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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 $X_{\mathrm{DMF}} = 0.28$.

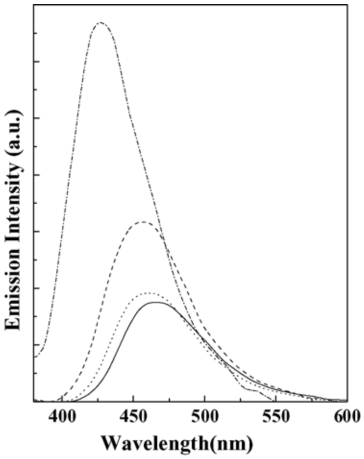

Fig. 1. Emission spectra of 4-AP in neat benzene (–·–), neat DMF (—), benzene–DMF mixture at mole fraction of DMF = 0.028 (- - -) and 0.28 (···) at $\lambda_{\mathrm{ex}} = 375$ nm.

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-

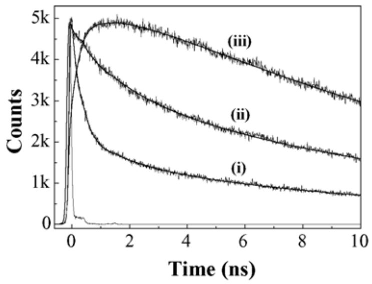

Fig. 2. Initial portion of the fluorescence decays of 4-AP in benzene–DMF mixture at mole fraction of DMF = 0.028 at (i) 410 nm, (ii) 430 nm and (iii) 555 nm.