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Guest-Host Systems with Anthraquinone Dyes: Thermodynamic and Structural Features†

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We report on experimental and theoretical investigations concerning the solubilities of pleochroic dyes in several liquid crystalline hosts. The solubilities of five anthraquinone dyes in these hosts were measured at different temperatures in the nematic phase and for three single-component hosts also in the isotropic phase. Owing to the fact that these measurements take rather long time we especially dealt with the question whether the solubilities of the dyes can be calculated on the basis of the thermodynamic properties of the compounds. For the calculations we used an equation that assumes ideal solutions as well as another one that takes into account the interactions between the molecules. The results will be discussed also with regard to the empirical experience as far as the influence of special terminal groups on the solubility is concerned.

The structures of four anthraquinone dyes in the crystalline phase are discussed with special regard to those structural details that may affect their behaviour in guest-host systems.

Keywords: guest-host systems, solubility parameters, anthraquinone dyes, thermodynamics, molecular structures

INTRODUCTION

A sufficient solubility of pleochroic dyes in a broad temperature range is a necessity for their applicability in guest-host liquid crystal displays. Only in the most recent years some data concerning this important

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point of view were reported.[1-9] Nevertheless till now there is no general approach available that shows which properties influence the solubilities in these guest-host systems. As the structures of some dyes in the crystalline phase are known,[10-13] the influence of molecular features on the solubilities could be studied. Another important aspect is the transferability of data from binary mixtures to multicomponent mixtures.

THEORETICAL APPROACH

The ideal approach

Owing to the small solubilities of the dyes and the logarithmic temperature dependence of the solubilities the usefulness of the ideal approach for the description of the saturated guest-host systems was investigated. Assuming an ideal behaviour of the mixture and neglecting the temperature dependence of the enthalpy of fusion of the solute equation (1) can be derived[14] from the known thermodynamic relations:

$$\ln \frac{1}{x_{2,id}} = \frac{\Delta \overline{H}_{m,2}}{R} \cdot \frac{T_{m,2} - T}{T_{m,2} \cdot T} \tag{1}$$

R is the gas constant. Therefore at a given temperature T the mole fraction of the solute $x_{2,id}$ in the saturated solution depends only on the melting point $T_{m,2}$ and the molar enthalpy of fusion $\Delta \overline{H}_{m,2}$ of the solute.

Although the ideal approach describes rather well the solubilities for a number of mixtures it has a great disadvantage: the equation does not contain any parameter of the solvent. A discussion of different solubilities of the dyes in various hosts on the basis of equation (1) is not possible.

The real approach

For a real approach one has to consider additional parameters, e.g. the interactions between solvent and solute molecules and the entropy of the mixture. The selection of the real approach was determined by the availability of data for the guest-host systems in question. As these data are very rare and we wanted to restrict the number of assumptions and approximations that were made, we chose an approach that only takes into account the energetic interactions between

solvent and solute molecules. Equation (2) was derived by Hildebrand and Scott[15] and a number of examples have proved its usefulness:

$$\ln \frac{1}{x_{2,re}} = \frac{\Delta \overline{H}_{m,2}}{R} \cdot \frac{T_{m,2} - T}{T_{m,2} \cdot T} + \frac{\overline{V}_2}{R \cdot T} \cdot [\delta_1 - \delta_2]^2 \cdot \varphi_1^2 \qquad (2)$$

$\overline{V}_2$ is the molar volume of the solute, φ_1 the volume fraction of the solvent, and δ_1 and δ_2 are the solubility parameters of the solvent and the solute, respectively. The solubility parameter is defined as

$$\delta = \left[\frac{\Delta \overline{E}^v}{\overline{V}}\right]^{1/2}$$

$\Delta \overline{E}^v$ is the molar energy of vaporization and $\overline{V}$ the molar volume of the compound in question.

The data that are additionally needed in comparison with the ideal approach are the solubility parameters (or the molar volumes and energies of vaporization of the compounds), the molar volume of the solute and the volume fraction of the solvent. As there is only a limited number of experimental data for solubility parameters[15,16] in the literature, one has to calculate these values from the energies of vaporization and the molar volumes. If these data are also lacking or difficult to determine, there is also the possibility to obtain the values from increment schemes. Some increment schemes have been reviewed by Fedors.[17]

Mixtures

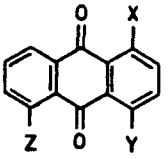
As we were interested in general statements concerning the solubility of pleochroic dyes in liquid crystals we mainly concentrated on binary systems with one mesogenic compound and one dye. Nevertheless, as for display applications multi-component mixtures are necessary, we also dealt with the question of the transferability of data from a single component host to host mixtures. Assuming an ideality of the mesogenic mixture, the solubility of a dye in the binary host should be characterized by the linear equation (3):

$$S_m = S_1 x_1 + S_2 x_2 \qquad (3)$$

S_m is the solubility of the dye in the binary host mixture, S_1 and S_2 the solubilities in the compounds, and x_1 and x_2 the mole fractions of the two host components in the host mixture.

TABLE I

Pleochroic dyes



dye	X	Y	Z
D-16	NH-(p-OC_9H_{19})C_6H_4	OH	H
D-27	NH-(p-$N(CH_3)_2$)C_6H_4	OH	H
D-35	NH-(p-C_2H_5)C_6H_4	H	NH-(p-C_2H_5)C_6H_4
D-43	NH-(p-OC_5H_{11})C_6H_4	H	NH-(p-OC_5H_{11})C_6H_4
D-52M	NH-(p-$N(CH_3)_2$)C_6H_4	H	H

EXPERIMENTAL

The dyes used for this investigation are listed in Table I. They were obtained from BDH Chemicals Ltd., Poole, UK, and used without further purification (concerning D-52M see Ref. 10). Some data of the dyes are listed in Table II. The melting points and the enthalpies of fusion of the dyes were determined with a DSC-2 equipment (Perkin-Elmer). The absorption maximum was obtained using a spectrometer Cary-17 (Varian).

As host phases four single component liquid crystals, a binary mixture PCH-7/CB-7, and the multicomponent mixture ZLI-1565 were chosen. The single component liquid crystals were selected due to their importance for multicomponent mixtures. ZLI-1565 is a nematic broad range mixture. The binary mixture PCH-7/CB-7 was chosen to investigate the transferability of data from single component hosts to host mixtures. All host phases are shown in Table III. The data

TABLE II

Properties of the pleochroic dyes

dye	M(g/mole)	T_m(°C)	$\Delta\bar{H}_m$(kJ/mole)	λ_{max}(nm)
D-16	457.6	101.8	32.1	589
D-27	358.4	230.9	39.0	595
D-35	446.6	222.1	36.2	542
D-43	562.7	194.8	38.7	543
D-52M	342.4	230.0	37.3	524

TABLE III

Liquid crystals

host	T_m(°C)	T_c(°C)
PCH-5	28.9	54.5
PCH-7	30.0	57.8
CCH-5	62.0	85.0
CB-7	28.4	42.2
PCH-7/CB-7[a]	≈30	47.7
ZLI-1565	−20	85

[a]50,0 % by weight

for the solubilities were derived from the absorption of a solution of the liquid crystal/dye mixture in chloroform. The experimental details have been described elsewhere.[3]

RESULTS AND DISCUSSION

Experimental solubilities

The experimental results are shown in Tables IV–IX. The clearing points of the saturated solutions were calculated using the data from Ref. 18.

For the description of the temperature dependence of the solubilities a logarithmic approach is useful. In the plot ln solubility vs. 1/T the experimental data for all mixtures can be described rather well by straight lines. An example is shown in Figure 1. Only the data below room temperature for the mixture ZLI-1565 are note-

TABLE IV

Solubilities in ZLI-1565 (mmole/l)

T(°C)	D-16	D-27	D-43	D-52M
−20			2.8	1.8
−15	23.6	1.4		1.8
0			3.0	2.3
3	26.2	1.7		2.3
25	75.4	3.3	5.3	5.3
50			19.5	
52	293	9.5		13.1
74	962	20.6		27.7
78			68.8	32.8

TABLE V

Solubilities in CCH-5 (mmole/l)

T(°C)	D-27	D-35	D-43
67	21.5	92.5	53.0
71	25.7	101	64.9
77	33.5	122	80.0
81	37.7	134	85.3
85	46.0	136	103

worthily greater than expected from the temperature dependence at higher temperatures. The enthalpies of solution $\Delta\overline{H}$ that are shown in Table X were calculated from the experimental data (for ZLI-1565 only for the temperature range from 25 to 78°C) assuming the relation:

$$\ln S = -\frac{\Delta\overline{H}}{R} \cdot \frac{1}{T} + C \tag{4}$$

S is the solubility of the dye, C is a constant.

Structural features

The details of the structure analyses and the numerical data have been published elsewhere.[10–13] In this work, we only want to discuss the following points of interest that are related to the other features in question:

—The dihedral angle θ between the anthraquinone system and the phenyl group(s)
—the occurrence of intramolecular hydrogen bonds
—the extension of the molecule

The main part of the molecule is similar for all the dyes in question. As an example the molecular structure of D-43 is shown in Figure 2.

TABLE VI

Solubilities in PCH-5 (mmole/l)

T(°C)	D-27	D-43
33	9.8	6.8
35	10.0	8.0
40	11.7	10.7
45	14.2	14.4
50	17.3	18.7

TABLE VII

Solubilities in PCH-7 (mmole/l)

T(°C)	D-27	D-35	D-43
33	7.0	29.6	7.1
38	9.2	33.6	8.4
44	14.0	41.4	11.4
50	24.6	48.6	15.5
56	29.9	56.9	20.3
64[a]	37.9	65.2	26.7
71[a]	44.9	73.0	36.8
78[a]	58.3	90.2	54.2

[a]isotropic

There is an almost planar anthraquinone system to which the phenyl rings of the substituents are arranged nearly perpendicular. The dihedral angles θ between anthraquinone system and phenyl rings are shown in Table XI. The values of about 70° for all the dyes except of D-35, where the angle is somewhat smaller, point to only small interactions between the resonance systems. This is supported by the geometric data of the —NH— group which point to an sp^2 hybridized N-atom that is part of the anthraquinone resonance system. The influence of these geometric conditions on the electronic spectra, experimental and theoretical investigations are under way, will be discussed elsewhere.[19]

Strong nonlinear intramolecular hydrogen bonds were observed in all cases when NHR— or OH— groups were located in α-positions of the anthraquinone system. The hydrogen atom and the bearing oxy-

TABLE VIII

Solubilities in CB-7 (mmole/l)

T(°C)	D-27	D-35	D-43
30	10.9	37.8	10.3
34	12.6	41.2	12.8
38	15.3	47.2	13.2
42	17.6[a]	50.4	13.3[a]
48[a]	23.2	54.0	14.6
56[a]	30.4	66.7	23.3
66[a]	41.9	86.4	41.1

[a]isotropic

TABLE IX

Solubilities in PCH-7/CB-7, 50.0% by weight (mmole/l)

T(°C)	D-27	D-35	D-43
34	11.7	36.1	10.3
39	17.9	43.2	10.8
43	19.3	47.7	13.0
49	25.9[a]	51.5	13.7[a]
57[a]	32.6	60.2	21.3
65[a]	43.8	74.8	33.8
73[a]	58.3	101	56.9

[a]isotropic

gen and nitrogen atom, respectively, are situated in the anthraquinone plane and the distance from hydrogen to the carbonyl oxygen atom is in the range from 1.837 to 1.896 Å for a N. . .H contact and 1.667 for O. . .H. This is in agreement with the data for similar anthraquinone derivatives.[20-25] The observed bond lengths confirm also the formation of an additional resonance system including the hydrogen bond (e.g. the system $C(6)^{I}$, C(14), C(1), N(1), H(1N), $O(1)^{I}$) that was postulated by Bailey.[22]

The longest extensions of the dye molecules including the van der Waals radii of the terminal hydrogen atoms are 18.1Å (D-27 and D-52M), 25.0Å (D-35), and 31.4Å (D-43). It was observed that there

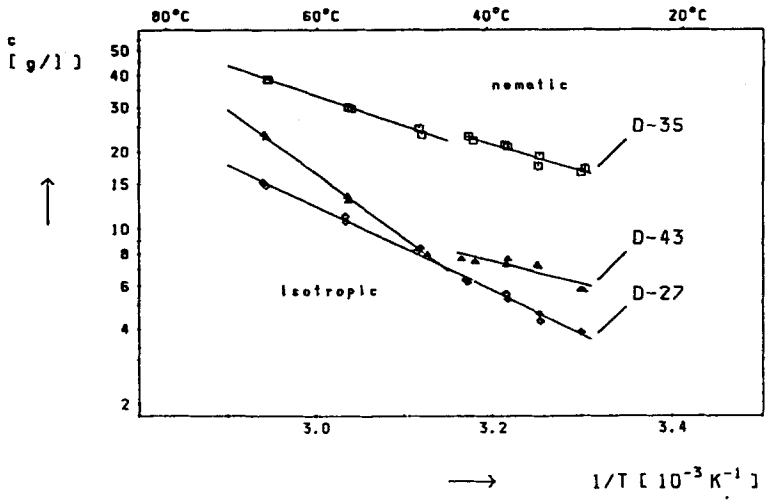


FIGURE 1 Solubilities of pleochroic dyes in CB-7.

TABLE X

Enthalpies of solution (kJ/mole)

	D-16	D-27	D-35	D-43	D-52M
ZLI-1565	41	31	—	43	30
CCH-5	—	40	23	33	—
PCH-5	—	28	—	46	—
PCH-7					
nematic phase	—	56	25	40	—
isotropic phase	—	31	24	42	—
CB-7					
nematic phase	—	35	20	17	—
isotropic phase	—	31	23	48	—
PCH-7/CB-7					
nematic phase	—	45	20	21	—
isotropic phase	—	31	30	53	—

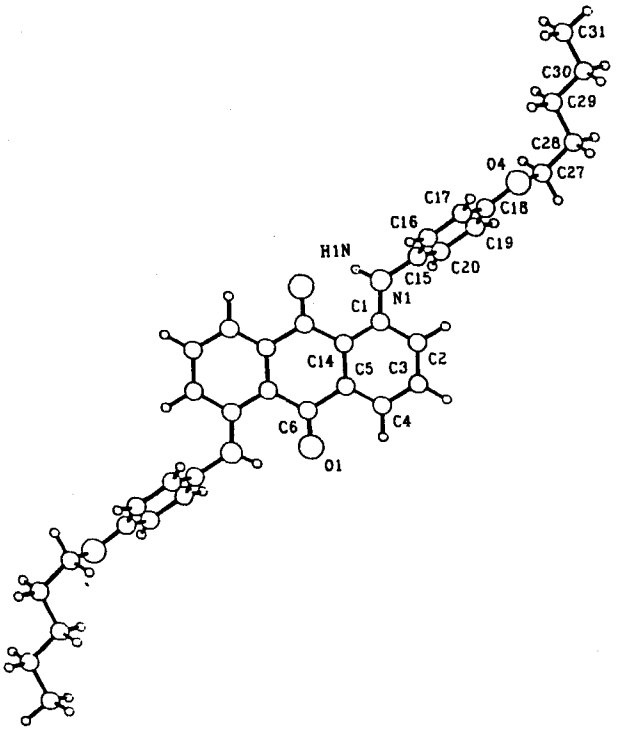


FIGURE 2 Molecular structure of D-43.

TABLE XI

Dihedral angles θ between anthraquinone and phenyl system

dye	θ(°)
D-27	69.5
D-35	50.3
D-43	75.1
D-52M	73.5

is a linear correlation between the longest molecular extensions of these dyes and their order parameters in a number of nematic hosts (e.g. ZLI-1565, CCH-5, PCH-7, and CB-7).[26]

Solubilities and molecular features

For the discussion of the experimental solubility data (Tables IV-IX) and a possible applicability of theoretical approaches the following points should be taken into consideration:

The solubilities of the pleochroic dyes in nematic liquid crystals are of the same order of magnitude as the values that were found for anthraquinone derivatives in isotropic solvents (see e.g. Ref. 27).

All the dyes have a similar structure. They only differ in the number of great substituents and the terminal groups of these substituents. The evident differences in the solubilities (see e.g. D-43 and D-35, where only the terminal pentyloxy groups are exchanged by ethyl groups) have to be correlated to properties of the dyes, that are strongly influenced by these groups.

In the one- and two-component host phases (Tables V–IX), D-35 shows the greatest solubility in the nematic as well as in the isotropic phase.

The values for D-27 and D-43 are similar, only in CCH-5 the solubility of D-43 is noteworthily greater.

The solubilities of the dyes in CB-7 are always greater than in the PCH phases.

The solubility of D-43 in CCH-5 is significantly greater, that of D-27 smaller than the solubilities in the isotropic phases of PCH-7 and CB-7 at the same temperature. So it seems that the more flexible CCH compounds are good hosts for dyes with an extended structure like D-43, not only as far as the order parameter is concerned,[26] but also concerning the solubility.

The solubilities of D-35 and D-43 in the binary mixture PCH-7/CB-7 (Table IX) can be well described by equation (3) using the

values from CB-7 and PCH-7 hosts. The agreement between experimental and calculated values is the best for temperatures where all the three hosts show the same phase (nematic or isotropic).

The solubility of D-43 in the *multi-component mixture ZLI-1565* (Table IV) that mainly consists of PCH compounds is comparable to that in the PCH hosts while the solubility of D-27 in the multi-component mixture is significantly smaller than in the PCH hosts.

The solubility of D-16 in ZLI-1565 is one to two orders of magnitude greater than those of the other dyes.

There are significant differences in the enthalpies of solution for the different guest-host systems (Table X). This is in agreement with the literature.[3,7–9] The dependence on the chosen host phase in the isotropic phase is smaller than in the nematic phase. Finally there is a relatively small temperature dependence of D-35 in all host phases.

Thermodynamical approaches

With the assumption that the densities of the pure hosts that were determined by Ibrahim[28] and Garg *et al.*,[29] can be taken for the densities of the solutions, the experimental mole fractions x_{exp} can be calculated.

Assuming an *ideal solution*, the mole fractions of the dyes in the saturated solutions were calculated from equation (1) using the data from Table II. Tables XII and XIII show the experimental and calculated values for the mixtures under investigation at a temperature in the nematic and in the isotropic phase, respectively.

There is a rather good agreement of the calculated data with the experimental values. The order of magnitude of the solubility is always correctly described.

The best agreement between calculated and experimental values was found for D-27 and D-52M. These are the most compact dye molecules which possess only one big substituent and have no long terminal alkyl chains. For D-35 and D-43, the dyes with the two bulky substituents, the best agreement between experimental and calculated values was observed for the CCH host.

The correct description of the comparatively high solubility of D-16, that is a consequence of the low melting point of this dye, illustrates the strong influence of the melting point and the enthalpy of fusion of the dye on the solubility in guest-host systems, at least if a special class of dyes is considered.

The calculated solubilities of D-43 and D-16 in all hosts are significantly higher than the experimental data. On the other hand, the

TABLE XII

Experimental and calculated (Eq. 1) mole fractions (nematic phase)

dye	host	T(°C)	$10^3 \cdot x_{exp}$	$10^3 \cdot x_{2,id}$
D-16	ZLI-1565	25	20	71
D-27	ZLI-1565	25	0.9	1.6
D-43	ZLI-1565	25	1.5	3.5
D-52M	ZLI-1565	25	1.5	2.2
D-27	CCH-5	77	9.8	17
D-35	CCH-5	77	35	26
D-43	CCH-5	77	23	35
D-27	PCH-5	38	3.0	3.1
D-43	PCH-5	38	2.5	6.7
D-27	PCH-7	38	2.8	3.1
D-35	PCH-7	38	10	5.5
D-43	PCH-7	38	2.5	6.7
D-27	CB-7	38	4.3	3.1
D-35	CB-7	38	13	5.5
D-43	CB-7	38	3.7	6.7
D-27	PCH-7/CB-7	38	4.3	3.1
D-35	PCH-7/CB-7	38	11	5.5
D-43	PCH-7/CB-7	38	3.2	6.7

calculated solubilities of D-35 are always smaller than the experimental values. The only difference between D-43 and D-35, e.g., is the nature of the terminal chain. D-43 has two pentoxy-, D-35 two alkyl-chains. It can be found more than once in the literature that substances with terminal alkyl chains show significantly greater solubilities in liquid crystals than the analogous alkoxy compounds.[1,3,9] Provided that the melting points and enthalpies of solution are similar, this is in agreement with our results that for dyes with terminal alkyl

TABLE XIII

Experimental and calculated (Eq. 1) mole fractions (isotropic phase)

dye	host	T(°C)	$10^3 \cdot x_{exp}$	$10^3 \cdot x_{2,id}$
D-27	PCH-7	66	12	11
D-35	PCH-7	66	20	18
D-43	PCH-7	66	9.7	23
D-27	CB-7	66	12	11
D-35	CB-7	66	24	18
D-43	CB-7	66	12	23
D-27	PCH-7/CB-7	66	13	11
D-35	PCH-7/CB-7	66	23	18
D-43	PCH-7/CB-7	66	11	23

groups there is a positive deviation from the calculated values while for alkoxy compound a negative deviation is observed.

According to our data, terminal dialkylamino groups and hydroxy groups that form intramolecular hydrogen bonds do not have a noteworthy influence on the solubility of the dyes.

There is no significant difference between the agreement of experimental and calculated data in the nematic and the isotropic phase. Therefore one can conclude that for the solubility of the pleochroic dyes that were under investigation in liquid crystalline phases the thermodynamic data are by far more important than any influence of the anisotropy of the solvent.

The logarithmic temperature dependence of the solubilities that was experimentally found, is also well described by the ideal approach.

A problem for the use of the *real approach* (equation (2)) for the guest-host systems in question is the lack of data, especially as far as the energies of vaporization of the dyes are concerned. A measurement of the latter would be made very difficult by the fact that the decomposition of the dyes begins already in the range of their melting points. Therefore we used the increment scheme suggested by Fedors[17] for the description of solutions of polymeric compounds in isotropic solvents. This procedure, unfortunately restricted to a temperature of 25°C, allows the calculation of molar volumes and molar energies of vaporization from increments for the groups that form the molecule. It could be proved that this procedure may also be applied to the guest-host systems in question, if there is a critical selection of the used increments. This is very important for the correct description of the anthraquinone system. As there is no value for the anthraquinone system given by Fedors, the increment for this basic structural element of the dyes has to be derived from the values of smaller groups. It was found that the energies of vaporization are by far to high, if the increments for carbonyl groups and, in the case of D-16 and D-27, for hydroxyl groups were used. This would lead to mole fractions of the dyes that are more than one order of magnitude smaller than the experimental values. The increments in question given by Fedors obviously reflect the occurrence of intermolecular hydrogen bonds formed by many well known solvents bearing CO- and OH- groups and their influence on the energy of vaporization. But taking into account the existence of the intramolecular hydrogen bonds, that were found in the crystalline state, another description of this part of the molecules led to much more realistic values.[26] This could be proved using the experimental data for other anthraquinone

derivatives.[16] Therefore the further procedure for the data selection was the following:

The energies of vaporization of dyes and host phases were taken from the increment scheme.

The molar volumes of the dyes were taken from X-ray data or (in the case of D-16) from the increment scheme.

The molar volumes of the liquid crystals were calculated or extrapolated from density data.

Because of the small concentrations of the dyes the volume fraction of the solvent was taken as 1.

The data for the molar volumes and the solubility parameters are given in Table XIV.

In Table XV there are listed the experimental mole fractions (for CB-7, PCH-7 and PCH-5 extrapolated from the nematic phase) together with the calculated data using equation (1) and (2), respectively, for 25°C.

For the comparison of the data, that were obtained from equation (2), with those obtained from equation (1) one has to take into consideration that the additional term in equation (2) is always positive. In consequence of this the resulting values for the mole fractions from the real approach are always smaller than the 'ideal values'. Therefore by no means a better description of the absolute solubilities of D-35 is possible using the real approach (2).

For all dyes, except of D-35, the data obtained from equation (2) are better or at least of comparable quality as the 'ideal values'. This confirms also the applicability of Fedors' increment scheme.

The better solubility of the dyes in CB-7 (and also E-7[1]) than in the PCH phases including ZLI-1565 is correctly described. For D-27 there is even the correct sequence within the PCH hosts.

TABLE XIV

Molar volumens (cm^3/mol) and solubility parameters $(cal/cm^3)^{1/2}$

Substance	$\bar{V}$	δ
D-16	371	10.5
D-27	260	11.2
D-35	351	10.9
D-43	453	10.5
D-52M	256	10.9
ZLI-1565	276	9.7
PCH-5	267	9.9
PCH-7	296	9.8
CB-7	284	10.2

TABLE XV

Experimental and calculated mole fractions at 25°C

dye	host	$10^3 \cdot x_{exp}$	$10^3 \cdot x_{2,id}$	$10^3 \cdot x_{2,re}$
D-16	ZLI-1565	20	71	47
D-27	ZLI-1565	0.9	1.6	0.6
D-27	PCH-7	1.1	1.6	0.7
D-27	PCH-5	1.8	1.6	0.8
D-27	CB-7	2.3	1.6	1.0
D-35	PCH-7	6.8	3.0	1.5
D-35	CB-7	9.0	3.0	2.2
D-43	ZLI-1565	1.5	3.5	2.1
D-43	PCH-7	1.3	3.5	2.4
D-43	PCH-5	1.1	3.5	2.6
D-43	CB-7	2.7	3.5	3.2
D-52M	ZLI-1565	1.5	2.2	1.2

The values for the mixtures with ZLI-1565 as host phase show that also multi-component hosts can be described by the procedure in question.

There could not be found any correlation between the calculated enthalpies of solution for the guest-host systems and the enthalpies of fusion of the dyes.

A general discussion of the enthalpies of solution could perhaps be made on the basis of more experimental data.

Besides the selection of increments can be taken as an additional indication for the existence of intramolecular hydrogen bonds in these anthraquinone dyes also in liquid crystalline solution.[26]

CONCLUSIONS

The applicability of the ideal and the real approach for the description of the solubilities of anthraquinone dyes in liquid crystalline phases was proved. The order of magnitude of the solubilities is correctly described. The influence of the host phase on the solubility can be described by the real approach. Because of the increment scheme the only experimental data that is indispensible for the calculations are melting point and enthalpy of fusion of the dye. Molar volumes of the compounds and densities, respectively, are usually available, so that the use of the increment scheme can often be limited to the data for the energies of vaporization.

At least the ideal approach can also be used to estimate the temperature dependence of the solubility. The real approach additionally offers the opportunity to estimate the solubility of anthraquinone dyes in other hosts when the data for some hosts are known.

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References

1. M. G. Pellatt, I. H. C. Roe and J. Constant, *Mol. Cryst. Liq. Cryst.*, **59**, 299 (1980).
2. S. Aftergut and H. S. Cole, Jr., *Mol. Cryst. Liq. Cryst.*, **78**, 271 (1981).
3. J. K. Foitzik and W. Haase, *Mol. Cryst. Liq. Cryst. Lett.*, **82**, 131 (1982).
4. F. C. Saunders, K. J. Harrison, E. P. Raynes and D. J. Thompson, *Proc. Intern. Liq. Cryst. Conference*, 19.-21.10. (1982), Cherry Hill, p. 126.
5. N. Basturk, J. Cognard and T. Hieu Phan, *Mol. Cryst. Liq. Cryst.*, **95**, 71 (1983).
6. J. K. Foitzik and W. Haase, *Mol. Cryst. Liq. Cryst.*, **97**, 231 (1983).
7. R. Eidenschink, Kontakte(Darmstadt), **1984(2)**, 25.
8. F. Jones and F. A. Kirby, *Mol. Cryst. Liq. Cryst.*, **108**, 165 (1984).
9. R. E. Sah, *Mol. Cryst. Liq. Cryst.*, **129**, 315 (1985).
10. J. K. Foitzik and H. Paulus, *Mol. Cryst. Liq. Cryst. Lett.*, **3**, 15 (1986).
11. J. K. Foitzik, H. Paulus and W. Haase, *Acta Cryst.*, **C42**, 106 (1986).
12. J. K. Foitzik, H. Paulus and W. Haase, *Acta Cryst.*, **C42**, 108 (1986).
13. J. K. Foitzik, H. Paulus and U. Quotschalla, *Acta Cryst.*, in press.
14. G. Kortüm, Einführung in die chemische Thermodynamik (Vandenhoeck & Ruprecht, Göttingen, 1972), 6th ed., p. 282.
15. J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes (Reinhold Publishing Corporation, New York, 1950), 3rd ed., p. 270.
16. R. C. Weast (editor), Handbook of Chemistry and Physics (CRC Press Inc., Cleveland, 1975/76), 56th ed., p. C-721.
17. R. F. Fedors, *Polym. Eng. Sci.*, **14**, 152 (1974).
18. P. Diot, J. K. Foitzik and W. Haase, *Revue Phys. Appl.*, **20**, 121 (1985).
19. U. Quotschalla and W. Haase, to be published.
20. G. D. Nigam and B. Deppisch, *Z. Kristallogr.*, **151**, 185 (1979).
21. M. Bailey and C. J. Brown, *Acta Cryst.*, **22**, 488 (1967).
22. M. Bailey and C. J. Brown, *Acta Cryst.*, **22**, 493 (1967).
23. M. Bailey and C. J. Brown, *Acta Cryst.*, **22**, 392 (1967).
24. J. Guilhem, *Bull. Soc. Chim. Fr.*, **1967**, 1656.
25. D. Hall and C. L. Nobbs, *Acta Cryst.*, **21**, 927 (1966).
26. J. K. Foitzik, Thesis, Darmstadt, D17 (1986).
27. H. Stephen and T. Stephen (eds.), Solubilities of Inorganic and Organic Compounds (Pergamon Press, Oxford, 1963), Vol. 1.
28. I. H. Ibrahim, Thesis, Darmstadt, D17 (1980).
29. A. K. Garg, V. K. Agarwal and B. Bahadur, *Mol. Cryst. Liq. Cryst.*, **130**, 11 (1985).