Thermochromic Absorption, Fluorescence Band Shifts and Dipole Moments of BADAN and ACRYLODAN

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Using the thermochromic shift method of absorption and fluorescence bands, the electric dipole moments in the ground (μ_g) and excited (μ_e) state are simultaneously determined for BADAN (6-bromoacetyl-2-dimethylamino-naphtalene) and ACRYLODAN (6-acrylolyl-2-dimethylamino-naphtalene) in ethyl acetate. For these compounds the same ratio $\mu_e/\mu_g = 2.9$ was found, which is similar to that of PRODAN (6-propionyl-2-dimethylamino-naphtalene).

The estimated empirical Onsager radii a for BADAN and ACRYLODAN are the same, and they are somewhat smaller than the calculated geometrical values.

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

1. Introduction

In our previous work [1], the dipole moments of BADAN (6-bromoacetyl-2-dimethylamino-naphtalene) and ACRYLODAN (6-acrylolyl-2-dimethylamino-naphtalene) in the ground μ_g, and excited μ_e, state, have been determined, using the solvatochromic method. These molecules are similar in shape to PRODAN (6-propionyl-2-dimethylamino-naphtalene). It has been found that in the case studied the values μ_e/μ_g for ACRYLODAN and BADAN are significantly different. This fact may be caused among others by the presence of two fluorescence bands of ACRYLODAN in polar solvents [2].

In the current paper, μ_e and μ_g are determined for BADAN and ACRYLODAN using the method of the thermochromic shifts. It is known that this method allows for a much more accurate determination of μ_e and μ_g, since it requires only one suitable solvent (for example ethyl acetate). Through the change in temperature, in this case from 193 K to 393 K, a continuous change of the dielectic permittivity ε and the refractive index n is obtained. This method narrows significantly the spread of experimental data and eliminates specific interactions at higher temperatures, which supports the analysis of the absorption and fluorescence band shifts observed.

2. Experimental

Absorption and fluorescence spectra of BADAN and ACRYLODAN in ethyl acetate were measured with the home constructed high pressure cell described in [3]. The permittivities ε and refractive indexes n were determined for different temperatures based on empirical formulas derived in [4]. For ε and n, determined as a function of T, the solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ were obtained (cf. (5), (12) and (13)) for ethyl acetate. From the broadened temperature scale (compared to [3]), ranging from 193 K to 393 K, the following dependencies of $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ on temperature T are obtained:

$$f(\varepsilon, n) = -\,0.00104\,T + 0.80164\,, \qquad (1)$$

$$\varphi(\varepsilon, n) = -\,0.0015\,T + 1.4320\,. \qquad (2)$$

Figures 1 and 2 show the behaviour of absorption and fluorescence spectra for BADAN and ACRYLODAN in ethyl acetate at 193 K to 393 K. With increasing temperature a blue shift of the spectra of both compounds and a decrease of the dielectric permittivity ε and refractive index n is observed, which leads to a decrease of the solvent polarity parameters. Similarly to PRODAN [3], strong temperature quenching of the fluorescence of both compounds is observed (Figs. 3 and 4).

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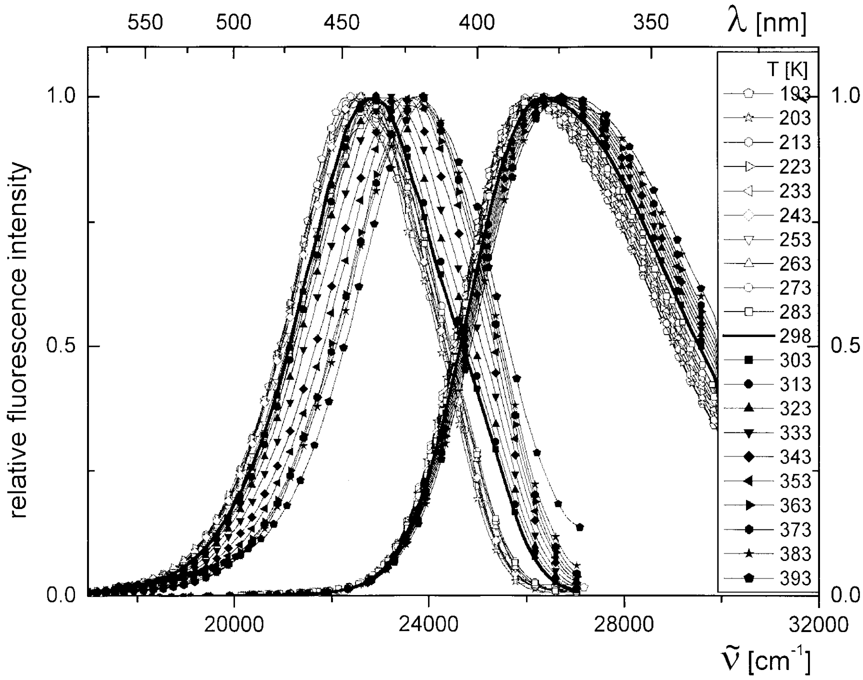

Fig. 1. Absorption (right) and fluorescence (left) spectra of BADAN in ethyl acetate from 193 K to 393 K (excitation wavelength $\lambda_{exc} = 360$ nm).

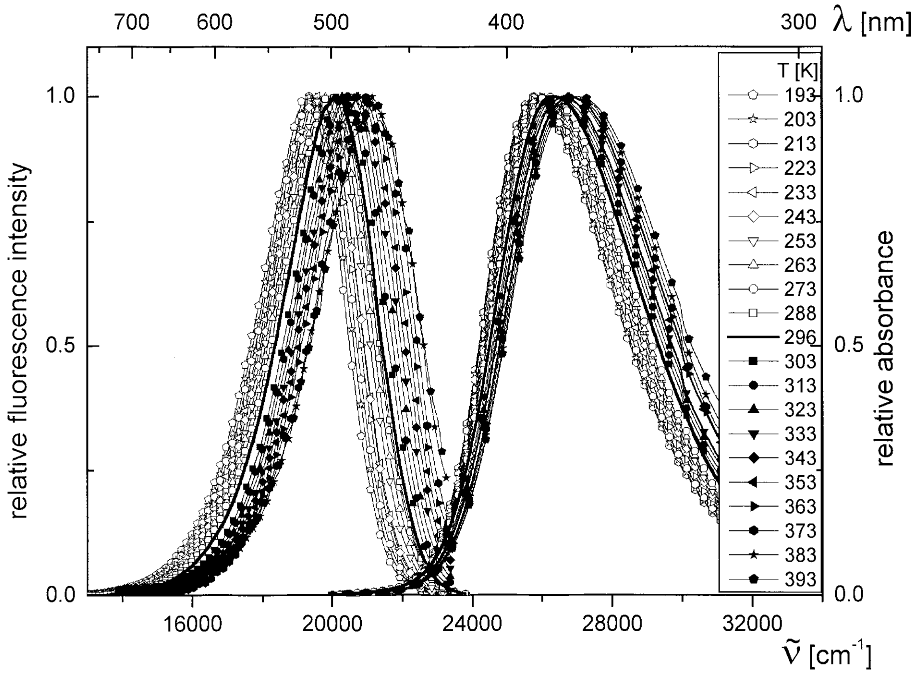

Fig. 2. Absorption (right) and fluorescence (left) spectra of ACRYLODAN in ethyl acetate from 193 K to 393 K (excitation wavelength $\lambda_{exc} = 420$ nm).

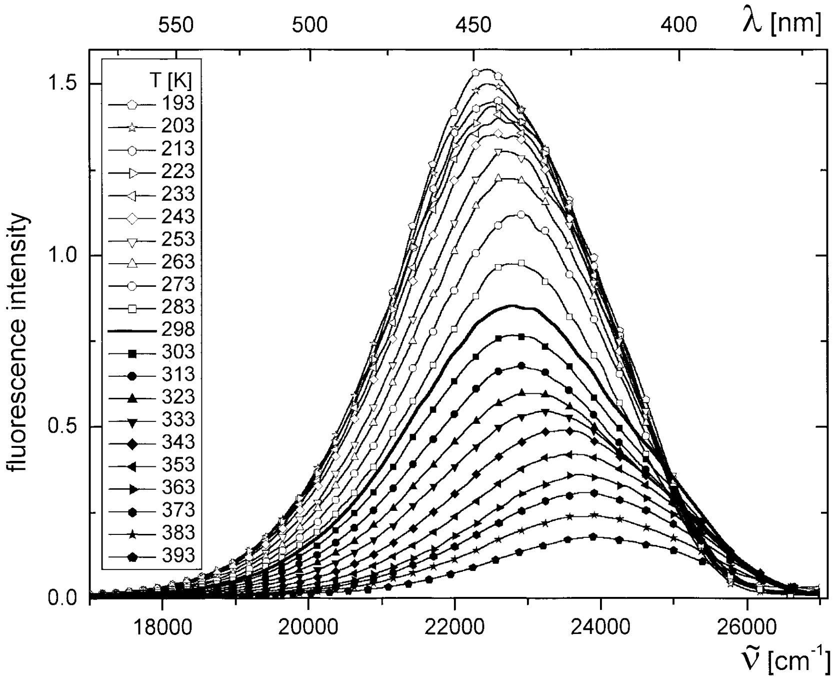

Fig. 3. The influence of temperature on the fluorescence intensity for BADAN in ethyl acetate from 193 K to 393 K (λ_{exc} = 360 nm).

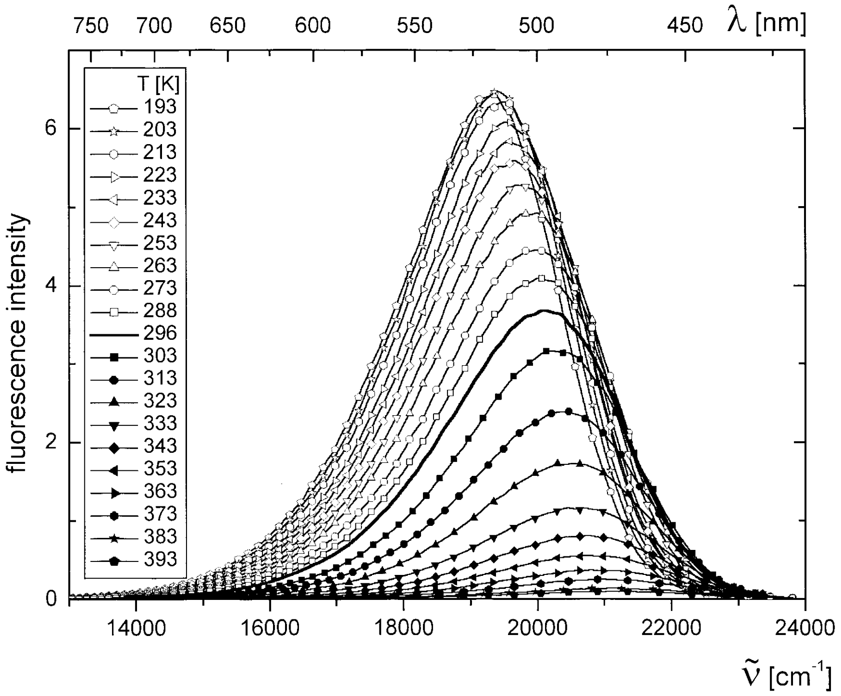

Fig. 4. The influence of temperature on the fluorescence intensity for ACRYLODAN in ethyl acetate from 193 K to 393 K (λ_{exc} = 420 nm).

3. Ground and Excited State Dipole Moments of BADAN and ACRYLODAN

The dipole moments μ_g and μ_e in the ground and excited state are determined from the equations describing the location of the maxima of the absorption ($\tilde{\nu}_a$) and fluorescence ($\tilde{\nu}_F$) bands as a functions of ε and n of the solvents used [5–7]:

$$\tilde{\nu}_A - \tilde{\nu}_F = m_1\, f(\varepsilon, n) + \text{const}\,, \tag{3}$$

$$\tilde{\nu}_A + \tilde{\nu}_F = -m_2\, \varphi(\varepsilon, n) + \text{const}\,, \tag{4}$$

where

$$\varphi(\varepsilon, n) = f(\varepsilon, n) + 2\, g(n)\,, \tag{5}$$

$$m_1 = \frac{2(\boldsymbol{\mu}_e - \boldsymbol{\mu}_g)^2}{h c a^3}\,, \tag{6}$$

$$m_2 = \frac{2(\mu_e^2 - \mu_g^2)}{h c a^3}\,. \tag{7}$$

Generally, if the Onsager cavity is taken as an ellipsoid of revolution ($b = c = a/p$, where a, b and c are its semi-axes), the solvent polarity parameters $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ can be determined from the following equations provided that $\alpha/a^3 = ½$ (α denotes the mean polarizability of the solute) [6, 8]:

$$f(\varepsilon, n) = \frac{\Phi - \Phi'}{(1 - \Phi)(1 - \Phi')^2}\,, \tag{8}$$

$$g(n) = \frac{\Phi'\left(1 - \frac{1}{2}\Phi'\right)}{(1 - \Phi')^2}\,, \tag{9}$$

where

$$\Phi = \frac{3A(1 - A)(\varepsilon - 1)}{2[\varepsilon - (\varepsilon - 1)A]}\,, \tag{10}$$

$$\Phi' = \frac{3A(1 - A)(n^2 - 1)}{2[n^2 - (n^2 - 1)A]}\,. \tag{11}$$

The constant A defines shape of the solute.

In the case of a sphere, for which $a = b = c$, $p = 1$ and $A = 1/3$, (10) and (11) have the following form

$$\Phi = \frac{\varepsilon - 1}{2\varepsilon + 1}\,, \tag{10$'$}$$

$$\Phi' = \frac{n^2 - 1}{2n^2 + 1}\,, \tag{11$'$}$$

and after substitution in (8) and (9) we obtain

$$f(\varepsilon, n) = \frac{2n^2 + 1}{n^2 + 2}\left(\frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n^2 - 1}{n^2 + 2}\right)\,, \tag{12}$$

$$g(n) = \frac{3}{2}\,\frac{n^4 - 1}{(n^2 + 2)^2}\,. \tag{13}$$

As has been shown in [8], the shape of the solute does not affect the values of determined dipole moments, but it affects the value of the Onsager interaction radius a. Therefore, the values of μ_g and μ_e were determined using (3)–(7) together with (12) and (13), assuming that $\boldsymbol{\mu}_g$ and $\boldsymbol{\mu}_e$ are parallel. Table 1 summarizes the values of the slopes m_1 and m_2, determined from the experimentally measured thermochromic shifts of the difference $\tilde{\nu}_A - \tilde{\nu}_F$ and the sum $\tilde{\nu}_A + \tilde{\nu}_F$ of the band maxima locations, and obtained according to (3) and (4) using the solvent polarity functions $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ given by (12) and (13) (cf. Figs. 5–8). Slight deviations of some experimental points from the linear dependence visible in Figs. 5 and 6 can result from the imperfect temperature stabilization at which the band locations were measured.

To determine μ_g and μ_e from (6) and (7), the Onsager radius a should be known. For BADAN and ACRYLODAN one can assume the same shape of the cavity as for PRODAN. Assuming the values a = 4.2 Å determined from crystallographic data [9] and a = 4.6 Å resulting from calculations of spherical cavity volumes being a sum of all atomic volumes [10], one can determine μ_g and μ_e for the values of m_1 and m_2 given in Table 1. Table 1 gives also the values of μ_g and μ_e calculated from (6) and (7) for two different Onsager radii a as well as the ratio μ_e/μ_g, which is equal to 2.9 for both compounds. A good agreement is observed for BADAN between the respective values of μ_g and μ_e determined from the thermochromic and solvatochromic methods

Table 1. Dipole moments (in Debye) determined from thermochromic shifts for BADAN and ACRYLODAN in two spherical cavities ($p = 1$, $A = 1/3$).

Molecule	a Å	m_1	m_2	μ_g	μ_e	$\Delta\mu$	μ_e/μ_g
		1 kK = 10^3 cm^{-1}		Debye			
BADAN	4.2	2.94	6.04	2.5	7.1	4.6	2.9
	4.6			2.8	8.1	5.3	2.9
ACRYLODAN	4.2	5.20	10.70	3.3	9.5	6.2	2.9
	4.6			3.7	10.8	7.1	2.9

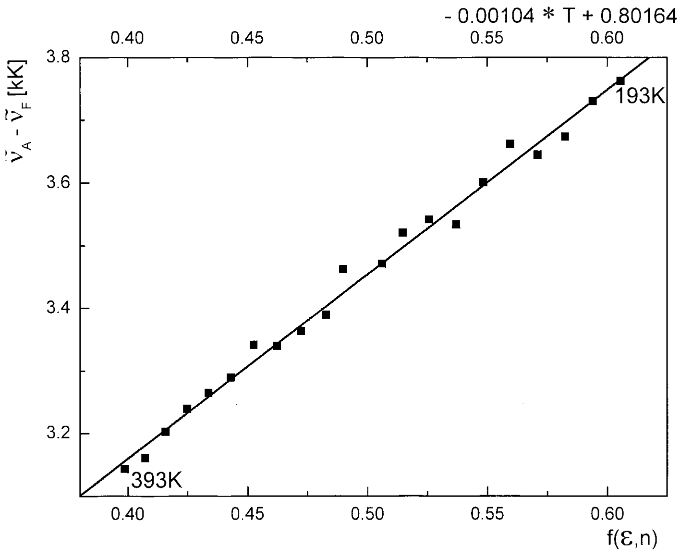

Fig. 5. Plots of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for BADAN in ethyl acetate at different temperatures T. Fit to (3) and (12) when $b = c = a$, $p = 1$ and $A = 1/3$.

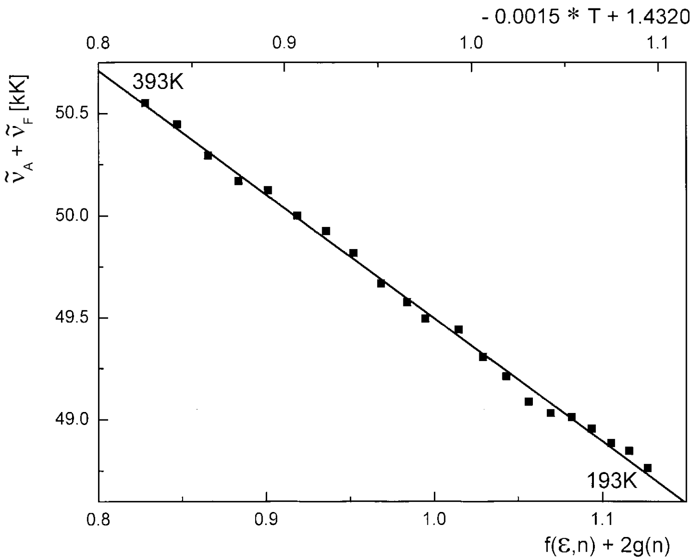

Fig. 6. Plots of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n)$ for BADAN in ethyl acetate at different temperatures T. Fit to (4) and (5) with (12) and (13) when $b = c = a$, $p = 1$ and $A = 1/3$.

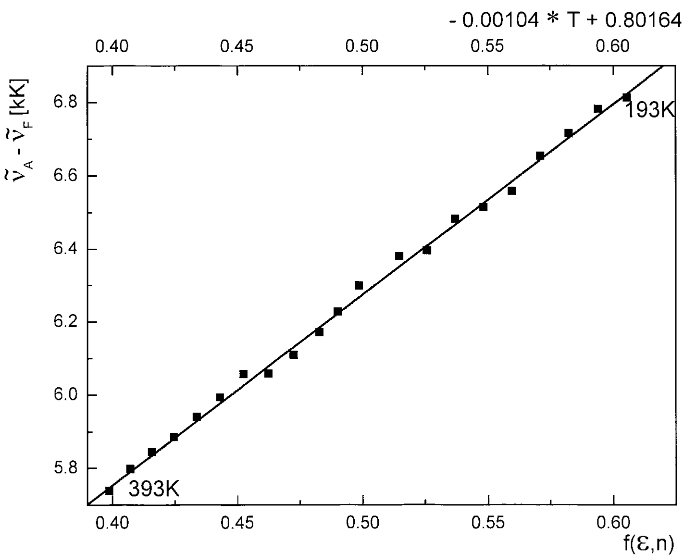

Fig. 7. Plots of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for ACRYLODAN in ethyl acetate at different temperatures T. Fit to (3) and (12) when $b = c = a$, $p = 1$ and $A = 1/3$.

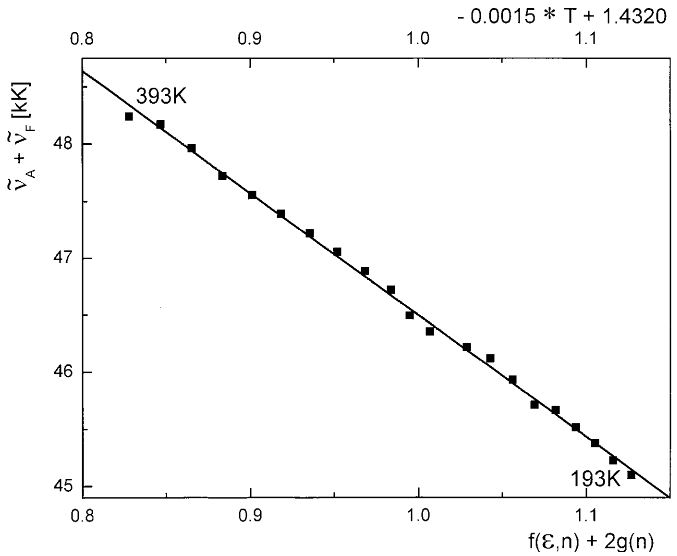

Fig. 8. Plots of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n)$ for ACRYLODAN in ethyl acetate at different temperatures T. Fit to (4) and (5) with (12) and (13) when $b = c = a$, $p = 1$ and $A = 1/3$.

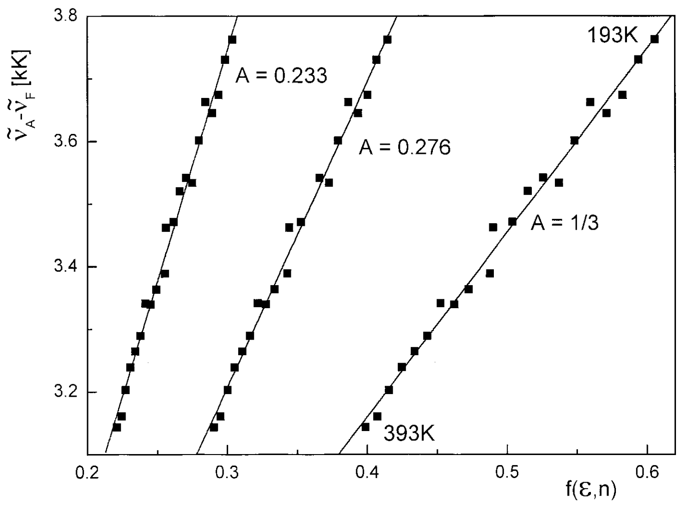

Fig. 9. Plots of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for BADAN in ethyl acetate at different temperatures and different molecular shape of the Onsager cavities: $A = 0.233$, $A = 0.276$ and $A = 1/3$. Fit to (3) and (8) with (10) and (11).

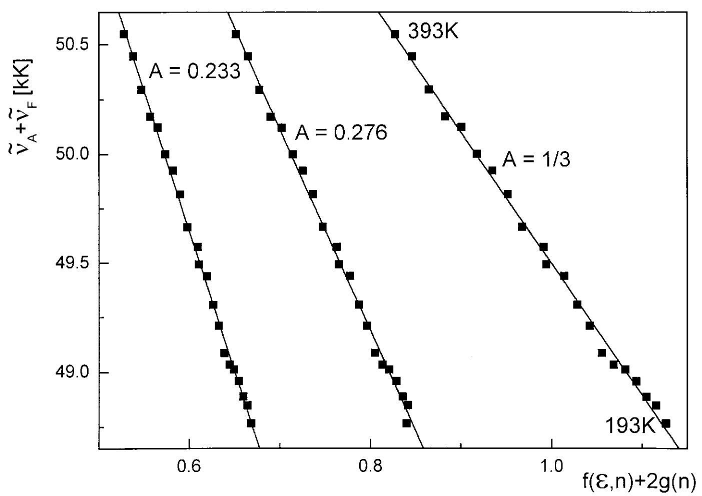

Fig. 10. Plots of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n)$ for BADAN in ethyl acetate at different temperatures and different molecular shape of the Onsager cavities: $A = 0.233$, $A = 0.276$ and $A = 1/3$. Fit to (4) and (5) with (8)–(11).

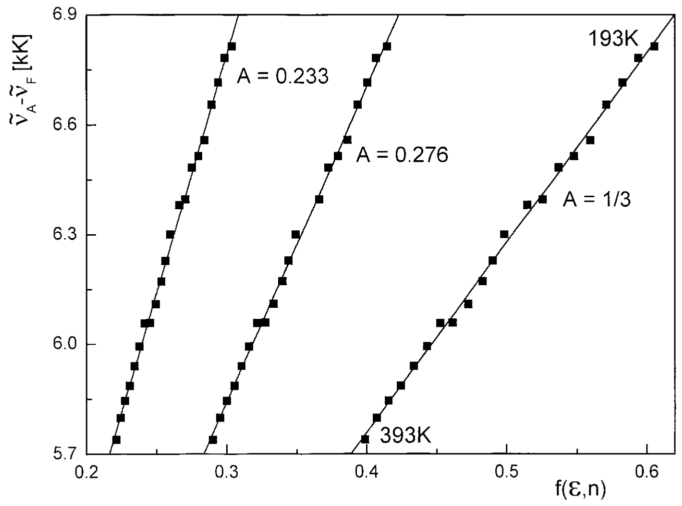

Fig. 11. Plots of $\tilde{\nu}_A - \tilde{\nu}_F$ versus $f(\varepsilon, n)$ for ACRYLODAN in ethyl acetate at different temperatures and different molecular shape of the Onsager cavities: $A = 0.233$, $A = 0.276$ and $A = 1/3$. Fit to (3) and (8) with (10) and (11).

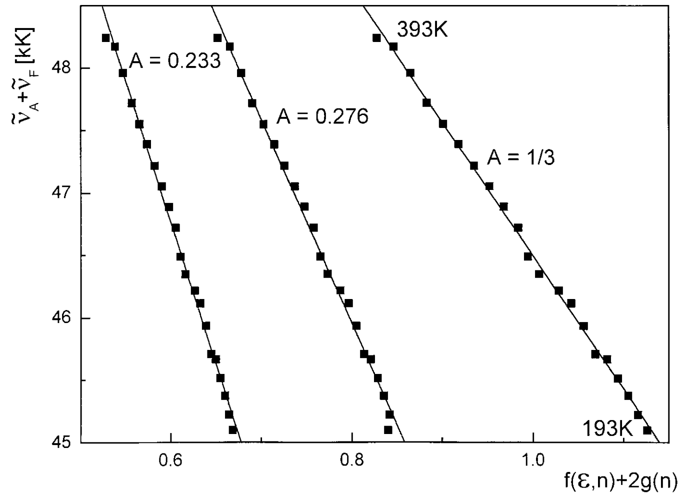

Fig. 12. Plots of $\tilde{\nu}_A + \tilde{\nu}_F$ versus $\varphi(\varepsilon, n)$ for ACRYLODAN in ethyl acetate at different temperatures and different molecular shape of the Onsager cavities: $A = 0.233$, $A = 0.276$ and $A = 1/3$. Fit to (4) and (5) with (8)–(11).

Table 2. Experimental Onsager parameters a determined from thermochromic shifts for BADAN and ACRYLODAN in cavities represented by prolate ellipsoid of revolution for two different calculated a values.

Molecule	A	m_1	m_2	Calculated values a	μ_g	μ_e	$\Delta\mu$	Empirical values a	
								Eq. (6)	Eq. (7)
		$1\ \text{kK} = 10^3\ \text{cm}^{-1}$		[Å]	in Debye			[Å]	[Å]
BADAN	0.276	4.88	9.21	4.2	2.5	7.1	4.6	3.5	3.6
				4.6	2.8	8.1	5.3	3.9	4.0
	0.233	7.35	12.90	4.2	2.5	7.1	4.6	3.1	3.25
				4.6	2.8	8.1	5.3	3.4	3.6
ACRYLODAN	0.276	8.6	16.39	4.2	3.3	9.5	6.2	3.6	3.65
				4.6	3.7	10.8	7.1	3.9	4.0
	0.233	12.90	22.79	4.2	3.3	9.5	6.2	3.1	3.3
				4.6	3.7	10.8	7.1	3.4	3.6

applied in [1]. In the case of ACRYLODAN, however, the ratio μ_e/μ_g obtained in [1] was 3.8, whereas now it amounts to 2.9, being the same both for BADAN and ACRYLODAN.

4. Estimation of the Empirical Onsager Interaction Cavity Radius for Ellipsoids of Revolution

To estimate the empirical cavity radius a for a molecule, the shape of which can be treated as an ellipsoid of revolution for which $b = c = a/p$, it is assumed for both the molecules studied that the parameter p exceeds 1 (model of a prolate ellipsoid of revolution). The value of the parameter p can be estimated from the shape of a molecule. For BADAN and ACRYLODAN the most suitable parameter is $p = 1.25$ or $p = 1.5$, corresponding to $A = 0.276$ or $A = 0.233$, respectively [11]. In order to estimate the empirical a values, the values of the functions $f(\varepsilon, n)$ and $g(n)$ were calculated from (8)–(11). According to (3) and (4), linear dependencies of $\tilde{\nu}_A - \tilde{\nu}_F$ and $\tilde{\nu}_A + \tilde{\nu}_F$ versus $f(\varepsilon, n)$ and $\varphi(\varepsilon, n)$ respectively, were obtained, and new slopes m_1 and m_2 were obtained for BADAN (Figs. 9–10) and for ACRYLODAN (Figs. 11–12). Based on these slopes, the empirical values of the cavity radii a were obtained from (6) and (7) for previously determined μ_g and μ_e for $p = 1$ and $A = 1/3$ (Table 1).

Table 2 lists the new values of m_1 and m_2 for $p = 1.25$ or $p = 1.5$, which differ significantly from those obtained for $p = 1$, as well as the empirical Onsager radii a for $A = 0.276$ or $A = 0.233$.

Both radii a determined from (6) and (7) are the same within the experimental error limits, and they are somewhat smaller than the calculated geometrical radius (Table 2). It should be noticed that both for BADAN and ACRYLODAN the empirical interaction radii a are not significantly different for the fixed value of the parameter A (i.e., 0.276 or 0.233), despite different values of μ_g and μ_e. This fact leads to the conclusion that the shape of the ellipsoid of revolution is the same for both compounds. Since the dipole moment of the solute is according to the Onsager theory approximated to a point dipole [11], the empirical radius a is smaller than the calculated geometrical radius (Table 2).

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