

Solvent Influence on the Electronic Absorption Spectra of Anthracene

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*The effect of some solvents on electronic absorption spectra of anthracene is studied here by using the cell model of a pure liquid proposed by Takehiro Abe. The linear dependence between the Abe parameters **a** and **b** for the studied solution makes possible estimation of the dipole moment and polarizability in the first excited state of anthracene. The obtained values are in a good agreement with the high degree of π -electron cloud delocalization in the anthracene molecule.*

Keywords: anthracene, electronic absorption spectra, dipole moment and polarizability in the electronic excited state

Anthracene is one of the most studied spectrally active molecules due to its good solubility in a great number of solvents and its physical properties, including an intense electronic spectrum both in absorption and in emission.

Anthracene is a complex molecule [1], built from three coplanar benzene rings. Its stability is due to a large delocalized π -electronic cloud, which also assures intramolecular redistributions of the excess vibration energy, reflected in the vibration structure of the anthracene electronic spectra.

The electronic bands of anthracene were attributed as follows [2,3]:

- the visible p -band with a vibronic structure appears due to the transition



It has a low intensity, $\log \epsilon \approx 4$.

- the ultraviolet β -band having $\log \epsilon > 5$ appears due to the transition:



The anthracene visible p -band [2] in the absorption spectrum and its homologous fluorescence band [3] have similar vibration structures. The ultraviolet β -band is more intense than the visible p -band and usually has two vibration components.

The solvent influence on the electronic spectra of some anthracene derivatives was studied by estimating the contribution of each type of universal interactions [4-6] (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.

Experimental part

In liquids, the universal interactions usually shift the molecular electronic spectra, compared to gaseous phase of the spectrally active molecule. The theories regarding the solvent influence on the electronic spectra states these shifts a function of the electro-optical parameters of the solvents and of the microscopic parameters of the spectrally active molecules [6-10]. These theories were used in order to estimate some electro-optical parameters of the spectrally active molecules [11].

The spectra of solutions are usually measured at very low concentrations of the spectrally active molecules and also in the wavelength regions in which the solvents do not absorb.

A modern theory that describes the solvent influence on the electronic spectra was developed [12,13]. The basic hypotheses of cell model are the following:

- the solvent and solute molecules are spherical and isotropic;

- the analysed system is composed of a spectrally active molecule ("u") and N solvent molecules ("v") which are arranged around the solute molecule in concentrically spheres, named solvation spheres;

- in the ground state of the system all molecules are in their ground state, while in the excited state of the system, the spectrally active molecule is in its excited state and the solvent molecules are in their ground state;

- the distance between the center of the spectrally active molecule and the center of a solvent molecule from the p^{th} sphere is [12]:

$$R_{uv(p)} = r_u + (2p - 1) \cdot r_v(p)$$

Two states of the solution were taken into consideration:

-ground state (g) in which all molecules are in their ground states;

- i^{th} excited electronic state (e) in which the solute molecule is in its i^{th} excited electronic state and all solvent molecules are in their ground states.

According to the Franck-Condon principle, the same positions of the molecules are appropriate to the ground and to the excited states of the solution. In order to estimate the solvation energy in a solution containing N identical solvent molecules and one solute molecule, only Van der Waals interactions were taken into account.

In the zeroth order of approximation, he considers that all spherical isotropic molecules are free of interactions. So, the energy states of the system in the zeroth order of approximation are the sums of the electronic state energies of the unperturbed molecules. So, the energies corresponding to the ground (W_g^0) and excited (W_e^0) states of the system in its gaseous phase are given, respectively, by:

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$$W_g^0 = W_g^0(u) + NW_g^0(v) \quad (3)$$

$$W_e^0 = W_e^0(u) + NW_g^0(v) \quad (4)$$

In solution, van der Waals interactions occur. They were taken into consideration by supplementary terms ΔW_g and ΔW_e for the ground and the excited states of the system, respectively, as it results from the relations (5) and (6), [12];

$$W_g^l = W_g^0 + \Delta W_g \quad (5)$$

$$W_e^l = W_e^0 + \Delta W_e \quad (6)$$

The wavenumber of the electronic absorption band ν_l of the spectrally active molecule in solution is expressed by relation (7):

$$hc(\nu_l - \nu_0) = \Delta W_e - \Delta W_g \quad (7)$$

In relation (7) ν_0 is the wavenumber of the studied electronic absorption band for the gaseous state of the spectrally active molecule. The solvation energies ΔW_g and ΔW_e correspond to the universal interactions in solutions of the spectrally active molecule which passes through its ground state to the excited electronic state. Finally, a relation between the dipole moments and polarizability of the spectrally active molecule and the parameters "a" and "b" of the solution was obtained.

$$[\mu_e^2(u) - \mu_g^2(u)] + a\alpha_e(u) = b \quad (8)$$

where:

$$a = \frac{\frac{3}{2} I_g(v) \alpha_g(u) \frac{I_g(u) - hc\nu_l}{I_g(v) + I_g(u) - hc\nu_l}}{3 \frac{M_V}{4\pi N_A \rho_V} \left[\frac{(\epsilon_V - n_V^2)(2\epsilon_V + n_V^2)}{\epsilon_V(n_V^2 + 2)^2} + \frac{n_V^2 - 1}{n_V^2 + 2} \right]} \quad (9)$$

$$b = \frac{-\frac{\nu_l - \nu_0}{C} + \frac{3}{2} \alpha_g(v) \alpha_g(u) \frac{I_g(u) I_g(v)}{I_g(v) + I_g(u)}}{3 \frac{M_V}{4\pi N_A \rho_V} \left[\frac{(\epsilon_V - n_V^2)(2\epsilon_V + n_V^2)}{\epsilon_V(n_V^2 + 2)^2} + \frac{n_V^2 - 1}{n_V^2 + 2} \right]} \quad (10)$$

In relations (8 and 9) I is the ionization potential, ϵ and n are the electrical permittivity and refractive index of the solvent, M and r are molar mass and density of the solvent, N_A is Avogadro number and C is a constant.

When only the van der Waals interactions are considered, relation (8) permits to estimate the dipole moments and polarizabilities in the electronic states responsible for the electronic band appearance [14-15]. The Abe model of a diluted solution has been applied in order to determine some electro-optical parameters of anthracene in its excited electronic state.

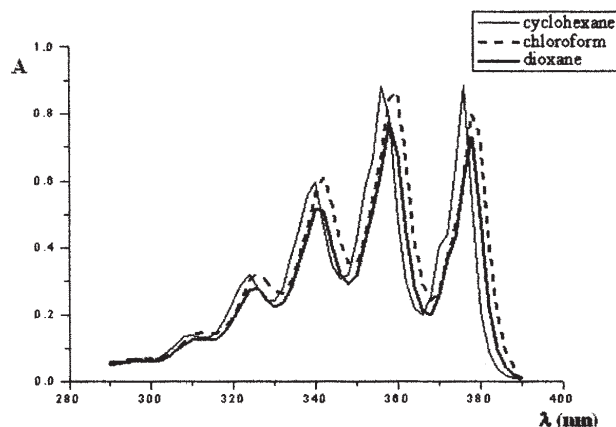


Fig. 1. Electronic absorption spectra of anthracene in some solvents

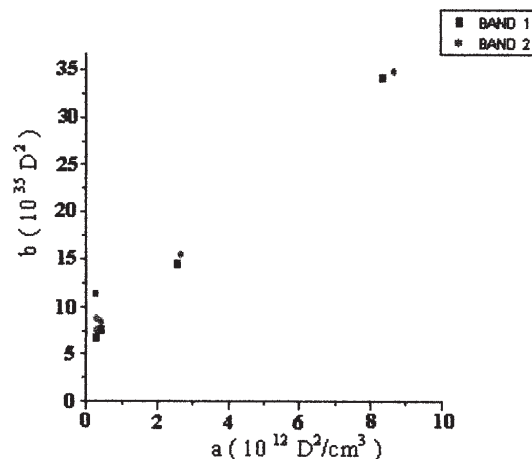


Fig. 2. b vs. a from relations (9) and (10) for visible anthracene vibronic bands 1 and 2

Materials and methods

The absorption spectra were recorded by means of a Specord M42 spectrophotometer, Carl Zeiss Jena, using 10 mm quartz cells.

The solvents used in this study were spectrally grade and purified by known methods [16] in order to eliminate the water traces.

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

Results and discussion

Assuming that all the molecules in the solution are spherical, and between them only van der Waals interactions act, T. Abe' theory is applied here in order to verify its applicability to the study of solvent influence on the visible vibronic band of anthracene.

The coefficients "a" and "b" were calculated using relations (9) and (10) and they were graphically represented in the plane (a, b). The dependences are

Table 1
WAVENUMBERS OF THE VIBRATION COMPONENTS OF THE VISIBLE ELECTRONIC ABSORPTION BAND OF ANTHRACENE

Solvent	$\nu(\text{cm}^{-1})$			
	Band 1	Band 2	Band 3	Band 4
Dioxane	32150	30770	29410	27930
Acetonitrile	31750	30860	29500	28090
Methanol	32360	30960	29590	28090
Ethanol	32260	30860	29500	28090
Chloroform	32050	30680	29240	27860
Cyclohexane	32260	30860	29500	28090

Table 2
MICROSCOPIC PARAMETERS IN THE EXCITED STATE OF ANTHRACENE

Vibronic bands	$\alpha_e (cm^3)$	$\mu_e (D)$
Band 1	$317.55 \cdot 10^{-25}$	8.49
Band 2	$318.67 \cdot 10^{-25}$	8.38
Band 3	$311.03 \cdot 10^{-25}$	6.99
Band 4	$301.68 \cdot 10^{-25}$	7.71

illustrated in figure 2 for two vibration components of the visible absorption band of anthracene.

A linear dependence of the type (8) between **a** and **b** was evidenced. In relation (8) $\alpha_e(u)$ represents the slope and $\mu_e^2(u) - \mu_g^2(u)$ represents the cut at ordinate for the resulting straight line (fig. 2). Having in view the D_2 symmetry of anthracene, the permanent electric dipole moment in its ground state is null. So, only the second term from the square difference of the dipole moments differs from zero. The cut at ordinate of the obtained straight line from figure 2 is equal to $\mu_e^2(u)$ in the case of anthracene.

When the electric dipole moment in the ground state of the spectrally active molecule is known, the electric dipole moment in the excited state can be estimated by using relation (8).

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, are listed in table 2.

From table 2 it results an increase 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 $\alpha_e(u)$ determined for the four vibration components of the visible electronic absorption band of anthracene are in limits of variation of the molecular electric dipole moment and of the polarizability in the vibration motions [17].

Conclusions

The spectral method derived from the Takehiro Abe' model of a pure, simple liquid can be successfully used to estimate some microscopic parameters in the excited states of anthracene, like polarizability and electric dipole

moments. The obtained values are in a good agreement with the large delocalization of the anthracene π -electronic cloud.

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