Estimation the dielectric properties of solvation shells and nano-cavities by solvatochromic shift of organic dye

A.S. Stepko¹, O.A. Savenko¹, P.V. Lebedev-Stepanov¹,²

¹FSRC 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: petrls@yandex.ru

Abstract. We investigated the preferential solvation effect of pyridinium-N-phenolate betaine (organic dye) taken as a molecular probe in two binary solvents (water-BuOH and water-BuNH₂) in concentration range 0-100%. The Onsager-Liptay model was used to connect the spectral solvatochromic shift in solvation shell of the dye with the dielectric permittivity of the environment around its chromophore. That makes it possible to estimate the effective dielectric constant in the microscopic region of the probe, based on the values of the experimentally measured solvatochromic shifts. It was shown that the solvation shell of the dye is significantly depleted with the second component of binary solvent in water solution. It is true both for the water-BuOH and water-BuNH₂ solvents. The absolute spectral shift in case of water-BuNH₂ solvent is greater than in the second case. However, the relative depletion is stronger in case of water-BuOH. The innovative potential of the method is in the development the nanoprobe devices to measure the dielectric constant of small objects and nano-regions, to control instantaneous solvent concentration into evaporating sessile droplet of binary solvent in different zones of the droplet.

1. Introduction

A study of the dielectric properties of the local environment of the dye molecule, which works like nano-probe, is a relevant problem from both theoretical and practical standpoints. The change of the absorption and luminescence spectra of a chromophore placed into nano-cavity, thin layer or specific solvation shell can be considered as a solvatochromic shift associated with the change of the dielectric properties of the chromophore surrounding. Theoretical description of the effective local dielectric permittivity allows predicting the magnitude of the solvatochromic shift of the dye spectrum upon complex formation, which is of interest when designing optical chemosensors.

The effective use of a dye as a nanoprobe that makes it possible to measure the local value of the effective dielectric permittivity of a cavitand upon the formation of a supramolecular complex with this dye is demonstrated in [1-2]. For this purpose, a solvent was selected experimentally to ensure the solvatochromic shift of the spectrum of a dissolved dye (rhodamine) equals to the shift produced upon complex formation between the dye and cavitand (cucurbituril). It is obvious that the use of this
method is limited by the solubility range of the dye in solvents with different dielectric constants. On the other hand, the calculation methods for the solvatochromic shifts of optical spectra based on various versions of the Onsager model [3] have been developed well over the past few decades [4-6]. The application of these techniques to the interpretation of the shifts of the dye spectrum, which are associated with placing it into a new local surrounding, for example, upon formation of a supramolecular complex, makes it possible to determine theoretically the local dielectric constant. 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 equation.

The cucurbituril cavity was considered as a polar environment into which the dye chromophore is placed. Positions of the maxima of the dye absorption spectra were measured experimentally in some solvents with known dielectric and optical properties. These values were used for parametrization of semi-empirical equation that can estimate the dielectric constant of local surrounding of dye placed in another solvent, nano-cavity or cavitand.

In this work, we used this method to study the properties of binary solvents. Investigation of the properties of binary and multicomponent solvents is an important area of modern fundamental and applied science. Most biochemical processes take place in complex multicomponent environments. Such environments are often the subject of research in medical diagnostics and sensing. The local concentrations of the components of the complex solvent near the molecule of solute, as a rule, differ from the average for the solution, so that the solvation shell is enriched with that component of the solvent to which the indicated molecule has a greater affinity.

Competition of the solvent particles for a place in the immediate vicinity of the solute molecule takes place. Molecular shell appears around the solute molecule, the microscopic composition of which, at least within the first coordination sphere, differs significantly from the macroscopic relative fraction of particles in solution. In the case of binary solvent, the concentration of binary solvent into such a shell differs from average concentration of binary solvent in bulk solution.

Thus, the value of the solvatochromic shift in the solvation shell can provide information on the deviation of the effective dielectric constant inside it from the macroscopic value of the indicated value. This difference indicates the preferential (selective) solvation of this chromophore, i.e. the perturbation of local concentration of the binary solvent components in the solvation shell in comparison with the macroscopic value of the solution concentration.

Comparison of this local concentration with the value of the dielectric permeability makes it possible to study the effect of selective solvation and the investigate the structure of solvation shell depending on the concentration of the binary solvent.

In this work, we used the pyridinium-N-phenolate betaine as a solute molecule (molecular probe). We investigated two binary solvents (water-BuOH and water-BuNH₂) in concentration range 0-100%. For the theoretical interpretation of the solvatochromic shifts in solvation shell of the dye, the Onsager-Liptay [1, 4-6] model was used, that makes it possible to estimate the effective dielectric constant in the microscopic region immediately adjacent to the chromophore, based on the values of the measured (experimental) solvatochromic shifts.

2. Model

The Onsager–Liptay model [1,2] was used to calculate solvatochromic shift. According to Onsager theory, the value of the absorption spectral 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 [2,3]. This model is a simple approach that accurately conveys the general physics of the effect. The dye molecule can be represented as a sphere of radius \( a \), and dipole moment placed in the center.

In this approximation, the energy shift of electronic states is described by nonspecific interactions, as follows from the theory of the Onsager’s reaction field, described by the equations:

\[
\begin{align*}
    \mathbf{E}_R &= \frac{2}{a^3} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right), \\
    f_{\text{ind}} &= \frac{2}{a^2} \left( \frac{n^2 - 1}{2n^2 + 1} \right),
\end{align*}
\]

where \( \mathbf{E}_R \) is Onsager reaction field strength; \( \mu \) is the dipole moment of the dissolved molecule; \( f_{\text{ind}} \) and \( f_{\text{or}} \) are induction and orientation factors; \( \mu_0 \) and \( \alpha \) are dipole moment and polarizability of the molecule in the vacuum respectively; \( a \) is the effective size of the molecule; \( \varepsilon \) and \( n \) are dielectric constant and refractive index of solvent. Then, according to the Onsager-Liptay theory [2-4], the change of the wave number \( \Delta \nu \) is determined by the equation:

\[
\begin{align*}
    h c \Delta \nu &= -2 \left( \frac{\mu_e - \mu_g}{a^3} \right) \varepsilon - 1 \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) \alpha - 2 \left( \frac{\mu_e - \mu_g}{a^3} \right) \varepsilon - 1 \left( \frac{\varepsilon - 1}{2\varepsilon + 1} \right) \alpha^{-1} - \\
    &- \alpha^2 \mu_g.
\end{align*}
\]

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

Eq. (2) allows identifying spectral shift for different values of \( \varepsilon \) and \( n \). As a result of the calculations, absorption spectrum shifts of dye for set of solvents with different dielectric permeability relative to H_2O can be obtained.

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

The extrapolation calibration graph for determination of dielectric permeability by experimental solvatochromic spectral gives the opportunity to estimate the parameter \( a \), the effective size of a molecule, which is a single fitting parameter.

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 (as it is shown in picture below). Van der Waals radii of the atoms [in Angstrom units] are 1.2 Å (H), 1.7Å (C), 1.52 Å (O), and 1.55 Å (N).

Algorithm of size estimation includes the next items.

1. A parallelepiped is constructed which completely includes the space region occupied by the given molecule.
2. This parallelepiped 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:

\[
V = \Delta V \sum_i \sum_j \sum_k g(i, j, k),
\]
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 \( g(i,j,k) = 0 \).

### 3. Calculations

We used the pyridinium-N-phenolate betaine as a solute molecule (molecular probe). We investigated two binary solvents (water-BuOH and water-BuNH\(_2\)) in concentration range 0-100%.

The experimental values of the spectral shifts were taken from [7]. For the theoretical interpretation of the solvatochromic shifts in solvation shell of the dye, the Onsager-Liptay model was used, that makes it possible to estimate the effective dielectric constant in the microscopic region immediately adjacent to the chromophore, based on the values of the measured (experimental) solvatochromic shifts.

We have calculated the molecular structure, dipole moments of the ground and excited states (in Debye units), and polarizability matrix (in atomic units) of the dye by the method TDDFT with functional CAM-B3LYP and basis 6-311G (d,p):

\[
\begin{align*}
\mathbf{\mu}_g &= (-0.69, -13.82, 4.39), \\
\mathbf{\mu}_e &= (-0.60, -6.53, 2.15), \\
\alpha &= \begin{pmatrix} 526.67 & -15.19 & -18.49 \\ -15.19 & 650.89 & -18.49 \\ -18.49 & -131.76 & 349.79 \end{pmatrix}
\end{align*}
\]

The orientation of the electric dipole vector is presented in Fig.1.

![Fig.1. Orientation of the electric dipole vector in pyridinium-N-phenolate betaine.](image)

Comparison of experimental data and calculation results are placed in Tables I and II and in Fig.2.
Table I. Experimental [7] and calculated spectral shifts of the dye relative to water in BuOH-water solvent.

| %mol BuOH | $\varepsilon_{\text{eff}}$ | $\lambda_{\text{max}}, \text{nm}$ | $v_{\text{max}}, \text{cm}^{-1}$ | Experimental shift, cm$^{-1}$ | Calculated shift, cm$^{-1}$ |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0         | 80.1            | 610.5           | 16380.0         | 0               | 0               |
| 5         | 76.9            | 582.5           | 17167.4         | -787.3          | -31.0           |
| 10        | 73.7            | 562.9           | 17765.1         | -1385.1         | -64.5           |
| 20        | 67.4            | 556.3           | 17975.9         | -1595.9         | -140.3          |
| 30        | 61.0            | 551.9           | 18119.2         | -1739.2         | -230.3          |
| 40        | 54.7            | 550             | 18181.8         | -1801.8         | -339.2          |
| 50        | 48.3            | 546.8           | 18288.2         | -1908.2         | -473.6          |
| 60        | 41.9            | 545.1           | 18345.2         | -1965.2         | -643.5          |
| 70        | 35.6            | 542.4           | 18436.6         | -2056.5         | -865.3          |
| 80        | 29.2            | 540.7           | 18494.5         | -2114.5         | -1167.1         |
| 90        | 22.9            | 538.8           | 18559.8         | -2179.7         | -1602.4         |
| 95        | 19.7            | 537.9           | 18590.8         | -2210.8         | -1901.0         |
| 100       | 16.6            | 535.8           | 18663.7         | -2283.6         | -2284.2         |

Table II. Experimental [7] and calculated spectral shifts of the dye relative to water in BuNH$_2$-water solvent.

| %mol BuNH$_2$ | $\varepsilon_{\text{eff}}$ | $\lambda_{\text{max}}, \text{nm}$ | $v_{\text{max}}, \text{cm}^{-1}$ | Experimental shift, cm$^{-1}$ | Calculated shift, cm$^{-1}$ |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 0             | 80.1            | 610.5           | 16380.0         | 0               | 0               |
| 5             | 76.34           | 577.6           | 17313.0         | -933.0          | -15.4           |
| 10            | 72.6            | 563.3           | 17752.5         | -1372.5         | -33.2           |
| 20            | 65.1            | 555.5           | 18001.8         | -1621.8         | -73.7           |
| 30            | 57.5            | 548.1           | 18244.1         | -1864.8         | -124.0          |
| 40            | 50.0            | 541.5           | 18467.22        | -2087.2         | -188.8          |
| 50            | 42.5            | 535.6           | 18670.6         | -2290.6         | -274.6          |
| 60            | 35.0            | 530.8           | 18839.5         | -2459.5         | -394.0          |
| 70            | 27.5            | 526.9           | 18978.9         | -2598.9         | -571.4          |
| 80            | 19.9            | 523.4           | 19105.8         | -2725.8         | -862.3          |
| 90            | 12.4            | 520             | 19230.8         | -2850.8         | -1430.0         |
| 95            | 8.7             | 517.8           | 19312.5         | -2932.5         | -1978.1         |
| 100           | 4.9             | 515.2           | 19409.9         | -3029.9         | -3028.3         |
Fig. 2. Experimental (*) and calculated (•) spectral shifts of the dye relative to water in BuOH-water solvent (left) and BuNH₂-water solvent (right).

It is clear that experimental shifts correspond to the average (bulk) concentrations of the binary solvent, while the theoretical shifts correspond to the local concentrations of solvent in the solvation shell around the dye molecule due to the chromophore interacts with its local surrounding. Fig. 2 shows that the local concentrations (calculated) differ from the bulk concentrations (experimental). Thus, the preferential solvation takes place in both cases of considered binary solvents in whole range of bulk binary concentration.

Comparison of the local and average (bulk) concentrations of the binary solvent shows that the calculation gives a smaller spectral shift value relative to the pure water than the experiment for a given average concentration. On the other hand, the solvatochromic shift determines strongly by the local concentration of the solvent around the chromophore. Then the solvation shell of the dye is significantly depleted in water. It is true both for water-BuOH and water-BuNH₂ solvents. The absolute spectral shift in case of water-BuNH₂ solvent is greater than in the second case. However, the relative depletion is stronger in case of water-BuOH solvent.

4. Conclusion

It was estimated the value of dielectric permittivity of the local environment of the dye molecule (pyridinium-N-phenolate betaine) dissolved in the binary solute by experimental determination of the solvatochromic shift of its chromophore in that solute. There is the preferential solvation effect. Solvation shell of the dye is significantly depleted with the second component of binary solvent in water solution.

It is reasonable to assume that this method could allow to study very wide intervals of dielectric permittivity by extrapolation of small sets of experimental beyond the initial interval of ε. The application of an extrapolation calibration graph could significantly reduce the number of experiments. Input data for extrapolation includes only set of the calculating values for Onsager-Liptay equation.

Investigation of the properties of multicomponent solvents is an important area of modern fundamental and applied science. Most biochemical processes take place in complex multicomponent environments. Such environments are often the subject of research in medical diagnostics and sensing. In particular, this method could allow to measure the local instantaneous concentration of a binary solvent in a dynamic system, such as an evaporating drop of a binary solution. This could make it possible to optimize the processes of self-organization and self-assembly in such a system [8].

The innovative potential of the method is in the development the nanoprobe devices for measurement the dielectric constant of small objects and nano-regions into bulk fluid volume, including small cavities in bulk liquid and pico- and femtoliter droplets of the liquid.
This work was supported by the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS and Russian Foundation for Basic Research, Grant 19-02-00937.

References

[1] Stepko A.S., Lobova N.A., Lebedev-Stepanov P.V. 2019 *Optics and Spectroscopy*. **126** (4) pp. 309-315
[2] 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
[3] Onsager L. 1936. *J. Am. Chem. Soc.* **58** pp 1486-1493.
[4] Liptay W.Sinanoglu O. (Ed.) Modern Quantum Chemistry Part II: Interactions 1965 *Academic Press New York* P. 282(Chapter5)
[5] Bakhshiev N.G. Photophysics of Dipole-Dipole Interactions: The Processes of Solvation and Complexation 2006 *SPb. Gos. Univ., St. Petersburg* [in Russian]
[6] Komarov P.V., Plotnikov V.G. 2012 *International Journal of Quantum Chemistry* **112** pp 3039-3045
[7] Kipkemboi P.K., Easteal A.J. 1994 *Aust. J. Chem.* **47** pp 1771-1781
[8] Savenko O.A.. Lebedev-Stepanov P.V. *International Conference Droplets* 2019. Durham, UK. Abstracts for Poster Session, Part II, p. 46.