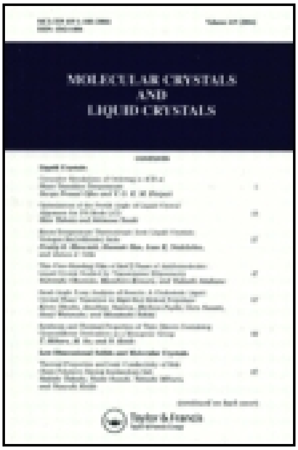

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Dielectric and spectral studies of molecular crystal - chloranil systems forming charge transfer complexes

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DIELECTRIC AND SPECTRAL STUDIES OF MOLECULAR CRYSTAL – CHLORANIL SYSTEMS FORMING CHARGE TRANSFER COMPLEXES

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Molecular crystal – chloranil systems forming charge transfer complexes were studied in solutions and as melts at precrystallization temperatures. Dielectric permittivity of chloranil mixtures with stilbene, naphthalene and diphenyl was measured as function of concentration and temperature, and absorption spectra of the same systems in CCl_4 solution were analyzed. The results obtained suggest the presence of additional molecular ordering in the melts at chloranil concentrations 0,5–5 mol.%. A model of such ordering accounting for both specific and non-specific intermolecular interactions is proposed.

Keywords: dielectric spectroscopy; charge transfer complexes; molecular ordering

INTRODUCTION

Optimization of the growth technology of stilbene, anthracene and other organic crystals is a problem of continuous interest. It has been found recently that introduction of certain acceptor dopants (e.g., chloranil) into the melt improves the structural perfectness of the grown crystals [1,2], which arises great interest in the effects caused by the dopant molecules upon the crystallization process. Physical and physico-chemical properties of such systems were studied in [3,4], though no connection to the crystal growth or structure was considered.

X-ray studies demonstrate that the optimal concentration of chloranil (CA) in the melt is not more than 1 wt.% [1,2]. However, this value substantially differs from stoichiometry of such complexes in solutions obtained by the electron spectroscopy studies [3,4], where the donor-acceptor ratio was 1:1 or 1:2. Dielectric measurements as an effective method for studying intermolecular interactions in different phase states [5] could allow us to determine the structure of CA charge transfer complexes formed with different donors. Complementary optical spectroscopy data were obtained in parallel experiments.

EXPERIMENTAL

The systems forming charge transfer complexes (CTC) were studied with stilbene, naphthalene and diphenyl chosen as donors (Fig. 1). Absorption spectra of molecular crystal + CA systems in CCl_4 solutions were measured using a Hitachi 330 spectrophotometer. CCl_4 was chosen as a solvent to avoid competition between the solvent and the donors [4].

CTC equilibrium constants k were calculated from the Benesi-Hildebrand equation:

$$\frac{[chloranil]l}{d} = \frac{1}{\varepsilon k[donor]} + \frac{1}{\varepsilon}, \tag{1}$$

where ε is extinction constant, k – equilibrium constant, l – the measurement cell thickness, d – optical density, and square brackets denote molar concentrations. Stoichiometry of the complexes was determined from the Job plots (maximal absorbance in the charge transfer band vs. mole fraction of CA).

Concentration and temperature dependences of dielectric permittivity were measured using our original experimental setup and a specially designed high-temperature measurement cell [6]. Measurements were conducted in a cooling mode during crystallization from the melt. The frequency of the external electric field applied to the 50 μm thickness sample was 1 KHz.

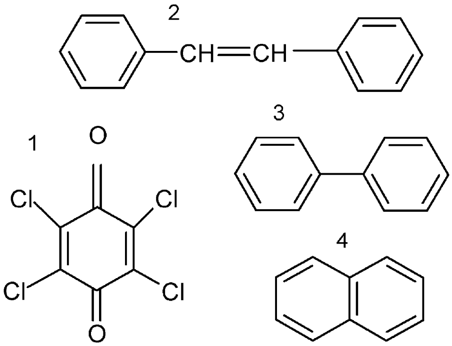

FIGURE 1 Chemical structure of the substances used: 1 – chloranil (CA), 2 – stilbene, 3 – diphenyl, 4 – naphthalene.

RESULTS

Absorbance Spectra

Analysis of charge transfer bands on absorbance spectra (Fig. 2) allowed us to determine stoichimetry and thermodynamical properties of CTC (Tab. 1).

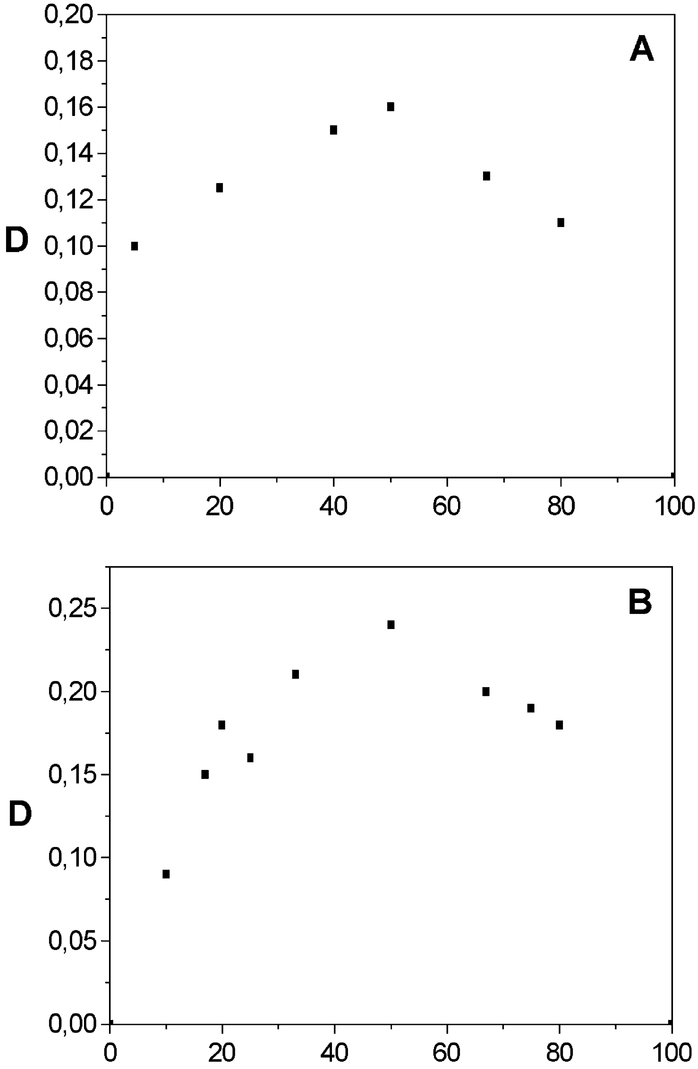

FIGURE 2 The Job plot (maximal absorbance vs. mol.% of CA) for CA complex formation with stilbene (a), naphthalene (b), biphenyl (c) in CCl_4.

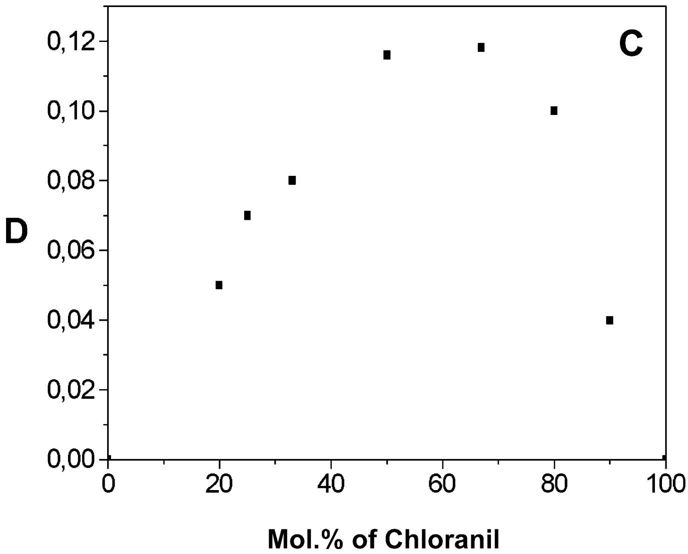

FIGURE 2 (Continued).

Wavelengths of maximal absorbance for the charge transfer bands and energies of electron transfer presented in Table 1 in good agreement with data obtained in [4]. However, our data on the complex formation constants and ΔG are somewhat different (probably, this discrepancy can be attributed to the use of different solvents). The donor-acceptor ratio 1:2 in system diphenyl + CA suggests that every molecule of diphenyl interacts with two CA molecules due to involvement of π-systems of both aromatic rings in the process. Evidently, it is caused by high conformational lability of the diphenyl ring system in comparison with stilbene (where lability

TABLE 1 Stoichiometry and Properties of the Charge Transfer Complexes Donor+ CA in CCl_4

Donor	k, l/mol	$-(\Delta G)$, kkal/mol	Donor-acceptor ratio	$\lambda_{\max}$ (CTC), nm	$h\nu$, eV	$\varepsilon_{\max} - \varepsilon_0$	μ_c, Debyes
Stilbene	17,3	7,7	1:1	512	2,37	0,50	2,1
Naphthalene	7,1	5,3	1:1	461	2,67	0,36	1,3
Diphenyl	19,6	11,8	1:2	440	2,81	0,44	1,5

of aromatic rings is limited by the double bond between them) and naphthalene (two conjugated aromatic rings).

In agreement with Mulliken's conception of complex formation [7,8], conditions for interaction of aromatic donors and acceptors is more favorable when the aromatic rings are parallel, oriented in the same way and their centers are located one above another. As the highest k and ΔG values were obtained for diphenyl + CA system, one may assume that this system satisfies these requirements better than two others.

Dielectric Studies

Analysis of absorption spectra has allowed us to determine the donor-acceptor ratio and interaction character of the CTC components in solutions. As a next step, plots of ε vs. T in the melt and in the solid phase at different concentrations of the components were measured. Dependences of ε vs. mol.% of CA in the melts are shown in Figure 3. Though dielectric measurements in melts are not possible at high CA concentrations due to limited CA solubility, the character of these plots in the concentration range 5–50 mol.% of CA allows us to expect the extrapolated maximal deviations from additive values at the same concentrations as the maximal intensity of the charge transfer band on the absorbance spectra in solutions.

The most interesting feature of the plots of Figure 3 is the presence of well-defined maximums observed at small CA concentrations (0.5–5 mol.%). It is important that CA concentrations corresponding to these maximums are substantially different from concentrations at which maximal intensity of the charge transfer absorption band is observed in solutions. It can be assumed that complexes or supramolecular structures of quite another type are formed at small CA concentrations where the charge transfer bands on the spectra are barely detectable or not observed at all.

The jumps of dielectric permittivity at the crystallization point are observed on $\varepsilon(T)$ plots both in non-activated naphthalene and diphenyl (Fig. 4, curve 1) and in naphthalene + CA and diphenyl + CA systems. Some features on $\varepsilon(T)$ plots, characteristic for polar molecular crystals, are observed with stilbene: peak of ε at crystallization appears with non-activated stilbene (curve 2); this peak becomes wider and higher when 0.6–1.5 mol.% of chloranil is added (curve 3) – a similar $\varepsilon(T)$ behavior is observed (curve 4) in weakly polar liquid crystals.[6,9] At large CA concentrations the shape of $\varepsilon(T)$ plots is similar to naphthalene and diphenyl.

For each donor, the difference $\Delta\varepsilon$ between the dielectric permittivity at the peak in Figure 3 and the value for the pure molecular crystal, as well as dipole moments μ_c of the CTC formed are presented in Table 1. The μ_c

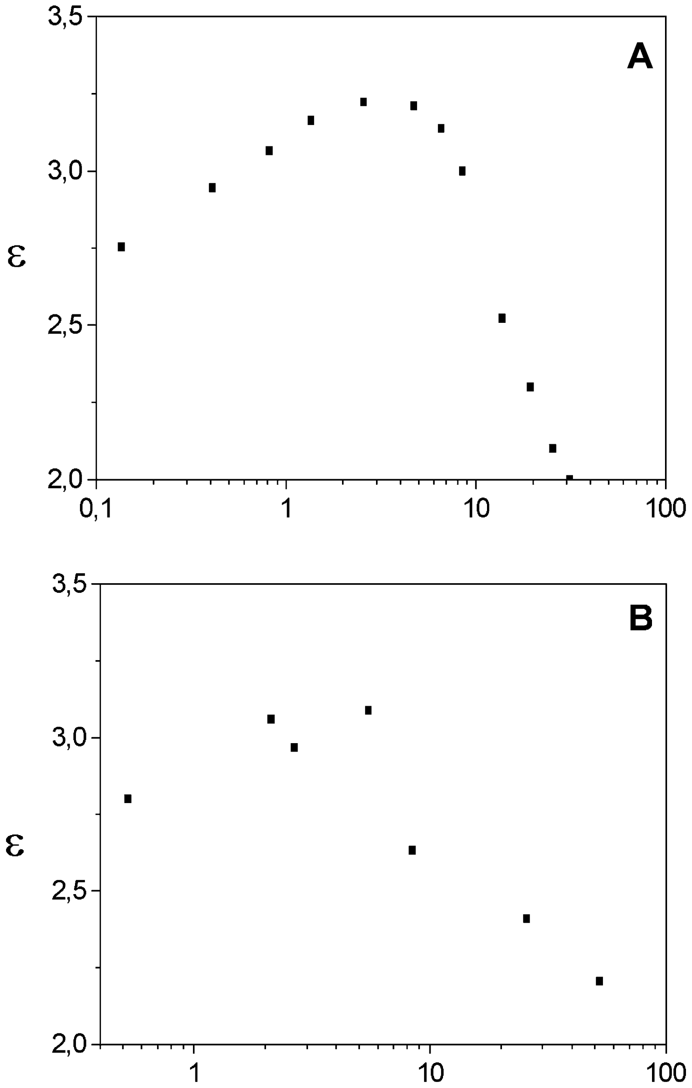

FIGURE 3 Dielectric permittivity vs. mol.% of chloranil in systems stilbene-CA (a), naphthalene-CA (b); biphenyl-CA (c) in melt at temperature just above crystallization point. The concentration range of the existence of a liquid crystal-like phase in system (a) is shaded.

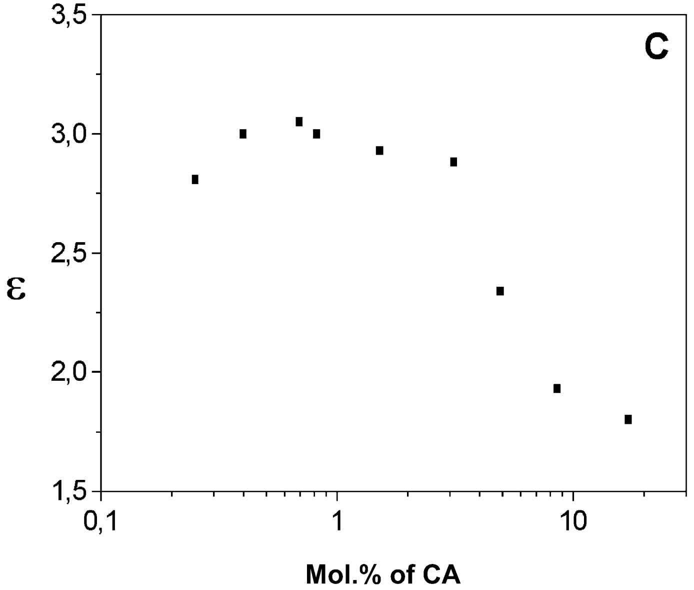

FIGURE 3 (Continued).

values were evaluated from the $\varepsilon(T)$ plots using the Langevin-Debye formula (2) in the form given in [10]:

$$\varepsilon - 1 = 4\pi N\left(\eta_0 + \frac{\mu^2}{3KT}\right), \tag{2}$$

where η_0 is the sum of electronic and ionic polarizability; μ – dipole moment; N – number of molecules per unit volume; K – Boltzmann constant; ε – dielectric permittivity; T – absolute temperature.

The results obtained in melts allow us to assume the existence of supramolecular structures, or clusters, consisting of 20–40 molecules. The CTC (which is the “nucleus” of the cluster) is formed due to a specific donor-acceptor interaction between CA molecule and one or two donor molecules. The charge redistribution in such “nucleus” leads to an increase in the dipole moment; thus, due to non-specific interactions (such as induction and dispersion interactions) an environment consisting of 20–40 donor molecules is formed around the “nucleus”. Such clusters become centers of crystalline phase formation during the crystallization from the melt, leading to improved crystal perfectness as compared with the non-activated crystal.

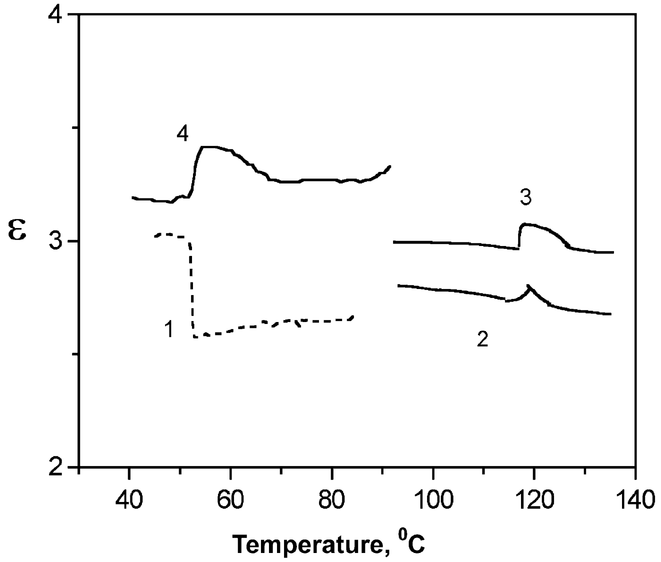

FIGURE 4 Temperature dependences of ε in the cooling mode: 1 – diphenyl, 2 – stilbene, 3 – stilbene + 1 mol.% of CA, 4 – cholesteryl nonanoate (data taken from [6]).

CONCLUSIONS

- The results obtained are an evidence of additional molecular ordering in the doped molecular crystal melts at CA concentrations 0.5– 5 mol.%.
- Dielectric permittivity behavior in the pre-crystallization region and at the crystallization point suggest the existence of liquid crystal-like ordering in the stilbene melt upon addition of 0.6–1.5 mol.% of CA. This result could probably bring a new insight into the assumed existence of liquid crystal-like ordering in the overcooled state of stilbene [11].
- Dielectric measurements are a useful tool in optimization of organic crystals growth technology, allowing one to account for the dipole moments and geometry of the complexes formed upon dopants addition and the resulting molecular ordering features.

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