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Abstract

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ON THE MANIFESTATION OF INTERMOLECULAR INTERACTIONS IN THE FLUORESCENCE SPECTRA OF SOLUTIONS OF ACETYLANTHRACENES IN SOLVENT MIXTURES

(Presented by Academician A. N. Terenin on 19 X 1959)

It is known that the position of the fluorescence spectra of many organic compounds depends very strongly on the solvent ([1–5]).

In studying the spectral properties of anthracene derivatives, we found that the fluorescence spectra of 1- and 2-acetylanthracenes also depend strongly on the solvent used.* Upon going from the nonpolar solvent, *n*-hexane, to one of the solvents that most strongly shifts the spectra, water, the position of the fluorescence maximum is shifted in 1-acetylanthracene from 22,450 cm^{-1} to 17,500 cm^{-1}, and in 2-acetylanthracene from 23,450 cm^{-1} to 18,500 cm^{-1}. In polar solvents the spectrum is continuous, whereas in nonpolar *n*-hexane a vibrational structure is observed, especially well pronounced for 2-acetylanthracene. The position of the absorption spectra changes very little in this case, and only a blurring of the vibrational structure in polar solvents is observed.**

It is noteworthy that especially strong shifts of the spectra are caused by hydroxyl-containing compounds: water, glycerin, ethylene glycol, and monohydric alcohols. One might try to associate this fact with the high value of the dielectric constant (ε) characteristic of this group of solvents ([3]); however, this is contradicted by the comparatively small influence of a number of other solvents that also have a high value of ε. Thus, for example, the maxima of the fluorescence spectra of 2-acetylanthracene in methyl ($\varepsilon = 33$), benzyl ($\varepsilon = 13$), and *n*-octyl ($\varepsilon = 10$) alcohols are shifted to the long-wavelength side relative to the maximum of the fluorescence spectrum in *n*-hexane by 3650, 3750, and 2740 cm^{-1}, respectively, whereas the shifts in acetone ($\varepsilon = 21.5$) and pyridine ($\varepsilon = 12.5$) amount to only 1200 and 1400 cm^{-1}. Evidently, in the case under consideration the strong influence of hydroxyl-containing solvents on the fluores-

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cence spectra cannot be due only to their dielectric properties, but apparently is to a significant degree connected with the specific interaction of hydroxyl groups with excited molecules of acetylanthracenes (most probably with their carbonyl groups).

The specificity of the influence of hydroxyl-containing solvents is also evidenced by the results obtained in the study of the fluorescence spectra of solutions of acetylanthracenes in solvent mixtures (Fig. 1).*** In nonpolar hexane the fluorescence spectra occupy the shortest-wavelength position, and their vibrational structure is the most resolved. In mixtures of hexane with pyridine (Fig. 1b) a gradual blurring of the vibrational structure and a shift of the spectrum into the region of lower frequencies are observed—

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* 9-Acetylanthracene does not fluoresce in the solvents we studied at room temperature. Acetylanthracenes were obtained by acetylation of anthracene with acetyl chloride (in benzene) in the presence of aluminum chloride and were separated by fractional crystallization (6). After purification by recrystallization and chromatography on aluminum oxide, 1-acetylanthracene had m.p. 107.5-109° and 2-acetylanthracene 187.5-188.5°.

** The influence of the solvent on the position and appearance of the absorption and fluorescence spectra of acetylanthracenes will be considered in more detail elsewhere.

*** The results obtained with 1-acetylanthracene are similar to the data shown in Figs. 1 and 2 for 2-acetylanthracene.

with increasing pyridine concentration,* while the addition of 1% pyridine to hexane is almost not reflected in the spectrum. A different picture is observed when alcohols are added to hexane. The introduction into hexane of even small additions of alcohol (0.1-0.2%) has a very strong effect on the form of the fluorescence spectrum. The vibrational structure is blurred, and its appearance forces one to assume that it is in fact formed by the superposition of at least two spectra that differ somewhat from each other.

Fig. 1. Fluorescence spectra of a solution of 2-acetylanthracene in hexane (dashed curve) and in solvent mixtures: **a** —hexane + methyl alcohol. Alcohol concentration: 1 —0.12; 2 —0.25; 3 —0.5; 4 —1. **b** —hexane + pyridine. Pyridine concentration: 1 —1, 2 —5, 3 —10, 4 —50. **c** —hexane + benzyl alcohol. Alcohol concentration: 1 —0.2; 2 —0.4; 3 —1. **d** —hexane + octyl alcohol. Alcohol concentration: 1 —0.3; 2 —0.6; 3 —1.7; 4 —3.4. (Concentrations are in volume percent.)

Fig. 2. Fluorescence spectra of a solution of 2-acetylanthracene

Figure 2: Fig. 2. Fluorescence spectra of a solution of 2-acetylanthracene

Fig. 2. Fluorescence spectra of a solution of 2-acetylanthracene in a mixture of hexane + 0.5% methyl alcohol + a third solvent. Concentration of the third solvent (in volume percent): 1 –0, 2 –1, 3 –5, 4 –10. Third solvent: **a** –ether, **b** –dioxane, **c** –pyridine, **d** –acetone; **d**, 5 –anisole (5%).

One of the possible explanations for the strong influence of small concentrations of alcohols on the spectra may be the assumption that an increased concentration of alcohol molecules is formed around the excited molecule of acetylanthracene, oriented with their hydroxyl groups toward the carbonyl oxygen. Such a mechanism has been proposed, for example, to explain a similar influence of small additions of alcohols on the fluorescence spectra of acridone (5). However, it seems more probable to us that the observed character of the changes in the spectra of acetylanthracenes as a function of alcohol additions to a neutral solvent is mainly a reflection of the formation of hydrogen bonds involving the hydroxyl hydrogen of the alcohol and the carbonyl oxygen of the excited acetylanthracene molecule. In this connection it should be borne in mind that, with increasing alcohol concentration in hexane, there should occur not only an increase concentrations of acetylanthracene complexes with individual alcohol molecules, but also the appearance of complexes with alcohol associates *.

It is known that the association of alcohols is destroyed when they are dissolved in certain solvents (ethers and amines are especially effective (7)), owing to the formation of a hydrogen bond between the alcohols and these solvents. Obviously, if the considerations stated above concerning the influence of alcohols on the spectra are correct, one should expect this influence to decrease to some extent in the presence in the solution of compounds that are also capable of interacting with alcohols.

Studies of the fluorescence spectra of acetylanthracene solutions in mixtures of two solvents, one of which was methyl alcohol, confirmed these assumptions. Thus, for example, if the shift of the maximum of the fluorescence spectrum of 2-acetylanthracene corresponding to one half of the total shift occurring on going from one solvent to another is observed in a hexane solution at a two-percent alcohol content, then, to obtain an analogous effect in mixtures of alcohol with acetone, dioxane, and pyridine, its concentration must be increased, respectively, to 20, 20, and 40%.

The effect of the interaction of alcohols with other solvents is especially clearly manifested in the fluorescence spectra of acetylanthracene solutions in mixtures of three solvents. Figure 2 presents changes in the spectra of solutions of 2-

* Similar results were also obtained in mixtures of hexane with acetone.

acetylanthracene in *n*-hexane containing 0.5% methyl alcohol when diethyl ether, pyridine, dioxane, acetone, and anisole are added to this solution. As is seen from Fig. 2, the introduction of increasing amounts of all these solvents (except anisole) leads to a successive shift of the spectra into the region of higher frequencies and to the appearance of vibrational structure in the spectrum, i.e., to neutralization of the influence of the alcohol. In the absence of interaction of these solvents with the alcohol, only the opposite picture could have been expected—a shift of the spectra into the region of lower frequencies (as is observed in the case of anisole), since their introduction into a solution of acetylanthracene in hexane in itself leads to a long-wavelength shift (see, for example, Fig. 1b).

From the influence on the fluorescence spectra one can also qualitatively estimate the order of interaction of this series of solvents with alcohol. Thus, from Fig. 2 it is seen that the addition of 1% acetone practically still has no effect on the spectrum; the addition of the same amount of ether causes a certain shift, while at the same content of pyridine and dioxane this shift is already ~ 600 cm^{-1}.

From consideration of the results set forth above it follows that the study of the fluorescence spectra of acetylanthracenes in solvent mixtures can be used to detect intermolecular interactions between them. It may also be thought that other compounds whose fluorescence spectra show a significant dependence on the solvent can be used for this purpose.

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* As is known (7), already at moderate concentrations of alcohols in nonpolar solvents associates consisting of several alcohol molecules are formed.

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