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**SPECTROSCOPY OF A NON-LUMINESCENT ASSOCIATE
OF INDIGO CARMINE IN SOLUTIONS**

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Abstract:

Introduction. *The food dye Indigo Carmine (E-132) was subjected to spectroscopic studies. It is shown that conditions for their participation in Association processes are created in aqueous and binary mixtures of solvents. The absorption bands against the background of the hypochromic effect in their electronic spectra are determined. Experimentally and by quantum chemical calculations, it is established that the dipole moments of the Indigo Carmine dye in the excited state increase up to 40 % and they contribute to the appearance of a strong dipole-dipole interaction, which results in the unification of Monomeric molecules into an associate. The interaction force (van der Waals) leads to resonant splitting of electronic States and changes in the probability of electron transition from the main excited levels of dye molecules.*

Research methods. *The choice of binary mixtures of solvents was due to the fact that in one of the components of the solvents the dyes under study dissolved well, in the other they practically did not dissolve. Electronic absorption spectra were recorded on a Specord 50 SA spectrophotometer (Analytikjena Germany), the optical density was measured with an accuracy of 0.3% and high resolution in the range of 190-1100nm. Microscopic studies were carried out on a biological microscope KSO 5001-1 "Anjeon precision optics Co, Htd" (South Korea) and on an electron microscope (SEM) TESCAN Mira3 (Russia). The fluorescence spectra were measured using a setup based on two MDR-76 monochromators with photoelectronic recording.*

Quantum-chemical calculation of the electronic structure and distribution of charges on the atoms of Indigo Carmine molecules was carried out using the MOPAC 2009 software package by the AM1 semiempirical method with a standard set of parameters

Results and discussions. *It has been shown experimentally that an increase in the concentration of the dye in solutions with a constant ratio of binary mixtures water + dioxane is accompanied by a drop in their integral absorption capacity. The long-standing increase in the concentration of the investigated compound leads to an increase in the process of falling of the electronic spectra of the solution, with a hypochromic effect observed, similar to that of an aqueous solution of a dye. Based*

on calculations, it was shown that for Indigo Carmine, the angle $88,96^{\circ}$ i.e. close to 90° . The diagram of the arrangement of molecules in associates of the dye Indigo Carmine can be attached as parallel vectors.

Conclusion. It is shown that an increase in the concentration of food dye in aqueous and binary mixtures of a solvent creates conditions for the association of Indigo Carmine identifying hidden bands of associated molecules. It is proved that the observed hypochromic effect during the association of Indigo Carmine molecules is due to resonant splitting of excited electronic levels under the action of the field forces of closely spaced food dye molecules. It was found that the ratio of the energy of the dipole-dipole interaction in the associate, " ΔE ", to the width of the Frank-Kondo electronic transition " $\Delta \varepsilon$ " has the ratio $\Delta E / \Delta \varepsilon > 1$.

Keywords: food dye, associate, aqueous solution dipole-dipole interaction, H-bond, van der Waals force, splitting of electronic States from the excited level.

Introduction. Indigo Carmine, the synthetic food dye (E-132), is widely used in the food industry as a coloring pigment and in pharmaceuticals for the production of capsules of various preparations. The absorbance of the dye is in the wavelength range $\lambda=400-700\text{nm}$ with the maximum adsorption capacity $\lambda=625\text{nm}$ [1]. Unlike other dyes, Indigo Carmine has three leucoforms. These leucoforms were obtained using the superoxide technique, which was accomplished by electron transfer. In this case, the radical is formed due to the autooxidation of two superoxide dye molecules [1]. The resulting form of Indigo Carmine was used to identify urological diseases [2].

In contrast to a neutral dye molecule, it has a luminescent ability. The optimum value of the wavelength for the excitation of the luminescence of the dye leucoform has been determined. The corresponding excitation length was $\lambda_e = 270\text{nm}$. In this case, the maximum of the luminescence spectrum falls on the $\lambda_{MAX}^f = 410\text{nm}$. It was used by the method of luminescence analysis for the quantitative determination of the dye in the drugs used [3,4]. Considering that Indigo Carmine is a synthetic dye, the use of its highly concentrated form can lead to undesirable effects in the food and pharmaceutical industries. An example is the fact that effective adsorbents are used to reduce the amount of dye in industrial wastewater. Such adsorbents may include searches of mustard or fat-free mustard gas [5].

Indigo Carmine can also be used for everyday life in expensive spheres of technology. One of such applications is due to the fact that, for the oxidation of hydrazine, an electrode made of carbon paste with nanoparticles of titanium oxide (Ti_2O) is used. In these cases, the volt-ampere characteristic of the modified current of the weeding systems turned out to be linearly dependent on the concentration of the hydrazine moiety, which was detected using an Indigo Carmine dye. In this case, the efficiency of the electrode is enhanced by the content of hydrazine [6]. Indigo Carmine dye is also used to evaluate the effectiveness of chemotherapy in clinical treatments. The effectiveness of the use of Indigo Carmine dye increases in the case of used leucoforms [7-9].

For the synthetic dye Indigo Carmine used in food technology and cosmetics in the form of concentrated solutions can be accompanied by the association of their molecules both in solutions and in capsules [10].

Determination of the spectral-optical characteristics of a dye in an associated state is one of the urgent problems of modern molecular spectroscopy. These studies will allow the development of a method for the effective use of the dye in various fields of technology.

The purpose of the study is to determine the conditions under which the dye E-132 is in an associated state. To determine the parameters of the associates and to establish the forces of interaction and the electronic nature of the associated molecules of Indigo Carmine in solutions.

Methods of the experiment. The object of the study was indigo carmine (E132), ChDA grade. As a solvent, bidistilled water, ethanol, dioxane, and acetone dimethyl sulfoxide (DMSO) purified were used according to a known method [11]. The choice of binary mixtures of solvents was due to the fact that in one of the components of the solvents the dyes under study dissolved well, in the other they practically did not dissolve. Electronic absorption spectra were recorded on a Specord 50 SA spectrophotometer (Analytikjena Germany), the optical density was measured with an accuracy of 0.3 % and high resolution in the range of 190-1100nm. Microscopic studies were carried out on a biological microscope KSO 5001-1 "Anjeon precision optics Co, Htd" (South Korea) and on an electron microscope (SEM) TESCAN Mira3 (Russia). The fluorescence spectra were measured using a setup based on two MDR-76 monochromators with photoelectronic recording.

Quantum-chemical calculation of the electronic structure and distribution of charges on the atoms of Indigo Carmine molecules was carried out using the MOPAC 2009 software package by the AM1 semiempirical method with a standard set of parameters [12, 13].

Binary mixtures of solvents were prepared in such a way that the concentration of the test compound remained constant and the ratio of the binary mixture of solvents changed. In the second case, the composition of the binary mixture of the solvent remained constant, the concentration of the dye changed. The positions of the absorption bands of self-aggregates were determined as Lorentz components as the total bands of monomers and dye associates.

The frequency of a purely electronic transition (ν_{00}) was determined based on the rule of V.L. Levshin using the mirror symmetry of the extraction absorption spectra [11]. Another method for determining (ν_{00}) is based on B.I. Stepanov's universal relation between the absorption and luminescence spectra

$$\frac{I_{\nu}}{\nu^3 \epsilon_{\nu}} = C e^{h(\nu_{00} - \nu)/KT}$$

where I_{ν}, ϵ_{ν} - is the emission power in relative units and the extinction coefficient, respectively, h, K - are the Planck and Boltzmann constants, respectively.

Results and discussions. 1. Spectroscopic studies of self-aggregation. The performed spectroscopic study showed that the absorption spectra of the dye in shape and intensity in a wide concentration range of 10^{-5} – 10^{-8} M remain unchanged and they refer to molecules in the monomeric state (Fig. 1a curve 1.1¹ and Fig. 1b curve 1). An increase in the concentration of the studied compounds in aqueous solutions from $5 \cdot 10^{-5}$ to $5 \cdot 10^{-3}$ M leads to a significant deformation of the electronic spectra (Fig. 1 a, b). As can be seen in Fig. 1a, an increase in the concentration of the dye in the introductory solutions leads to a decrease in the integral absorption capacity (hypochromic effect). In this case, both bathochromic and hypochromic broadening of the absorption spectrum of the aqueous solution of the dye are observed. The observed deformations of the spectra can be explained by the following considerations. In the case when the dye (Indigo Carmine) is in a soluble medium, each dye molecule (E-132) is solvated by the solvent molecules. In such solutions, the molecule of the test compound will be in a monomer state. For multidimensional molecules, intermolecular interactions (MMI) are excluded. When the concentration of the dye increases in the solvent shell of the solvent, a volume with a high concentration of the dye is formed [14]. As a result of the Brownian motion of these multidimensional molecules, some of them leave the solvation shell. In this case, conditions are created for the appearance of an interaction MMI between the molecules released from the solvent shell of the solvent. The MMI molecule promotes the onset of the dye association process. The process of molecular association is accompanied by the formation of dimeric and more complex dye associates [15].

The process of molecular association leads to a decrease in the number of monomeric molecules. As a result, the absorption intensities of monomers decrease, resulting in a hypochromic effect in the adsorption spectra. This reasoning is confirmed by the temperature studies carried out. The result of temperature studies shows that heating the solution where the hypochromic effect occurs, an increase in the absorption capacity of the solution is observed. It was found that when heating a solution with associative molecules, the effect of heating to a temperature of 65-80⁰C (depending on the nature of the solvents used), the absorption spectra of the solution will be identical to the absorption capacity of the diluted solution related to multidimensional dye molecules. Using the results of temperature studies, the binding energies of the associates are determined [15]. According to this method, the binding energy of associates is determined by the equation:

$$\Delta H = \frac{RT_1T_2}{T_2 - T_1} \ln \frac{D_1(D_2 - D_0)}{D_0(D_1 - D_2)}$$

where R- is the gas constant, D_0 - is the optical density of a diluted solution in which the molecules are in the monomeric state, D_1 and D_2 - are the optical densities at T_1 and T_2 respectively. Calculations show that the binding energy values correspond to 16-20 kJ / mol.

For a detailed study of the process of association, provided excrement in a binary mixture of solvents water + dioxane (Fig. 1b).

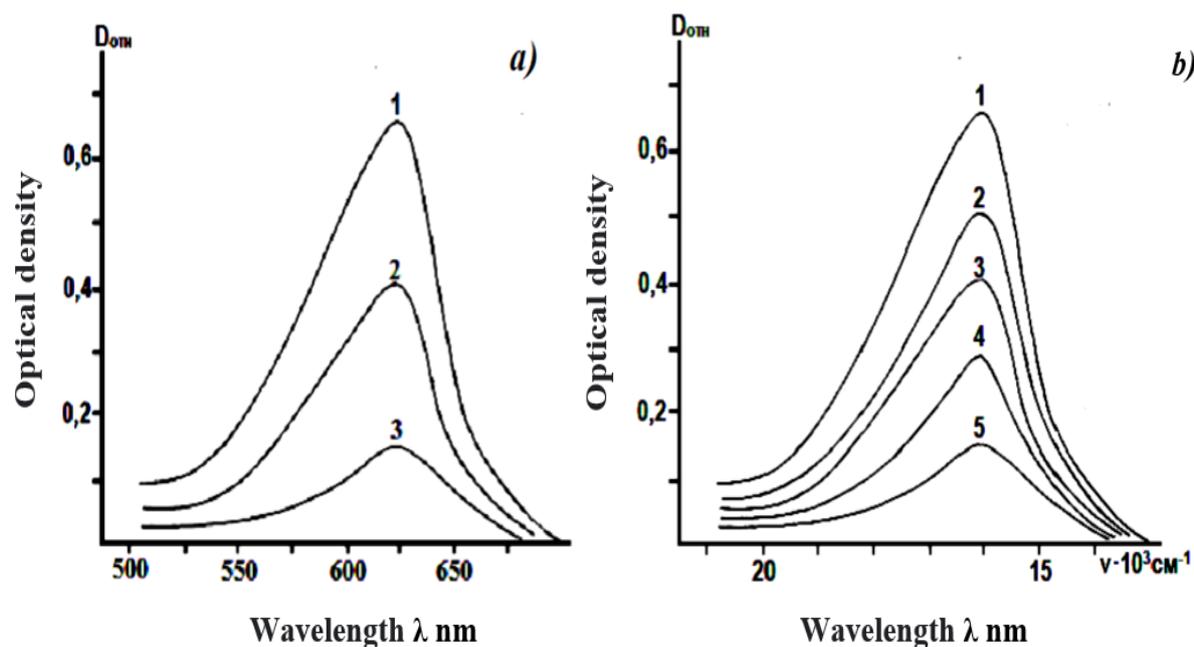
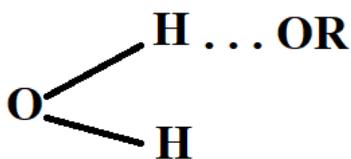


Fig. 1. The concentration dependence of the absorption spectra of Indigo Carmine in water $C=10^{-6}$ M (curve 1) 10^{-5} (1), 10^{-4} (2), 10^{-3} (3) M (a) and in a binary mixture water-dioxane (0,4:0,6) 10^{-5} (1), $5 \cdot 10^{-5}$ (2), 10^{-4} (3), $5 \cdot 10^{-4}$ (4), 10^{-3} (5) M (b)

As can be seen from Fig. 1b, while maintaining a constant composition of the volumes of the binary mixture of solvents water + dioxane (0,4+0,6) at a solution concentration of $C=10^{-5}$ M, the absorption spectrum in shape and absorption maximum coincide with the absorption spectrum of monomeric Indigo Carmine molecules (compare curve 1 Fig. 1a and b). It has been shown experimentally that an increase in the concentration of the dye in solutions with a constant ratio of binary mixtures water + dioxane is accompanied by a drop in their integral absorption capacity. The long-standing increase in the concentration of the investigated compound leads to an increase in the process of falling of the electronic spectra of the solution, with a hypochromic effect observed, similar to that of an aqueous solution of a dye.

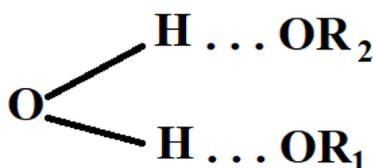
Spectroscopy of Indigo Carmine Associates. The process of association of Indigo Carmine molecules was studied in solutions of a binary mixture of water + dioxane at a constant concentration of $C=10^{-5}$ M. The result of these experimental studies shows that, in the composition of binary mixtures, an increase in the insoluble component (dioxane) leads to deformation of the electronic absorption spectra with a hypochromic effect. The addition of the insoluble dioxane component to the dye solution leads to a decrease in the solvate energy due to the formation of a hydrogen bond between the hydrogen of water and the oxygen of the added components (dioxane). An increase in the proportion of an insoluble component leads to an intensification of the interaction process between the components of the solvents. In this case, the energy of the solvate weakens to such a level that the molecules of the solute are displaced from it, while there is an opportunity for direct interaction between the molecules of the solute. The expected decrease in the O-H stretching

vibration of water with the possible formation of a hydrogen bond is carried out with a dioxane molecule or two H-bonds.



The binding energies of the associates were also determined in the case of using a binary solution dioxane + water. To elucidate the nature of energy in binary mixtures, the association process was studied for molecules of arythylenes (AE) and arylpolythylenes (AP), which were model compounds for food dyes (PC). The research results showed that for solutions of AE and AP in binary mixtures to solvents (water + dioxane), a decrease in the absorption and luminescence capacity with a hypochromic effect is also observed. Heating ethylene solutions with a hypochromic effect is carried out by restoring the absorption capacity of monomeric molecules. An increase in the heating temperature of the solution to 75⁰C leads to a complete restoration of the absorption capacity of diluted solutions of the test compound. From the temperature dependence of the spectrum absorbed, the binding energy of the associimets was determined. The obtained values of the binding energy corresponded to 16-20 kJ / mol. However, in the structure of many molecules of AE, AP and food dyes, there are no groups that could form H-bonds are formed between the given pretexts that are binary mixtures of solvents with the components.

According to Chulanovsky's theory, natural water is interconnected by hydrogen bonds in the form of a kind of grid. In this case, the hydrogen of one molecule forms bonds with the oxygen of another molecule. These connections will appear in the form of a non-melting chain both horizontally and vertically [11].



The hydrogen chain and form a solvation shell around the monomeric molecules of the compounds under study. An increase in the temperature of the solution will lead to the rupture of the hydrogen bond chain and the monomeric molecules, as a result of their chaotic movement, will be in a non-solvate. In this case, the conditions for their unification by the forces of Van der Waals arise. Van der Waals forces can exist in the form of three components of forces. They can be dispersive, inductive and dipole-dipole interactions. Dispersive forces arise when the value of the premature index of the solvents used is different. For systems of the same solvent, they will remain unchanged. Inductive forces are manifested as a result of the creation of a condition by the appearance of an inductive charge. Dipole-dipole interaction form when polar molecules approach each other. Taking into account the above, for AE and AP molecules, the dipole moments of diamine-mixed and dinitro-mixed arythylyene derivatives were calculated theoretically. As a result of quantum chemical calculations, it was shown that for molecules of arythylyenes and arylpolythylenes, the values of dipole moments are in the range of 2.0÷6.0 Db. In an

excited state, these values increase by 40 %. [monograph Lambert]. On the basis of these considerations, it was established that the associations of food dyes are combined by dipole-dipole interactions of van der Waals forces.

Thus, we can conclude that the bond energy 20-22 kJ / mol refers to the hydrogen bond of solvent systems. Associates AE, AP, and PC are united by the dipole-dipole MMI of van der Waals forces.

In order to clarify the nature of the hypochromic effect in the processes of molecular association, first of all, the absorption spectra of monomers (curve 1) with bands of associates of dye molecules (curve 5 in Fig. 1) obtained in binary mixtures with a higher concentration of the dye (Fig. 1b) were normalized.

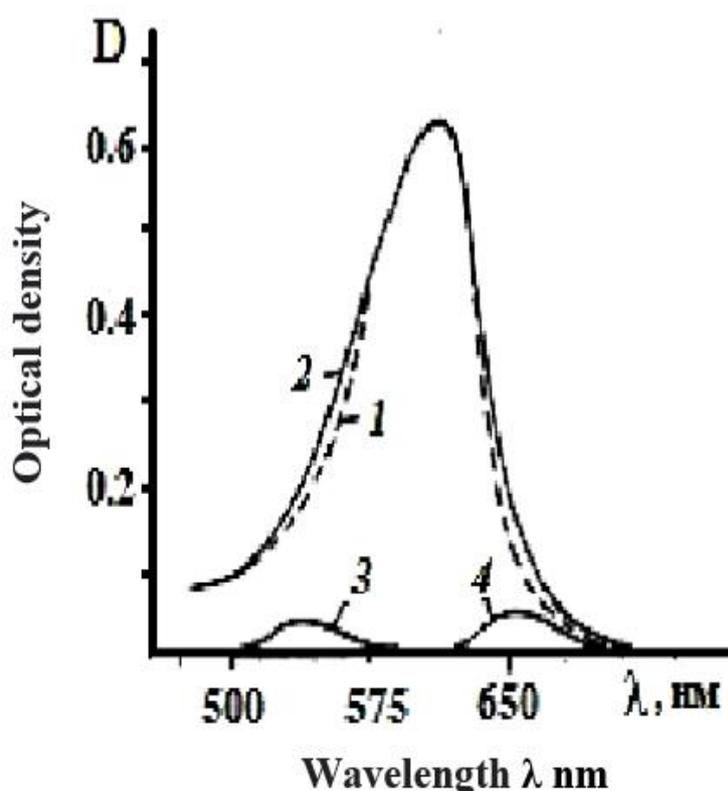


Fig. 2. Absorption spectra of monomers (1), associates (2) and algebraic difference (3,4), Indigo Carmine molecules, as well as a diagram of electronic transitions of its monomers and associates

In the process of normalization of the spectra, 3 it was taken into account that long-wavelength and short-wavelength broadening of the spectrum with respect to the band of monomeric dye molecules are observed for the Indigo Carmine associates. However, in these cases, the apparent bands of associates turned out to be hidden.

The results of the comparison of the normalized spectra are shown in Fig. 3. As can be seen from Fig. 2. To the algebraic sum of the bands of monomers and associates appear in curves 3,4 (Fig. 2). Curve 3,4 are the Larintsev's components of the total bands 1 and 2 (Fig. 2). The 3,4 bands are hidden, broken components that form in trace exciton interactions. Excitonic interactions occur between two closely spaced Indigo Carmine molecules that combine to form an associate. These Bands of Associates are hidden split components resulting from excitonic interaction, and they

arise in the process of dye association. These experimental results prove that the process of association of Indigo Carmine is completely obeyed by the exciton theory of A.S. Davidov. It was found that the hidden bands of Indigo Carmine associates correspond to maxima with frequencies of $\nu_1^a = 18100\text{cm}^{-1}$ and $\nu_2^a = 14750\text{cm}^{-1}$. The half-widths of these bands are practically equal to each other $\sigma_1^a = \sigma_2^a = \sigma_3^a = 1000\text{cm}^{-1}$.

In order to determine the electronic nature of the process of association of the Indigo Carmine dye, we determined the frequencies of the 0-0 purely electronic transition for monomeric and associated molecules of Indigo Carmine. The frequency of purely electronic transitions was determined according to the method [11]. For this purpose, the imaginary luminescence spectra are calculated using the universal relation of B.I. Stepanov. Calculations show that for monomeric molecules of the E-132 dye, the ν_{00} values correspond to $\nu_{00}^m = 14100\text{cm}^{-1}$ $\nu_{00}^a = 13200\text{cm}^{-1}$, the most probable absorption frequencies for monomers correspond to $\nu_m^a = 15800\text{cm}^{-1}$ and in associate $\nu_1^a = 18500\text{cm}^{-1}$ и $\nu_2^a = 14750\text{cm}^{-1}$. respectively.

Using the values of the frequencies of a purely electronic transition and the most probable frequencies in the absorption of monomers and associates of the Indigo Carmine dye, a diagram of electronic transitions from the ground and excited electronic levels of Indigo Carmine dye molecules was constructed (Fig. 3).

As can be seen from Fig. 3. for associates of the dye E-132, in comparison with monomeric molecules, resonant splitting of electronic levels occurs. In the diagram, the line thicknesses correspond to the intensity ratios for the electron transitions of monomers and associated molecules. According to the theory of A.S. Davidov, in the case of the formation of complex associations, the value of the value of the splitting energy in relation to dimeric molecules \sim two cut will be larger. Data items (see Figure 3). In the case of the formation of folded associates according to the theory of A.S. David, the splitting energies in relation to dimeric molecules will be 2 times higher, which is confirmed by (see Fig. 3) \sim 2 times. Thus, electronic transitions to absorption for monomers correspond to 15800 cm^{-1} for dimeric molecules 14700 . For complex associates of Indigo Carmine 18100 cm^{-1} .

All these results show that in the process of the association of closely spaced monomeric molecules, resonant splitting of excited electronic levels occurs with the observation of the Davidov doublet, which is a manifestation of hidden banding (Fig. 3). For a dimeric unit cell in a molecular crystal with dipole-dipole interaction between monomer molecules, the following relationship is fulfilled:

$$\Delta E_D = \Delta E_M + \Delta D + V_{12}$$

where ΔE_D and ΔE_M - the energy of the electronic transition in the dimer and monomer, respectively; ΔD - is the difference between the interaction energy of the excited and normal monomer molecules with another monomeric molecule in the dimeric unit cell of the associated dye.

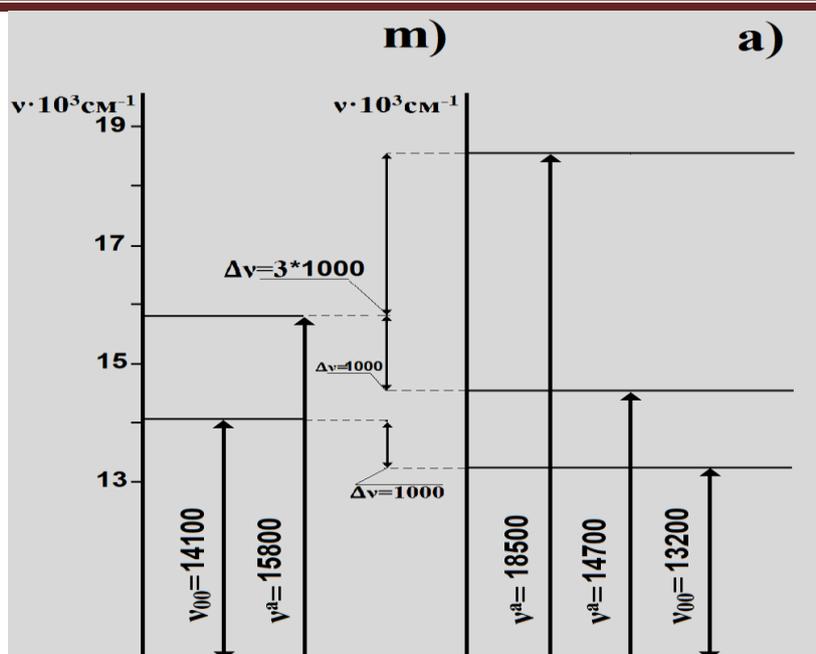


Fig. 3. Scheme of the main and excitation levels of monomers (M) and asbestos cements (a) Indigo Carmine molecules

The energy of exciton interaction between monomer molecules in the dimeric unit cell of the Indigo Carmine associate (Figs. 3a, b) is $V_{12} = 37500 \text{ cm}^{-1}$, which is characteristic of the strong dipole-dipole interaction between molecules observed in crystals of molecular nature. The resonant lifetime of an exciton in such a molecular crystal is $t = h/2V_{12}$. For a dimeric unit cell of Indigo Carmine, it is about $3 \cdot 10^{-16} \text{ s}$. This time is characteristic of a free exciton, the resonance lifetime of which is shorter than the relaxation time of the molecular crystal lattice. The rate of transfer of excitation between molecules in a dimeric unit cell (resonance rate) $n = 1/t = 3 \cdot 10^{15} \text{ s}^{-1}$. It is obvious from Fig. 4 that the difference in the interaction energy between the excited and normal molecules in the dimeric unit cell of the Indigo Carmine associate $\Delta D = +37500 \text{ cm}^{-1}$. The shift of the center of the exciton absorption band of the associate relative to the absorption band of monomeric Indigo Carmine to the blue region of the spectrum is due to the fact that the energy of interaction between molecules in the dimeric unit cell in the ground state is higher than in the excited one [11].

Energy parameters in associative food dyes and due to the fact that the components of the Davydov doublet in the absorption spectrum of the aggregate have approximately the same amplitude, it was concluded that the interacting dipole corresponds to the force perpendicular to each other. In this case, the radius – vector connecting both dipoles is not parallel to one of them.

The angles between the dipole moments of the transitions of molecules in associates were determined according to

$$\frac{f_k}{f_D} = \frac{1 + \cos \Theta}{1 - \cos \Theta}$$

where f_k and f_D - are the oscillator forces of the short-wave and long-wave absorption bands of associates.

Based on calculations, it was shown that for Indigo Carmine, the angle $88,96^{\circ}$ i.e. close to 90° . The diagram of the arrangement of molecules in associates of the dye Indigo Carmine can be attached as parallel vectors (Fig. 4). These data associates of dyes can be represented by Indigo Carmine in the form of parallel vectors.

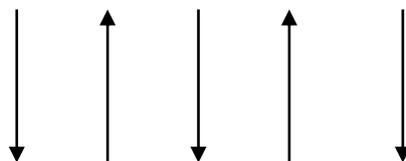


Fig. 4. Diagram of the arrangement of molecules in associates

We have shown that dimers of food dyes in binary solvents are formed under the action of Van der Waals forces. Multivariate food dyes also appear to be formed by Van der Waals forces. The validity of this assumption is confirmed by the conducted temperature studies. An increase in the temperature of the solution, where the association of the molecules of the studied compounds is observed, leads to the dissolution of the precipitate and the restoration of the absorption spectra of monomeric molecules. The calculation of the binding energy of the associates showed that they correspond to the binding energy of the dimers.

It is important to note that from the temperature experiments and the dependences of the absorption spectra, it is very difficult to distinguish the bands corresponding to dimers and complex associates that appear at the second and third stages of aggregation. When aggregating food dye molecules, there is only a drop in the absorption capacity, which is restored to its original form when heated. The results obtained coincide with those obtained for another class of compounds (phthalomides) [12].

In order to clarify the structure of complex associates, the absorption-polarization properties of aggregated food dye molecules were studied. The formation of complex associates from food dye dimers is confirmed by removing the temperature dependences of the polarization spectra. From the given temperature dependence of the linear dichroism spectra of 3,5-diglucoside cyanidine at the third stage of association. For complex associates of 3,5-diglucoside cyanidine at room temperature, the value is deg. As the temperature increases, not only does the value decrease, but also a significant deformation of the linear dichroism spectra is observed. At a temperature of 341 K, the spectra of the linear dichroism in the size and shape of the band completely coincided with the spectra of dimer molecules of the food dye. A further increase in temperature leads to the development of the process and at 353 K the absorption and linear dichroism spectra coincide with the electron bands of monomeric molecules of food dyes. All these results show that complex food dye molecules are formed from dimers and the binding energy of complex associates is 2 times less than the energy obtained with respect to dimeric molecules.

The non-dimeric nature of the polarization and absorption of the amplitudes of the long-wave splitting of food dye aggregates can be caused by the electron interaction in the dimeric unit cell, in which the intensities and polarizations can be

borrowed from neighboring bands. Our study of the dependence of the optical density of food dye aggregates and their angles of non-gyrotropic rotation of the polarization plane on the total dye concentration at a constant ratio of the binary mixture showed that the optical density value increases faster (by almost 2 orders of magnitude) at high concentrations of food dyes. This may be due to the fact that the orientation ability of the aggregated dye at high concentrations is significantly higher than its orientation ability of the low-concentration aggregated form, which has a rod-shaped structure, apparently due to its large size. Since the absorption-polarization spectra of complex associates, along with other bands, retain a dimeric character, we have the structure of associates, which is formed from a dimeric unit cell, where exciton and electron interactions are played out, which determine the nature of the splitting of the absorption spectrum and the non-gyrotropic rotation of the polarization plane.

The formation of multimers in the form of aggregated food dye molecules, as well as dimers, apparently obeys the exciton theory of Davydov A.S. Indeed, according to the calculation formula of the exciton theory, when complex associates are formed, the exciton band shifts to the red region of the spectrum, as was observed by the authors [10] for Rhodamine S and methylene blue. For food coloring molecules, a similar pattern of changes in the absorption spectra and linear dichroism is also observed, as in the case of Rhodamine S and methylene blue.

The acceptability of the exciton theory to the structural formation of aggregated food dye molecules is also confirmed by the correspondence of exciton bands with the spectra of non-gyrotropic rotation of the polarization plane.

As an experimental result, it should be noted that the components of the Davydov doublet in the absorption spectrum of the aggregate have approximately the same amplitude. This shows that the interacting dipoles in the dimer cell of complex associates are perpendicular to each other, which is qualitatively consistent with the experimental results. In this case, the radius vector connecting both dipoles is not parallel to either of them. Based on the estimated data and the possibility of the formation of Van der Waals forces between the dye multimers, we can present a model of complex associates of food dyes (Fig.5).

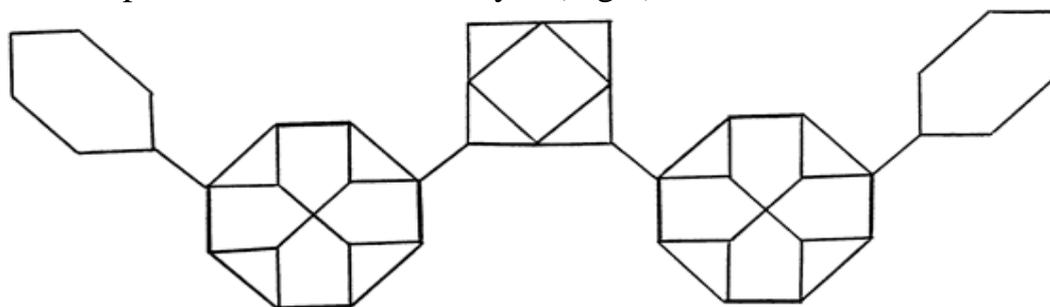


Figure 5. Model of complex associates of anthocyanin derivatives

From the above scheme (Fig.5), it follows that the dipole moments of exciton band transitions in the aggregated dye should be located with respect to the growth axis of the aggregate at an angle of $\sim 45^\circ$. The arrangement of complex dye associates shown in Fig.5 can explain the well-known fact that the binding energy of dimers is 2 times higher than the energy of complex associates. In this case, dimers are formed

by interacting naphthyl groups. At the same time, complex associates are united by the interaction of phenyl groups of dimeric molecules. Moreover, the energy of the electron bonds of naphthyl groups is 2 times higher than the corresponding energy values of the phenyl groups.

Another proof of the reliability of the scheme of the structure of complex associates is the fact that the quantum yield of the glow of complex associates is higher than the fluorescence capacity of dimers. In fact, the light excitation caught on complex associates can quite effectively migrate along parallel dipoles, while falling on a luminescent defect of a structural nature, the probability of which is high in large (in size) associates.

Thus, speaking about the gravitational nature of the orientation of associates in a solution, it is necessary to keep in mind the orientation mainly of the solution as a whole, the mass of which significantly exceeds the mass of individual associates, which makes the gravitational forces large in their magnitude and quite real.

In addition, as a result of absorption-luminescence and polarization studies, it was found that the molecules of anthocyanin, flavone, betalaine, tartrazine and indigocarmine derivatives at the second and third stages of association in binary mixtures of solvents form complex associates from the dimers of the studied molecules with the following properties:

- the structure of complex associates is needle-shaped or rod-shaped. In this case, the angle between the planes of the dimers in the associate is $\sim 90^\circ$, and with respect to the growth axis of the aggregates has a value of $\sim 45^\circ$.

- complex aggregates of food dyes in binary solvent mixtures are ordered under the influence of the Earth's gravitational field. In these cases, the optical activity of the studied molecules increases by about an order of magnitude.

Conclusions. It is shown that an increase in the concentration of food dye in aqueous and binary mixtures of a solvent creates conditions for the association of Indigo Carmine identifying hidden bands of associated molecules.

It is proved that the observed hypochromic effect during the association of Indigo Carmine molecules is due to resonant splitting of excited electronic levels under the action of the field forces of closely spaced food dye molecules.

It was found that the ratio of the energy of the dipole-dipole interaction in the associate, " ΔE ", to the width of the Frank-Kondo electronic transition " $\Delta \epsilon$ " has the ratio $\Delta E / \Delta \epsilon > 1$.

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