Fluorescence Quenching and Solvation Processes of Fluorenone and 4-hydroxyfluorenone in Binary Solvents

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Steady state and time-resolved spectroscopic measurements of fluorenone and 4-hydroxyfluorenone dissolved in binary nonpolar, polar and polar protic mixed solvents have been performed at room temperature. The absorption and emission spectra show that, apart from the free molecules, hydrogen bond complexes exist in the ground and excited states in the mixed solvents used. The data obtained were used to determine the stoichiometric equilibrium constants. The fluorescence decay data point that in the binary used solutions the radiation appears from an assembly of luminescence centers emitting fluorescence light of different wavelengths and decay times. Molecules forming simple hydrogen bond complexes (with fluorenone) show different photophysical properties from those where a proton-relay complex (with 4-hydroxyfluorenone) is established.

Key words: Fluorenone; 4-hydroxyfluorenone; Emission Spectra; Fluorescence Decay Times; Binary Solvents.

1. Introduction

The solvation phenomena in mixed solutions of polar molecules with closely located excited states of different character ($n\pi^*$ or $\pi\pi^*$) have been the subject of many publications [1 – 8]. It has been shown that in the ground state the non-bonding lone pair electrons are particularly suitable for forming hydrogen bonds, whereas this capacity is largely lost when one of these electrons is excited to the π^* system. Also, that the packing of the polar molecules around the ground state of the solute molecule is very different from the packing around the excited state. This causes the appearance of same relaxation processes that occur on the nanosecond time-scale, e.g., intermolecular proton transfer (IMPT) [9, 10], red-edge excitation effects [11 – 13], initial shock effect in the luminescent centres [14, 15], the formation of solvated radical-ions, charge-transfer complexes [16, 17], etc. All the relaxation processes cause changes in the luminescence properties of the solute molecules, e.g., the appearance of a new fluorescence band, excitation-wavelength dependence of the fluorescence intensity and fluorescence quenching, i.e. the decrease of the fluorescence quantum yield and the fluorescence decay time.

The fluorescence changes stated above depend on the nature of the electronic states involved in the radiation process, and on the kind of solvent. Recently a very scrupulous study of the fluorescence quenching processes in hydrogen-bonded complexes of fluorenone with a series of alcohols were performed by Fujii et al. [3] and Biczok et al. [4]. Their results show that the S_1 state of fluorenone in mixed solvents, comprising alcohol – nonpolar solvent (cyclohexane), has mainly an $n\pi^*$ character while a $\pi\pi^*$ character in polar aprotic solvents, and also that the kinetics of the dynamic fluorescence quenching of the S_1 and T_1 states by various alcohols is caused by the vibronic coupling to the ground state via the hydrogen bond. As a consequence one would expect that the fluorescence decay curves for mixed solutions should be monoexponential. Recently performed measurements of the fluorescence decay curves of fluorenone (9Fl) and 4-hydroxyfluorenone (4HOFl) in various solutions have shown that monoexponential fitting of the decay curves is obtained only for nonpolar and polar aprotic solvents [13]. The fluorescence decay data of mixed sol-

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vents comprising alcohol-cyclohexane (methylcyclohexane) and alcohol-acetonitrile can satisfactoroly be fitted by a sum of two or three exponential functions only. This indicates that in mixed solvents the fluorescence appears from a mixture of hydrogen-bonded complexes. This finding has been confirmed by redegde effect studies [13].

Taking into account the above findings, it was tempting to repeat the measurements of the fluorenone fluorescence quenching by alcohol and to extend them by additional measurements on the 4HOFl molecule, for which the solvation processes show a different dynamics than for 9Fl. In this paper we report the results of steady state spectroscopic and fluorescence lifetime measurements. The obtained data are used to calculate the equilibrium constants of bonding with ethanol molecules in the ground, K_g, and excited, K_e, states and the Stern-Volmer quenching constant, K_ST, for both molecules. Also, a detailed study of the fluorescence emission processes of the hydrogen-bonded complexes of 9Fl and 4HOFl are given.

2. Experimental Details

Fluorenone and 4-hydroxyfluorenone were purchased from Aldrich Chemical Co. and purified by recrystallization from toluene. Its purity was checked chromatographically. All solvents were of the highest grade commercially available: ethanol (99.9%) was reagent grade; all others were Aldrich spectal or HPLC grade. CH was distilled before use from a sodium potassium amalgam, to ensure that it is pure and free of water.

Absorption and fluorescence spectra were recorded using a Shimadzu UV-2401 PC spectrophotometer and a Shimadzu RF-5301 spectrofluorometer with 5.0 nm band-width for excitation and emission. The radiation was observed perpendicular to the direction of the exciting beam. Samples for fluorescence measurements were prepared in 1 cm quartz cuvettes. The concentration of the solutions was ca. $5 \cdot 10^{-4}$ M. The luminescence spectra have been corrected for the spectral response of the photomultiplier (Hamamatsu R-928), but not for reabsorption.

The fluorescence decay data were collected by the time-correlated single photon counting apparatus (the pico / femto second laser system, thermoelectrically cooled MCP-PTM R3809U-05) at the Laboratory of Ultrafast Laser Spectroscopy, A. M. University, Poznań, Poland [18]. The samples have been excited with a spectraphysics picosecond laser system: argon-pumped Ti-Sapphire-Tsunami 720 – 850 nm laser. The second (360 – 500 nm) harmonic of the Ti-Sapphire laser generates picosecond pulses at a repetition rate in the range from 4 MHz to single shot. The exciting and the fluorescence beam are polarised. The fluorescence light is monitored at the magic angle with respect to the plane of polarisation of the exciting beam. The pulse timing and data processing systems emploied a biased TAC model TC 864 (Tennelec) and an emission detector MCP-PMT R3809U-05, thermoelectrically cooled and equipped with an appropriate Hamamatsu preamplifier. The photon count rate was limited to 20 kHz when the repetition rate of exciting pulses was 4 MHz. The time between the exciting pulses was at least 5-times longer than the measured fluorescence decay time, ensuring excitation of a fully re-equilibrated sample with each laser pulse.

The fluorescence decay data were fitted by the interactive convolution to the sum of exponentials

$$I(t) = \sum_i \alpha_i \exp\left(\frac{-t}{\tau_i}\right),$$

where a_i and τ_i are the pre-exponential coefficient and the decay time of the i-th fluorescence component. All time-resolved measurements were performed at room temperature.

3. Results

3.1. Absorption Spectra in Mixed Solvents

The absorption spectra of 4HOFl in cyclohexane-ethanol and acetonitrile-ethanol mixed solvents are presented in Figs. 1A and 1B. The spectra are arranged in the order of increasing concentration of ethanol, keeping the solute concentration constant. The absorption spectra of 9Fl in these solvents, as well as both molecules in methylcyclohexane-ethanol and tetrahydrofuran-ethanol show big similarities. Moreover the 9Fl spectra can be found in [3, 5] and therefore will not be presented here.

As can be seen, the absorption spectra of 4HOFl in both mixed solutions form isosbestic points at 278 and 376 nm in CH—EtOH and at 282 and 379 nm in AcN—EtOH systems, respectively. This suggests that an equilibrium is established between two species, i.e. free molecules and their hydrogen bonded 4HOFl

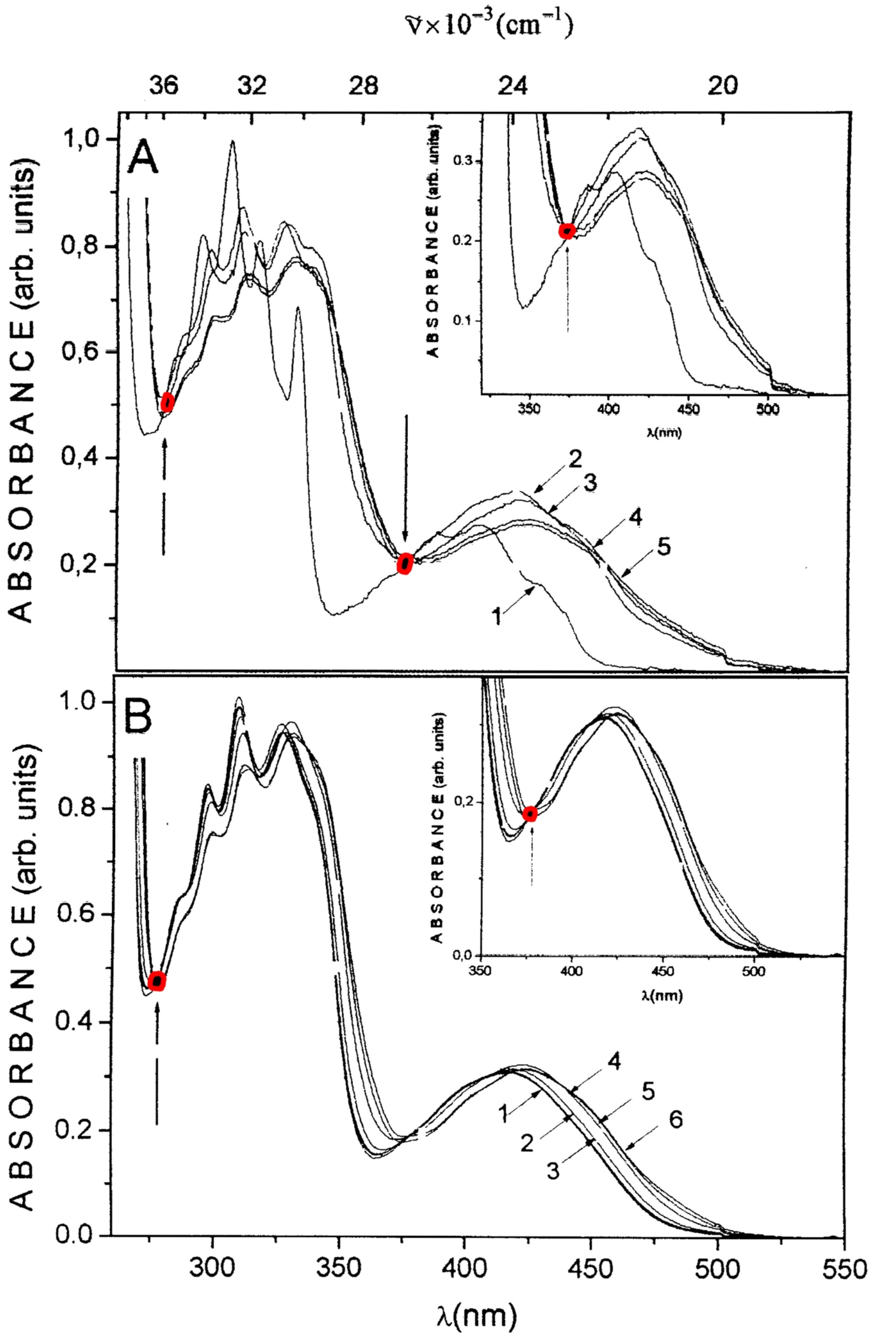


Fig. 1. The absorption spectra of 4HOFl in cyclohexane-ethanol (A) and acetonitrile-ethanol (B) binary mixed solvents. Concentration of ethanol is A 1: 0; 2: 0.17; 3: 1.70; 4: 17.0; 5: neat EtOH; and B 1: 0; 2: 0.17; 3: 0.34; 4: 1.70; 5: 17.0; 6: neat EtOH (mol dm^{-3}).

and 9Fl complexes. Both kinds absorb in the same region. The appearance of isosbestic points in the absorption spectra indicates that in the mixed solvents the hydrogen-bond formation is 1:1 between the molecules studied (M) and its complexes with ethanol (MC) (where the ethanol molecule is denoted as C═HO—R)

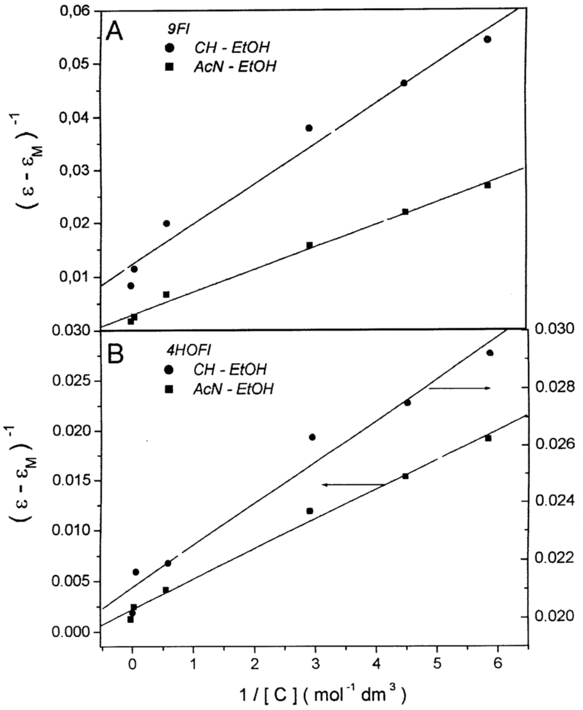


Fig. 2. Plot of $(\epsilon - \epsilon_\mathrm{M})^{-1}$ versus 1/[C] for fluorenone (A) and 4-hydroxyfluorenone (B) for cyclohexane-ethanol and acetonitrile-ethanol binary mixtures.

in the ground state ($\mathrm{S_0}$). The equilibrium state between them describes the relation [2, 19]

$$\mathrm{M} + \mathrm{C} \overset{K_\mathrm{g}}{\longleftrightarrow} (\mathrm{MC}), \tag{1}$$

where the equilibrium constant, defined as

$$K_\mathrm{g} = \frac{[\mathrm{MC}]}{[\mathrm{M}][\mathrm{C}]}, \tag{2}$$

can be calculated using the relationship given by Ketelaar et al. [19]

$$\frac{1}{\epsilon - \epsilon_\mathrm{M}} = \frac{1}{K_\mathrm{g}(\epsilon_\mathrm{MC} - \epsilon_\mathrm{M})} \cdot \frac{1}{[\mathrm{C}]} + \frac{1}{\epsilon_\mathrm{MC} - \epsilon_\mathrm{M}}. \tag{3}$$

In (3) ϵ, ϵ_MC and ϵ_M are the apparent absorption coefficient, the absorption coefficient of the complex and studied molecule, respectively. Figures 2A and 2B shows the plot of (3), made using experimental data taken from the absorption spectra. As can be seen, a linear dependence of $1/(\epsilon - \epsilon_\mathrm{M})$ on $1/[\mathrm{C}]$ is accomplished for fluorenone and 4-hydroxyfluorenone in both solvent mixtures. On the basis of these drawings the equilibrium constants, K_g, of studied molecules has been determined with satisfactory accurateness. The obtained K_g values are assembled in Table 1.

Table 1. The equilibrium constant between the solute molecule and its hydrogen-bond complex in the ground, $\mathrm{S_0}$, and excited, $\mathrm{S_1}$, state and the Stern-Volmer quenching constant, K_ST.

Equilibrium constant	9FL		4HOF	
	AcN + EtOH	CH + EtOH	AcN + EtOH	CH + EtOH
K_g (dm^3/mol)	0.66 0.6 ± 0.2[a]	1.62	0.71	14.00
K_e (dm^3/mol)	0.30 1.6[a]		0.49	
K_ST(dm^3/mol)	1.95		3.55	

[a] data obtained by T. Fujii et al. [3].

3.2. Fluorescence Spectra

The fluorescence spectra of fluorenone and 4-hydroxyfluorenone in cyclohexane-ethanol and acetonitrile-ethanol mixed solvents are shown in Figures 3 and 4. As follows from these figures, the fluorescence spectra undergo very complex changes on adding EtOH to CH and AcN, i.e., they are shifted to longer wavelength, possess changed half widths and band profiles of the emission spectrum. This behaviour indicates, that in such a solution an extra factor contributes to the well known dipole-dipole interaction, i.e., hydrogen-bonding interactions between the 9Fl and 4HOFl molecules and the alcohol, not only in the $\mathrm{S_0}$ state, but also in the excited, $\mathrm{S_1}$, state. In order to make it more evident in the inserts of the Figs. 3B and 4B, the normalised fluorescence spectra of both molecules in an AcN and EtOH are shown.

We note that for CH-THF mixtures an increase of the fluorescence intensity and a red shift of the fluorescence band maximum occurs. Both effects increase by adding to a nonpolar solvent an aprotic polar admixture. The observed behaviour of the fluorescence spectrum indicates that the $\mathrm{S_1}$ state changes in character from $n\pi^*$ to $\pi\pi^*$. Such an interchange of close lying states of different characters, induced by solvent polarity, is understandable, has been suggested in [9] and will be discussed briefly in Section 4.

The changes of the fluorescence spectra noted in Figs. 3 and 4 indicate that ethanol added to a nonpolar as well as to a polar nonprotic solvent quenches the fluorescence. This phenomenon is caused by hydrogen-bonds. This specific interaction indicates that the molecules in the excited state, $\mathrm{S_1}$, are quenched.

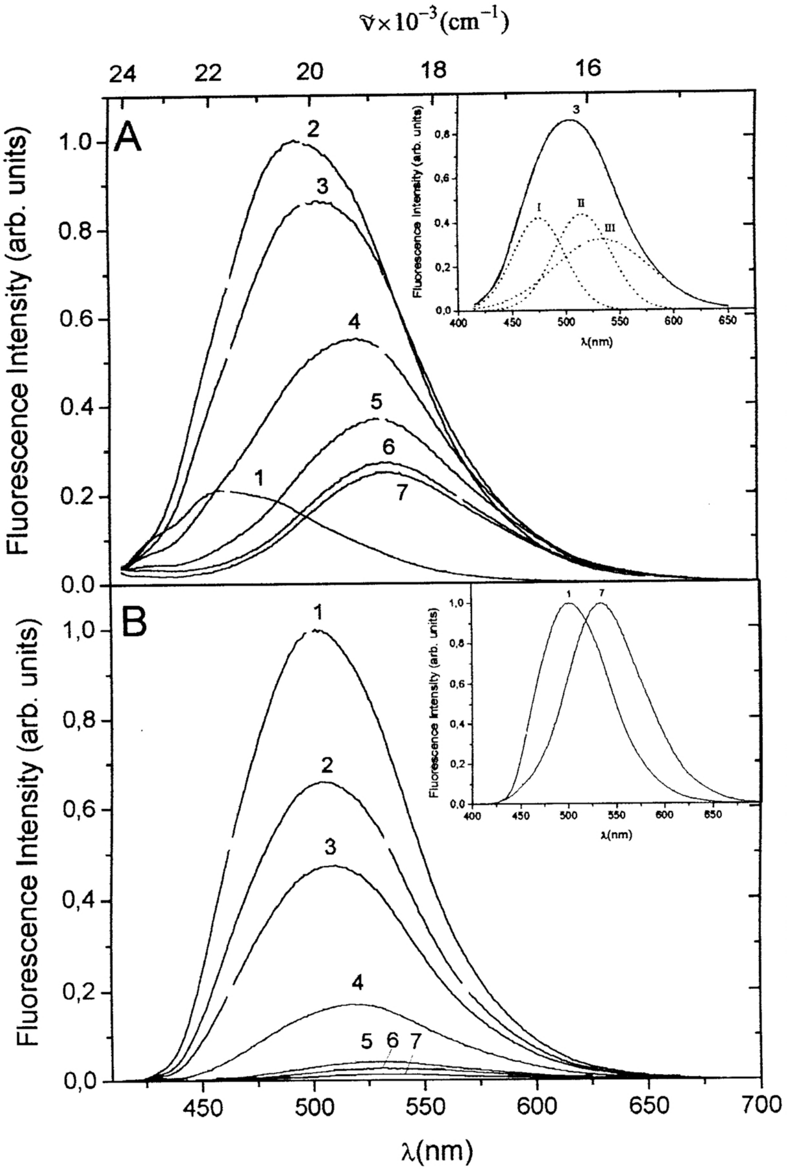


Fig. 3. The fluorescence spectra of fluorenone in binary mixture of cyclohexane-ethanol (A) and acetonitrile-ethanol (B). Concentration of ethanol is: 1: 0; 2: 0.17; 3: 0.34; 4: 1.70; 5: 17.0; 6: 170; 7: neat EtOH (mol dm^{-3}).

Taking into account the above findings, we must assume that in the S_1 state a stoichiometric equilibrium exists between the excited-state molecules, M^*, and the excited hydrogen-bonded complexes (M^*C), described by the reaction

$$M^* + C \xleftrightarrow{K_e} (M^*C). \tag{4}$$

The equilibrium constant of the excited state is defined as

$$K_e = \frac{[(M^*C)]}{[M^*][C]}, \tag{5}$$

where $[M^*]$ and $[(M^*C)]$ are the concentrations of the studied molecule and the hydrogen-bonded complex

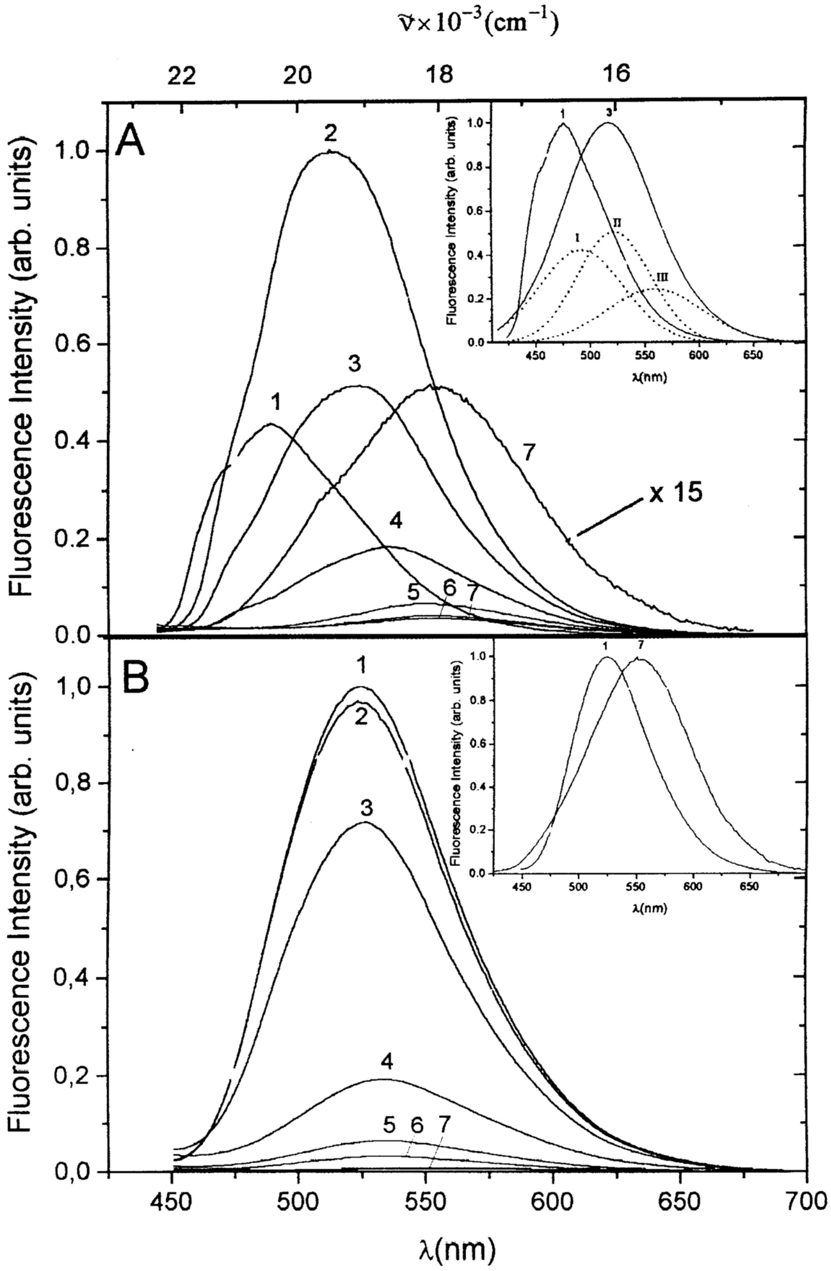


Fig. 4. The fluorescence spectra of 4-hydroxyfluorenone in binary mixture of cyclohexane-ethanol (A) and acetonitrile-ethanol (B). Concentration of ethanol is: 1: 0; 2: 0.17; 3: 0.34; 4: 1.70; 5: 17.0; 6: 170; 7: neat EtOH (mol dm^{-3}).

in the S_1 state, respectively. Here (M^*C) denotes the collision complex which, as it will be shown later, transforms into different forms. Accepting the formation and decomposition reactions of hydrogen bonded complexes, as given in [2], the changes of the fluorescence intensity caused by the ethanol molecules are described by the equation

$$\left(\frac{I}{I_0}-1\right)\cdot\frac{1}{[\mathrm{C}]}\cong\alpha\left(\frac{\tau}{\tau'}\right)K_\mathrm{e}-\frac{\tau}{\tau'}K_\mathrm{e}\left(\frac{I}{I_0}\right) \quad (6)$$

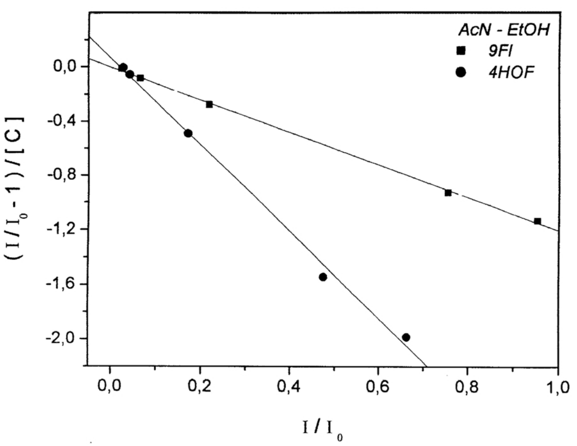
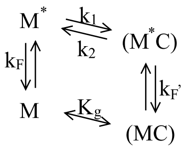


Fig. 5. Plot of $(I/I_0 - 1)/[C]$ versus I/I_0 of fluorenone and 4-hydroxyfluorenone in acetonitrile-ethanol binary mixed solvent.

In (6) I and I_0 are the fluorescence intensities with and in the absence of ethanol molecules, respectively, [C] is ethanol concentration, τ and τ' are the fluorescence decay times of the studied molecule M^* and its hydrogen bonded complex (M^*C), and α describes the ratio of fluorescence quantum yields of (M^*C) and M^*.

Figure 5 shows $(I/I_0 - 1)/[\mathrm{C}]$ versus I/I_0 for the binary AcN—EtOH mixture. Such a plot could not be drawn for a CH—EtOH mixture since in this case the fluorescence intensity increases for small alcohol concentrations, reaches a maximum and decreases for high [C] (see Figures 3A and 4A). The linear dependence plotted in Figs. 2 and 5 also for the decreasing part of the fluorescence intensity given on Figs. 3A and 4A, which are not presented, indicates that the photophysical processes appearing in the S_0 and S_1 states of the solutions studied can be presented by the simplified Scheme 1.



Scheme 1.

This reaction scheme has been scrupulously discussed in [2, 9, 20] without taking into account that between the collision complex (M^*C) and the ground state complex (MC) there exist some intermediate forms of hydrogen bonded solvates [9]. This will be discussed in Section 4. The theoretical fitting curves, the straight lines on Fig. 5, are given by the equations

$$(I/I_0 - 1)[\mathrm{C}]^{-1} = 0.064 - 3.2I/I_0;$$

$$(I/I_0 - 1)[\mathrm{C}]^{-1} = 0.003 - 1.11I/I_0$$

for 9Fl and 4HOFl, respectively. The excited state equilibrium constant, K_e, of fluorenone and 4-hydroxyfluorenone in the binary AcN—EtOH mixed solvent possess the values 0.3 $\mathrm{M}^{-1}\mathrm{dm}^3$ and 0.49 $\mathrm{M}^{-1}\mathrm{dm}^3$. The K_e constant for the CH—EtOH mixtures could not be determined for the reasons mentioned earlier. The obtained K_g and K_e data are collected in Table 1, where the values of other authors are given for comparison.

Analysing the determined K_g and K_e values it is evident that the appearance of hydrogen bond complexes of both molecules is more probable in the CH—EtOH mixture than in AcN—EtOH mixed solvents. Also, the equilibrium constants K_g and K_e of the 9Fl and 4HOFl differ significantly. This points distinctly a difference in the hydrogen bond complex formation of fluorenone and 4-hydroxyfluorenone.

3.3. Time-resolved Fluorescence Measurements

The fluorescence decays were measured using a fixed excitation wavelength ($\lambda_\mathrm{exc} = 360$ nm) at the magic angle for six emission wavelengths (at λ_max values of the 9Fl and 4HOFl fluorescence spectra in neat solvent: CH, AcN, EtOH, see Tables 2 and 3). Figure 6 shows decay curves of both molecules. A satisfactory agreement between the measured fluorescence decay data and the theoretical fitting function has been obtained using a monoexponential function in the case of a neat nonpolar and aprotic solvent and using a sum of two or three exponential functions for the binary mixed solvents as well as for pure EtOH. In agreement with results of other authors [7, 8, 21 – 23] the fluorescence decay curves of 9Fl in CH and AcN are well fitted by a simple exponential function. The obtained fluorescence decay times determined for two emission wavelengths are collected in Tables 2 and 3. The experimental error of τ_F equals 0.04 for decay times in the region < 0.5 ns and about 2% for the long decay components.

4. Discussion

The absorption and fluorescence spectra of 9Fl and 4HOFl in mixed binary solvents undergo complex changes, i. e. they are shifted to longer wavelength

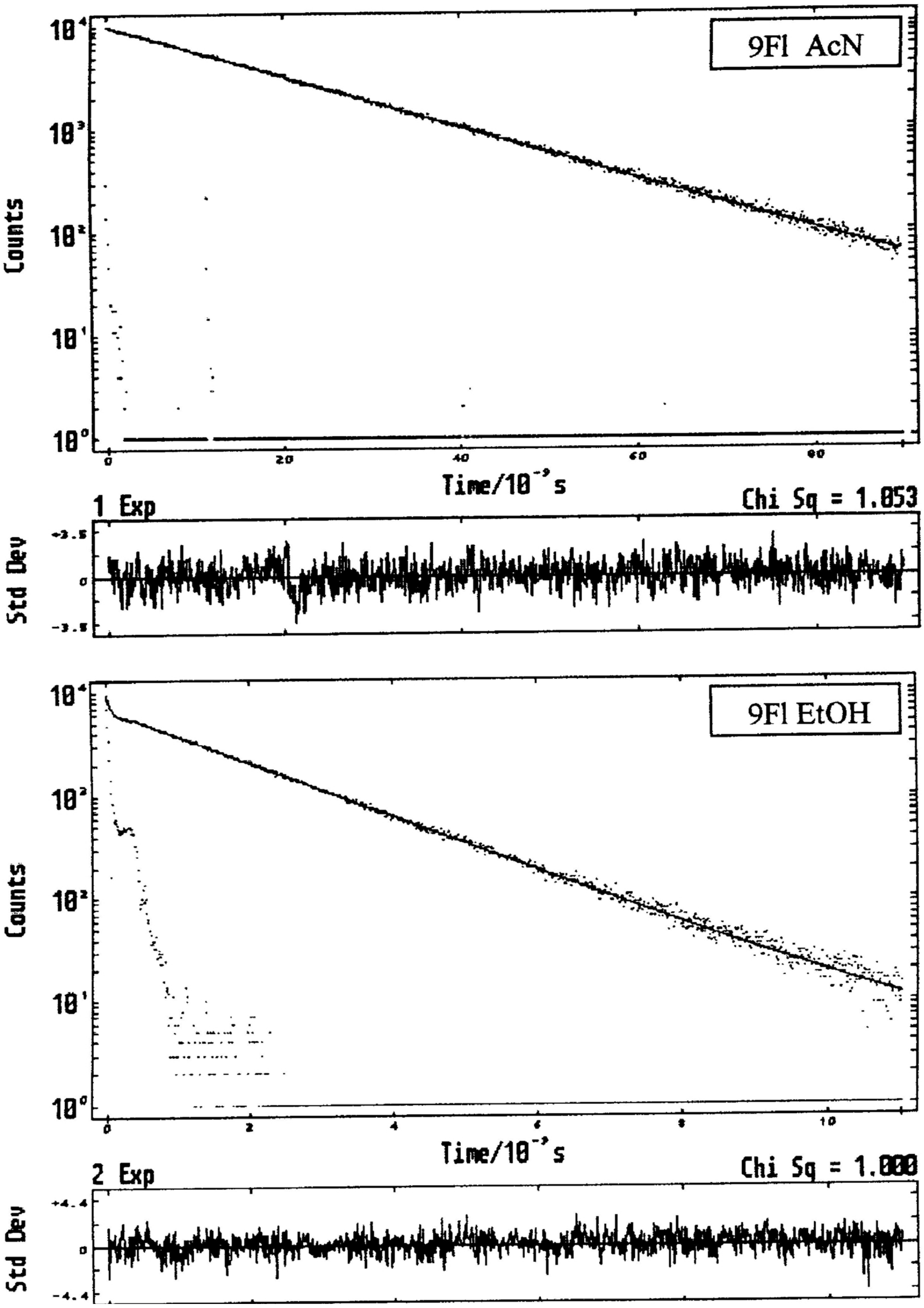


Fig. 6. The fluorescence decay curves of 9Fl in AcN and EtOH solutions at 293 K. Below are given the weighted residuals obtained by fitting the experimental data to sum of the exponentials.

Table 2. Fluorescence lifetimes of fluorenone and 4-hydroxyfluorenone in cyclohexane-ethanol binary mixed solvent.

CH—EtOH Mixture		9Fl						4HOF					
		$\lambda_{\text{obs}} = 460$ nm			$\lambda_{\text{obs}} = 535$ nm			$\lambda_{\text{obs}} = 476$ nm			$\lambda_{\text{obs}} = 550$ nm		
		τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2
CH	τ_1	0.132	100	1.15	0.129	100	1.14	0.48	100	1.05	0.47	100	1.10
200:1	τ_1	0.130	71	1.18	0.138	53	1.14	0.138	53	1.14	0.138	53	1.14
	τ_2	2.61	29		3.53	47		2.76	29		3.12	32	
100:1	τ_1	0.125	30	1.18	0.125	8	1.11	0.50	36	1.05	0.49	65	1.14
	τ_2	1.92	70		3.73	92		3.14	15		2.84	35	
	τ_3							0.21	49				
50:1	τ_1	0.107	22	1.04	0.104	3	0.94	0.20	37	1.10	0.18	23	1.11
	τ_2	3.68	58		4.77	94		2.50	16		2.64	27	
	τ_3	0.76	20		0.76	3		0.64	47		0.56	50	
10:1	τ_1	0.086	23	1.12	0.077	3	1.01	0.091	18	1.12	0.082	19	1.07
	τ_2	2.53	54		2.71	90		2.64	56		2.82	14	
	τ_3	0.44	23		0.43	7		0.34	26		0.49	67	
1:1	τ_1	0.046	21	1.11	0.066	4	0.99	0.033	10	1.08	0.052	15	1.09
	τ_2	2.43	67		2.12	94		2.91	75		2.79	31	
	τ_3	0.42	12		0.27	2		0.57	15		0.34	54	
1:10	τ_1	0.022	21	1.01	0.043	21	0.98	0.022	11	1.09	0.036	19	1.04
	τ_2	2.33	67		1.80	67		3.06	72		2.77	28	
	τ_3	0.42	12		0.96	12		0.55	17		0.28	53	
EtOH	τ_1	0.019	21	1.10	0.041	4	1.11	0.030	36	1.10	0.035	22	1.11
	τ_2	2.04	67		1.67	96		2.86	28		2.56	15	
	τ_3	0.37	12					0.28	36		0.27	63	

and show intensity and half width changes. Generally, the shift of the absorption band is smaller than that of the fluorescence spectrum. For 4HOFl the differences between the maxima of the absorption and emission bands determined in CH and EtOH equal $\tilde{\nu}^{\text{A}}_{\text{CH}} - \tilde{\nu}^{\text{A}}_{\text{EtOH}} \cong 1130\ \text{cm}^{-1}$ and $\tilde{\nu}^{\text{F}}_{\text{CH}} - \tilde{\nu}^{\text{F}}_{\text{EtOH}} \cong 2870\ \text{cm}^{-1}$. The respective $\tilde{\nu}$ differences for the AcN—EtOH mixtures are by one order of magnitude smaller. The half width of the fluorescence spectrum of both molecules decreases with increasing ethanol concentration, e.g., $\Delta\tilde{\nu}_{1/2} \cong 3600\ \text{cm}^{-1}$ versus 3425 cm^{-1} for cyclohexane and pure EtOH, respectively. In addition, the intensity distribution of the fluorescence spectrum of both molecules under study changes from an asymmetric (detected in CH, AcN, and MCH) are to a symmetric one in neat EtOH (see inserts on Figures 3B and 4B). These findings, in accordance with [11, 22, 23] and our earlier work [13], may be explained on the basis of specific solute-solvent configuration changes which undergo fast relaxation in comparison to the fluorescence decay. For solutions of low viscosity, where an inhomogeneous band broadening is observed [24], the relaxation time of the solute-solvent and the fluorescence decay time satisfy the inequality $\tau_{\text{R}} < \tau_{\text{F}}$. Our earlier studies show that viscous and glassy solvents, where $\tau_R > \tau_F$, no fluorescence band broadening is observed for the studied molecules [13].

In addition to the fluorescence intensity distribution changes by increasing ethanol percentage in nonpolar solvent, the fluorescence intensity first considerably increases, reaching a maximum and decreases at higher EtOH concentration (see Figures 3A and 4A). We would like to mention that in the case of binary aprotic and protic solvent mixtures (AcN—EtOH) a continued decrease of the fluorescence intensity is noted. As has been mentioned earlier, these changes, are in part, due to the fluorescence quenching of 9Fl and 4HOFl by the alcohol molecules. This means that the hydrogen-bond complexes ($\text{M.}^*\text{C}$) and free molecules M^* in the S_1 state (see Scheme 1) form a stoichiometric equilibrium. In the dynamics of the formation of excited hydrogen bond complexes of different kinds, the same non-radiative processes take place. In accordance with [2, 9, 20], the formation of solvated radical-ions (M^-C^+) is responsible for the fluorescence quenching. From Scheme 1 it follows that radiative and non-radiative processes in the S_1 state may occur in part form the dye molecules and hydrogen complexes. In accordance with Scheme 1, the absorp-

Table 3. Fluorescence lifetimes of fluorenone and 4-hydroxyfluorenone in acetonitrile-ethanol binary mixed solvent.

AcN—EtOH Mixture		9Fl						4HOF					
		$\lambda_{\text{obs}} = 501$ nm			$\lambda_{\text{obs}} = 535$ nm			$\lambda_{\text{obs}} = 525$ nm			$\lambda_{\text{obs}} = 550$ nm		
		τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2	τ[ns]	α[%]	χ^2
AcN	τ_1	17.48	100	1.05	17.48	100	1.18	6.52	100	1.06	6.48	100	0.98
100:1	τ_1	13.23	100	1.14	13.18	100	1.07	4.05	100	1.18	4.01	100	1.03
50:1	τ_1	10.52	100	1.18	10.53	100	1.18	3.07	100	1.16	3.03	100	1.03
10:1	τ_1	5.47	100	1.07	5.42	100	0.96	1.15	87	1.14	1.11	93	1.07
	τ_2							0.24	13		0.27	7	
1:1	τ_1	2.28	93	1.14	2.26	97	1.07	0.35	50	1.06	0.36	69	1.05
	τ_2							2.20	28		2.66	17	
	τ_3	0.063	7		0.57	3		0.047	22		0.052	14	
1:10	τ_1	1.79	91	1.17	1.76	96	1.08	0.28	42	1.10	0.27	65	1.10
	τ_2							2.60	25		2.45	13	
	τ_3	0.041	9		0.051	4		0.033	33		0.034	22	
EtOH	τ_1	1.68	94	1.04	1.67	96	1.01	0.28	36	1.11	0.27	43	1.09
	τ_2							2.86	28		2.56	24	
	τ_3	0.042	6		0.040	4		0.030	36		0.035	33	

tion process in the solutions under study is described as follows:

$$\mathrm{M} + \mathrm{C} + hv_{\mathrm{A}} \rightarrow \mathrm{M}^* + \mathrm{C} \rightarrow \mathrm{M} + \mathrm{C} + hv_1^{\mathrm{F}}, \tag{7a}$$

$$\begin{aligned} \mathrm{M} + \mathrm{C} + hv_{\mathrm{A}} &\rightarrow \mathrm{M}^* + \mathrm{C} \underset{k_1}{\overset{k_2}{\rightleftarrows}} (\mathrm{M}^*\mathrm{C})_{\mathrm{coll}} \\ &\rightarrow \left(\mathrm{M}^-\mathrm{C}^+\right)^*_{\mathrm{FC}} \rightarrow \left(\mathrm{M}^-\mathrm{C}^+\right)^*_{\mathrm{R/V}}, \end{aligned} \tag{7b}$$

$$\mathrm{MC}_{\mathrm{EQ}} + hv'_{\mathrm{A}} \rightarrow \mathrm{MC}^*_{\mathrm{EQ,FC}} \rightarrow \mathrm{M} + \mathrm{C} + hv_3^{\mathrm{F}}, \tag{7c}$$

$$\begin{aligned} \mathrm{MC}_{\mathrm{EQ}} + hv'_{\mathrm{A}} &\rightarrow \mathrm{MC}^*_{\mathrm{EQ,FC}} \\ &\rightarrow (\mathrm{MC})^*_{\mathrm{V/R}} \rightarrow (\mathrm{M}^-\mathrm{C}^+)^*_{\mathrm{V/R}}, \end{aligned} \tag{7d}$$

where the first link (7a) describes the normal fluorescence emission, the second the formation of a collision complex followed by the formation of the Franck-Condon exciplex [24]. In (7b) proton (or electron) transfer takes place in the collision complex, thus the process is independent from diffusion. When the exciplex passes to a thermolised state, non-radiative decay processes to the triplet and ground state compete with the fluorescence from a vibrationally relaxed state, $(\mathrm{M}^-\mathrm{C}^+)^*_{\mathrm{V}}$, or from the fully relaxed thermal equilibrium state $(\mathrm{M}^-\mathrm{C}^+)^*_{\mathrm{R}}$, which follows as a result of thermal reorientations with solvent molecules. These exciplex states are also populated by direct excitation of the hydrogen bond complex from the ground state, as shown in (7d). The emission processes named above are

$$(\mathrm{M}^-\mathrm{C}^+)^*_{\mathrm{V/R}} \rightarrow \begin{cases} (\mathrm{M} + \mathrm{C}) + hv_2^{\mathrm{F}}, & \text{(8a)} \\ (\mathrm{M}^-\mathrm{C}^+)_{\mathrm{g}} + hv_2^{\mathrm{F}'}, & \text{(8b)} \\ (\mathrm{M}^-\mathrm{C}^+)_{\mathrm{V}} + hv_2^{\mathrm{F}''}, & \text{(8c)} \\ {}^3\mathrm{M} + \mathrm{C} + \Delta_{\mathrm{th.energy}}. & \text{(8d)} \end{cases}$$

Independently from that, the excited solvates in the vibrationally relaxed state can pass to a fully relaxed state as a result of the reorientational motion of the solvent molecule. This process is followed by fluorescence emission or by radiationless decays as follows:

$$\left(\mathrm{M}^-\mathrm{C}^+\right)^*_{\mathrm{V}} \rightarrow \left(\mathrm{M}^-\mathrm{C}^+\right)^*_{\mathrm{V}} \rightarrow \left[(\mathrm{M}^-\mathrm{C}^+)_{\mathrm{V}}\right]^*_{\mathrm{EQ}}$$

$$\rightarrow \begin{cases} \mathrm{M} + \mathrm{C} + hv_2^{\mathrm{F}'''}, & \text{(9a)} \\ [(\mathrm{M}^-\mathrm{C}^+)_{\mathrm{V}}]_{\mathrm{EQ}} + hv_2^{\mathrm{F}^{\mathrm{IV}}}, & \text{(9b)} \\ {}^3\mathrm{M} + \mathrm{C} + \Delta_{\mathrm{th.energy}} & \text{(9c)} \\ \text{or } (\mathrm{M}^-\mathrm{C}^+)_{\mathrm{g}'} + \Delta'_{\mathrm{th.energy}}. & \end{cases}$$

The deactivation processes of the singlet excited state presented above indicate that in the fluorescence decay one should expect at least three radiation modes distinguished by different rate constants and emission wavelengths; see (7a, 7c, 8a, 8b, 8c, 9a, 9b). This supposition is well confirmed by the fluorescence decay data of 9Fl and 4HOFl, measured in binary solvents (see Tables 2 and 3). Additionally, in order to confirm this supposition, the τ_F values have been detected at two emission wavelengths, i.e. at $\lambda_\mathrm{em} = 460$ and 535 nm for 9Fl in CH—EtOH and at $\lambda_\mathrm{em} = 501$ and 535 nm in AcN—EtOH mixtures. The respective wavelengths for 4HOF are: 476 and 550 nm in CH—EtOH, and 525 and 550 nm in AcN—EtOH. Apart from the τ values of the decay modes, Table 1 and 3 collect the preexponential factors describing its contribution to the total emission and the χ^2 parameter describing the goodness of the fitting procedure.

Analyzing the experimental decay data collected in Tables 2 and 3, it follows that the fluorescence decays of both molecules in pure CH and AcN are very well fitted by a mono-exponential function for both selected wavelengths of the emission band. The obtained τ_F values do not depend on λ_em. As has been mentioned earlier, in binary mixed solvents the fluorescence decay data can be fitted by a sum of two or three exponential functions only. On the basis of the performed analyses of the experimental τ_i and α_i data (see Table 2 and 3), we suppose that in the mixed solvents two or three fluorescence emitting centers exist. Their emissions are represented by the reactions (7a), (7c), (8), and (9). The emitted photons possess different wavelengths, and the fluorescence decays are characterised by different times, e.g., τ_1, τ_2, and τ_3. The emission bands of the hydrogen bond complexes (see (7c), (8), and (9)) are shifted to longer wavelengths. They appear in the long wavelength wing of the emission band. Its λ_max value are 510 and 515 nm, respectively, for 9Fl and 4HOFl in ethanol [13]. The decay of the hydrogen bond complexes is represented by the longest decay time, i.e., τ_2. The τ_2 values change from 2 to 4 ns. The preexponential factors of the decay components of 9Fl and 4HOFl in CH—EtOH, determined at longer wavelengths are higher than those determined at shorter wavelengths. This dependence is not obtained for the long time decay components of 4HOFl in AcN—EtOH mixture (see Table 3). Generally, the participation of the long time decay component in the total emission is constant for high concentrations of EtOH.

For EtOH mixtures higher than 100:1 CH—EtOH v/v an additional decay component appears in the fluorescence decay, i.e., τ_3. Its decay times vary from 0,40 to 0,90 ns for 9Fl and from 0,27 to 0,64 ns for 4HOFl. The emission of this component contributes more at short wavelengths of the luminescence spectrum of 9Fl whereas in the case of 4HOFl it contributes more in the long wavelength part. Also the relative contributions to the total luminescence differ significantly, i.e., about 15 and 6 percent versus about 27 and 55 percent for the short and long wavelength part of the luminescence band of fluorenone and 4-hydroxyfluorenone, respectively.

In AcN-EtOH mixed solvent the third decay component appears at ethanol concentrations of 1:1 v/v AcN—EtOH. the decay times are in the ps region (33 – 60 ps), they contribute to the total luminescence of 9Fl and 4HOFl by about 6 and 26 percent, respectively. We suppose that the luminescence center of the third decay component of both molecules in CH—EtOH and AcN—EtOH solution possesses different origins, e.g., appearing from radiative collision complexes or Franck-Condon exciplexes.

The fluorescence decay time of 9Fl and 4HOFl determinated in neat AcN is about two orders of magnitude longer in comparison to that measured in CH (see Table 3 and [21]). This large change of τ_F with the noted increase of the fluorescence quantum yield is a consequence of the change of character of the lowest energy level from $n\pi^*$ to $\pi\pi^*$ [2, 25]. This phenomenon maybe explained by the energy shift of the electronic states caused by the dielectric media, and the mixing of states caused by strong hydrogen bonding interactions of protic solvents [2, 20]. The fluorenone fluorescence in AcN is quenched already by adding small quantities of EtOH, i.e., the fluorescence decay time, τ_F, and the fluorescence intensity decrease significantly (see Table 3 and Figures 3B and 4B).

Analyzing the data in Tables 2 and 3, it follows that the τ_1 value decreases systematically with increasing EtOH admixture. It is obvious that the τ_1 values are a continuation of the fluorescence decay data obtained for neat solvent (CH and AcN). This conjunction, and the observed decrease of the fluorescence intensity of both molecules under study point out that the fluorescence is quenched by EtOH molecules (see Figures 3B and 4B).

The differences of τ_1, τ_2, and τ_3 noted among those determined for 9Fl and 4HOFl confirm the stability of the relay proton-transfer chain formed between the oxygen atom and the hydroxy functional group of 4HOFl. The 4-hydroxyfluorenone molecules show higher resistibility against quenching caused by EtOH molecules.

The inserts of Figs. 3A and 4A show the fluorescence spectra of both molecules obtained in binary mixed solvents (CH—EtOH mixture 50:1 v/v) and decomposed in the three separated bands which correspond to the emission modes discussed above. In the performed decomposition of the fluorescence spectrum into the separated bands we established the $\lambda_{\max}$ value of the I-st and III-rd band and their half width, measuring a gaussian profile of intensity distribution. The λ values of the I-st and III-rd band are taken from measurements made for a pure CH solvent and from the red-edge effect studies of both molecules in EtOH [13]. As a result of those calculations we found that the three bands participate in the fluorescence spectrum in the ratio 0.7:0.6:1 for 9Fl and 1:0.9:0.6 for 4HOFl. These ratios agree with those obtained using the respective preexponential factors $\alpha_i (i = 1, 2, 3)$ of the multiexponential intensity decay by 80 percent (see Table 2). The decomposition of the other fluorescence spectra of other EtOH admixtures give also participation coefficients which agree with those determined from the fluorescence decay analysis. This supports strongly our supposition concerning the complexity of the fluorescence emission of 9Fl and 4HOFl in the binary mixed CH—EtOH solvents, and that each emission mode originates from molecules possessing different solvation shells.

The discussion concerning the fluorescence decay data can be summarised as follows:

- the first decay component, $\alpha_1 \exp(-t/\tau_1)$, can be attributed to the emission of an excited molecule being in the vibrationally relaxed electronic state,
- the second component, $\alpha_2 \exp(-t/\tau_2)$, appears from the luminescence of the hydrogen bond complexes. These complexes possess the fluorescence band at longer wavelength, in the wing of the regular fluorescence. Their maximum can be determined by the use of the red-edge effect [13]. The complexes emit from an excited state at full thermal equilibrium, i.e. in the vibrational and solvent reorganisation coordinates,
- the third decay component, $\alpha_3 \exp(-t/\tau_3)$, represents radiative transitions of different complexes of intermediate configurations – unrelaxed CT states.

The decay data assembled in Tables 2 and 3 behave differently on increasing the concentration of EtOH molecules in the binary solvent. The luminescence radiation described by the first component is quenched. This process is satisfactorily described by the Stern-Volmer equation. Graphically, the Stern-Volmer dependencies τ_1^0/τ_1 and I_1^0/I_1 versus EtOH concentration [C] are presented by a straight line, which is not given here. We would like to mention that for high EtOH concentrations (above 10:1 of CH/EtOH v/v) this dependence breaks down. The Stern-Volmer quenching constant, K_{ST}, for 9Fl and 4HOFl are equal to 1.95 M.$^{-1}$ and 3.6 M.$^{-1}$.

5. Conclusions

The spectroscopic properties of fluorenone and 4-hydroxyfluorenone in binary, nonpolar-protic and polar-protic, mixed solvents show that:

- Both molecules in nonpolar-protic and polar-protic binary solvent mixtures form hydrogen-bond complexes in the ground and excited states. At room temperature the stoichiometric equilibrium constant between free molecules and their complexes in the S_0 state is bigger then that in the S_1 state. Both constants are significally bigger for 4HOFl (about 7.5 and 63 percent for the S_0 and S_1 states).
- The luminescence of both molecules in CH—EtOH mixtures consists of three radiation modes (they correspond to three kinds of luminescence centres) characterised by a defined wavelength and decay time. The relative contributions of the radiation modes depend on the EtOH concentration and the wavelength of the luminescence spectrum.
- The fluorescence quenching process follows the Stern-Volmer law for EtOH concentrations lower than 10:1 v/v mixtures of both types of binary solvents.
- Analyzing the photophysical data of 9Fl and 4HOFl, determined in steady state, and time resolved-spectroscopic measurements we state that the proton-relay complexes (formed in the case of 4HOFl) show a higher K_{g} and K_{e} and smaller fluorescence quantum yield, and the decay time changes by increasing the EtOH concentrations. These differences point out that the 4HOFl hydrogen complexes are more stable and are less quenched by EtOH than 9-Fluorenone hydrogen complexes.

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