The aqueous-polyelectrolyte dye solution as an active laser medium

A I Akimov, A M Saletskii

Abstract. The spectral, luminescent, and lasing properties of aqueous solutions of a cationic dye rhodamine 6G with additions of anion polyelectrolytes – polyacrylic and polymethacrylic acids – are studied. It is found that the energy and spectral properties of lasing of these solutions depend on the ratio of concentrations of polyelectrolyte and dye molecules. It is also found that the lasing parameters of aqueous-polyelectrolyte dye solutions can be controlled by changing the structure of the molecular system. The variation in the structure of aqueous-polyelectrolyte solutions of rhodamine 6G resulted in an almost five-fold increase in the lasing efficiency compared to that in aqueous dye solutions.

1. Introduction

It is known that the spectral and luminescent properties of organic compounds and, hence, their lasing properties substantially depend on a solvent. The probability of intersystem crossing to the triplet state in dye molecules, the efficiency of association and photochemical transformations of dyes, and the probability of energy transfer between dye molecules change depending on the solvent [1].

The ethanol solutions of dyes are most often used as liquid active media. However, along with a high lasing efficiency, these solutions have high induced optical inhomogeneities, which results in the deterioration of their lasing properties. Water used as a solvent possesses a number of advantages over organic solvents, in particular, because of its low thermooptical losses. However, purely aqueous solutions of dyes have not received wide acceptance because of the efficient association of dye molecules in them. It is because of the loss caused by dye associates that the lasing efficiency of aqueous solutions of dyes is low [2].

Many studies of different authors have been devoted to the development of active laser media with the low efficiency of dye aggregation. Thus, to decrease the degree of dimerisation, a detergent was added to the solution [3] or polymer systems were used [4]. The solid polymer matrices doped with dye molecules have received wide acceptance as active elements for lasers [5]. However, the presence of optical inho-

mogeneities and photochemical and mechanical instability of polymer elements represent their substantial drawback.

The use of aqueous-polyelectrolyte solutions of ionic dyes as active laser media is promising. By varying the dye and polyelectrolyte concentrations in such systems, one can change the distance between active dye molecules adsorbed on polyion macromolecules. As the distance between such adsorbed monomer molecules is increased, the interaction between them strongly weakens, resulting in a decrease in the degree of aggregation of dye molecules, thereby increasing the lasing efficiency [6, 7].

In this paper, we present the results of our study of spectral, luminescent, and lasing properties of aqueous-polyelectrolyte solutions of rhodamine 6G (R6G).

2. Experimental

We studied lasing of dye solutions in a laser consisting of a nonselective cavity with plane mirrors with reflection coefficients $r_1 \approx 100\%$ and $r_2 \approx 68\%$ and a cell with the cross section 1×1 cm. The transverse pumping scheme was used. The dye solutions were excited by the second harmonic of a ruby laser at 347 nm. The pump energy was $E_0 = 50-70$ mJ and the pump pulse duration was ~ 25 ns. The lasing spectra were detected with an ISP-51 prism spectrograph on photographic plates. The output energy was measured with a thermocouple power meter.

The luminescence spectra of dye solutions were detected with a laser spectrofluorimeter consisting of an LG106M argon laser, an MDR-6 monochromator, and a FEU-79 photomultimlier operating in the photon counting mode. The absorption spectra were recorded using a Specord M-40 spectrophotometer.

We used in our experiments polyelectrolytes (PEs) of polyacrylic (PAA) and polymethacrylic (PMAA) acids, the rhodamine 6G dye of the DKE type, and doubly distilled water. The initial concentration of the dye in solution was chosen close to the optimal one for pumping to produce lasing.

In solutions with the constant dye concentration and different concentrations of polyacids (PAs), the ratio of the concentrations $n = C_{PE}/C_{R6G}$ determines the number of monomer chains of the PA macromolecule per one dye molecule.

3. Results

The absorption and luminescence spectra, as well as lasing parameters of aqueous solutions of the dye exhibited considerable variations in the concentration range $C_{PAA} =$

A I Akimov, A M Saletskii Department of Physics, M V Lomonosov Moscow State University, Vorob'evy Gory, 119899 Moscow, Russia

$3 \times 10^{-5} - 3 \times 10^{-1}$, which depended on the amount of PA added to the solution. These variations were caused by changes in the solution structure, which in turn depended on the relative concentration n.

The addition of PA into aqueous solutions of dyes causes specific variations in their absorption spectra. The deformation of the absorption spectrum observed in this case is typical for processes of association of molecules [1]. We will estimate the deformation of the spectrum from the ratio D_d/D_m of optical densities at the absorption maxima of the short-wavelength (D_d) and long-wavelength (D_m) bands. Fig. 1 (curve 1) shows the dependence of such deformations on the ratio of concentrations of PAA and R6G molecules, as well as the dependences of the relative luminescence intensity (curve 2) and position of the maximum of the luminescence spectrum of R6G on n (curve 3). One can see from Fig. 1 that three regions of relative concentrations, $n \leqslant 2$ (I), $2 < n < 50$ (II), and $n > 50 - 100$ (III), can be distinguished according to the type of deformations observed in the spectra. Consider the spectral, luminescence, and lasing properties of solutions in these concentration intervals.
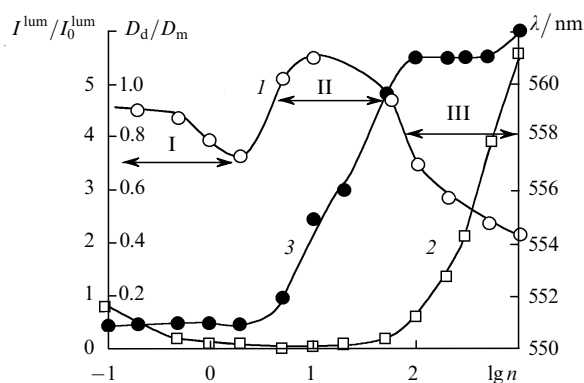

Figure 1. The ratio D_d/D_m (1), the relative luminescence intensity I^{lum}/I_0^{lum} (2), and the wavelength λ (3) of the maximum of the luminescence spectrum of R6G as functions of the relative concentration n.

3.1. Region of low relative concentrations $n \leqslant 2$

The wavelengths 526 and 501 nm of the maxima of absorption bands of R6G in the spectra of solutions containing PAA coincide with the wavelengths of these bands in the spectrum of the aqueous solution of R6G. As the concentration n increases, the intensity of the short-wavelength (dimer) absorption band decreases compared to that of the long-wavelength absorption band. This suggests that the degree of association of dye molecules decreases (curve 1 in Fig. 1).

Such spectral variations mean that when the amount of PA increases in the region $n \leqslant 2$, the dye concentration in the liquid phase of the solution decreases because a fraction of dye molecules form insoluble complexes with PE. These complexes are formed due to the interaction of dye cations with ionised carboxyl groups $-COO^-$ of polyacid. The formation of complexes in not observed at concentrations $C_{PAA} \leqslant 6 \times 10^{-5}$ mol l^{-1} ($n \leqslant 0.2$) when a fraction of the dye removed from the solution is small.

Upon addition of PA in small amounts, when $n < 1$, the luminescence intensity of R6G rapidly decreases (curve 2 in Fig. 1). This decrease is caused by the reduction in the absolute concentration of the dye in a liquid phase and by

electronic energy transfer from R6G monomer molecules remaining in the liquid phase of the solution not only to its dimers in the solution but also to nonluminescent dimers in dye-polymer complexes.

The processes proceeding in this concentration interval can be described in the following way. In the region of low relative concentrations ($n < 1$), the absolute concentrations of PA in solution are low ($C_{PAA} < 3 \times 10^{-4}$ mol l^{-1}) and, hence, the degree of ionisation of its ionogen groups is great. This means that dye molecules adsorbed on these groups are located close to each other, which results in their dimerisation. The complexes formed represent long-chain polymer PA molecules with dye dimers attached to ionogen sites.

Upon further addition of PA, complexes are formed. As a result, as shown in Fig. 1 (curve 2), the luminescence intensity continues to decrease, and luminescence becomes in fact completely quenched in solutions with relative concentrations $n = 5$ and 10.

Therefore, the decrease in the luminescence intensity with increasing concentration of PA in solution can be explained both by a decrease in the number of emitting monomer dye molecules in the liquid phase of the solution and by relaxation of the excitation energy of monomers due to losses on dye dimers in the solution and in complexes, as well as on their aggregates existing in the solution.

The lasing spectra of aqueous solutions of R6G with additions of PEs exhibit two bands (Fig. 2). Their intensity depends on the amount of PE added to the dye solution.
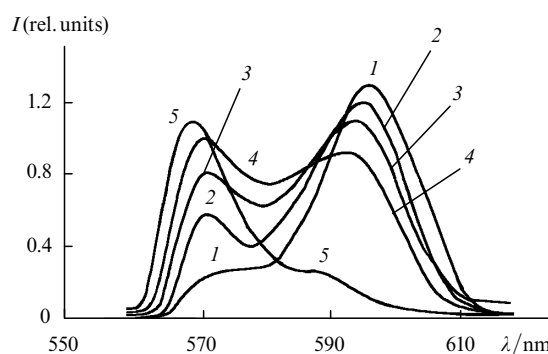

Figure 2. Lasing spectra of aqueous-polyelectrolyte solutions for $n = 0$ (1), 0.2 (2), 0.5 (3), 1 (4), 2 (5) and $C_{R6G} = 3 \times 10^{-4}$ mol l^{-1}.

One can see from Fig. 2 that the increase in the PAA concentration reduces the intensity of the long-wavelength (dimer) lasing band almost to zero at $n = 2$, whereas the intensity of the short-wavelength (monomer) lasing band increases.

These variations in the lasing spectra are caused by the decrease in the dye concentration in the liquid phase of the solution resulting in the increase in the fraction of monomer molecules compared to that of dimers. The latter circumstance causes the redistribution of the emission intensity in the lasing spectrum in favour of the short-wavelength monomer band (spectrum 5 in Fig. 2).

3.2. Variations in the absorption, luminescence, and lasing spectra in the region of relative concentrations $2 < n < 50$

The region of relative concentrations $2 < n < 10 - 50$ is an intermediate region where the passage to a new phase state of the aqueous-polyelectrolyte dye solution occurs. Varia-

tions in the structure of the solutions are accompanied, as one can see from Fig. 1, by an abrupt change in the deformations in the absorption spectrum, which means the increase in the concentration of dye dimers compared to the concentration of monomers. This probably occurs due to the enhancement of dimerisation of PE – R6G molecular complexes, which make the additional contribution to the absorption spectrum in such a way that the intensity of the short-wavelength (dimer) absorption band increases stronger than that of the long-wavelength (monomer) band.

Simultaneously with variations in the intensities of the absorption bands, an abrupt red shift of the luminescence spectrum is observed (curve *3* in Fig. 1), as well as the long-wavelength broadening of the absorption spectra, which is especially pronounced for solutions with $n = 10$. These variations in the spectra suggest that the solution structure drastically changes.

Because the distance between R6G dimers adsorbed on a polymer chain increases, their decay begins to play a significant role so that the number of adsorbed R6G monomers increases. This is accompanied by the redistribution of the intensities between the short-wavelength (dimer) and long-wavelength (monomer) absorption bands, as one can see from the change in the type of deformation in the absorption spectrum for $n > 10$ (Fig. 1).

The increasing absorption of dimers in the intermediate region of relative concentrations and the corresponding increase in the electronic energy relaxation caused by energy transfer to nonluminescent complexes and their aggregates result in the virtually complete luminescence quenching (curve *2* in Fig. 1) and complete suppression of lasing of the solutions (curves *1* and *2* in Fig. 3).
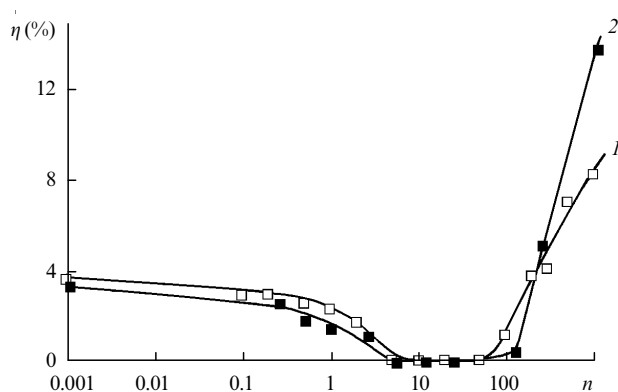

Figure 3. Lasing efficiency η of aqueous solutions of R6G with additions of PAA (*1*) and PMAA (*2*) at $C_{R6G} = 3 \times 10^{-4}\,\text{mol}\,l^{-1}$ as a function of n.

Thus, the region of relative concentrations $n \leqslant 50$ is of no practical interest for obtaining efficient lasing.

3.3. Variations in the absorption, luminescence, and lasing spectra in the region of relative concentrations $n > 50 - 100$

A further addition of PA into the solution and the passage to the third concentration region (Fig. 1) cause the inverse effect: the solution structure changes again. The aggregate precipitation formed earlier dissolves completely in the excess PA, the solution becomes homogeneous, and strong scattering of light disappears. The variations in the phase composition of the solution are accompanied by substantial changes in the absorption, luminescence, and lasing spectra.

One can see from Fig. 1 that the direction of deformations in the absorption spectra drastically changes in the interval $n = 50 - 100$. This means that because of the structural transformation of the solution, the formation of adsorbed dye dimers gave way to the process of their gradual decay with the formation of adsorbed monomers. As the number of polymer molecules in the solution further increases, when $n > 100$, the number of monomer dye molecules adsorbed on the polymer also increases, while the number of dimers decreases correspondingly.

The increase in the number of monomer dye molecules adsorbed on the polymer chain of PA results in the restoration of luminescence of solutions on passing from low concentrations $n \leqslant 1 - 2$ to high concentrations $n > 50 - 100$. The luminescence intensity becomes finally substantially greater than its initial intensity, which is typical of aqueous solutions of the dye. The corresponding variations in the luminescence intensity are shown in Fig. 1 (curve *2*).

The luminescence intensity of the solution with $n = 1000$ was 5.5 times greater than that of the solution without PAA and $400 - 800$ times greater than that of the solution with $n = 5 - 10$, where the luminescence was almost completely quenched.

After the formation of a new phase state in the solution for $n \geqslant 100$, the shift of the luminescence spectrum was terminated (curve *3* in Fig. 1). The maximum of the luminescence band proved to be shifted by 10 nm compared to its position in the aqueous solution of R6G ($\lambda \approx 551$ nm).

The shift of the luminescence spectrum in passing from the region of low concentrations to the region of high concentrations of PE ($n \geqslant 100$) shows that the energy state of emitting monomer dye molecules changes compared to their state in the aqueous solution. The spectral shift observed in the region of relative concentrations $1 - 2 < n < 50$ results from the overlap of the luminescence spectra of monomers in solution and the spectra of adsorbed monomers and depends on the relation between amounts of these monomers.

When more than $50 - 100$ elementary units of PA correspond to a single dye molecule, adsorbed R6G molecules prove to be widely separated and the energy of interaction between them decreases. In this case, the concentration of adsorbed monomers increases due to the partial decomposition of adsorbed dye dimers. The decrease in the number of dimers is accompanied by a decrease in the loss of the excitation energy on them. This occurs due to a decrease in the inactive absorption and in losses related to energy transfer from excited adsorbed monomers to dimers. This facilitates the luminescence rise and lasing becomes possible.

One can see from Fig. 3 (curve *1*) that the increase in the PAA concentration in solution up to $n = 50 - 100$ results in lasing. The lasing intensity is close to the threshold one and is limited both by the low concentration of adsorbed monomers and losses on nondissociated R6G dimers. A further increase in the PA concentration ($n > 100$) is accompanied by the corresponding increase in the number of adsorbed dye monomers and by the simultaneous decrease in the number of R6G dimers in the polymer chain caused by their further dissociation. This process is accompanied by the reduction of the radiative and nonradiative losses, which further enhances the intensity of luminescence (curve *2* in Fig. 1) and lasing (curves *1* and *2* in Fig. 3) of the solutions.
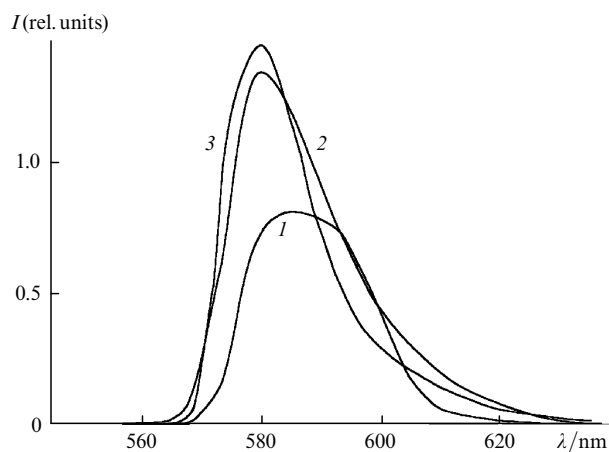
I (rel. units)

Figure 4. Lasing spectra of aqueous solutions of R6G with the addition of PAA for $n = 100$ (*1*), 300 (*2*), and 500 (*3*).

η (%)

Figure 5. Lasing efficiency of the aqueous solution of R6G with the addition of PMAA as a function of the R6G concentration for $n = 1450$.

The lasing spectra of R6G molecules adsorbed on PA macromolecules at $n > 100$ (Fig. 4) substantially differ from those obtained at low ($n < 1$) concentrations of PA (Fig. 2). Instead of the two lasing bands observed for $n < 1$, the lasing spectrum observed at $n > 100$ exhibits one band, which is related to R6G monomers adsorbed on PA macromolecules (this concerns both PAA and PMAA).

One can see from Fig. 4 that the lasing spectrum shifts to the blue with increasing n and, hence, with increasing distance between adsorbed monomer dye molecules. However, even for $n \geqslant 100$, lasing occurs at a considerably longer wavelength ($\lambda_{max} = 579$ nm for $n = 500$) than lasing of the strongly diluted aqueous solution of R6G monomers ($\lambda_{max} \approx 568$ nm). The shift of the lasing spectrum of R6G monomers adsorbed on PAA relative to the lasing spectrum in the aqueous solution is $\Delta\lambda_{las} \approx 10$ nm. This shift is caused by the red shift $\Delta\lambda_{lum} = 10$ nm of the luminescence spectrum, which almost coincides with the shift of the lasing spectrum.

The properties of the absorption, luminescence, and lasing spectra of aqueous solutions of the R6G dye with additions of PAA are also typical for the solutions containing PMAA. However, these PAs differently affect the lasing efficiency of R6G in aqueous solution. Fig. 3 compares the dependences of the lasing efficiency of R6G solutions on n for these two PAs (curves *1* and *2*).

One can see from Fig. 3 that the first two of the concentration regions considered above (when $n < 50 - 100$) are of no interest from the point of view of the practical use of the corresponding solutions as active media because the lasing efficiency in the first region is lower than that in the aqueous solution, whereas in the second region no lasing observed. Of practical interest is only the third region of relative concentrations in which n is substantially greater than 100. Thus, one can see from Fig. 3 that the lasing efficiency at $n \sim 1000$ increases by a factor of 2.3 after the addition of PAA and by a factor of 4.5 after the addition of PMAA compared to the lasing efficiency of the aqueous solution without PA. By adding PMAA at the optimal concentration, the lasing efficiency of the aqueous solution of R6G can be further increased.

One can see from Fig. 5 that the lasing efficiency η of the aqueous solution of R6G with the addition of PMAA at $n = 1450$ is 20.4 %. This value is close to the lasing efficiency $\eta = 22$ % of the ethanol solution of R6G [8] pumped at 347 nm into its secon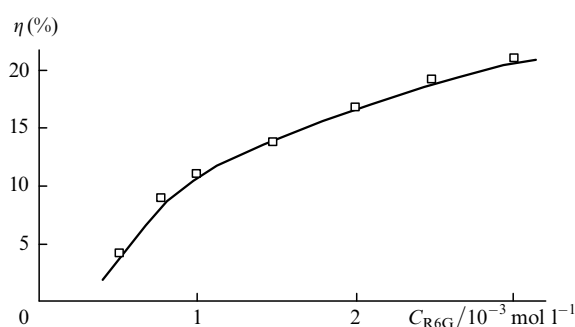d absorption band. It is obvious that pumping into the main absorption band will provide a further increase in the lasing efficiency.

4. Conclusions

Our studies showed that by varying the ratio $n = C_{PE}/C_{R6G}$ of concentrations of PE and R6G in the aqueous solution and thereby changing the dye structure, we can control the spectral, luminescent, and lasing properties of the solution. When the PE concentration is low, the distance between the adsorbed dye molecules is small (of the order of 5 Å) and their strong interaction results in the formation of associates. The associates strongly absorb the pump radiation, resulting in the luminescence quenching and an increase in the lasing threshold.

Such dye solutions have a low lasing efficiency. As the PE concentration increases, the number of charged segments, which has no dye molecules attached to them, increases. This leads to the increase in the distance between adsorbed R6G molecules, resulting in the dissociation of associates and increase in the number of adsorbed R6G monomers. The increase in the number of R6G monomers causes the luminescence rise, thereby enhancing the lasing efficiency.

Therefore, changing the arrangement of dye molecules on the polymer chain by varying the relative concentration n, one can control the energy and spectral parameters of lasing and obtain the high lasing efficiency in aqueous solutions of the dye. The maximum lasing efficiency of aqueous solutions of R6G was achieved for $n > 100$. The variation of n in this region resulted in the change in the lasing efficiency from ~ 4 to ~ 20 %. This change was accompanied by the red shift of the lasing spectrum and its broadening. This method for controlling the lasing efficiency allowed us to obtain the record lasing efficiency for the aqueous solution of the dye (upon pumping into the second absorption band of the dye), which is close to that for the ethanol solution [8].

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