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Solvation dynamics of 4-aminophthalimide in dioxane–water mixture

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Abstract

Solvation dynamics of 4-aminophthalimide (4-AP) in dioxane–water mixtures display a slow component of 350–500 ps. This is attributed to transient dioxane–water clusters and rupture of water–dioxane hydrogen bond. A detailed analysis indicates that there is no preferential solvation of 4-AP in dioxane–water mixture. The solvent shift of the emission maximum of 4-AP in a solution is shown to be controlled by hydrogen bond parameters of the solvent.

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1. Introduction

Solvent polarity plays a crucial role in chemistry. Dynamics and equilibrium of polar chemical reactions, solubility and chromatographic separation may be markedly altered by ‘tuning’ solvent polarity. A very convenient way of varying solvent polarity is to use a mixture of two solvents of drastically different polarity. For an ideal mixture, one expects that any equilibrium property (A) in a binary liquid (e.g., solvation energy, composition, etc.) is a weighted average of that in the two solvents e.g., $A = x_1A_1 + x_2A_2$, where x_i is the mole fraction of the i th component in the binary mixture. However, most binary mixtures deviate significantly from the ideal behavior. In a non-ideal mixture, because of preferential solvation, the local composition around a polar solute may be very different from that in the bulk [1]. In a mixture containing a non-polar solvent of mole fraction x_N in bulk and a polar solvent of bulk mole fraction x_P , the corresponding mole fractions y_N and y_P next to a polar solute may be very different from those in bulk. The mole ratio in bulk, $X = x_N/x_P$ is related to that near the solute, $Y = y_N/y_P$ as $Y = Xe^{-Z}$ [1]. Z is a

measure of preferential solvation. For a solute of dipole moment μ , Z is given by [1]:

$$Z = \frac{1}{4\pi\epsilon_0} \frac{CM\mu^2\Delta F_{N,P}}{2\delta RT\tau^6}, \quad (1)$$

$$\Delta F_{N,P} = F_P - F_N, \quad (2)$$

where $\Delta F_{N,P}$ is the difference of the Onsager’s reaction field, $F(\epsilon) = 2(\epsilon - 1)/2\epsilon + 1$, of the pure polar and non-polar solvents and is a positive quantity. M and δ are the mean molar weight and density of the two solvents, respectively. Since $Z > 0$, according to Eq. (1) the relative concentration of the polar solvent near the solute is higher than that in the bulk.

In recent years, there has been considerable progress in understanding solvation dynamics in pure (one component) liquids. More recently, it has been reported by many groups that solvation and hydrogen bond dynamics in liquid mixtures and particularly, complex biological systems are very different from those in a pure liquid [2–5]. There have been many theoretical [6,7] and experimental studies [8–19] and simulations [20–24] on dielectric relaxation [6,8], solvation dynamics [8–23] of binary liquids and also their glass forming properties with a view to develop new cryopreservatives [24]. Using a microscopic theory, Chandra and Bagchi [6,7] predicted that the continuum model is inadequate to describe a binary mixture and that the solvation dynamics

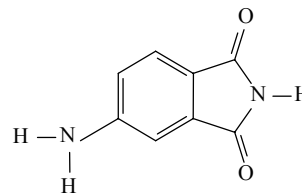
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and dielectric relaxation in a binary liquid mixture is highly non-exponential. They showed that the non-ideality (i.e., preferential solvation), is found even in the absence of any specific solute–solvent interaction (e.g., hydrogen bonding) [7]. The non-ideality depends strongly on the size and dipole moment of the solvent molecules [7]. Subsequent simulations suggested that the solvent response in binary liquids consists of an ultrafast inertial response and a relatively slow translational diffusion of the polar solvent molecules [20–23].

Many groups have investigated solvation dynamics in binary liquids using coumarin dyes (C153 and C102) as a solvation probe [9–18]. Gardecki and Maroncelli [11] reported that in a binary mixture of two polar aprotic solvents (acetonitrile and propylene carbonate) the solvation dynamics of C153 is described by a biexponential decay and the amplitudes of the decay components are linearly related to the mole fraction of the individual components. An extreme case of preferential solvation is formation of complexes [8,12]. Moog et al. [12] detected that trifluoro-ethanol becomes attached to C153 to form a 1:1 complex. Chicos et al. [13] studied solvation dynamics of C153 in several mixtures containing hexane as one component and alcohols of various chain lengths as the other. They detected a very slow component of solvation dynamics which varies from 200 to 6000 ps [13]. This ultraslow component is absent in the individual components and is substantially slower than that in lower chain alcohols (e.g., in methanol solvation is complete in a few ps). They attributed this slow component to preferential solvation and translational diffusion of the polar solvent molecules into the first solvation shell of the solute following creation of the dipole by exciting the solute. This is supported by computer simulations [21–23]. Such a slow component have been reported for C153 and C102 in several other solvent mixtures, e.g., hexane–methanol [17], hexane–propionitrile [18], and dioxane–water [18]. Molotosky and Huppert [18] ascribed the slow dynamics in dioxane–water mixture to the formation of transient clusters. Levinger and co-workers [16] studied the ultrafast component (<35 ps) of solvation dynamics of C153 in a non-associated solvent mixture consisting of a dipolar (acetonitrile) and a quadrupolar (benzene) solvent. They found that the average solvation time decreases with increase in the mole fraction of acetonitrile [16].

Among various solvent mixtures dioxane–water is very popular for tuning solvent polarity for the following reasons: First, viscosity and density of the two solvents are very much similar and hence, one does not have to worry about changes in the viscosity and density during variation of polarity. Secondly, the two components are miscible in all proportions. In this work, we employed 4-aminophthalimide (4-AP, Scheme 1) as a solvation probe to study solvation dynamics in dioxane–water mixtures.



Scheme 1. Structure of 4-aminophthalimide.

Absorption and emission properties of 4-AP are very strongly dependent on the hydrogen-bonding ability of the solvent [25]. Emission maximum of 4-AP shifts by 25 nm from 435 in dioxane ($\epsilon = 2.2$ and $E_T(30) = 36$) to 460 in a more polar solvent acetonitrile ($\epsilon = 37.5$ and $E_T(30) = 46$) [28]. However, in protic solvents 4-AP displays a dramatic red shift. For instance in *t*-butanol ($\epsilon = 12.42$ and $E_T(30) = 43.5$) which is less polar than acetonitrile, the emission maximum of 4-AP is at 500 nm. We will first analyze the steady-state spectral properties of 4-AP in terms of the Kamlet–Taft solvent parameters, e.g., polarity (π^*), hydrogen bond donor acidity (α) and hydrogen bond acceptor basicity (β) [26]. The hydrogen bond donor acidity (α) denotes ability of a solvent to donate a proton for solvent-to-solute hydrogen bonding. Obviously, $\alpha = 0$, for an aprotic solvent (e.g., dioxane). The hydrogen bond acceptor basicity (β) is a measure of the solvent's ability to accept a proton to form a hydrogen bond. Dioxane (and other ethers) though aprotic and non-polar, displays a marked affinity ($\beta = 0.37$) to accept a proton to form a hydrogen bond because of the presence of the oxygen atoms. We will show that hydrogen bond parameters (α and β) are much more important for 4-AP than the polarity parameter (π^*). This is in contrast to the coumarin dyes where the polarity parameter dominates over hydrogen bonding [17]. We will then show that in a dioxane–water mixture the preferential solvation of 4-AP by water is negligible. We will finally show that in a dioxane–water mixture 4-AP exhibits a very slow component of solvation dynamics. We will discuss the possible origin of this slow component.

2. Experimental

4-Aminophthalimide (4-AP, Kodak) was purified by repeated recrystallization from methanol–water mixture. The steady-state absorption and emission spectra in different dioxane–water mixtures 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 using a picosecond diode laser (IBH Nanoled-07). The emission was collected at a magic angle polarization using a Hamamatsu MCP photomultiplier

(2809U). The time correlated single photon counting (TCSPC) setup consists of an Ortec 935 QUAD 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 is about 100 ps.

3. Results and discussions

3.1. Steady-state spectra of 4-AP in neat solvents

We will first examine the role of different solvent parameters on the marked solvent shift of steady-state spectra of 4-AP in neat liquids. Absorption and emission maxima of 4-AP in many solvents are reported in the literature [25]. We have listed the absorption and emission maxima of 4-AP in 14 solvents along with the relevant solvent parameters (Table 1). We fitted the absorption frequency of 4-AP to the Kamlet–Taft parameters [26] as

$$\nu_{\text{abs}} = \nu_{0,\text{abs}} + p\pi^* + a\alpha + b\beta. \quad (3)$$

The linear regression fit yielded $\nu_{0,\text{abs}} = 29.533 \times 10^3 \text{ cm}^{-1}$, $a = -623 \text{ cm}^{-1}$, $b = -1648 \text{ cm}^{-1}$ and $p = -1351 \text{ cm}^{-1}$ with a correlation coefficient $R = 0.99$. In this case, the hydrogen bonding parameters, α and β contribute, respectively, about 17% and 45% while the polarity parameter (π^*) contributes about 38%. Evidently for 4-AP the combined contribution of the two hydrogen bonding parameters (α and β) are greater than that of the polarity parameter. This is in contrast to the case of C153 for which the contribution of the polarity parameter is about three times larger [17].

For the emission maxima we used the following equation:

$$\nu_{\text{em}}^* = \nu_{0,\text{em}}^* + p^*\pi^* + a^*\alpha + b^*\beta. \quad (4)$$

In this case $\nu_{0,\text{em}}^* = 24.995 \times 10^3 \text{ cm}^{-1}$, $a^* = -3191 \text{ cm}^{-1}$, $b^* = -1545 \text{ cm}^{-1}$ and $p^* = -3134 \text{ cm}^{-1}$ with a correla-

tion coefficient $R = 0.95$. It is evident that for 4-AP, there is a five fold increase in α . This suggests that the amino and imino protons of 4-AP form stronger hydrogen bonds in the excited state. In this case also, the hydrogen bonding parameters, (α and β) contribute more than the polarity parameter (π^*).

3.2. Steady-state spectra of 4-AP in dioxane–water mixtures

Addition of water to dioxane causes a marked red shift in the absorption and emission maxima of water (Table 2). Fig. 1a and b describe the solvent shift in absorption and emission maxima with increase in mole fraction of water (x_w), respectively. It is readily seen the solvent shift in absorption maxima is almost linear in x_w . However, the plot of emission maxima against x_w is non-linear. Suppan [1] and Zurawsky and Scarlata [27] showed that the non-linearity of the plot of emission maxima incorrectly predicts preferential solvation and arises mainly from the non-linear dependence of the dielectric constant (ϵ) of the mixture on the mole fraction of the polar component. They suggested that a continuum reaction

Table 2

Absorption and emission maxima of 4-AP in dioxane–water mixture at various mole fractions of water

Mole fraction of water (x_w)	$\nu_{\text{abs}} \times 10^{-3} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{em}} \times 10^{-3} \text{ (cm}^{-1}\text{)}$
0	28.169	22.988
0.046	28.089	22.321
0.14	27.932	21.141
0.22	27.700	20.618
0.35	27.548	20.161
0.43	27.397	19.960
0.50	27.322	19.762
0.55	27.247	19.685
0.60	27.173	19.646
0.63	27.173	19.569
0.66	27.173	19.531
0.71	27.027	19.493

Table 1

Kamlet–Taft parameters [23], absorption and emission maxima of 4-AP in different solvents [19]

Solvent	π^*	β	α	$\nu_{\text{abs}} \times 10^{-3} \text{ (cm}^{-1}\text{)}$	$\nu_{\text{em}} \times 10^{-3} \text{ (cm}^{-1}\text{)}$
Hexane	−0.08	0	0	29.611	25.965
CCl ₄	0.28	0	0	29.166	23.827
1-BuOH	0.47	0.88	0.79	26.888	19.482
2-PrOH	0.48	0.95	0.76	26.888	19.620
1,4-Dioxane	0.49	0.37	0	28.169	22.988
EtOH	0.54	0.77	0.83	27.027	19.275
THF	0.55	0.55	0	27.944	22.379
CHCl ₃	0.58	0	0.44	28.333	21.000
MeOH	0.6	0.62	0.93	27.111	19.206
MeCN	0.66	0.31	0.19	28.111	21.740
Acetone	0.71	0.48	0.08	27.861	21.827
DMF	0.88	0.69	0	27.166	21.275
DMSO	1.00	0.76	0	26.805	20.862
Water	1.09	0.18	1.17	27.083	18.520

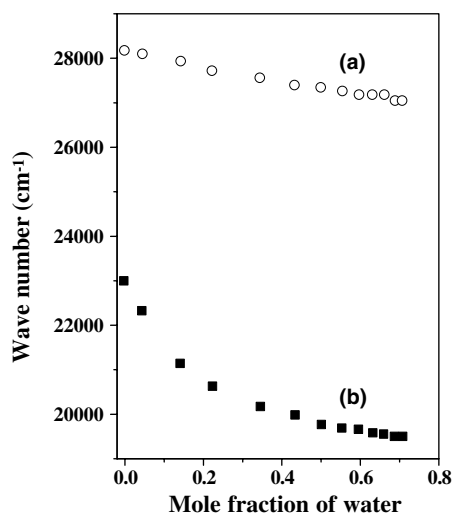


Fig. 1. Plot of (a) absorption maxima and (b) emission maxima of 4-AP in dioxane–water mixtures against the mole fraction of water.

field, $F(\varepsilon) = 2(\varepsilon - 1)/2\varepsilon + 1$ based on experimentally measured ε provides a much better description. The values of ε of dioxane–water mixtures are available in the literature [28]. Using this we now determine the extent of preferential solvation (Z_{ps}) of 4-AP as follows.

According to Kaufmann and co-workers [29], Z_{ps} is related to the experimentally obtained ‘non-linearity ratio’, ρ_{exp} . The latter is given by

$$\rho_{exp} = \frac{2 \int_0^1 (v_{exp} - v_{linear,bulk}) dx_w}{\Delta v_{w,d}} \quad (5)$$

For the solute (4-AP) in the ground state, v_{exp} is the experimental absorption frequency at a water mole fraction x_w and $v_{linear,bulk} = x_w v_{abs,water} + x_d v_{abs,dioxane}$ is the calculated absorption frequency. $\Delta v_{w,d}$ is the difference in absorption frequencies of 4-AP in water and dioxane. For the excited state of 4-AP one uses the emission frequencies.

ρ_{exp} is a sum of contribution of preferential solvation (ρ_{ps}) and dielectric non-ideality (ρ_{ni}),

$$\rho_{exp} = \rho_{ps} + \rho_{ni}, \quad (6)$$

where ρ_{ni} may be determined using the experimental ε of dioxane–water mixtures and have been estimated to be 0.28 [18]. Kaufmann and co-workers [29], have shown that for $\rho_{ps} < 1$, the relationship between ρ_{ps} and Z_{ps} is well approximated by the expression

$$\rho_{ps} = 0.31 Z_{ps}. \quad (7)$$

Using Eq. (5), we found that for the ground state of 4-AP, ρ_{ps} is -0.004 and hence, from Eq. (7), Z_{ps} is -0.013 . For the excited state of 4-AP, we determined ρ_{ps} to be 0.042 and hence, Z_{ps} is 0.135 . The very low value of Z_{ps} indicates that preferential solvation plays a very minor role in the case of 4-AP in dioxane–water mixtures.

3.3. Time resolved fluorescence Stokes shift of 4-AP in dioxane–water mixtures

Fig. 2 describes fluorescence decays of 4-AP in a mixture of dioxane and water at $x_w = 0.5$. It is readily seen that in a dioxane–water mixture, fluorescence decays of 4-AP depends markedly on the emission wavelength. For example at $x_w = 0.5$, the decay at the blue end (at 440 nm) may be fitted to a biexponential with components of 190 ps (80%) and 11.5 ns (20%). On the other hand at the red end (at 605 nm) a decay of 10.6 ns component is preceded by a distinct growth with a component of 250 ps. 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

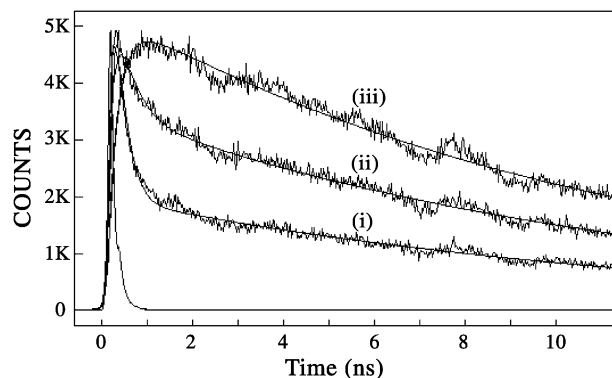


Fig. 2. Fluorescence decays of 4-AP in dioxane–water mixture at a mole fraction of water = 0.5 at: (i) 440 nm; (ii) 475 nm; (iii) 605 nm.

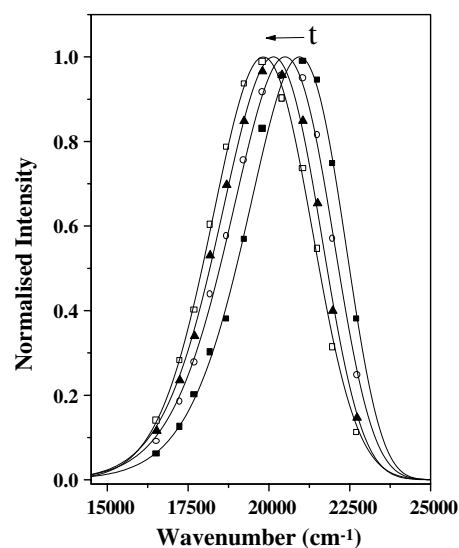


Fig. 3. Time resolved emission spectra of 4-AP in dioxane–water mixture at a mole fraction of water = 0.5 at 0 ps (■), 150 ps (○), 400 ps (▲) and 3000 ps (□).

$$C(t) = \frac{v(t) - v(\infty)}{v(0) - v(\infty)}, \quad (8)$$

where $v(0)$, $v(t)$ and $v(\infty)$ are the peak frequencies at time 0, t , and ∞ , respectively. The decay of $C(t)$ of 4-AP in a mixture of dioxane and water at $x_w = 0.5$ is shown in Fig. 4. Decay components of $C(t)$ at different x_w are given in Table 3. It is readily seen that the decay of $C(t)$ exhibits a slow component of about 350 ± 50 ps (at $x_w = 0.5$) to 500 ± 50 ps (at $x_w = 0.22$). This is substantially slower than the solvation dynamics of water in bulk which is complete within 1 ps [31–33].

There may be several sources of the slow (350–500 ps) component of solvation dynamics detected for 4-AP in dioxane–water mixtures. Chicos et al. [13] proposed that the ultraslow component of solvation dynamics arises from a translational diffusion of the polar solvent molecules into the first solvation shell displacing the non-polar solvent molecules. The diffusion coefficient of water is $2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [33]. According to the relation $\langle Z^2 \rangle = 2Dt$, a water molecule travels $\sim 13 \text{ \AA}$ in 350 ps and $\sim 15 \text{ \AA}$ in 500 ps. This is about 2–3 times larger than

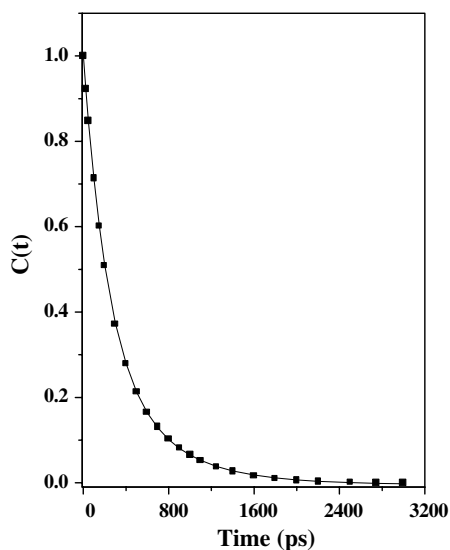


Fig. 4. Decay of response function, $C(t)$ of 4-AP in dioxane–water mixture at a mole fraction of water = 0.5. The points (■) denote the actual values of $C(t)$ and the solid line denotes the best fit to a biexponential decay.

Table 3

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

Mole fraction of water (x_w)	$\Delta\nu^a$ (cm^{-1})	a_1	τ_1^b (ps)	a_2	τ_2^b (ps)	$\langle \tau_s \rangle^{bc}$ (ps)
0.22	860	0.90	400	0.10	1430	500
0.35	1090	0.80	270	0.20	980	400
0.50	1120	0.65	220	0.35	570	350

^a $\pm 100 \text{ cm}^{-1}$.

^b ± 50 ps.

^c $\langle \tau_s \rangle = a_1 \tau_1 + a_2 \tau_2$.

the length of a dioxane molecule (4.8 \AA). 13 \AA corresponds to 5–6 water layers (thickness of each water layer being 2.4 \AA). It is doubtful whether solvation dynamics involves diffusion over such a long distance.

Very recently, Yoshida et al. [34] determined diffusion coefficient in a binary mixture consisting of butoxyethanol and water using neutron spin echo. According to them neutron spin echo probes a much faster time scale compared to dynamic light scattering (DLS). They found that the diffusion coefficient in this mixture is of the order of $10^{-11} \text{ m}^2 \text{ s}^{-1}$ which is about 100 times smaller than that in water. They attributed this slow dynamics to the formation of transient clusters involving dioxane–water of nanosecond lifetime. Rayleigh scattering of dioxane–water mixture suggests dissociation of dioxane–water clusters into dioxane and water molecules [35]. Most recently, Orzechowski et al. [8] reported that dielectric relaxation of a mixture of propionic acid and triethylamine exhibits a nanosecond component which has been ascribed to the formation of complexes involving the two components of the binary mixture. Following these studies we propose that the rate determining step in the solvation dynamics of 4-AP in dioxane–water mixture is the dissociation of the dioxane–water clusters.

It may be recalled that in order to explain the slow dynamics in an aqueous solution of a protein, Nandi–Bagchi proposed a dynamic exchange between the almost immobile ‘bound’ water molecules and ‘free’ water molecules. In the limit of high binding energy, the slow component (τ_{slow}) is given by [2,5]

$$\tau_{\text{slow}} \approx k_{\text{bf}}^{-1}, \quad (9)$$

where, k_{bf} denotes the rate constant for bound-to-free interconversion. Following this model, we propose the rate constant in dioxane–water mixture as

$$\tau_{\text{slow}}^{-1} = \left(\frac{k_B T}{h} \right) \exp \left(\frac{-\Delta G}{RT} \right), \quad (10)$$

where ΔG is the activation energy for solvation dynamics in the dioxane–water mixture. From Eq. (10), the 350 ps component corresponds to $\Delta G = -4.5 \text{ kcal mol}^{-1}$ and 500 ps to $\Delta G = -4.7 \text{ kcal mol}^{-1}$. Obviously, this is on the order of a hydrogen bond energy. Thus, the rate determining step may be rupture of a hydrogen bond between dioxane and water.

4. Conclusions

This work shows that 4-AP exhibits an ultraslow component (350–500 ps) of solvation dynamics in dioxane–water mixture. In this mixture, no preferential solvation of 4-AP is detected. The slow component of solvation dynamics is suggested to be due to the formation of transient dioxane–water clusters and rupture

of a hydrogen bond between dioxane and water is proposed to be the rate determining step. The solvent shift of the emission maximum of 4-AP is shown to be controlled by hydrogen bond parameters of the solvent.

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