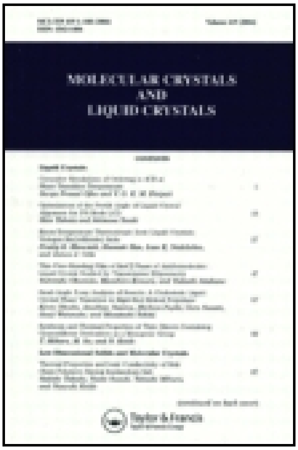


Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

On the Solubilities of Pleochroic Dyes in Liquid Crystalline Phases

J. K. Foitzik [a] & W. Haase [a]

[a] Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, Petersenstraβe 20, 6100, Darmstadt, Federal Republic of Germany

Version of record first published: 17 Oct 2011.

To cite this article: J. K. Foitzik & W. Haase (1983): On the Solubilities of Pleochroic Dyes in Liquid Crystalline Phases, Molecular Crystals and Liquid Crystals, 97:1, 231-240

To link to this article: http://dx.doi.org/10.1080/00268948308073153

Mol. Cryst. Liq. Cryst., 1983, vol. 97, pp. 231–240
0026-8941/83/9704–0231/$18.50/0

On the Solubilities of Pleochroic Dyes in Liquid Crystalline Phases†

J. K. FOITZIK and W. HAASE

Institut für Physikalische Chemie der Technischen Hochschule Darmstadt, Petersenstraße 20, 6100 Darmstadt, Federal Republic of Germany

(Received January 31, 1983)

Solubilities of pleochroic dyes in the liquid crystalline phases ZLI-1565, PCH-5, PCH-7 and CCH-5 are reported. The dyes used were 1,4- and 1,5-disubstituted anthraquinones. We found rather different values for the anthraquinones studied and also noteworthy temperature dependences. The enthalpies of solution were calculated. The influence of the structures of the dyes as well as of the liquid crystalline phases on the solubility and its temperature dependence is discussed.

INTRODUCTION

Problems concerning guest-host displays[1,2] are the subject of many recent reports. This is due to the fact that guest-host displays promise to offer some advantages for the producer as well as for the user, in comparison with twisted-nematic displays. In this respect one might mention that polarizers become dispensible and that a greater viewing angle can be attained.[2]

One of the most important fields of investigation is centered around the search for appropriate pleochroic dyes[3–14] which have hitherto proved to be one of the major problems. This is caused by the fact that a single molecule has to satisfy a number of different requirements.

The most important properties that are demanded of such a molecule are:

— a large extinction coefficient,
— high dichroism,

†Presented at the Ninth International Liquid Crystal Conference, Bangalore, December 6–10, 1982.

— sufficient solubility in liquid crystalline phases,
— high order parameter in liquid crystalline phases,
— stability to illumination (UV/VIS), and
— chemical stability.

For a long time the main problem was the stability of the dyes to illumination. For example, a large number of azo dyes were available and showed high dichroism, order parameters and extinction coefficients, as well as sufficient solubilities. Owing to their rapid decomposition, however, when they were exposed to light, they were unsuitable for use in displays.[15,16] Recently some new azo dyes have been synthesized which seem to exhibit a greater stability.[17,18]

Thus interest concentrated on other types of dyestuffs which had proved to be distinctly more stable to illumination. These types of dyes however did not include any substance that could fulfil all the above-mentioned requirements simultaneously. The order parameter especially proved to be a major problem. Therefore new dyes had to be synthesized with the aim of optimizing this property. Today anthraquinone derivatives are of great interest because the dyes obtainable through appropriate substitution, foremost in 1- and 4- or 1- and 5-positions, show high order parameters in nematic phases.[11,19–21]

In contrast to the azo dyes, these anthraquinones have molecular structures quite different to those of commercial liquid crystals. Thus the question of solubility is accentuated. Investigations at 25°C using E 7 as the nematic host showed rather different saturation solubilities for several anthraquinone dyes.[11] At the same time, a number of these solubilities are of the order of magnitude demanded for a sufficient contrast ratio. Thus for LCDs which are exposed to great changes in temperature, the possibility of separation of the dye by crystallization has to be considered. In order to prevent this, the solubilities of the dyes at the temperatures concerned must be known.

Furthermore the question of stability of supersaturated solutions, i.e. metastable systems, and the conditions of their occurrence become increasingly important. It was also an aim to get information on correlations between the structures of dyes and liquid crystals on the one hand and the solubility of the dyes in the nematic phases on the other.

EXPERIMENTAL

One problem in the determination of solubilities of pleochroic dyes in liquid crystalline phases is the fact that there are usually only rather small amounts of dye and liquid crystal available. Therefore the procedure has to be carried out on small amounts of the substances.

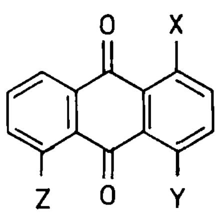
A further problem is that the existence of saturated solutions must be confirmed. The presence of solid dye particles, even some days after starting the intermixing procedure, cannot be taken as the only proof of having a saturated solution. Only after the concentration of the dye in solution approaches a limiting value as a function of time can this be applied as a proof of having reached the saturation concentration.

A third problem is the fact that supersaturated solutions can exist for rather a long time.

To confirm that we had thermodynamically stable saturated solutions, we determined the solubility for a system twice for each temperature. First, we started with the pure components (liquid crystal, dye) or saturated solutions at lower temperatures, and then we began with a saturated solution at higher temperatures. If the two curves of concentration vs time approached the same value, then this was taken to be the value of the saturation concentration. The formation of supersaturated solutions should also be recognizable by this double determination.

The fact that this procedure unfortunately takes rather a long time has already been mentioned elsewhere.[22] The details of the procedure were also reported there.

The dyes we investigated had the general structure and are listed in Table I.



We restricted our investigations to anthraquinones because when we started this work, they were assumed to be one of the most favorable types of dyes for guest-host displays. Their stability to illumination is very good and there were dyes available which have an adequate order parameter and

TABLE I

Structures of the investigated dyes*

DYE	X	Y	Z
D-16	$NH\text{-}C_6H_4\text{-}OC_9H_{19}$	OH	H
D-27	$NH\text{-}C_6H_4\text{-}NMe_2$	OH	H
D-35	$NH\text{-}C_6H_4\text{-}C_2H_5$	H	$NH\text{-}C_6H_4\text{-}C_2H_5$
D-43	$NH\text{-}C_6H_4\text{-}OC_5H_{11}$	H	$NH\text{-}C_6H_4\text{-}OC_5H_{11}$
D-52	$NH\text{-}C_6H_4\text{-}NMe_2$	H	$NH\text{-}C_6H_4\text{-}NMe_2$

*See general structure quoted earlier in the text.

TABLE II

List of liquid crystalline phases

Liquid crystal	T_f (°C)	T_c (°C)
ZLI-1565	−20	+85
PCH-5	+30	+55
PCH-7	+30	+57
CCH-5	+62	+85

T_f: temperature of fusion, T_c: clearing temperature.

dichroism. Besides this, we had a number of technically interesting dyes with the same general structures. All dyes were procured from BDH Chemicals Ltd., Poole, England. The liquid crystals used (all from E. Merck, Darmstadt, W. Germany) are given in Table II.

RESULTS AND DISCUSSION

As there were no data to be found in the literature, we first wanted to obtain some general information concerning the temperature dependence of the solubilities of pleochroic dyes in mesogenic mixtures of practical relevance. We therefore selected ZLI-1565 as nematic host. This multi-component mixture offers the advantage of a technically interesting phase with a broad liquid crystalline range. It was therefore possible to study solubilities over a wide temperature range.

For the purpose of interpretation, simpler systems, i.e. one-component liquid crystalline phases, were used for further investigations. This also proved necessary because of the deviation of the solubility values from the Arrhenius-plot at low temperatures for the ZLI-1565/dye mixtures as described below. Phenyl-and cyclohexylcyclohexanes were chosen with the following aspects in mind:

— These types of liquid crystals, especially the PCH compounds, are components of many broad range mixtures, *e.g.* ZLI-1565.[23]

— Some PCHs and CCHs exhibit a nematic phase from only a few degrees above room temperature, with a range of 20–30°C. This temperature range, besides being easy to handle, renders results of greater relevance to display devices.

— From homologous sequences of biphenyls, phenylcyclohexanes and cyclohexylcyclohexanes, information should be obtainable concerning the influence of the respective ring system on the solubility.

The temperature dependence of the solubilities of the investigated dyes in the hosts ZLI-1565, PCH-5, PCH-7 and CCH-5 are shown in Figures 1–4.

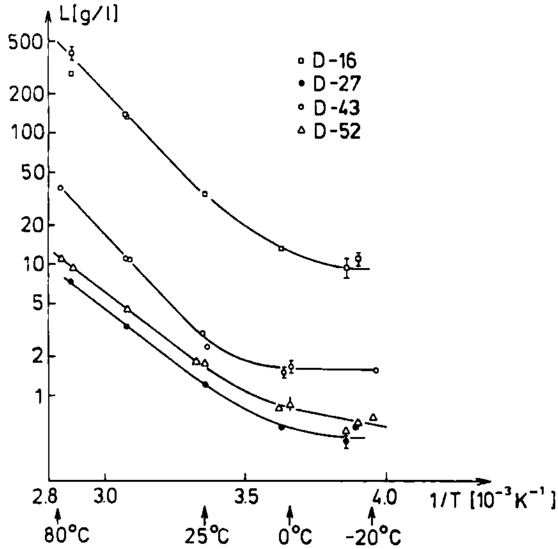


FIGURE 1 Solubilities of anthraquinone dyes in ZLI-1565.

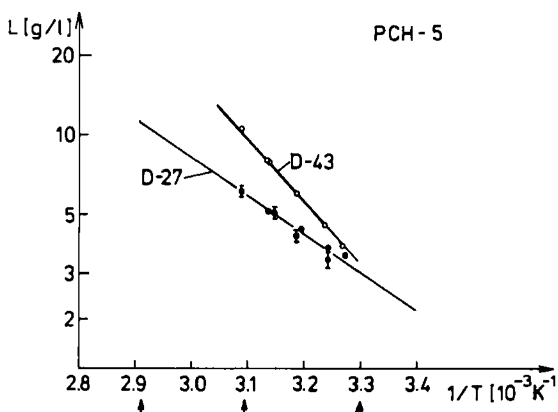


FIGURE 2 Solubilities of anthraquinone dyes in PCH-5.

1. Solubilities in the phase ZLI-1565

One finds a substantial temperature dependence in the range −20 to +75°C. We also observed great differences in the absolute values for the various dyes. The solubility of D-16 is greater than 1% by weight even at temperatures much lower than 0°C, and mixtures of almost 1 : 1 by weight are found to be stable above 70°C. The values for the other dyes are

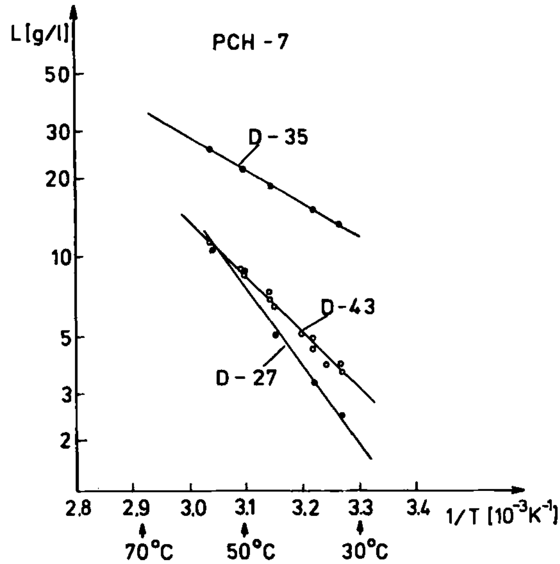


FIGURE 3 Solubilities of anthraquinone dyes in PCH-7.

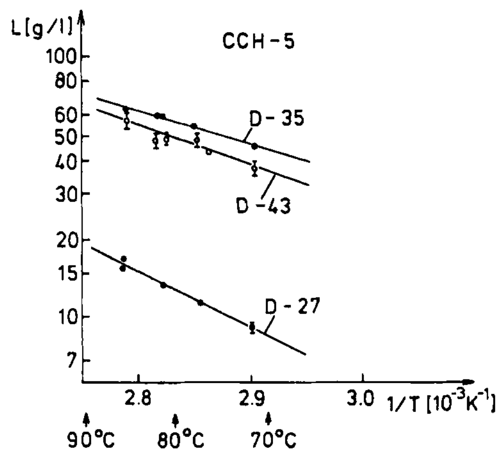


FIGURE 4 Solubilities of anthraquinone dyes in CCH-5.

noticeably smaller and solubilities of more than 1% are stable only above room temperature. For the whole temperature range investigated, solubilities increased in the sequence D-27 < D-52 < D-43 < D-16.

We found a great deviation from the Arrhenius-plot, but are confident that the values which are required to give a linear plot lie well beyond the margin of error. There is not yet enough information to interpret this behavior of the systems at low temperatures. Moreover this behavior may be caused by the occurrence of other phases or the formation of aggregates of mesogenic and dye molecules.

2. Solubilities in single-component liquid crystals

The solubility values for single-component liquid crystals can be described quite well by straight lines. The solubilities in the temperature range studied decreased in the sequence D-35 > D-43 > D-27 for all hosts. Some selected values are given in Table III.

One might mention the solubilities of D-27 and D-43 in PCH-5 and PCH-7. While the differences between the values in each host are not so serious for D-43, they are quite remarkable for D-27, especially as far as their temperature dependence is concerned. This is shown in Figure 5. Comparing the phase ZLI-1565 with the single-component systems, one finds a lower solubility of D-27 in the mixture at the same temperature. Concerning D-43, the solubilities in ZLI-1565 and the PCH-hosts are quite similar, while the solubility in CCH-5 is again higher. If one extrapolated the solubility data from CCH-5 to 50°C, one obtains higher values for D-35, as well as D-43, and lower values for D-27 in comparison with the PCH-phases at the same respective temperatures. This may be brought about by the flexibility of the molecules. Dyes with larger "side chains," *e.g.* D-43 and D-35, seem to be more soluble in CCH-compounds which consist of two of the more flexible cyclohexane rings.

The values found for ZLI-1565 at 25°C are rather different from those reported for E-7.[11] This must be caused by the fact that E-7 consists to a great extent of biphenyls while the former is a mixture based on PCH

TABLE III

Solubilities in different nematic hosts [g/l]

	ZLI-1565	E-7[+]	CCH-5	PCH-5	PCH-7
D-16	34.5[1]	22.0[1]			
D-27	1.2[1]	8.0[1]			
	3.1[2]			6.0[2]	8.9[2]
	7.4[3]		10.0[3]		
D-35			52.0[3]		22.0[2]
D-43	3.0[1]	4.0[1]			
	10.9[2]			10.4[2]	8.8[2]
	38.7[4]		49.8[4]		
D-52	1.8[1]	8.0[1]			

[+]According to Ref. 11.
[1]At 25°C.
[2]At 50°C.
[3]At 74°C.
[4]At 78°C.

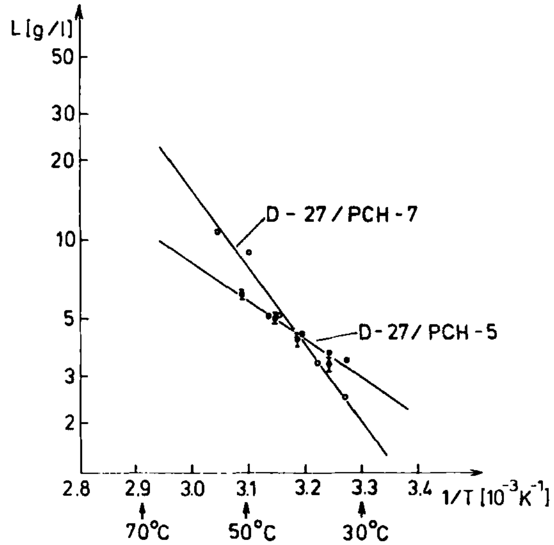


FIGURE 5 Solubilities of D-27 in PCH-5 and PCH-7.

compounds and analogous esters. Some selected data for the solubilities in different hosts are given in Table III.

3. Influence of temperature

The temperature dependence of the solubility of a solute in a liquid phase is described by the equation

$$a = K \cdot \exp(-\Delta H/RT)$$

where a is the activity of the solute, ΔH the enthalpy of solution and K a constant.

Based on this, one can write (to a good approximation) for our solutions

$$L \sim \exp(-\Delta H/RT)$$

where L is the solubility in g/l.

The ΔH values of the systems studied are given in Table IV. The data for ZLI-1565 are taken from the straight part of the curve. For ZLI-1565 as nematic host, the solution enthalpies lie in the range of 30–42 kJ/mol. The values for D-43 in the mixture are similar to those in the PCH systems but different from the CCH-5 data. Great differences between the individual values seem to occur for D-27. Interesting, especially for technical application, is the small solution enthalpy of D-35 in PCH-7, as well as in CCH-5. As this compound has a somewhat high solubility at the higher temperatures at which the measurements had to be performed, and also owing

TABLE IV

Calculated enthalpies of solution [kJ/mol]

	D-16	D-27	D-35	D-43	D-52
ZLI-1565	41	32		42	30
PCH-5		28		47	
PCH-7		57	25	41	
CCH-5		41	21	28	

to its small enthalpy of solution, one can expect it to be readily soluble even at very low temperatures. Thus from the point of view of solubility, this dye may be a favorable one to use in guest-host displays exposed to low temperatures.

4. Influence of dye structure

Although up to now the available data are limited, one can nevertheless make some general statements:

— It seems as though the size of the molecule as a whole is not a decisive factor with respect to solubility. This is confirmed by the fact that the dye with the smallest total molecular dimension, i.e. D-27 possesses the least solubility.

— There were not found to be any general differences between 1,4- and 1,5-disubstituted anthraquinones.

— Amino-substituents in the phenyl rings seem to lead to lower solubilities in comparison with alkyl- or alkoxy-substituents, as shown especially by the results for ZLI-1565.

— For PCH-7 and CCH-5, one observes that dyes with small solubilities at low temperatures correlate with a rather high temperature dependence of their solubilities. Therefore with an increase in temperature, the solubility may be subject to a compensatory effect.

Acknowledgments

The authors would like to thank the Deutsche Forschungsgemeinschaft for financial support. A part of this work was supported by VDO-Adolf Schindling AG, Schwalbach. The liquid crystals were a gift from E. Merck, Darmstadt.

References

1. G. H. Heilmeier and C. A. Zanoni, *Appl. Phys. Lett.*, **13**, 91 (1968).
2. D. L. White and G. N. Taylor, *J. Appl. Phys.*, **45**, 4718 (1974).
3. T. Uchida, C. Shishido, H. Seki and M. Wada, *Mol. Cryst. Liq. Cryst.*, **34**, 153 (1977).
4. A. Bloom and E. B. Priestley, *IEEE Trans. Electron. Dev.*, **ED-24**, 823 (1977).

5. T. Shimomura and S. Kobayashi, *Appl. Opt.*, **20**, 819 (1981).
6. J. Constant, J. Kirton, E. P. Raynes, I. A. Shanks, D. Coates, G. W. Gray and D. G. McDonnell, *Electron. Lett.*, **12**, 514 (1976).
7. A. Bloom, P. L. K. Hung and D. Meyerhofer, *Mol. Cryst. Liq. Cryst.*, **41**, 1 (1977).
8. A. Bloom and P. L. K. Hung, *Mol. Cryst. Liq. Cryst.*, **40**, 213 (1977).
9. A. Bloom and P. L. K. Hung, *Mol. Cryst. Liq. Cryst.*, **44**, 323 (1978).
10. H. S. Cole Jr. and S. Aftergut, *Appl. Phys. Lett.*, **31**, 58 (1977).
11. M. G. Pellatt, I. H. C. Coe and J. Constant, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980).
12. R. J. Cox, *Mol. Cryst. Liq. Cryst.*, **55**, 1 (1979).
13. P. L. K. Hung and A. Bloom, *Mol. Cryst. Liq. Cryst.*, **59**, 1 (1980).
14. T. Jones and T. J. Reeve, *Mol. Cryst. Liq. Cryst.*, **60**, 99 (1980).
15. J. Cognard and T. Hieu Phan, *Mol. Cryst. Liq. Cryst.*, **68**, 207 (1981).
16. H. Seki, C. Shishido, T. Uchida and M. Wada, *Mol. Cryst. Liq. Cryst.*, **66**, 209 (1981).
17. H. Seki, T. Uchida and C. Shishido, *Jpn. J. Appl. Phys.*, **19**, 501 (1980).
18. H. Seki, C. Shishido, S. Yasui and T. Uchida, *Jpn. J. Appl. Phys.*, **21**, 191 (1982).
19. G. Heppke, B. Knippenberg, A. Möller and G. Scherowsky, *Proceedings of Eurodisplay '81*, 25 (1981).
20. J. Cognard and T. Hieu Phan, *Mol. Cryst. Liq. Cryst.*, **70**, 1279 (1981).
21. F. C. Saunders, K. J. Harrison, E. P. Raynes and D. J. Thompson, *Proc. of Intern. Display Research Conference* (Oct. 19–21), p. 121 (1982).
22. J. K. Foitzik and W. Haase, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 131 (1982).
23. G. Weber, F. Del Pino and L. Pohl, 10. Freiburger Arbeitstagung Flüssigkristalle (1980).