Computation of dielectric properties of nano-probe local surroundings by solvatochromic spectral shift measurement of organic dye molecule

A. S. Stepko¹, P. V. Lebedev-Stepanov¹ ²

¹Photochemistry Center of FSRC Crystallography & Photonics RAS Novatorov St., 7a/1, Moscow, 119421, Russia
²National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), 31 Kashirskoe shosse, 115409, Moscow, Russia

E-mail: tousen@bk.ru

Abstract. Study of dielectric properties of the macrocyclic molecules cavity that can form inclusion complexes with dye molecules is an important problem. Changes in absorption spectra of chromophore inserted into macrocyclic cavity with the formation of the supramolecular complex can be considered as solvatochromic shift. This shift caused by changes of dielectric properties of the environment around the chromophore when it moves from water solution to macrocyclic cavity. Theoretical model that can describe the effective dielectric permittivity of the cavity allows predicting solvatochromic spectral shift of dye molecules due to non-covalent supramolecular complexation. Such a dye molecule could apply as a nano-probe for measurement of the effective dielectric constant of any local surrounding media in which its chromophore can be inserted.

1. Introduction

Theoretical model allows to work with a wide range of dielectric permittivity therefore there are no constraints as in the experimental study. The method needs only set of values for parameterization of the Onsager–Liptay equation. In the present work we have been using this approach for determination of dielectric properties of cavitand (cucurbit [7] Apr (CB [7])) which involved in complexation with styryl dye molecules.

Experimental and theoretical study of the dependence of optical spectra on the position of dyes chromophore (1-(2-ammonioethylnyl)-4-[[(E)-2-(3,4-dimethoxyphenyl)ethylnyl]pyridinium diperchlorate (D1), 1-(3-ammoniopropyl)-4-[[(E)-2-(3,4-dimethoxyphenyl)ethylnyl]pyridinium diperchlorate (D2), and 1-(5-ammoniopentyl)-4-[[(E)-2-(3,4-dimethoxyphenyl)ethylnyl]pyridinium diperchlorate (D3), containing two, three, and five methinyllene groups, respectively ) were carried out in previous work [1].

Our calculations showed that in the D1@CB [7] and D2@CB [7] inclusion complexes (where @ is the conventional symbol for supramolecular complex), the pyridinium residue of the dye is located inside the CB [7] cavity, which is less polar than water. This leads to a bathochromic (red) shift of absorption bands of the D1@CB[7] and D2@CB[7] complexes as compared with the spectra of these dyes in water. On the contrary, in the spectrum of D3@CB [7] the chromophore moiety of which...
remains in an aqueous environment, a weak hypsochromic (blue) shift of the long wavelength absorption band is observed (fig. 1).

![Absorption spectra](image1)

### Figure 1

Upper panel: absorption spectra of the dyes and their complexes (A is a dye, and AB is a complex). Lower panel: optimized structures of the D1@CB[7], D2@CB[7], and D3@CB[7] complexes (L is the distance between the centers of masses of SD and CB[7] in complexes.

The changes in the spectra of D2 in different solvents and by complexation with CB[7] can be understood on the basis of the ideas of the Onsager theory [2] about the dipole–dipole (universal) interaction of styryl dye (SD) with water molecules and with the CB [7] cavity. Water is one of the most polar solvents. It is known that the more polar the solvent, the larger the short-wavelength shift of their absorption bands of pyridine derivatives. In our experiments, on the contrary, the addition of CB[7] cavitand with a nonpolar cavity to the water leads to a transition of the dye from the polar medium to the nonpolar one, which should be accompanied by a red shift of the long-wavelength absorption band. This is actually observed for D1 and D2 since their pyridine residues are located in the CB[7] cavity.

2. Model

In the present work, we have been using Onsager–Liptay [2-4] theory to calculate solvatochromic shift. Our experimental study of solvatochromic effect was carried out for D2 with a set of different solvents: methanol, ethanol, I-propanol, n-butanol and water with known dielectric and optical properties (fig. 2).
According to Onsager theory, the value of the absorption spectra shift of a molecule in solution relative to the same molecule in vacuum can be represented as the sum of contributions of dispersion, dynamic polarization and orientation-induction interactions.

Essence of the effect is that the orientation polarization contribution of the dipole moments of ground and excited state changes under the action of the solvent reaction field. The difference in the energies of the ground and excited states also changes, so that is the basis for calculating the shift of the spectral line. Thus, the Onsager model gives a quite rough approximation due to the difference in shape of the studying molecules from the spherical one for which the theory was developed. This model allows to describe solvatochromic processes for different systems as it was shown in many works \cite{4, 5}. Nevertheless, this model is an estimate and simple approach that accurately conveys the general physics of the effect.

According to the theory, the dye molecule can be represented as a sphere with radius $a$ and dipole moment placed in the center. In this approximation, the energy shifts of electronic states caused by nonspecific interactions, as follows from the theory of the Onsager reaction field, described by the equations:

$$
\mu = \mu_0 + \alpha \varepsilon E_R, \quad E_R = (f_{ind} + f_{aur}) \mu,
$$

$$
f_{aur} = \frac{2}{a} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right), \quad f_{ind} = \frac{2}{a} \left( \frac{n^2 - 1}{2n^2 + 1} \right),
$$

where $E_R$ is Onsager reaction field strength; $\mu$ is the dipole moment of the dissolved molecule; $f_{ind}$ and $f_{aur}$ are induction and orientation factors; $\mu_0$ and $\alpha$ are dipole moment and polarizability of the molecule in the vacuum; $a$ is the effective size of the molecule; $\varepsilon$ and $n$ are dielectric constant and refractive index of solvent respectively. In the case of charged molecule (for example, dication), $\mu$ and $\mu_0$ are the orientation-induction contribution to the total dipole moment of the dye molecule in solution and in vacuum respectively. This contribution is invariant relative to coordinate transformation. Then, according to the Onsager-Liptay theory \cite{2-4}, the change of the wave number $hc\Delta\nu$ is determined by the equation:

![Figure 2. Shifts of D2 absorption spectra depending on permittivity of the solvent.](image-url)
$h\epsilon\Delta \nu = -\frac{1}{2} \frac{2}{a^3} \left[ \frac{n^2 - 1}{2n^2 + 1} \right] \mu_e - \mu_g \left[ 1 - \frac{2}{a^3} \left( \frac{n^2 - 1}{2n^2 + 1} \right) \alpha \right]^{-1} - \frac{2}{a^3} \frac{\mu_e - \mu_g}{\epsilon - 1} \left[ 1 - \frac{2}{a^3} \left( \frac{\epsilon - 1}{2\epsilon + 1} \right) \alpha \right]^{-1} \mu_g,$

(2)

where $h$ is Planck constant, $c$ is a light velocity, $\mu_e$ and $\mu_g$ are dipole moments of the ground and excited states of dye molecule respectively, $\Delta \nu$ is a solvatochromic frequency shift, $\alpha$ is polarizability of the molecule.

3. Calculations

Quantum chemical method TDDFT with functional CAM-B3LYP and basis 6-311G (d,p) implemented in Gamess-US software package was used to calculate molecular structure, dipole moments of the ground (39.7 D) and excited (34.3 D) states, and polarizability (609.3 a.u,) of the dye molecule.

Formula (2) allows identifying spectral shift for different values of $\epsilon$ and $n$. As a result of the calculations, absorption spectrum shifts of D2 for set of solvents with different dielectric permeability relative to H2O were obtained. These results (fig. 2) are presented in Table 1 in comparison with our experiments. The extrapolation calibration graph for determination of dielectric permeability by experimental solvatochromic spectral shift is presented in figure 3. This graph was obtained by the formula (2) with using a single fitting parameter, the effective size of the molecule $a$. The fitted value of $a$ is 5.6Å.

On the other hand, an effective size of the molecule can be estimated by calculation of its volume, taking into account van der Waals radii of atoms and their mutual overlap (fig.4). Van der Waals radii of the atoms are 1.2 Å (H), 1.7Å (C), 1.52 Å (O), and 1.55 Å (N).

Algorithm of size estimation includes he next items.

1. A paralleleppipered is constructed which completely includes the space region occupied by the given molecule (fig. 4).
2. This paralleleppipered is divided into many small identical parallelepipeds with the volume of $\Delta V = \Delta x \Delta y \Delta z$ with the sizes of the sides $\Delta x$, $\Delta y$, $\Delta z$ which are much smaller than van der Waals radii of the atoms.
3. The total volume of the molecule is calculated by the formula:

$$V = \Delta V \sum_i \sum_j \sum_k g(i, j, k),$$

(3)

where $g(i,j,k)=1$ if a small parallelepiped with coordinates $(i, j, k)$ located inside of at least one of Van der Waals spheres of the molecule; in the opposite case, this value is given by $g(i,j,k)=0$.

The estimated volume of the dye molecule (fig 4) is 296 Å$^3$. This volume corresponds to a sphere with a radius of 4.2 Å. It is quite close to fitted value of characteristic size of the molecule. We found that solvatochromic shift of CB[7] cavity corresponds to effective dielectric constant 13.6 (fig. 3).

According to experimental data [5], the dielectric constant of the cucurbit[7]uril cavity is comparable to octanol ($\epsilon = 10.3$). This result is quite close to our estimation.
Table 1. Calculated and experimental absorption spectrum shifts of D2 for set of solvents with different dielectric permeability relative to H$_2$O

| Solvent | E  | N   | Calculated shift relative to H$_2$O, cm$^{-1}$ | Experimental shift relative to H$_2$O, cm$^{-1}$ |
|---------|----|-----|-----------------------------------------------|-----------------------------------------------|
| H$_2$O  | 80.1| 1.333| 0                                             | 0                                             |
| MeOH    | 32.6| 1.327| 605                                           | 825                                           |
| EtOH    | 24.3| 1.361| 859                                           | 1070                                          |
| i-PrOH  | 20.8| 1.378| 1068                                          | 887                                           |
| n-BuOH  | 17.8| 1.399| 1291                                          | 1251                                          |

Figure 3. Extrapolation calibration curve for determination of the effective permittivity of the cavity of CB [7] based on the theoretical dependence of the solvatochromic shift on $\varepsilon$ (formula (1)).

Figure 4. The space region occupied by the molecule 1-(3-ammoniopropyl)-4-[(E)-2-(3,4-dimethoxyphenyl)ethinyl]pyridinium diperchlorate (D2).

4. Conclusion
Our approach gives the value of the effective dielectric constant of the local environment of the dye molecule which works like nano-probe, by experimental determination of the solvatochromic shift of
nano-probe inserted in such environment (fig. 4). The method allows working with wide intervals of dielectric permittivity by extrapolation of small sets of experimental beyond the initial interval of $\varepsilon$ by formula (2). The use of an extrapolation calibration graph can significantly reduce the number of experiments. Input data for extrapolation includes only set of the calculating values for Onsager-Liptay equation (2). The characteristic size of the dye is a fitting parameter, the value of which is in good comparison with exact calculation (3).

The innovative potential of the method is in development of nano-probe devices for measuring the dielectric constant of small objects and nano-regions into bulk fluid volume.

**Acknowledgements**

This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS in part of quantum chemistry calculation and experimental study of solvatochromic effect. In addition, this work was supported by the “Improving of the competitiveness” program of the National Research Nuclear University MEPhI (Moscow Engineering Physics Institute) in part of molecule volume and characteristic size determination.

**References**

[1] Avakyan V.G., Stepko A.S., Lobova N.A., Grushnikova E.Yu., Sazonov S.K., Gromov S.P., Plotnikov V.G., Lebedev-Stepanov P.V. 2017 *Doklady Physical Chemistry* **476** pp 406-409
[2] Liptay W. Sinanoglu O. (Ed.) Modern Quantum Chemistry Part II: Interactions 1965 *Academic Press New York* pp 282(Chapter 5)
[3] Komarov P.V., Plotnikov V.G. 2012 *International Journal of Quantum Chemistry* **112** pp 3039-3045
[4] Komarova K.G., Sakipov S.N., Plotnikov V.G., Alfimov M.V. 2015 *Journal of Luminescence* **164** pp 57-63
[5] Khaleel I. A., Werner M. N. 2015 *Chemical Society Reviews* **44** pp 394-418