

RESULTS AND DISCUSSION

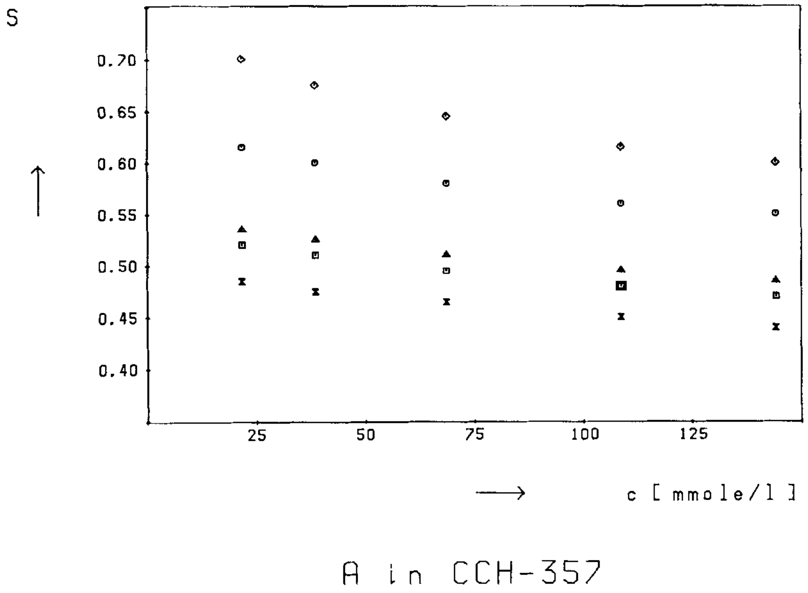
Order parameter

The order parameters S of the dyes D-35 and A were determined as a function of their concentrations in the hosts CCH-357, PCH-7 and

K-15. The results are shown in Figures 1–2. The greatest concentration in every figure is the value of the solutions saturated at room temperature.

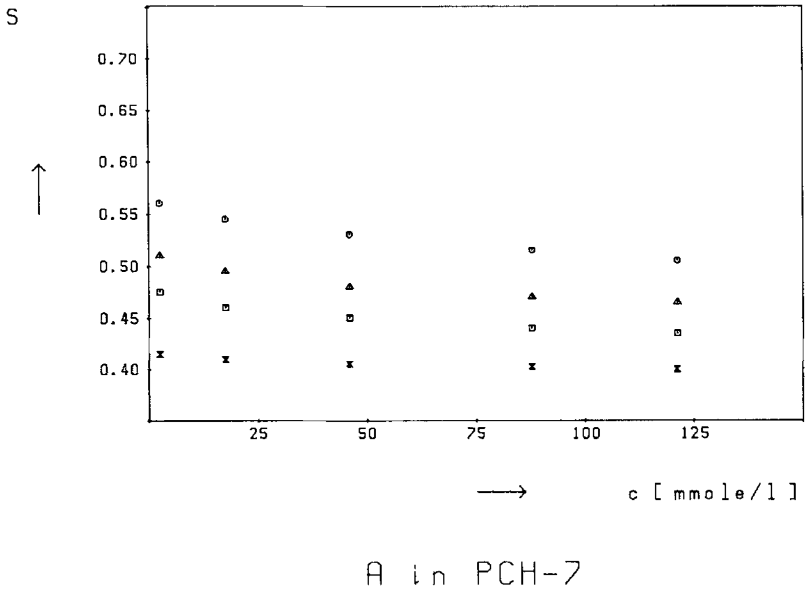
As there are great differences in the lengths of the longest axes of the dye molecules and also in the directions of the electronic transition moments[17] of the compounds in question the absolute S data differ. The order parameter of D-35 in all hosts is ≈0.05 to 0.1 higher than that of dye A in the same solvent. This better orientation of the dye with the greater longest axis in the rod-like hosts is in agreement with the data in the literature.[7,13,18]

In all mixtures there is a noteworthy dependence of the order parameter on the dye concentration. This dependence is rather small at high dye concentration, but significantly greater in the low concentration range. So it seems that there is a limit of the order parameter at high concentrations which is almost reached at dye concentrations of ≈125 mmole/l or higher. This behaviour is more expressed at lower reduced temperatures than at higher ones.

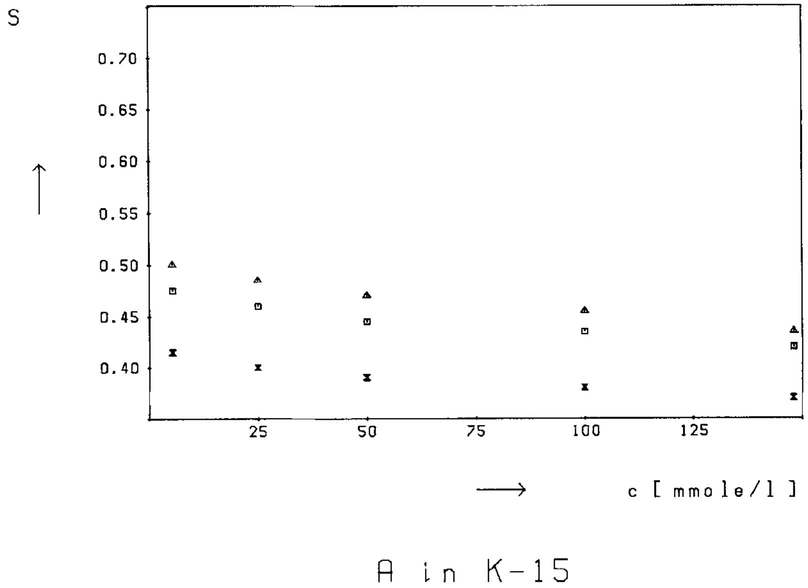


(a)

FIGURE 1 Order parameter S of Dye A as a function of his concentration in the various hosts:
a) in CCH-357 at reduced temperatures: ◇ 0.870, ⊙0.920, △0.960, ⊡0.975, X̲0.990
b) in PCH-7 at reduced temperatures: ⊙0.930, △0.960, ⊡0.975, X̲0.990
c) in K-15 at reduced temperatures: △0.960, ⊡0.975, X̲0.990

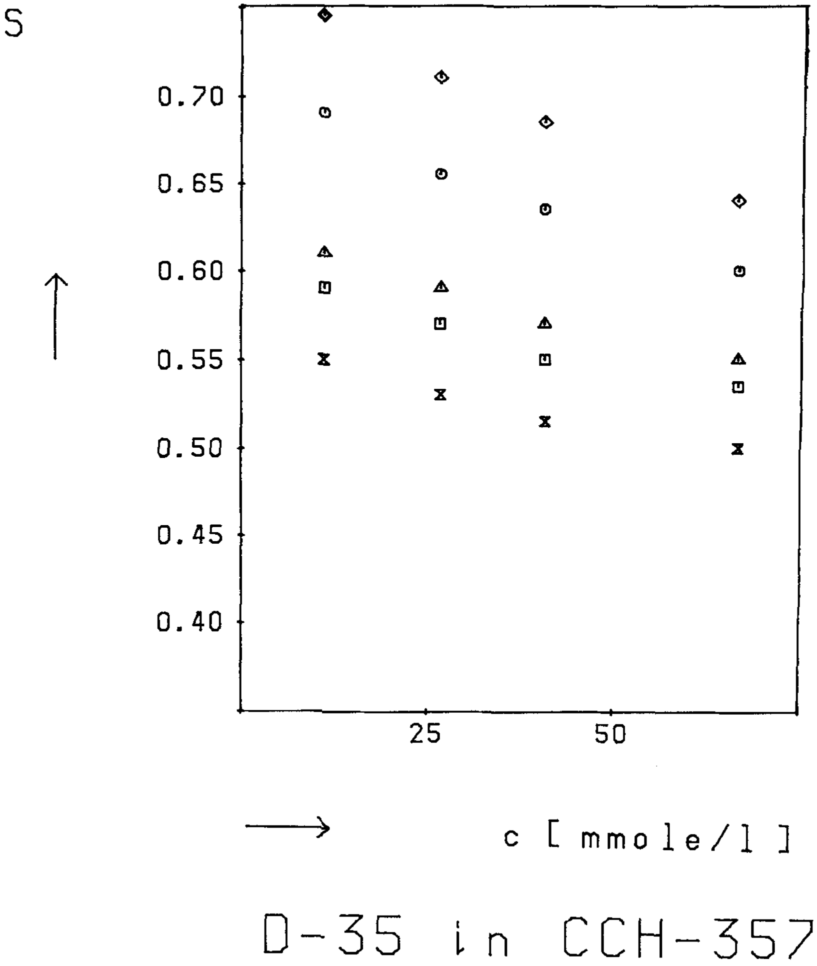


(b)



(c)

FIGURE 1 (*continued*)

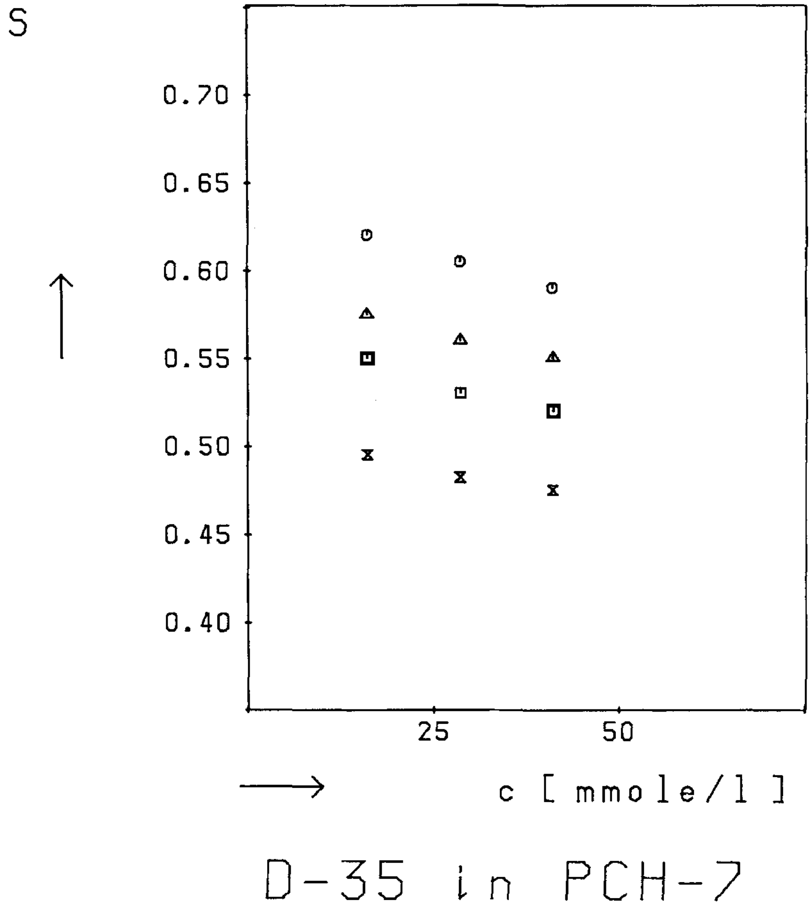


(a)

FIGURE 2 Order parameter S of dye D-35 as a function of his concentration in the various hosts:
a) in CCH-357 (reduced temperatures: see 1a)
b) in PCH-7 (reduced temperatures: see 1b)
c) in K-15 (reduced temperatures: see 1c)

It should be noted that in the concentration range which is normally used for the determination of the order parameters, the value for S shows a significant correlation to the dye concentration. This is in agreement to earlier observations of nonfamiliar guest host systems.[18]

The concentration dependence of the order parameter for D-35 is

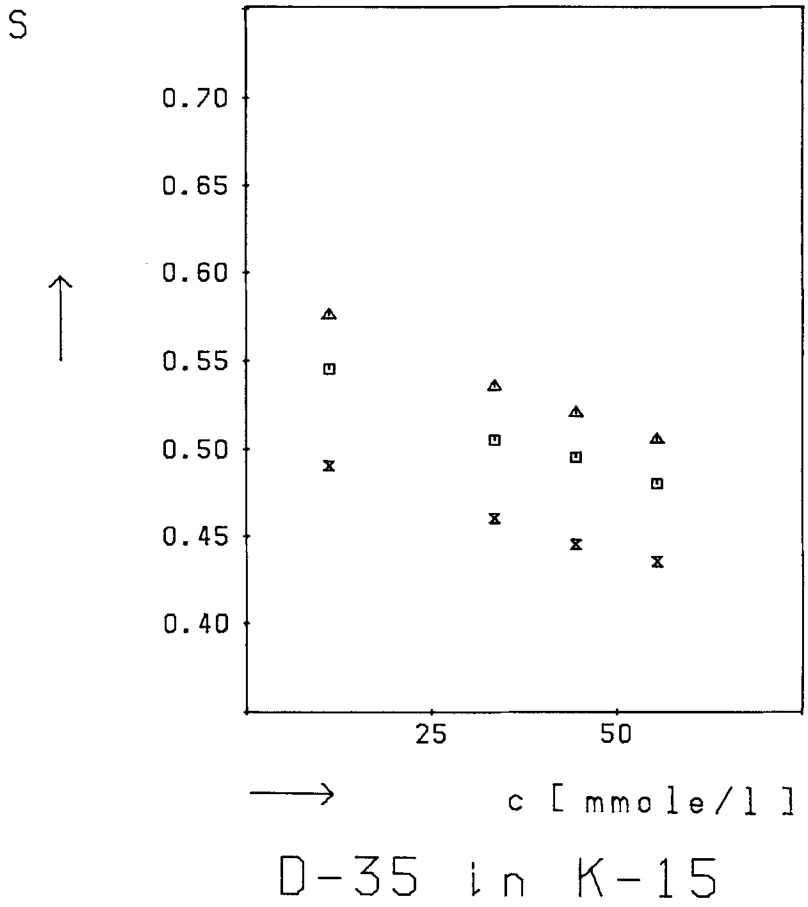


(b)

FIGURE 2 (*continued*)

significantly greater than for A. We interpret this behaviour in terms of the different molecule extensions of the compounds.

The type of the nematic host has also a remarkable effect on the order parameter of the dye in solution. Both dyes have the highest order parameters in the CCH mixture. The values in K-15 and PCH-7 are similar to each other and smaller than those in the CCH host. This is in agreement with other investigations[13] where anthraquinone dyes were found to have higher order parameters in CCH hosts than in PCH and CB ones, respectively. From this one can conclude that the molecular shape of the CCHs has some advantages for the dis-



(c)

FIGURE 2 (*continued*)

solved dyes. The more flexible CCH molecules allow a better orientation of the dye molecules in the direction of the director of the host than do the aromatic, more rigid biphenyl and phenylcyclohexyl derivatives. This influence of the chosen host mixture becomes greater if the temperature approaches to the clearing point as it is shown in Figure 3.

Influence on the phase behavior of the host

The melting points of the hosts are decreased in all cases by the addition of the pleochroic dye. The freezing point depression is in good

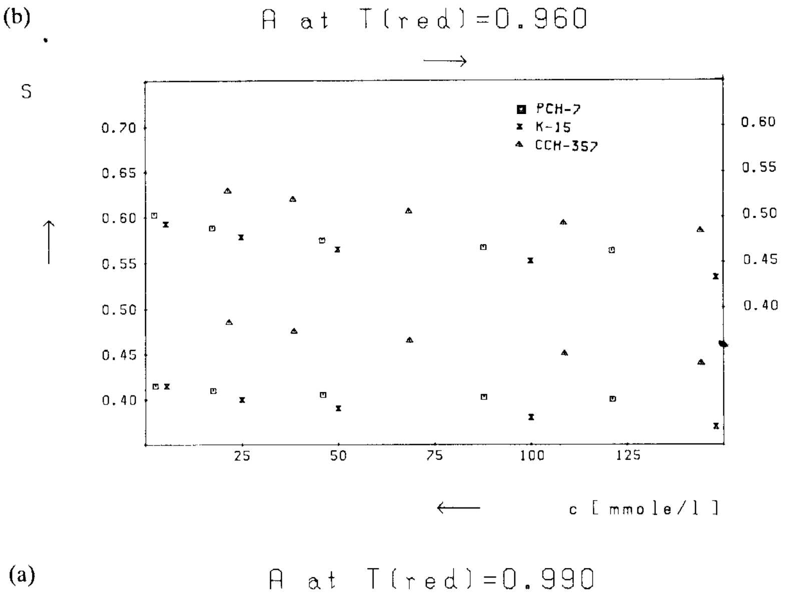


FIGURE 3 Concentration dependence of order parameter S from dye A in the different hosts:
a) at the reduced temperature of 0.990
b) at the reduced temperature of 0.960

agreement with the values that were calculated assuming an ideal behaviour of the mixture and nonmiscibility in the solid phase. This is shown for dye D-16 as an example in Table III. These results confirm the observation that guest-host systems with pleochroic dyes can be reasonably described by approaches which assume ideal behaviour of the mixture.[13–14]

The influence of the dye in solution on the clearing point is more complex. As we reported elsewhere,[15] there can be either an increase or a decrease of the clearing temperature with increasing dye con-

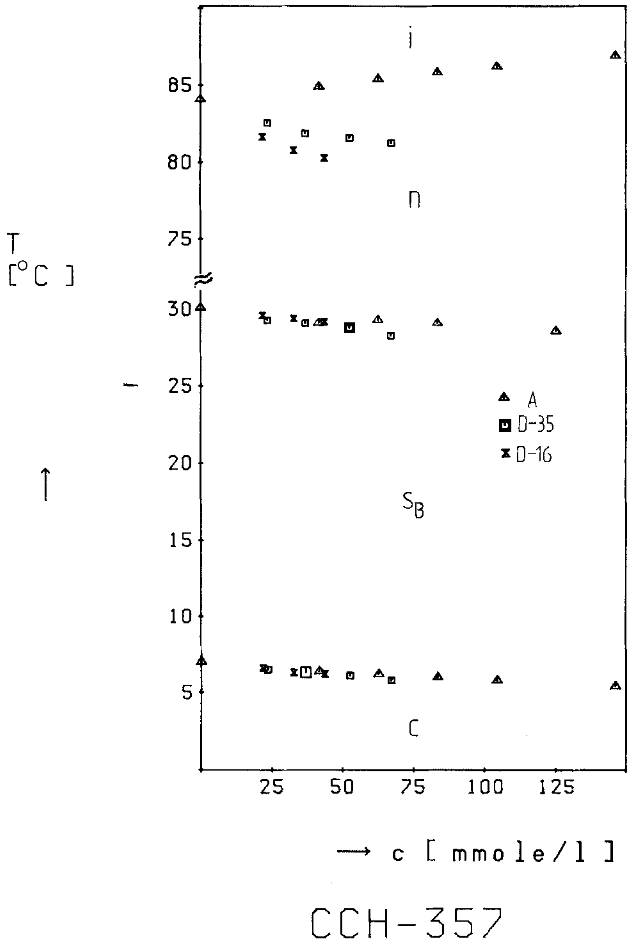
TABLE III

Experimental and calculated values for the freezing-point depression for D-16

c(mmole/l)	ΔT(K) experimental	ΔT(K) calculated
5.50	0.15	0.10
10.90	0.25	0.21
21.85	0.50	0.43
43.68	0.90	0.86

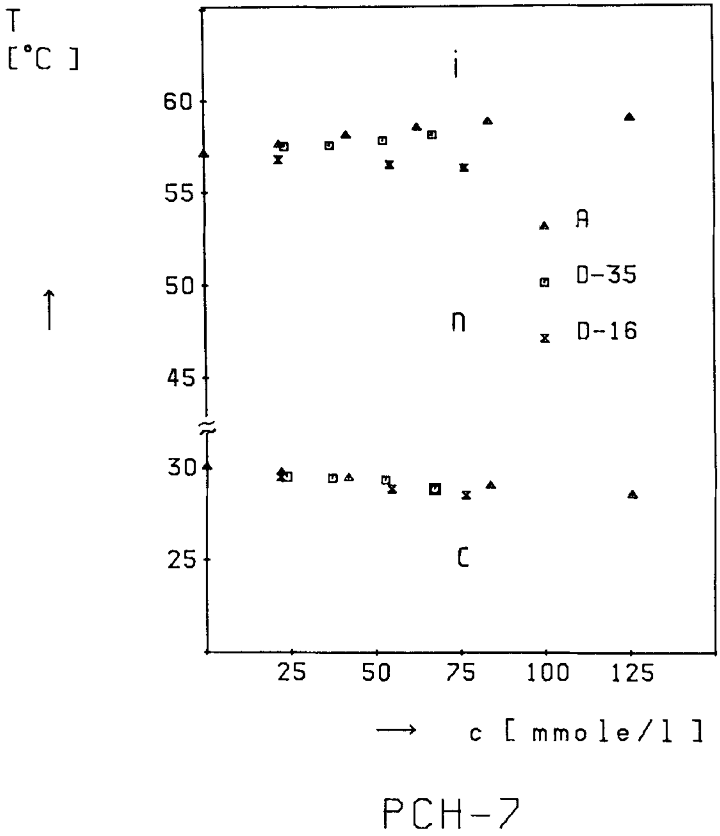
centration. The results for the systems under investigation are shown in Figure 4.

The addition of dye A to the nematic phase leads in all cases to an increase of the clearing point. D-16 causes either an increase (K-15) or a decrease (PCH-7, CCH-357) of the clearing temperature, so



(a)

FIGURE 4 Variation of the transition temperatures for the three dyes A, D-16, and D-35 in the various hosts:
a) in CCH-357
b) in PCH-7
c) in K-15



(b)

FIGURE 4 (*continued*)

do D-35 (increase: K-15, PCH-7; decrease: CCH-357). For all hosts, one observes a sequence A > D-35 > D-16 for enlarging the range of the mesophase.

The temperature for the transition smectic B-nematic is hardly influenced by the dye in solution.

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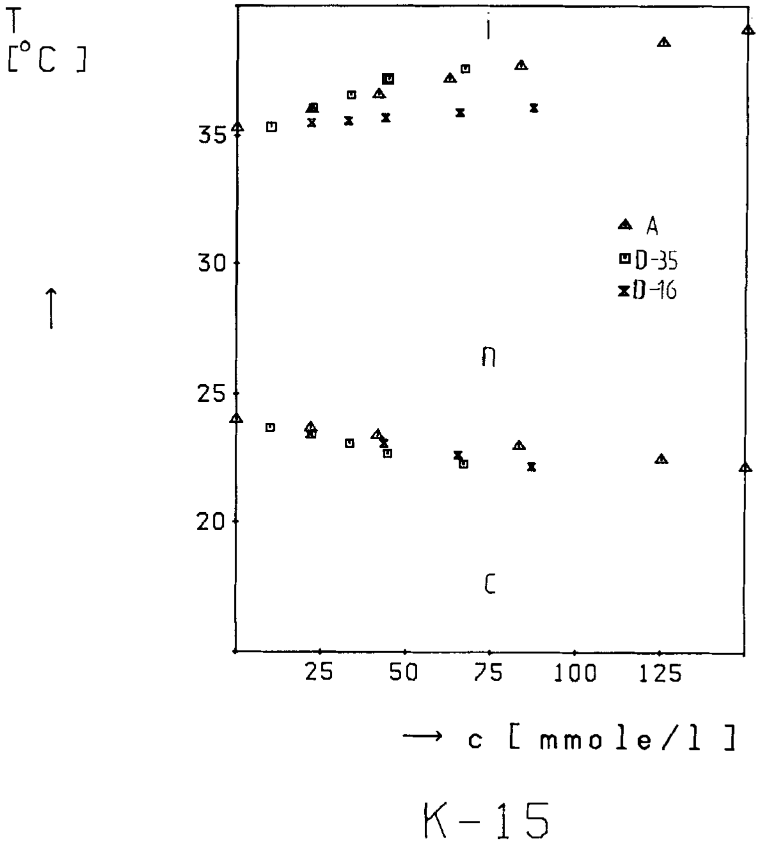

(c)

FIGURE 4 (*continued*)

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