Solvent Influence on the Electronic Fluorescence Spectra of Anthracene

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The electronic fluorescence spectra of anthracene in different solvents were analyzed from the point of view of intermolecular interactions using Abe model of a simple liquid. From the obtained correlations some information about the dipole moment and polarizability of anthracene in excited vibronic states were formulated. The values of the dipole moments and polarizabilities of anthracene in its excited vibronic states are in the limits of the variations of these parameters in vibration motions.

Keywords: anthracene, fluorescence spectrum, spectral shifts, dipole moment and polarizability in excited vibronic states.

Anthracene is a fused ring aromatic hydrocarbon consisting of three benzene rings. Polycyclic aromatic hydrocarbons are of interest in various domains due to their unique characteristics such as high photoreactivity, strong π- π absorption coupled with high fluorescence yield, high solubility in organic solvents. Like most polycyclic aromatic hydrocarbons, anthracene can be used to obtain dyes, scintillation counters, insecticides, coating materials, etc. [1-5].

Anthracene is a complex, planar molecule having three orthogonal C_2 axes of symmetry; it belongs to D_{2h} point group of symmetry and consequently its dipole moment in the ground electronic state is zero [6].

Anthracene is a non-polar molecule characterized by a great polarizability due to the large delocalization of π-electrons inducing an important interaction between vibration movement and electron cloud. This interaction determines the vibration structure of the anthracene electronic spectra with intramolecular redistribution of the excess vibration energy [7]. Anthracene is a complex molecule for which the selection rule $\Delta\nu = \pm 0.1$ for the vibration transitions is encroached upon due to the high interactions between electronic and nuclear motions.

The visible electronic (absorption and fluorescence) band of anthracene was assigned to a $^1B_{2u} \leftarrow {}^1A_{1g}$ transition (p- band) with the transition moment polarized along the short molecular in plane axis. This band has a well resolved vibration structure consisting of five vibration sub-bands [6, 8].

The anthracene visible absorption p-band and its homologous fluorescence band have similar vibration structures [8].

The solvent influence on the absorption and fluorescence electronic spectra provides valuable information related to some physico-chemical properties such as dipole moment or/and polarizability in the electronic states responsible for the electronic band appearance.

Changes in solvent are associated with changes in the dielectric constant, polarity or polarizability of the surrounding medium of the spectrally active molecule. Modifications of the electron density in the molecular states determine changes both in the dipole moments and polarizability of the spectrally active molecules. The solvents differently influence the spectrally active molecule both in its ground and excited states. Consequently, the analysis of the solvatochromic effect is useful in studying the excited states of this kind of molecules, especially in the case of weak intermolecular interactions in their ground electronic state.

The solvatochromic effect in some solutions of anthracene derivatives was studied by estimating the contribution of each type of universal interactions (dispersive, inductive, polarization) to the total spectral shift registered by passing the spectrally active substance from its gaseous phase into a homogeneous solution achieved in solvents with various physical properties [9-15].

In a previous article [16], the solvent influence on the electronic absorption spectra of anthracene was investigated by using Abe model developed for simple liquids.

The purpose of this paper is both to verify the applicability of Abe model in studying the solvent influence on the fluorescence spectrum of anthracene and to determine the dipole moment and the polarizability of anthracene molecule in its vibronic states on the basis of the same theory.

Theoretical notions

The bases of the theoretical model developed [17, 18] in order to describe the spectral shifts due to the universal intermolecular interactions in simple liquids were detailed in [16]. In Abe model the contributions of all universal intermolecular interactions are expressed by known terms dependent on the microscopic parameters of the interacting molecules and also on the macroscopic parameters of the solvent. There are a great number of articles in which the theory of intermolecular interactions in simple liquids is verified [19-22] by spectral means.

The theoretical model developed by Abe is important especially when some electro-optical parameters of the spectrally active molecules must be estimated [23,24].

The fluorescence spectra are usually studied in very low concentrations of the spectrally active molecules. Consequently the spectrally active molecules do not interact between themselves and only the interactions between solvent-solvent or solvent-spectrally active molecules could be reflected in the electronic spectra

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[14,17,18]. The solvent-solvent interactions in solutions are not evidenced in electronic spectra due to the fact that the electronic transitions are very quick and the solvent arrangement around the spectrally active molecules remain the same in the electronic states participating in the studied transition.

Thus, relation (1) between the dipole moments μ and polarizability α of the spectrally active molecule and the parameters "**a**" and "**b**" of the solution was obtained. The indices **g** and **e** refer to the ground and excited states of the spectrally active molecule noted by **u**, while the solvent molecules are noted by **v**.

$$[\mu_e^2(u) - \mu_g^2(u)] + a\alpha_e(u) = b \quad (1)$$

The solvent parameters "**a**" and "**b**" from relation (1) can be expressed by relations (2) and (3).

$$a = \frac{\frac{3}{2} I_g(v)\alpha_g(u) \frac{I_g(u) - hc\nu_1}{I_g(v) + I_g(u) - hc\nu_1}}{\frac{3}{4\pi N_A} \frac{M}{\rho} [\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2+2)^2} + \frac{n^2-1}{n^2+2}]} \quad (2)$$

$$b = \frac{-\frac{\nu_1 - \nu_0}{C} + \frac{3}{2}\alpha_g(v)\alpha_g(u)\frac{I_g(u)I_g(v)}{I_g(v)+I_g(u)}}{\frac{3}{4\pi N_A} \frac{M}{\rho} [\frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{\varepsilon(n^2+2)^2} + \frac{n^2-1}{n^2+2}]} \quad (3)$$

In relations (2) and (3) ν_0 and ν_1 are the wavenumbers measured in the maximum of the studied vibration component of the fluorescence vibronic spectra of anthracene in its gaseous phase and in binary solution achieved in a given solvent, respectively; I is the ionization potential, ε and n are the electrical permittivity and refractive index of the solvent, M and p are molar mass and density of the solvent, N_A is Avogadro number and C is a constant [17,18] computed by using relation (4).

$$C = \frac{1}{hc}\sum_p R_{uv(p)}^{-6} = \frac{16\pi^3 N_A^2}{9hc}\left(\frac{\rho_v}{M_v}\right)^{\frac{2}{3}}\left\{\left[\left(\frac{M_u}{\rho_u}\right)^{\frac{1}{3}} + \left(\frac{M_v}{\rho_v}\right)^{\frac{1}{3}}\right]^{-4} + \left[\left(\frac{M_u}{\rho_u}\right)^{\frac{1}{3}} + 3\cdot\left(\frac{M_v}{\rho_v}\right)^{\frac{1}{3}}\right]^{-4} + \ldots\right\} \quad (4)$$

Relation (1) permits to estimate the dipole moments and polarizabilities in the electronic states responsible for the electronic band appearance [18,19,23,24].

Experimental part

The electronic fluorescence spectra were recorded on a LS55 PerkinElmer spectrofluorimeter.

The refractive indices of the solvents were measured at an Abbe refract meter and a RL Oehme DK-meter (7MHz) was used to measure the electric permittivity.

Spectral grade solvents were achieved from Merck Company. Anthracene (A) was achieved from Merck Company and used as received.

Results and discussion

Six solvents (table 1), having various physico-chemical properties, were used in this study and the visible electronic fluorescence spectra of the anthracene derivatives in these solvents were analyzed. The wavenumbers in the maxima

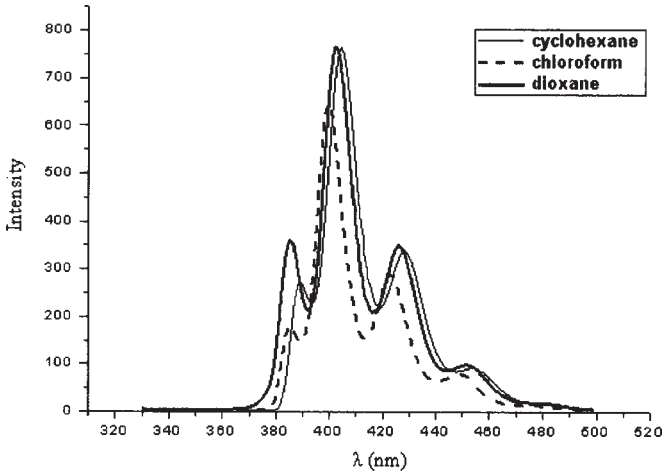

Fig. 1. Fluorescence spectra of anthracene in different solvents

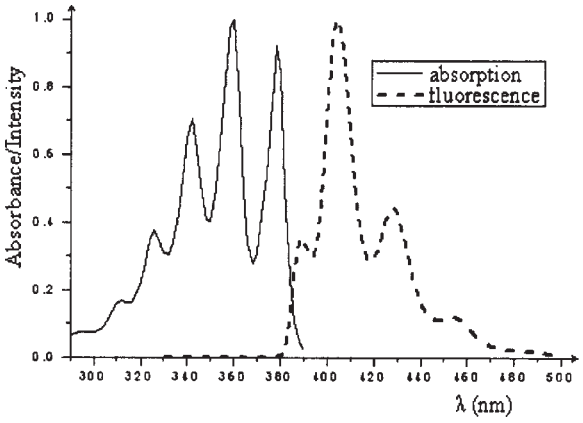

Fig. 2. Mirror symmetry of visible electronic-absorption and fluorescence– spectra of anthracene in chloroform

Nr.	Solvent	$\bar{\nu}_1(cm^{-1})$	$\bar{\nu}_2(cm^{-1})$	$\bar{\nu}_3(cm^{-1})$	$\bar{\nu}_4(cm^{-1})$
1.	Cyclohexane	25907	25000	23585	22222
2.	Dioxane	26042	24876	23364	22124
3.	Chloroform	25641	24631	23364	22026
4.	Ethanol	26178	25000	23585	22321
5.	Methanol	26178	25000	23697	22321
6.	Acetonitrile	26042	24876	23585	22173
Total spectral shift $\Delta\bar{\nu}(cm^{-1})$		537	369	333	197

Table 1
WAVENUMBERS OF VIBRONIC COMPONENTS IN FLUORESCENCE SPECTRUM OF ANTHRACENE

of the visible absorption vibronic bands are listed in table 1. The electronic fluorescence spectra of anthracene in cyclohexane, chloroform and dioxane are given in figure 1.

The mirror symmetry of anthracene electronic absorption and fluorescence spectra is illustrated in chloroform (fig. 2).

The total shifts measured in the considered solvents are strongly dependent on the vibration motion in the anthracene molecule, as it results from table 1. This fact demonstrates that the solvents affect especially the vibration components situated to higher wavenumbers in the fluorescence spectra (characterized by great values of Δv, v being the vibration number).

Assuming that all molecules from solution are spherical, and between them only van der Waals interactions take place, T. Abe' theory is used here in order to verify its applicability to the study of solvent influence on the fluorescence vibronic band of anthracene. In this purpose, C constant was estimated by using relation (4) and the coefficients "**a**" and "**b**" were calculated with relations (2) and (3) and then were graphically represented in the plane **(a, b)**. The dependences of the parameters "**a**" and "**b**" are illustrated in figures 3-6 for the vibronic components of the visible fluorescence band of anthracene.

A linear dependence of the type (2) between "**a**" and "**b**" was evidenced. In relation (2) $\alpha_e(u)$represents the slope and $\mu_e^2(u) - \mu_g^2(u)$ represents the cut at ordinate for the resulting straight lines (figs. 3-6) in the plane ("**a**", "**b**"). Having in view the D_2 symmetry of anthracene, the permanent electric dipole moment in its ground state is null. So, only the first term from the square difference of the dipole moments differs from zero. The cut at ordinate of the obtained straight lines from figures 3-6 is equal to $\mu_e^2(u)$ in the case of anthracene.

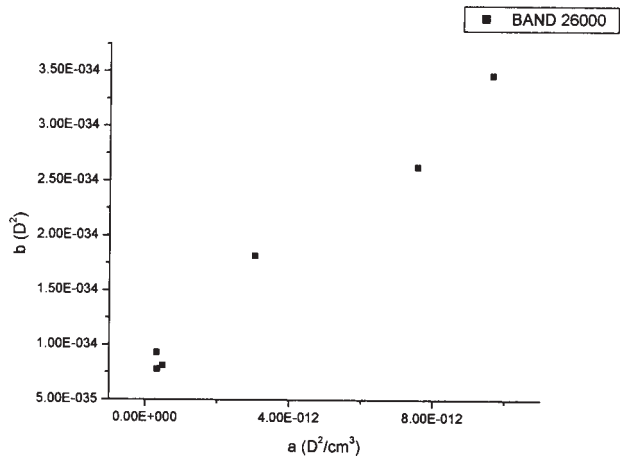

Fig. 3. **b** vs. **a** from (3) and (4) for anthracene visible fluorescence vibronic band at 26000 cm^{-1}

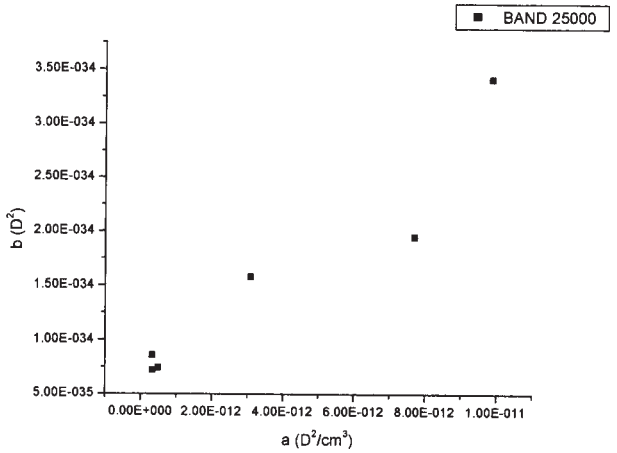

Fig. 4. **b** vs. **a** from (3) and (4) for anthracene visible fluorescence vibronic band at 24000-25000 cm^{-1}

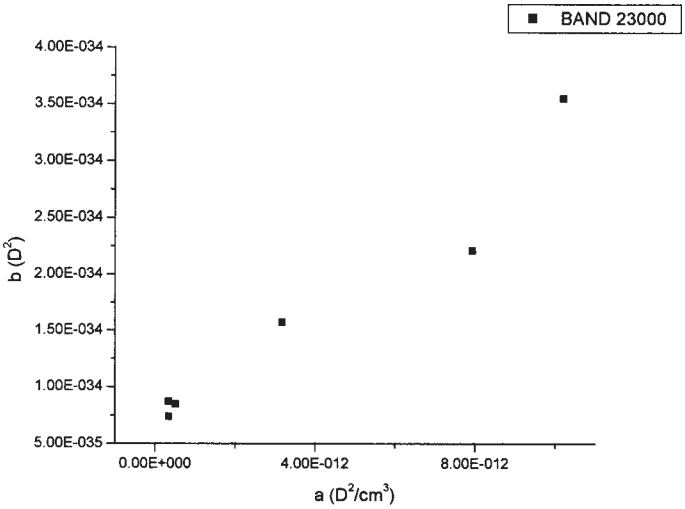

Fig. 5. **b** vs. **a** from (3) and (4) for anthracene visible fluorescence vibronic band at 23000

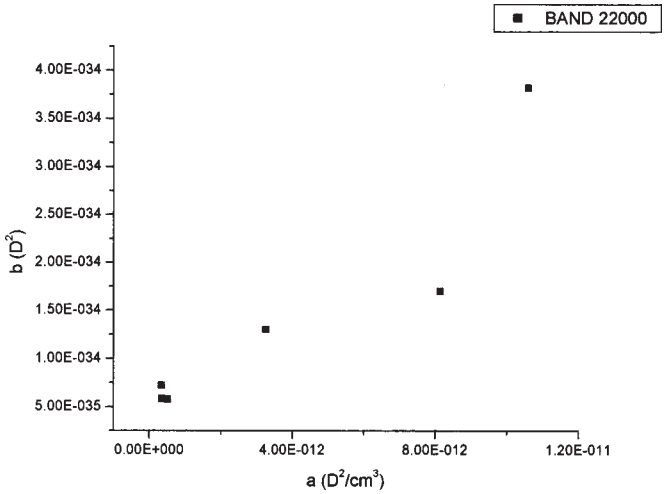

Fig. 6. **b** vs. **a** from (3) and (4) for anthracene visible fluorescence vibronic band at 22000

Table 2
MICROSCOPIC PARAMETERS IN THE EXCITED VIBRONIC STATES OF ANTHRACENE DETERMINED FROM FLUORESCENCE SPECTRA

Wavenumber (cm^{-1})	$\alpha_e(10^{25} cm^3)$	$\mu_e(D)$
Band 1 (26000)	270.34	8.82
Band 2 (25000)	237.51	8.24
Band 3 (23000)	246.80	8.40
Band 4 (22000)	256.57	6.76

When the electric dipole moment in the ground state of the spectrally active molecule is known (null for anthracene), the electric dipole moment in the excited state can be estimated by using relation (2), on the basis of Abe model of simple liquids.

The microscopic parameters $\alpha_e(u)$ and $\mu_e^2(u)$ in the excited electronic state of anthracene molecule, as they were determined by Abe model applied to the vibration components of anthracene fluorescence spectra are listed in table 2. From table 2 it results a decrease both in the dipole moment and in polarizability of anthracene by excitation. In the limits of approximations in which T. Abe' model was developed, the values obtained for the dipole moment and polarizability of anthracene in the vibration levels of the first excited electronic state can be considered as being in a good agreement with its molecular structure. The differences between the values of $\mu_e^2(u)$ and α_e(u) determined for the four vibration components of the visible electronic fluorescence band of anthracene are in the limits of variation of the molecular electric dipole moment and polarizability in the vibration motions [25, 26]. These results are also concordant with the values obtained from solvent influence on the absorption spectra of anthracene [16].

Conclusions

The spectral method derived from the Abe' model of a simple liquid can be successfully used to estimate some microscopic parameters in the excited vibronic states of anthracene, like polarizability and electric dipole moment. The obtained values are in a good agreement with the large delocalization of the anthracene π-electronic cloud. One can affirm that the model proposed by T. Abe can be applied to study solvent influence both on the absorption and fluorescence spectra of anthracene.

The existence of some aberrant points in the dependences of "**a"** and "**b"** coefficients of Abe suggest us to extend this study to a greater number of solvents with various physico-chemical parameters in order to verify what are the solvents and the spectrally active molecules obeying the theory developed by T. Abe. This study would contribute to a more precise evaluation of microscopic parameters of anthracene or anthracene derivatives.

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Manuscript received: 8.10.2009