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ELECTRONIC ABSORPTION SPECTRA AND DIMERIC PROPERTIES OF RHODAMINES IN SOLUTIONS*

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Measurements of the concentration and temperature dependence of the electronic absorption spectra of rhodamine B, rhodamine 3B, rhodamine 3G and rhodamine S in water solutions have been carried out. On the basis of these measurements the dimerization constant, pure dimer and monomer spectra as well as the binding energy of a monomer unit in the dimer have been calculated. In each dimer spectrum the occurrence of two bands has been found. The oscillator strengths of the monomer band and dimer bands as well as the magnitude of excitonic splitting were determined. From these data, for each dye dimer the angle between the transition moments of the adjacent molecules and the separation distance between these molecules were calculated.

1. Introduction

Investigations of the associations of dye molecules have been in progress for many years [1–8]. Recently they were intensified due to the application of dye solutions as active media in lasers.

A particularly great number of papers has been devoted to the investigations of the associations of rhodamine B and rhodamine 6G [9–15]. In this work we present the experimental results for the electronic absorption spectra of a larger family of rhodamines in water solutions, namely, rhodamine B, rhodamine 3B, rhodamine 3G and rhodamine S. We shall also present a discussion of the structure of dimers of the above mentioned rhodamines in solutions.

2. Experimental

The object of the investigation were solutions of rhodamines whose characteristics are listed in Table I. Rhodamine B produced by Schuchardt was purified by manyfold crystallization from ethanol and vacuum evaporation of the solution. Rhodamine 3B of Gurr turned out to be a mixture of rhodamine B and rhodamine 3B. The dyes

TABLE I

Data characterizing rhodamines in solutions

1	2	3	4	5[a]	6[b]
				The range of concentration	
System	Dye	Molecular weight	Solvent	M/l	
I-RB/H$_2$O	Rhodamine B C$_{28}$H$_{31}$Cl N$_2$O$_3$	479.03	water	$10^{-6} \div 5 \times 10^{-3}$	$10^{-6} \div 10^{-2}$
II-R3B/H$_2$O+HCl	Rhodamine 3B C$_{30}$H$_{35}$Cl N$_2$O$_3$	507.08	water +1% 10n HCl	$5.6 \times 10^{-6} \div 10^{-3}$	$5.6 \times 10^{-6} \div 2 \times 10^{-2}$
III-R3G/H$_2$O+HCl	Rhodamine 3G C$_{25}$H$_{25}$Cl N$_2$O$_3$	437.0	water +1% 10n HCl	$3.1 \times 10^{-6} \div 10^{-3}$	$3.1 \times 10^{-6} \div 10^{-2}$
IV-RS/H$_2$O+HCl	Rhodamine S C$_2$H$_{23}$Cl N$_2$O$_3$	374.88	water +1% 10n HCl	$3.1 \times 10^{-6} \div 10^{-3}$	$3.1 \times 10^{-6} \div 2 \times 10^{-2}$

[a] in which it was assumed that mainly monomers and dimers appear,
[b] in which the systems were investigated.

were separated on a column with silica gel and developed in a chloroform-benzene solution. After having washed rhodamine B, rhodamine 3B was eluted by ethanol. It was crystallized from the chloroform-ether system to chromatographical purity.

Rhodamine 3G of Gurr was dissolved in ethanol and evaporated under vacuum. The remnants were crystalized from the ethanol, ethyl ether, petroleum benzine system to chromatographical purity.

Rhodamine S of Gurr was changed into a free base by the action of an ammonia solution. The precipitate was dried and again changed into a hydrochloride by dissolving it in benzene. Then the hydrochloride was crystallized by vacuum evaporation.

The absorption spectra were measured on a VSU2-P sepctrophotometer under the conditions described formerly [16]. The absorption spectra of monomers $\varepsilon'(\lambda)$ and dimers $\varepsilon''(\lambda)$ were obtained based on the experimental values of the absorption coefficients of solution $\varepsilon^{exp}(c_i, \lambda_j)$ from the entire range of the absorption band and from the concentration range in which the appearance of trimers and associates of higher orders could be neglected. The ranges of the mentioned concentrations for each system are given in column 5 of Table I. The procedure for finding the spectra $\varepsilon'(\lambda)$, $\varepsilon''(\lambda)$ and dimerization constant K by applying the method of least squares, has been described in Ref. [16].

3. Experimental results and discussion

In Fig. 1 we present the electronic absorption spectra of the systems listed in Table I for several concentrations of dye molecules. All the curves for each system pass through the isosbestic points which shows that in the ranges of concentration mentioned[1] there

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[1] Column 5 gives the ranges in which appear mainly monomers and dimers, and column 6 the ranges in which the systems were investigated.
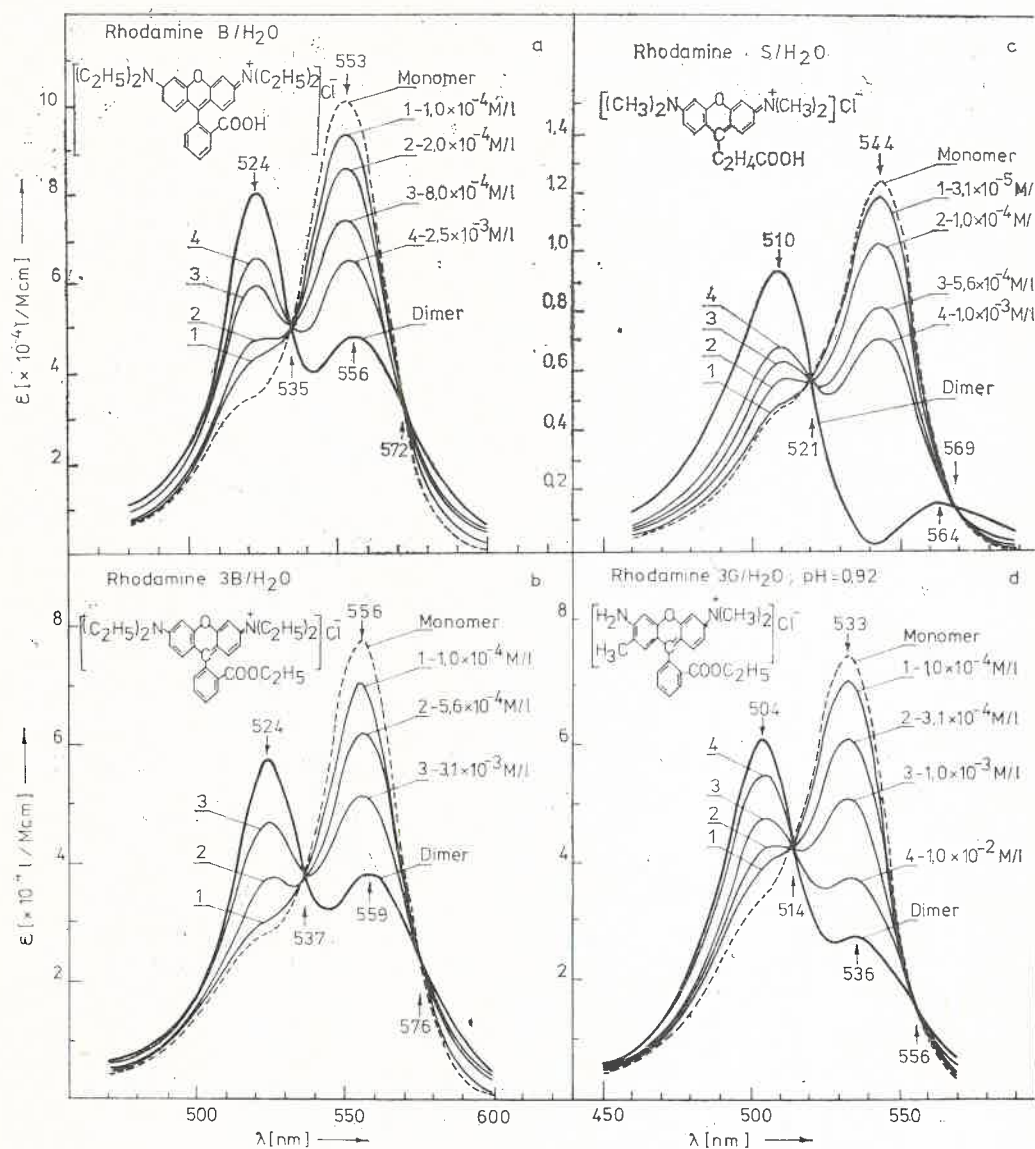
Fig. 1. The absorption spectra of water-solutions of rhodamines for different dye concentrations (concentrations in M/l)

appear mainly monomers D and dimers $D_{/}$. The concentration range in question were also found through measurements of absorption spectra dependencies (corresponding to each particular concentration) on temperature.

In **Fig. 2** are presented the absorption spectra of rhodamine S in water for a higher range of concentration than in Fig. 1. Isosbestic points do not occur here. It can be seen that the monomer maximum at $\lambda = 544$ nm decreases systematically with concentration,

434

whereas the maximum at $\lambda = 510$ nm, corresponding to dimers (Fig. 1) does not increase but shifts systematically towards the shortwave side. This new band, which appears on the shortwave side of the dimer maximum can be ascribed to higher associates. This point
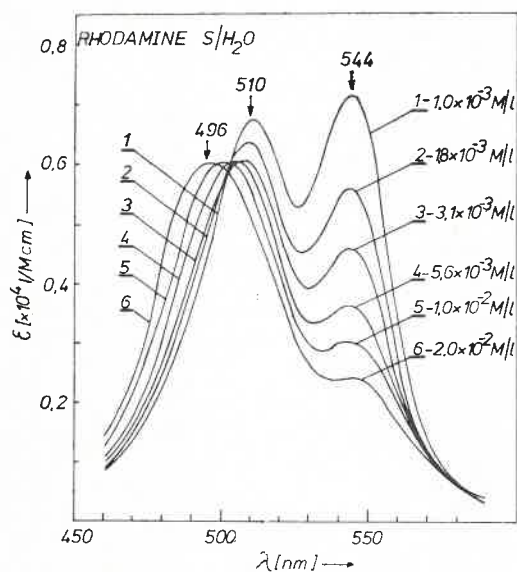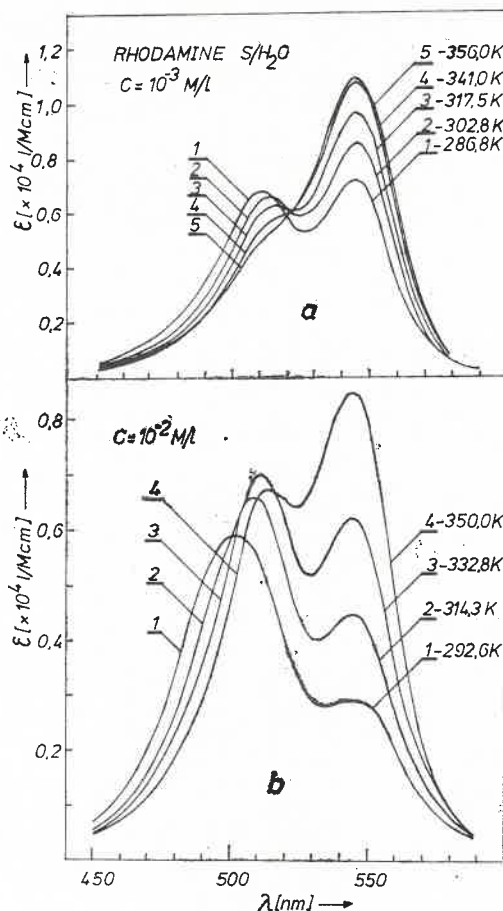

Fig. 2. The electronic absorption spectra of rhodamine S in the range of high concentrations

Fig. 3. The absorption spectra of water solutions of rhodamine S for different temperatures

of view is confirmed by the investigations of the dependence of the absorption spectra on temperature.

Figures 3a and 3b illustrate the change in the absorption spectra with temperature of a solution of concentration $c = 10^{-3}$M/l at which the appearance of higher associates can be neglected, and of a solution of concentration $c = 10^{-2}$M/l. In the latter case isosbestic points do not appear and observed changes in the absorption spectra confirm the presence of higher associates in the solution.

The investigations of the temperature dependence of the absorption spectra of a solution with a fixed concentration allowed the finding of the value of the dimerization constant

for each temperature. This aim has been achieved in the following way. First there was found the dependence of coefficient ratio $\varepsilon(\nu')/\varepsilon(\nu_H)$ corresponding to the maxima of the absorption bands of monomers and the shortwave absorption band of dimers from the fraction x of the monomer molecules in the solutions, based on the family of the absorption spectra obtained at room temperature for different concentrations of solution. Assuming, as in Ref. [17], that the same fraction of monomers in solution correspond to the same value $\varepsilon(\nu')/\varepsilon(\nu_H)$ at temperature changes and at concentration changes of the spectra, the values of x were found and thus value K for different temperatures.

From relation

$$K = A \exp\left(\frac{Q}{RT}\right), \tag{1}$$

where R — gas constant, we have found the binding energy Q of monomer units in the dimer. The found values of K, corresponding to each particular temperature and fixed concentration, lie very well along a straight line in the coordinate system $\left(\ln K, \dfrac{1}{T}\right)$. From the slope of the straight line we found the binding energy Q which amounts to 7.5 kcal/M for the water solution of rhodamine S of concentration 10^{-3} M/l. The binding energy of dimers has been found in the same way for the remaining systems. Values of Q and K have been listed in Table II. We should mention that the binding energy Q was

TABLE II

Comparison of the values of the dimerization constant and binding energy of the rhodamines in solutions

1	2	3	4	5	6
System	K 1/M	T °K	Q kcal/M	C M/l	Ref.
I−RB/H$_2$O	1352	293	—	5×10^{-3} [a]	this work
	1300	298	—	—	[7]
	1000	298	—	—	[20]
	1500	—	—	—	[2]
	1370	303	—	—	[21]
	6010	303	—	—	[22]
	1470	295	—	—	[13]
	—	—	9.9	1×10^{-3}	
	—	—	10.0	4×10^{-3}	[19]
	—	—	10.2	2×10^{-2}	
	—	—	11.2	3×10^{-2}	
II−R3B/H$_2$O + HCl	790	293	5.85	10^{-3} [a]	this work
	700	293	5.17	10^{-3} [a]	[17]
III R3G/H$_2$O pH=0.92	945	293	6.9	10^{-3} [a]	this work
IV RS/H$_2$O + HCl	710	293	7.5	10^{-3} [a]	this work

[a] The maximal value of concentration c from the ranges presented in column 5 of Table I in which a monomer-dimer equilibrium occurs.

found for different concentrations of the dye in the case of each investigated system. There was observed a certain increase in values of Q in the range of higher concentrations, which can be associated with the appearance of higher associates in the solution[2]. However, in the range of the concentrations to which correspond the plots in Fig. 1, those changes were slight. Taking this into consideration as well as the appearance of well determined isosbestic points we could accept that in the concentration ranges given in Fig. 1 mainly monomers and dimers appear in the solutions.

In Fig. 1a are presented the absorption spectra of rhodamine B for different dye concentrations. The measurements were carried out in neutral water solutions in which rhodamine B occurs mainly in the form of a bipolar ion. However, in the range of higher concentrations where the participation of the cation form can be noticeable, both forms still have practically identical absorption spectra [7, 8, 18, 19]. Thus the observed concentrational changes of these spectra cannot be ascribed[3] to the relative concentration changes of ion forms of rhodamine B.

In Fig. 1a we have also presented the pure spectrum of monomers $\varepsilon'(\lambda)$ and dimers $\varepsilon''(\lambda)$. For rhodamine B similarly as for the remaining systems the dimer spectra have two maxima $\varepsilon''_{max\,(H)}$ and $\varepsilon''_{max\,(J)}$ respectively at wavelengths λ smaller and larger than the value of λ corresponding to the maximum of the monomer band ε'_{max}.

The investigation of the absorption spectra of rhodamine B in water at concentration changes was the subject of numerous papers [2, 7, 13, 19–23]. The parameter values characterizng the absorption spectra of rhodamine B in water, found by the quoted authors are close to the results obtained in the present work. It refers particularly to the position of isosbestic points[4] as well as to coefficient values ε'_{max} and $\varepsilon''_{max\,(H)}$. The value of dimerization constant K, obtained by us, is close to the value of K obtained in papers [7, 21]. The binding energy Q was not found in this work. However, for the system of rhodamine B in a glycerin-water solution we obtained formerly [24] value $Q = 10$ kcal/M very close to the value obtained in Ref. [19].

In Fig. 1b there are presented the absorption spectra of rhodamien 3B for several concentrations, as well as the spectra of monomers and dimers. The numerical characteristic of these spectra are closest to the results obtained by Levshin and Baranova [25] who obtained for ε'_{max} and $\varepsilon''_{max\,(H)}$ values 0.8×10^5 l/Mcm and 0.52×10^5 l/Mcm, respectively; the isosbestic points they found at wavelengths 537 nm and 580 nm.

In Fig. 1c and 1d there are presented the absorption spectra of water solutions of rhodamine S and rhodamine 3G. In the case of rhodamine S a big separation of dimer bands $\varepsilon''_{max\,(H)}$ and $\varepsilon''_{max\,(J)}$ draws our attention; as well as a much smaller (almost of one order of magnitude as compared with the remaining systems) value of coefficients ε'_{max} and $\varepsilon''_{max\,(H)}$.

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[2] A similar increase of value Q was found in Refs [17, 16].

[3] In contradistinction to the case of concentrational changes of the absorption spectra of rhodamine B in ethyl alcohol [13, 14].

[4] The positions of the isosbestic points found by Rohatgi and Singhal [21] remarkably differ from the results of other authors. It also refers to the value of $\varepsilon'_{max(H)}$. The reasons for the difference have been discussed in Ref. [13].

We have not found any information in literature concerning rhodamine 3G and rhodamine S in water. The results obtained by us prove that the association properties of water solutions of rhodamine 3G are very close to the analogous properties of water solutions of rhodamine 3B.

Rhodamine S, however, exhibits in the range of high concentrations, exceptionally large deformations of the absorption spectra conditioned by the presence of higher associates in the solution.

The values of the binding energy Q in the case of the investigated systems are contained within the limit $5 \div 10$ kcal/M. It proves that the association of monomer units in a dimer occurs by hydrogen bonds coming into existence either between the dye molecules, in the case when they possess active groups $N-H$, or with the participation of water molecules as was shown in Refs [17, 26, 27].

4. The structure of dimers

The dimer spectra of rhodamines presented in Fig. 1 show a structure appearing as two bands. The maximum of one of them $\varepsilon''_{\max (H)}$ is shifted towards the shortwave side versus the monomer maximum $\varepsilon'_{\max}$; the maximum of the other one $\varepsilon''_{\max (J)}$ occurs on the longwave side of $\varepsilon'_{\max}$.

The relative intensities of these bands as well as the dimer band splitting into components can be explained by the theory of molecular excitons developed for interactions
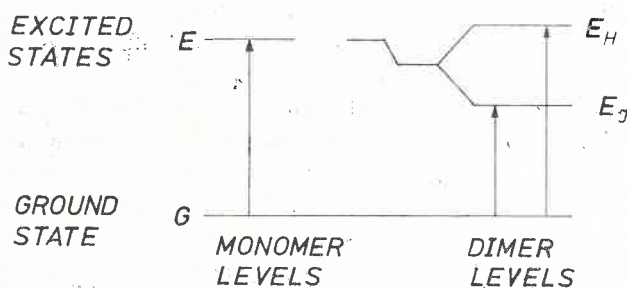

Fig. 4. Electronic energy levels diagram for a monomer and dimer

among chromophors of monomer units in a dimer [28–30]. Optical transitions between the energy levels presented in Fig. 4 correspond to the mentioned dimer as well as the monomer bands. Knowing the pure spectra of a monomer and dimer we can obtain certain information as to the structure of the dimer by regarding its simpler models.

For the explanation of the dimer band splitting in the case of dye molecules two models allowing transitions $E_H \leftarrow G$ i $E_J \leftarrow G$ [31, 32] were accepted. The schemes of these models are presented in Fig. 5. The arrows denote the transition dipole moments in the monomer molecules and α is the angle between the transition dipoles in the dimer; ϑ is the angle between the transition dipoles and the line connecting the centres of molecules separated by a distance R. Rig. 5a presents a parallel plane twist angle model and Fig. 5b —

an in-plane oblique angle model. In order to find the intermolecular distance R and angle α between the monomer units in the dimer we shall apply model a. It is the simplest model allowing for the existence of band H with a larger intensity than band J in the dimer spectrum which corresponds qualitatively to experimental results obtained in this work.
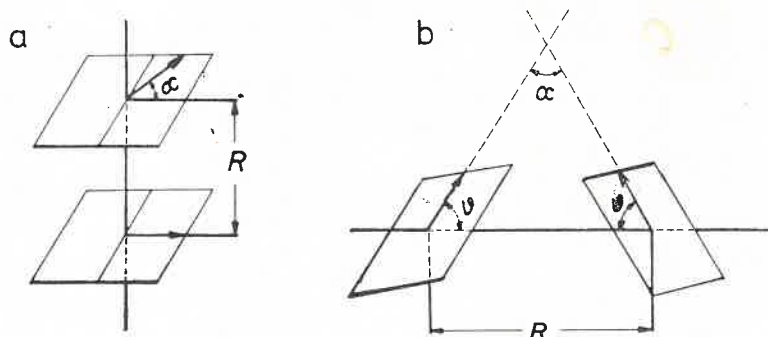

Fig. 5. Schematic diagrams of dimer models: a — parallel plane dimer model; b — oblique plane dimer model

Besides, the plain parallel dimer model corresponds to the most stable configuration of the approximate planar dye molecules.

In the dipole-dipole approximation the magnitude of exciton splitting is given by [33]:

$$\Delta v = \frac{2|\vec{M}|^2 \cos \alpha}{hcR^3} = \frac{2D \cos \alpha}{hcR^3} , \tag{2}$$

where $\vec{M}$ is the transition moment for the singlet-singlet transition in the monomer and D — the dipole strength. The square of the transition moment $\vec{M}$ is a measure of the oscillator strength f for the transition. Thus the "dipole strength" is related to the oscillator strength by:

$$D = \frac{3he^2}{8\pi^2mc} \frac{f}{v} = 1.07 \times 10^{-14} \frac{hcf}{v} \, [\text{erg cm}^3], \tag{3}$$

where m is the electron mass and e the electron charge. The oscillator strength has been found by integrating the molar absorption coefficient $\varepsilon'(v)$ over the monomer band

$$f = 4.32 \times 10^{-9} \int_{\text{band}} \varepsilon'(v) dv \tag{4}$$

[numerical factor in (4) is expressed in cm² Ml⁻¹]. Angle α can be computed from relation [29, 31]

$$2D_H = D(1 + \cos \alpha), \quad 2D_J = D(1 + \cos \alpha) \tag{5}$$

where D_H, D_J and D are "the dipole strengths" of the transition for energy levels E_H, E_J and E, respectively. The factors "2" in Eq. (5) appeared because $\varepsilon''(v)$ was expressed per

monomer unit [cf. Eq. (8)]. According to (3) the dipole strengths are proportional to the appropriate oscillator strengths. Hence

$$\mathrm{tg}^2 \frac{\alpha}{2} = \frac{f_J \nu_H}{f_H \nu_J},$$

(6)

where f_J and f_H are oscillator strengths for the J and H bands in the dimer spectrum and ν_J and ν_H are maximum positions of these bands.
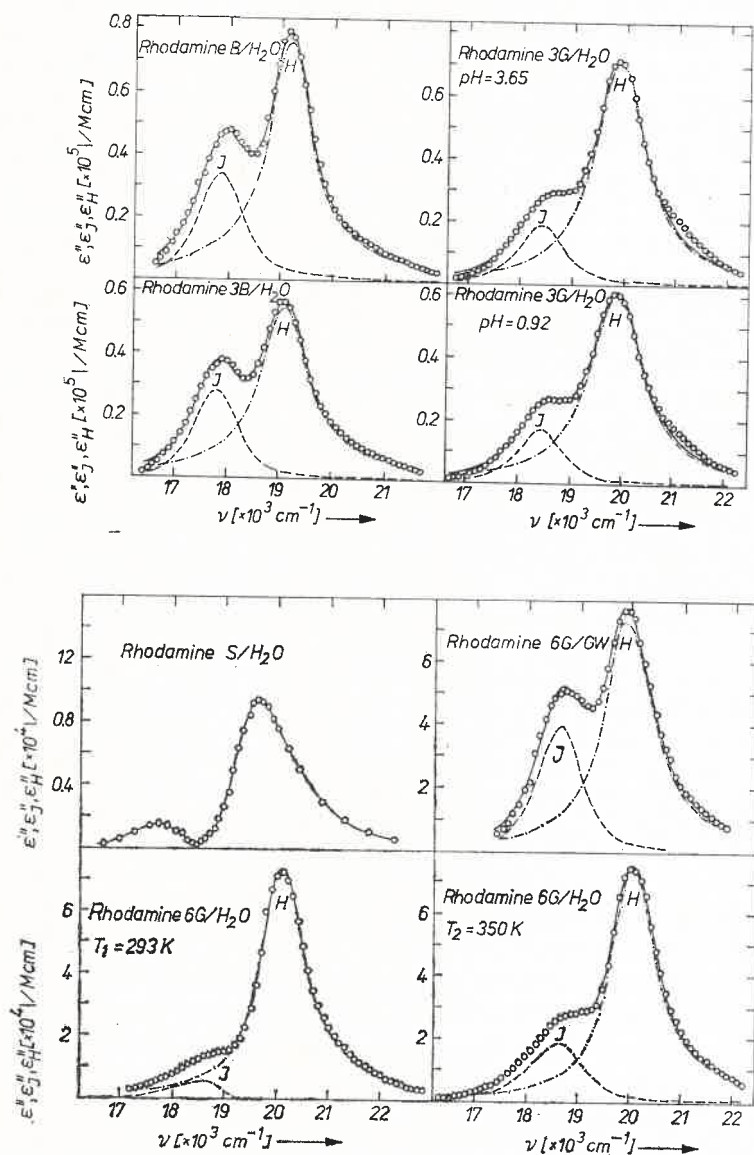

Fig. 6. Rhodamines dimer spectra and their separations into H and J bands

The intermolecular distance R can be computed from Eq. (2). Taking (3) into account one obtains:

$$R = \left(\frac{2.14 \times 10^{10} f \cos \alpha}{\nu \Delta \nu}\right)^{1/3} \text{[Å]}. \tag{7}$$

Finding angle α on the basis of (6) requires first a computation of the value of the oscillator strengths f_J and f_H. In order to achieve it we have decomposed the dimer spectrum into component bands ε_J'' and ε_H'' applying the procedure worked out by Stone [34] which leads to the applying of the method of least squares to nonlinear functions[5] and finding the best fit of the curve computed to the experimental curve by the way of successive iterations.

Fig. 6 presents the dimer spectra and their decompositions for rhodamines listed in Table III. Circles mark the experimental spectra of dimers and solid and dashed lines — approximated by the linear combination of the Gauss and Cauchy function — dimer spectra and component bands H and J, respectively.

TABLE III

Spectral peak positions for monomer and dimer molecules and splitting $\Delta \nu$ computed according to (2)

1. System	2. ν' cm^{-1}	3. ν_H cm^{-1}	4. ν_J cm^{-1}	5. $\Delta\nu - \nu_H - \nu_J$ cm^{-1}	6. $\Delta\nu'$ [b] cm^{-1}
I — RB/H$_2$O	18080	19140	17840	1300	1100
II — R3B/H$_2$O	18000	19100	17800	1300	1100
III — R3G/H$_2$O, pH = 0.92	18760	19860	18440	1420	1380
III' — R3G/H$_2$O, pH = 3.65	18720	19820	18380	1440	1420
IV — RS/H$_2$O	17620	19630	17720	1910	1180
V — R6G/H$_2$O, T_1 = 293 K	19020	20100	18600	1500	1240
V' — R6G/H$_2$O, T_2 = 350 K	19000	20040	18660	1380	1320
VI — R6G/GW[a], η = 1.7 poise	18760	19840	18620	1220	1090

[a] GW-glycerin-water solutions,
[b] half width of monomer band.

In all the investigated cases we observe strong H bands and relatively weak J bands. In Table III there are listed the values of wave numbers determining the position of the maxima of the monomer band, the dimer bands H and J as well as the values of exciton splitting $\Delta \nu$. In column 6 for comparison, are given the values of the half width $\Delta \nu'$ of

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[5] Similarly as in Ref. [35] we assumed that spectra $\varepsilon''(\nu)$, $\varepsilon_J''(\nu)$ and $\varepsilon_H''(\nu)$ can be approximated by a linear combination of Gauss and Cauchy functions.

the monomer band. Values Δv surpass $\Delta v'$ for all the investigated sytems[6] so these systems correspond to the strong coupling case where vibronic interactions can be neglected.

In Table IV we listed the values of the oscillator strengths f, f_H and f_J of the monomer band as well as those of bands H and J and the values of the computed structural parameters

TABLE IV

Oscillator strengths of the monomer band and of dimer bands H and J and the values of the computed structural parameters of dimer

1	2	3	4	5[a]	6[b]	7[a]	8[b]	9	10	11	12
System	f	f_H	f_J	ε_H'' x10^{5}l/Mcm		ε_J'' x10^{5}l/Mcm		α deg			R Å
I – RB/H$_2$O	0.657	0.541	0.200	0.763	0.800	0.340	0.480	64.4	67.4	75.5	6.4
II – R3B/H$_2$O	0.550	0.407	0.153	0.547	0.575	0.283	0.377	64.8	71.4	78.0	6.0
III – R3G/H$_2$O, pH = 0.92	0.586	0.461	0.088	0.610	0.610	0.170	0.270	48.8	55.7	67.3	6.7
III' – R3G/H$_2$O, pH = 3,65	0.554	0.531	0.095	0.717	0.718	0.190	0.293	47.4	54.5	65.1	6.8
IV – RS/H$_2$O	0.087	0.066	0.008	0.094	0.094	0.016	0.016	40.2	44.3	44.3	3.5
IV' – R6G/H$_2$O, T_1 = 293 K	0.605	0.562	0.027	0.747	0.730	0.057	0.141	25.6	30.8	47.5	7.4
V' – R6G/H$_2$O, T_2 = 350 K	0.600	0.507	0.116	0.740	0.753	0.170	0.270	52.7	51.2	61.8	6.7
VI – R6G/GW, η = 1.7 poise	0.587	0.513	0.225	0.730	0.773	0.410	0.510	68.7	73.7	78.2	5.8

[a,b] The values of the maxima of bands H and J in the case of a separated and not separated dimer spectrum $\varepsilon''(v)$. The values α in column 9 computed from relation (6); in columns 10, and 11 on the basis of (6') for the values ε_H'', ε_J'' from columns 5, 7 and 6, 8.

α and R for dimers. In the Table IV there are also given the values of the maxima of bands H and J found after the decomposition of the dimer spectrum into component bands (columns 5 and 7) and those found directly from the dimer spectra (columns 6 and 8). In column 9 the values of angles computed from relation (6) have been listed, and in columns 10 and 11 — those found from the relation [21]

$$\text{tg}^2 \frac{\alpha}{2} = \frac{f_J}{f_H} \approx \frac{\varepsilon_J''}{\varepsilon_H''}. \tag{6'}$$

Values α from column 10 were obtained on the grounds of the values ε_J'' and ε_H'' from columns 5 and 7 and values α listed in column 11 on the basis of the data from columns 6 and 8. It can be seen that the approximated Eq. (6') gives values α much higher than Eq. (6) (cf. columns 10, 11 and 9) first of all when for ε_H'' and ε_J'' were taken the values for the not decomposed dimer spectrum. It is understandable that the approximation of the ratio of the oscillator strengths f_J/f_H by $\varepsilon_J''/\varepsilon_H''$ is a rough approximation on account of a much bigger relative half width of J band as compared with H band (cf. Fig. 6). Besides,

[6] In Table III there are also given the suitable data for rhodamine 6G whose spectral properties we investigated formerly [16].

on account of a partial overlapping of bands H and J mainly in the region of H band the values $\varepsilon''_{max\,(H)}$ of the separated H bands are much lower than the analogous values found from the not decomposed dimer spectrum. Values $\varepsilon''_{max\,(J)}$ are, in fact, unchanged in both cases.

The obtained value α for the system RB/H$_2$O is remarkably higher than the value 52° obtained in Ref. [21] for the reason that angle α was found on the grounds of an approximated formula (6′) giving values of α which were too large. However, the intermolecular distance R turned out to be slightly smaller than in Ref. [21] where for R they obtained the value 8.3 Å.

Also the strong hypochromic effect connected with dimerization observed in the cited reference for the system RB/H$_2$O has not been confirmed.
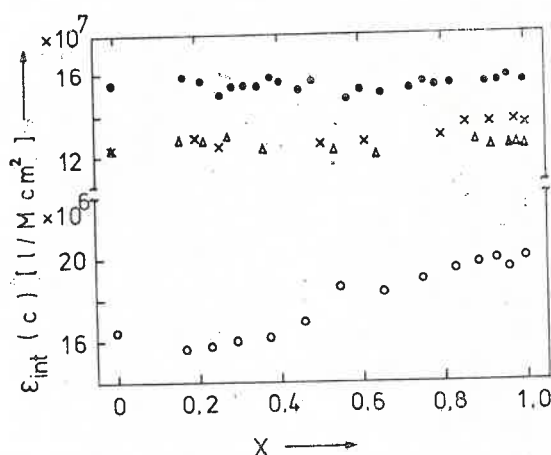

Fig. 7. Dependence of integrated absorption coefficient ε_{int} (c) vs the fraction x of monomer in solution: ● — RB/H$_2$O; × — R3G/H$_2$O, pH — 0.92; △ — R3B/H$_2$O; ○ — RS/H$_2$O

In Fig. 7 we present the dependence of the integrated absorption coefficient vs the monomer fraction x in solution[7]. Similar dependencies are presented for the remaining systems from Table I. For the system RB/H$_2$O $\varepsilon_{int}(c)$ is in fact constant for the entire range of changes x and thus concentration c.

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[7] The absorption coefficient of solution $\varepsilon(\nu, c)$ for the wave number ν and concentration c can be presented as:

$$\varepsilon(\nu, c) = \varepsilon'(\nu)x + \varepsilon''(\nu)(1-x). \tag{8}$$

After integrating (8) over ν we obtain

$$\varepsilon_{int}(c) = (\varepsilon'_{int} - \varepsilon''_{int})x + \varepsilon''_{int}, \tag{8'}$$

where

$$\varepsilon_{int}(c) = \int \varepsilon(\nu, c)\, d\nu.$$

The dimer molar extinction coefficient $\varepsilon''(\nu)$ in expressed here per monomer unit.

As it results from (8') it is possible in the case when $\varepsilon'_{int} = \varepsilon''_{int}$. Values $\varepsilon_{int}(c)$ for $x = 0$ and $x = 1$ corresponding to ε''_{int} and ε_{int} are also marked in the figure. A slight hypochromic effect is observed for the system R3B/H$_2$O and a slightly bigger one for the system RS/H$_2$O.

We have also investigated the influence of pH on the structure of the dimer of rhodamine 3G in water. Pure absorption spectra of dimers and monomers for two different values of pH are presented in Fig. 8. These spectra differ slightly which results in a slight
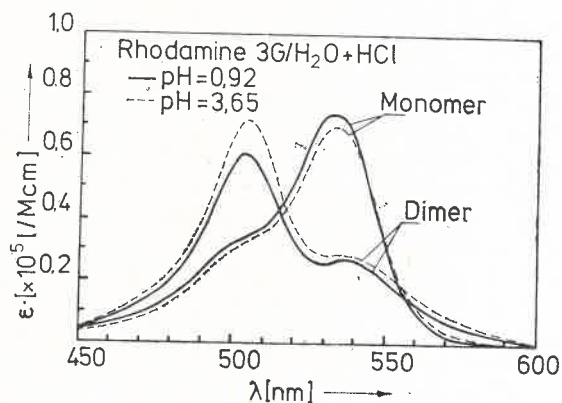

Fig. 8. The absorption spectra of monomers and dimers of rhodamine 3G in water for different values of pH

difference of the structural parameters value α and R (cf. Table IV). However, the values of the dimerization constant K and binding energy Q at a larger value of pH are noticeably lower[8]. The direction of those changes is the same as in Ref. [32] and proves that an ionized molecule has a less stable dimer state than a neutral molecule.

Knowledge of the pure spectrum of a dimer and monomer allows one to obtain certain information as to the structure of a dimer on the basis of a very simple model. Still, in the cases when the absorption spectra have a more complex structure [8, 15] the simple theory of molecular exciton is not sufficient to its explanation.

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[8] At pH = 3.65 we obtained $K = 460$ l/M and $Q = 6.1$ kcal/M but at pH = 0.92 values K and Q amount to 945 l/M and 6.9 kcal/M, respectively.

444

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