Preferential Solvation of Coumarin 153—The Role of Hydrogen Bonding

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Preferential solvation of solvatochromic probe coumarin 153 has been studied in toluene−acetonitrile and toluene−methanol solvent mixtures. Solvatochromic shifts of absorption and fluorescence spectra of coumarin 153 in these nonideal systems are analyzed as a function of solvent polarity. There is no apparent preferential solvation of coumarin 153 in the ground state. For the excited-state molecule preferential solvation is observed in toluene−acetonitrile mixtures and it is confirmed by a theoretical model. For the excited C153 in toluene−methanol mixtures strong nonlinearity in the fluorescence solvatochromic shifts is attributed mainly to formation of a hydrogen bond between methanol and C153. IR spectra of C153 in solvent mixtures containing methanol confirm formation of a hydrogen bond between methanol and C153. The presence of a hydrogen-bonded C153 in toluene−methanol mixtures causes an unusual dependence of the C153 fluorescence lifetime on the mole fraction of methanol in solution.

Introduction

It has been long recognized that solvation processes are essential to our understanding of chemical reactions in the liquid phase. The understanding of solvation of electronically excited molecules was greatly advanced over 40 years ago by the seminal works of Lippert[1] and Mataga,[2] which were concerned with static absorption and fluorescence solvatochromism. In the 1960s and 1970s, the foundations of the study of transient solvatochromism were pioneered by Bakshiev and Mazurenko.[3,4] During last 20 years there has been growing interest in solvation dynamics studies mainly due to development of femtosecond laser spectroscopy which enables the real-time measurements of ultrafast dynamical processes in liquids. The recent progress in this area is leading to unprecedented knowledge on the microscopic motion of polar solvents. In many investigations of solvation dynamics the time-resolved fluorescence spectroscopy of polar fluorescent probes with a large dipole moment that depends on electronic state has been used. Ultrafast optical excitation of an equilibrated ground-state probe produces a nonequilibrium configuration of the solvent around the excited state of the probe. Subsequent relaxation is accompanied by a time-dependent fluorescence spectral shift toward lower frequencies that can be monitored and analyzed to quantify the dynamics of solvation.[5] There have been many studies of solvation dynamics in polar solvents[5−8] and few in nonpolar solvents.[9−11] Recently, there is growing interest in solvation dynamics studies in binary mixtures of solvents.[12−18] In mixtures of solvents of different polarity a process of preferential solvation described as dielectric enrichment occurs in the solvation shell of dipolar solute molecules.[19,20] In the immediate neighborhood of a polar solute molecule the concentration of the more polar solvent will be greater than the bulk concentration since the solute−solvent stabilization energy which results from electrostatic interactions increases with solvent polarity. In these systems two processes contribute to solvation of the excited polar solute: reorientation of polar solvent molecules and translational diffusion of more polar solvent molecules contributing to dielectric enrichment in the solvation shell.

Coumarin 153 (C153) has been used in many studies as a probe of solvation dynamics.[5,6,11,12] The molecule is a particularly useful solvation dynamics probe as it is rigid, soluble in a broad range of solvents, and has a large radiative rate constant. The dipole moment of the excited C153 (14 D)[21,22] is larger than that of the ground state (6.5 D). The subject of the present study is to analyze solvation of the fluorescence probe C153 in binary solvent mixtures toluene−acetonitrile and toluene−methanol. These systems have been chosen to study the effect of hydrogen bonding between C153 and methanol on preferential solvation and photophysical properties of C153. Acetonitrile and methanol have similar dielectric properties, while the latter one can form hydrogen bonds with C153 as shown in this work.

Experimental Section

Coumarin 153 (C153) was obtained from Sigma and used without further purification. All solvents were either HPLC grade or they were purified by distillation; toluene and the solvents used in IR measurements were also dried over molecular sieves. The steady-state absorption spectra were recorded using a Carl-Zeiss Specord UV−Vis spectrophotometer equipped with a digital recording system. Emission spectra were recorded at room temperature for air-saturated samples using a conventional spectroflurometer with a cooled photomultiplier EMI 9558B operating in a single photon counting mode. The fluorescence spectra were corrected for instrumental response and were converted from a linear wavelength to a linear frequency representation. Fluorescence quantum yields were measured using quinine sulfate (0.05 M H_2SO_4) as a fluores-

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TABLE 1: Solvent Properties[a]

solvent	μ/D	ϵ	n	$F(\epsilon,n)$	r_1/Å
toluene	0.31	2.38	1.495	0.02	2.86
acetonitrile	3.53	35.7	1.342	0.71	2.24
methanol	1.7	32.7	1.328	0.71	2.05

toluene−acetonitrile

$n = 1.495 - 0.084x_p + 0.003x_p^2 - 0.072x_p^3$ ($\pm$0.0005)
$\epsilon = 2.38 + 14.6x_p - 4.16x_p^2 + 22.9x_p^3$ ($\pm$0.05)
$F = 0.034 + 1.649x_p - 1.737x_p^2 + 1.923x_p^3$ ($\pm$0.01)
$x_p = -0.015 + 0.571F - 0.145F^2 + 1.923F^3$ ($\pm$0.005)

toluene−methanol

$n = 1.495 - 0.063x_p + 0.014x_p^2 - 0.117x_p^3$ ($\pm$0.0005)
$\epsilon = 2.38 + 6.13x_p + 0.14x_p^2 + 24.03x_p^3$ ($\pm$0.05)
$F = 0.020 + 0.855x_p + 0.119x_p^2 - 0.293x_p^3$ ($\pm$0.01)
$x_p = -0.039 + 1.531F - 1.850F^2 + 2.490F^3$ ($\pm$0.005)

[a] ϵ and n are the dielectric constant, and refractive index of the solvents at 20 °C. μ is the dipole moment from refs 11, 37. $F(\epsilon,n)$ solvent polarity scale based on dielectric continuum theory $F = F(\epsilon,n) = (\epsilon - 1)/(\epsilon + 2) - (n^2 - 1)/(n^2 + 2)$. x_p is the molar fraction of a polar component of a binary mixture. r_1 is the van der Waals radius.[35] The formulas for n, F, ϵ, and x_p are obtained by fitting the experimental data.

cence standard, whose quantum yield was assumed to be 0.55.[23] The quantum yields were calculated by using a quadratic correction for refractive index of the solvent and a correction for percent light absorbed by the samples. For the measurements with excitation at 365 nm, samples with absorbance less than 0.1 at 365 nm were employed. Fluorescence quantum yields and fluorescence lifetimes were measured using samples which were thoroughly degassed by several freeze−pump−thaw cycles and were subsequently sealed off. Fluorescence decay functions were recorded using the time-correlated single photon counting technique with a nanosecond flashlamp as an excitation source (1.2 ns pulse width at 365 nm). The detection wavelength was set near the maximum of the fluorescence band. The spectral resolution was near 20 nm. The fluorescence lifetimes were calculated by fitting the experimentally recorded fluorescence decay functions to the convolution of a monoexponential decay function and an excitation profile. Dielectric constant measurements of solvent mixtures were carried out using a Radelkis OH-301 dielectrometer. Refractive indexes of mixtures were measured using a conventional refractometer. The concentration of C153 was around 3×10^{-5} M and 5×10^{-6} M in absorption and fluorescence measurements, respectively, which corresponds to a maximum optical density of about 0.7 and 0.1 in a 1 cm cell. IR spectra were recorded using a Perkin-Elmer Spectrum 1000 FT-IR spectrometer in a 0.2 mm cell. In this case the concentration of C153 was roughly 2.5×10^{-2} M. All measurements were performed at room temperature, 20 $\pm$ 2 °C.

Results and Discussion

Basic properties of the pure solvents are listed in Table 1. Both acetonitrile and methanol are strong polar solvents with similar dielectric constants ϵ and refractive indexes n. The reaction field factor

$$F(\epsilon,n) = \frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 - 1}{n^2 + 2} \quad (1)$$

which is often used as a measure of solvation energy[11,19] has the same value for both solvents. The data in Table 1 show

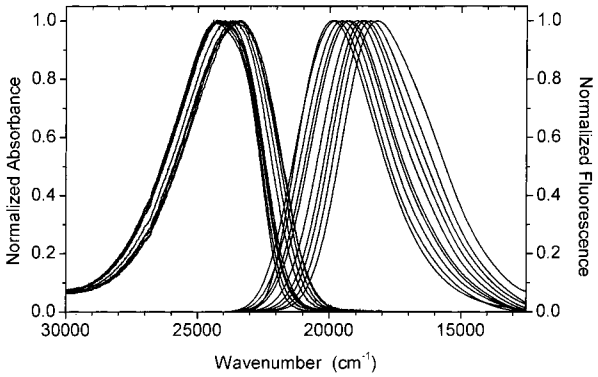

Figure 1. Normalized absorption and fluorescence spectra of C153 in toluene−methanol mixtures for alcohol mole fractions $x_P = 0.0$, 0.02, 0.04, 0.06, 0.08, 0.2, 0.4, 0.6, 0.8, 1.

that polarities of acetonitrile and methanol are very similar. The main difference between these two solvents, important in a discussion of solute−solvent interactions, is the ability of methanol to form hydrogen bonds. One can expect that in alcohols C153 can form a hydrogen bond localized on its carbonyl group similarly to coumarin 102.[24,25] Chudoba et al. have shown formation of hydrogen bonds between similar coumarin 102 and phenol using femtosecond IR spectroscopy.[24,25] Recently, Cichos et al. using molecular dynamics simulations have studied solvation of C153 in methanol/hexane mixtures[15] and later solvation of C153 in pure acetonitrile or methanol.[26] The simulations show that methanol can form hydrogen bonds with C153, while this is not the case for acetonitrile.

Solvatochromic Shifts. The steady-state absorption and fluorescence spectra of C153 in mixtures of toluene−methanol at different methanol concentrations are shown in Figure 1. The shape of the absorption band of C153 in toluene is slightly different than that in more polar solvent mixtures indicating some contribution of vibrational structure. The absorption band shifts to the red with increasing concentration of a polar component in solvent mixtures. The red shift can be observed already at very small concentrations of methanol. In toluene the band is centered at 24900 cm^{-1}, while in acetonitrile and methanol at 24380 and 24230 cm^{-1}, respectively. That gives the maximum shift between the spectra of C153 in neat toluene and neat polar component, 520 and 670 cm^{-1} for acetonitrile and methanol, respectively.

The fluorescence bands of C153 in Figure 1 do not show any vibrational structure even in neat toluene. The observed red shift of the fluorescence band due to increasing solvent polarity is bigger than that of the absorption spectra. The fluorescence band is centered at 19860, 18110, and 17280 cm^{-1} in toluene, acetonitrile, and methanol, respectively. Therefore, the maximum shift of the fluorescence band for toluene−acetonitrile mixtures is 1750 cm^{-1} and for toluene−methanol mixtures 2580 cm^{-1}. The spectra presented in Figure 1 show that the red shifts of the absorption and fluorescence bands of C153 in toluene−methanol mixtures are not a linear function of polar solvent concentration. To analyze solvatochromic shifts it is convenient to employ the reaction field factor $F(\epsilon,n)$ as the solvent polarity scale. The dielectric continuum theory predicts that solvatochromic shifts of the absorption and fluorescence spectra for a molecule in solvents of different polarity should be proportional to $F(\epsilon,n)$.[11,19] It is often assumed that $F(\epsilon,n)$ for a binary mixture of polar and nonpolar solvents is a linear function of the molar fraction of the polar component x_p

$$F(\epsilon,n) = x_n F(\epsilon_n,n_n) + x_p F(\epsilon_p,n_p) \quad (2)$$

Absorbance or fluorescence solvatochromic shifts are then analyzed as a function of x_p. Equation 2 applies to some ideal mixtures. However, in general binary mixtures are not ideal and $F(\epsilon,n)$ should be calculated from eq 1 using experimental ϵ and n. We have measured the values of ϵ and n for each mixture and from the best fit of the experimental data the equations given in Table 1 are obtained. Figure 2 shows the polarity function $F(\epsilon,n)$ calculated from experimental values of ϵ and n for toluene−methanol and toluene−acetonitrile mixtures. The toluene−acetonitrile mixtures show nonideal behavior in the whole concentration range. Such a behavior was expected due to the well-known self-association properties of acetonitrile molecules.[19] For the toluene−methanol mixtures the linear dependence of $F(\epsilon,n)$ on the mole fraction of the polar component x_p is valid at low concentrations ($x_p < 0.1$). Therefore, the mole fraction of the polar component x_p is not a good measure of bulk solvent polarity. The nonlinear solvatochromic shifts of the absorption and fluorescence bands of C153 in toluene−acetonitrile and toluene−methanol binary mixtures should be analyzed as a function of $F(\epsilon,n)$ instead of molar fraction x_p of polar component. Figure 3 shows plots of solvatochromic shifts of C153 in the studied binary mixtures as a function of x_p and $F(\epsilon,n)$. The two plots differ significantly. Nonlinear solvatochromic shifts of the absorption and fluorescence bands are observed in Figure 3a (where the results are plotted as a function of x_p), even at low concentration of polar component. Figure 3b shows the same solvatochromic shifts as a function of $F(\epsilon,n)$. For the toluene−acetonitrile mixtures, the nonlinear dependence for the absorption band disappears completely up to the $x_p = 0.5$ and the solvatochromic shift of the fluorescence band shows also very weak nonlinearity for the whole x_p range. For the toluene−methanol mixtures we observe a weak nonlinearity for the absorption band and a quite strong nonlinear dependence for the fluorescence band. As the scale with $F(\epsilon,n)$ does correct the nonlinear solvatochromic shifts of C153 in toluene−acetonitile mixtures that indicates that there is almost no dielectric enrichment for the ground and excited state of C153. In contrast, in the toluene−methanol mixtures the non linearity still remains for the absorption band and becomes even stronger for solvatochromic shifts of fluorescence spectra.

Preferential Solvation. Several theoretical models have been proposed to describe preferential solvation phenomena. All these models were developed using the theory of solvatochromic shifts, which is based on an Onsager description of electrostatic solute−solvent interactions.[27] The first model of solvation in mixtures of solvents was developed by Bakshiev and co-workers[28] and it was applied to systems where polar and nonpolar solvents have similar molecular radii and refractive index n values. The second approach proposed by Mazurenko[29] is based on a cage model of solvent with several additional assumptions: (i) the first solvation shell of the solute consists of N cells with N_P polar and N_N nonpolar molecules of solvents, (ii) replacement of any nonpolar molecule by a polar one in each of whole cells leads to an equal gain in energy, (iii) the probability distribution of filling cells by polar and nonpolar molecules in the equilibrium is given by the binominal distribution. It follows from the assumption (ii) that the model cannot be applied to systems with site-specific interactions between solute and solvent molecules.

Finally, the third model known as the theory of dielectric enrichment was developed by Suppan and co-workers.[19] Recently, the model has been extensively explored by several authors.[14,17,18,30−33] For an ideal dielectric mixture, the local composition in the near vicinity of a dipolar solute is given by

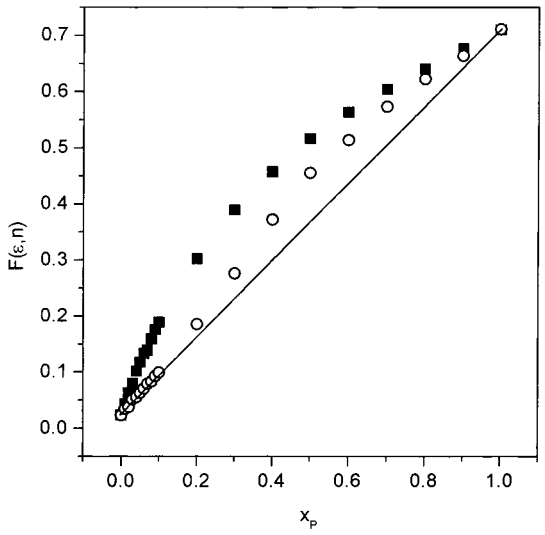

Figure 2. The polarity function $F(\epsilon,n)$ plotted as a function of the mole fraction of polar solvents: toluene−methanol mixtures are shown as circles, toluene−acetonitrile mixtures as squares.

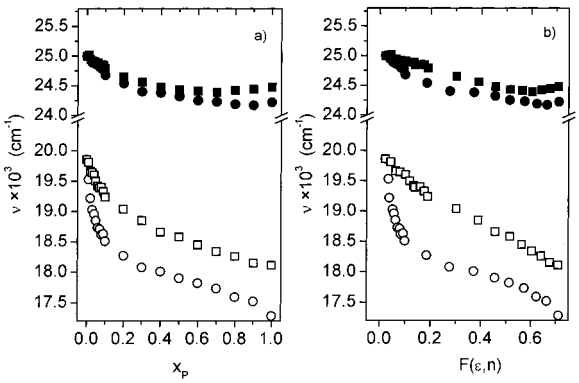

Figure 3. Average frequencies (first moments) of absorption (filled symbols) and fluorescence (open symbols) spectra plotted (a) as a function of the mole fraction of polar solvents, (b) as a function of the reaction field factor $F(\epsilon,n)$. Toluene−methanol mixtures are shown as circles, toluene−acetonitrile mixtures as squares.

$$\frac{y_n}{y_p} = \frac{x_n}{x_p} e^{-Z} \quad (3)$$

where Z is referred as the index of preferential solvation. x_n (x_p) and y_n (y_p) are the bulk and local mole fractions of the nonpolar (polar) component of the solvent, respectively. In the single shell approximation Z can be calculated according to

$$Z = \frac{1}{4\pi\epsilon_0} \frac{3\mu^2 M \Delta f(\epsilon)}{8\pi R T \delta r^6} \quad (4)$$

where M and δ are the mean molar mass and the mean density of the two solvent components, respectively. r is the mean distance between solute and solvent molecules of the first solvation shell. $\Delta f(\epsilon) = f(\epsilon_p) - f(\epsilon_n)$, where $f(\epsilon)$ is the Onsager polarity function given by the expression

$$f(\epsilon) = \frac{2(\epsilon - 1)}{2\epsilon + 1} \quad (5)$$

TABLE 2: Local Mole Fractions of the Polar Solvent Component around Excited C153 and *Z* values in Toluene−Acetonitrile and Toluene−Methanol Mixtures

x_p	y_p	*Z* (from eq 3)	*Z* (from eq 4)
		Toluene−Acetonitrile	
0.03	0.048	0.49 (±0.05)	0.53
0.05	0.083	0.54	0.53
0.1	0.16	0.56	0.53
0.3	0.34	0.19	0.53
0.6	0.63	0.14	0.52
0.8	0.83	0.17	0.50
		Toluene−Methanol	
0.03	0.26	2.4 (±0.1)	0.52
0.05	0.31	2.2	0.53
0.1	0.42	1.9	0.53
0.3	0.57	1.1	0.54
0.6	0.69	0.4	0.53
0.8	0.81	0.1	0.49

Recently Kauffman et al.[18] have compared different methods of approximation of the index of preferential solvation *Z* based on eq 4 or on experimental data.

It is important to note that all presented models describe the process of dielectric enrichment as a result of electrostatic solute−solvent interactions. Therefore, the process of dielectric enrichment does not account for any specific solute−solvent interactions such as hydrogen bonding. It was discussed by Suppan[34] that eq 3 is not suitable for specific associations and in fact can be used to distinguish between specific and unspecific interactions. We apply this procedure to analyze fluorescence Stokes shifts of C153 in toluene−acetonitrile and toluene−methanol mixtures. For different bulk molar fractions x_p we calculate local molar fractions y_p and then *Z* values.

For a given value of x_p we have an experimental value of the polarity function $F(\epsilon,n)$ of the bulk (Table 1) and the observed fluorescence shift. However, the fluorescence Stokes shift corresponds to the local composition of the solvent near solute molecules and to a local polarity function $F_l(\epsilon,n)$. For a given solute molecule, solvatochromic shifts in different solvents due to dipole−dipole interactions are[19]

$$\Delta\nu = aF(\epsilon,n) + b \tag{6}$$

This relationship holds well for C153 as it was shown by Maroncelli et al.[11] Therefore we can assume that the observed fluorescence shift is described by the equation

$$\Delta\nu_f = aF_l(\epsilon,n) + b \tag{7}$$

This relationship can be applied to calculate $F_l(\epsilon,n)$ for a given $\Delta\nu_f$ and then the local molar fraction y_p from the equation given in Table 1. The parameters *a* and *b* in eq 7 are calculated from the positions of fluorescence bands of C153 in pure polar and nonpolar components. Table 2 gives the local molar fraction of polar component y_p and *Z* values obtained from the above procedure for different solvent mixtures. Results in Table 2 show very different behavior of C153 in toluene−acetonitrile and toluene−methanol mixtures. For toluene−acetonitrile mixtures, for x_p higher than 0.2, the value of y_p is very close to that of x_p and the *Z* value is almost constant and can be estimated as 0.18 ± 0.03. For that mixture at $x_p < 0.2$, values of y_p are slightly higher than that of x_p and the *Z* value is around 0.53. However, an average Z = 0.36 can be used to calculate y_p in the whole concentration range (0.03−0.8) with accuracy near 15%. For toluene−methanol mixtures, the y_p values are higher than that of x_p, mainly at low concentrations of methanol. The *Z* value increases continuously from 0.1 at $x_p = 0.8$ up to 2.4 at $x_p = 0.03$. In this case, eq 3 fails completely as the *Z* value strongly depends on the concentration of methanol. This result suggests that solvatochromic shifts observed for C153 in toluene−methanol mixtures are strongly affected by specific interactions. Similar analysis for the absorption spectra of C153 in toluene−methanol mixtures gives *Z* values increasing from 0.3 at $x_p = 0.8$ up to 1.4 at $x_p = 0.03$. Apparently hydrogen bonding is weaker for the ground-state C153 but still eq 3 cannot be used to calculate the local concentration of methanol around the solute. Similar strong dependence of the *Z* values on alcohol concentration for C153 in alkane−alcohol mixtures was observed by Cichos et al.[14]

At very low concentrations of a polar component in solution the steady-state fluorescence solvatochromic shifts can be affected by slow diffusion of polar molecules. We can observe apparent deviations in the calculated *Z* values for x_p smaller than 0.01. This is in agreement with measurements of Cichos et al.[14] where they estimated a Stokes shift time constant τ_s = 1.8 ns for C153 in 0.01 M MeOH in hexane.

The index of preferential solvation Z can be also calculated from eq 4. The calculation requires the estimation of the solvent density, δ, solvent molar mass, *M*, and the distance between the cavity center and the first solvation sphere, *r*. For δ and *M*, we use mole fraction weighted averages of the pure components. *r* is calculated as a sum of van der Waals radius of the solute r_1 and solvent r_2. As a measure of r_2 we use bulk-mole-fraction-weighed van der Waals radius of the solvent.[17,18] van der Waals radii of pure solvents obtained using the method of Bondi[35] are given in Table I. The same method gives $r_1 = 3.87$ Å for C153 assuming that the solute is spherical. In Table 2, *Z* values calculated from eq 4 are compared with that obtained from experimental data and eq 3. For toluene−acetonitrile mixtures calculated values are in reasonable agreement with the experimental data particularly at low concentrations. Acetonitrile and methanol have very similar dielectric properties as shown in Table 1. Therefore, *Z* values calculated from eq 4 are very similar for both mixtures (Table 2). This result confirms that strong nonlinear solvatochromic shifts for C153 in toluene−methanol mixtures are a result of specific interactions, i.e., hydrogen bonding. In this case solvatochromic shifts cannot be used to calculate the preferential solvation index *Z*.

Fluorescence Lifetimes and Fluorescence Quantum Yields. Fluorescence lifetimes and fluorescence quantum yields of C153 in toluene−methanol and toluene−acetonitrile mixtures are given in Table 3. For the toluene−acetonitrile mixtures, the fluoresecence lifetime τ_f of C153 gradually increases with solvent polarity as shown in Figure 4. Different behavior is observed for C153 in toluene−methanol mixtures. The fluorescence lifetime of C153 increases with increasing solvent polarity for $x_p < 0.2$ and then decreases with increasing solvent polarity for $x_p > 0.2$. The plot of the fluorescence lifetime τ_f of C153 versus molar fraction of methanol x_p has a maximum near $x_p = 0.2$ (Figure 4).

The fluorescence quantum yield decreases with increasing mixture polarity. The radiative rate constant k_r of C153 in toluene−methanol mixtures decreases with increasing concentrations of methanol (Table 3). The nonradiative rate constant k_{nr} increases with increasing concentration of methanol. Values of the radiative rate constants k_r are similar to that observed in the toluene−methanol mixtures. The k_r value for C153 in neat methanol is approximately the same as in toluene and equals 1.1×10^8 [s^{-1}]. The nonradiative rate constant k_{nr} of C153 in toluene−acetonitrile mixtures does not change significantly with mixture polarity.

TABLE 3: Fluorescence Quantum Yields, Lifetimes. and Rate Constants for Radiative and Nonradiative Decay for Degassed Solvents

mole fraction of polar component x_P	fluorescence quantum yield φ_F (±5%)	fluorescence lifetime τ_F [ns] (±0.05)	rate constant: radiative $k_r \times 10^8$ [s^{-1}] (±0.05)	rate constant: nonradiative $k_{nr} \times 10^8$ [s^{-1}] (±0.05)
		Toluene−Methanol		
0.0	0.82	5.2	1.6	0.3
0.1	0.82	5.5	1.5	0.3
0.2	0.82	5.6	1.5	0.3
0.4	0.76	5.5	1.4	0.3
0.6	0.68	5.3	1.3	0.6
0.8	0.68	5.0	1.4	0.6
0.9	0.56	4.8	1.2	0.9
1.0	0.46	4.2	1.1	1.3
		Toluene−Acetonitrile		
0.0	0.82	5.2	1.6	0.3
0.1	0.79	5.3	1.5	0.4
0.2	0.79	5.4	1.5	0.4
0.4	0.83	5.6	1.5	0.3
0.6	0.91	6.0	1.5	0.1
0.8	0.82	6.2	1.3	0.3
0.9	0.78	6.4	1.2	0.3
1.0	0.69	6.5	1.1	0.5

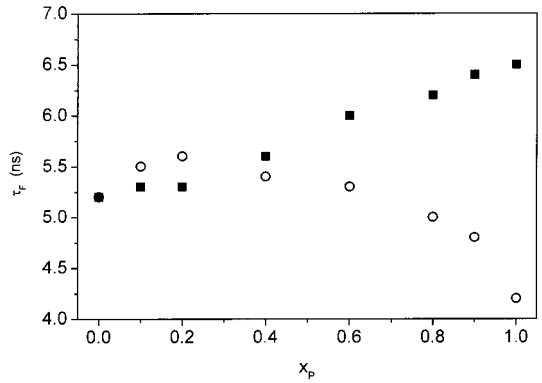

Figure 4. Fluorescence lifetimes (τ_f) of C153 in toluene−methanol (circles) and toluene−acetonitrile (squares) mixtures. x_p is the molar fraction of polar solvent.

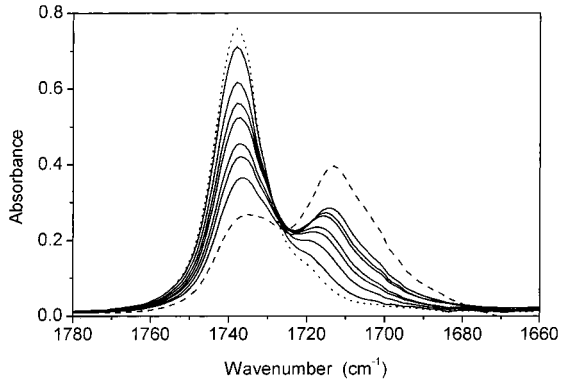

Figure 5. IR spectrum of carbonyl stretching mode of C153 in toluene−methanol mixtures for alcohol mole fractions $x_P = 0$ (dotted line), $x_P = 0.03, 0.06, 0.09, 0.12, 0.18, 0.23, 0.32$ (solid lines), and $x_P = 1$ (dashed line). Due to relatively poor solubility of C153 in neat methanol the last spectrum was recorded at three times lower concentration of the solute and then multiplied by factor 3.

The unusual dependence of the fluorescence lifetime of C153 on solvent polarity in toluene−methanol mixtures can be explained by presence of two different fluorescing species in solutions. Good candidates are C153 and hydrogen-bonded C153. In neat toluene non-hydrogen-bonded C153 has the fluorescence lifetime $\tau_f = 5.2$ ns. In neat methanol C153 is hydrogen bonded (see section on IR spectra) and it has the fluorescence lifetime $\tau_f = 4.2$ ns. The fluorescence lifetime of non-hydrogen-bonded C153 increases with solvent polarity as can be seen from the data for toluene−acetonitrile mixtures (Table 3). However, at higher concentrations ($x_p > 0.3$) mostly the hydrogen-bonded form is present in toluene−methanol mixtures. Apparently the fluorescence lifetime of the hydrogen-bonded C153 decreases with increasing solvent polarity which results in the unusual dependence of τ_f on solvent polarity with a maximum as shown in Figure 4.

At low concentrations of methanol a dependence of the fluorescence lifetime on the detection wavelength can be observed. The measurements for $x_p = 0.03$ give $\tau_f = 5.2$ ns at 22 100 cm^{-1} and $\tau_f = 5.7$ ns at 16 650 cm^{-1}. The fluorescence lifetime measured on the blue side of the fluorescence band corresponds mostly to non-hydrogen-bonded C153. The hydrogen-bonded C153 has a fluorescence spectrum shifted to the red. Therefore the measurement on the red side of the fluorescence band probes mostly the hydrogen-bonded C153. We do not observe any wavelength dependence of the fluorescence lifetimes for $x_p > 0.6$. Formation of hydrogen-bonded-C153 can be observed in IR spectra of C153 in solvent mixtures containing methanol as discussed in the next section.

For C153 in toluene−acetonitrile mixtures we do not observe any wavelength dependence of the fluorescence lifetime.

IR Spectra. Figure 5 shows the IR spectrum of the carbonyl stretching mode of C153 in toluene−methanol mixtures. In neat toluene the absorption band is centered at 1738 cm^{-1} and its intensity decreases with increasing concentration of the polar component in the mixture. Subsequently a new red-shifted band appears which is centered at 1713 cm^{-1} in neat methanol. For mixtures of relatively low polarity ($x_p \leq 0.12$) an isosbestic point can be clearly seen near 1730 cm^{-1} showing the presence of an equilibrium at the ground state between the hydrogen-bonded and the non-hydrogen-bonded form. At higher concentrations hydrogen-bonded complexes C153$(MeOH)_n$ can be formed. For the excited C153 concentration of the hydrogen-bonded form is higher due to stronger electrostatic interactions between C153 and methanol.[15] In an additional set of IR experiments (not shown here) we used a polar component with stronger hydrogen-bond-donating abilities, namely, phenol. For this system we have observed similar behavior of C153, however, for about 10 times lower concentrations of phenol.

These results are in agreement with the fact that in the mixtures two fluorescing species are present which we attribute to non-hydrogen-bonded C153 and hydrogen-bonded C153.

Conclusions

In this work we present results of our studies on preferential solvation of solvatochromic probe coumarin 153 in toluene−acetonitrile and toluene−methanol solvent mixtures. For these mixtures solvent polarity function $F(\epsilon,n)$ is not a linear function of the molar fraction x_p of the polar component. Therefore the absorption and fluorescence solvatochromic shifts of C153 are analyzed as a function of $F(\epsilon,n)$ instead of x_p. For the excited state of C153, preferential solvation is observed in toluene−acetonitrile mixtures and it is reasonably well described by the theoretical model developed by Suppan et al. For the excited C153 in toluene−methanol mixtures strong nonlinearity in the fluorescence solvatochromic shifts has to be attributed mainly to formation of a hydrogen bond between methanol and C153. In this case a simple model of preferential solvation fails completely. IR spectra of C153 in solvent mixtures containing methanol confirm formation of a hydrogen bond between methanol and C153. The presence of hydrogen-bonded C153 in toluene−methanol mixtures causes an unusual dependence of the C153 fluorescence lifetime on the molar fraction of methanol x_p with a maximum near $x_p = 0.2$. The results presented in this paper show that the fluorescence probe of solvation dynamics C153 can form hydrogen-bonded complexes in solvents such as alcohols. The dynamics of the excited-state formation and rearrangement of the hydrogen-bonded complexes can contribute to the time-dependent Stokes shift and therefore to the measured solvation dynamics. Yu and Berg[36] have analyzed the time-dependent fluorescence Stokes shift of resorufin in several polar solvents. For resorufin the change in dipole moment on excitation is very small and the time-dependent Stokes shift observed in hydrogen-bonding solvents was attributed mainly to the dynamics of the solute−solvent hydrogen bonding. In ethanol and ethylene glycol they have found a hydrogen-bond equilibration time of 40 ps for both the ground and excited states. The results presented in this paper show that for C153 both polar solvation and hydrogen-bond dynamics can contribute to the measured solvation dynamics in some hydrogen-bonding solvents or mixtures.

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