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Evidence of the specific solvation of selected fluorescent dyes with methoxy group and its analogues derivatives of the 7H-indolo[1,2-a]quinolinium system

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Abstract

The fluorescence quantum yield of the 5-(4-methoxyphenyl)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium perchlorate and its analogues was determined in 12 selected solvents of the hydroxyl and CH-acid type and in the dichloromethane–acetonitrile binary system at constant and variable temperature. The quenching process, which depends on the dye and solvent structure, in hydroxylic ones was caused by dissociation of the solvent–dye complex. A rare phenomenon of the dye fluorescence quantum yield raising along with the increase in temperature is observed. It has been proved that methoxy group and its derivatives is a negatively charged complexing centre and the complex stability raises along with the increasing electron donor character of alkyl fragment. This conclusion is supported by theoretical calculations of bonding energy. The important role of a local dielectric constant and the method of its calculation are discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Solvent dipolar interaction; Electrostatic potential of polar solvents; Local dielectric constant; Fluorescence quantum yield; 5-(4-R-phenyl)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium salts; Solvates stability constants; Weak bonding energy determination

1. Introduction

Sometimes photochemical reactions can proceed very selectively e.g., photosynthesis of starch, but in most cases they generate a mixture of many products, difficult to separate and purify. Therefore photocyclization and dehydrogenation of compounds, described by us, containing 3-azoniahexa-1,3,5-triene system, which run as 6π -electrocyclic process, seem to be a very nice exception [1–5]. Many classes of compounds undergo that reaction, including hemicyanine-like dye derivatives of 3H-indole [1–3]. Photo-products show more rigid and compact constitution than substrates and more extended π -electronic system. Those features cause a high photostability of the photoproducts and a strong fluorescence both in solid state and in solutions. Therefore they have found numerous practical applications, e.g. as major components of active media in tunable dye lasers [6]. Searching for an optimum solvent for one of the laser dyes we observed an unexpected phenomenon – laser action quenching by acetonitrile. It was surprising, because the same dye works very effectively in dichloromethane

solution and displays the fluorescence quantum yield near unity in this solvent [7].

This paper is an attempt to explain the above mentioned phenomenon, which was undoubtedly caused by a specific solvent–solute interaction. It is well known, that the intermolecular solute–solvent interaction forces can occur in several forms such as ion–dipole forces, dipole–dipole forces, dipole-induced dipole forces, hydrogen bonding and charge transfer or electron pair donor–acceptor forces. All of them cause changes in position, intensity and shape of the absorption and emission bands of the chromogene or luminogene part of the solute molecule.

In this paper we would like to present results of solvent–solute interaction study when the 5-(4-R-oxyphenyl)-7H-indolo[1,2-a]quinolinium dyes were taken as the solute. A substituted oxygen atom connected directly with chromogene/luminogene system of the solute is a critical point of their structure. The effect of changes in the surroundings of an oxygen atom was studied.

Parent solute was the 5-(4-methoxyphenyl)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium perchlorate IQ4OME, emission characteristics of which were measured in 12 solvents: acetonitrile, ethanol, dichloromethane, 1,2-dichloroethane,

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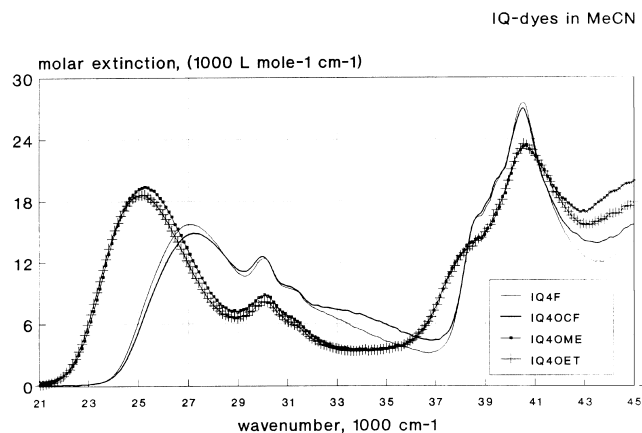


Fig. 1. The UV–VIS absorption spectra of IQ-dyes in acetonitrile solution.

1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, diethylene glycol, ethylene glycol, diethylene glycol monomethyl ether, diethylene glycol dimethyl ether and ethylene glycol monomethyl acetate at constant and varied temperature. The parent solute of IQ4OME and its analogues were examined also in an acetonitrile–dichloromethane binary solvent system at constant temperature. UV–VIS absorption spectra of IQ4-dyes are shown in Fig. 1.

The large red-shift caused by –OMe and –OEt substituents of more than 1000 cm^{-1} is very close to that observed in many classes of dyes of hemicyanine-like structure derivatives of pyrylium, pyridinium or benzo[c]quinolinium cation [8,9] and the same shift is observed in corresponding fluorescence spectra [5,6]. Moreover, the shape of absorption/emission spectra is independent from the temperature [5,9]. On this background we can conclude, that in absorption/emission processes the same electronic states are involved.

2. Experimental data and discussion

Fluorescence quantum yields of selected dyes' derivatives of the 7H-indolo[1,2-a]quinolinium cation were determined in isothermic conditions using a dozen neat solvents. Moreover, for the IQ4OME dye, additional measurements were taken both in binary solvent system of acetonitrile–dichloromethane and at variable temperature.

Comparison between absorption and fluorescence spectra of IQ4OME dye is shown in Fig. 2. The first series of experiments indicated the existence of a certain solvent's dipole moment threshold, below which a strong fluorescence is observed as opposed to a very weak fluorescence above that threshold.

Moreover, it was observed, that the fluorescence quantum yield increases parallelly with the increase in temperature. The assumption that a dye–solvent complex exists, which effectively disperses the excitation energy radiationless, seems to be a logical explanation for both phenomena.

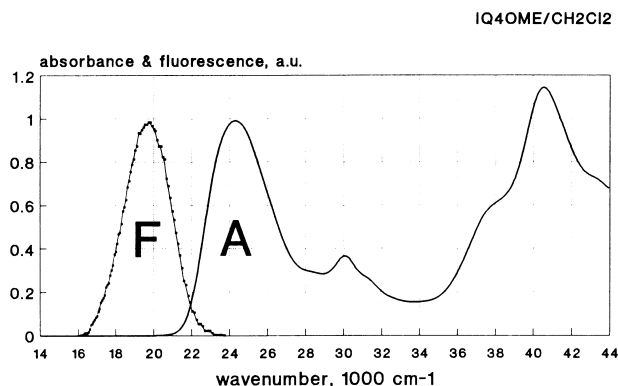


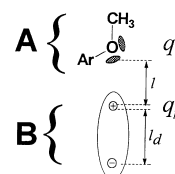
Fig. 2. The absorption and fluorescence spectra of IQ4OME dye measured in dichloromethane solution.

The stability of the complex, in which the solvent dipole interacts electrostatically with an appropriate negatively charged part of the dye-molecule, depends upon the kind of the solvent and the complex can dissociate in a thermal way. A dye-molecule devoid of a solvent partner can stay in excited state relatively for a long time losing its energy through radiation process with a high fluorescence efficiency.

Model of such a complex and its experimental verification are described ahead.

2.1. Proposition of the solvent–dye electrostatic interaction model

A complex of two interacting molecules is presented: A – dye with the lone electron pair located on oxygen atom of the 4-methoxyphenyl group connected in position 5 with 7,7-dimethyl-7H-indolo[1,2-a]quinolinium moiety (dye IQ4OME) and B – molecule of the solvent. Both components of the complex, electrostatically interacting at the distance l , have partial electrical charges; negative $-q_o$ of the dye, and positive q_p of the solvent.



The energy of ionic bond originating from intermolecular forces between A and B dipoles can be described by the Coulomb's law

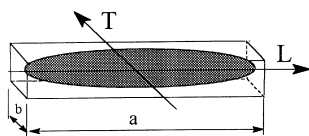
$$E = \int_l^\infty F dl = \frac{q_o q_p}{\varepsilon_{loc}} \times \int_l^\infty \frac{dl}{l^2} = \frac{1}{\varepsilon_{loc}} \times \frac{q_o q_p}{l} \quad (1)$$

where ε_{loc} means a local dielectric constant.

The partial electrical charge, situated at the active end of the solvent molecule, can be calculated from its dipole moment μ

$$q_p = \frac{\mu}{l_d} \quad (2)$$

Therefore, the calculation of the dipole length is a separate problem requiring some introduction. If the solvent molecule is approximated as an ellipsoid inserted in a cage of cuboidal shape with a square base and the shape factor s equal to a/b ,



where a and b denote respectively the longer/shorter linear dimension of a cuboid of the known volume, the length of dipole can be calculated from the volume of cuboid by following formula:

$$V = ab^2 = \frac{M}{d_{20}^4 N} \quad (3)$$

and $s = a/b$.

For the longitudinal direction, $l_d = a$

$$l_d = \sqrt[3]{\frac{s^2 M}{d_{20}^4 N}} \quad (4)$$

and for the transversal direction, $l_d = b$

$$l_d = \sqrt[3]{\frac{M}{s d_{20}^4 N}} \quad (5)$$

where M is the molar mass of the solvent, d is its density and N is the Avogadro's number.

Thus the energy of that bonding can be expressed by the following formula:

$$E = \frac{q_o \mu}{\epsilon_{loc} l} = \frac{q_o \mu}{\epsilon_{loc} l} \sqrt[3]{\frac{d_{20}^4 N}{M}} f(s) = q_o \cdot U(s) \quad (6)$$

where

$$\begin{cases} f(s) = s^2 & \text{longitudinal} \\ f(s) = 1/s & \text{transversal} \end{cases} \quad (7)$$

and $U(s)$ is the electrostatic potential generated by polar solvent molecule.

The local dielectric constant ϵ_{loc} and the bond length l constitute a separate problem.

2.2. Local dielectric constant

The space among the electrically charged ends of two interacting dipoles is too small to hold numerous solvent molecules. Therefore a macroscopic dielectric constant is not supported by any physical background. This important (on the molecular scale) problem remains unsolved. We would like to present here its approximate solution, fully realising the fact that it is only a rough approach.

If the space between two electrical dipoles is divided into two parts: the first one without any molecules of the surrounding phase and the second one with those molecules, you get an object resembling two parallel connected capacitors: a vacuum one and a capacitor with the dielectric filling. The vicarious dielectric constant of that system, when the geometrical dimension of capacitors remains invariable and degree of filling with dielectric is changed, can be described by Eq. (8),

$$\epsilon_{loc} = \epsilon_o [1 + \alpha(\epsilon - 1)] \quad (8)$$

where ϵ_o denotes the dielectric permittivity of vacuum, ϵ is the macroscopic static relative dielectric constant of the solvent and α is the degree of capacitor filled with dielectric.

If the geometry of interacting dipoles is known, and assuming that the molecules of dielectric solvents are inserted into a solid with the volume equal to that of the molecule, the degree of capacitor filling by that solid is possible to estimate.

In this case the mathematical problem boils down to determination of the volume share of the solvent solid remaining in the space surrounding the interacting dipoles. For the simplify, let the length of the solvent dipole-dye bonding is equal to one of the dimensions of the solid containing the dielectric solvent molecule.

The calculations done for a sphere are presented ahead. According to the situation presented in the figure the volume of a sphere sector may be calculated and compared to the half-volume of the sphere with diameter D .

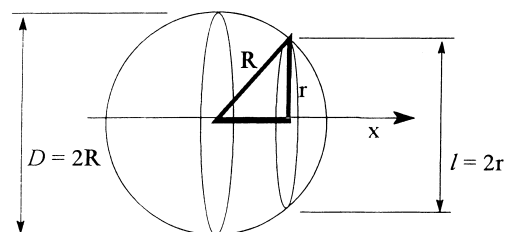
It arises from the marked triangle that

$$x = \sqrt{R^2 - r^2} \quad (9)$$

$$\begin{aligned} V_p &= \int_{x_1}^{x_2} \pi r^2 dx = \int_{\sqrt{R^2 - r^2}}^R \pi (R^2 - x^2) dx \\ &= \pi R^3 \left[\frac{2}{3} - \left(1 - \frac{r^2}{R^2}\right)^{1/2} + \frac{1}{3} \left(1 - \frac{r^2}{R^2}\right)^{3/2} \right] \end{aligned} \quad (10)$$

in relation to the sphere half-volume it is equal to

$$\begin{aligned} \alpha &= \frac{V_p}{\frac{1}{2}V_s} = \frac{2\pi R^3 \left[\frac{2}{3} - \left(1 - r^2/R^2\right)^{1/2} + \frac{1}{3} \left(1 - r^2/R^2\right)^{3/2} \right]}{\frac{4}{3}\pi R^3} \\ &= 1 + \frac{1}{2} \left(1 - \frac{r^2}{R^2}\right)^{3/2} - \frac{3}{2} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \end{aligned} \quad (11)$$



The sphere diameter D can be determined from Eq. (12), by calculating its volume using the molecular weight, specific density and Avogadro's number

$$D = \sqrt[3]{\frac{6M}{\pi d_{20}^4 N}} \quad (12)$$

Analogical calculations can be done for various elongatedly shaped solids, which may approximate the shape of solvent molecule. The symbol s denotes the shape factor, i.e. the solid's longer to the shorter dimension ratio. The results are presented.

Di axial elongated ellipsoid

$$\alpha = 1 + \frac{1}{2} \left(1 - \frac{r^2}{R^2}\right)^{3/2} - \frac{3}{2} \left(1 - \frac{r^2}{R^2}\right)^{1/2} \quad (13)$$

$$R_{\text{short}} = \frac{D}{2} \sqrt[3]{\frac{1}{s}} \quad (14)$$

$$R_{\text{long}} = \frac{D}{2} \sqrt[3]{s^2} \quad (15)$$

Cylinder

$$\alpha = \begin{cases} 0 & R > r \\ 1 & R \leq r \end{cases} \quad (16)$$

$$R_{\text{short}} = \frac{D}{2} \sqrt[3]{\frac{2}{3s}} \quad (17)$$

$$R_{\text{long}} = \frac{D}{2} \sqrt[3]{\frac{2s^2}{3}} \quad (18)$$

Regular cuboid

$$\alpha = \begin{cases} 0 & R > r \\ 1 & R \leq r \end{cases} \quad (19)$$

$$R_{\text{short}} = \frac{D}{2} \sqrt[3]{\frac{\pi}{6s}} \quad (20)$$

$$R_{\text{long}} = \frac{D}{2} \sqrt[3]{\frac{\pi s^2}{6}} \quad (21)$$

Spherocylinder (cylinder with spherical bases)

$$\alpha = \begin{cases} 1 + \frac{1}{2} \sqrt{\left(1 - \frac{r^2}{R^2}\right) \left(\left(1 - \frac{r^2}{R^2}\right) - 3\right)} & R_{\text{short}} > r \\ 1 & R_{\text{short}} \leq r \end{cases} \quad (22)$$

$$R_{\text{short}} = \frac{D}{2} \sqrt[3]{\frac{2}{3s-1}} \quad (23)$$

$$R_{\text{long}} = D = \frac{s}{2} \sqrt[3]{\frac{2}{3s-1}} \quad (24)$$

Dicone (two cones sharing one common base)

$$\alpha = \left(\frac{r}{R}\right)^3 \quad (25)$$

$$R_{\text{short}} = \frac{D}{2} \sqrt[3]{\frac{2}{s}} \quad (26)$$

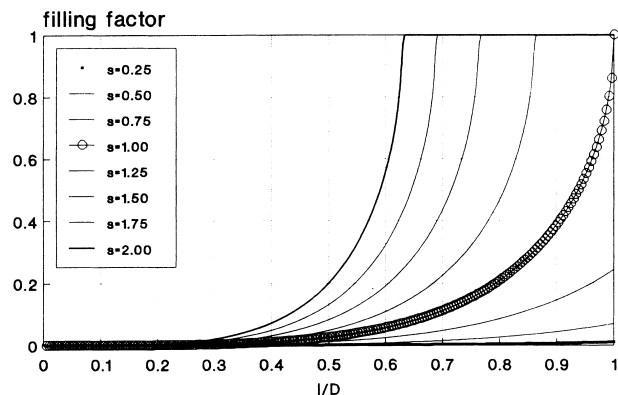


Fig. 3. The filling factor α as a function of relative dye-solvent bond length calculated for ellipsoids with different shape factor s . The circles-marked curve was found for a sphere ($s=1$). A narrow plots were computed for elongated ellipsoids ($s>1$), while more flats were found for disk-like ones ($s<1$).

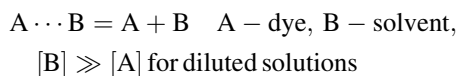
$$R_{\text{long}} = \frac{D}{2} \sqrt[3]{2s^2} \quad (27)$$

The Fig. 3 illustrates the dependence of the degree of filling α on the l/D proportion and selected shape factors s for an ellipsoid.

Disposing the method of the bonding solvent dipole-dye energy calculation, it is possible to analyse quantitatively the relationship between the fluorescence quantum yield and the solvent complex ability to form using a simple model presented ahead.

2.3. Thermal dissociation of the solvent dipole-dye complex

The dissociation of the complex can be expressed by the following equation:



The adequate equilibrium constant of that reaction, combined with the Arrhenius relation brings:

$$K = \frac{[A][B]}{[A \cdots B]} = k_0 \exp\left(-\frac{E}{kT}\right) = k_0 \exp\left(-\frac{q_o q_p}{kT \epsilon_{\text{loc}l}}\right) \quad (28)$$

The total concentration C of the dye can be formulated following:

$$C = [A] + [A \cdots B] \quad (29)$$

Practically, if the inequality $[B] \gg [A]$ is true, the solvent concentration remains constant, and to simplify the form, a new constant K_a , defined below, can be used

$$\frac{[A]}{[A \cdots B]} = \frac{K}{[B]} \equiv K_a \quad (30)$$

The concentrations of both components can be expressed by

$$[A] = C - \frac{[A]}{K_a} = C \times \frac{K_a}{1 + K_a} \quad (31)$$

$$[A \cdots B] = \frac{[A]}{K_a} = C \times \frac{1}{1 + K_a} \quad (32)$$

If the fluorescence quantum yield φ_A of dye A is greater than fluorescence quantum yield of the complex $A \cdots B$, the apparent (experimentally available) fluorescence quantum yield can be calculated directly from the defining equation

$$\varphi = \frac{n_{em}}{n_{abs}} = \frac{n_{A,em} + n_{AB,em}}{n_A + n_{AB}} \quad (33)$$

where,

$$n_A = \alpha[A] \text{ number of quanta absorbed by the dye A} \quad (34)$$

$$n_{AB} = \alpha[A \cdots B] \text{ number of quanta absorbed by the complex } A \cdots B \quad (35)$$

$$n_{A,em} = \alpha\varphi_A[A] \text{ number of quanta emitted by the dye A} \quad (36)$$

$$n_{AB,em} = \alpha\varphi_{AB}[A \cdots B] \text{ number of quanta emitted by the complex } A \cdots B \quad (37)$$

In relations presented above α is constant, if the absorption spectrum of A remains close to the $A \cdots B$ spectrum. In other cases specific molar extinction coefficients should be used.

From Eqs. (31)–(37) the measured fluorescence quantum yield can be expressed by the following formula:

$$\varphi \frac{\alpha\varphi_A[A] + \alpha\varphi_{AB}[A \cdots B]}{\alpha[A] + \alpha[A \cdots B]} = \frac{\varphi_A[A] + \varphi_{AB}[A \cdots B]}{[A] + [A \cdots B]} \quad (38)$$

$$\varphi = \frac{\varphi_A \frac{cK_a}{1+K_a} + \varphi_{AB} \frac{c}{1+K_a}}{c \frac{K_a}{1+K_a} + c \frac{1}{1+K_a}} = \frac{\varphi_A K_a + \varphi_{AB}}{1 + K_a} \quad (39)$$

This equation can be transformed into a more convenient form, enabling direct reading its parameters from the plot

$$\varphi = \varphi_{AB} + \frac{\varphi_A - \varphi_{AB}}{1 + \exp[G/T(q_p - q^0)]} \quad (40)$$

where q^0 denotes the half-position of the S-shaped function plot and is given by the relation

$$q^0 = \frac{T}{G} \ln \left(\frac{k_0}{[B]} \right) \quad (41)$$

A theoretical expression of G , according to Eq. (28) is as follows:

$$G = \frac{q_0}{kl\varepsilon_{loc}} = \frac{1}{k} U \quad (42)$$

where U is an electrostatic potential measured at the distance l from the solvent's positive pole.

2.4. Experimental determination of the fluorescence quantum yield of IQ4OME in acetonitrile at variable temperature

In order to verify the conception of electrostatic model the fluorescence quantum yield of IQ4OME dye was determined in acetonitrile solution as the function of temperature and followed the bond energy. Then the energy was compared with the values theoretically determined for different solids approximating solvent molecule shape, various solvent dipole–dye bond lengths and different electrical charge densities located at the oxygen atom of the methoxy group of IQ4OME dye. It made possible the estimation of an optimum bond length. The electrical charge densities were calculated by means of HyperChem programme [10] applying several semiempirical methods available in the programme.

The last step of the verification procedure consisted in calculating electrostatic potentials related to the solvent series dipole at the distance equal to the expected solvent–dye complex's bond length counting from the positively charged end.

If the relation between the fluorescence quantum yield of the IQ4OME dye and the electrostatic potential of the solvent dipole, determined on the basis of the acetonitrile data at variable temperature, properly explained the results obtained for other solvents at constant temperature, then the suggested model could be judged as experimentally proved.

Following the above mentioned plan the energy of solvent–dye IQ4OME bonding was calculated on the basis of the data obtained from experiments at variable temperature.

The maximum fluorescence quantum yield, corresponding to a free dye-molecule, and the minimum fluorescence quantum yield, corresponding to the solvent–dye complex, were determined based on the data obtained from experiments with other solvents.

The results of experiments and the data required for the calculations are presented in Table 1.

According to the Arrhenius equation the temperature dependence of the fluorescence quantum yield and the intermolecular complex equilibrium constant can be formulated as follows:

$$K = k_0 \exp \left(-\frac{E}{kT} \right) = \left(\frac{\varphi - \varphi_{AB}}{\varphi_A - \varphi} \right) \quad (43)$$

Table 1
Fluorescence quantum yields of acetonitrile solution of the IQ4OME dye as the function of temperature

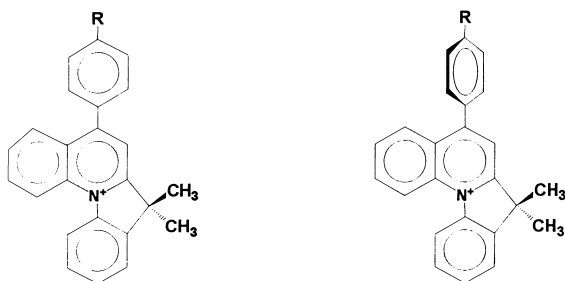
Temperature (K)	Fluorescence quantum yield (φ)	$\ln \left(\frac{\varphi - 0.12}{1 - \varphi} \right)$
278.15	0.128	−4.690
283.15	0.136	−3.989
298.15	0.157	−3.126
315.15	0.169	−2.831

The experimental data show that $\varphi_{AB} = 1$ and $\varphi_A = 0.12$. Using the least square method for the logarithmic equation (Eq. (18)) the following regression equation (Eq. (19)) has been determined

$$\ln\left(\frac{\varphi - \varphi_{AB}}{\varphi_A - \varphi}\right) = \ln(K_a) \\ = 10.746 \pm 0.755 - (4220 \pm 221) \times (1/T) \quad (44)$$

$n = 4$, $s = 0.326$, $r = 0.9491$, $F(1,2) = 18.15$,
random = 75%

The next step is to estimate the electrical charge that was present in the bonding energy formula. The charge at the oxygen atom of the IQ4OME dye was calculated for two extreme rotamers, planar and twisted one, using several semiempirical quantum-chemical methods [10].



The obtained results are presented in Table 2.

Those values were used in theoretical estimation of $O \cdots H$, $O \cdots C$, and $O \cdots HC$ bonding energies through calculating characteristic temperatures Θ of a thermodissociation process.

The value determined from the Eq. (45) displays the sense of characteristic temperature Θ of the dissociation process, which can be expressed by several formulae,

$$\frac{\Delta E}{k} = \Theta = \frac{1}{k\varepsilon_{loc}} \frac{q_o q_p}{l} = \frac{e^2}{k\varepsilon_o l_o} \frac{\rho_o \rho_p}{\varepsilon_{loc} \lambda} = \frac{e}{k} \rho_o U \quad (45)$$

where e is the electron charge, k is the Boltzmann constant, ε_o is the electrical permittivity of vacuum and $l_o = 100$ pm is the length, the electronic densities ρ_o (describing the dye)

Table 2

The results of the quantum-chemical calculations of the electron density localised at the oxygen atom of the methoxy-group in IQ4OME. The dye geometry optimised in the MM+ force field

Quantum method applied	Electrical charge density	
	Conformer	
	Planar	Twisted
AM1	0.192	0.184
MNDO	0.256	0.250
MINDO3	0.411	0.404
INDO	0.259	0.250
CNDO	0.205	0.195
Average	0.265±0.09	0.257±0.09
	0.261±0.08	

and ρ_p (describing the solvent) expressed in electron charge scale, the relative local dielectric constant ε_{loc} and λ the length of the ionic bond given in hundreds of pm. The sense of U is the electrostatic potential of solvent dipole at the distance of l .

In Eq. (45), the following substitutions were applied

$$q_o = \rho_o e, \quad q_p = \rho_p e, \quad l = l_o \lambda, \quad \varepsilon_{loc} = \varepsilon_o \varepsilon_{loc}$$

Substituting the values of the above mentioned universal constants gives the following relationship

$$\Theta = 1.16027 \times 10^4 \rho_o U \quad (46)$$

in which

$$U = U_o u = \frac{e}{\varepsilon_o l_o} \frac{\rho_p}{\varepsilon_{loc} \lambda} \quad (47)$$

$$U_o = \frac{e}{\varepsilon_o l_o} = 1.809105 \times 10^4 \quad (48)$$

$$u = \frac{\rho_p}{\varepsilon_{loc} \lambda} \quad (49)$$

The distance between the oxygen atom and the solvent dipole was assumed to be equal to

$$l_{O \cdots X} = k \times (r_1 + r_2) \quad (50)$$

$$l_{O \cdots HC} = k \times (r_1 + 2r_2 + r_3) \quad (51)$$

where r_1 – r_3 corresponds to atomic radii of the elements that build bonds [11], and the constant $k > 1$ is a correction factor to the Van der Waals radius. The $O \cdots HC$ bond length should be equal to 300 pm as the expected value calculated on the basis of the data obtained from the thermal experiment together with the electron densities from the quantum-chemical semiempirical calculations. From the comparison of the values of atom radii sum and that expected the value of correction factor can be approximated as $k=1.331$. In this manner the calculated bond lengths of the $O \cdots H$ bonding is 147.9 pm, $O \cdots C$, 201.2 pm, and $O \cdots HC$, 300.0 pm respectively. These values seem to be similar to real bond lengths. Taking into account the crystallographic data, the O – H bond is 95.8 pm length and $O \cdots H$ – O in hexagonal ice is 275 pm length [11]. From this data we can conclude that $O \cdots H$ bond in ice is 179 pm length with respect to ca. 148 roughly approximated by Eq. (51).

The results are presented in Table 3.

The results indicate that ellipsoid or cylinder with spherical bases (spherocylinder) is the best shape for the solvent molecule.

Both shapes suggest a reasonable length of $O \cdots HC$ bond, amounting to 282.7–302.6 and 272.3–308.3 pm in comparison to 300 pm accepted by us.

The last step of verification was to calculate the electrostatic potential for series of the examined solvents and to prepare graphical relation: experimental fluorescence quantum yield vs. calculated electrostatic potential. For the calculations an elliptical shape of the solvent molecule was taken. The shape factors s were calculated based on molecular models optimised in MM+ force field using

Table 3

The optimum bond lengths and average values of characteristic temperatures obtained for various solids approximating the solvent (acetonitrile) molecule shape. Calculations for $s=1.706=14.5/8.5$

Solid (critical diameter, pm) range of calculations	Characteristic temperature Θ , (K)	Characteristic temperature standard deviation*	Optimal bond length, pm	Bond length standard deviation*
Sphere ($D=549.17$) 310–370	4756	+2276 –1269	334.69	+11.86 –12.09
Ellipsoid ($D=459.61$) 270–330	4607	+2295 –1378	292.73	+9.82 –10.05
Spherocylinder ($D=4316.8$) 230–340	5057	+3712 –2163	287.02	+21.27 –14.72
Dicone ($D=579.07$) 240–280	4809	+2196 –1156	257.53	+10.24 –11.43
Cylinder ($D=401.51$) 340–450	7166	+7745 –6830	–	– –
Cuboid ($D=370.44$) 340–400	7446	+8280 –7076	–	– –

* Due to the asymmetrical standard error distribution two values of standard deviation are given.

HyperChem programme [10]. The results are presented in Table 4 and Fig. 4.

The graphical presentation of the obtained experimental and calculated results (Fig. 4) indicates a high degree of conformity. Hence the presented model is valid.

In discussed model it was assumed, that a lone electron pair located on the oxygen atom of the methoxy group is that the place of dye-molecule which attracts the solvent. In order to verify this assumption structurally modified analogues of the IQ4OME dye were prepared and studied. The structural modifications concerned the surroundings of the oxygen atom of the dye-molecule. The IQ4OCF dye with an electron-withdrawing group of $-\text{OCF}_3$ should display a decreased electron density on oxygen atom, hence the stability of appropriate solvates should be lower. A reverse effect was expected in case of the dye IQ4OET with $-\text{OEt}$ group, which should have an increased electron density on oxygen atom and should form more stable solvates. The elimination of the attractive centre of the dye-molecule,

which takes place in the case of IQ4F dye with $-\text{OMe}$ group replaced by $-\text{F}$ group should protect the dye against the stable solvates formation and in fact, it was observed.

In our opinion, the occurrence of the expected phenomena can prove entirely the validity of the model discussed.

Especially, the expected impact of the modified methoxy group should be examined applying quantum-chemical methods. The compounds with the discussed groups connected with an acceptor molecule should serve as the models. The pyrylium moiety was taken as an acceptor and the calculations were done for the compounds of a general structure.

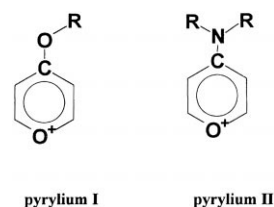


Table 4

Solvents used in determination of fluorescence quantum yield of the IQ4OME dye and their polar characteristics

Solvent	F.W.	Density (d_{20}^4 , g/cm ³)	Dipole moment (μ , 10 ⁻³⁰ C m)	Relative dielectric constant (ϵ) ^a	Bond type	Shape factor a/b direction ^b	Solvent local potential (V)	Fluorescence quantum yield of dye IQ4IME
Ethylene glycol	62.07	1.113	7.72	37.7	O··H	18.5/10 T	12.370	0.085
Diethylene glycol	106.12	1.118	7.71	31.7	O··H	18.5/7 T	12.125	0.166
Diethylene glycol monomethyl ether	120.15	1.010	6.81	15.0	O··H	19/6.5 T	10.287	0.099
Ethanol	46.07	0.785	5.81	24.5	O··H	15/9 T	9.125	0.125
2-Ethoxyethyl acetate	132.16	0.975	7.11	8.3	O··C	17.8/7.1 T	7.174	0.105
Diethylene glycol dimethyl ether	134.18	0.937	6.61	5.8	O··HC	19.5/6.5 T	4.659	0.243
Acetonitrile	41.05	0.786	11.79	35.9	O··HC	14.5/8.5 L	4.370	0.157
1,1,1-Trichloro-ethane	133.41	1.338	5.71	7.2	O··HC	11/10 L	2.762	0.780
1,2-Dichloro-ethane	98.96	1.256	6.11	10.4	O··HC	15.5/9 L	2.434	0.869
Dichloro-methane	84.93	1.325	5.21	8.9	O··HC	16/10.5 L	2.357	0.923
1,1,2,2-Tetrachloroethane	167.85	1.586	4.54	8.2	O··HC	16/11 L	1.849	1.000
1,1,2-Trichloro-ethane	133.41	1.435	2.71	3.4	O··HC	13/9.3 L	1.207	1.000

^aData taken from [12–15].

^bMain diameters of molecule, in arbitrary units, and direction of polarisation related to the shape of the solvent molecule: L (longitudinal), T (transversal).

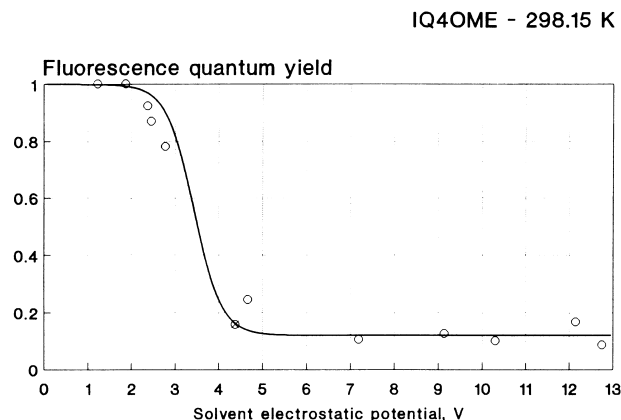


Fig. 4. Fluorescence quantum yield of IQ4OME dye measured in selected solvents as the function of solvent electrostatic potential.

These simple compounds contain a strong electron acceptor ring and electron donating R-oxy or di-R-amino groups. The changes in electrical character of radicals R should influence the electron density of exocyclic heteroatom, and the better should influence the C–O or C–N bond length. The stronger the electron donating character of R, the stronger the oxygen or nitrogen atom should be attracted to the pyrylium ring and the shorter should be the mentioned bonding.

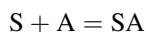
The results presented in Table 5 confirm entirely this thesis.

To test experimentally the quantitative relation between the methoxy group modifications and appropriate solvate stability, the fluorescence quantum yields were determined using binary solvent system. Acetonitrile and dichloromethane were taken as the strong interacting solution and the inert solvent, respectively.

Experiments were performed at isothermal conditions and constant concentration of the dye. The solvates stability constants were calculated based on the theory presented ahead.

2.5. Fluorescence quantum yield of the IQ dyes in the binary solvent system

The dissociation process in the binary solvent mixture can be described as follows:



where A is the more polar solvent.

Table 5

Effect of an alkyl-substituents modification on the substituent's heteroatom – *ipso*-carbon atom bond length in the model pyrylium cations. Geometry optimisation in the AM1 base

Substituent R	Pyrylium I O–C bond length (pm)	Pyrylium II N–C bond length (pm)
Et	133.072	134.407
Me	133.582	135.016
CF ₃	134.584	136.954

The total concentration C_S of the solvent A in that system can be expressed as follows:

$$C_S = [S] + [SA] \quad (52)$$

The equilibrium constant of that reaction is defined as follows:

$$K = \frac{[SA]}{[S][A]} = \frac{[SA]}{(C_S - [SA])[A]} \quad (53)$$

The concentration of the complex and solute can be formulated as

$$[SA] = C_S \frac{K[A]}{1 + K[A]} \quad (54)$$

$$[S] = C_S - [SA] = \frac{C_S}{1 + K[A]} \quad (55)$$

The concentration of solvent [A] using the molar fraction in mixture is given

$$[A] = \frac{x_a}{x_a V_a + (1 - x_a) V_b} \quad (56)$$

where V_a and V_b are a molar volumes of solvents applied.

The fluorescence quantum yield depends on the value of [S] and [SA]. In the case of interaction between dye and solvent – the fluorescence quantum yield is smaller and in the case of absence or very low intensity of this interaction the fluorescence yield is higher. In the fluorescence measurement experiments in a binary solvent system it is possible to determine the normalised value of fluorescence quantum yield φ_n in the (0,1) range of

$$\varphi_{\max} = \beta \times [A] + k \quad (57)$$

$$\varphi_{\min} = \beta \times [SA] + k \quad (58)$$

The concentration of solvent [A] reaches the maximum value, when

$$x_a = 1, \text{ then } [A]_{\max} = (1/V_a)$$

and the normalised fluorescence quantum yield is defined as

$$\varphi_n = \frac{\varphi - \varphi_{\min}}{\varphi_{\max} - \varphi_{\min}} = \frac{1 - V_a[A]}{1 + K[A]} \quad (59)$$

If the molar fraction of the solvent is changed, the equilibrium constant K should be determined on the basis of the collected fluorescence data.

$$K = \frac{1 - \varphi_n - V_a[A]}{\varphi_n[A]} \quad (60)$$

There are a few methods available for determination of K , e.g. if the molar fraction of the most polar solvent is

$$x_a = 0.5, \text{ then } [A]_{0.5} = 1/(V_a + V_b)$$

and

$$K = V_b \frac{1 - \varphi_n}{\varphi_n} - V_a \quad (61)$$

Table 6

Relative fluorescence quantum yield of selected dyes in dichloromethane–acetonitrile solvent system at 298.2 K, and results from the theoretical relationship

Molar fraction of MeCN	Quantum yield of IQ4F (predicted)	Quantum yield of IQ4OCF (predicted)	Quantum yield of IQ4OME (predicted)	Quantum yield of IQ4OET (predicted)
0.000	>0.88(0.88197)	0.93754(0.91130)	0.84390(0.88475)	0.84735(0.88565)
0.085	0.87551(0.88392)	0.81164(0.84160)	0.77408(0.72267)	0.73632(0.67065)
0.170	0.89240(0.88608)	0.74515(0.78471)	0.62416(0.59562)	0.55374(0.52229)
0.259	0.90337(0.88861)	0.75010(0.73536)	0.50132(0.48901)	0.39935(0.40935)
0.352	0.88027(0.89158)	0.71121(0.69227)	0.38180(0.39854)	0.29077(0.32075)
0.450	0.88091(0.89518)	0.65460(0.65405)	0.29686(0.32028)	0.21534(0.24891)
0.544	0.90885(0.89917)	0.62455(0.62281)	0.22173(0.25763)	0.16271(0.19434)
0.650	0.91130(0.90448)	0.60270(0.59260)	0.17858(0.19813)	0.12512(0.14478)
0.760	0.91709(0.91118)	0.57992(0.56572)	0.14948(0.14608)	0.13068(0.10310)
0.877	0.90581(0.92013)	0.55053(0.54110)	0.10973(0.09913)	0.07665(0.06679)
1.000	0.93733(0.93252)	0.48758(0.51876)	0.08730(0.05709)	0.06383(0.03526)
φ_{\min}	0.882±0.011	0.519±0.012	0.057±0.017	0.035±0.022
φ_{\max}	0.933±0.013	0.911±0.014	0.885±0.021	0.0886±0.031
K	0.0568±0.0023 ^a	0.0967±0.0003	0.1158±0.0004	0.1813±0.0008
100×R ²	68.069	97.132	98.791	98.399
Random, %	50.0	36.4	36.4	27.3

^aCalculated for the solvent complex with dichloromethane.

Another method consists in fitting the theoretical equation to the experimental data using a non-linear least-square method. Statistical tests of the fit quality can be calculated at the same time. The φ_{\min} , φ_{\max} and complex (solvate) stability constant K were calculated using the second of the above mentioned methods.

Numerical calculation of φ_{\min} and φ_{\max} is justified, because any measured value remains a random variable. Therefore in relationships where it is located at ‘strategic position’, it is more safer to substitute it for its estimated value. The experimental data used in calculations and the results of non-linear regression applied are presented in Table 6.

The comparison between experimental data and the theoretical plots is presented in Fig. 5.

On the other hand, in case of the acetonitrile–IQ4OME dye complex the dissociation activation energies were calculated independently using experimental results obtained at variable temperature. They can be expressed by the Eq. (62).

$$\Delta E = k\Theta \quad (62)$$

It seems, that individual dyes differ from one another with the stability energies of solvates only, while the entropic factor remains constant. This last assumption was not verified, but if above hypothesis is true, the decomposition activation energy of solvent complexes with IQ4OCF and IQ4OET dyes can be calculated using the following relation:

$$\Delta E_1 = \Delta E_0 - kT \ln \left(\frac{K_1}{K_0} \right) \quad (63)$$

The calculated values of the activation energy in kJ mole^{-1} , being simultaneously the bonding energy, amount respectively to

IQ4OCF	34.71
IQ4OME	35.11
IQ4OET	36.27

These values are similar to a typical value of the hydrogen bonding energy varying from 4 to 40 kJ mole^{-1} [16]; they are many times lower than the energy of atomic bonding, e.g. for a C–C bonding the energy varies from 346 for a

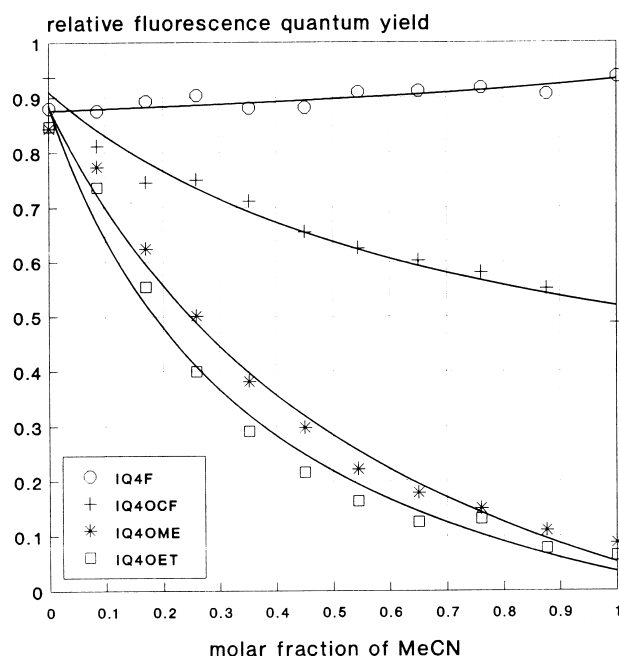


Fig. 5. Relative fluorescence quantum yield of IQ-dyes as the function of acetonitrile mole fraction in mixtures with dichloromethane. Points showed experimental data, while lines were calculated using the discussed model.

Table 7
Characteristics of 5-(4-R-phenyl)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium perchlorates

Compound Molecular formula (Molecular weight)	UV-VIS ν (1000 cm^{-1})/log ϵ MeCN (298 K)	$^1\text{H NMR}$ (400 MHz, CDCl_3 /300 K)	
Compound Melting range ($^\circ\text{C}$) Molecular formula (Molecular weight)		Atom: δ (ppm)	
		Atom: J (Hz)	
(IQ4F) 254–255	Maximum: 27.079 (4.197), 30.023 (4.095), 40.496 (4.442) Minimum: 29.666 (4.044), 36.677 (3.500), 43.558 (4.080) Shoulder: 23.872 (2.785), 28.544 (4.108), 29.666 (4.044), 31.665 (3.493), 39.293 (4.252), 41.071 (4.382) Maximum: 27.211 (5.325), 29.887 (5.237), 40.449 (5.578) Minimum: 29.174 (5.203), 36.681 (4.709), 43.501 (5.230) Shoulder: 23.798 (3.744), 28.409 (5.269), 29.539 (5.209) Maximum: 25.245 (4.288), 33.960 (3.547), 40.611 (4.368) Minimum: 28.900 (3.856), 33.790 (3.541), 34.316 (3.542), 42.927 (4.229) Shoulder: 22.359 (3.193), 27.501 (4.051), 29.584 (3.892), 30.568 (3.906), 39.822 (4.265), 41.578 (4.314) Maximum: 25.085 (4.298), 30.029 (3.933), 40.612 (4.391) Minimum: 28.876 (3.857), 33.932 (3.511), 43.155 (4.211) Shoulder: 21.918 (2.913), 27.287 (4.073), 29.515 (3.081), 31.846 (3.727), 39.655 (4.272), 41.739 (4.318)	1: 9.2239 2: 8.3232 3: 7.9487 4: 8.3124 6: 8.1377 7Me ₂ : 1.905 8: 7.772 9: 7.7260 10: 7.802 11: 8.6828 2'/6': 7.7801 3'/5': 7.3756 1: 9.2143 2: 8.3041 3: 7.9343 4: 8.2710 6: 8.1266 7Me ₂ : 1.8816 8: 7.7562 9: 7.7453 10: 7.7149 11: 8.6703 2'/6': 7.8460 3'/5': 7.5100 1: 9.2234 2: 8.3448 3: 7.9510 4: 8.4356 5'OMe: 3.9373 6: 8.1407 7Me ₂ : 1.8875 8: 7.761 9: 7.757 10: 7.779 11: 8.6917 2'/6': 7.7678 3'/5': 7.2066 1: 9.2308 2: 8.3569 3: 7.9593 4: 8.4511 5'OMe: 4.1954 5'OMe: 1.5092 6: 8.1381 7Me ₂ : 1.8949 8: 7.755 9: 7.7019 10: 7.7905 11: 8.6989 2'/6': 7.7614 3'/5': 7.1941	1,2: 8.83 1,3: <0.5 1,4: <0.5 2,3: 9.12 2,4: <0.7 3,4: 8.65 8,9: 6.65 8,10: 1.6 8,11: <0.5 9,10: 6.5 9,11: <0.8 10,11: 8.26 2',3': 8.51 2'F: 4.9 3'F: 8.5 1,2: 8.94 1,3: 0.76 1,4: <0.5 2,3: 7.03 2,4: 1,27 3,4: 7.58 8,9: 8.68 8,10: 2.12 8,11: <0.5 9,10: 7.44 9,11: 1.85 10,11: 8.18 2',3': 8.76 1,2: 8.86 1,4: 0.74 1,4: <0.5 2,3: 7.07 2,4: 1.46 3,4: 8.53 8,9: ca 7 8,10: 1.6 8,11: <0.5 9,10: ca 7 9,11: 0.8 10,11: 8.38 2',3': 8.73 1,2: 8.90 1,3: 0.8 1,4: <0.5 2,3: 7.07 2,4: 1.50 3,4: 8.47 5'OMe: CH ₃ : 6.96 8,9: 7.2 8,10: 1.75 8,11: <0.5 9,10: 7.2 9,11: <0.5 10,11: 8.54 2',3': 8.79
$\text{C}_{24}\text{H}_{19}\text{NCIF}_4$ (439.87)			
(IQ4OCF) 253–254			
$\text{C}_{25}\text{H}_{19}\text{ClF}_3\text{NO}_5$ (514.87)			
(IQ4OME) 271.5–273			
$\text{C}_{25}\text{H}_{22}\text{ClNO}_5$ (451.91)			
(IQ4OET) 293–295			
$\text{C}_{26}\text{H}_{24}\text{ClNO}_5$ (464.87)			

single bond to 835 kJ mole⁻¹ for a triple one [17]. In case of the IQ4F dye lack of fluorescence quantum yield decreasing while dichloromethane was changed by acetonitrile means that any specific dye–acetonitrile interaction does not occur and therefore the bonding energy of similar as above type is equal to zero.

3. Experimental details

3.1. Dyes

The 5-(4-R-phenyl)-7,7-dimethyl-7H-indolo[1,2-a]quinolinium perchlorates were prepared and purified following literature [1–6] methods. The purity of all dyes was checked by the ¹H NMR (80 and 400 MHz) and thin layer chromatography (Kieselgel Alufolien 60 F 254 plates, Merck) eluted with mixture of butan-2-one:acetic acid:*n*-propanol (2:2:1, v/v).

The 7H-indolo[1,2-a]quinolinium perchlorates were prepared photochemically from corresponding 3H-indolium hemicyanines according to the known methods [1–4].

R	Common name of a dye
4-F	IQ4F
4-OCF ₃	IQ4OCF
4-OCH ₃	IQ4OME
4-OC ₂ H ₅	IQ4OET

The spectral characteristics of dyes studied is presented in Table 7.

3.2. Solvents

Most of the solvents used were of Uvasol[®] grade from Merck of spectrofluorimetric or spectroscopic purity.

3.3. Instrumentation

The UV–VIS spectra were recorded on UVIKON 930 (Kontron Instruments, USA) and SPECORD M40 (Carl Zeiss Jena, Germany) spectrometers equipped in interface and software from MEDSON [19]. The fluorescence spectra were recorded with the MPF-2A (Hitachi-Perkin-Elmer) and SFM 25 spectrofluorimeters (Kontron Instruments, USA) and SPECORD M40 spectrometer (Carl Zeiss Jena, Germany) supplemented by fluorimetric device.

The NMR spectra (¹H, ¹³C and ¹H – ¹³C COSY) were measured on BRUKER DPX-Avance (400 MHz) and TESLA BS 487C (80 MHz) spectrometers in CDCl₃ or TFA using TMS as internal standard.

The absolute fluorescence quantum yields, φ_f were determined at 298 K using 10-methyl-9(10)H-acridone ($\varphi = 0.98$ in ethanol) as a standard, according to the published procedure [20–23].

4. Conclusion

The presented paper has demonstrated that solvents are able to form complexes with some dyes containing negative charged centres. The stability of those complexes is similar to the stability of strong hydrogen bonds. The complexes undergo thermal dissociation. If the complexing centre is located in luminogenic moiety of the dye, the formation of solvate entails a decrease in fluorescence efficiency.

A rare phenomenon of the dye fluorescence quantum yield raising along with the increase in temperature is observed. It has been proved that methoxy group and its derivatives is a negatively charged complexing centre and the complex stability raises along with the increasing electron donor character of alkyl fragment.

It has been pointed out that the forces between dye and permanent solvent dipole have an electrostatic character. A threshold value of the solvent electrostatic potential occurs dividing the solvent series into two parts. If the absolute value of the solvent's electrostatic potential exceeds the threshold value, the fluorescence is absent or very weak, otherwise it is intensive.

Fluorescence efficiency of the dyes without methoxy group or its analogues within the limits of the dye luminogenic does not depend upon kind of the solvent.

Determination of a local dielectric constant near to solvent-dye bond is a very important element of our theoretical explanation of experimental data. A new method of calculation based on the macroscopic data and geometric relations of the association centre has been developed and applied with good results.

During and after the solvation process there are no vacancies in the solution and therefore the effect of pressure can be neglected, similarly as it took place in the case of dielectric constant of acetonitrile [18].

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