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Solvation Statics and Dynamics of Coumarin 153 in Hexane−Propionitrile Solvent Mixtures

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We have studied the solvation statics and dynamics of coumarin 153 dye in binary hexane−propionitrile solvent mixtures. The static and dynamic solvation of coumarin 153 in hexane−propionitrile shows that preferential solvation occurs in both the ground and excited states. We analyzed both the statics and dynamics of preferential solvation of coumarin 153 in hexane−propionitrile using Agmon's model, which is based on extension of the Smoluchowski aggregation model to the reversible case.

Introduction

Solvation statics and dynamics have been extensively studied.[1−6] The spectral shifts of both the static absorption and fluorescence spectra of many probe molecules were compared to the gas-phase spectra in different solvent environments. Ultrashort laser pulses, of picosecond and femtosecond time duration, have been used during the last two decades to study solvation processes on a femto−picosecond time scale. In these studies, the solvation dynamics were monitored via the time dependent spectral shift of the fluorescence band of a probe molecule dissolved in the solvent under study. The solvation dynamics of probe molecules in polar liquids is bimodal. The short component ($<$100 fs) is attributed to inertial rotation of the solvent molecules. The long component is about 10 times longer and arises from the diffusive rotational motion of the solvent molecules. Recently, studies of solvent dynamics were also conducted in mixtures of nonpolar and polar solvents.[7−20]

Suppan[7] studied the effect of solvent mixtures on the absorption and emission of polar solute probes. In several solvent mixtures, of different dielectric polarities, a process of preferential solvation, described as "dielectric enrichment", occurs in the solvation shell of dipolar solute molecules. Dielectric enrichment requires the translational diffusion of solvent molecules, and its extent depends on solvent viscosity and time. When the probe solute does not disturb the "bulk" solvent mixture composition, the solvatochromic shift of fluorescence or absorption bands is linear with respect to the polar solvent mole fraction, x_P. On the other hand, a local enrichment of one solvent component around the solute leads to deviations from this linear dependence. This happens due to various interactions (i.e., electrostatic forces and hydrogen bonding) of the solute with the two different solvent components. In most cases, large dipole moments of both the polar solvent component and the solute cause dielectric enrichment. The result is that the solute interacts with a higher mole fraction of this component than exists in the "bulk" of the solvent mixture. Due to this preferential solvation, the solvatochromic shift is not proportional to the bulk mole fraction, x_P. The deviation from the linear behavior is a measure of the strength of the preferential solvation.

A similar solvation system of a dipolar probe in a solvent mixture is the solvation in an electrolyte solution of polar organic solvents. We have studied the solvation energetics and dynamics of coumarin 153 in various electrolyte solutions of polar organic solvents.[21,22] We used a model of two distinct solvates to explain the experimental data. The first distinct solvate was a coumarin dye molecule surrounded by *n* solvent molecules in the first solvation shell, PS_n (PS_n denotes a probe molecule surrounded by *n* solvent molecules in the first solvation shell). In the second distinct solvate, one of the surrounding solvent molecules in the first solvation shell was replaced by a cation, $PS_{n-1}I$. Upon photoexcitation of the coumarin dye, an ion−solvent exchange reaction occurred, followed by time-resolved fluorescence measurements. The model was successfully applied to coumarin 153 dye in all the solvents used, as well as a wide range of electrolyte concentrations. Maroncelli and co-workers[23] used an extended model, which also included aggregates with several ions in the first solvation shell around the solute. Recently, Agmon[24] applied the theory of a reversible diffusion influenced reaction to the solvation statics and dynamics of a probe molecule in binary mixtures. The theory involves many aggregates of a solute surrounded by various compositions of the mixture. The two extreme cases of aggregates are the ones containing either *n* nonpolar molecules, PS_N^n, or, in the opposite case, *n* polar solvent molecules in the first solvation shell, PS_P^n. The general case is several polar solvent molecules in the first solvation shell, such as $PS_N^{n-i}\,S_P^i$, where $i > 1$. This assumption is similar to Maroncelli's extended ionic solvation model.

Another class of binary solvent solutions is the mixture of two polar solvents with approximately the same polarity. Barbara and co-workers[25] and, recently, Maroncelli and co-workers[26] studied the solvation dynamic characteristics of a probe molecule in two polar liquid mixtures. The neat liquids are both aprotic solvents, the equilibrium solvation properties of which are sufficiently similar that the occurrence of preferential solvation is not expected in their binary mixtures. Gardecki and Maroncelli[26] found that the steady-state solvent nuclear reorganization energy in these mixtures is essentially invariant to the composition in these mixtures. Solvation times in the binary mixtures vary, between the pure solvent limits, with the composition of solvent mixtures. The dependence of the characteristic solvation times on composition is related to other dynamic properties,

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such as solute rotation times and solution viscosity. Furthermore, the dependence of the dynamics on composition can be described by a linear function of the mole fraction of one of the solvent mixture constituents.

In this study, we measure the solvation energetics and dynamics of coumarin 153 in hexane−propionitrile mixtures. The solvation in hexane−propionitrile shows that distinct preferential solvation occurs both in the ground and excited states. We used Agmon's model for preferential solvation to explain both the static and dynamic spectroscopic results.

Experimental Section

Time-resolved fluorescence was detected using a time-correlated single−photon-counting (TCSPC) technique. As a sample excitation source, we used a continuous wave (cw) mode-locked Nd:YAG-pumped dye laser (Coherent Nd:YAG Antares and a cavity dumped 702 dye laser) that provided a high repetition rate of short pulses (2 ps at full width at half-maximum (fwhm)). The TCSPC detection system is based on a multichannel plate Hamamatsu 3809 photomultiplier and a Tennelec 864 TAC and 454 discriminator. A personal computer was used as a multichannel analyzer and for data storage and processing. The overall instrumental response was about 40 ps (fwhm). Measurements were taken at 10 or 20 ns full scale. The samples were excited at 310 nm (the second harmonic of the Rhodamine 6G dye laser). At this wavelength, a sample is excited to S_2, the second excited electronic state. The transition dipole moment S_0-S_2 is perpendicular to S_0-S_1. Therefore, a polarizer set at an angle complementary to the "magic angle" was placed in the fluorescence collection system.

Absorption spectra were acquired with a Perkin-Elmer model 551S UV−vis spectrometer. Steady-state fluorescence spectra of the samples were recorded on an SLM-Aminco-Bowman 2 luminescence spectrometer and corrected according to manufacturer specifications.

Coumarin 153 (C153) was purchased from Exciton and used without further purification. Hexane and propionitrile were purchased from Aldrich and used without further purification. All experiments were performed at room temperature (23 ± 2 °C).

Data Analysis of Static Absorption and Emission Spectra

The emission band of hexane−propionitrile mixtures is broad and structureless and can be described by a log-normal distribution function.

$$I(\nu) = h\begin{cases} \exp[-\ln(2)[\ln(1+\alpha)/\gamma]^2] & \alpha > -1 \\ 0 & \alpha \leq -1 \end{cases} \qquad (1)$$

with

$$\alpha \equiv 2\gamma(\nu - \nu_p)/\Delta$$

where $I(\nu)$ is the fluorescence intensity at frequency (ν), h is the peak height, ν_p is the peak frequency, γ is the asymmetry parameter, and Δ represents the band's width. The relevant parameters for the analysis of these mixtures are given in Table 1.

TABLE 1: Characteristic Parameters for a Single Lognormal Fit of the Emission Band of C153 in Hexane/Propionitrile Mixtures[a]

x_{PN}	γ	$10^3\nu_p$ [b] (cm^{-1})	Δ [b] (cm^{-1})
0	−0.32	22.20	2800
0.0062	−0.27	21.80	3150
0.012	−0.23	21.45	3150
0.025	−0.23	21.20	3200
0.05	−0.22	20.80	3100
0.1	−0.23	20.40	3025
0.15	−0.24	20.20	3000
0.2	−0.24	20.10	2950
0.3	−0.26	20.00	2925
0.4	−0.27	19.90	2850
0.6	−0.28	19.75	2825
0.8	−0.30	19.65	2800
1	−0.30	19.45	2750

[a] γ is the asymmetry of the peak, ν_p is the location of the peak maximum, and Δ is the peak width (see text). [b] We estimate the error in the determination of ν_p to be ±50 cm^{-1}, and for Δ, ±25 cm^{-1}.

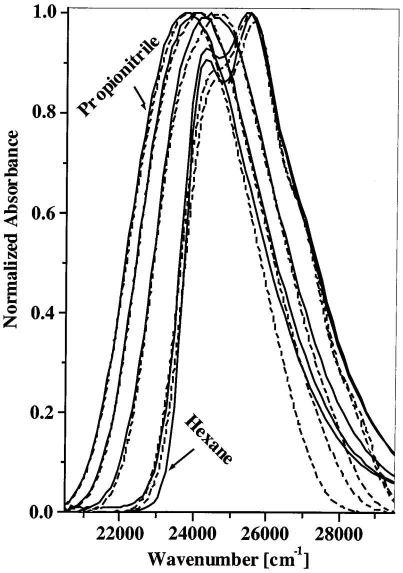

Figure 1. Normalized absorption spectra of coumarin 153 in hexane−propionitrile mixtures with propionitrile (mole fraction right to left: x_P = 0, 0.013, 0.2, 0.6, 1). Solid lines are the experimental data and dashed lines are the calculated fit.

The shape of the absorption hexane−propionitrile mixtures could not be fitted with a log-normal distribution because the vibronic structure in the absorption spectrum is preserved to about a 0.2 mole fraction of propionitrile. To fit the absorption, $A(\nu)$, of C153 at all mixtures, from 0 to 1 mole fractions, we used[27]

$$A(\nu) = \sum_{k=0}^{\infty}\frac{S_0^k}{k!}\exp\left\{-cc\left[\left(\frac{\nu-\nu_p}{\nu_{st}}\right) - k\frac{\nu_0}{\nu_{st}}\right]^2\right\} \qquad (2)$$

where $cc = h\nu_{st}/2k_BT$ is the curvature of the ground- and excited-state parabola in the solvent coordinate, S_0 is the vibronic displacement of the excited-state parabola, ν_{st} is the Stokes shift, and ν_0 is the vibronic frequency modulating the spectral shape. The peak position of the absorption band is defined as $\nu_p = \nu_{12} - \nu_{st}$. ν_{12} is the electronic origin of the transition in the gas phase. The band position shifts as a function of mixture composition because ν_{st} increases with x_p.

Results

Steady-State Absorption and Fluorescence Spectra. Figure 1 shows the absorption spectra of C153 in hexane−propionitrile mixtures along with the fit to the spectra using eq 2. As the polar component increases, the vibronic structure is less

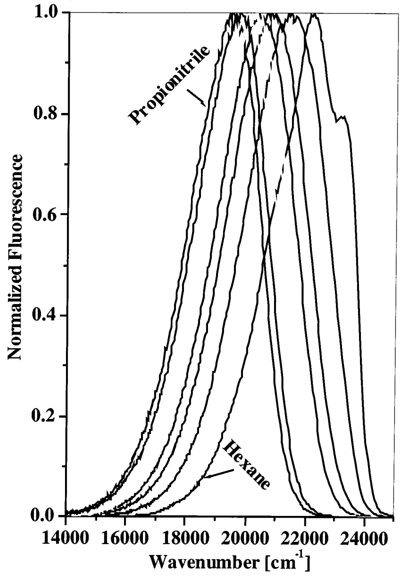

Figure 2. Fluorescence spectra of coumarin 153 in hexane−propionitrile mixtures with propionitrile (mole fraction right to left: $x_{\mathrm{P}} = 0$, 0.012, 0.05, 0.1, 0.8) and in neat propionitrile. Excitation wavelengths are at the absorption maximum.

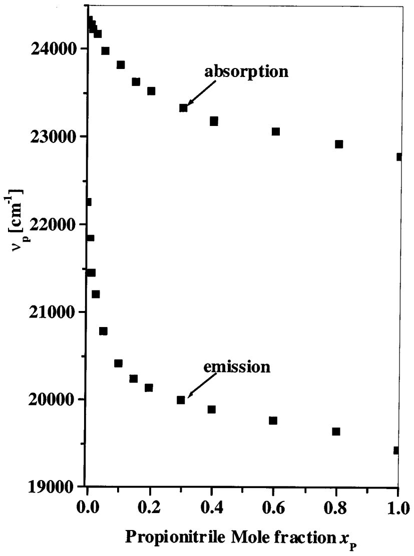

Figure 3. Peak of the absorption and emission spectra as a function of propionitrile mole fraction.

pronounced. The vibronic structure disappears when $\nu_{\mathrm{st}} \sim 2\nu_0$. In our case, we took five vibrations, $k = 4$, and $S_0 = 1.15$. For neat hexane $\nu_{\mathrm{st}} = 1700$ cm^{-1} and $\nu_0 = 1350$ cm^{-1}. For the absorption spectrum of C153 in neat propionitrile $\nu_{\mathrm{st}} = 3000$ cm^{-1}. From the fit of the absorption spectrum of C153 in neat hexane, we find $\nu_{12} = 26\,000$ cm^{-1}. Hexane polarity[28] is considered in several polarity scales to be zero; its dielectric constant is 1.9[29] and the dipole moment is zero.[29] Propionitrile is a polar liquid with a dielectric constant, $\epsilon = 28$,[29] and a dipole moment of 3.6 D;[29] the polarity on the π^* [28] scale is 0.55 and on the $E_{\mathrm{T}}^{\mathrm{N}}$ [29] scale 0.401. Both neat hexane and neat propionitrile have low viscosities of 0.31 and 0.45 cP,[29] respectively at 25 °C, and their mixtures also exhibit low viscosity.

Figure 2 shows the emission spectra of C153 in hexane−propionitrile mixtures. The spectral shifts of both the absorption and emission of hexane−propionitrile mixtures as a function of the propionitrile mole fraction is shown in Figure 3. Both the absorption and emission shifts deviate strongly from linear behavior. Using Suppan's model[7] and assuming that the solvent mixture behaves as an ideal mixture, we find *Z* values for the absorption and emission shifts of 1.8 and 3.0, respectively. From Suppan's model, large *Z* values indicate local enrichment of the polar solvent around the solute, which leads to a spectral shift deviation from a linear dependence of the shift with x_{P}. A more detailed analysis, which takes into account the dielectric "nonideality" of the binary solvent mixture, is given in the discussion section.

Time-Resolved Emission. Time-correlated single photon counting has a limited instrument response function (IRF) of ~40 ps, which limits the time resolution to about 20 ps. The time-resolved emission of coumarin 153 in either neat hexane or propionitrile, measured by time-correlated single photon counting cannot provide the solvation response in the neat solvents because of its poor time resolution. The time-resolved emission of coumarin 153 in binary mixtures shows a slow solvation component of about ~100−1000 ps depending on the propionitrile concentration. To estimate the contribution to the solvation energy of the ultrafast components of solvation, we used Maroncelli's procedure[30] to find the band position at "$t = 0$" immediately after the laser pulse excitation. The emission spectrum at about $t = 10$ ps is determined from the constructed time-resolved spectra. The difference in the band position at $t = 0$ and its position at $t = 10$ ps is attributed to the fast solvation components. We find that for $x_{\mathrm{P}} = 0.4$ the fast components contribute about 1000 cm^{-1} to the spectral shift. The short components arise from the rotational motion of both propionitrile and hexane molecules.

Time-resolved spectra were constructed and analyzed by a procedure given by Maroncelli and co-workers.[1] The time-resolved emission data, collected at 10 nm intervals, were analyzed using a convoluted procedure with the system IRF and a sum of exponentials. We constructed time dependent spectra, which were fit to a log-normal function. From the spectral shift of the fluorescence band maximum of coumarin 153, we constructed the solvation correlation function

$$C(t) = \frac{\bar{\nu}_0 - \bar{\nu}(t)}{\bar{\nu}_0 - \bar{\nu}_\infty} \tag{3}$$

where $\bar{\nu}(t)$, $\bar{\nu}_0$, and $\bar{\nu}_\infty$ are the band maximum position at time *t*, time zero, and long times, respectively. We fit *C*(*t*) to a sum of exponentials. Figure 4 shows plots of the solvation correlation function *C*(*t*) of coumarin 153 in hexane−propionitrile mixtures as a function of time for several mixtures. The function *C*(*t*) is nonexponential and could be reasonably fitted by two exponentials. Its average relaxation time is a function of the polar solvent concentration. A dependence of *C*(*t*) on the polar mole fraction, x_{P}, is expected for the dynamics of a dielectric enrichment process. The larger the polar solvent mole fraction, the faster the *C*(*t*) relaxation, provided that the change of the diffusion constant of the polar liquid in the mixtures is small compared to the concentration dependence of *C*(*t*). Table 2 shows the relaxation parameters of *C*(*t*) in the studied mixtures.

Discussion and Model Calculations

In general, binary mixtures composed of nonpolar and polar liquids show effects of preferential solvation of a probe molecule by the polar component in the mixture. Suppan measured several mixtures and found that some mixtures behave "ideally" (the cyclohexane−tetrahydrofuran system) whereas others show slight (diisopropyl ether−dimethylformamide) or relatively large (*n*-hexane−propionitrile) deviations from linearity. The dynam-

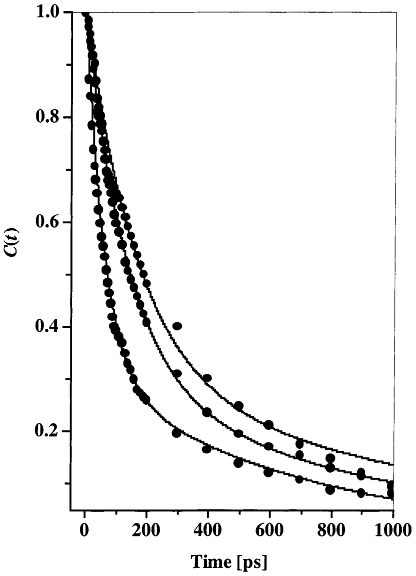

Figure 4. Normalized solvation response function, $C(t)$, of coumarin 153 in hexane−propionitrile mixtures at different propionitrile mole fractions. Top to bottom: x_P = 0.025, 0.05, and 0.1. Circles are experimental data, and solid lines are biexponential fits to the experimental data.

TABLE 2: Relevant Parameters for Time-Resolved Measurements of Hexane/Propionitrile Mixtures

	$C(t)$ Fitting parameters[a,d]					
x_{PN}	a_1	τ_1 (ps)	a_2	τ_2 (ps)	$\langle\tau\rangle^b$ (ps)	$\Delta\nu^c$ (cm^{-1})
0.025	0.69	170	0.31	1200	490	1000
0.05	0.69	140	0.31	900	370	1100
0.1	0.69	60	0.31	680	250	1450

[a] Biexponential fit to the experimental data. [b] Average solvation time ($\langle\tau\rangle$). [c] Spectral shift ($\Delta\nu$). [d] The estimated error in the solvation time τ_1, τ_2, and $\langle\tau\rangle$ is ±10%.

ics of preferential solvation of coumarin 153 in hexane−alcohol mixtures was studied by Rempel and co-workers.[12] They analyzed the normalized spectral shift of both the absorption and emission band according to the theory of Suppan.[7] The solute−solvent interaction energy is a linear function of the solvent polarity. The polarity of a solvent is defined as a function F of the dielectric constant ϵ. Onsager's function is given by

$$F = \frac{2(\epsilon - 1)}{2\epsilon + 1} \tag{4}$$

The polarity of an "ideal" mixture of two solvents composed of nonpolar, N, and polar, P, solvents whose dielectric constants are ϵ_N and ϵ_P, respectively, is a simple linear combination according to their mole fraction x_N and x_P

$$F_{\text{linear,bulk}} = x_N F_N + x_P F_P \tag{5}$$

When the polarity of the two cosolvents is very different, their distribution next to a dipolar solute is then not the same as the undisturbed bulk. If x_N and x_P are the mole fractions of the bulk, then next to the solute, the mole fractions become y_N and y_P. The mole ratios $X = x_N/x_P$ and $Y = y_N/y_P$ are then related by $Y = Xe^Z$. A single shell approximation to Z is given by Suppan[7]

$$Z = \frac{1}{4\pi\epsilon_0} \frac{CM\mu^2 \Delta F_{N,P}}{2\delta R T r^6} \tag{6}$$

$$\Delta F_{N,P} = F_P - F_N \tag{7}$$

where $\Delta F_{N,P}$ is the difference of the Onsager's functions of pure polar and pure nonpolar solvents, the solvent dipoles, set at a fixed distance, from the solute dipole center, C, in a numerical factor in the order of unity, μ is the solute dipole moment, M is the mean molar weight of the polar and nonpolar solvents, R is the gas constant, T is the temperature, and δ is the mean density of the two solvent components.

Dielectric "nonideality" of a binary solvent system refers to the deviation of the Onsager reaction field function from linearity in the polar mole fraction of the solvent mixture. A dipolar fluorophore, dissolved in an ideal dielectric mixture, exhibits a solvatochromic shift that is linear in the solvent polar mole fraction in its solvation sphere. As a result, the "local composition" easily can be determined from the peak shift. Kauffman and co-workers[8,9] have identified conditions under which the linear approximation is justified and find that for most cases of practical importance the linear approximation will not provide accurate estimates of the local solvent composition from solvatochromic studies. Similarly, solvatochromic shifts can only be accurately predicted from theoretical local compositions if dielectric nonideality is taken into account. The Z value, due to preferential solvation, Z_{PS}, is related to experimental spectral shift data by employing the so-called "nonlinearity ratio" ρ_{exp}.[7−9] This quantity can be calculated from measured quantities using the expression

$$\rho_{\text{exp}} = \frac{2\int_0^1 (E_{\text{exp}} - E_{\text{linear,bulk}})\, dx_P}{\Delta E_{N,P}} \tag{8}$$

where E_{exp} is the experimental peak energy of the fluorophore at bulk polar mole fraction x_P and $E_{\text{linear,bulk}} = x_P E_P + x_N E_N$ is the calculated peak energy of the fluorophore, assuming it is dissolved in an ideal binary mixture at bulk polar mole fraction x_P. $\Delta E_{N,P}$ is the difference in peak energies in the neat polar and nonpolar solvents. Two factors contribute to the difference between E_{exp} and $E_{\text{linear,bulk}}$, preferential solvation and dielectric nonideality. The experimental nonlinearity ratio, ρ_{exp}, can be expressed as the following sum:

$$\rho_{\text{exp}} = \rho_{\text{ps}} + \rho_{\text{ni}} \tag{9}$$

in which ρ_{ps} and ρ_{ni} are the contributions of preferential solvation and dielectric nonideality to the experimental nonlinearity ratio, respectively. The dielectric nonideality contribution, ρ_{ni}, can be calculated from experimental dielectric constant measurements using the expression

$$\rho_{\text{ni}} = \frac{2\int_0^1 (F_{\text{exp}} - F_{\text{linear,bulk}})\, dx_P}{\Delta F_{N,P}} \tag{10}$$

where $\Delta F_{N,P}$ is given by eq 7, F_{exp} is the real dielectric function that we took from the data in ref 7, and $F_{\text{linear,bulk}}$ is calculated for an ideal dielectric mixture from eq 5. Equations 8−10 provide a means of calculating ρ_{ps} from experimental data. Kauffman and co-workers[8,9] have shown that when ρ_{ps} is less than 1, the relationship between ρ_{ps} and Z_{ps} is well approximated by the expression

$$\rho_{\text{ps}} = 0.31 Z_{\text{ps}} \tag{11}$$

Equations 8−11 can be used to calculate Z_{ps} from experimental spectroscopic and dielectric data. Using this procedure for both the absorption and emission data of the solution, we obtain ρ_{ps} = 0.12 and 0.52, respectively. The preferential solvation Z_{ps}

values of C153 in hexane−propionitrile in the ground and excited states (calculated from eq 11) are $Z_{ps} = 0.4$ and $Z_{ps} = 1.7$, respectively. These values are smaller, by about 0.5, than Z values calculated for an "ideal" mixture. Recently, Jarzeba and co-workers[20] studied the preferential solvation of C153 in toluene−acetonitrile and they found a Z value of ∼0.5 for the excited state.

Reversible Aggregation Model

The main aim of this study is to analyze the spectral static and dynamic data using a molecular approach, based on successive reversible aggregation, developed by Agmon[24] of the polar solvent with the probe molecule. Polar probe molecules in hexane−propionitrile mixtures were found to show distinctive dielectric enrichment properties. Supan[7] used a continuum model to describe preferential solvation. Petrov et al.[11] extended the Onsager model to an electrostatic shell model for which the shift in the electrostatic "reaction-field" for m polar molecules, ΔR_m, is $\Delta R_m/\Delta R_0 \approx 1/(1 + m)$ and ΔR_0 is the reaction field of a neat polar liquid. (This neglects specific solvation effects such as hydrogen-bonding.) Thus, the first polar molecule in the first solvation shell contributes to solvation more than the subsequent polar molecules. Preferential solvation may be thought of as a successive reversible aggregation process of polar solvent molecules, B, around the probe molecule denoted by A. If the aggregation process is limited to the binding of only one B molecule in a single step, then it can be described by

SCHEME 1

$$\mathrm{A} + \mathrm{B} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{AB}$$

$$\mathrm{AB} + \mathrm{B} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{AB_2}$$

$$\mathrm{AB_2} + \mathrm{B} \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{AB_3}$$

where k_a and k_d are the association and dissociation rate coefficients at the "contact" radius, $r = a$. Recently, Agmon[24] used the theory of reversible diffusion influenced reactions and extended the Smoluchowski coagulation theory for irreversible reactions to successive reversible reactions. Both the steady-state and time-resolved emission of preferential solvation of an excited solute could be formulated using Scheme 1. In the model, D is the relative A−B diffusion coefficient and only one B molecule may bind to A in a single step. In the limit that A is spherical and static, the B's do not interact with each other, the rate constants for the different binding steps are identical (in particular, there is no limit to the number of B particles that may bind to A), and the diffusion equations decouple and admit an analytic solution.[24] The model provides both the steady-state and transient aspects of preferential solvation. The assumptions leading to B particle independence restrict the model to a small polar solvent concentration, c, but the restriction is not severe because it is known (e.g., from gas-phase cluster studies)[31,32] that only the few first-shell solvent molecules induce a sizable spectral shift. The model leads to an expression for the time-resolved spectral shift.

$$\left\langle \frac{\Delta R(t)}{\Delta R_0} \right\rangle = \frac{1 - \exp[-cK_{eq}S(t|*)]}{cK_{eq}S(t|*)} \tag{12}$$

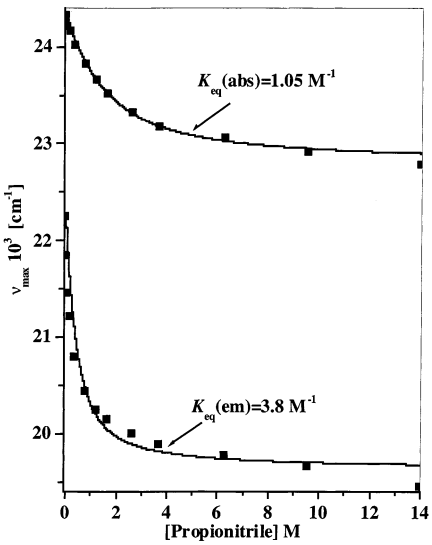

Figure 5. Dependence of the peak of the fluorescence spectrum of coumarin 153 in hexane−propionitrile mixtures on the propionitrile concentration. Squares are experimental data, and the solid line is a fit to eqs 14a and 14b.

Here $S(t|*)$ is the "separation" probability for an initially bound A−B pair, with a reversible boundary-condition at contact;[24] $K_{eq} \equiv k_a/k_d$ is the equilibrium (association) constant. To convert these results to frequency shifts, it is assumed that the average (or peak) emission frequency, ν_{max}, is known for the neat polar and nonpolar solvents (ν_p and ν_N, respectively). With the assumption that the time dependent shift is proportional to $\langle \Delta R(t) \rangle$, one has

$$\nu_{max}(t) = \nu_p + (\nu_N - \nu_p)\langle \Delta R(t)/\Delta R_0 \rangle \tag{13}$$

$S(t|*)$ can be calculated using the SSDP program of Krissinel and Agmon.[33] Equation 13 provides a simple model for solvatochromic shifts induced by preferential solvation. At long times, an isolated A−B pair separates with certainty, $S(\infty|*) = 1$. The average steady-state shift, $\langle \Delta R(\infty)/\Delta R_0 \rangle$, is obtained by setting $S(\infty|*) = 1$. Although, $cS(t|*)$ appears in the denominator, it is easy to see that $\langle \Delta R(\infty)/\Delta R_0 \rangle \to 1$ when $cS(t|*) \to 0$, as should be. This applies to both the $t = 0$ and $c \to 0$ limits. The steady-state shift is given by

$$\left\langle \frac{\Delta R(\infty)}{\Delta R_0} \right\rangle = \frac{1 - \exp[-cK_{eq}]}{cK_{eq}} \tag{14a}$$

$$\nu_{max}^{SS} = \nu_p + (\nu_N - \nu_p)\left[\frac{1 - \exp[-cK_{eq}]}{cK_{eq}}\right] \tag{14b}$$

We used eq 14b to fit the position of the absorption and emission spectra, ($\nu_N = 22.2 \times 10^3$ cm^{-1}, $\nu_P = 19.4 \times 10^3$ cm^{-1}). From the fit, we obtained the ground- and excited-state equilibrium constants for coumarin 153 in hexane−propionitrile mixtures. Figure 5 shows the fit to the position of the absorption and emission spectra. We find that the ground- and excited-state equilibrium constants are 1.05 and 3.8, respectively. Using the derived excited-state equilibrium constant from steady-state fluorescence and eq 13, we were able to fit the nonexponential solvation dynamics derived from the time-resolved emission studies. Figure 6 shows the fit to the time-resolved solvation of several hexane−propionitrile mixtures. As seen, the fit is good. We chose the value of the contact radius as $a = 5$ Å. Because ν_N, ν_P, and K_{eq} are derived by independent measurements, the

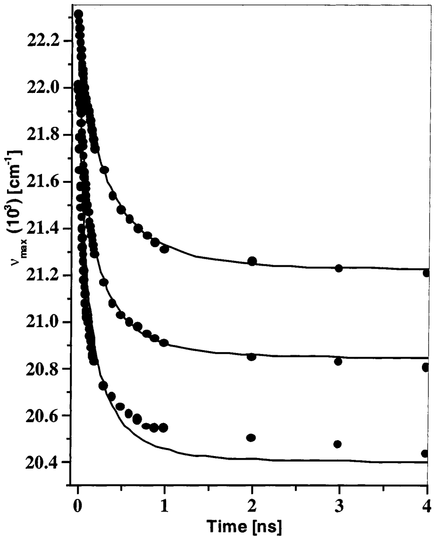

Figure 6. Time-resolved Stokes shift for the coumarin 153 in hexane−propionitrile mixtures. Circles are experimental data. Top to bottom: $c = 0.2$, 0.4, 0.8 M. Solid lines are fits to eqs 12 and 13.

time-resolved fit has only two free parameters, the diffusion constant, $D = 3 \times 10^5$ cm^2/s, which was found to be constant for all the mixtures studied and one of the rate parameters. We find k_a and k_d to be 5.7×10^{10} M^{-1} s^{-1} and 1.5×10^{10} s^{-1} respectively, with their ratio $K_{eq} = 3.8$.

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