

Configurational Relaxation of "Van der Waals Complexes" in Solution

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Novel measurements on the microscopic solvation dynamics of 3-amino-*N*-methylphthalimide (3ANMP) in nonpolar decalin (decahydronaphthalene) solutions with small concentrations of ethanol and other polar additives have been made, using the time-dependent fluorescence Stokes shift (TDFSS) technique. It is found that the experimentally measured TDFSS slightly differs from that predicted by the theory of the generalized Smoluchowski-Vlasov equation (SVE). The essentially slower character of the TDFSS in binary solutions than given by the SVE approach may be explained by the control of the solvation behavior by the large-wavevector processes involving nearest-neighbor molecules.

KEY WORDS: Solvation dynamics; configurational relaxation; binary solvent; spectral shift.

INTRODUCTION

The study of the solvation dynamics in liquids has become an active area of research due to its importance in charge transfer reactions in solutions and biological systems. The dynamics of the time-dependent response of binary solvents to a charge redistribution in a polar solute molecule after electronic excitation has been a subject of considerable theoretical and experimental investigation [1–6]. The basic experiment is as follows:

1. Before optical excitation, the dipole molecules in solution are configurationally ordered and have the minimum value of their free energy. Ultrashort optical excitation produces a nonequilibrium configuration of the polar solute and solvent molecules.

2. After optical excitation, intermolecular configurational relaxation in solution takes place, which leads

to the appearance of the time-dependent fluorescence Stokes shift (TDFSS).²

Usually, the TDFSS is monitored and analyzed via the spectral shift correlation function

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

Here $\bar{\nu}(0)$, $\bar{\nu}(t)$, and $\bar{\nu}(\infty)$ represent the frequencies of the intensity maximum of the fluorescence spectrum immediately after excitation, at some time t , and at a time sufficiently long in comparison with the time of configurational relaxation.

Picosecond spectroscopy was first applied to a dynamic solvation study in binary solvents for 2-amino-7-nitrofluorene in benzol with 2-propanol additives [1]. The authors came to the conclusion that a time-dependent fluorescence shift occurs as the result of 2-propanol selective solvation of dye molecules.

Recently the spectral shift correlation function $C(t)$ for simple liquids and binary mixtures has been studied using coumarin 152 and coumarin 153 as probes by a femtosecond laser spectrometer [3]. The authors demonstrated that in general the average solvation time τ_s

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² Abbreviations: 3ANMP, 3-Amino-*N*-methylphthalimide; TDFSS, time-dependent fluorescence Stokes shift; SVE, Smoluchowski-Vlasov equation; VWC, van der Waals complexes; DMF, dimethylformamide; MSA, mean spherical approximation.

determined from the $C(t)$ function was different from the average solvation time calculated within the continuum model. But in some binary solvents (for example, in mixtures of acetonitrile and benzonitrile) the experimentally determined average solvation time showed unexpected agreement within experimental error with the value following from the continuum model.

Pulse fluorimetry studies of dye molecules in binary solvents mainly study the influence of specific donor-acceptor and nonspecific van der Waals interactions on the behavior and ratio of time-dependent spectral shifts. Therefore, in spite of the significance of the TDFSS in binary solvents where specific donor-acceptor interactions are absent, the number of such investigations is still low. This is mainly due to the lack of necessary dielectric constant values on binary solvents for a wide range of solvents, because only for some mixtures have the frequency dependences of the dielectric permittivity been measured. This leads to substantial difficulties in the interpretation of TDFSS measurement results and solvation mechanisms in such systems.

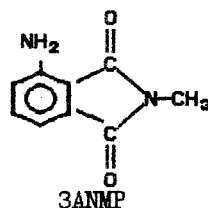
Some experimental results of $C(t)$ investigations in binary solutions of 3-amino-*N*-methylphthalimide (3ANMP) have been published recently [4,5]. It was shown that due to selective solvation of the dipole solute molecules by polar additives in binary solvents the interactions between the molecules in such systems are reminiscent of the interaction in van der Waals complexes (VWC). The correlation function of the spectral shift in binary solvents is substantially nonexponential. There is an increase in the contribution to $C(t)$ of the fast picosecond component as the polar additive concentration in solution grows. The magnitude of the TDFSS increases with concentration of polar solvent molecules and depends on the excitation frequency. Electronic spectra of 3ANMP in binary solvents are dynamically inhomogeneously broadened.

In the present paper we study $C(t)$ of 3ANMP in binary solvents both experimentally, using a time-resolved technique, and theoretically by the Smoluchowski-Vlasov equation (SVE) approach.

EXPERIMENTAL

Kinetic measurements were made by a subnanosecond laser spectrofluorimeter which employed as an excitation source a dye laser with distributed feedback pumped by a TEA-nitrogen laser with pulse duration of 1.2 ns. After a monochromator (MSD-1) the fluorescence was measured by a fast photomultiplier FEU-164 with time resolution of about 1 ns and a stroboscopic

voltmeter with time gate about 2 ns. The detection system provided measurement of two characteristics of the fluorescence: the kinetics of the fluorescence and instantaneous fluorescence spectra. The spectral width of the slit in the recording monochromator was 3 nm. The coefficients for correction of the spectral sensitivity of the detection system were determined by comparing the spectra of liquid solutions of reference substances when recorded on a standard SLM-4800 fluorimeter and our setup. The processing of experimental data was done with a computer. 3ANMP was twice sublimed at $T = 90^\circ\text{C}$



Decalin ($\text{C}_{10}\text{H}_{18}$)

and commercial decalin ($\epsilon = 2.2$) was purified by the conventional method until the fluorescence of organic impurities become negligible compared with the fluorescence of 3ANMP at concentration of 10^{-5} M. The polar additives were chromatographic grade. The solutions were dark stored and protected from water absorption.

RESULTS AND DISCUSSION

Introduction of slight ethanol additives (even 0.1 vol %) into a 3ANMP neutral solution results in smooth absorption and a fluorescence spectral shift that is proof of selective solvation of the dipole luminophore molecules by the molecules of polar additives (Fig. 1). As was shown in a number of papers [7-9], the interaction of 3ANMP molecules and the polar solvents is exclusively van der Waals, i.e., nonspecific, and the effect of intermolecular H bond for 3ANMP is negligibly small.

The energy of the dipole-dipole interaction for equidirected dipoles is expressed by the simple equation $E = -\mu_1\mu_2/r^3$, where μ_1 and μ_2 are the dipole moments of 3ANMP and ethanol molecules, respectively, and r is the distance between them in the solution. Estimations show that $E = 3.5 \times 10^{-21}$ J in the ground state and 6.6×10^{-21} J in the excited state for 3ANMP dipole moments in the ground and excited states of 2.6 and 4.9 D, respectively, $\mu_2 = 1.68$ D [10], and $r = 5$ Å (order of the size of dye molecules). At the same time the value of the thermal energy $k_B T$ at room temperature (293°K) is 4.04×10^{-21} J. Consequently, the van der Waals com-

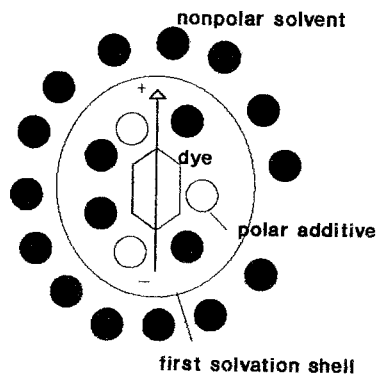


Fig. 1. Scheme of van der Waals-like complex in binary solution. Open circles represent the molecules of polar additive and closed circles are the molecules of nonpolar solvent. Due to dipole-dipole interactions with dye the polar additive molecules concentrate in the first solvation shell.

plex (VWC) in a binary solvent should be stable in the ground state as well as in the excited state. Therefore there are reasons to consider the selective solvation of dye molecules by polar molecules in a nonpolar solvent as the formation of VWC and examine it as a VWC-supermolecule. Such an approach is logical, as the main spectroscopic properties of the solution are defined by the process occurring in such supermolecules during the absorption-emission light cycle.

The addition of ethanol and other polar solvents into a neutral solution of 3ANMP in decalin leads to the appearance of the TDFSS, which is absent in pure decalin. Figure 2a shows instantaneous fluorescence spectra of 3ANMP in decalin with the addition of 0.8% of ethanol. It should be noted that in all cases (different concentrations and types of additives) the time-dependent spectral shift is smooth and is only accompanied by an increasing half-width of the instantaneous spectrum with detection time (Fig. 2b). The last phenomenon may be quantitatively described by the so-called inhomogeneous broadening function [11].

Ethanol is a protic solvent and can form a hydrogen-bonded complex with the solute molecules. To elucidate the possible role of H-bond formation, we performed experiments with aprotic solvent additives, namely deuterium ethanol and dimethylformamide (DMF). The small deviation of instantaneous fluorescence spectral positions for solutions with additions of ethanol and deuterium ethanol (Fig. 3a) indicates that the effect of intermolecular hydrogen bonding for 3ANMP is negligibly small and in binary solvents the TDFSS of 3ANMP is mainly caused by nonspecific solvation dynamics. It is most likely that 3ANMP mole-

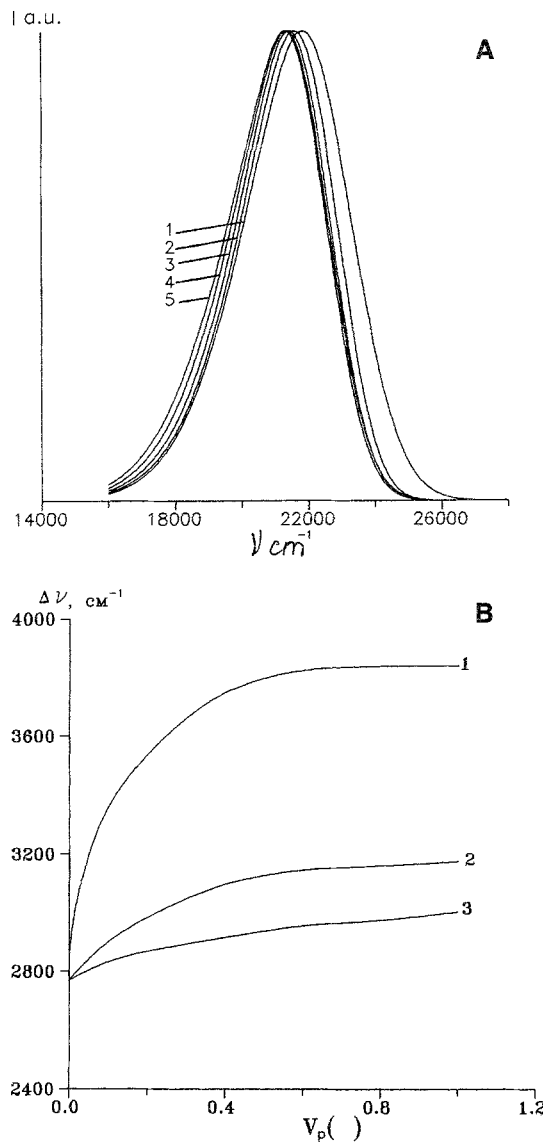


Fig. 2. (A) Instantaneous fluorescence spectra of 3ANMP in decalin with 0.8% of ethanol at times (1) 0, (2) 2, (3) 6, (4) 12, (5) 20, and (6) 30 ns after the onset of the excitation pulse, and (B) the dependence of spectral half-width on concentration of ethanol additives for different times of detection (1) 0, (2) 6, and (3) 20 ns after the onset of the excitation pulse. $\lambda_{\text{ex}} = 337 \text{ nm}$, $T = 20^\circ\text{C}$.

cules form intramolecular hydrogen bonds that fix the position of the amino group and one of the carbonyl groups [12] so they are not sensitive to some intramolecular hydrogen-bond effects.

Figure 3b shows the positions of the time-resolved fluorescence spectral maxima of 3ANMP in decalin with 0.8% addition of DMF and ethanol. Dimethylformamide ($\epsilon = 37.7$) is a more polar solvent than ethanol ($\epsilon = 24.69$, $T = 25^\circ\text{C}$), but in the presence of DMF the mag-

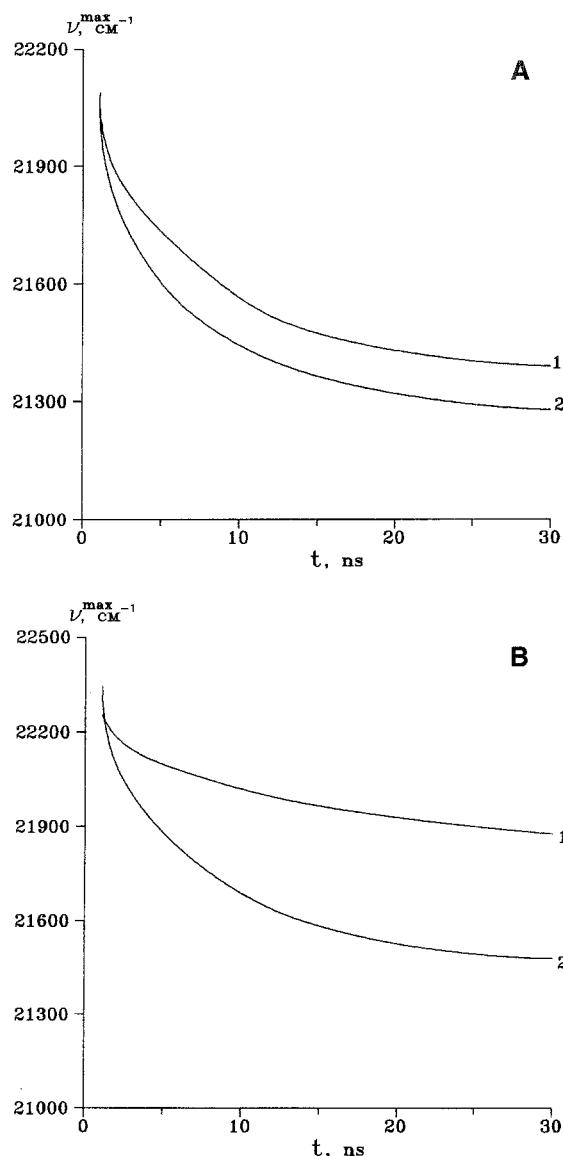


Fig. 3. Positions of fluorescence spectral maxima for solutions with different additives: (A) 0.8% deuterium ethanol (1) and 0.8% ethanol (2); (B) 0.4% dimethylformamide (1), 0.4% ethanol (2). $\lambda_{\text{ex}} = 337$ nm, $T = 20^\circ\text{C}$.

nitude of the TDFSS decreases. This difference in magnitude of the TDFSS may be explained by the different size of DMF and ethanol molecules. The DMF molecule is much larger than the ethanol one, and in agreement with modern molecular theories of solvation [13], the magnitude of the TDFSS should be smaller for DMF solutions.

We have performed calculations of the TDFSS using a Smoluchowski–Vlasov equation combined with the mean spherical approximation (MSA) in the way de-

scribed in Ref. 14. The time-dependent solvation energy in Fourier space is related to the solvent polarization relaxation $\delta\bar{P}(\bar{k}, t)$ by the expression

$$E_{\text{solv}}(t) = -1/2 (2\pi)^{-3} \int d\bar{k} \bar{D}(\bar{k}) \delta\bar{P}(\bar{k}, t) \quad (2)$$

where $\bar{D}(\bar{k})$ is the Fourier transform of the isolated dipole or ion electric field. The resulting equation for the relaxation of the polarization in a homogeneous system in Fourier space has the form

$$\partial\delta\bar{P}(\bar{k}, t)/\partial t = -(2D_R + D_T k^2) \delta\bar{P}(\bar{k}, t) + \rho_0(2D_R + D_T k^2) C(\bar{k}) \delta\bar{P}(\bar{k}, t)/3 \quad (3)$$

Here D_T and D_R are, respectively, the translational and rotational diffusion coefficients of the solvent, ρ_0 is the average number density of the liquid, and $C(\bar{k})$ is the tensor, which can be decomposed into the usual MSA anisotropy parts C_Δ and C_D of the direct correlation function [15].

Equation (3) can be solved to obtain the longitudinal component which is responsible for the TDFSS of the k -dependent polarization

$$P_L(\bar{k}, t) = P_L(\bar{k}) \exp[-t/\tau_L(k)] \quad (4)$$

with

$$\tau_L(k) = (2D_R)^{-1} \left\{ \left[1 + p'(k\sigma)^2 \right] \left[1 - \rho_0 \left(C_\Delta(k) + 2C_D(k) \right) / 3 \right] \right\}^{-1} \quad (5)$$

where $p' = D_T/(2D_R\sigma^2)$ is a dimensionless solvent parameter that characterizes the relative importance of translational modes, and σ is the molecular diameter of a solvent molecule. As C_Δ and C_D we used the usual MSA anisotropy functions [15]. In the limit $k \rightarrow 0$ the k -dependent polarization is given by

$$P_L(\bar{k}) = 1/4\pi [1 - 1/\epsilon(\bar{k})] D_L(\bar{k}) \quad (6)$$

where $D_L(\bar{k})$ is the Fourier transform of the external field and $\epsilon(\bar{k})$ is the wavevector-dependent longitudinal dielectric function, which is given by the equation

$$\epsilon(\bar{k}) = \left\{ 1 - 3Y \left[1 - (C_\Delta(\bar{k}) + 2C_D(\bar{k})) \rho_0 / 3 \right] \right\}^{-1} \quad (7)$$

where $3Y = 4\pi\mu^2\rho_0/3k_B T$, k_B is the Boltzmann constant, T is the temperature, and μ is the dipole moment of a solvent molecule.

Using the above equations, it is possible to calculate the time dependence of the solvation energy $E_{\text{solv}}(t)$

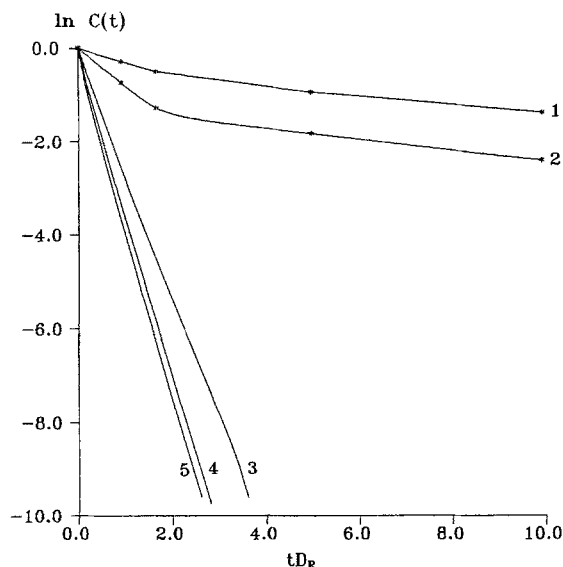


Fig. 4. Comparison of experimental (1, 2) and SVE-MSA (3–5) results. The concentration of ethanol was (1) 0.1% and (2) 1.0%. The calculations were performed for the dimensionless solvent translational diffusion parameter p' equal to (3) 0, (4) 0.2, and (5) 0.5 and solute/solvent size ratio and dielectric constant $R = 5$ and $\epsilon = 2$, respectively.

and solvation time correlation function

$$C(t) = \frac{E_{solv}(t) - E_{solv}(t=\infty)}{E_{solv}(t=0) - E_{solv}(t=\infty)} \quad (8)$$

which has the same physical meaning as the function $C(t)$ defined by Eq. (1).

The experimental and calculated functions of $C(t)$ are compared in Fig. 4. The TDFSS calculated by the SVE theory is essentially more rapid than the experimentally measured shift of $C(t)$. The measured $C(t)$ also seems to show a greater degree of nonexponential behavior.

As mentioned above, the experimentally found [3] average solvation time for coumarin probes in binary solvents showed unexpected agreement with its value calculated by the continuum model. Unfortunately, there

is no information on dielectric constant values for mixtures of decalin with polar additives used in this work and that is why it was not possible to calculate the TDFSS for 3ANMP in a binary solvent using the continuum model.

The author of Ref. 16, in a comment at a conference on solvated electrons, assumed that the solvent far from the electron would relax faster than the solvent near the electron and so the short time decay of the TDFSS is dominated by the small-wavevector processes. The modern molecular theories of solvation dynamics show this effect. So the slightly slower spectral relaxation in binary solvents than in the SVE approach found in the present paper may be explained by a selective solvation of dipole solvent molecules near the probe and controlling the solvation behavior by large-wavevector processes involving nearest-neighbor molecules.

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