Spectroscopic and thermodynamic studies of binary mixtures composed of nematogenic and non-nematogenic components

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Spectroscopic and thermodynamic studies of binary mixtures composed of nematogenic and non-nematogenic components

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The effect of a non-nematic guest, tetracyanoethylene (TCNE), on the liquid-crystalline state of the host, 4-*n*-pentyl-4'-cyanobiphenyl (5CB), has been investigated. It was shown by absorption spectroscopy that TCNE forms a 1 : 1 charge transfer complex with 5CB in the nematic phase, similar to that in the isotropic solution. The effect of TCNE on the transition temperature was investigated by comparison with a normal guest, 2,3-dimethylbutane (DMB), which has a molecular volume comparable with that of TCNE but has no specific interaction with the host. TCNE was found to lower the transition temperature much more strikingly than DMB, suggesting the peculiar effect of complex formation. The theoretical background is given based on molecular field theory.

1. Introduction

There has been considerable interest, both experimental and theoretical, in the effect of non-nematogenic guest molecules on the liquid-crystalline state of the host [1–4]. Such studies have dealt mainly with the effect of a general type due to the guest with no specific interactions with the host. In this paper we investigate the effect of a remarkable electron acceptor tetracyanoethylene (TCNE) as a guest in the nematic host of 4-*n*-pentyl-4'-cyanobiphenyl (5CB).

As suggested by the bright red colour, formation of a TCNE–5CB charge transfer complex has been confirmed by a spectroscopic investigation. The existence of two different conformations of the complex is suggested by the dichroic absorption study. The behaviour of the nematic–isotropic transition temperature indicates the strong interference by TCNE with the nematic state of 5CB, and this is discussed using molecular field theory [5, 6].

2. Experimental

TCNE was purified by repeated vacuum sublimation before use, and commercial 5CB (Chisso) was used without further purification. The red colour observed on mixing TCNE with 5CB was confirmed not to be due to reaction products, using thin layer chromatography.

3. Results and discussion

The U.V.–visible absorption spectrum of the solution of TCNE ($0.01 \, \mathrm{mol \, dm^{-3}}$) and 5CB ($0.10 \, \mathrm{mol \, dm^{-3}}$) in 1,2-dichloroethane is shown in figure 1, together with
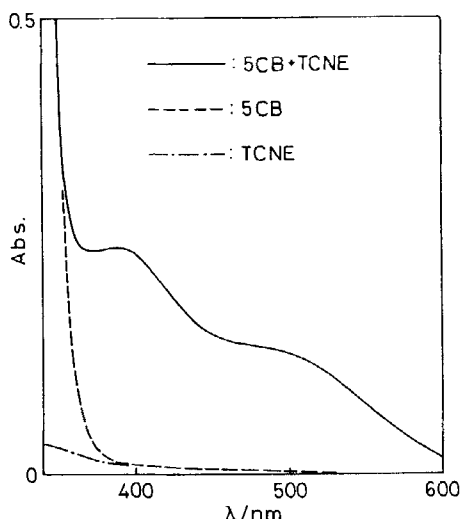
Figure 1.   U.V.-visible absorption spectrum of TCNE, 5CB and their mixture in 1,2-dichloro-ethane solution. [5CB] = 0·1, [TCNE] = 0·01 mol/dm³.

Temperature dependence of the equilibrium constant for TCNE–5CB change transfer complex formation in a 1,2-dichloroethane solution and the thermodynamic constants.

t °C	20	25	30	35
K mol^{-1} dm^3	0·167	0·154	0·142	0·127
$-\Delta H = 14\cdot98\,\mathrm{kJ\,mol^{-1}}$		$-\Delta S = 26\cdot55\,\mathrm{J\,K^{-1}\,mol^{-1}}$		

those of the individual components. Two new absorption bands are observed in the same region as in other biphenyl derivatives with TCNE, and are most probably attributable to the formation of a charge transfer complex [7]. The longer (about 500 nm) and shorter (about 400 nm) wavelength bands are assigned to electronic transitions from the HOMO and next HOMO of 5CB molecule to the LUMO of TCNE. Through the absorbance measurement at 490 nm as a function of concentration [8], the formation of a 1 : 1 complex was confirmed in the present system. The equilibrium constant and the resultant thermodynamic quantities are given in the table.

The absorption spectra of a homogeneously aligned sample of the TCNE–5CB mixture are shown in figure 2 for polarization parallel and perpendicular to the director. The spectral features are essentially unchanged from those in figure 1, indicating a similar complex formation to that in the isotropic solution. The dichroic ratios ($D = A_{\parallel}/A_{\perp}$) near the maxima of both charge transfer bands are plotted in figure 3 for various temperatures up to the phase transition T^N. The D value reflects the orientational order associated with each transition moment. If the moment vector makes an angle $\Delta\beta$ from the molecular long axis of 5CB, the dichroic ratio is related to the order parameter $\bar{P}_2$ of the host liquid crystal by

$$\bar{P}_2\,P_2(\cos\Delta\beta) \;=\; (D - 1)/(D + 2), \tag{1}$$

where $P_2(\cos\Delta\beta)$ is the second Legendre polynomial. Using the observed D values and $\bar{P}_2$ given in [9], $\Delta\beta$ is estimated to be 55° for the 490 nm band and 45° for the 390 nm band.
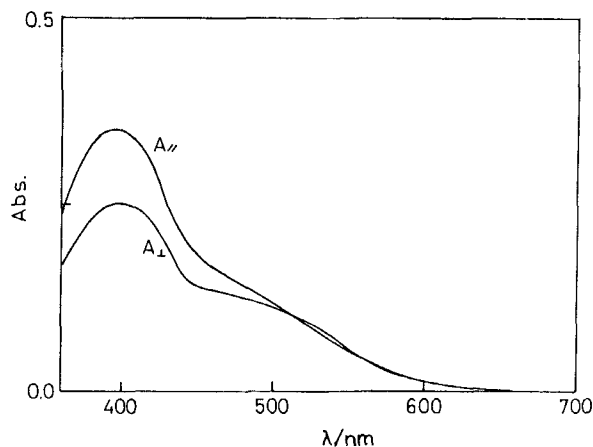
Figure 2. Polarized U.V.-visible absorption spectra of homogeneously aligned liquid-crystalline TCNE (0·9 mol %)/5CB mixture.
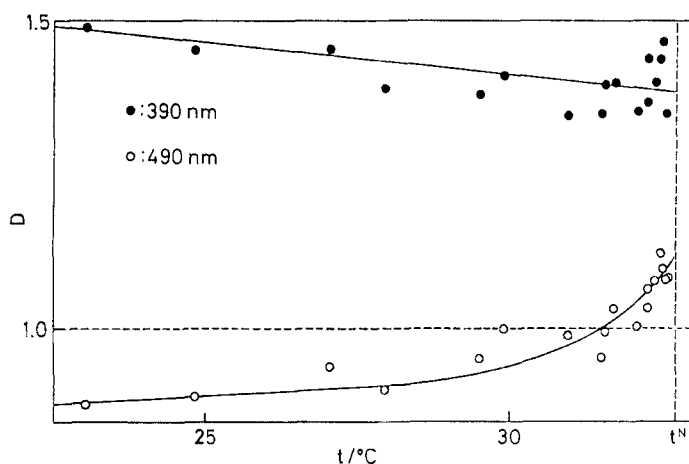
Figure 3. Dichroic absorption ratio of liquid-crystalline TCNE/5CB sample measured at two CT bands maxima, 390 nm and 490 nm. Base-line correction is taken into consideration.

Since liquid-crystalline cyanophenylcyclohexane, which corresponds to the 5CB molecule without the π-electrons in the phenyl ring with the attached alkyl chain, does not form a complex with TCNE; the TCNE molecule in the present complex is very probably attached to the alkylated ring of 5CB. A simple molecular orbital calculation suggests that the two conformations of the complex shown in figure 4 are quite

Figure 4. Possible structures of TCNE–5CB charge transfer complex.

reasonable. In that case, it is known from symmetry that only the 490 nm (HOMO of 5CB → LUMO of TCNE) transition is allowed in c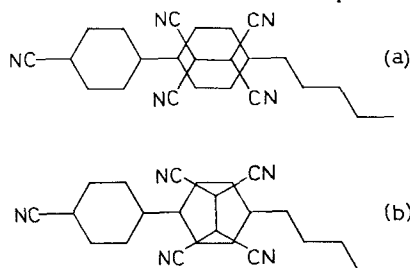onformation (*a*) and only the 390 nm band is allowed in conformation (*b*). Therefore, the appearance of two charge transfer bands as observed means that both (*a*) and (*b*) conformations exist simultaneously under the present conditions. $\Delta\beta$ given by the molecular orbital calculations is about 50° for both transitions.
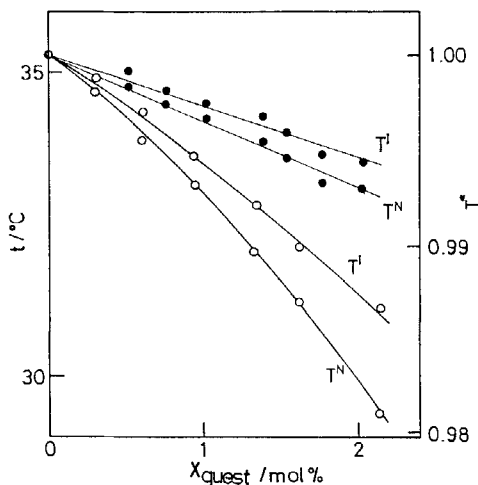

Figure 5.   Phase diagram of TCNE/5CB (—o—o—o—) and DMB/5CB (—●—●—●—) binary mixtures. Concentration is given by mol %.

Figure 5 shows the change of transition temperature as a function of the TCNE concentration in 5CB, where T^N is the temperature at which droplets of isotropic phase first appear in the nematic sample and T^I is the temperature at which the nematic phase disappears completely. Those transition temperatures are lowered approximately linearly with the guest concentration. The figure also shows comparable results for the DMB–5CB system; the molecular volume of DMB has almost the same value as TCNE [10] but it shows no evidence of complex formation with 5CB. Comparison between two systems shows that the admixture of TCNE results in a much steeper depression of the transition temperature than that of DMB.

The difference between DMB and TCNE binary systems was investigated by using the Marcelja's formulation of the molecular field theory [5, 6], which treats a pure nematic as a hypothetical binary mixture composed of core and alkyl chain parts. In the present study, the anisotropic molecular field (X_a) acting on a host liquid-crystalline molecule (A) and a guest non-nematogenic molecule (B) is written as

$$
\left.
\begin{aligned}
-X_A &= \phi_A v_{AA} \eta_A + \phi_B v_{BA} \eta_B, \\
-X_B &= \phi_B v_{AB} \eta_A,
\end{aligned}
\right\}
\tag{2}
$$

where η_I and ϕ_I are, respectively, the order parameter and volume fraction of component I, and v_{IJ} represents the strength of orientational field from component I to J. The orientational part of the chemical potential is given by [1–4]

$$
\left.
\begin{aligned}
\mu_A(\beta, X_A, \phi_B) &= -\tfrac{1}{2} X_A \eta_A - (1/\beta) \ln Z_A(\beta, X_A, \phi_B), \\
\mu_B(\beta, X_B, \phi_B) &= -\tfrac{1}{2} X_A \eta_B - (1/\beta) \ln Z_B(\beta, X_B, \phi_B),
\end{aligned}
\right\}
\tag{3}
$$

where $\beta = 1/kT$ and Z_I is the orientational partition function of component I. It can be shown by a little manipulation that the host chemical potential μ_A is related to that of the pure liquid crystal μ_A^0 by

$$\mu_A[(v_{AA}\eta_A/X_A)\beta, \ X_A, \ \phi_B] \ = \ [X_A/(v_{AA}\eta_A)]\mu_A^0(\beta, \ v_{AA}\eta_A). \tag{4}$$

This shows that the effect of non-nematogenic impurity is taken into account by simply modifying the temperature argument in the same chemical potential formula.

At the transition temperature of the pure liquid crystal $T_{NI}^0 = k/\beta_{NI}^0$

$$\mu_A^0(\beta_{NI}^0, \ v_{AA}\eta_{A,NI}^0) \ = \ 0 \tag{5}$$

is satisfied, where $\eta_{A,NI}^0$ is the critical order parameter. If we simplify the discussion by assigning the transition temperature T^I or T^N to the temperature (T^{NI}) at which the orientational chemical potential of the host nematic becomes zero, i.e. the temperature at which the orientation of the host becomes completely random, we have from equations (4) and (5)

$$\mu_A\left(\frac{\beta_{NI}^0}{1 - [1 - v_{BA}\eta_{B,NI}/(v_{AA}\eta_{A,NI}^0)]\phi_B}, \ \phi_A v_{AA}\eta_{A,NI}^0 + \phi_B v_{BA}\eta_{B,NI}, \ \phi_B\right) \ = \ 0. \tag{6}$$

From equation (6) we find the following conclusions

$$
\left.
\begin{aligned}
&(A) \quad T_{NI}/T_{NI}^0 = 1 - S\phi_B, \quad S = [1 - v_{BA}\eta_{B,NI}/(v_{AA}\eta_{A,NI}^0)], \\
&(B) \quad \eta_{A,NI} = \eta_{A,NI}^0 \text{ irrespective of } v \text{ and } \phi \text{ values}, \\
&(C) \quad \eta_A \approx \eta_A^0 \text{ for the same reduced temperature } \beta_{NI}^0/\beta^0 = \beta_{NI}/\beta.
\end{aligned}
\right\} \tag{7}
$$

Although our treatment described here is a considerably simplified one, it is notable that the last two results ((B) and (C)) provide theoretical support for the outstanding experimental observations by Patterson *et al.*; namely that the second rank order parameters of host nematics in various binary systems lie on a universal curve when they are plotted against the reduced temperature of binary systems and have the same critical value irrespective of the concentration and kinds of the non-nematogenic guests. The first conclusion (A) gives the effect of the non-nematogenic guest on the transition temperature in an explicit form. Under the usual condition of $v_{BA}\eta_{B,NI} > 0$, (A) indicates that the rate of depression of the transition temperature, S, is smaller for a guest which aligns well following the orientation of the host. For a spherical guest molecule, S would take the largest value of unity. Using values of the molecular volume 68·24, 68·82 and 245 cm^3 mol^{-1} for DMB, TCNE [10] and 5CB [12], respectively, we find $T^N/T_{NI}^0 = 1 - 1\cdot05\phi_B$, $T^I/T_{NI}^0 = 1 - 0\cdot93\phi_B$ for DMB–5CB system from figure 5. This shows that the effect of DMB on the transition temperaturre is very close to that expected for a spherical guest molecule.

On the other hand, for the TCNE–5CB system, we obtain $T^N/T_{NI}^0 = 1 - 3\cdot06\phi_B$ and $T^I/T_{NI}^0 = 1 - 2\cdot25\phi_B$. It should be noted that the depression rate, S (cf. equation (7)) is considerably larger than unity, which is expected for a spherical guest molecule. Complexed TCNE attaches to the core part of 5CB and so it would align well following the host orientation in contrast to the behaviour of DMB, and much slower depression rate, S, than DMB would be expected from equation (7) in contrast to the experimental observation. This difficulty may be overcome by assuming a negative value for v_{BA} in equations (7). 5CB molecules are known to form a cluster (cybotactic group) [12] or dimer [13] in the liquid-crystalline state. Since TCNE molecules are

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attached to the core part of 5CB, the clustering or dimerization may be obstructed in the complexed system more effectively than foreign molecules with no specific interaction. This would destroy the liquid-crystallinity of 5CB more effectively than a spherical guest molecule, resulting in the much stronger depression of the transition temperature ($S > 1$, hence $v_{BA} < 0$). The interrelation between the magnitude and sign of v_{IJ} and the destruction of clustering or dimerization of the host nematic will be the subject of a future study.

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