

Fig. 3. Relative location of the absorption spectra of (1) silver NPs, (2) R6G, and (3) fluorescence of the dye in aqueous solution.

cles are added into the solution of the dye ($C = 10^{-5}$ mol/L). Similar dependences are observed for aqueous alcohol solutions (curves 2–5). They differ from aqueous solution and from one another in that the concentration of silver NPs at which the absorption maximum of the dye is observed is shifted toward lower values as the proportion of alcohol in the solution rises.

This increase of the optical density of the dye's absorption spectrum is due to the effect of the NPs electromagnetic field. The excitation of numerous plasmons in the particle results in efficient light scattering and the formation of an enhanced electromagnetic field near the surfaces of NPs. Scattered light can be reabsorbed by the molecules of R6G [9], and the overlap of the SPR absorption bands of silver NPs and R6G promote this reabsorption (Fig. 3), substantially increasing the amount of light absorbed by the system as a whole. A drop in the optical density of R6G in the presence of silver nanoparticles was also observed in [10].

The fluorescence of the dye undergoes similar changes upon changing the ratios of water and alcohol (Fig. 5): with an increase in the volume fraction of alcohol, the bend point is shifted toward lower concentrations of silver nanoparticles. According to [11, 12], the reason for the enhanced fluorescence of the molecules near metal NPs is an increase of the rate of fluorescence excitation due to localized plasmon resonance. At the same time, when the molecules are near the metal or in contact with it, nonradiative energy is transferred from the molecules to the NPs, reducing the probability of radiative decay of the excited molecules.

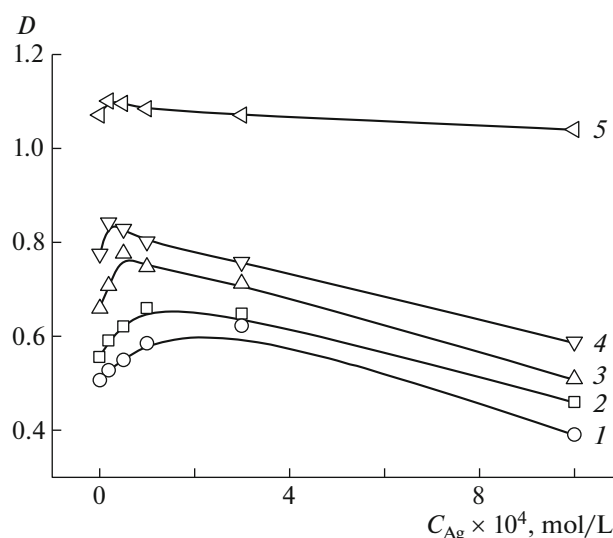


Fig. 4. Dependence of optical density of R6G on concentration of silver NPs in aqueous alcohol solution. Water/alcohol ratios, %: (1) 100 : 0, (2) 90 : 10, (3) 70 : 30, (4) 50 : 50, (5) 30 : 70.

The difference between the structures of water and aqueous alcohol solutions must be considered in order to explain the obtained dependences [13–18]. In contrast to a pure aqueous solution, in an aqueous solution diluted with alcohol, some of the dye molecules are surrounded by the solvation shells of alcohol molecules, which are weaker than those of water. This means the lifetime of an alcoholic solvation shell is shorter than those of the solvates of water molecules. In the periods between the collapse and formation of solvation shells, the molecules of the dye and NPs can

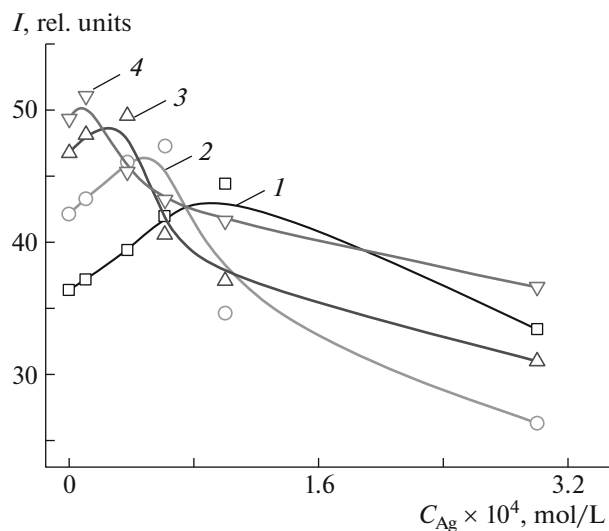


Fig. 5. Dependence of fluorescence spectra of R6G on concentration of silver NPs in an aqueous alcohol solution. Water/alcohol ratios, %: (1) 100 : 0, (2) 90 : 10, (3) 70 : 30, (4) 50 : 50.

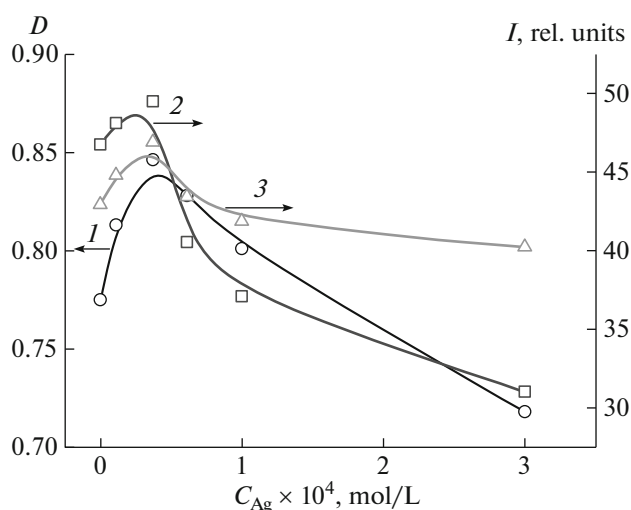


Fig. 6. Dependences of (1) optical density, (2, $\lambda = 564$ nm) intensity of fluorescence, and (3, $\lambda = 563$ nm) intensity of R6G generation in aqueous alcohol solution at a ratio of the components of 50 : 50% on the concentration of silver NPs.

close to the distances needed for interaction. Since the frequency of the rearrangement of solvates of alcohol molecules is higher than that of water, the probability of molecule–NPs pairs forming in an alcohol medium is higher than in water. This probably explains the drop in the concentration of silver NPs in order to obtain absorption and fluorescence maxima upon increasing the volume fraction of alcohol in binary solutions.

Measuring the properties of the stimulated emission of R6G dye in aqueous alcohol mixtures depending on the concentration of silver NPs revealed the same dependence as for absorption and fluorescence. Figure 6 shows curves for three processes at a water-to-alcohol ratio of 50 : 50%. For all curves, the bend maximum is observed at almost the same concentration. The relative increase in the values also remains approximately the same.

CONCLUSIONS

Our studies of the effect the plasmon resonance of silver NPs have on absorbance and the spontaneous and stimulated emission of dye molecules in aqueous alcohol solutions showed that the critical concentra-

tions of silver NPs at which absorption and emission maxima are observed fall as the volume fraction of alcohol rises in the mixture. This indicates that the probability of molecules and silver NPs converging is higher in alcoholic media than in water due to structural features of the solvation shells of the solvents.

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Translated by L. Grineva