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Aggregation of dye molecules and its influence on the spectral luminescent properties of solutions

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ABSTRACT. The principal results of studies carried out in recent years on the molecular aggregation of organic dyes and pigments in solutions are examined and surveyed in the present review. Attention is concentrated on the influence of association on the photoenergetics of the dye molecules. Theoretical studies on the spectral-luminescent spectroscopic characteristics of the molecular aggregates are briefly considered. Studies on the anisotropy of the absorption and on the emission from the associated species are described. Investigations of the concentration depolarisation and concentration quenching of the fluorescence of dye solutions are subjected to a critical analysis. The results of studies of the mixed association of dye molecules and of its influence on the lasing characteristics of the solutions are presented. The physicochemical conditions affecting the efficiency of the association process are examined.

The bibliography includes 251 references.

Contents

I. Introduction 613
II. Theoretical study 613
III. The photoenergetics and structure of the associated species 615
IV. Polymethine dyes 618
V. Mixed association 620
VI. Polarisation studies 621
VII. Concentration-induced depolarisation and the quenching of luminescence 622
VIII. Association and lasing properties of the solutions. Factors influencing the effectiveness of association 623

I. Introduction

The wide-scale employment of organic dyes in science and engineering has stimulated research into the photophysical and photochemical properties of their molecules. Since dyes are most often used in liquid and solid solutions, where their spectral luminescent characteristics are complicated by intermolecular interactions, studies on the associated molecular forms of such compounds have become important. One may point out several aspects responsible for the interest in molecular association. This is in the first place the necessity to create a non-contradictory theory of the liquid state and solutions. The study of the photoenergetics of dye solutions always requires the knowledge of the spectral-luminescent characteristics of their molecular aggregates in order to be able to isolate in a pure form the optical manifestations of various intermolecular interactions, which are frequently complex and varied. It is impossible to overestimate the importance of studies on molecular association for the investigation and modelling of biological processes at the molecular level since under these conditions the molecules, functioning as reaction centres, are usually associated.

The employment of dye solutions as the lasing media in lasers has given rise to interest in problems such as that of the influence of solvents and various additives on the development of molecular association, which has a negative effect on the lasing efficiency. The application of dye solutions in quantum electronics as passive modulators, optical filters, shutters, etc., when appreciable absorption in the absence of luminescence is required, has given rise to additional interest in their associated molecular forms. Under these conditions, the appreciably different spectral-luminescent properties of the associated dye molecules and their monomeric forms can serve as a factor expanding their application in this field. The idea of a shift from the set of elements used in electronics to the molecular level will greatly expand the research into the problem of the molecular dye aggregates which is thus related to a number of fundamental aspects. Since the association of dye molecules lead as a rule to the quenching of the luminescence, it is essential to know the physicochemical factors inducing association or reducing its effectiveness. On the other hand, luminescent associated species can be used in concentrators of light energy, which requires conditions for the intensification of the association process. It is virtually true that whatever aspect of the study or use of dyes is considered (the study of relaxations of different kinds, Langmuir-Blodgett films, micellar systems, etc.), the problem arises of molecular association and its luminescence-spectroscopic manifestations. This is in fact why the number of studies devoted to the association of dye molecules and their spectroscopy has been continuously increasing. The previous review devoted to this problem[1] no longer reflects the current state of research in this field. The development of the spectroscopic techniques and the use of quantum-chemical modelling methods have made it possible to obtain a series of new luminescence-spectroscopic effects, arising on dimerisation of organic dye and pigment molecules. This review is based on studies published during the last 15 years.

II. Theoretical study

The luminescence-spectroscopic properties of the molecules of organic compounds in aggregates are a result of their collective interaction and are caused by the change on association of the oscillator strengths for optical transitions and selection rules and by

the manifestation of vibronic interactions. They involve the splitting of spectral bands, the displacement of electronic spectra, and changes in the intensity and anisotropy of absorption and emission and in molecular vibration frequencies, and the appearance of new vibrational transitions.

As regards their theoretical aspect, many of these problems have still not been solved even in a general form and for this reason there has been no weakening of interest in the theoretical description of the optical spectra of molecular aggregates (absorption, luminescence, and circular dichroism spectra), attention being concentrated on the effects of vibronic interaction.[2] The following aspects of the theoretical study of the molecualr aggregates have yielded most results: (1) the classical theory of the polarisability of bound oscillators; (2) the study of the exciton–phonon interaction as a stoichastic process which depends on time and the potential; (3) numerical calculation of the positions of the lines and intensities on the basis of a simple microscopic model; (4) the application of the sums rule as the theorem of moments for a vibronic band.

However, the quantitative application of theoretical methods to real systems remains problematical and the optical characteristics of associated species are calculated only for ordered structures, for example, sandwich type structures.

The most significant results have been obtained using the theory of excitons. The shape of the absorption bands of molecular dimers has been predicted with the aid of the model of incoherent exciton scattering.[3] The Hamiltonian of the dimer is represented by the sum of the Hamiltonians of the monomers and of the intermolecular interaction operator, whose matrix elements are expressed in terms of the eigenfunctions of the monomers. The energy levels and the matrix elements of the dipole moments of the dimer have been calculated in this way. The absorption coefficient and the absorption contours are expressed in terms of these quantities for different molecular interaction energies. The form of the absorption spectrum of the dimer depends on the relation between the nuclear relaxation and the exchange energy between the monomers. As an example, the absorption spectrum of the 9-chloroanthracene dimer was calculated and was found to be close to the experimental spectrum.

Allowance for the exciton effects, the electron–phonon interaction, and the local disorder among phosphor molecules made it possible to calculate the form of these individual transitions in the vibronic spectra of the molecular aggregates.[4] Best agreement between calculation and experiment was then achieved for pseudocyanine on the assumption that the aggregates contain eleven molecules arranged helically.

The same workers proposed a method for calculating the electronic absorption spectra of aggregates permitting the separate description of the vibrational structure of the non-uniform broadening.[5] The applicability of the method was demonstrated for the *J*-aggregates of 1,1-diethyl-*N*,*N*′-isocyanine chloride in water. It was found that the aggregate consists of six monomers.

A new approach to the calculation of the optical properties of molecular aggregates is based on allowance for the non-uniform spectra broadening caused by the non-equivalence of the environments of phosphor molecules comprising the molecules of the medium.[6] One considers an assembly of chemically identical aggregates in an isotropic medium (liquid, glass, etc.) in which it is necessary to take into account the distribution of non-equivalent states and to average out the form of the spectral lines with respect to the distribution. The functional form of the Hamiltonian corresponding to each six system is uniform but the magnitude of the parameter can differ from system to system. In this model, the medium is characterised by vibrations (modes) which can be divided into strong and weak in terms of their interaction with the aggregates. Strong modes are regarded as the usual exciton–phonon interaction and weak modes are responsible for the statistical non-uniformity. The Hamiltonian is constructed as follows:

$$H = \sum_i \varepsilon_i A_i^+ A_i + \sum_n \omega_n B_n^+ B_n + \\ + \sum_j \sum_i \sum_n g_{ij}^n \omega_n \left(B_n + B_n^+\right) A_i^+ A_j ,$$

where ε_i are the electronic energy levels of the aggregates, A and B are operators of the exciton–phonon formation and annihilation, and g_{ij}^n is the parameter of the exciton–phonon coupling for a separate mode on transition between levels i and j. The vibrational modes ω_n of the solvent and the molecule are grouped in the last two terms. Non-uniform local perturbations of any of the parameters (ε, ω, g) can differ for different species in the ensemble, but it is postulated that during the absorption of a photon the parameters are constant. Calculation showed that even in simple systems dimer spectra can be completely different from the monomer spectrum (depending on the vibronic and non-uniform contributions to the line width and the variation of any one parameter). The possibility of applying these theoretical results to real molecular systems, in which individual vibronic lines are not resolved, has been discussed in a study,[7] where analytical expressions were obtained for the form of the absorption and circular dichroism bands of the dimer.

The study of exciton–nuclear interactions in aggregates showed[8,9] that such interactions predominate in real dimers. The parameters used in this case were obtained by adjusting the theoretical spectra to agree with the experimental spectra of solutions of xanthene dyes (rhodamine B, pyronines B and Y).

The dimers of eosin Y have been investigated.[10] The visible absorption spectrum of its monomers refers to a single electronic transition, but includes several different vibration bands. The spectra of the dimers are therefore regarded as a result of their exciton interaction between vibronic levels. The difficulties in the interpretation of the experimental spectra proposed by Jones, et al.[11] are indicated and an approximation, constituting a further development of the exciton theory, is proposed for the analysis of the spectra of the dimers. It is suggested[10] that such spectra be considered on the basis of exciton interactions between vibronic states.

The electronic transitions between the split components of the electronically excited dimers have been analysed using perturbation theory.[12] It was shown that the one-photon transition between the ground state and one of the components of the excited state is prohibited for dimers in the case where the transition moments of the monomers constituting the associated species are parallel. However, the components forbidden in a one-photon transition can be manifested in a two-photon process. The theoretical treatment adopted in the above study[12] is equivalent to the strong bond limit.

The properties of the electronic states of metalloporphyrin dimers have been investigated by quantum-chemical methods.[13,14] Calculations have been carried out for the sandwich dimer, where the centres of the monomers are located on the axis perpendicular to the molecular plane.[13] The singlet and triplet states of the dimers of this compound have been obtained[14] for structures where the molecules are in one and in different parallel planes. Quantitative

agreement with experiment were not always obtained but the parameters of the structure attributed to the dimers agree with EPR data.

The dimers of a series of porphyrins[15] with different geometries[16] were investigated by this method. The energy changes and the orbital nature of the excited electronic states of the xanthene dyes during their dimerisation were established by direct quantum-chemical calculation,[17] dimers with a sandwich structure being considered.

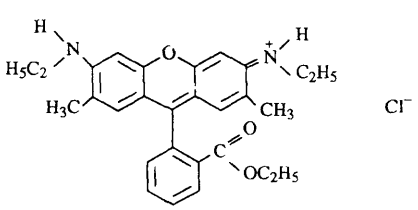
The results obtained when the theoretical parameters are determined from experimental data are of interest.[9,10,18] Not only the form of the electronic spectra of the dimers but also quantities such as the association constant, the quenching constant etc. are then obtained. Thus, using the method of least squares and the experimental spectra of Acridine Orange in the hydrochloride form, the dimerisation constant and the molar exctinciton coefficients of the dimers were obtained.[19] However, in their analysis the authors had to assume that the dye solutions consists only of monomers and dimers.

The approach to the description of the contours of the electronic bands of associated dye molecules, based on the hypothesis that the total absorption spectrum consists of "elementary" spectra (uniform relaxation components), has been proposed.[20] The initial postulate is that the line width and the probability of the transition between two electronic states are functions of the transition frequencies only. With the aid of the expression obtained for the description of the spectra of associated species and the experimental spectra, the parameters of the absorption spectra of the associated species were determined by minimising the corresponding function. No temperature dependence of the width of the Lorentzian component of the spectra of the associated species was observed for rhodamine 6G, in contrast to the monomers where such a dependence exists.

The optical properties of aggregates of chromophores have been studied theoretically using the incoherent dynamics model in the theory of Green's functions.[21]

III. The photoenergetics and structure of the associated species

Aggregates are molecular objects which occupy an important place in traditional spectroscopic research whose aim is the elucidation of spectral-luminescent changes occurring on association, the influence of this process on photophysical phenomena in solutions of dyes (the quenching of luminescence, the migration of energy), the influence on the lasing properties of solutions etc. The association of dye molecules alters significantly the probabilities of their vibronic transitions. The redistribution of the radiative and non-radiative transitions in associated rhodamine 6G species, occurring when their structure and composition are altered, has been investigated.[22,23]

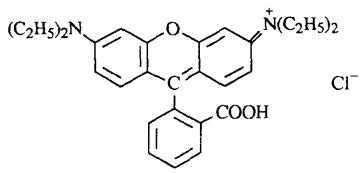


Rhodamine 6G

Earlier studies on aggregates of this compound have already been reviewed.[24] Different degrees of association of the dye were obtained in mixtures of polar and non-polar sovlents. The associated species are arbitrarily divided into "simple" and "complex" (the simple species arise when the content of the non-polar component is up to 90% of the volume of the mixture and the complex species arise when its content is higher). The luminescence with λ_{max} - 570 nm (20% of ethanol and 80% of CCl_4) was attributed to type *P* slow fluorescence due to the triplet–triplet annihilation of the simple associated species. For a higher CCl_4 content the intensity of the above glow falls and a new band arises with a maximum in the region of 620 nm, which is attributed to slow type *E* fluorescence due to the thermal activation of the associated triplet molecules to the excited singlet state with subsequent emission. For complex rhodamine 6G associated species, the $S_1 - T$ splitting is ~ 1500 cm^{-1}. The association of the molecules of this dye in binary mixtures takes place with participation of the anion[23] and the latter behaves as a heavy atom accelerating the intersystem crossing processes in the simple associated dye species.

The luminescence maximum at $\lambda = 670$ nm is attributed[22,23,25] to the phosphorescence of the rhodamine 6G associated species.

The absence of sensitised phosphorescence or slow fluorescence of stilbene has in fact been explained by the aggregation of rhodamine 6G following its adsorption from aqueous solution on the surface of a stilbene crystal.[26] This is associated with the fact that the *T* level of stilbene lies above the S_1 level of the rhodamine 6G aggregates. The aggregation of the molecules of rhodamines B and 3B, adsorbed on crystals (SnO_2, ZnO, etc.)[27–29] and on amorphous quartz,[30] is responsible for the anomalous spectroscopic-kinetic effects and the electron and hole injection in such systems.



Rhodamine B

Comparison of the optical properties of the associated species formed under different conditions can allow conclusions about their structure and the nature of the forces inducing association. The comparison for rhodamine 6G showed[31] that in dye solutions with $c \simeq 10^{-4}$ M and with a non-polar component content up to 90%, associated species are formed with a geometry such that they are incapable of luminescence. An increase in the content of the non-polar component (to 98–99%) increases the degree of association of the dye molecules and alters the geometry of the associated species (the angle between the planes of the molecules becomes less than 90°), whereupon the associated species fluoresce. More complex associated species, which do not fluoresce, are formed in virtually non-polar media. The fluorescence spectra of the rhodamine 6G associated species, formed in alcoholic solutions at –150 °C and in a binary mixture with a 99% content of the non-polar component, are identical.[31,32]

A more complete study of the optical properties of the luminescent associated species formed in cooled highly concentrated alcoholic solutions of dyes with different molecular structures (rhodamine 6G, Neutral Red, Crystal Violet, and Methylene Blue) showed that there is a definite qualitative agreement between the

luminescence-spectroscopic characteristics of the associated species of these dyes, despite the fact that the optical characteristics of the monomeric forms differ significantly.[32] Thus the fluorescence quantum yield of the associated species of the dyes investigated is low even at 77 K ($\sim 10^{-2}$), while the phosphorescence yield is lower still by 2–3 orders of magnitude. The electronic spectra of Neutral Red in ethanol at $c = 3 \times 10^{-2}$ M, where the dye molecules are almost all associated, are presented in Fig. 1, while Table 1 lists the wavelengths of the maxima in the spectra of the different types of luminescence, their quantum yields, and the phosphorescence decay times. The luminescence excitation spectra of the associated species have an appreciable maximum on the long-wavelength edge of the absorption band where the extinction coefficient is extremely low. Studies have shown[32] that complex associated species with non-uniformly broadened electronic spectra luminesce.

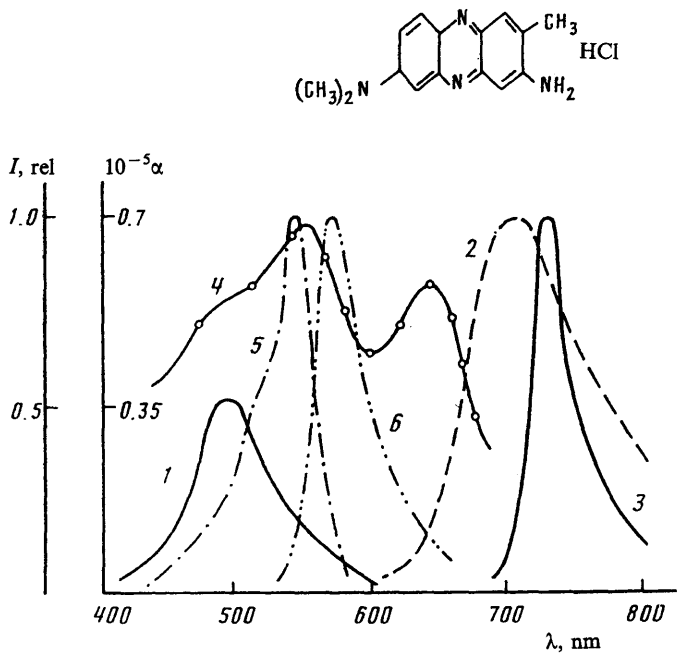


Figure 1. Electronic absorption (α) (curve *1*), fluorescence (curve *2*), phosphorescence (curve *3*), and excited fluorescence (*I*) (curve *4*) spectra of Neutral Red associated species in ethanol at 77 K; curves *5* and *6*—absorption and fluorescence spectra of the monomeric form at 77 K.[32]

It is essential to note that in binary mixtures of polar and non-polar solvents, the structure of the dye aggregates and the composition of their solvation shells vary non-linearly with the ratio of the solvent components.[33] This is related to the fact that the macroproperties of the binary solvent differ appreciably in the majority of instances from its microproperties, which exert a decisive influence on the spectral-luminescent characteristics of the phosphor molecules.[34] The polarisation characteristics of the luminescence and the axial moments of inertia of the rhodamine 6G assocated species give grounds for the assumption that in such mixtures their geometry is either of the "house of cards" or sandwich type.[33] The same geometry has been postulated for rhodamine B dimers in aqueous solutions. The separate aggregation of this dye in the neutral and cationic forms has been considered.[35] The energy of the exciton interaction (~ 560 cm^{-1}) and the angle between the dipole moments of the monomers ($\sim 70°$) of both forms are virtually identical, but the greater tendency towards the association of the neutral form is due to the electrostatic interaction between the carboxy- and xanthene groups of the monomers. The monomeric molecular forms of rhodamine B in water have also been investigated.[36]

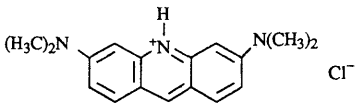
Table 1. The wavelengths of the maxima in the absorption (λ_a), fluorescence (λ_{fl}) and phosphorescence (λ_{ps}) spectra, the fluorescence (B_{fl}) and phosphorescence (B_{ps}) quantum yields, and the phosphorescence decay times (τ_{ps}) of associated dye species in ethanol and $T = 77$ K.[32]

Dye	λ_a, nm	λ_{fl}, nm	λ_{ps}, nm	B_{fl}	B_{ps}	τ_{ps}, ms
Rhodamine 6G	502 534	628	695	$3 \cdot 10^{-2}$	$2 \cdot 10^{-6}$	1200
Crystal Violet	584 592	732	745	$5 \cdot 10^{-3}$	$4 \cdot 10^{-4}$	345
Neutral Red	514	715	732	$8 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	200
Methylene Blue	569	700	-	$3 \cdot 10^{-2}$	-	-

The maxima in the induced absorption spectra of the rhodamine 6G and B associated species in aqueous solutions are respectively at $\lambda \simeq 430$ and 510 nm, while the lifetimes of the excited states are $\tau \simeq 160$ and 120 ps.[37] Smirl, et al.[38] obtained $\tau = 100$ ps for rhodamine B.

The formation of associated species of different types has been established for ethanol solutions of Arcridine Orange at 77 K[39] and the total emission spectra undistorted by reabsorption were obtained for different concentrations of the solutions. The authors were able to isolate four fluorescence bands of different aggregates, characterised by different durations τ of the afterglow, with maxima at $\lambda = 535$ nm ($\tau = 12$ ns), which is attributed to the dimers, $\lambda = 572$ nm ($\tau = 24$ ns), $\lambda = 605$ nm ($\tau = 42$ ns), and $\lambda = 645$ nm ($\tau = 33$ and 25 ns); τ for the monomers was 6 ns. It was proved that the higher aggregates do not phosphoresce. The increase in the average lifetime of the excited states for more complex aggregates implies an increase in the forbiddeness for the lowest sublevel, i.e. the approach of the angle between the molecular planes of the dye in the associated species to 90°. We observed an increase in the yield and duration of the luminescence of the associated species of acridine compounds also in polymer matrices at room temperature.[40] It was found[41] that $\tau = 4.2$ ns for Acridine Orange monomers in alcoholic solutions and $\tau = 14.7$ ns for the aggregated forms.

The study with the aid of Stark modulation spectroscopy of the aggregation of rhodamine 6G,[42] acriflavin, and Acridine Orange[43] in polymer matrices also confirmed that the structure of the dimers is of the house of cards type, but in Acridine Orange the molecular planes are almost parallel.



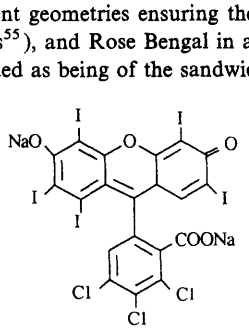
Acridine Orange

It was established that the dipole moments of the associated species of the compounds investigated change by less than a factor of 2 on electronic excitation as compared with monomers. Theoretical study within the framework of the simple exciton theory of the Stark effect in the aggregates confirmed this.[44]

Despite the fact that, in the first approximation of the theory, the triplet states of the aggregate should not differ from the monomer states in the case of large aggregates the T_1 states differ signifciantly. The phosphorescence band of Acridine Orange with λ_{max} = 680 nm has been atttributed[45] to the luminescence of large aggregates, while the phosphorescence band with λ_{max} = 615 nm, which virtually coincides with the phosphorscence spectrum of the monomers, was attributed to simple associated species. The long-wavelength phosphorescence quantum yield is ~0.05 and τ = 0.3 s (smaller by a factor of 15 than for the monomers).

The conclusions reached concerning the structure of the associated species of xanthene dyes, based on optical spectroscopy, have been confirmed also by NMR spectroscopy.[45,47] The molecular pattern in the associated species of azo-dyes in water and their micro-environment have been established by this method.[48,49]

The structures of the dimers in aqueous solutions of benzothiazole[50] (distance between the molecules 3.8 Å, angle between the molecules 18–25°, bond energy 5 kcal mol^{-1}), β-dicarbonyl compounds,[51] acetophenone in methylcyclohexane and isopentane glasses at 77 K (appreciable deformations in the phosphorescence spectra of highy concentrated solutions of this compound have been demonstrated[52]), xanthone,[53] thionine in H_2O and D_2O,[54] phenanthrene (it is assumed that the dimers of this compound have different geometries ensuring the stacking interaction of the chromophores[55]), and Rose Bengal in aqueous and methanol solutions[56] are regarded as being of the sandwich type.



Rose Bengal

It is believed[57] that the aggregation of Rose Bengal in aqueous solutions containing added KNO_3 develops in two stages: a neutral complex is formed initially between the dye anion and the K^+ ion, which is followed by the reaction between the neutral complex and a second dye anion. Multistage association with increase in concentration has also been proposed for vat dyes, which give rise to dimers and trimers in aqueous solutions.[58] The concentration variations of the absorption spectra of stilbene in a water–dioxane mixture have shown that association takes place directly between the molecules of this compound by virtue of van der Waals forces.[59] Certain aggregation parameters for dyes in solutions, obtained in the studies quoted above, are listed in Table 2.

Table 2. The dimerisation constants K, bond energies ΔH, the angles θ, and the distances R between the molecules in the associated species.[18,35,48,49,54,57,59]

Dye	Solvent	K, litre mol^{-1}	ΔH, kcal mol^{-1}	θ, deg	R, Å
Rhodamine 6G					
dimers	Ethanol	0.27	–	82	5.0
trimers		44.5	–		
Rhodamine B	Water	2100	10.0	64	6.4
	Ethanol	1.7	–	–	–
Rhodamine 3B	Water	790	5.8	67	6.7
Rhodamine 3G	"	945	6.9	48	6.8
Rhodamine S	"	710	7.5	40	3.5
Rhodamine 19	"	4400	–	–	–
Fluorescein	"	5.0	5.8	76	4.6
Rose Bengal	"	56700	–	82	–
Thionine	"	–	7.4	–	–
Methylene Blue	"	2400	6.7	–	–
Pseudoisocyanine	"	–	1.8	–	–
Azo-dye	"	510	3.5	–	–
Stilbene	Water + dioxane	–	4.8÷7.5	–	–

The photoenergetics of associated dye species and its relationship with structure can be understood by studying the aggregates of other compounds with a similar molecular structure, for example, porphyrins. The photophysics of the aggregates of these compounds has been thoroughly investigated.[60–70] From the standpoint of the problem considered in this review, the principal results of these studies reduce to the following.

Aggregation does not alter the probability of fluroescence per molecule, while the probability of intersystem crossing increases. There is a significant increase in the probability of internal conversion, while the probability of intersystem deactivation of the triplet state hardly changes on aggregation. The relative positions of the molecules in the associated species and the distances between them play an important role in altering the probability of non-radiative transitions. The electronic spectra of chemical dimers are determined by the exciton interaction of the dipole moments of the transitions of the monomers and by the intermolecular vibronic interaction. However, such interactions do not cause significant changes in the probability of non-radiative deactivation processes involving singlet and triplet excited states compared with the monomers and the main pathway to the deactivation of excitation in vibrationally linked dimers is interconversion to the T state. The overlap of the π-conjugated systems plays a significant role in the spectroscopic and energetic properties of the associated species. The

structure of the dimers was established and the oscillator model of the interacting chromophores was justified on the basis of spectroscopic-polarisation studies, data for the linear dichroism of oriented polymer films, and ^{1}H NMR data.

A series of covalently bonded Zn–H_2 porphyrin dimers have been investigated.[71] Two representatives of porphyrin dimers joined via the benzene ring have been studied by resonance Raman spectroscopy,[72] whilst in another study,[73] the photoelimination of the dip in the absorption spectra of aetioporphyrin in organic glasses showed that in the case of dimers the phase and energy relaxation of the excited electronic state are faster than for the monomers.

Both hypsochromic and bathochromic band shifts are observed in the electronic absorption spectra on formation of physical dimers of porphyrin compounds. The structure of the associated species is determined by the nature of the solvent and the substituents in the porphyrin ring.[74,75] The quantum yield of the luminescence of the dimers of certain porphyrins [for example, *meso*-tetrakis(*N*-methyl-4-pyridyl)porphin] is similar to the yield of the monomeric forms which aggregate at very low concentrations (10^{-7} M).[76] In contrast to the monomer, the aetioporphyrin I dimers exhibit optical activity and their fluroescence yield is 0.9 of the yield of the monomer.[70] Tetra(4-aminophenyl)porphin and its derivatives exhibit a high tendency to associate in solutions and in films.[77–79] The form of the associated species, having their own characteristic features of deactivation of the electronic excitation, depends greatly on the conditions in the association process and on the nature of the solvent. Thus in dimethylformamide the associated species of this compound exhibit, in addition to the fluorescence with a maximum at λ = 702 nm, a broad luminescence band with $\lambda_{max} \simeq 1000$ nm.[80] The pathways to the deactivation of the excitation of porphyrin associated species depend to a considerable extent on their structures and on the characteristic features of the interaction of the monomeric molecules in them. These questions have also been discussed in other communications.[81,82]

The structure of the associated species indicated by the appreciable influence of the properties of the solvent affects very greatly their spectra and energetics. However, hitherto there has been no unanimous view concerning the nature of the spectral changes in the association of dye molecules. In a number of studies,[83–91] this problem was solved taking into account the solvation of phosphor molecules. It was shown that the change in the absorption spectra on association of the same dye molecules can be various depending on the composition and structure of the sovlation shells. The concentration-induced changes in the absorption spectra of rhodamines, anthracene, erythrosine, trypaflavin, and other compounds have been investigated in various solvents and their mixtures at different temperatures of the solutions. The authors initial postulate was that, when the dye molecules are in the immediate vicinity of one another, the deformation of their electronic absorption spectra is caused by resonance interactions. For an intermolecular distance of ~10 Å, the molecules in the associated species are surrounded by individual solvation shells whose structures are not the same and are dynamic in character as a consequence of the thermal motion of the solvent molecules. On the other hand, a change in the immediate environment of the phosphor molecules infringes the resonance conditions and leads to an increased role of dispersion forces. Therefore, it is suggested in the above studies that the main cause of the hypsochromic effect on association is the dispersion interaction between the molecules in the aggregate when each monomeric molecule of the latter has its own solvation shell. Associated species having a common solvation shell give rise to a splitting in the absorption spectrum. The conditions have been examined for the occurrence and the spectroscopic manifestation of aggregation, wheruepon associated species of both types (contact and solvent separated) may be formed in the solution.[87]

It is noteworthy that the question of the solvation of the aggregates is extremely complex and has been solved only in a broad outline.

Studies of mixed solutions of rhodamine 6G, Bromothymol Blue, and benzopurpurine 4B,[88] showed that the nature of the distortions of the electronic absorption spectra on association of dye molecules of different kinds is similar to that for homogeneous associated species.

The study of this problem for ultraviolet absorpt on spectra[91] showed that the nature of the distortion of such spectra on association is the same.

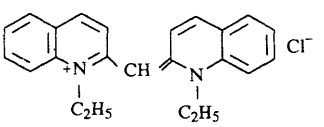
Thus the wide variety of concentration-induced changes in the absorption and luminescence spectra of dye solutions have been explained[83–91] from a single standpoint postulating the possibility of the formation of associated complexes differing in the nature of the solvation processes.

IV. Polymethine dyes

Until recently, the association of polymethine dyes was investigated in polar, mainly aqueous, solutions.[92–95] Attention was concentrated on *J*-aggregates (Scheibe aggregates).[96–100] The study of these compounds in weakly polar media is hindered by their sparing solubility and the problem is solved by introducing "aliphatic" groups into their molecules. Such cyanine dyes with long alkyl chains readily form Langmuir–Blodgett layers,[101–105] which have found extensive applications in various branches of science and engineering.[106]

J-Aggregation occurs not only in solutions but also in adsorption on the surfaces of microcrystals,[107,108] on oppositely charged polymer units,[109] and in adsorption of dyes from solution to give monolayers[110,111] or porous bilayers.[112,113] Cyanine dyes without long alkyl chains form *J*-aggregates at the air-water interface[110,114] if they are moderately soluble in water. In Langmuir–Blodgett films, the occurrence of aggregation has been established not only for cyanine dyes but also for other compounds, for example spiropyrans[115] and pyrene.[116]

The development of the spectroscopic technique has made it possible to obtain additional data about the development of the aggregation of cyanine dyes. A new model of aggregation and a critical discussion of earlier concepts concerning such aggregation have been described in a study[117] where aqueous solutions of pseudoisocyanine (PIC) were considered, while the *J*-band (the sharp peak at λ = 573 nm at room temperature and $c \simeq 10^{-3}$ M) was measured with a high spectral resolution (~5 cm^{-1}) on excitation by a dye-based laser.



Pseudoisocyanine

It has been established that the PIC monomers exist only at a very low concentration and at fairly high temperatures. As the temperature of the solution is reduced (the concentration is increased), dimers of the above dye are formed with a bond energy of ~ 1.8 kcal mol^{-1} and an angle between the monomeric transition moments of about 70°. Before the *J*-band appears in the spectrum, virtually all the molecules are in the dimeric state.[118] A further decrease in temperature leads to aggregation, the constant position of the *J*-band indicating a rapid growth of large aggregates with a narrow distribution of *n*-meric species, which are highly extended with their dipole moments parallel to the long axis. By studying the long-wavelength edge of the *J*-band for very low absorption coefficients, Kopainsky, et al.[117] established that the aggregates have an intrinsic absorption "tail" and that the *J*-band is to a large extent non-uniformly broadened.[119] Aggregation at very low concentrations ($\sim 10^{-6}$ M) has been demonstrated for solutions of furocoumarins.[120] The authors believe that only aggregated forms of furocoumarins exhibit an appreciable fluorescence, but these conclusions are rather tentative and require a more rigorous experimental justification.

It has been established by non-linear spectroscopic methods that the PIC *J*-aggregates have a fluorescence lifetime of 600–800 ps, but, for high intensities of the exciting light, it diminishes to 15 ps.[121] The emission time has been established for PIC bromide *J*-aggregates in ethylene glycol and water glasses with the aid of the photon echo method (~ 14 ps).[122] The luminescence lifetime of the 1,1-diethyl-2,2-cyanine bromide *J*-aggregates in water is 20 ps, while for the monomers it is 300 ps[123] and for microcrystals adsorbed on AgBr it amounts to 230 ps.[108]

At the same time, the question of the architecture of the *J*-aggregates and of its influence on the fluroescent properties remains open.[124] Aggregation numbers both ranging from 4 to 100 molecules[121] and amounting to 500 molecules[122] have been quoted for PIC. The effectiveness of the association of cyanine dyes can be increased by adding certain compounds to the solution.[125] The question of the structure of Scheibe aggregates can be of fundamental importance in the practical use of such systems. For example, when a thiacyanine dye is introduced into a monolayer of an oxacyanine dye organised into *J*-aggregates and present at a concentration greater by a factor of 10^4, an anomalously pronounced transfer of excitation energy from the "host" to the "guest" is observed,[126] its effectiveness depending greatly on the temperature of the system. The determination of the degree of association of naphthalocyanines in water, toluene, and acetone, showed that the associated species are either dimers or trimers.[127–130]

The influence of association on the spectral-luminescent properties of polymethine dyes with one chromophore as a function of their structure in mixtures of polar and non-polar solvents has been investigated.[131–134] The increase in the content of the non-polar solvent (hexane) to 90% induces a sharp fall in the intensity of the long-wavelength absorption band and an increase in the short-wavelength band. The latter is then narrower than the band in the spectrum of the solution in pure chloroform and undergoes a hypsochromic shift, whilst the long-wavelength band undergoes a bathochromic shift. These spectroscopic changes are accompanied by the quenching of fluorescence. The spectroscopic effects noted above depend on the characteristics of the molecular structure of the dyes and on the nature of the anion. On the basis of electronic and NMR spectra, it has been established that polymethine dyes whose molecules contain no bulky substituents form ion pairs with a sandwich structure. In weakly polar media, the structure of these associated species is more stable since the cations of their constituent molecules are rigidly fixed at both ends by anions as a consequence of the electrostatic attraction of unlike charges. Owing to the dissociation of the dyes, in polar solutions the counterion does not participate in association, which takes place as a result of dispersion interactions. The same cationic cyanines form different types of associated species in media of different polarity depending on the electronic and steric structures of the dye molecules.

The aggregation of cyanines with two chromophores was first examined by Herz,[96] but the chromophores of the test compounds were not rigidly linked, so that the spectroscopic changes were caused not only by aggregation but also by the change in the angle between the chromophores. Depending on the molecular structure of biscyanines with rigidly fixed chromophores, their association leads to the appearance of new short-wavelength or long-wavelength absorption and luminescence bands.[135,136] The effects in the absorption spectra occuring with increase in the content of the non-polar component depends on the nature of the anion. The results of these studies confirmed the marked dependence of the spectral-luminescent characteristics of the associated species on the nature of their solvation.[83–86] In contrast to cyanines with one chromophore, biscyanines exhibit a considerable tendency to associate.[137,138]

The form of the absorption bands of polymethines in a polymeric matrix is determined by the capacity of their ion pairs for association.[139] This process can be consistently regulated by introducing bulky substituents into the heterocyclic residues and the polymethine chain and also by altering the polarity of the polymeric medium.

The study of the molecular **aggregates of dyes in polymers** has become important, because such systems are used as scintillators,[140] radiation converters,[141] carriers for the recording of holograms,[142,143] laser media,[144,145] materials for the recording of information,[146] etc. The dye molecule association processes in polymeric media and its influence on the spectral-luminescent characteristics of these systems were analysed in a review.[147] Here we may note that dye molecules usually associate in polymers less effectively than in liquids, but the photophysical properties of the associated molecules can differ appreciably from the monomeric ones. For example, the associated species of Golden Yellow vat dye (dibenzopyrenequinone) in poly(vinyl alcohol) are more photostable than the monomers[148] and the sensitising effect in such a system depends on the ratio of the molecular and associated forms and on the operation of factors inducing the deaggregation of the dye. The fluorescence quantum yield of the dimers of a series of acridine dyes in polymers is higher than the yields of the monomeric molecules[149] but more complex associated species formed at $c > 2.5 \times 10^{-3}$ M have a low fluorescence yield.

In such systems, it is difficult to determine the degree of association of phosphor molecules. This has been done[150] for acridines and rhodamines in poly(vinyl alcohol) films, where the equilibrium constants of monomers and dimers were also determined. However, no account was taken in the above study of complex aggregates. The concentrations of the dimers and complex associated species of acridines were determined in our study[149] and their absorption spectra were identified ($\lambda_{max} = 470$ nm for the dimers and 435 nm for complex associated species), while in another study[40] their fluorescence spectra were identified and the decay times were estimated (8.0 and 2.0 ns respectively). The study of the kinetics of the polarisation of the fluorescence of these compounds showed that, in contrast to the monomeric forms, in poly(vinyl

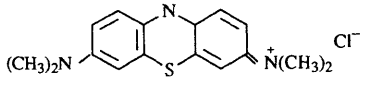
alcohol) the associated species of acridine compounds do not rotate after their photoexcitation.[151]

The association of dye molecules exerts a significant influence on the activity of the systems employed. Thus the polymeric lattices with incorporated dyes used in biotechnology and medicine undergo a change in their properties[152] and the diffraction efficiency of gelatine grids activated by Methylene Blue is impaired at high dye concentrations.[153]

V. Mixed association

Mixed association is the aggregation of the molecules of different dyes. In the literature, this is referred to as heterogeneous association. The study of mixed association processes has become important in connection with the fact that mixtures of different dyes are used as working media in dye lasers,[155] in radiation converters,[141] and in other systems based on the phenomenon of sensitised luminescence.[156] The study of heterogeneous association is complicated because it occurs against the background of homogeneous association which as a rule takes place more efficiently.

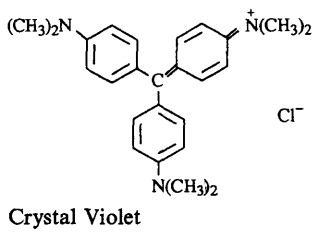
Heterogeneous association is manifested in the study of the electronic excitation energy migration processes in mixed solutions of dyes. In the study of the concentration dependences of the yield of the luminescence and of its polarisation,[157] it was noted that the main role in the quenching of the luminescence of rhodamine 6G is played by associated species comprising this dye and benzopurpurine 4B. It has been shown by absorption spectroscopy[83,88] that, on formation of mixed associated species of these compounds, there is an appreciable diminution of the absorbing capacity of the solutions. The procedure has been proposed[157,158] for the determination of the degree of heterogeneous association based on the measurement of the luminescence characteristics of the dye solutions. Thus the degree of heterogeneous association for an aqueous solution of rhodamine 6G ($c = 2 \times 10^{-6}$ M) and Methylene Blue ($c = 1 \times 10^{-4}$ M) at room temperature was found to be 0.33.



Methyl Blue

The bond energies in such associated species (4.6 kcal mol^{-1}) are smaller by a factor of ~2 than the bond energy in homogeneous rhodamine 6G associated species in water.[159]

The heterogeneous association of the same compounds as well as Crystal Violet, Methylene Red, Brilliant Yellow, and Methylene Orange in water has been studied[160] and the absorption spectra of such aggregates have been identified. The splitting of the absorption band characteristic of homogeneous associated species is absent from such spectra.

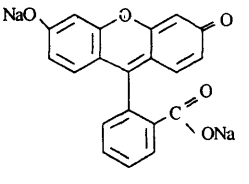


Crystal Violet

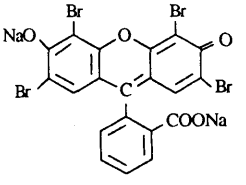
This can be understood bearing in mind that the splitting of the electronic levels on association is induced by resonance interactions which are impossible for molecules of the individual compounds. It was concluded[160] that heterogeneous associated species are formed as a result of dispersion interaction forces. The stability of such aggregates may depend on the addition of electrolytes to the solution.[161] Mixed associated species comprising rhodamine 6G and oxazine 17 are formed also in polar organic solvents.[162] The solvents apparently exert their main influence on the heterogeneous association of dye molecules through their microproperties, i.e the properties of solvent molecules in the solvation shells and the composition of the latter. This conclusion was reached[163] in a study of the spectroscopic characteristics of mixtures of rhodamine dyes with Methylene Blue in various solvents (water, glycerol, ethanol, formamide), the effectiveness of mixed asociation depends on the parameter which reflects the ability of the solvent to form hydrogen bonds. The major role of the nature of the solvent in mixed association of dyes has been pointed out also by Dzhumadinov, et al.[164] However, like homogeneous association, heterogeneous association is most effective in binary mixtures of polar and non-polar solvents. In such media, it was possible to record not only fluorescence but also slow fluorescence and phosphorescence for mixed associated species of rhodamines with Methylene Blue.[165,166] Since the singlet level is appreciably lowered and the energy gap between the S_1 and T_1 levels diminishes in such association, this leads to the quenching of the fluorescence and the excitation of slow fluorescence. It has been established with the aid of IR spectrosocpy that mixed associated species of these compounds are formed via hydrogen bonding.

The heterogeneous association of rhodamines and Methylene Blue has been studied in solutions of polyelectrolytes[167,168] and in aqueous solutions of surfactants[169,170] but an unambiguous interpretation of its spectral-luminescent manifestations in such systems is difficult. The mixed association of Methylene Blue and organic anions (naphthalene-1-disulphonate, etc.) in water has been detected with the aid of absorption and luminescence spectra, which undergo a bathochromic shift under these conditions.[171] The thermodynamic quantities and equilibrium constants were determined for such complexes and it was concluded that they arise in the reaction between the Methylene Blue cation and the aromatic ring of the organic anion. At high concentrations of the polyanion (naphthalene-2,7-disulphonate) such complex formation predominates over the dimerisation of the dye.

The formation of mixed sandwich dimers in aqueous solutions of a number of basic dyes has been established.[172,173] Such aggregation in the presence of natural or synthetic polymers occurs at lower concentrations.[174] The temperature dependences of the absorption and fluorescence spectra of mixtures of Na-fluorescein Na-eosine, trypaflavin, and Acridine Orange showed that the mixed associated species are formed by those dyes whose molecules are capable of being linked by a hydrogen bond.[175]



Na-Fluorescein



Na-Eosine

Mixed aggregation has been observed also for cyanine dyes in Langmuir–Blodgett monolayers.[176] For a certain combination of Na-octadecyl-substituted cyanines in films formed from the solution, mixed *J*-aggregates are produced, whose single absorption and luminescence bands occupy, in spectroscopic terms, an intermediate position between the spectra of *J*-aggregates of the individual components of the dyes. It was established that the appearance of such aggregates requires a very particular compatibility of the molecules, since even slight structural changes in them disrupt the mixed association. Thus the dyes 1′methyl-3-octadecylthia-2′-cyanine and 1-methyl-3-octadecylselena-2′cyanine form mixed aggregates with 1′-methyl-1-octadecyl-2,2′-cyanine but not with 1′-methyl-3-octadecyloxa-2′-cyanine. The luminescence spectra of such mixed *J*-aggregates undergo a slight Stokes shift, while the homogeneous *J*-aggregates exhibit resonance fluorescence.

The formation of mixed associated species has been demonstrated for many dyes, but the available data on their photoenergetics are in the main qualitative. These systems require much attention by investigators using modern methods. Thus it has been established by differential spectrosocpy that the absorption spectrum of mixed associated species of rhodamine 6G and Crystal Violet in poly(vinyl alcohol) matrices contains four maxima,[177] which agrees fully with the general pattern in the electronic absorption spectra of dye dimers.[178]

VI. Polarisation studies

According to the exciton theory, the oscillators of the sandwich dimers, referring to different absorption bands, should be mutually perpendicular and hence should be polarised in different directions. This is also indicated by the theory of the circular dichroism of aggregates.[179] However, there are virtually no theoretical data on the characteristics of the polarisation of the luminescence of the aggregates and the experimental data are not numerous and are contradictory. This is associated with the fact that the degree of polarisation of the emission by the dye associate species has different causes (both the structure of the emitter and the depolarising factors).[180]

An attempt has been made to devise a theory of the polarised luminescence of dimers with the aid of the non-linear Schrödinger equation.[181] The donor–acceptor pair of identical molecules, whose transition dipole moments are either located in a single plane or are mutually perpendicular, was adopted as the dimer model. The average degree of polarisation of the fluorescence of the dimers was calculated as a function of the parameter characterising the non-linearity of the interaction of the molecules, which was varied from 0.7 to 0.776. However, the applicability of the results for practical purposes is extremely problematical.

The depolarisation of the fluorescence of molecular aggregates as a result of energy transfer between the molecules within the framework of the model of a randomly arranged pair of electronically linked molecules[182] has been investigated in a study[183] where the theory was compared with experiment for chlorophyll and phaeophytin. As the author himself notes, analysis of the equations obtained is difficult. Nevertheless, using experimental results together with the equations, it is possible to obtain a number of parameters characterising the energy transfer in the associated species.

At the same time, the polarisation methods for the investigation of aggregation make it possible to extract valuable information, which is frequency difficult to obtain by other methods. Thus by investigating the polarisation fluorescence and circular dichroism of covalently linked ethylene–bisporphyrin dimers in viscous solvents in a magnetic field, it was established that electronic-vibrational exchange with participation of both totally symmetric and non-totally symmetric vibrations is intensified in such dimers. Such exchange smoothes out the polarisation spectra of the dimers, while the changes in the circular dichroism spectra in the region of the Soret band are due to exciton effects.[63]

It has been shown with the aid of absorpton-polarisation measurements that the absorption spectra of the rhodamine 6G associated species in poly(methyl methacrylate) matrices have four absorption bands with maxima at λ = 491, 512, 547, and 561 nm, the bands of the short-wavelength doublet having identical amplitudes and being polarised at right angles to one another.[184,185] Since the dimer contour of the short-wavelength doublet is retained at different dye concentrations, the authors concluded that the rhodamine associated species consists of many molecules in the form of a polymer chain with a dimeric unit cell in which the exciton and vibronic interactions determine the nature of the splitting in the absorption spectrum. The energy of the exciton interaction between the molecules and the associated species has been estimated as 430 cm^{-1}. A similar absorption spectrum of the associated species has been observed also for rhodamine B in aqueous solutions at low temperatures.[186]

Measurements of the polarisation characteristics of the fluorescence and dichroism makes it possible to determine the structure of the associated species. This method has been demonstrated on alcoholic solutions of rhodamine 6G.[187] It has thus been shown that the hydrogen-bonded dimers of pyrromethenone amides have a nearly coplanar structure.[188] Polarisation measurements and the use of the Levshin–Perren formula[180] made it possible to determine the composition of the associated species of asphaltenes.[189] The effect of the association of the molecules of rhodamine dyes, eosine, and erythrosine in aqueous glycerol solutions on the polarisation of the fluorescence has been investigated.[190–193] The increase in the degree of polarisation of the long-wavelength luminescence of the solution with increase in the concentration of the dyes was explained by the formation of their luminescent associated species but no evidence was adduced to show that the associated species in the test solutions are capable of luminescing. The increase in the degree of polarisation of the fluorescence can apparently be explained in this case by the non-uniform broadening of the electronic spectra and by directional energy transfer (the Weber effect).[194] Furthermore, calculation showed that the degree of polarisation of the luminescence of the dimers is smaller than that of the monomers.[195] It has been established[196] that the degree of polarisation of the fluorescence of different forms of *p*-(dialkylamino)benzylidenemalononitrile in poly-(vinyl acetate) matrices diminishes in the sequence monomer (0.5) > dimer (0.2) > complex associated species (0.03). However, it has been found for a series of dyes in frozen ethanol solutions that the degree of polarisation of the luminescence of the associated species can be both smaller and greater than the degree of polarisation of the luminescence of their monomeric forms.[32]

VII. Concentration-induced depolarisation and the quenching of luminescence

When dyes are used in different systems, the problem of the quenching of the luminescence is of primary importance. Numerous studies have established that the concentration-induced quenching in solutions of organic dyes is associated with molecular association,[1] whilst the concentration-induced depolarisation of the fluorescence is associated with electronic excitation energy transfer.[180,197] Until recently, it was assumed that the associated dye molecules do not fluoresce under the usual conditions.[1] However, modern experimental techniques make it possible to record the luminescence of associated species for which the luminescence quantum yield is very low.[198–200] The luminescence of associated species of rhodamine dyes in alcoholic[201] and aqueous[202] solutions at room temperature was observed. The luminescence spectrum of the associated dye molecules is appreciably displaced towards longer wavelengths relative to the spectra of the monomers.

The question of the contribution to the concentration-induced quenching of luminescence by the migration of the electronic excitation energy between the monomers remains controversial. It has been shown for rhodamine dyes in various solvents and for different degrees of association, taking into account the diffusion of molecules, that non-radiative energy transfer between identical monomeric molecules does not lead to the quenching of luminescence.[203,204] Energy is transferred without losses from acriflavin to rhodamine B.[205] The energy transfer between the molecules of different dyes can lead to non-radiative deactivation in the molecules of an acceptor dye and the effectiveness of such losses depends on the spectral luminescent characteristics of the test dyes.[206] The migration of excitation between the monomeric molecules under the conditions of spectral non-uniformity of the systems can induce the quenching of fluorescence.[207–212]

The problem of the concentration-induced depolarisation of fluorescence has been solved for solid solutions by assuming that the probability of transfer is isotropic.[213] The influence of fluctuations in the concentration of the luminescing molecules on the anisotropy of the emission has been examined in a study[214] where an expression was obtained for the anisotropy as a function of the concentration of the molecules, which was identical with the formula derived by Bodunov.[213] These problems were examined in detail by Gaisenok and Sarzhevskii.[180]

The expression for the concentration induced depolarisation of the fluorescence of non-viscous solutions, examined on the basis of Boyarskii's theory[1,215] and the Levshin–Perren formula,[180] has been obtained[216] (in terms of the anisotropy of the emission r):

$$r/r_0 = d_m/d_d,$$

where r_0 is the anisotropy of the "frozen" highly dilute solution in the absence of acceptor associated species and d_m the depolarising factor due to the transfer of excitation both between the monomers and from monomers to the associated species:

$$d_m = (1-\alpha\left[1+\frac{1}{2}\frac{(\alpha f)^2}{1-\frac{3}{4}(\alpha f)^2}\right],$$

$$f\sqrt{\pi}\gamma\exp(\gamma^2)\left[-\frac{2}{\sqrt{\pi}}\int_0^{\gamma}\exp(-t^2)dt\right],$$

$$\alpha = \alpha_0\left[\frac{\gamma_m}{\gamma_m+\gamma_a}\right],\ \gamma = \gamma_m+\gamma_a = \frac{\sqrt{\pi}}{2}\left(\frac{c_m}{c_{0m}}+\frac{c_a}{c_{0a}}\right),$$

where c_m, c_{0m}, c_a, and c_{0a} are the concentrations and critical concentrations of the monomers and associated species, α_0 is the probability that the excitation energy is not degraded during migration between the monomers, and d_d is the rotational depolarising factor:

$$d_d = 1-\frac{3}{2}<\sin^2\theta>$$

(θ is the angle between the directions of the moments of the transition when the molecule is excited and deactivated).

The averaging procedure was carried out[217] and reabsorption and secondary emission, which exert a significant influence on r at high concentrations, were taken into account in another study.[218]

The above expressions were confirmed experimentally for aqueous glycerol solutions of rhodamine 6G.[219] At high concentrations of dyes, the theoretical relations indicated an increase in anisotropy, which was in fact observed experimentally for both Stokes and anti-Stokes excitation.

On the assumption of a multistep non-radiative energy transfer from the monomers to the associated species, an expression was obtained for the relative decay time τ of the fluorescence of phosphors:[220,221]

$$\frac{\tau}{\tau_0} = \frac{1+\gamma^2-(1.5+\gamma^2)f(\gamma)+\alpha_0\alpha f(\gamma)\left[f(\gamma)+\gamma^2-0.5\right]-\alpha_0\alpha\gamma^2}{[1-f(\gamma)]\,[1-\alpha_0\alpha f(\gamma)]}.$$

It was tested experimentally for rhodamine dyes in solutions where the dye molecules exhibit different tendencies to associate.[222–224]

A critical analysis of the above formulae was carried out by Bodunov and co-workers.[225] Using the graphical method proposed by Loring, et al.,[226] theoretical expressions were obtained for the anisotropy r and the yield B of the luminescence, with the aid of which it is possible to analyse the experimental data:

$$\frac{r}{r_0} = 1+\frac{\pi}{2\sqrt{2}}q^{0.5}\gamma_m+0.1887q\gamma_m^2+(0.3832-\delta)q\gamma_m\gamma_a,$$

$$\frac{B}{B_0} = q\frac{r_0}{r},$$

$$q = \left\{-\frac{\pi}{4}\gamma_a-\frac{\pi}{4\sqrt{2}}\gamma_m+\left[1+\left(\frac{\pi}{4}\gamma_a+\frac{\pi}{4\sqrt{2}}\gamma_m\right)^2-\right.\right.$$

$$\left.\left.-0.5258\gamma_m^2-(0.13716-\delta+\beta)\gamma_m\gamma_a\right]^{0.5}\right\}[1-0.371\gamma_a^2-$$

$$-0.1887\gamma_m^2-(0.13716-\delta+\beta)\gamma_m\gamma_a],$$

$$\gamma_{m(a)} = \frac{c_{m(a)}}{c_{0m(a)}}.$$

δ and β have been tabulated.[226]

The above formulae agree with the exact theoretical results obtained previously[180] in the corresponding limiting cases.

For an experimental test of the above formulae, it is essential to know the degree of association (the fraction of the associated dye molecules) and the order of the association (the number of molecules in the associated species) of the solutions. These characteristics permit the determination of the concentration of the monomers and associated species in dye solutions. A number of methods for their

determination have been described.[1] The dimerisation constant has been calculated from the quenching of the fluorscence of rhodamine and acridine compounds in poly(vinyl alcohol) matrices[150,227] and a method for the determination of the degree of association has been proposed.[228]

At the same time, the formulae quoted above can be used to determine the degree of association (the concentration of associated molecules). For this purpose, it is essential to obtain experimentally the concentration variations of r/r_0, B/B_0, and τ/τ_0. The numerical solution of the resulting equations makes it possible to determine the degrees of association for different concentrations of the solutions. The concentration dependence of the degree of association of rhodamine 6G molecules in poly(vinyl alcohol) matrices was obtained by this method[229] and is illustrated in Fig. 2 (curve *4*). The same figure presents the experimental concentration dependences of the anisotropy of the emission (curves *1*), the quantum yield (curve *2*), and the lifetime of the fluorescence (curve *3*). Curve *1* in Fig. 2 shows that, at high concentrations of rhodamine 6G, an increase in the relative anisotropy of the emission r_{rel} is observed.

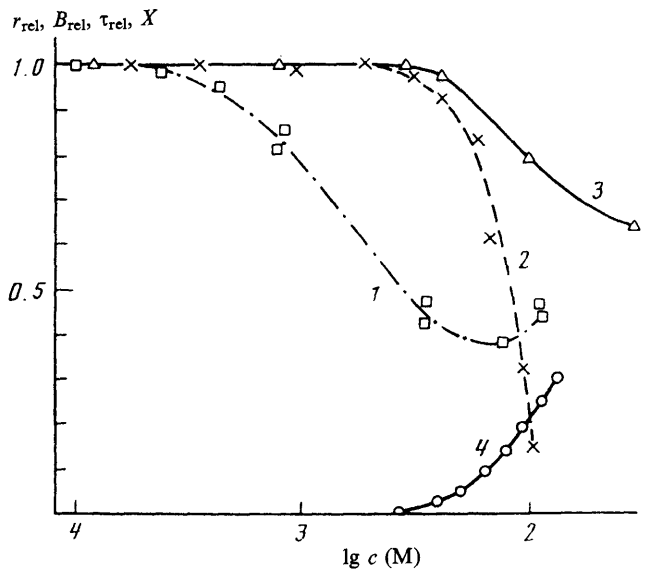


Figure 2. Concentration variation of the relative anisotropy of the emission (curve *1*), relative quantum yield (curve *2*), and relative decay time (curve *3*) of the fluorescence of rhodamine 6G in poly(vinyl alcohol) films; curve *4*—fraction of associated rhodamine 6G molecules (X).[229]

Comprehensive analysis of the association processes and of the concentration-induced quenching of fluorescence in different media linked to them has been performed for dyes widely used in science and engineering. The structural aspects of the fluoroescein aggregates in water have been examined in a study[18] where the association constants were determined by absorption spectroscopy and the absorption spectra of the dimers and trimers of this dye were identified. The calculated exciton parameters for the dimers satisfy two different geometrical models ("sandwich" and "jointed"). The trimers appear at $c \simeq 10^{-1}$ M. The authors suggest that the exciton theory predicts an increase in the trimerisation constant. The quenching of the fluorescence in water occurs up to limiting concentrations ($\sim 3 \times 10^{-1}$ M) and is due both to the migration of excitation between monomeric molecules and to energy transfer to aggregates, quenching by trimers being more effective.[230]

The aggregation of coloured neutral and cationic forms of rhodamine B in aqueous solutions has been studied.[35,231] The greater effectiveness of the association of the neutral form is caused by the electrostatic attraction between the carboxyl and xanthene groups of the monomers. The thermodynamic characteristics of the dimerisation of both forms are similar.

The quenching of the luminescence of rhodamine 6G in ethanol and water takes place starting from concentrations of $\sim 5 \times 10^{-3}$ M and 2×10^{-4} M respectively.[232,236] The quenching is attributed to the formation of dimers and trimers and to the transfer to them of excitation energy from their monomers via the Forster mechanism. However, the authors believe that in the case of ethanol solutions energy is transferred also via an exchange mechanism and that molecular diffusion plays a major role. Quenching by trimers is more effective as a consequence of their greater size compared with dimers, while migration of excitation via monomers does not lead to quenching.[18,237] For aqueous solutions of rhodamine 6G, the collision mechanism does not play a role. The association and quenching processes involving rhodamine 19 have been examined by Arbeloa, et al.,[238] while the mechanisms of the concentration-induced quenching of the luminescence of sulphorhodamine,[101] encapsulated in phospholipid vesicles, has been examined by Plant,[239] who investigated the influence of concentration on the fluorescence lifetime, which becomes shorter for higher concentrations owing to energy transfer to complexes and the collisions between dye molecules.

It is noteworthy that, in the study of the lumienscence of dye solutions, the above investigators[230–238] did not take into account the role of the inactive absorption by associated species in this process. The considerations which they have put forward concerning the formation of dye trimers and the quenching effect of the migration of excitation energy between monomers are not very convincing.

VIII. Association and lasting properties of the solutions. Factors influencing the effectiveness of association

The association of the molecules of laser dyes leads to an appreciable impairment of the lasing properties of their solutions. Polar organic solvents are usually employed for laser dyes. They prevent the development of the self-association of their molecules. However, as noted above, associated species are formed at high concentrations also in such media. Numerous studies have been devoted to the influence of association on the lasing characteristics of dye solutions.[162,240–243] It was established that an increase in dye concentrations in a series of lasing systems entails a fall in the laser energy and shifts of the laser emission spectrum. The spectral shifts are particularly notable in the case of two-component solutions.[162] At the same time lasing by rhodamine 6G associated species has been noted in aqueous solutions[202] in which the associated species do not luminesce under the conditions of stationary excitation. The wavelength of the laser radiation is 640 nm and, although the lasing

efficiency is not high it is nevertheless almost the same as the efficiency of the monomers in aqueous solutions of rhodamine 6G.

The effectiveness of the association process in dye solutions depends on many factors and it is not always a simple problem to determine whether it occurs or not. Association is determined by the molecular structure of the dyes and the nature of the solvents. It increases for molecules containing groups capable of forming hydrogen bonds and also for weakly polar solvents where the dye molecules are not surrounded by a solvation shell which prevents their mutual approach.

The association fof dyes is also prevented by the addition of detergents to the solutions.[41,244,245] In the case of aqueous solutions, the addition of electrolytes diminishes the degree of association of dye molecules,[246] while in the case of alcoholic solutions salts (electrolytes) do not affect the association process[247] but induce an additional orientational broadening of the spectrum. For rhodamine 6G in mixtures of polar and non-polar solvents, the addition of salts to the solution disrupts the complex associated species into monomers, which shows that the association of the molecules of this compound in weakly polar media involves the formation of ion pairs.[137,248] A decrease in the degree of association of dyes is observed after the addition of cyclodextrins and water-soluble polymers to the solution.[249] Data indicating an increase in the association of rhodamine dyes at high (up to kbar) pressures have been published.[250,251]

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Investigators working in the field of quantum electronics, spectroscopy, photochemistry, molecular biology, etc. have devoted much attention at the present time to the molecular aggregation of dyes and its physicochemical manifestations. This is related both to the wide-scale application of dyes and to the good prospects for the use of individual organic molecules and their aggregates as information processing elements, high speed memory devices, etc. The study of the photonics of the molecular aggregates of dyes will make it possible in the future to regulate the radiative and non-radiative relaxation of the excited states of organic molecules at the structural level.

Definite views based on a series of theories, which agree to some extent with experimental data, have arisen in the literature as regards the spectral luminescent manifestation of aggregation. The influence of aggregation on the probabilities of various transitions in molecular systems has been established for many compounds. The view that, together with dimers, complex associated species with characteristic optical properties are formed under certain conditions has been generally accepted. The problems of the influence of the solvent microenvironment on the structure of the aggregates and on their spectral luminescent characteristics have been solved in broad outline. Vigorous studies have been initiated on associated molecules in polymeric media. The problem of the concentration-induced depolarisation and quenching of the luminescence of dye solutions can be regarded as solved in broad outline taking into account molecular aggregation. Extensive data are available on the development of the association process in solutions of a large series of dyes and of the influence of various factors on it.

However, despite the availability of numerous experimental data, there is so far no unanimous view on the nature of the changes in the spectroscopic characteristics of molecules during their association. The elucidation of this process would make it possible to solve the converse problem—the determination of the nature and energetics of intermolecular interactions in the aggregation of dye molecules. The cause of the loss of capacity for luminescence by aggregates and the structure and photochemical properties of complex dye species (including those of dimers) need to be elucidated. For this purpose, it is essential to determine the orbital structure of the excited electronic states of the associated molecules. One should note that, despite the elucidation of the general characteristics of the optical manifestations of aggregation, the individual properties of compounds frequently play a decisive role in such manifestations. It is therefore so far impossible to carry out a sufficiently complete analysis of the results of studies on aggregation in terms of classes of dyes, since many problems (the influence of the medium, of the structural characteristics of dye molecules, of the nature of the counterion, etc.) have been investigated sporadically. The relations between the structure of aggregates and their spectral-luminescent characteristics have been established mainly only for dimers and ordered *J*-aggregates, while for complex associated species this problem still has to be solved. The establishment of these relations will make it possible to use organic dyes more effectively and studies on the aggregation of their molecules and of its influence on the spectral-luminescent properties of their solutions therefore still remain of current interest.

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