

Selective Nonspecific Solvation Under Dielectric Saturation and Fluorescence Spectra of Dye Solutions in Binary Solvents

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The influence of selective nonspecific solvation on the fluorescence spectra of three substituted *N*-methylphthalimides in a binary solvent system consisting of a nonpolar (*n*-heptane) and a polar (pyridine) component has been studied under conditions close to dielectric saturation. The substantially nonlinearity of the effect is confirmation that the spectral shifts of fluorescence bands depend on the number of polar solvent molecules involved in solvating the dye molecule. The measured fluorescence spectral shifts determined by substituting one nonpolar solvent molecule with a polar one in the proximity of the dye molecule agree quantitatively with the forecasts of the previously proposed semiempirical theory which describes this nonlinear solvation phenomenon.

KEY WORDS: Nonlinear solvation; fluorescence in binary solvents.

INTRODUCTION

Considerable advances have been made in studying the phenomenon of selective nonspecific solvation occurring in dilute solutions of polar organic substances (dyes) in binary solvents consisting of nonpolar and polar (active) components. The substantially nonlinear relationship between the spectral properties of the dye and the composition of such solutions can be explained by the fact that the dye molecules are solvated predominantly by the polar component of the binary solvent. The microscopic composition of the solvation shell of a dissolved molecule can differ markedly from the macrocomposition of the solution determined by volumetric ratios of components. Figure 1 [1–6] shows typical examples of spectral-luminescent dependence, indicating qualitative agreement between the experimental results, which cover a wide range of solution components, and

the predictions of the semiempirical theory of equilibrium selective nonspecific solvation.

In the last few years evidence has emerged that behavior of the type shown in Fig. 1 is explained not only by the abrupt spatial heterogeneity of such systems, as mentioned above, but also by a change in the mechanism of orientational interaction between polar molecules of the dye and solvent in a specific range of solvent composition. This range (indicated by the arrow in Fig. 1) corresponds to very low concentrations of the active component of the binary solvents and has not been adequately studied. At these concentrations the solvate contains a single molecule of the active component and the essence of the solvation process resides in a nonlinear twin interaction between polar dye and solvent molecules. This effect is similar, in its nature, to the dielectric saturation effect, and ultimately results in the formation of ordered local molecular structures [7–10].

The present paper extends the study of this new nonlinear solvation phenomenon—selective nonspecific solvation near dielectric saturation and, in particular, fo-

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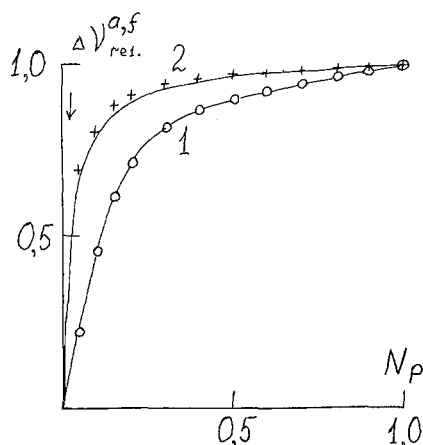


Fig. 1. Experimental (lines) and calculated (points) values of relative shifts of absorption (1) and fluorescence (2) bands of solutions of 3-aminophthalimide in a binary solvent system (*n*-heptane + *n*-butanol) versus the mole fraction of the polar component (room temperature). The arrow indicates the region of nonlinear solvation processes.

cuses on the effect of solvation on the fluorescence spectra of dyes in a binary solvent system. Three dyes were selected from a group of substituted *N*-methylphthalimides: 3-amino-*N*-methylphthalimide (3ANMP), 4-amino-*N*-methylphthalimide (4ANMP), and 4-dimethylamino-*N*-methylphthalimide (4DMANMP). By varying the substituent group, the effect of molecular structure on the character of the solvation can be explored. Note that the electronic transition responsible for the fluorescence of these compounds is an intramolecular charge transfer from the amino group to one of the carbonyl groups [11]. It is also important to note that in the molecule 4DMANMP, as distinct from the two others, the specific interaction with the active solvent in the amino group is missing. Mixtures of *n*-heptane with pyridine were used as the binary solvents. These mixtures underwent thorough purification (dehydration, in particular) according to appropriate techniques.

Stationary fluorescence spectra of the solutions were measured with an apparatus built around the DFS-42 spectrometer (LOMO-corporation, Leningrad). The measured spectral contours were then decomposed into "elementary" bands representative of specific solvate compositions as described in Refs. 9–12.

This method of analysis relies on two principal assumptions. First, the experimentally measured fluorescence spectrum, $I^f(\nu)$, of the ensemble of excited molecules represents a superposition of elementary fluorescence spectra $I_i^f(\nu)$, each arising from a subensemble of excited

molecules which are solvated by i molecules of the active component of the binary solvent, i.e.,

$$I^f(\nu) = \sum_{i=0}^{\infty} \gamma_i I_i^f(\nu) \quad (1)$$

where γ_i is the fraction of the i th type of solvate ($\sum_{i=0}^{\infty} \gamma_i = 1$). For a nonpolar solvent $\gamma_0 = 1$, and $I^f(\nu) = I_0^f(\nu)$. Second, the main contribution to the spectral-luminescent properties is made by solvent molecules in the first coordination sphere of the dye molecule. In addition to the method developed here, a wealth of evidence exists to support these assumptions (see, e.g., Refs. 4, 6, and 11).

The procedure for obtaining $I_i^f(\nu)$ for $i > 1$ is the following. Since the fluorescence spectrum $I^f(\nu)$ of a given three-component system monotonically shifts to longer wavelengths with increasing fraction ϕ of the polar solvent component [2,4–6, 9–12], one can assert that the very short-wavelength region of the spectrum is due to dye molecules solvated only by nonpolar solvent molecules ($i = 0$). Thus, the behavior of the value $k_0 = I_0^f(\nu)/I^f(\nu)$ in the ultrashort-wave region can help follow a decrease in solvates of this type ($i = 0$) with increasing polar solvent fraction ($\gamma_0 = 1/k_0$). This makes it possible to obtain at $\tilde{I}_1^f(\nu)$ the spectrum:

$$\tilde{I}_1^f = I^f(\nu) - 1/k_0 I_0^f(\nu) \quad (2)$$

which is the total spectrum of solvates having the number of polar component molecules $i > 1$:

$$\tilde{I}_1^f(\nu) = \sum_{i=1}^{\infty} \gamma_i I_i^f(\nu) \quad (3)$$

Given an extremely small polar solvent fraction (i.e., given the smallest value ϕ at which spectrum $\tilde{I}_1^f(\nu)$ is isolated), the spectrum $\tilde{I}_1^f(\nu)$ thus obtained seems to represent the spectrum $I_1^f(\nu)$ of the subensembles of the dye molecules whose solvate shells contain only one polar component molecule.

By conducting a similar operation with an $\tilde{I}_1^f(\nu)$ spectrum family, it is easy to get values k_1 , spectra $\tilde{I}_2^f(\nu)$, $I_2^f(\nu)$, etc. As before, the k_i values are determined for the ultrashort region of the spectrum $\tilde{I}_i^f(\nu)$:

$$k_i = I_i^f(\nu)/\tilde{I}_i^f(\nu) \quad (4)$$

At this,

$$\tilde{I}_{i+1}^f(\nu) = \tilde{I}_i^f(\nu) - 1/k_i I_i^f(\nu) \quad (5)$$

$$I_i^f(\nu) = \sum_{i=1}^{\infty} \gamma_i I_i^f(\nu) \quad (6)$$

$$\gamma_i = (1/k_i) \prod_{j=0}^{j=i-1} (1 - 1/k_j) \quad (7)$$

For a more detailed description of this procedure, see Ref. 9.

Given as an example in Fig. 2 are the fluorescence spectra $I_i^f(\nu)$ of 3ANMP under different solvation conditions. A summary of the data is given in Table I. Here, ν_0^f and ν_{∞}^f are frequencies of dye fluorescence maxima in nonpolar and polar solvents, respectively, and ν_1^f , ν_2^f , etc., are analogous values for binary solvents. The subscripts refer to solvate shells wherein one, two, etc., molecules of the nonpolar component are replaced by polar ones.

In order to discuss the results, it is first necessary

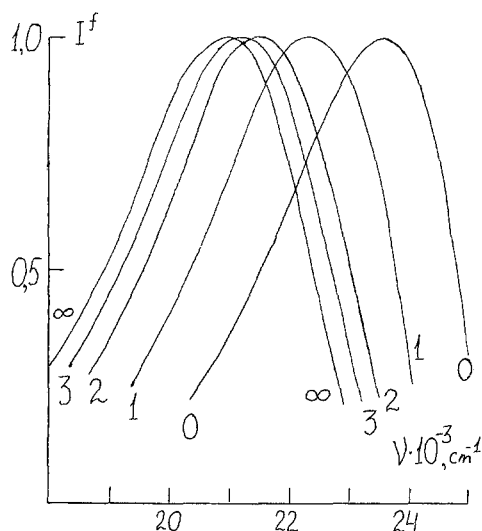


Fig. 2. Fluorescence spectra of 3ANMP under different solvation conditions (room temperature). 1, 2, and 3 are solutions in a mixture of *n*-heptane and pyridine (the solvation shell includes, besides *n*-heptane molecules, 1, 2, and 3 pyridine molecules, respectively). (0) Solution in *n*-heptane; (∞) solution in pyridine.

Table I. Frequencies of Maxima of Fluorescence Spectra Under Different Solvation Conditions (cm^{-1})

Molecule	ν_0^f	ν_{∞}^f	ν_1^f	ν_2^f	ν_3^f
3ANMP	23,500	21,000	22,300	21,600	21,300
4ANMP	24,000	20,300	22,500	21,700	21,200
4DMANMP	23,300	20,000	22,300	—	—

to note the substantially nonlinear dependence of the fluorescence band shift on the number of molecules of the polar component of the binary solvents involved in the solvate shell of dye molecule (Fig. 3). The enormous influence exerted by the first molecule of the polar component ($\Delta\nu_{0-1}^f = \nu_1^f - \nu_0^f$) comprising 30–50% of the entire shift of the fluorescence spectrum in going from the individual nonpolar solvent to the polar one ($\Delta\nu_{0-\infty}^f = \nu_{\infty}^f - \nu_0^f$) is particularly noteworthy. This confirms, in our view, the existence of the nonlinear character of the twin interaction between polar molecules of the dye and the solvent. The data presented here also permit the conclusion that the character of this interaction, which manifests itself almost equally in the spectral shifts of molecules of different structures, is predominantly nonspecific (dipole–dipole).

Finally, we attempt a quantitative interpretation of the experimental data using the results given in Ref. 10. Remember that, according to Ref. 10, the general expression for the shift in the radiative spectrum by an amount $\Delta\nu_{0-1}^f$ caused by the appearance, in the nearest environment of the dye molecule, of the first molecule of the polar component of the binary solvent has the following form (provided there is dielectric saturation):

$$\Delta\nu_{0-1}^f = [(\sqrt{2} \mu'/a^3) (\mu_g \cos \nu - \mu_e)] + [3\Pi/2(I + I')] [(\alpha_g - \alpha_e) (\alpha' - \alpha_0)]/2a^6 \quad (8)$$

Here μ_g , μ_e and α_g , α_e are the dipole moment and the average value of polarizability of a dye molecule in the ground (g) and excited (e) states (see Fig. 4), ν is the angle between the moments, μ_g , μ_e and μ' , α' are the

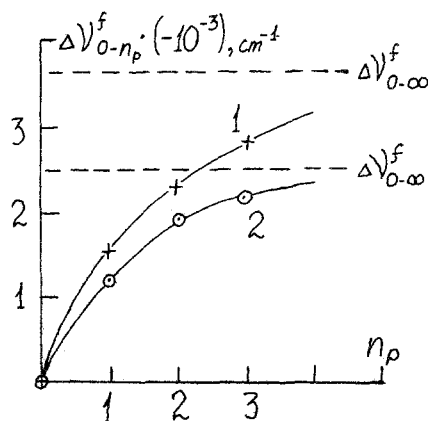


Fig. 3. Dependence of fluorescence spectral shifts of 4ANMP (1) and 3ANMP (2) on the number of pyridine molecules n_p involved in the composition of their solvation shells.

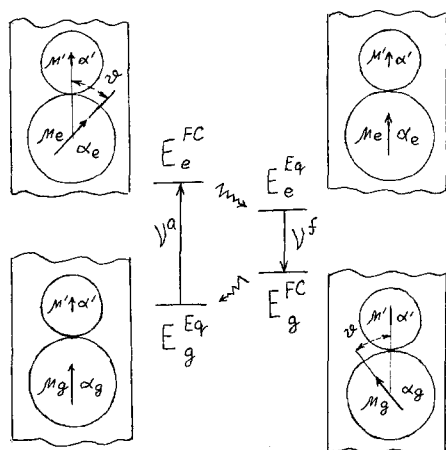


Fig. 4. Diagram of electron states and solvate structure models illustrating the radiation process in selective nonspecific solvation proceeding under dielectric saturation.

dipole moment and polarizability of the polar solvent molecule, α_0 is the polarizability of a nonpolar solvent molecule, I and I' are the first ionization potentials of the dye and polar solvent molecules, and a is the effective radius of interaction (Onsager's radius of a dye molecule [6,11]). The values of dipole moments of all molecules in the solution (μ_i) are related to the analogous gas phase values (μ_i^0) by the expression

$$\mu_i = \mu_i^0 (2n_0^2 + 1)/(n_0^2 + 2) \quad (9)$$

where n_0 is the refractive index of the ground (nonpolar) component of the binary solvent.

For the compound studied here, according to Ref. 10, it is the first (orientational) part of expression (8) that contributes the most to the value $\Delta\nu_{0-1}^f$, so that we rewrite (8) as follows:

$$\Delta\nu_{0-1}^f = \sqrt{2} \mu' (\mu_g \cos\vartheta - \mu_e)/a^3 \quad (10)$$

All of the electrical and structural parameters which are necessary to perform the calculations for the compounds studied here are taken from Refs. 6, 11, and 13 and are also given in Table II. The results of the final calculation and appropriate experimental data are given in Table III. It can be readily seen that the values are in good quantitative agreement and testify to the ability of this simple physical model [7-10] and the corresponding semiempirical theory to describe correctly the observed nonlinear solvation phenomena.

The results presented here as well as those reported in Refs. 7-10 allow one to put forward some preliminary qualitative statements about the character of resolution

Table II. Electrical and Structural Parameters of the Compounds Studied [6, 11, 13]

Molecule	μ_g^0 (D)	μ_e^0 (D)	ϑ (deg)	a^3 (\AA^3)
3ANMP	2.6	5.2	20	50
4ANMP	3.5	7.1	15	50
4DMANMP	3.5	7.1	15	70

Table III. Experimental and Calculated Values of Solvation Shifts of Fluorescence Bands

Molecule	$\Delta\nu_{0-1}^f$ (cm^{-1})	
	Experiment	Calculation
3ANMP	-1200 ± 100	-1300 ± 200
4ANMP	-1500 ± 100	-1700 ± 300
4DMANMP	-1000 ± 100	-1200 ± 200

processes of polar dye molecules in a binary solvent system consisting of nonpolar and polar components, depending on the solvent composition. At the initial stage, i.e., in the region corresponding to very low concentrations of the polar component (see Fig. 1), the selective nonspecific solvation proceeds under conditions close to dielectric saturation. This is consistent with the predominance of 1:1 Van der Waals complexes in the solution, which consist of polar dye and solvent molecules solvated by the nonpolar component, characterized by ordering of the microstructure, and leading to abnormally large spectral shifts. As the concentration of the polar component increases, the degree to which it fills the solvation shell of the dye molecule also increases, destroying the local molecular structure which results from multiparticle dipole-dipole interactions between polar molecules [14], and the system moves to the region of common (linear) phenomena. As noted, in this region the offbeat vs composition nonlinearity shown in Fig. 1 is determined primarily by the spatial heterogeneity of such solutions.

To sum up, the particular character of the twin nonlinear interaction of polar molecules, which is similar in nature to the dielectric saturation effect, as well as the role of this interaction in the formation of microstructure and optical properties of dye solutions, is, in our view, worthy of further comprehensive study.

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