On the Estimation of Excited-State Dipole Moments from Solvatochromic Shifts of Absorption and Fluorescence Spectra

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The effect of the solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ appearing in solvatochromic theories, and the effect of the molecular shape of the Onsager cavity (sphere, ellipsoid of revolution) on the determined electric dipole moments μ_e in the singlet excited state are studied. It is found that the shape of the solute does not exhibit a significant effect on the determined values of μ_e, but only on the solvent parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ as well as on the Onsager radius a. Passing from a sphere to an ellipsoid leads to such a change in the scale that induces a proportional change in the slope coefficients m_1 and m_2. Also the effect of α/a^3 (α and a are the mean isotropic polarizability of the solute and the Onsager cavity radius in a homogeneous dielectric, respectively) on the determined values of μ_e has been studied, and it is found that the assumption $\alpha/a^3 = 1/2$ is valid in many cases.

Key words: Solvatochromic Absorption and Fluorescence Band Shifts; Dipole Moments in the Ground and Excited States; Shape of the Onsager Cavity.

1. Introduction

Due to the fast progress in photochemistry, studies of electric dipole moments in excited states (μ_e) gain more and more importance. From the numerous ways of determining μ_e, i.e. electrooptical methods (electrochromism of absorption and fluorescence bands, the effect of an external electric field on the fluorescence anisotropy, Stark splitting of rotational levels of the 0–0 vibrational band) [1, 2], the solvent-shift method is the simplest and the most widely used one.

Since in different solvatochromic theories different solvent polarity parameters appear, in the present paper their applicability is discussed. The effect of the solutes shape on the determined dipole moments μ_e and the validity of the assumptions $\alpha/a^3 = 1/2$ [3, 8] made in most theories devoted to the solvent effect on the absorption and fluorescence spectra of solutes is studied.

Most theories [4–10] of the solvent effect on the location of the absorption, $\tilde{\nu}_A$, and fluorescence, $\tilde{\nu}_F$, bands lead, in spite of different assumptions, to similar expressions for the $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ (see (15) and (16)) with the difference, however, that the applied solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ differ significantly. The discussed solvatochromic method of dipole moment (μ_e) determination in the first singlet excited state S_1 is based on the position change of the absorption and fluorescence bands caused by an internal electric field (Onsager model).

2. Theoretical Basis

By employing the simplest quantum – mechanical second – order perturbation theory and taking into account Onsager's model, the following two equations have been obtained for the $\tilde{\nu}_A$ and $\tilde{\nu}_F$ band shifts (in wavenumbers) in any solvent relative to the band positions of a free molecule (in the gaseous state) [8, 11, 12]:

$$\begin{aligned}\Delta\tilde{\nu}_{A,F} = {} & -m_{A,F}(1-\alpha f')^{-1} \\ & \cdot [f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] \\ & - \frac{\mu_e^2-\mu_g^2}{2hc}(2-\alpha f')\, f'(1-\alpha f')^{-2} \qquad (1)\end{aligned}$$

(for $\tau_R \ll \tau_F$, τ_R being the relaxation time for the rearrangement of the solvent molecules and τ_F the lifetime of the molecule in the excited state),

where for absorption

$$m_A = \frac{\boldsymbol{\mu}_g(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)}{hc} \qquad (2)$$

and for fluorescence

$$m_F = \frac{\boldsymbol{\mu}_e(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)}{hc}\,. \qquad (3)$$

Based on (1), the following expressions are obtained for $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ [12, 13]:

$$\tilde{\nu}_A - \tilde{\nu}_F = \frac{(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)^2}{hc}(1-\alpha f')^{-1} \cdot [f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] + \text{const}, \tag{4}$$

$$\tilde{\nu}_A + \tilde{\nu}_F = -\frac{(\boldsymbol{\mu}_e^2 - \boldsymbol{\mu}_g^2)}{hc}\{(1-\alpha f')^{-1} \cdot [f(1-\alpha f)^{-1} - f'(1-\alpha f')^{-1}] + f'(2-\alpha f')(1-\alpha f')^{-1}\} + \text{const}, \tag{5}$$

where μ_e and μ_g are the excited and ground state dipole moments, respectively, and α is the mean static isotropic polarizability of the solute. f and f' are the so called reaction field factors depending on the shape and the Onsager cavity radius a of the solute and on the electric permittivity ε and the refractive index n of the solvent.

Generally, the Onsager cavity is given by an ellipsoid with the principal axes $2a$, $2b$ and $2c$. If the directions of the axis $2a$ and the electric field coincide, the factors of the reaction fields f and f' are [14, 15]

$$f = \frac{2}{abc}\,\frac{\varepsilon - 1}{2\varepsilon + 1}\,F(\varepsilon, A) \tag{6}$$

and

$$f' = \frac{2}{abc}\,\frac{n^2 - 1}{2n^2 + 1}\,F(n^2, A), \tag{7}$$

where

$$F(\varepsilon, A) = \frac{3A(1-A)(2\varepsilon + 1)}{2[\varepsilon - (\varepsilon - 1)A]}, \tag{8}$$

$$F(n^2, A) = \frac{3A(1-A)(2n^2 + 1)}{2[n^2 - (n^2 - 1)A]}, \tag{9}$$

and the constant A is given by

$$A = \frac{abc}{2}\int_0^\infty \frac{\mathrm{d}s}{(s+a^2)^{3/2}(s+b^2)^{1/2}(s+c^2)^{1/2}}, \tag{10}$$

where s is the integration parameter. As useful approximations of (6) and (7) the following formulas can serve [10]:

$$f = \frac{2}{a^3}\,\Phi, \tag{11}$$

and

$$f' = \frac{2}{a^3}\,\Phi', \tag{12}$$

where

$$\Phi = \frac{\varepsilon - 1}{2\varepsilon + 1}\,F(\varepsilon, A) \tag{13}$$

and

$$\Phi' = \frac{n^2 - 1}{2n^2 + 1}\,F(n^2, A). \tag{14}$$

Therefore α must be treated as an empirical parameter. The integral (10) can be reduced to elementary functions only if two of the three axes are parallel. For ellipsoids of revolution in which $b = c = a/p$ and the symmetry axis a is longer than b ($a > b$) we have the case of prolate molecules, and for $a < b$ the case of oblate discoidal molecules*. For instance, for an ellipsoid of revolution $p = 2.0$, $A = 0.174$; for a sphere $p = 1.0$ and $A = 1/3$; and for an oblate shape $p = 0.4$ and $A = 0.583$ [15].

Equations (4) and (5) can be written in the simple form

$$\tilde{\nu}_A - \tilde{\nu}_F = m_1 f(\varepsilon, n) + \text{const}, \tag{15}$$

$$\tilde{\nu}_A + \tilde{\nu}_F = -m_2\,\varphi(\varepsilon, n) + \text{const}, \tag{16}$$

where

$$\varphi(\varepsilon, n) = f(\varepsilon, n) + 2g(n), \tag{17}$$

$$m_1 = \frac{2(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)^2}{hca^3}, \tag{18}$$

and

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{hca^3}. \tag{19}$$

Solvent polarity parameters in different theories are given below. From the theory of Bilot and Kawski [8, 11] follows that

$$f(\varepsilon, n) = \frac{\Phi - \Phi'}{\left(1 - \frac{2\alpha}{a^3}\Phi\right)\left(1 - \frac{2\alpha}{a^3}\Phi'\right)^2}, \tag{20}$$

$$g(n) = \Phi'\,\frac{\left(1 - \frac{\alpha}{a^3}\Phi'\right)}{\left(1 - \frac{2\alpha}{a^3}\Phi'\right)^2}. \tag{21}$$

The factors f and f', given by (11) and (12), are simplified when a spherical cavity ($a = b = c$, $A = 1/3$ and $F(\varepsilon, A) = F(n^2, A) = 1$) of radius a is assumed, which may be regarded as a sufficient approximation. In this case (20) and (21) have the form

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* The values of A for selected ratios of semiaxes are given in the appendix of [16].

$$f(\varepsilon,n)=\frac{\dfrac{\varepsilon-1}{2\varepsilon+1}-\dfrac{n^2-1}{2n^2+1}}{\left(1-\dfrac{2\alpha}{a^3}\,\dfrac{\varepsilon-1}{2\varepsilon+1}\right)\left(1-\dfrac{2\alpha}{a^3}\,\dfrac{n^2-1}{2n^2+1}\right)^2}\,, \tag{22}$$

$$g(n)=\frac{\dfrac{n^2-1}{2n^2+1}\left(1-\dfrac{\alpha}{a^3}\,\dfrac{n^2-1}{2n^2+1}\right)}{\left(1-\dfrac{2\alpha}{a^3}\,\dfrac{n^2-1}{2n^2+1}\right)^2}\,. \tag{23}$$

If the polarizability of the solute is neglected, i.e. $\alpha = 0$, the equation for $f(\varepsilon, n)$ obtained by Lippert [6] and Mataga et al. [17] results from (22):

$$f_{\mathrm{LM}}(\varepsilon,n)=\frac{\varepsilon-1}{2\varepsilon+1}-\frac{n^2-1}{2n^2+1}\,. \tag{24}$$

For an isotropic polarizability of the solute, the condition $2\alpha/a^3 = 1$ is frequently satisfied, and (22) and (23) are then considerably simplified [18–22]**:

$$f_{\mathrm{BK}}(\varepsilon,n)=\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right), \tag{25}$$

$$g_{\mathrm{BK}}(n)=\frac{3}{2}\,\frac{n^4-1}{(n^2+2)^2}\,. \tag{26}$$

According to McRea's theory [5]

$$f_{\mathrm{MR}}(\varepsilon,n)=\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right). \tag{27}$$

In Bakhshiev's theory [9, 29] the functions of the solvent polarity are

$$f_{\mathrm{B}}(\varepsilon,n)=\frac{2n^2+1}{n^2+2}\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right) + p^{\mathrm{a-f}}\,\frac{n^2-1}{n^2+2}\,, \tag{28}$$

$$\varphi_{\mathrm{B}}(\varepsilon,n)=\frac{2n^2+1}{n^2+2}\,\frac{\varepsilon-1}{\varepsilon+2}+p^{\mathrm{s}}\,\frac{n^2-1}{n^2+2}\,, \tag{29}$$

where $p^{\mathrm{a-f}}$ and p^{s} are the parameters dependent on the solute properties***.

By neglecting the second term in (28) we receive (25). The parameters m_1 and m_2 in [8, 11], (18) and (19), and Bakhshiev's [9, 29] parameters $\Delta c^{\mathrm{a-f}}$ and C_2 fulfill the relations

$$m_1 = \Delta C^{\mathrm{a-f}}, \quad m_2 = -2\,C_2\,.$$

For an ellipsoidal molecule of isotropic polarizability it follows from the general theory of Liptay [10] that the solvent parameters are ((102) and (103) in [10])

$$f_{\mathrm{L}}(\varepsilon,n)= \tag{30}$$

$$=\frac{\dfrac{\varepsilon-1}{2\varepsilon+1}F(\varepsilon,A)-\dfrac{n^2-1}{2n^2+1}F(n,A)}{\left(1-\dfrac{2\alpha}{a^3}\,\dfrac{\varepsilon-1}{2\varepsilon+1}F(\varepsilon,A)\right)\left(1-\dfrac{2\alpha}{a^3}\,\dfrac{n^2-1}{2n^2+1}F(n,A)\right)}\,,$$

and

$$\varphi_{\mathrm{L}}(\varepsilon,n)=\frac{\dfrac{\varepsilon-1}{2\varepsilon+1}F(\varepsilon,A)}{1-\dfrac{2\alpha}{a^3}\,\dfrac{\varepsilon-1}{2\varepsilon+1}F(\varepsilon,A)}\,, \tag{31}$$

and for $F(\varepsilon, A) = F(n, A) = 1$ ($p = 1$, $A = 1/3$, $2\alpha/a^3 = 1$), (30) and (31) yield

$$f_{\mathrm{L}}(\varepsilon,n)=\left(\frac{\varepsilon-1}{\varepsilon+2}-\frac{n^2-1}{n^2+2}\right), \tag{32}$$

and

$$\varphi_{\mathrm{L}}(\varepsilon,n)=\frac{\varepsilon-1}{\varepsilon+2}\,. \tag{33}$$

Equation (32) is identical with (27).

The expressions (1), (5) and (17) do not contain dispersive interactions caused by Van der Waals forces, which ar present in all solvent – solute systems and are distinctly weaker than dipolar interactions between the solute and the solvent molecules (so called dielectric effect) in diluted solutions. In view of that they do not affect the determination of electric dipole moments when the difference $\Delta\boldsymbol{\mu} = \boldsymbol{\mu}_{\mathrm{e}} - \boldsymbol{\mu}_{\mathrm{g}}$ for the investigated molecules is not small.

** The authors of [23] have not cited our earlier works [18–22] but irrelevant works which do not concern the transformation of our general Eqs. (4) and (5). This led to the fact that some later authors [24–28] regard expressions (15) and (16) together with (25) and (26) as derived originally in [23].

*** The parameters $p^{\mathrm{a-f}}$ and p^{s} can be determined either by plotting a line through a point for vapours (a free molecule) or, if no data for vapours are available, by preserving the best linearity of the relation examined. Formulas (7.18), (7.19) and (6.18), (6.19) given in [30] and [31], respectively, are incorrect.

Generally, when dipole moments $\boldsymbol{\mu}_e$ and $\boldsymbol{\mu}_g$ are not parallel to each other but form an angle φ, the use of (18) and (19) leads to [8, 32]

$$\mu_e = \left(\mu_g^2 + \frac{1}{2} m_2\, hca^3\right)^{1/2}, \tag{34}$$

$$\cos\varphi = \frac{1}{2\,\mu_g\,\mu_e} \cdot \left[(\mu_g^2 + \mu_e^2) - \frac{m_1}{m_2}(\mu_e^2 - \mu_g^2)\right]. \tag{35}$$

Assuming that the symmetry of the investigated solute molecule remains unchanged upon electronic transition, and the ground and excited state dipole moments are parallel, based on (18) and (19) one obtains

$$\mu_g = \frac{m_2 - m_1}{2}\left(\frac{hca^3}{2\,m_1}\right)^{1/2}, \tag{36}$$

$$\mu_e = \frac{m_1 + m_2}{2}\left(\frac{hca^3}{2\,m_1}\right)^{1/2}, \tag{37}$$

or by dividing (37) by (36):

$$\mu_e = \frac{m_1 + m_2}{m_2 - m_1}\,\mu_g = \frac{m_F}{m_A}\,\mu_g\,, \quad (m_2 > m_1). \tag{38}$$

The parameters m_1 and m_2 occurring in (15) and (16) for the difference $\tilde{\nu}_A - \tilde{\nu}_F$ and the sum $\tilde{\nu}_A + \tilde{\nu}_F$ of the wavenumbers, which are linear functions of the solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$, can be determined from the slopes of the straight lines. Only two of the four parameters m_1, m_2, m_A, and m_F are independent. They are bound by the relations (38).

The short-range specific interactions between the solvent and the solute molecules, as hydrogen bonding, the tendency of polar solvent molecules to form aggregates of two or more molecules, etc., which are observed as deviations from the dielectric solvatochromic plot $f(\varepsilon, n)$, are not taken into consideration in all mentioned theories.

3. Application of Different Solvent Parameters for the Determination of μ_e

To check the effect of the solute shape on the determination of the electric dipole moment in the excited state μ_e, and in particular also on μ_g, (15) and (16) were used for different solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ present in different theories. In the case of 4-dimethylamino-4′-mitrostilbene (DNS) and 4-dimethylamino-4′-cyanstilbene (DCS) use was made of Lippert's measurements of absorption ($\tilde{\nu}_A$) and fluorescence ($\tilde{\nu}_F$) maxima locations in different solvents [6], as well as our measurements for 4-amino-4′-nitrostilbene (ANS) [36]. The values of m_1 determined from (15) for $f_{MR}(\varepsilon, n)$, (27), and for $f_{BK}(\varepsilon, n)$ (25), differ significantly, which according to (18) affects μ_e. Table 1 gives the values of m_1 and μ_e for μ_g obtained by the dielectric method. These values concern DNS and DCS in the case of a spherical cavity ($a = b = c$, $p = 1$, $A = 1/3$). In the same Table 1 the values of m_1 can be found for a molecule treated as an ellipsoid of revolution ($b = c = a/p$, $p = 2$, $A = 0.174$) using $f_L(\varepsilon, n)$, (30), and $f_{BK}(\varepsilon, n)$, (20), as well as Onsager radii a determined from (18), if for μ_e the values measured by the electrochromical method are taken [33, 34]. The Onsager radii determined in such a way should be treated as empirical parameters. For comparison, the values of μ_e obtained based on $f_{LM}(\varepsilon, n)$, (24), and $f_B(\varepsilon, n)$, (28), as well as μ_e obtained based on the electrochromical method [1] are listed also in Table 1. It is readily seen that signifi-

Table 1. Dipole moments (in Debye) determined from solvatochromic shifts for DNS and DCS in cavities represented by spherical and prolate ellipsoids of revolution.

Molecule	$a = b = c$, $A = 1/3$, $\alpha/a^3 = 1/2$						$b = c = a/p$, $p = 2$, $A = 0.174$, $\alpha/a^3 = 1/2$							μ_e Electro-chromism
	a	m_1	m_1	μ_g	μ_e	μ_e	m_1	m_1	μ_e	a	a	μ_e	μ_e	
	[6]	(15), (27)	(15), (25)	[33, 34]	(15), (18), (27)	(15), (18), (25)	(15), (30)	(15), (20)	[33, 34]	(15), (18, 30)	(15), (18, 20)	(15), (18), (24)	(15), (18), (28) [35]	[1]
	Å	1 kK = 10^3 cm^{-1}			Debye		1 kK = 10^3 cm^{-1}		Debye	Å			Debye	
DNS	8	7,6	6,15	7.2	26.8	24.8	25	22	25.4	5.1	5.3	31.2	24.8	26, 25
DCS	8	5.2	4.1	7.1	23.3	21.5	18.5	17	20.7	4.65	4.75	30.1	–	20, 21

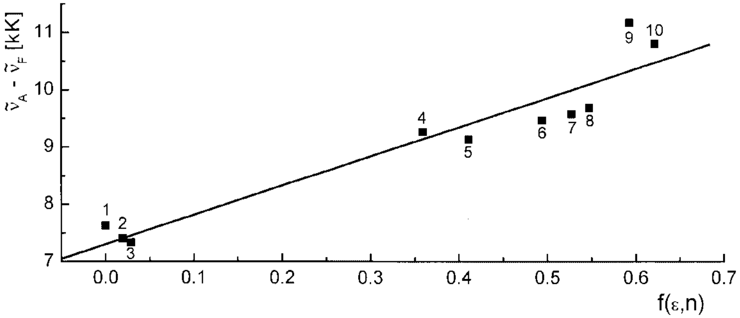

Fig. 1. Plot of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for ANS in different solvents: 1 = tetralin, 2 = toluene, 3 = m-xylene, 4 = bromobenzene, 5 = fluorobenzene, 6 = ethyl acetate, 7 = butyl chloride, 8 = methyl acetate, 9 = methylene chloride, 10 = ethylene chloride. Fit to (15) and (22) when $a = b = c$, $p = 1$ and $A = 1/3$.

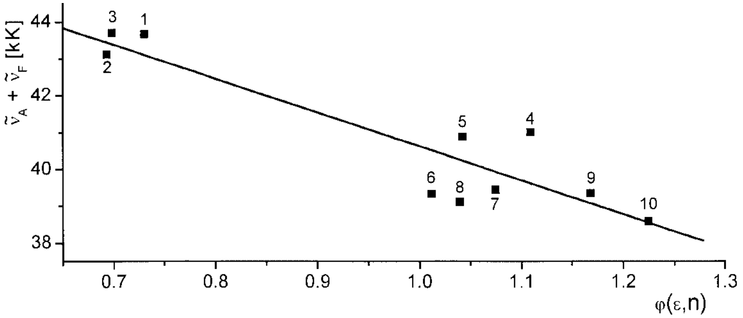

Fig. 2. Plot of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n) = f(\varepsilon, n) + 2g(n)$ for ANS in the same solvents as in Figure 1. Fit to (16), (22) and (23) when $a = b = c$, $p = 1$ and $A = 1/3$.

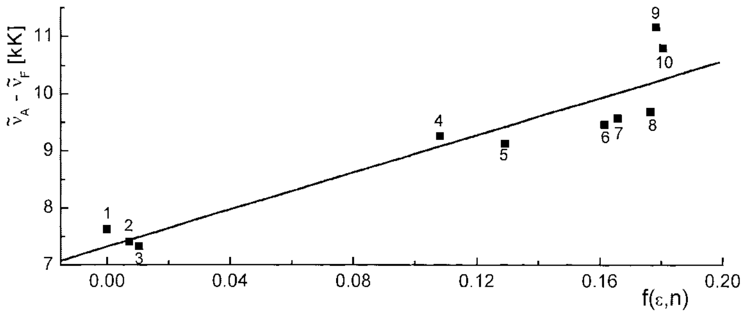

Fig. 3. Plot $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for ANS in different solvents (the same as in Figure 1). Fit to (15) and (20) when $b = c = a/p$, $p = 2$ and $A = 0.174$.

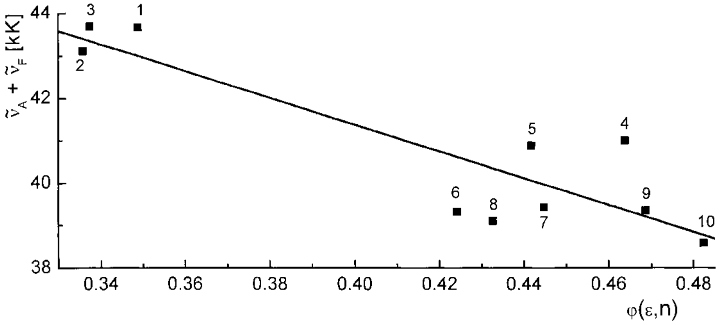

Fig. 4. Plot of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n) = f(\varepsilon, n) + 2g(n)$ for ANS in the same solvents as in Figure 1. Fit to (16), (20) and (21) when $b = c = a/p$, $p = 2$ and $A = 0.174$.

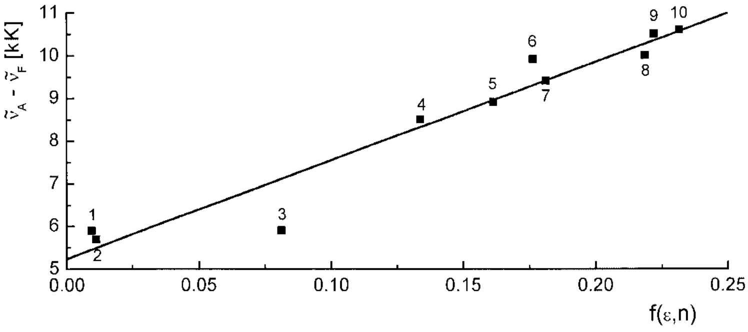

Fig. 5. Plot of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for DNS in different solvents: 1 = tetrachloromethane, 2 = cyclohexene, 3 = triethylamine, 4 = diethylether, 5 = ethyl acetate, 6 = methyl acetate, 7 = trifluorotuluene, 8 = isobutyl alcohol, 9 = methyl ethyl ketone, 10 = acetone. Fit to (15) and (20) when $b = c = a/p$, $p = 2$ and $A = 0.174$.

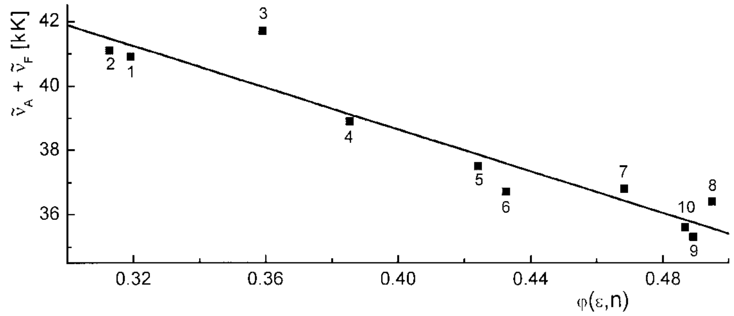

Fig. 6. Plot of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n) = f(\varepsilon, n) + 2g(n)$ for DNS in the same solvents as in Figure 5. Fit to (16), (20) and (21) when $b = c = a/p$, $p = 2$ and $A = 0.174$.

Table 2. Dipole moments (in Debye) determined from solvatochromic shifts for ANS and DNS in cavities represented by spherical and prolate ellipsoids of revolution.

Molecule	μ_g	(15), (16) and (22), (23) $a = b = c$, $p = 1$, $A = 1/3$, $\alpha/a^3 = 1/2$				(15), (16) and (20), (21) $b = c = a/p$, $p = 2$, $A = 0.174$, $\alpha/a^3 = 1/2$				Electrochromism [1]	
		m_1	m_2	μ_e	a	m_1	m_2	μ_e	a	μ_e	μ_e
	Debye	1 kK = 10^3 cm^{-1}		Debye	Å	1 kK = 10^3 cm^{-1}		Debye	Å	Debye	
ANS	6.5	5.1	9.65	21.1	7.5	16.3	31.0	20.9	5.06	22	23
DNS*	7.2	6.15	11.45	23.9	8.0 (7.7)	22.5	41.0	24.7	5.16	26	25
	7.6			25.2	8.0			26	5.3	–	–

* The values of μ_e determined for DNS by Crosetti and Kohler [37] are incorrect.

cant differences exists between these values. Hence, taking into account α/a^3 in (20–23) and (30–31) is important. Since the actual values of α/a^3 are for many compounds not known, for the calculation of $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ the condition $\alpha/a^3 = 1/2$ was assumed, which is in most cases justified.

To obtain more accurate information on μ_e (in particular if $\boldsymbol{\mu}_e$ and $\boldsymbol{\mu}_g$ are parallel), (15) and (16) should be applied and the parameters m_1 and m_2 should be determined. Figures 1–4 present a comparison between $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ for ANS in solvents of different ε and n for spherical ($p = 1$, $A = 1/3$) and ellipsoidal ($p = 2$, $A = 0.174$) cavities. For DNS, in Figs. 5 and 6 a comparison is given for the difference and sum mentioned with the theory for the ellipsoid of revolution ($p = 2$, $A = 0.174$). For the spherical cavity a suitable comparison between experiment and theory is presented in [8]. For ANS and DNS suitable quantities of m_1, m_2, μ_e, μ_g and a are

Table 3. Comparison of excited dipole moments μ_e determined for different α/a^3 values, (15) – (17) and (22), (23).

Molecule	α/a^3	μ_g	μ_e	a
		Debye		Å
ANS	0.60 [38]	6.5	20.7	7.5
	0.50	6.5	21.1	7.5
DNS	0.68 [38]	7.2	23.1	8.5
	0.50	7.2	23.9	8.0
DCS	0.53 [38]	7.0	22.3	8.3
	0.50	7.1	23.3	8.0
3-amino-phthalimide	0.62 [3]	2.6	5.0 ($\varphi = 17°$)	3.8
	0.50	2.6	5.6 ($\varphi = 15°$)	3.8

given in Table 2. It can be noticed that in both cases ($p = 1$ and $p = 2$) almost the same values of μ_e are obtained, which are within the limit of experimental error. Similarly as previously, the estimated values of a should be treated as empirical parameters.

A visible effect of μ_g on both μ_e and a can be seen (DNS in Table 2). From these results the essential conclusion can be drawn that the shape of the solute does not influence significantly the value of μ_e obtained by the solvatochromic method. The same values of μ_e are obtained for spherical and ellipsoidal molecules. The shape of the solute affects only the solvent parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ and causes a change of scale (cf. Figs. 1 and 3 as well as Figs. 2 and 4).

For parallel $\boldsymbol{\mu}_\mathbf{g}$ and $\boldsymbol{\mu}_\mathbf{e}$, (38) can be used if the dipole moment in the ground state μ_g is known from independent measurements. In such a case the knowledge of the Onsager radius a is not necessary. This is true for the investigated stilbene derivatives.

Quite an independent issue is the assumption $\alpha/a^3 = 1/2$. In most cases the value of α/a^3 is unknown. Only for phtalimide and stilbene derivatives it was experimentally found that the values of α/a^3 range from 0.41 to 0.62 [3] and from 0.53 to 0.68 [38], respectively. The comparison of the excited state dipole moments μ_e determined for experimental values of α/a^3 and for $\alpha/a^3 = 1/2$ is presented in Table 3. The relative spread in the μ_e values obtained amounts to 10% and is within the limit of experimental error. Hence, the assumption $\alpha/a^3 = 1/2$ is justified.

4. Final Remarks

The different sequence of experimental points (1, 4, 8) in Figs. 2 and 4 compared to that in Figs. 1 and 3 is caused by big changes in the refractive index n (i.e., for point 4: bromobenzene $n = 1.5577$, for point 8: methyl acetate $n = 1.361$) which affects significantly the function $g(n)$ and thus $\varphi(\varepsilon, n)$ given by (17). To avoid this and to eliminate the influence of specific interactions, one selected solvent of moderate electric permittivity ε should be applied. The solvent polarity parameter $f(\varepsilon, n)$, (22) and (25), changes most strongly for ε ranging from 2 to 10. A decrease in ε and n is obtained by increasing the temperature (T) in a high pressure cell. The values of ε and n as a function of T can be derived from empirical equations given in [12, 39–41] for several different polar solvents as well as for mixtures of polar and unpolar solvents. Hence values of ε and n are obtained which change continuously, which supports the analysis of the absorption and fluorescence spectra shifts observed.

In summary, it should also be emphasized that the shape of the solute studied does not affect the value of the determined dipole moment μ_e but only the value of the Onsager interaction radius a. Assuming $\alpha/a^3 = 1/2$ in the mentioned theories is justified and does not significantly influenc the determined value of μ_e.

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