On a Specific Intermolecular Interactions in Nematic Liquid Crystal Systems

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Abstract. The aim of this study was the investigation of the molecular structure of Nematic Liquid Crystal Systems that are based on polar liquid crystals, whose molecules have a large dipole moment directed along the long axis of the molecule. The investigation has a practical importance in the development of the new LC materials for electro-optical systems. In this work, the investigation of a specific intermolecular interaction – the formation of charge transfer complexing (CTC) in LC systems − was carried out by UV and IR spectroscopy. A long−wavelength shift of the CTC absorption band is found. The complicated dependence of optical density of the absorption band of the donor and CTC on the initial donor concentration has been obtained. The correlation between the optical density of the absorption bands of the CTC and donor, on the one hand, and the phase diagram, on the other, was demonstrated to occur in the investigated systems. The analytical expressions for equilibrium constants of complexation process were derived, and the concentrations of the complexes were determined based on the absolute rates reaction theory.

Electron donor–acceptor liquid crystals have been attracting considerable attention due to possible applications in optoelectronics and photonics. The creation of such charge transfer complexes is a powerful and flexible instrument for modifying the structures and properties compared to those of the initial components [1−3]. The aim of this study was the investigation of the molecular structure of nematic liquid crystal (NLC) systems that are based on polar liquid crystals, whose molecules have a large dipole moment directed along the long axis of the mole-cule (such as 4−n−buthyl−4′−n′−heptanoiloxyazoxybenzene {I}; n−cyanophenyl ester of n′−heptylbenzoic acid {II}; 4−heptyloxy−4′−cyanobiphenyl {III}; 4−methoxy−4′−n−butylazoxybenzene {IV}).
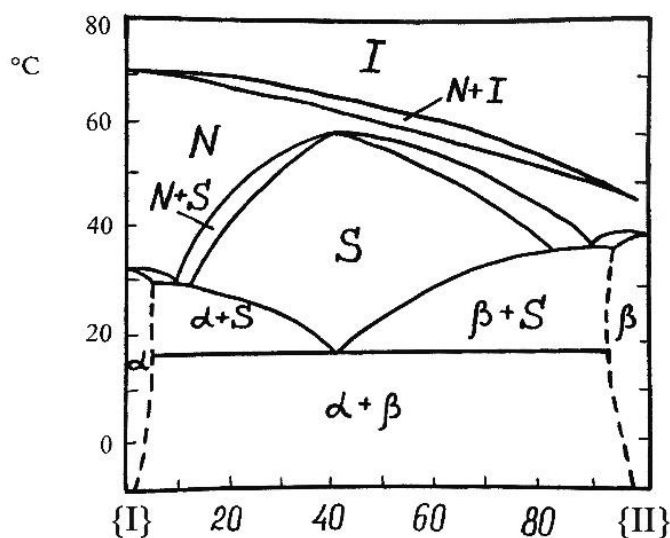

Fig. 1. Phase diagram {II}/{I}.

The investigation is both important in terms of understanding the anomalous behavior of elastic modules and other physical parameters, and has a practical importance in the development of the new LC materials for electro−optical systems.

In the present work the investigation of a specific intermolecular interaction – the formation of charge transfer complexing (CTC) in LC systems − was carried out by UV and IR spectroscopy on "Pye Unicam", "Uvidec−610" and "IR75" spectrometers. The UV spectra were recorded by using specially designed fused quartz cuvettes. The thickness of the investigated LC layer is 20□ μm. The temperature required for recording the spectra was kept constant with an accuracy of ±0,1°C. The UV spectra of individual compounds show that LC {I} has three absorption bands with maxima at wavelengths: 333 nm, 236 nm, 191 nm; and LC {II} has two bands with maxima at 248 and 198nm. The position of these maxima does not depend on temperature changes. When these compounds are mixed− in {I}/{II} LC system, a new absorption band have been found. The wavelength maxima of the new band varies in the range from 300 to390 nm, depending on the composition and temperature of the medium. In the LC systems under consideration, where the molecules of each of the components have several electron−donor groups, the emergence of a new band seems to be possible to explain by the formation of the CTC of various compositions. It can be seen that in LC {I} both the carboxyl and azoxy groups can act as a donor, while in LC {II} these can be the carboxyl and cyano groups.

The long−wavelength parts of the absorption spectra of binary {I}/{II} LC systems at different temperatures are shown in Fig. 2. The spectra are recorded relative to 100 % {II}.

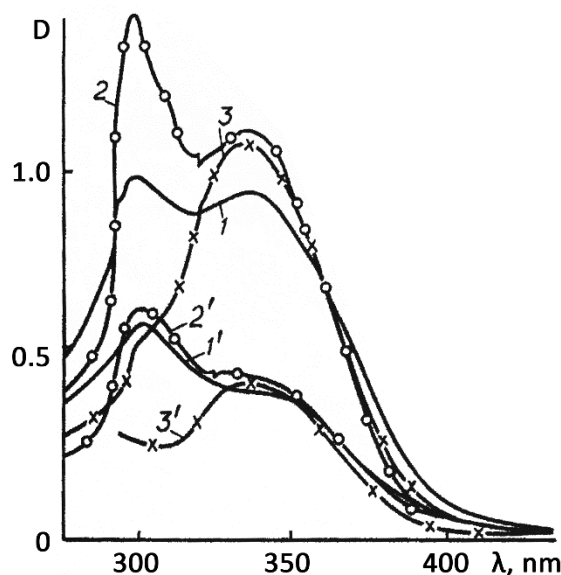**Fig. 2.** Long−wavelength absorption bands of UV spectra of the {II}/{I} systems:
(1mol% {II} / 99mol% {I} (1−3), 0,1mol% {I} / 99,9mol% {I I} (1′−3′))
at a temperature of 42°C (1, 1′), 55°C (2,2′) and 65°C (3, 3′).

Two absorption bands with maxima at 300 nm and 340 nm are observed. The intensities of these bands increases when the temperature rises from 40°C to 55°C. Moreover, the short−wavelength band intensity increases faster. Its line half−width is much less than the long−wavelength line half−width. Above 55°C the decreases of the intensity of short−wavelength band are observed. At the 65°C the short−wavelength band almost completely disappears. The given features of the spectra can be explained by the following reasons. According to Fig. 1, in the temperature range 44−56°C the matrix in which {I} is dissolved is in NLC state. In this phase, the dissolved compound acquires a long−range orientational order and the intermolecular interaction leads to a narrowing of the absorption band, as well as to an increase of its intensity [6]. As for the

band at $300\,nm$, it can be explained by the formation of CTC in an LC system. Apparently, in non−oriented matrix, λ_{max} of the CTC should be in a longer wavelength range. However, since the CTC is in an LC system, then, due to the orienting influence of this ordered matrix, λ_{max} is shifted to shorter wavelength. Indeed, at temperatures higher than 55°C, when LC system is in isotropic phase, λ_{max} is shifted to longer waves by $5-6\,nm$. Note that a further concentration increases of the {I} in {I}/{II} system leads to the decrease in ordering of LC system [4], to the broadening of the absorption bandwidth and to their merging. The results of a UV study of the alcohol solutions of {III}, {IV} and their mixtures confirm the assumption about the CTC formation. The spectra are shown in Fig. 3. Computer processing of the spectra shows that the CTC with an optical density of 0,02 is formed in this solution.
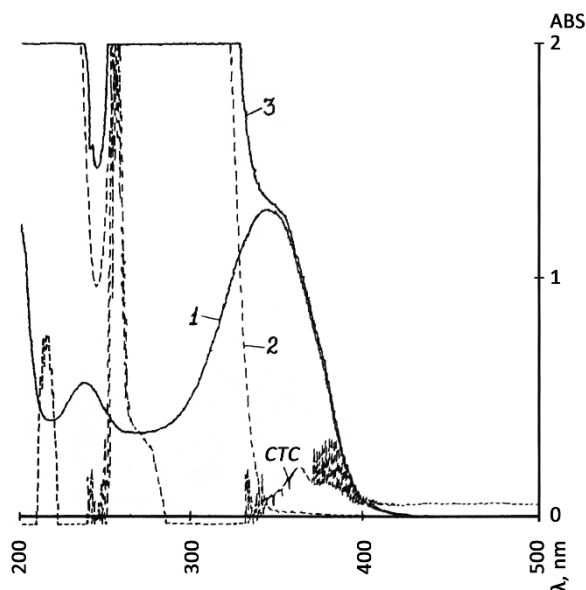

Fig. 3. Absorption band of CTC in alcohol solution {III + IV}, 1− alcohol solution of {IV}, 2− alcohol solution of {III}, 3−alcohol solution 0.0667 mol/l {III}/ 0.0083 mol/l{IV} at a temperature of 25°C.

Taking into account the conformational features of LC {I} and LC {II} molecules [4], as well as, the calculations [5] of the mutual orientation of molecules, it can be argued that the carboxyl group of {I} is most probable to act as a donor. Thus, in the considered LC system the formation of the CTC occurs by the partial delocalization of an electron from the carboxyl group of {I} to the benzene ring of {II}. This process of complexation is preceded by the process of disassociation of the molecules of a strong polar compound [4].

If in the {I}/{II} LC system the concentration of {I} is relatively low (< 5 mol%), the CTC of a simple composition (1:1) is formed. Then with an increase of {I} concentration in the LC system the CTC of a more complex composition are formed. Three absorption bands in long−wavelength range of the spectrum are observed in Fig. 4. ($\lambda_{1max} = 300\,nm$, $\lambda_{2max} = 336\,nm$, and λ_{3max} in the range $300-400nm$, depending on the composition and temperature of the LC system.

Actually, only one broad absorption band is visible in Fig. 4. However, two bands are clearly visible in LC system at {I} concentrations of 0,1 and 1 mol% (Fig. 2), the existence of three bands at high {I} concentrations in the system becomes obvious. With increasing the {I} concentration the bands broaden and overlap with each other. As for the third band at $\lambda_{1max} = 300\,nm$, its wavelength does not depend on the concentration and only weakly depends on the temperature. The intensity of this band increases with an increase in the {I} concentration in LC system. Using the expression [7] for the energy of charge−transfer band:

$$hv = I_D - E_A + C \qquad (1)$$

where I_D- is the ionization potential of the donor, E_A- is the acceptor electron affinity energy, $C-$ are other interactions, the short−wavelength band can be assumed to be absorption band for one of the complex types: DA_2, DA_3, D_2A, D_3A.
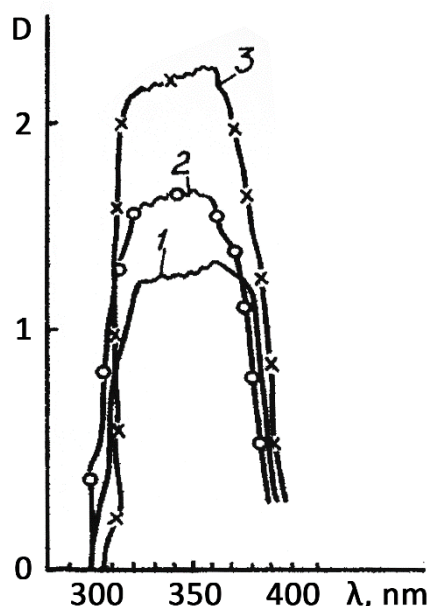

Fig. 4. Long-wavelength absorption bands of UV spectra of the {II}/{I} systems: (5mol% {I} / 95mol% {II} −1, 7mol% {I} / 93mol% {II} −2, 10mol% {I} / 90mol% { II} −3).

According to our semi empirical calculations [5] by atom−atom potential method two molecules in LC are arranged in such a way that the planes of the corresponding benzene rings become mutually parallel; for two molecules in pair the relative shift of the centers of the gravity of molecules along the long axis is 2−3 Å; with the exception of the oxygen atom of the carboxyl group of {I}, all the heteroatoms are in the planes of corresponding benzene rings and the dihedral angle between the planes of two benzene rings in each molecule is $15 − 20^0$. All this indicates that in the LC systems under consideration the formation of complex complexes is impossible without the external influences leading to the certain conformational changes. Such external influences can be the local fields and the other solvation effects. The process of solvation leading to the formation of D_2A type CTC can be represented as follows. The molecule of the {I} comes close to the molecule of {II} in such a way that the cloud of the lone pair electrons of the oxygen of carboxyl group is partially delocalized to the aromatic ring of the heptylbenzoic acid and, thus, a complex is formed in accordance with the Mullikan's theory of the CTC formation. It is obvious, that both the Coulomb and covalent parts of the donor−acceptor interaction lead to the increase of the reactivity of CTC for the formation of more complex CTC. In the case of such complexation, the dipole moments of the donor and acceptor are antiparallel. Coulomb forces increasingly repulse the negative charge from the heptylbenzoic acid to the cyano group. Due to the presence of the conjugation chain, the lone pairs of electrons of the azoxy group are involved in the process of transferring the electron cloud from the molecule of {I} to the molecule of {II} by means of the carboxylic oxygen of the {I} through the aromatic ring of benzoic acid. In the formation of the D_2A type CTC the conformational changes, caused by the reaction field or other solvation interactions, do not play a significant role. For the formation of the CTC the conformational changes should be such as to remove the steric hindrance for the direct connection of the $N = N$ donor group of {I} into a covalent bond with the acceptor {II}. I.e. either the angle between the two benzene rings of

{I} should increase, or the oxygen atom of the azoxy group should leave the plane of the benzene ring in which it is located. According to [8], the additional rotation of the benzene ring with the butyl group around the $C-N$ bond by 20^0, requires $\sim1,0\ kcal/mol$ energy, and for the $-\overset{N}{\underset{\underset{O}{|}}{}}-$ group the exit from the plane of another benzene ring by at least by 5^0 requires $\sim0,5\ kcal/mol$ energy. For the system under consideration the interaction energy of Onsager reaction field with surrounding medium is $\sim0,2\ kcal/mol$, i.e. it is insufficient for the above mentioned deformation of bond angles in the donor molecule. A possible mechanism of the formation the CTC of DA or D_2A type is schematically shown in Fig. 5.
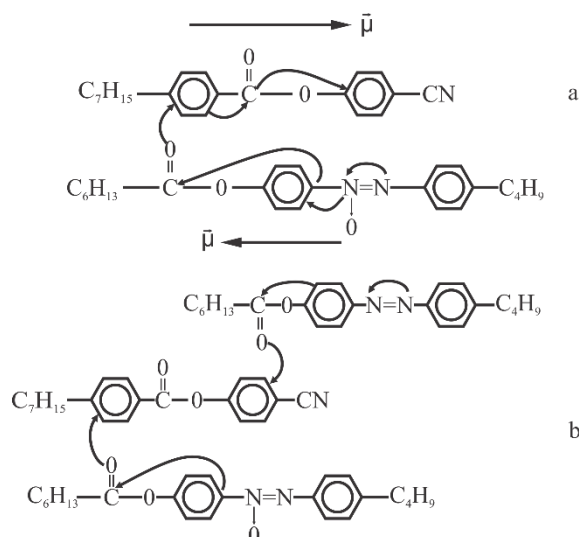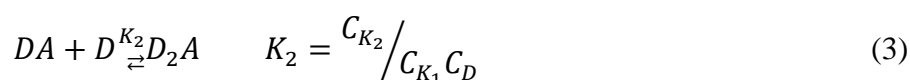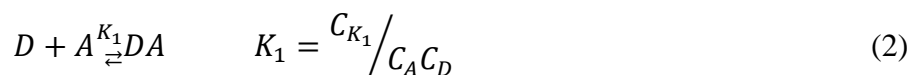

Fig. 5. Schematic representation of an electron transfer from a donor to an acceptor.

It is impossible to give preference to one of the possible options of "attachment" of the hydrogen atom of the carboxyl group of the donor to the phenyl or cyano group of the acceptor. However, it is obvious that for any of the options the molecular length of the CTC l_{CTC} is in the range: $l_0 < l_{CTC} < 2l_0$, where l_o is the length of the donor molecule. Hence it becomes obvious that a unit system of molecules builds the induced smectic A_d phase in LC systems. Based on the parameters of the spectra of the investigated particular LC systems, the number of the DA type CTC is observed to be greater than the number of D_2A type.

The concentrations of the complexes are determined based on the absolute rates reaction theory and the analytical expressions for equilibrium constants of complexation process are derived. Thus in binary {I}/{II} LC system complexation occurs according to the scheme:

$$D + A \overset{K_1}{\rightleftarrows} DA \qquad K_1 = {C_{K_1}}\big/{C_A C_D} \tag{2}$$

$$DA + D \overset{K_2}{\rightleftarrows} D_2A \qquad K_2 = {C_{K_2}}\big/{C_{K_1} C_D} \tag{3}$$

where A - is acceptor; D - is donor {II}; K_1, K_2 - are corresponding equilibrium constants; C_{K_1}- is the equilibrium concentration of DA type CTC; C_{K_2} - is the equilibrium concentration of D_2A type CTC.

Let us consider the process of the CTC formation as a chemical reaction. Then, in presence of the statistical equilibrium in reacting systems, the number of activated complexes $[D^\#]$ per unit of volume will be equal to:

$$[D^{\#}] = [A][D]\frac{kT}{h\nu}\frac{Q_{D^{\#}}}{Q_A Q_D}exp\left(-\frac{E_0}{kT}\right) \qquad (4)$$

where $D^{\#}$ - is the number of activated complexes in per unit of volume; $Q_A, Q_D, Q_{D^{\#}}$ - are the statistical sums, referred to a per unit of volume of acceptor, donor and activated complex; $[A], [D]$ - are the concentrations of reagents; E_0 - is the difference between the energies of zero levels of the activated complex and the initial reagents. The combination $\frac{Q_{D^{\#}}}{Q_A Q_D}exp\left(-\frac{E_0}{kT}\right)$ in (4) is numerically equal to the constant of chemical equilibrium between the starting reagents and the activated complex $K_{D^{\#}}$. According to [7] for $K_{D^{\#}}$ we have:

$$K_{D^{\#}} = e^{-\Delta G^{\#}/RT} \qquad (5)$$
$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#} \qquad (6)$$
$$K = \varkappa\frac{KT}{h}e^{\frac{-\Delta H^{\#}}{RT}+\frac{\Delta S^{\#}}{R}} \qquad (7)$$

where $\Delta G^{\#}$ - free energy activation; $\Delta H^{\#}$ - activation enthalpy; $\Delta S^{\#}$ - activation entropy; $\varkappa$ - transmission ratio; K - reaction constant. Assuming that $K_1 = K_{D^{\#}}$, for K_1 we will have:

$$K_1 = \frac{C_{K_1}}{(C_{A_0}-C_{K_1})(C_{D_0}-C_{K_1})} \qquad (8)$$

$$C_{K_1} = \frac{C_{A_0}+C_{D_0}+\frac{1}{K_{D^{\#}}}\pm\sqrt{\left(C_{A_0}+C_{D_0}+\frac{1}{K_{D^{\#}}}\right)^2-4C_{A_0}C_{D_0}}}{2} \qquad (9)$$

where C_{D_0} and C_{A_0} are the initial concentrations of donor and acceptor.

When the concentration of the {I} is up to 5 $mol\%$ the only DA type complexes are formed in {I}/{II}LC system. The equilibrium concentrations of the acceptor C_A and donor C_D can be found from the relations [7]:

$$C_{A_0} = C_A + C_{K_1} \qquad (10)$$
$$C_{D_0} = C_D + C_{K_1} \qquad (11)$$

Required for calculations value of $\Delta H^{\#}$ was determined through the activation energy E_a. The activation energy of rotational for {I}/{II} LC systems of various compositions was determined from the EPR spectra described in [4]. These measurements showed that E_a depending on donor concentration in LC system varies from 10 to 4 $kcal/mol$. $\Delta S^{\#}$ determined according to the [7,12] while taking into account the complex structure of molecules, the linear dependence of $\Delta S^{\#}$ on $\Delta H^{\#}$, the composition of the LC system. $\Delta S^{\#}$ is chosen equal $15-20$ $cal/mol \cdot K$. The calculation for some LC systems according to the given equations are summarized in Table 1.

Table 1. K_1 equilibrium constants and C_{K_1} equilibrium concentrations of DA−type CTC in {II}/{I}LC systems.

^{o}K	C_{A_0},mol/l	C_{D_0}, mol/l	E_a kkal/mol	S, kal/mol°C	K_1	C_{K_1}, mol/l
318	3,00	0,09	8,8	18	0,022	0,01
318	2,92	0,15	8,6	20	0,08	0,03
318	2,84	0,20	8,2	20	0,15	0,06
318	2,74	0,30	7,8	20	0,29	0,13
328	3,0	0,09	8,8	18	0,03	0,01
328	2,92	0,15	8,6	20	0,12	0,04
328	2,84	0,20	8,2	20	0,23	0,09

328	2,74	0,30	7,8	20	0,42	0,16

For the LC samples with a high donor concentration $- C_{D_0} \geq 15 \; mol\%$, the processing of UV spectra can be carried out in accordance with scheme (2) and (3). In this case, when the DA D_2A type CTC are formed in LC system, the equilibrium constant is determined from material balance equations [7] and relations (2), (3), (8), (9):

$$C_{K_1} = K_1 C_A C_D \tag{12}$$
$$C_{K_2} = K_1 K_2 C_A C_D^2 \tag{13}$$
$$C_{A_0} = C_A + C_{K_1} + C_{K_2} \tag{14}$$
$$C_{D_0} = C_D + C_{K_1} + C_{K_2} \tag{15}$$

We used the extrapolation method [9] in order to determine the concentration and the extinction coefficient of the D_2A type CTC at the high donor's concentrations.

The dependence of the optical density of the absorption band of the donor and CTC on the donor concentration at a constant temperature are shown in Fig. 6 and 7.
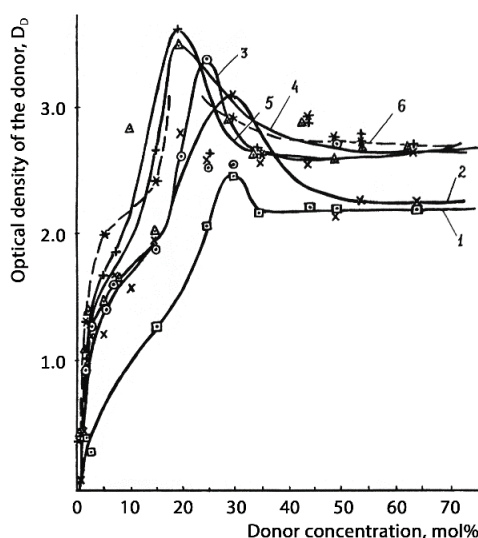

Fig. 6. The dependence of the optical density of the absorption band (λ=336nm) of the donor on its concentration in the {I}/{II} system at a temperatures of 35°C −1, 40°C −2, 45°C −3, 50°C −4, 60°C −5, 55°C −6.
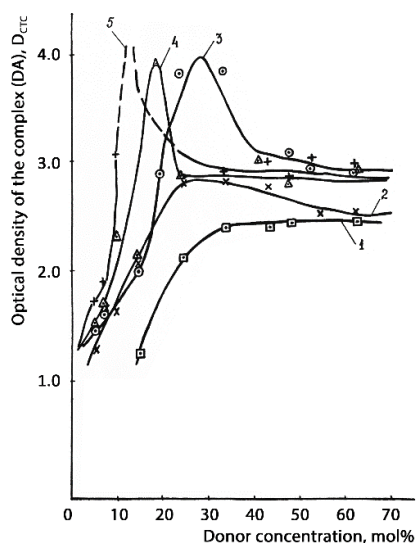
Fig. 7. The dependence of the optical density of the absorption band of the DA complex on the donor concentration in the {I}/{II} system at a temperatures of 35°C −1, 40°C −2, 45°C −3, 50°C −4, 60°C −5.

The optical density of both the donor band and the CTC does not depend on the C_{D_0} in the concentration range $35\ mol\% \le C_{D_0} \le 65\ mol\%$. On the other hand, the intensity of the band at $\lambda_{1max} = 300\ nm$ increases with increase of the C_{D_0}. This means that starting from the C_{D_0} of $35\ mol\%$ all newly formed DA type CTC turn into D_2A type. In the mentioned concentration range at temperature of $35-55°C$ the LC system is in smectic phase (Fig. 1). The presented results indicate a correlation between the optical densities of the absorption band of the CTC and the donor on the one hand and the phase diagram on the other. The increase of the optical density of the D_2A type CTC is observed in the temperature and the concentration range of the smectic phase existence. The complexation promotes the formation of the smectic phase. Another feature of the UV spectra: with the increase of the donor concentration the λ_{max} of the absorption band of the DA type CTC is shifted to longer wavelength by $90\ nm$. Such a shift in molecular crystals is explained by the static interaction [10]. The described shift of the absorption band in the investigated LC system seems to be possible to explain as follows: increase in the concentration of the donor leads to the deterioration of the LC system ordering [11] and the static shift becomes insignificant. On the other hand, the disassociating effect of the donor [11] leads to the change in the energy of intermolecular interaction between the donor and the acceptor. In addition, the increase of the polarity of the LC system due to disassociation leads to the increase of the electronegativity of the acceptor. Then, according to the equation (1), the energy of charge−transfer band decreases, which is observed in UV spectra.

IR study was carried out to clarify the structure of CTC. The changes observed in the vibrational spectra of CTC in comparison with the spectra of the initial components can be attributed to the following four types: 1−changes in the vibration frequencies in the donor and acceptor molecules, caused by the change in the nature of bonds in these molecules during complexation; 2− the appearance of the previously forbidden (by the selection rules) vibrations as a result of the change in the symmetry of molecules; 3− change in the intensity of some absorption bands of the initial molecules; 4− the occurrence of the new intermolecular vibrations, i.e. vibrational motions of atoms and groups of atoms relative to the donor−acceptor bond. A shift in the frequency of the absorption band of groups: $C=O$; C_6H_4 and a change in the intensity of these bands are observed. Only one new absorption band is observed in the spectra of the studied systems at a frequency of $\nu = 1125 sm^{-1}$.

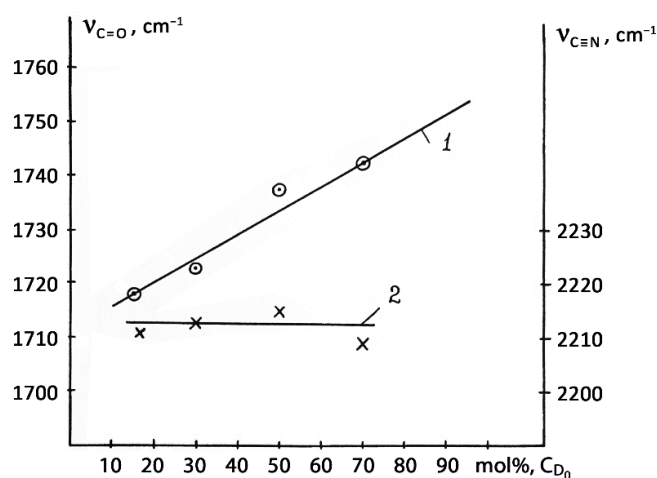**Fig. 8.** The dependence of the frequencies of the absorption bands of the C=O and C≡N groups in the {I}/{II} system on the donor concentration at a temperature of 50°C: 1− C=O group, 2− C≡N group.

An increase of the vibrational frequency can be caused only by the kinematic effect of the interactions of the stretching vibrations of the donor and vibrations of DA bonds (of the same types of symmetry). Similar effects in the investigated systems can be due to their phase state. In fact, it should be assumed that the increase in the frequency of the $C = O$ group is due to the increase of force constants of the $C = O$ bond during the formation of CTC.

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