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

[a] Institut für Physikalische Chemie der TH Darmstadt, Petersenstrasse 20, D-6100, Darmstadt, FRG

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THE DETERMINATION OF SOLUBILITIES OF PLEOCHROIC DYES IN NEMATIC PHASES.

J.K.FOITZIK and W.HAASE
Institut für Physikalische Chemie der TH Darmstadt,
Petersenstrasse 20, D-6100 Darmstadt, FRG

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ABSTRACT: A procedure to determine the solubilities of pleochroic dyes in nematic liquid crystals is described and discussed. The solubilities of some commercial pleochroic dyes were measured as a function of temperature and also the phenomenon of supersaturation was investigated.

INTRODUCTION

One difficulty using guest-host displays (1,2) with dichroic dyes is the requirement that these dyes have to show a number of properties that are difficult to combine in a single molecule. These properties are, amongst others, a high order parameter, high dichroism, sufficient solubility in nematic phases, chemical stability and stability to illumination.

For LCDs which are exposed to unsteady environmental factors there are some additional problems. If there are great changes in temperature, as in motor-cars, the temperature dependence of the solubility of the dyes may become a decisive factor. Concerning the order parameters, dichroism and stability of the dyes, there have been many investigations (3-13). On the other hand, there are only a few data relating to solubilities reported in the literature (10,11,13) and hardly any concerning the temperature dependence of solubility.

In principle, solubilities of dyes can be obtained by various methods. Because of the fact that the solubility of dichroic dyes in liquid crystalline phases is often rather small, it was considered advisible to use VIS-spectroscopy for the determination (10,11). Because of the special properties of liquid crystalline systems, one must take into account that there may occur difficulties in getting thermodynamically stable systems. Therefore it was important for us to choose an experimental procedure which allowed us to relate the determined data to thermodynamically stable systems. The procedure should also require only small amounts of the substances and also be applicable for temperatures below room temperature.

EXPERIMENTAL

The determination of the solubilities was realized using the following procedure: 1-2 ml of the liquid crystal and an adequate amount of the finely pulverized dye were put into a little test-tube with a side tube. In the side tube there was a filter of grade 4 porosity. After closing tube and side tube with ground glass stoppers, intermixing of the dye and the nematic phase was realized by rocking the glass-apparatus - which was completely immersed in a bath - through an angle of about 120°, approx. 10 times per minute.

After certain periods, a part of the solution was sucked through the filter. After this filtration we could be sure that no solid dye particles existed in the sample volume. According to the solubility of the dye, we took samples of 10, 20 and 50 μl with a micro-pipette and dissolved them in 5 to 250 ml of chloroform. The extinction of this solution was determined with a CARY 17 (Varian) spectrophotometer. Comparing this extinction with those of solutions of known concentrations, the solubility of the dye in the liquid crystalline phase could be calculated.

Samples were taken over adequate periods till the concentration of the dye was constant. This seems to be an indispensible feature of the method, because the time to reach the saturation limit was in some cases rather long and also dependent on the temperature. This is shown in FIGURE 1. It is not possible to take the presence of solid dye particles existing some time after mixing the compounds as the only proof of having reached the saturation concentration. On the other hand, the usual way to obtain a guest-host system, i.e. to dissolve the guest molecules in the isotropic phase of the host, followed by cooling the system in the nematic state, may lead to supersaturated solutions. This would simulate a greater solubility than that corresponding to a stable equilibrium state of the mixture. Because of these facts, the solubilities were determined twice at each temperature. First, as decribed above, beginning with the pure components or a saturated solution at a lower temperature, and second starting with a saturated solution at higher temperatures.

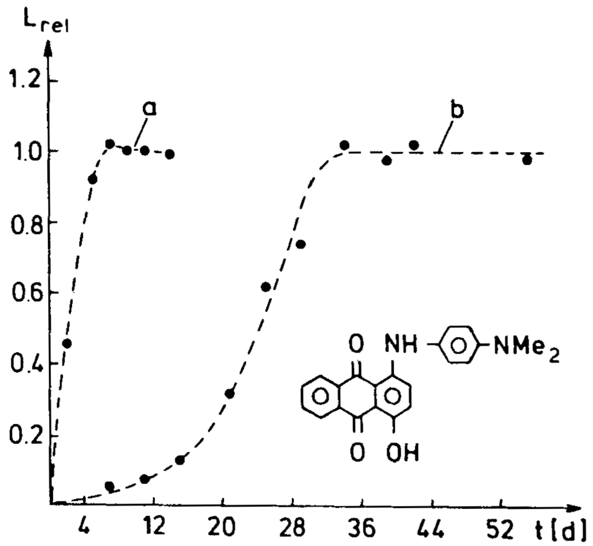

FIGURE 1 Solubility of D-27 in ZLI-1565 a) at 74°C; b) at −17°C (saturation solubility = 1)

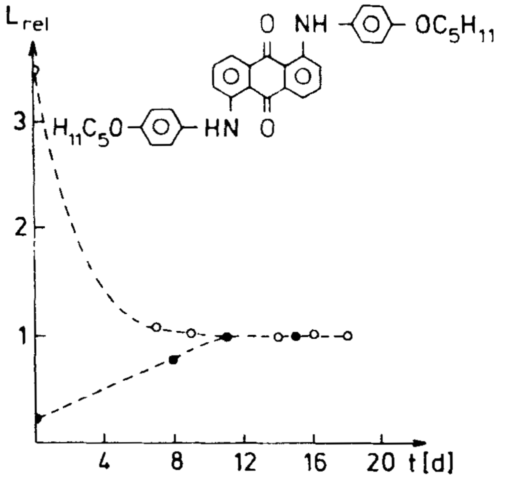

FIGURE 2 Solubility of D-43 in ZLI-1565 at 51.5°C, starting at higher or lower concentrations of the dye in solution (saturation solubility = 1)

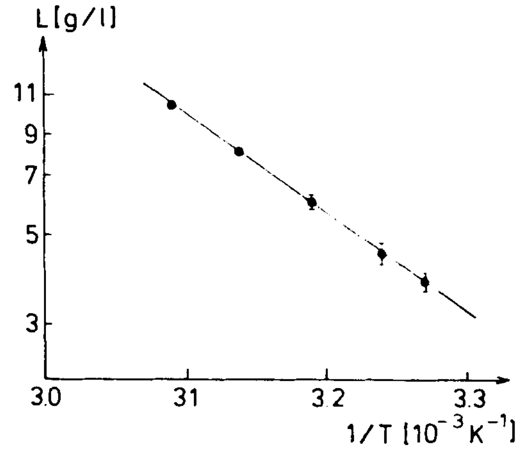

FIGURE 3 Solubility of D-43 in PCH-5 (T_{NI} = 55°C)

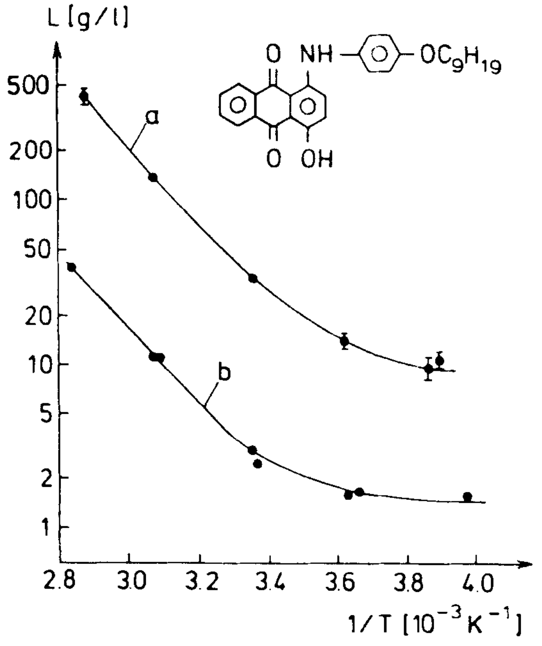

FIGURE 4 Solubilities of a) D-16, b) D-43 in ZLI-1565 (T_{NI} = 85°C)

If the two curves for the concentration of dye in solution vs. time approach the same limiting value this should be the value of the saturation solubility. This is shown in FIGURE 2.

To verify this procedure, the solubilities of certain anthraquinone dyes (BDH) in pure phenylcyclohexanes and in the multicomponent mixture ZLI-1565 (Merck) were determined. The measurements were made over a broad temperature range in the mesophase. An important reason for using the anthraquinone dyes was their great stability to illumination. Nevertheless the systems were protected by exclusion of illumination. Only in one case (D-52) did a noticeable decomposition of the dye occur during the investigation period. In this case the spectrum showed an increasing blueshift of the absorption maximum and the data for the solubility increased to unrealistic values.

The reproducibility of the results was of the order 1-5%, depending on the different dyes and temperatures.

RESULTS AND DISCUSSION

Some solubility curves are shown in FIGURE 3 and 4. We used the plot ln L vs. 1/T where L is the solubility in g/l and T the temperature in K. According to the usual behaviour of the solubilities of solid compounds in liquids, straight lines should be obtained in this plot. For the system shown in FIGURE 3 we found a good correspondence to this ideal behaviour. However, at low temperatures, the solubilities of the dyes in the multi-component mixture ZLI-1565 show a rather large deviation from this behaviour. This phenomenon will be discussed later (14). Remarkable also are the great differences found for the solubilities of a dye in different nematic host phases (11,14). The good conformity of the limits found when starting at higher or lower concentrations are a proof that thermodynamically stable systems were achieved. Therewith the method satisfies the conditions mentioned above.

A disadvantage of the method is that it takes a rather long time (as shown in FIG.1 and 2) to get the values. At low temperatures and starting with the pure components, this is caused by the duration of the dissolution process. This process may be shortened if one replaces the rocking of the glass-apparatus by intensive stirring, but then the problems of having a closed system and small volumes have to be remembered. It also takes rather a long time to confirm the values of the saturation solubility by several measurements. Also when starting at higher temperatures some days are usually required for the supersaturated solution to become a saturated solution despite the fact that almost ideal conditions for crystallization exist because of the presence of solid particles to act as crystal nuclei and the permanent rocking. In some cases considerably supersaturated solutions were stable for some weeks.

These results show not only the necessity to study the concentration of the dye as a function of time, but also the utility of the chosen method for determining duplicate equilibrium values. Without crystal nuclei the tendency to form metastable systems should increase, leading to supersaturated solutions that exist for rather long times and simulating solubilities much higher than the values for thermodynamically stable systems.

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