Relaxation Dynamics of Inhomogeneous Spectral Width in Binary Solvents Studied by Transient Hole-Burning Spectroscopy

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We have performed transient hole-burning spectroscopy of cresyl violet in binary solvents of different polarity components in order to detect the relaxation of inhomogeneous spectral bandwidths (relaxation of dispersion around average energy) in addition to that of spectral peak shift (relaxation of average energy). We proposed in our previous paper (*J. Phys. Chem. A* **1997**, *101*, 5729) that the relaxation process of spectral width and that of average energy of the system should be characterized by different relaxation modes of solvent molecules. In the binary solvents a slow relaxation process was observed especially for the spectral width, which was assigned to the translational diffusion of polar component of solvent molecules. On the other hand, the relaxation of average energy was not effectively affected by the solvent mixing, which could be attributed mainly to fast relaxation processes, the libration and/or rotational diffusion of solvent molecules in the closest solvation shell. Even if the distribution of the solvent shell would be disturbed by the slower translational diffusion mode of polar solvent molecules, the average energy could be immediately compensated by the fast relaxation of solvent surroundings. The developments of the molecular theory on the translational dynamics should be necessary for essential understanding of the results obtained here.

Introduction

Solvation dynamics in polar solute−solvent systems has attracted extensive interests owing to its close relation to chemical reaction in solution phase, which should be the reason many experimental[1−9] as well as theoretical[10−18] studies have been devoted to it in the past decade. Recent investigations[3,4,8,16] have particularly focused on the elucidation of the fastest part of the solvent response, which covers the relaxation of average energy of the solute−solvent system. From a viewpoint of chemical reaction, however, it must be of crucial importance to detect not only the relaxation of average energy but the relaxation of dispersion around average energy. For a type of reaction that can be considered in the transition-state theory in solution, the vast majority of molecules in the system stay in the reactant potential well and a small fraction of molecules are subjected to the reaction driven by a solvent fluctuation.[19] Although in this model a (quasi-)equilibrium process is presupposed, in an actual system a relaxation process of energy dispersion must occur in the reactant well and should cause essential influence over the reaction process. Under such motivation, we have performed comparative studies on the relaxation of inhomogeneous spectral broadening corresponding to energy dispersion and that of average energy, by means of transient hole-burning (THB) and time-resolved fluorescence (TRF) spectroscopy of polar dyes in polar solvents.[9,20]

Within a realm of dielectric continuum model under an approximation of linear response for the system,[21,22] energy of the Stokes shift ΔE_{SS} is proportional to the square of the difference between the solute dipole moment in the ground state and that of the excited state. On one hand, energy ΔE_w that corresponds to the spectral width of the steady-state absorption and fluorescence spectra can be characterized by $\Delta E_w = (2k_BT\Delta E_{SS} \ln 2)^{1/2}$, where k_B and T are the Boltzmann constant and temperature, respectively. On the basis of spectral time evolution obtained from experiments, the dynamic response function $\rho_e(t)$ of the relaxation process of average energy can be given as

$$\rho_e(t) = \frac{\tilde{\nu}(t) - \tilde{\nu}(\infty)}{\tilde{\nu}(0) - \tilde{\nu}(\infty)} \qquad (1)$$

where $\tilde{\nu}(t)$ is the spectral maximum of the ground-state hole or fluorescence at time t. On the other hand, the dynamic response function of the relaxation of spectral band broadening $\rho_w(t)$ can be derived by using the time-dependent spectral width $\tilde{\sigma}(t)$ of hole or fluorescence spectra corresponding to eq 1:[12]

$$\rho_w(t) = \sqrt{\frac{\sigma|(t)^2 - \sigma|(\infty)^2}{\sigma|(0)^2 - \sigma|(\infty)^2}} \qquad (2)$$

Under conventional treatments, both $\rho_e(t)$ and $\rho_w(t)$ are considered to be characterized by a normalized time correlation function of the solvent fluctuation, which is assumed to be the same in the ground and excited states of the solute molecule. In such a case, $\rho_e(t)$ and $\rho_w(t)$ should correspond to each other. However, recent studies have reported that more than 50% of the relaxation of average energy could be achieved by a fast librational or inertial process of the solvent in the nearest solvation shell.[3,4,6] On the other hand, our previous results[5,9,20] derived from both THB and TRF measurements have revealed

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TABLE 1. Solvent Properties of THF, ACN, and Mixtures TA1−TA3 Employed for THB Spectroscopy and Steady-State Absorption Spectral Width $\tilde{\sigma}_h$ of CV

solvent	mole ratio (THF to ACN)	μ/D	ϵ_0[a]	$\tilde{\sigma}_h/10^3$ cm^{-1} [b]
THF	100:0	1.8	7.6	1.48
TA1	97:3		8.2	1.43
TA2	85:15		11	1.30
TA3	72:28		14	1.30
ACN	0:100	3.5	37.5	1.41

[a] Assumed to be proportional to the mole-fraction volume. [b] Derived from the half-width at half-maximum at the higher energy region of the steady-state absorption spectra. The spectral resolution due to the spectrometer was about 60 cm^{-1}.

that in polar fluid solvents at room temperature $\rho_w(t)$ relaxes much more slowly compared to $\rho_e(t)$, but their relaxation times become comparable in viscous alcoholic solvents at lower temperature. We thus presented a mechanism such that the translational diffusion mode of the solvent may characterize the relaxation of the spectral width while the rapid rotational diffusion should be largely responsible for the relaxation of average energy, whereas at lower temperature owing to relative preponderance of the translational diffusion, both relaxation times agree with each other.

In this paper, we present further insight of the relaxation of inhomogeneous spectral broadening by means of THB spectroscopy of a laser dye molecule, cresyl violet (CV), in binary solvents of different-polarity components at room temperature. Possible mechanisms for the relaxation of the inhomogeneous spectral broadening and that for the spectral peak shift will be discussed. The present results can be explained by the framework that is consistent with the previously proposed mechanism.[9]

Experimental Section

Details on our experimental setup for THB spectroscopy have been described previously.[9,20] Briefly, a smaller fraction (≈10%) of an output of an amplified dye laser (ca. 0.3 mJ/pulse, 50 Hz) was employed as an excitation source. The remainder of the laser pulse was focused into D_2O to generate a white continuum that was used as a probe light. A part of the probe light was detected as a reference. The difference optical density (ΔOD) spectra were acquired by two pairs of a combination of a multichannel photodiode array detector attached to a spectrograph. Temporal and spectral resolutions of the equipment were about 150 fs and 3 nm, respectively.

Selection of the solute and solvent molecules in this study was performed as follows: CV was used as a solute molecule, which slightly increases its dipole moment μ according to the laser excitation. For solvents, tetrahydrofuran (THF: relative permittivity $\epsilon = 7.6$, $\mu = 1.8$ D), acetonitrile (ACN: $\epsilon = 37.5$, $\mu = 3.5$ D), and their binary mixtures being rich in less polar component, TA1 (contains 97% of THF in mole fraction), TA2 (85%), and TA3 (72%), were employed. Solvent properties of the binary system are given in Table 1. The excitation wavelength was 606−609 nm corresponding approximately to the 0−0 absorption band of the solute molecule.[23] Sample solutions were contained in a quartz cuvette with 2 mm optical path length. The solute concentration of the sample solution was about 10^{-6} M. All measurements were performed at room temperature (295 K).

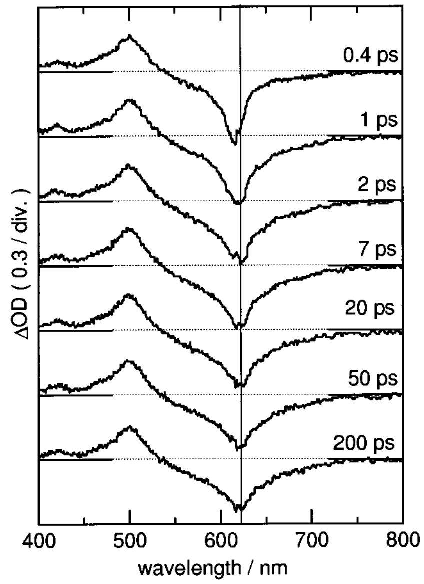

Figure 1. ΔOD spectra of **CV** in the binary solvent TA2 where THF and ACN were mixed by 85:15 in the molar fraction. Delay times after the excitation are indicated within the figure.

With respect to the selection of the solute, **CV**, as a probe molecule for THB spectra, we have made a careful discussion in our previous report;[9] the Stokes shift between the steady-state absorption and fluorescence spectra of **CV** even in polar solvents such as ACN was rather small (ca. 700 cm^{-1}), and the observed $S_n \leftarrow S_1$ absorption spectrum of **CV** rose by the response time of the detecting system and decayed by the fluorescence lifetime of the solute molecule. We thus conclude that given the experimental conditions substantial time evolution of the THB spectra of **CV** in the solvents should be solely ascribed to the solvation processes, not to intramolecular relaxation processes of the solute or to the electronic structure change of the excited solute molecule.

Results

Steady-state absorption and fluorescence spectra of **CV** in pure solvents THF and ACN and in their mixtures show relatively good mirror images. Table 1 also summarizes the half-width at half-maximum (hwhm) of the steady-state absorption spectrum of **CV**, $\tilde{\sigma}_h$, in pure and binary solvents. Here $\tilde{\sigma}_h$ was derived from the higher energy region of the steady-state absorption spectra for the sake of the analysis of the transient hole width, as will be stated later. In the binary solvents TA2 and TA3 relatively narrower values of $\tilde{\sigma}_h$ were observed compared to those in pure solvents. This results implies that the inhomogeneity around the ground-state solute molecule in the binary solvents TA2 and TA3 would be a different type compared to that in pure solvents.

Figure 1 depicts time-dependent ΔOD spectra of **CV** in the binary solvent TA2 detected at room temperature. The spectral correction due to group velocity dispersion of the white continuum probe pulse was already completed, using the procedure given elsewhere.[20] The nominal spectra before 0.3 ps of the delay time was omitted here because of coherent interaction between the pump and probe lights. The absorption band with the maximum at 500 nm is largely ascribed to the $S_n \leftarrow S_1$ absorption spectrum of **CV**. The analysis for evaluation of the dynamic broadening of the ground-state hole width is the same as our previous method for pure solvents:[20] the suitably weighted $S_n \leftarrow S_1$ absorption spectrum of **CV** was subtracted from the ΔOD spectra observed at each delay time. In our experimental apparatus, there existed some difficulty in observing accurate TRF spectra at the same time resolution as ΔOD spectra detected in this work. Then the hwhm of the hole

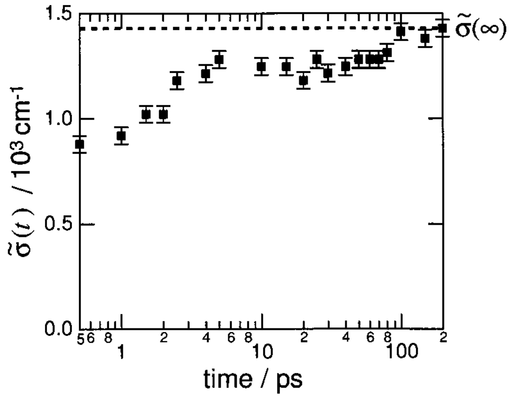

Figure 2. Time dependence of the hwhm of the hole spectrum of **CV** in the binary solvent TA1 where THF and ACN were mixed by 97:3 in molar fraction. The dotted line corresponds to the value of $\tilde{\sigma}(\infty)$. The error bar was estimated according to the spectral resolution of the spectrometer used.

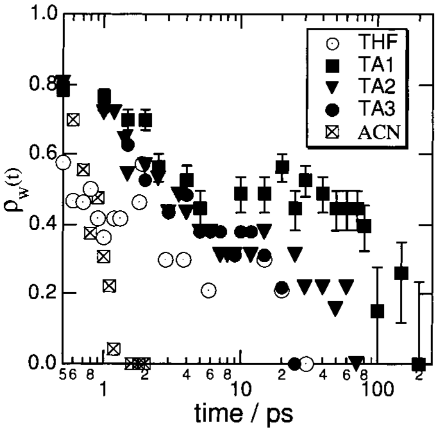

Figure 3. Normalized dynamic response functions $\rho_w(t)$ derived from time evolution of the hole width of **CV** in THF (open circles), ACN (open squares), and their mixtures TA1 (filled squares), TA2 (filled triangles), and TA3 (filled circles). See Table 1 for properties of solvent mixtures. The error bar estimated for the data in TA1 was estimated according to the spectral resolution of the spectrometer used.

spectra at the higher energy region was employed, as stated in our previous paper.[9] Figure 2 displays the time dependence of the hwhm of the hole spectra in the mixture TA1 as typical. The error bar indicated in the figure was estimated according to the spectral resolution of the detecting spectrometer. $\rho_w(t)$ was then calculated according to eq 2, where $\tilde{\sigma}(\infty)$ was the same as $\tilde{\sigma}_h$, and $\tilde{\sigma}(0) = 30$ cm^{-1} was the spectral width of the exciting laser pulse. Figure 3 compares $\rho_w(t)$ detected in the binary solvents observed in this work and those in pure components taken from our former publication.[9] For the plot of TA1, relatively larger error bars were estimated when ρ_w(t) approaches zero according to the definition of ρ_w(t) as given in eq 2. Errors for TA2 and TA3 were also estimated as in the case of TA1.

In Figure 1, at 0.4 ps after the laser excitation an obvious depression appears around the excitation wavelength (606−609 nm), where the contribution from the $S_n \leftarrow S_1$ absorption is very small. This depression is attributed to the sum of the ground-state hole (at the blue side) and induced emission (the red side) spectra. As the delay time is increased the depression shifts its peak toward the red and broadens its spectral shape. The peak shift of the depression, which is equivalent to the relaxation of the average energy, ceases within 2 ps after the excitation. It is emphasized that in all the binary solvents investigated here the depression shift was completed within 2 ps, while the total amount of the depression shift was almost the same among the mixture. In pure THF, the average energy relaxation was achieved within 0.7 ps after the excitation, and in ACN the depression shift was too fast to be detected by the time resolution of the equipment used there (150 fs).[9]

On the other hand, the time evolution of the hole spectral width was dramatically slowed in the binary solvents. The observed $\rho_w(t)$'s in the binary solvents relax slower than those obtained in their pure component of the solvent. About 50% of the relaxation of $\rho_w(t)$ in the mixtures was achieved in the first 3−4 ps (Figure 3). This fast relaxation process seems to be rather independent of the fraction of the component. However, the remaining processes that are responsible for the relaxation of $\rho_w(t) \rightarrow 0$ are dramatically affected by the ingredients of the solvent mixture. The solvent with smaller fraction of ACN showed the slower relaxation process. In particular, for the binary solvent TA1, it took up to 200 ps to complete the recovery of the hole width. In Figure 2, we are aware that the behavior of $\tilde{\sigma}(t)$ between 5 and 80 ps seems to be unclear. The time dependence of $\tilde{\sigma}(t)$ at that time domain would be essentially a plateau, or another interpretation such that $\tilde{\sigma}(t)$ once slightly narrows (5−20 ps) and then broadens (20−80 ps) might also be possible. We do not have further discussion with regard to the origin of this dynamic behavior because it is too subtle to be distinguished by our present measurement. Additional experiments to clarify this point would indeed be desirable.

As a result, the relaxation of average energy was not largely influenced if the binary solvents were used; on the other hand, the slower relaxation processes of the spectral width were observed in the binary solvents compared to that in the pure solvents used as their ingredients.

Discussion

In the binary solvents studied here the relaxation of average energy was completed within a few picoseconds, which was much faster compared to that of the spectral width, a situation that is quite similar to that generally detected in pure solvents in our previous study.[9] It is plausible that the relaxation of average energy would also be achieved by the fast rotational relaxation process and libration of solvent molecules located at just around the solute molecule. However, the time domain of the slowest component of $\rho_w(t)$ observed especially in THF-rich binary solvents could not be explained simply by some librational modes nor dielectric response of the bulk solvent. Actually, when the slowest decay component of $\rho_w(t)$ that gives rise to the process of $\rho_w(t) \approx 0.5 \rightarrow 0$ observed in the binary solvent system TA1 is assumed to be exponential, its time constant τ is estimated to be 130 ps. We can then consider that the slowest process to be originated from a diffusive mode.

According to the increase of the dipole moment of the solute molecule, which is induced by laser excitation, we suggest that more polar component of the binary solvents come close to the solute molecule. We suppose this approach to be diffusive process. On the basis of Smoluchowski's diffusion model, the diffusion-controlled rate constant k_D in the present case can be given as

$$k_D = 4\pi(D_{CV} + D_{ACN})R \tag{3}$$

where D_{CV} and D_{ACN} are the diffusion coefficients for **CV** and ACN in a solvent THF, respectively. R is usually called the critical reaction radius: when two target molecules that are in diffusion approach at the distance R, a reaction occurs with a probability of unity. In our present context we propose that R

roughly gauges the distance resulting from a diffusive walk by solvents, which is required for the rearrangement of the closest solvation shell. We use an empirical method, the Wilke−Chang equation, to provide D_{CV} and D_{ACN}[24]

$$D_i = 7.4 \times 10^{-8}(\phi M_w)^{1/2} T \eta^{-1} V^{-0.6} \tag{4}$$

where $i = \mathbf{CV}$ and ACN and ϕ stands for the association factor of solvent. M_w, T, and η are the molecular weight of the solvent, temperature, and viscosity of the solvent, respectively. V is the molal volume of solute at its normal boiling temperature. On the basis of eqs 3 and 4, k_D for the system TA1 employed for the experiment has been estimated as typical. In the estimation, R was assumed to be 8.1 Å, which would correspond to the closest solvation shell around **CV**, on the basis of the summation of the molecular radii of **CV** (4.8 Å) and THF (3.3 Å), where the radii were derived as the summation of the van der Waals volume of each atom of the molecules. $\phi = 1$ was assumed for a nonassociating solvent THF.[24] $T = 295$ K and $\eta = 0.55$ cP for THF was adopted. $V = 260$ cm^3 g^{-1} mol^{-1} for **CV** and $V = 60$ cm^3 g^{-1} mol^{-1} for ACN were employed on the basis of the Le Bas method.[24] Given the conditions, k_D was estimated to be 2.5×10^{-10} s^{-1} M^{-1} for TA1. The actual reaction rate k can be derived as

$$k = k_D \cdot C \tag{5}$$

where C is the concentration of the diffusing species. Under the present experimental condition, C for **CV** was about 10^{-6} M as noted in the Experimental Section; on the other hand, C for ACN in the system TA1 was 0.38 M. In this case, if we adopt C of ACN as it has dominant concentration, finally $k^{-1} = 100$ ps was obtained. We should emphasize here that despite rather the crude diffusion model assumed here k^{-1} represents a relatively similar order of magnitude of τ.

The above estimation implies that the slower part of the relaxation of $\rho_w(t)$ in the binary solvents must be attributed to the translational diffusion process of the polar component of the solvent molecule that is approaching closer toward the solute molecule. Followed by the increase of μ of the solute molecule due to the laser excitation, the solvent distribution near the solute in the equilibrated excited state should be abundant in the more polar component than that in the ground state. Actually, the binary system containing the smaller portion of ACN showed the slower decay of $\rho_w(t)$. As described in the Results section, in the binary solvents $\rho_w(t)$ relax in a rather similar way in the course of a few picoseconds after the excitation, but the distinguishable difference of the relaxation process depending on the fraction of the polar component appeared after that time region. We thus suggest that the translational relaxation process of the polar component would have essential influence on the relaxation of the spectral width at least at the time domain where the fraction-dependent slower relaxation was detected. Alternately stated, about 50% of the relaxation of $\rho_w(t)$ would be substantially characterized by the slower translational diffusion process.

The above mechanism would suggest that the rearrangement (or replacement) of the solvent component in the closest solvation shell should require 10−100 ps. We have found related results with respect to such a type of diffusive motion in solution that is obtained through an analysis of a transient effect observed for fluorescence quenching at high quencher concentration in the system of coumarin fluorescence quenched by *N*,*N*-dimethylaniline.[25,26] If we applied conventional Smoluchowski's model where a continuum was assumed for the solvent, even though it employed the transient effect, it failed to explain the behavior of experimental results in the subpicosecond to picoseconds region when the concentration of the quencher was higher than 0.1 M.[25] We propose that in the subpicosecond to few picoseconds region the continuum model would not be suitable because substantial reactions with quencher molecules that distribute around neighbors of the fluorescent molecule according to the radial distribution function should be predominant. We have instead employed a diffusion equation that takes into consideration the quencher distribution at initial conditions derived from the intermolecular average potential.[26] In the model the Percus Yevick equation for hard spheres was adopted as a closure.[27] In this treatment, we have found that within a realm of a few picoseconds after the excitation, when the concentration of the quencher is about 1 M, molecules in the closest solvation shell around the fluorescent molecules would dominantly take part in the quenching reaction. In addition, molecules in the second or farther shell would play a role after the tens of picoseconds time region. In the tens of picoseconds to subnanosecond time domain, on the other hand, simple Smoluchowski's diffusion model without considering the intermolecular average potential could be applicable for the analysis of the observed fluorescence decay curves.[26]

This result with respect to the transient effect may be interpreted that at least in the time region of subpicosecond to few picoseconds the component of the closest solvation shell should not be disturbed, whereas after the tens of picoseconds domain the diffusion process of the solvent can be treated as the bulk model and the replacement of the member of the closest shell should be achieved in this time scale. We suppose that this picture should reinforce our assignment of the slower relaxation in the binary solvents detected in the present work. It takes not less than tens to hundreds of picoseconds in order to achieve the complete relaxation of the hole spectral width in the binary solvents with smaller fraction of the polar component. Such a slower time scale would really agree with that of the translational diffusion process of solvent molecules, where the rearrangement of the closet solvation shell might be involved.

On the other hand, it is stressed that the slower relaxation in the binary solvents was observed only for the relaxation of the spectral width, while the relaxation of average energy was affected only marginally by the solvent mixing. We then propose that energy relaxation can be achieved by fast relaxation processes such as rotational diffusion or librational motion of solvent molecules in the closest solvation shell. In the course of the relaxation process of the spectral width, the slower translational diffusion of the polar component of the solvent would bring about the rearrangement of the solvent distribution, which might well disturb the energy of the system. Such disturbance of the energy could be compensated largely by the fast relaxation process of the solvents surrounding the neighbor of the solute molecule. However, minor contribution to the average energy due to the exchange of the polar solvent molecule would be detected with a slower component, although we could not detect the depression peak shift within our spectral resolution. To clarify this point, an extensive observation with much higher spectral resolution is indeed desirable. Actually we are preparing an upgraded version of the measurements of the THB and TRF spectroscopy according to this line. The mechanism presented above should be rather consistent with the proposed relaxation of energy and the spectral width obtained from the THB and TRF spectroscopy in pure polar solvents reported in our previous work.[9,20]

The recent developments of the molecular theory of liquids have elucidated that not only the rotational dynamics of the solvent but also the translational dynamics would contribute to essential understanding of the experimental results described here. Chong and Hirata[28] have developed a molecular theory to study collective excitations in polyatomic fluids under the framework of the interaction-site model. They have succeeded in separating the collective motions into acoustic and optical modes, which are essentially originated from the translational and rotational motions of solvent molecules, respectively.[28] Patey et al.[18] have developed time-dependent density fluctuational theory for a single solute particle in binary solvents. They applied the theory for the dynamics of selective solvation and reported that in binary solvents the reorganization of the closest solvation shell should play an essential role for the relaxation mechanism particularly at longer time scales. Such relaxation processes should intrinsically involve the translational motions of the solvents.[18] We would state that the above theoretical frameworks elaborated by Chong et al. and Yoshimori et al. may shed a closer molecular view for relaxation mechanisms in liquids. Further progress of theories that reveal the importance of the translational relaxation modes of solvents as proposed in our work should highly be desirable.

Recently Petrov et al.[29] performed TRF spectroscopy in polar/nonpolar binary solvents using 3′-*N*,*N*-dimethylamino-3*H*-4,5-benzonaphthantracene as a solute where pyrene rigidly coupled with *N*,*N*-dimethylaniline. Cichos et al.[30] have reported TRF spectroscopy of coumarin 153 in binary mixtures of alkanes and alcohols. A direct comparison with our present results should be rather difficult because the fluorescence probes employed in their studies increase μ drastically according to the excitation, where a specific solute−solvent coupling would be much more effective than that of our case. At any rate, they also discussed that in binary solvents local enrichment of one component solvent around the solute, which is referred to as preferential solvation, should be substantial. To our knowledge, however, the present work first correlates the translational diffusive mode of a component of the binary solvent with the relaxation dynamics of the inhomogeneous spectral broadening.

Conclusions

Time-resolved hole-burning (THB) spectra of cresyl violet in binary solvents consisting of components of different polarity being rich in less polar component were observed at room temperature. In the binary solvents, the dynamic response function $\rho_w(t)$ derived from the spectral broadening of the hole relaxes much more slowly compared to those observed in each pure solvent. The slower part of the relaxation process of $\rho_w(t)$ depends drastically on the fraction of the component of the mixture: in the smaller the fraction of polar component of the solvent, much more time was needed to complete the recovery of the hole spectral width. On the other hand, the relaxation of the average energy of the system detected through the spectral peak shift of the summation of the hole and induced fluorescence spectra was marginally affected by the solvent mixing. We propose the mechanism that the relaxation of the spectral broadening (relaxation of dispersion around average energy) can be mainly governed by the translational diffusion mode of the solvent, while the relaxation of average energy can be mostly achieved by fast rotational and/or librational processes of the solvent in the vicinity of the solute molecule. The above picture of the relaxation of the spectral width and energy presented on the basis of the present results in the binary solvents agrees with the mechanism obtained in our previous work observed in pure polar solvents.

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