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Abstract

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THE INFLUENCE OF FLUORESCENCE QUENCHERS ON THE FLUORESCENCE SPECTRA OF SOLUTIONS OF CERTAIN ANTHRACENE AND PHTHALIMIDE DERIVATIVES IN SOLVENT MIXTURES

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It has been shown in a number of works that the fluorescence spectra of 1- and 2-acetylanthracenes (^{1}), 9-aminoanthracene (^{2}), and phthalimide derivatives ($^{3-5}$) depend very strongly on the solvent. When solvents such as water or alcohols are used instead of saturated hydrocarbons, in which the fluorescence spectra occupy the most short-wavelength position, the maxima of the spectra are shifted by several thousand reciprocal centimeters toward lower frequencies. The absence of any substantial difference in the influence of different solvents on the absorption spectra of these compounds, the decrease in the shifts of the fluorescence spectra in hydroxyl-containing solvents as their viscosity increases (^{6}), and also the character of the changes in the form of the fluorescence spectra and the shift of their position upon the addition of small amounts of "active" solvents to inert ones (^{1,2,7}) made it possible to conclude that the solvent interacts with excited molecules considerably more strongly than with unexcited ones, and that during the lifetime of molecules in the excited state a process of reorientation of the surrounding solvent molecules takes place in the direction of establishing a new equilibrium distribution.

If the time required to attain equilibrium orientation (depending, in particular, on the viscosity of the solvent) is comparable with the duration of the excited state, then the experimentally observed fluorescence spectrum should be the result of the superposition of emissions from different emitting centers—excited molecules with different degrees of orientation of the solvent molecules around them. In this case, the most long-wavelength emission should be due mainly to molecules that have spent the longest time in the excited state, since the distribution of solvent molecules around them will be closest to the equilibrium one and, consequently, their effect will be strongest.

This assumption was confirmed by us by direct measurements carried out on an IF-39 phase fluorometer.* It was found that, upon excitation by modulated light of the fluorescence of a solution of 2-acetylanthracene in glycerol, the radiation isolated from the long-wavelength part of the spectrum (~520 mμ) is shifted in phase relative to the radiation isolated from the short-wavelength part (~436 mμ). The greatest value of the phase difference, observed at a temperature of −5°, was equal to 28°, which, under exponential decay laws, would correspond

Fig. 1

Figure 1: Fig. 1

to an $8 \cdot 10^{-9}$ longer duration of the long-wavelength emission in comparison with the short-wavelength emission.

The presence of different emitting centers may also manifest itself in changes in fluorescence spectra when fluorescence quenchers are introduced into the solution, the most probable result being a shift of the spectra toward the short-wavelength side owing to the shorter duration of the excited state of the centers responsible for the short-wavelength emis—

* The work was carried out jointly with V. I. Shirokov.

···quenching.* However, the detection of this effect in single-component solvents appears difficult because, at low solvent viscosities, the equilibrium state may be established in a time considerably shorter than the lifetime of the excited state, whereas at high viscosities the diffusion rate of the solvent is low. We investigated at room temperature the fluorescence spectra of solutions of 2-acetylanthracene in methyl and isobutyl alcohols containing *p*-toluidine, which is an effective quencher (Fig. 1). Although in these solvents, at toluidine concentrations $> 10^{-1}$ mol/liter, some shift of the spectra toward shorter wavelengths is observed, the possibility of changes in the properties of the solvent itself at such high quencher concentrations does not allow this phenomenon to be interpreted unambiguously.

Quite clear results were obtained by us in studying the influence of quenchers on the fluorescence spectra of solutions of certain derivatives of anthracene and phthalimide in solvent mixtures. It had previously been shown $(1, 2)$ that the addition of even small amounts of "active" solvents (causing a strong shift of the spectra) to hexane solutions of acetylanthracenes or aminoanthracene produces a strong long-wavelength shift of the fluorescence spectra, which is associated with the formation of associates of excited molecules with molecules of the active solvent. Additions of certain solvents to solutions of a number of phthalimide derivatives have an analogous effect. In this case, at certain concentrations of the "active" solvent, as in single-component solvents at certain viscosities, the fluorescence spectra are complex, and the most long-wavelength emission must be emitted by excited molecules around which the distribution of active-solvent molecules most closely approaches equilibrium. Evidently, these will mainly be the longest-lived excited molecules, and, consequently, one may expect stronger quenching of them (if the probability of quenching in a single collision is not significantly greater for the short-lived centers).

Fig. 1. Dependence of the fluorescence quantum yields of 2-acetylanthracene (1 –5) and 3-aminophthalimide (6–8) on the quencher concentration $[T]$. 1–4 – solvents, respectively, *n*-hexane, *n*-butanol, methanol, hexane + methanol (0.25 mol/liter), T –*p*-toluidine; 5 –solvent, hexane + methanol (0.25 mol/liter),

Fig. 2. Effect of fluorescence quenchers on fluorescence spectra

Figure 2: Fig. 2. Effect of fluorescence quenchers on fluorescence spectra

T —*p*-dimethoxybenzene; 6–8 —solvents, respectively, *n*-hexane, *n*-heptane + *n*-butanol (0.017 mol/liter), *n*-heptane + pyridine (0.015 mol/liter), T — *p*-toluidine.

Fig. 2. Effect of fluorescence quenchers on the fluorescence spectra of 2-acetylanthracene (*a*, *v*), 3-aminophthalimide (*g*, *d*) and 4-dimethylamino-N-methylphthalimide (*b*, *e*). Solvents: *a* —hexane + methanol (0.25 mol/l) + *p*-toluidine (1, 2, 5); *v* —hexane + methanol (0.25 mol/l) + *p*-dimethoxybenzene (1, 3, 5, 6); *b* —hexane + butanol (0.017 mol/l) + toluidine (1-4), *e* (1); *b* —hexane + butanol (0.068 mol/l) + toluidine (9, 10); *g* —heptane + butanol (0.017 mol/l) + toluidine (1-3, 5); *d* —heptane + pyridine (0.015 mol/l) + toluidine (1, 2, 5); *e* —hexane + butanol (0.017 mol/l) + dioxane (0.6 mol/l) (11); *a*–*g* —hexane (heptane) + toluidine (7, 8). Quencher concentrations: 1, 7, 9 —0; 2 —$5 \cdot 10^{-3}$; 3—10^{-2}; 4—$2 \cdot 10^{-2}$; 5, 10—$3 \cdot 10^{-2}$; 6—$5 \cdot 10^{-2}$ mol/l. Luminophore concentrations: $2 \cdot 10^{-5}$–$5 \cdot 10^{-5}$ mol/l.

We investigated the influence of quenchers (*p*-toluidine and *p*-dimethoxybenzene) on the position of the fluorescence spectra of solutions of 2-acetylanthracene, 3-aminophthalimide, and 4-dimethylamino-*N*-methylphthalimide** in *n*-hexane (*n*-heptane) containing small amounts, 0.015-0.25 mol/liter, of active solvent. The results obtained are presented in Fig. 2, from which it is seen that the presence in hexane solutions of acetylanthracene—methanol (0.25 mol/l), in solutions of phthalimides—*n*-butanol (0.017 mol/l) or pyridine (0.015 mol/l) causes a shift of the fluorescence maxima by 1000-1800 cm^{-1} toward lower frequencies. In the case of 2-acetylanthracene, which in pure hexane has a spectrum with a well-pronounced vibrational structure, the addition of alcohol also causes complete blurring of the vibrational structure. If, however, a quencher is added to these solutions, then simultaneously with a decrease in the total fluorescence yield (Fig. 1) a shift of the spectra toward higher frequencies is also observed, bringing them, as the concentration of the quencher increases, closer to the position characteristic of pure hexane solutions. In the case of acetylanthracene, not only a shift of the spectrum is observed, but also the appearance of vibrational

* We note in passing that the long lifetime of the centers responsible for the long-wavelength part of the spectrum may, upon excitation with polarized light, cause the appearance of a dependence of fluorescence polarization on the fluorescence spectrum (an increase in depolarization in the long-wavelength part) in the region of solvent viscosities insufficient to exclude rotational depolarization.

** We take this opportunity to express our gratitude to V. V. Zelinskii for providing the phthalimide samples.

structure, i.e., in its form the spectrum increasingly begins to resemble the spectrum in pure hexane. Comparison of the influence of *p*-toluidine and *p*-dimethoxybenzene (Fig. 2, *a* and *v*) shows that, at the same content in solution, the latter produces a smaller effect, in full agreement with

its lower quenching ability (Fig. 1). When a quencher is introduced into hexane solutions that do not contain an active solvent, only fluorescence quenching is observed, and no changes whatever in the fluorescence spectra occur (Fig. 2, *a* and *d*).

It should be noted that an effect analogous to the action of quenchers was observed earlier (^{7}) when such solvents as ether, dioxane, and pyridine were added to solutions of 2-acetylanthracene in hexane containing small amounts of alcohol. Additions of these substances also cause the spectrum to shift toward lower frequencies and to approach the form characteristic of the spectrum in pure hexane; however, their action was explained by the formation of hydrogen bonds with the alcohol, weakening its influence on the excited molecules of acetylanthracene. Although this effect may occur under the action of quenchers (the quenchers used are capable of forming hydrogen bonds with acetylanthracene and phthalimides), its role should not be significant. This follows from the fact that the influence of ether, dioxane, and pyridine becomes noticeable only at concentrations close to the alcohol concentration or exceeding it, whereas quenchers produce a noticeable shift of the spectrum at concentrations almost two orders of magnitude lower. Moreover, the interaction forces of the excited molecules of the phthalimides studied with alcohols are apparently stronger than in the case of acetylanthracenes, and the addition to their solutions of substances capable of forming hydrogen bonds with alcohol has only an insignificant effect on the spectra. Thus, for example, the presence in a hexane solution of 4-dimethylamino-*N*-methylphthalimide of 0.017 mole/liter (0.125 vol. %) *n*-butanol shifts the maximum of the fluorescence spectrum by 1700 cm^{-1} (Fig. 2,*b*). The addition to this solution of even large amounts of dioxane does not cause a short-wavelength shift of the spectrum (Fig. 2,*e*), whereas with a toluidine content of only $5 \cdot 10^{-3}$ mole/liter an entirely appreciable shift is already observed.

From the data obtained in studying the influence of fluorescence quenchers on fluorescence spectra it follows that the interaction of an active solvent with excited molecules is a process competing with the quenching process, i.e., it occurs over a time comparable with the lifetime of the excited state. This result is of interest in connection with the fact that the addition of an active solvent to hexane solutions of acetylanthracenes leads to an increase in the fluorescence quantum yield (^{8}), and, consequently, there is greater reason to believe that the deactivation processes responsible for the lower yield in a pure hexane solution are not "instantaneous," but also proceed over a time of the order of the lifetime of the excited state.*

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* Such an assumption was made earlier ([9]) also on the basis of the closeness of the values of τ_0, calculated from the long-wavelength absorption band, to the values of the ratios τ_{exp} to the fluorescence quantum yields ([10]).

Note: Figure translations are in progress. See original paper for figures.

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