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Slow solvation dynamics of 4-AP and DCM in binary mixtures

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Abstract

In a binary mixture of benzene and dimethylformamide (DMF), solvation dynamics of 4-aminophthalimide (4-AP) and 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM) displays a slow component. As mole fraction of DMF increases from 0.028 to 0.28 the average solvation time ($\langle\tau_s\rangle$) for 4-AP decreases from 830 to 450 ps while for DCM it decreases from 450 to 100 ps. In dioxane–water mixtures $\langle\tau_s\rangle$ for DCM is 250 ps which remains unaffected as mole fraction of water increases from 0.22 to 0.50.

Keywords: Solvation dynamics; Binary liquids

1. Introduction

Structure and dynamics of binary mixtures have been a subject of many recent studies [1,2,14]. Structure of binary liquids has been studied using mass spectrometry of binary clusters [3], NMR cryoporometry in sol–gel glass [4], quasi-elastic neutron scattering [5]. Dynamics in binary liquids has been studied using dielectric relaxation [6] and more recently, using femtosecond [7–9], picosecond [10–13,15] and nanosecond [16] time resolved emission spectroscopy. At a very low temperature (90 K) solvation dynamics in a porous glass filled with binary liquid mixture occurs in millisecond to several seconds time scale [17]. There have been many theoretical studies [1,2,18] and simulations [19–23] on solvation dynamics in binary liquids. Chandra and Bagchi showed that the non-ideality (i.e. preferential solvation) depends on both the molecular size and dipole moment of the solvent molecules constituting the binary mixture and that the non-ideality is observed even in the absence of any specific solute–solvent interaction (e.g. hydrogen bonding) [1,2]. Subsequent simulations revealed that the solvent response in binary liquids consists of an ultrafast inertial response and a relatively slow translational diffusion of the polar solvent molecules [19–23].

In pure water and many other polar solvents such as methanol, acetonitrile, dimethylformamide (DMF), solvation dynamics occurs in a time scale of <1 ps [7,24–31]. However, in many binary mixtures solvation dynamics exhibits a component of 100–1000 ps time scale. In binary mixtures of hexane and an alcohol Chicos et al. [11] detected a very slow component of solvation dynamics which varies from 200 to 6000 ps depending on the composition and length of the alkyl chain of the alcohol. They attributed the slow component to translational diffusion of the polar solvent molecules into the first solvation shell of the solute [11]. This is supported by computer simulations [20]. Similarly, slow components of solvation dynamics have been reported for hexane–propionitrile mixture [13] and water–dioxane mixtures [13,15]. Gardecki and Maroncelli reported that in a binary mixture of two polar aprotic solvents (acetonitrile and propylene carbonate) the ultrafast part of solvation dynamics (<100 ps) is described by a biexponential decay and the amplitudes of the decay components are linearly related to the mole fraction of the individual components [8]. Levinger and co-workers studied the ultrafast (<35 ps) component of solvation dynamics in a non-associated mixture consisting of a quadrupolar solvent (benzene) and a polar aprotic solvent (acetonitrile) [9].

Picosecond studies in binary aprotic liquids are still few except that by Molotsky and Huppert on hexane–propionitrile mixture [13]. In the present work, we have studied a

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mixture of benzene and a polar aprotic solvent dimethylformamide (DMF). This mixture has not been studied by solvation dynamics before. As a probe, we used 4-aminophthalimide (4-AP) and 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4H-pyran (DCM).

2. Experimental

4-Aminophthalimide (4-AP) was purchased from Kodak and was purified by repeated recrystallization from methanol–water mixture. Laser grade DCM (Exciton) was used without further purification. Benzene (SRL grade, >99.9% purity) was dried by refluxing over sodium and benzophenone. DMF (Spectrochem) was distilled under reduced pressure. The steady-state absorption and emission spectra were recorded in a Shimadzu UV-2401 spectrophotometer and a Perkin-Elmer 44B spectrofluorimeter, respectively.

For lifetime measurements, the samples were excited at 405 nm for DCM and 375 nm for 4-AP using a picosecond diode laser (IBH Nanoled-07) in an IBH Fluorocube apparatus. The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier (5000U-09). The time correlated single photon counting (TCSPC) setup consists of an Ortec 9327 CFD and a Tennelec TC 863 TAC. The data is collected with a PCA3 card (Oxford) as a multi-channel analyzer. The typical FWHM of the system response using a liquid scatterer is about 80 ps. The fluorescence decays were deconvoluted using IBH DAS6 software.

3. Results

3.1. Steady-state results

The absorption maximum of 4-AP in neat benzene and neat DMF are at 349 and 369 nm, respectively. In a mixture containing benzene and DMF as mole fraction of DMF (X_{DMF}) increases from 0.028 to 0.28 the absorption maximum of 4-AP exhibits a red shift from 355 to 365 nm.

In pure benzene, 4-AP exhibits intense emission, with emission maximum at 427 nm (Fig. 1). In neat DMF, the emission maximum of 4-AP is at 470 nm (Fig. 1) [14]. On addition of DMF to benzene, the emission maximum of 4-AP shifts from 457 nm at $X_{\mathrm{DMF}} = 0.028$ to 460 nm at $X_{\mathrm{DMF}} = 0.28$ (Fig. 1).

The absorption maximum of DCM is at 460 nm in dry benzene and at 472 nm in DMF. In a binary mixture of benzene and DMF, the absorption maximum of DCM is at 462 nm at $X_{\mathrm{DMF}} = 0.028$ which shifts to 469 nm at $X_{\mathrm{DMF}} = 0.28$.

The emission maximum of DCM in benzene and DMF are at 540 and 620 nm respectively. In a mixture of benzene and DMF, the emission maximum of DCM is observed to be at 560 nm at $X_{\mathrm{DMF}} = 0.028$ and at 600 nm at $X_{\mathrm{DMF}} = 0.28$.

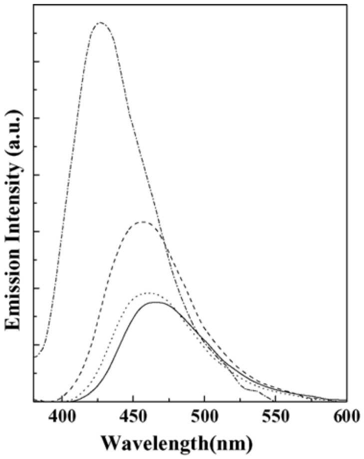

Fig. 1. Emission spectra of 4-AP in neat benzene (–·–), neat DMF (—), benzene–DMF mixture at mole fraction of DMF = 0.028 (- - -) and 0.28 (···) at $\lambda_{\mathrm{ex}} = 375$ nm.

3.2. Time resolved fluorescence stokes shift

3.2.1. 4-AP in benzene–DMF mixture

In dry benzene, fluorescence of 4-AP exhibits a biexponential decay with two components of 4.5 ± 0.1 ns (20%) and 14.0 ± 0.2 ns (80%). In this case, the fluorescence decays do not exhibit any wavelength dependence. This indicates that solvation dynamics of 4-AP in benzene is too fast to be detected in a picosecond setup. This is consistent with a recent report on very fast solvation in neat benzene [9].

In a mixture of benzene and DMF, the fluorescence decays of 4-AP display marked emission wavelength dependence in picosecond time scale. At $X_{\mathrm{DMF}} = 0.028$, the decay at the blue end (410 nm) may be fitted to a triple exponential with components of 250 ± 50 ps (70%), 1.8 ± 0.1 ns (10%) and 13.4 ± 0.2 ns (20%). On the other hand, at the red end (555 nm) a decay of 13.4 ns component is preceded by two rise times of 250 ± 50 ps and 2.1 ± 0.1 ns (Fig. 2). The amplitude of the 1.8 ns component increases from 10% at 410 nm to 25% at 440 nm and then decreases. But at 450 and 460 nm, the 250 ps component exhibits a rise while the 1.8 ns component exhibits a decay. Thus the two components of 250 ps and 1.8 ns cannot be ascribed to a photochemical interme-

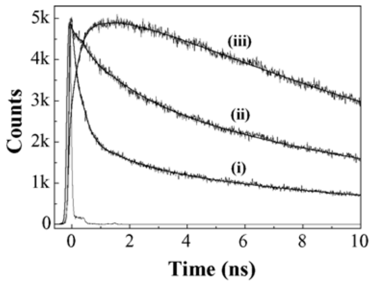

Fig. 2. Initial portion of the fluorescence decays of 4-AP in benzene–DMF mixture at mole fraction of DMF = 0.028 at (i) 410 nm, (ii) 430 nm and (iii) 555 nm.

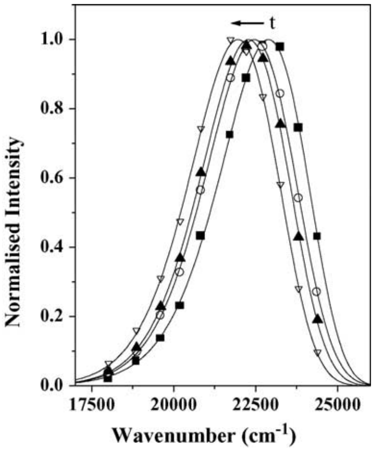

Fig. 3. Time resolved emission spectra of 4-AP in benzene–DMF mixture at mole fraction of DMF = 0.028 at 0 ps (■), 200 ps (○), 400 ps (▲) and 10,000 ps (▽).

diate and the observed time dependent spectral shift is due exclusively to solvation dynamics.

From the parameters of the best fit to the emission decays and using the steady-state emission spectra, time resolved emission spectra (TRES, Fig. 3) of 4-AP have been constructed following the procedure described by Maroncelli and Fleming [30]. The solvation dynamics is described by the decay of the response function, $C(t)$, which is defined as

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \quad (1)$$

where $\nu(0)$, $\nu(t)$ and $\nu(\infty)$ are the peak frequencies at time 0, t and ∞, respectively. The decay of $C(t)$ of 4-AP in a mixture of benzene and DMF at $X_{\mathrm{DMF}} = 0.028$ is shown in Fig. 4. The solvent correlation function, $C(t)$ is fitted to a biexponential decay. The decay parameters of $C(t)$ are given in Table 1. At $X_{\mathrm{DMF}} = 0.028$, decay of $C(t)$ (hence, solvation dynamics) displays two components of 200 ps (70%) and 2300 ps (30%) (Table 1). In this case, the average solvation time is 830 ± 50 ps. This is substantially slower than the solvation dynamics of DMF in bulk which is complete within ~1 ps [9,24]. The total Stokes shift for 4-AP in this mixture ($X_{\mathrm{DMF}} = 0.028$) is 950 ± 100 cm^{-1}.

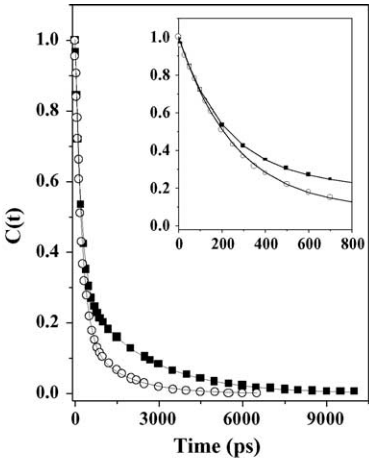

Fig. 4. Decays of response function, $C(t)$ of 4-AP in benzene–DMF mixture at mole fraction of DMF = 0.028 (■) and 0.28 (○). The points denote the actual values of $C(t)$ and the solid lines denote the best fit to a biexponential decay. The initial parts of the decays of $C(t)$ are shown in the inset.

Table 1
Decay parameters of $C(t)$ of 4-AP and DCM in benzene–DMF mixture at various mole fractions of DMF

Probe	X_{DMF}	$\Delta\nu$ (cm^{-1})[a]	a_1	τ_1 (ps)[b]	a_2	τ_2 (ps)[b]	$\langle\tau_s\rangle$ (ps)[b,c]
4-AP	0.028	950	0.70	200	0.30	2300	830
	0.28	350	0.83	240	0.17	1400	450
DCM	0.028	350	0.47	120	0.53	760	450
	0.28	500	0.53	60	0.47	160	100

[a] ±100 cm^{-1}.
[b] ±50 ps.
[c] $\langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$, where $\langle\tau_s\rangle$ is 1.54 ps in pure DMF [7] and ~1 ps in neat benzene [9].

At $X_{\mathrm{DMF}} = 0.28$, the $C(t)$ of 4-AP is described by two components of 240 ps (83%) and 1400 ps (17%) with an average solvation time of 450 ± 50 ps (Table 1 and Fig. 4). The total Stokes shift is 350 ± 100 cm^{-1} (Table 1).

3.2.2. DCM in benzene–DMF mixture

In dry benzene, fluorescence decay of DCM is found to be single exponential with a time constant (τ_f) of 200 ± 50 ps whereas in neat DMF the life time (τ_f) of DCM is 2100 ± 100 ps, i.e. 10 times longer.

The fluorescence decays of DCM in a mixture of benzene and DMF depend markedly on the emission wavelength. For example, in the binary mixture consisting of DMF mole fraction, $X_{\mathrm{DMF}} = 0.028$, the observed decay at the blue end (515 nm) may be fitted to a biexponential with components of 150 ± 50 ps (45%) and 550 ± 50 ps (55%). On the other hand, at the red end (640 nm) a decay of 500 ± 50 ps component is preceded by a distinct growth of 450 ± 50 ps.

The decay of $C(t)$ for DCM in a mixture of benzene and DMF for both the mole fractions ($X_{\mathrm{DMF}} = 0.028$ and 0.28) are shown in Fig. 5. Decay components of $C(t)$ for DCM at different X_{DMF} are given in Table 1. In this mixture, the average solvation time, $\langle\tau_s\rangle$ decreases from 450 ± 50 ps at $X_{\mathrm{DMF}} = 0.028$ to 100 ± 50 ps at $X_{\mathrm{DMF}} = 0.28$. In this case, the observed solvation time in the binary mixture are substantially slower than the ultrafast solvation dynamics observed in either benzene [9] or DMF [7] in bulk which is complete within ~1 ps.

3.2.3. DCM in dioxane–water binary mixture

A similar wavelength dependence in the time resolved fluorescence decays was also observed for DCM in dioxane–water mixtures. In this case, the decay of $C(t)$ could be fitted to a single exponential with solvation time $\tau_s = 250 \pm 50$ ps (Table 2). Interestingly in the dioxane–water mixtures, solvation time of DCM is almost independent of the relative amount of water (Table 2).

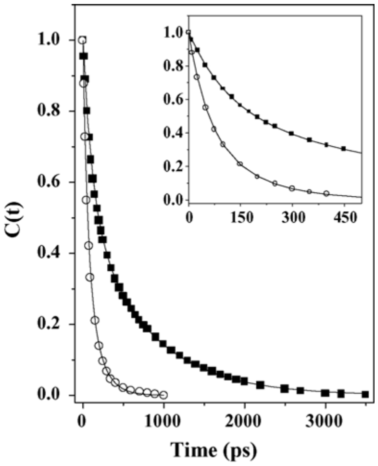

Fig. 5. Decays of response function, $C(t)$ of DCM in benzene–DMF mixture at mole fraction of DMF = 0.028 (■) and 0.28 (○). The points denote the actual values of $C(t)$ and the solid lines denote the best fit to a biexponential decay. The initial parts of the decays of $C(t)$ are shown in the inset.

Table 2
Decay parameters of $C(t)$ of 4-AP and DCM in dioxane–water mixture at various mole fractions of water

Probe	X_{water}	$\Delta\nu$ (cm^{-1})[a]	a_1	τ_1 (ps)[b]	a_2	τ_2 (ps)[b]	$\langle\tau_s\rangle$ (ps)[b,c]
4-AP[d]	0.22	860	0.90	400	0.10	1430	500
	0.50	1120	0.65	220	0.35	570	340
DCM	0.22	300	1.00	250	–	–	250
	0.50	400	1.00	250	–	–	250

[a] ±100 cm^{-1}.
[b] ±50 ps.
[c] $\langle\tau_s\rangle = a_1\tau_1 + a_2\tau_2$. In pure water $\langle\tau_s\rangle$ is ~0.20 ps [25,31].
[d] From Ref. [15].

4. Discussion

The solvation dynamics of 4-AP and DCM in benzene–DMF binary mixture clearly shows the presence of a component which is substantially slower than the solvation dynamics in pure DMF (1.54 ps) [7] and that in neat benzene (~1 ps) [9]. In the case of benzene–DMF mixture, there is no scope of formation of a hydrogen bond between the quadrupolar solvent benzene and the aprotic solvent DMF. Thus it appears that specific interaction, such as hydrogen bonding is relatively unimportant in the slow component of solvation dynamics in a binary mixture. Similar conclusion was reached earlier by Chandra and Bagchi in a theoretical analysis of solvation dynamics in a binary liquid [1,2].

The average solvation time, $\langle\tau_s\rangle$ in benzene–DMF mixture is found to decrease with increase in relative amount of DMF. For 4-AP, $\langle\tau_s\rangle$ decreases from 830 ps at $X_{DMF} = 0.028$ to 450 ps at $X_{DMF} = 0.28$ while for DCM it decreases from 450 to 100 ps (Table 1). It is readily seen that $\langle\tau_s\rangle$ differs by a factor of 2–4 for the two probes and hence, it may be concluded that the slow dynamics depends on the nature of the solute though not very strongly.

Theory [1,2] and simulations [19–23] suggest that the solvation dynamics in a polar–quadrupolar mixture consists of two processes, electrostriction and redistribution. The former refers to increase in the local density of both the components in the vicinity of the dipolar solute (excited probe). The second is dielectric enrichment i.e. increase in the local concentration of the more polar component at the expense of the less polar one [1,2,12,14,20]. According to the simulations, following creation of dipole the polar solvent molecules diffuse from outer shells to the first solvation shell replacing the less polar solvent [19–23]. Following this model, we propose that the ultraslow component of solvation dynamics in a benzene–DMF mixture arises from translational diffusion of the polar DMF molecules into the first solvation shell displacing the nonpolar benzene molecules. This results in a local enrichment of DMF around the excited probe (4-AP or DCM).

It is interesting to note that in dioxane–water mixture, $\langle\tau_s\rangle$ for 4-AP decreases from 500 ps at $X_{water} = 0.22$ to 340 ps at $X_{water} = 0.50$ [15]. However, in this work we observed that for DCM, solvation dynamics is found to be independent of the composition of dioxane–water mixture and exhibits a solvation time, 250 ps. In an earlier work, Molotosky and Huppert reported that the solvation time for the coumarin 153 (C153) in dioxane–water mixture is more or less independent of the composition and displays a component 200 ± 40 ps [13]. This is very close to the solvation time detected in our work using DCM. The near constancy of the solvation time of DCM and C153 is in sharp contrast with the decrease in of solvation time with increase in water content observed for 4-AP. However, the solvation time of 4-AP in dioxane–water mixtures differ from those of DCM and C153 at most by a factor of 2. This once again shows that solvation dynamics in a binary mixture depends on the solvation probe.

5. Conclusion

In summary, the observation of a slow component of solvation dynamics in a few hundred ps time scale in a binary mixture seems to be a general phenomenon. The present study involving two probes and two solvent mixtures demonstrates that the phenomenon is observed for both protic (i.e. hydrogen bonding) and aprotic (non-hydrogen bonding) solvents. The exact magnitude of solvation time and nature of its dependence on composition of the binary mixture depend slightly on the probe. However, the probe dependence is small (2–4 times). The observation of the slow dynamics in a totally non-hydrogen bonding binary mixture involving benzene and DMF (and also in hexane–propionitrile [13]) suggests hydrogen bonding is unimportant in the slow solvation dynamics. Following earlier experiments and simulations it is suggested that the slow component arises from the changes in local density and dielectric enrichment in the vicinity of the dipolar solute.

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