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Transient dynamics of solvatochromic shift in binary solvents

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Using the picosecond spectro-streak method we monitored the dynamics of preferential solvation of charge-transfer dipoles in binary mixtures of solvents strongly different in dielectric constants. The observed slow ($\leqslant 1$ ns) spectral red-shift of the charge-transfer (exciplex) fluorescence is considered to be mainly due to the formation and the dielectric enrichment of the solvation shell around the solute molecules in their dipolar excited charge transfer state by diffusion of polar molecules from the bulk of the solvent mixture. As a fluorescent probe molecule we used 8-N,N-(dimethylamino)-11H-indeno[2,1-a]pyrene. The characteristic time of the solvatochromic shift varies from 400 ps to 140 ps for toluene/DMSO (dimethylsulfoxide) mixtures as the volume fraction of the polar component increases. Typical Stokes shifts are of the order of 1000–3000 cm^{-1}. A basic concept of the classical Onsager model has been modified and adapted for binary solvents considering a spherical cavity surrounded by a solvent layer with the permittivity of the polar component. To describe the transport of polar molecules to the first coordination shell of the excited dipole we applied the Smoluchowski diffusion model which leads to hyperbolic kinetics that compare reasonably well with the experimental Stokes shift data. © *1998 American Institute of Physics.* [S0021-9606(98)51006-9]

I. INTRODUCTION

For nearly half a century the great importance of chemical reactions in solution has motivated a great many studies for understanding the solvation of polar solutes in solvents of varying permittivity. Over the past decade attention has shifted from the equilibrium energetics of solvation to time-dependent aspects of solvation in polar solvents.[1–3]

The use of spectro-streak methods[4] allows the study of solvatochromic shift of intramolecular exciplex fluorescence in binary solvents on a picosecond time scale. Recently, we have found[5] that slow ($\leqslant 1$ ns) spectral red-shifts of exciplex fluorescence arise in binary mixtures of solvents strongly different in dielectric permittivity. These features are associated with the dielectric enrichment of the first solvation shell around a fluorescent dipolar probe molecule. Such studies of the solvation dynamics provide direct access to the short-time kinetics of diffusion-influenced processes.

A solute–solvent dielectric interaction in a neat solvent is usually considered in terms of the Onsager model[6] which also might be adapted to a case of binary liquid mixtures. However, a modification made recently[7] is suitable for the steady state rather than for the transient. In the work reported here, being interesting mainly in the physical sense of the problem, we try first to adapt the original Onsager model to binary solvent mixtures in a form suitable to the transient solvation and, second, to use molecular transport theory in order to explain the data obtained in mixtures of toluene ($\epsilon = 2.38$) and DMSO ($\epsilon = 49$) at room temperature.

II. THEORETICAL DESCRIPTION

A. An extension of the Onsager model

First, we try to modify and adapt the classical Onsager model to the case of time-resolved solvatochromic shift in binary mixtures. Onsager[6] considered a point dipole of moment m in a spherical cavity of radius a in a homogeneous dielectric with permittivity ϵ. The dipole polarizes the dielectric so that a reaction field R appears which acts on the dipole as a result of its action on the dielectric. In the spherical cavity this field is uniform and parallel to the dipole moment. The change in the dipole energy is

$$\Delta U = -mR, \tag{1}$$

where according to Onsager[6]

$$R = \frac{2m}{a^3} \frac{(\epsilon - 1)}{(2\epsilon + 1)}. \tag{2}$$

The solvatochromic shift in fluorescence and absorption spectra, observed in liquid solutions, can be explained in the framework of Onsager's model. This approach is common. However, it is worth noting that this model has an intrinsic contradiction between the macroscopic consideration of the problem (isotropic dielectric continuum) and a molecular scale of the system (a single dipole in a cavity). In particular, as Onsager noted, it is a real problem to connect the radius of the cavity with molecular parameters of the light-emitting dipole.

In order to apply the Onsager model to binary solvents we must modify it. Suppose that in a binary solvent mixture,
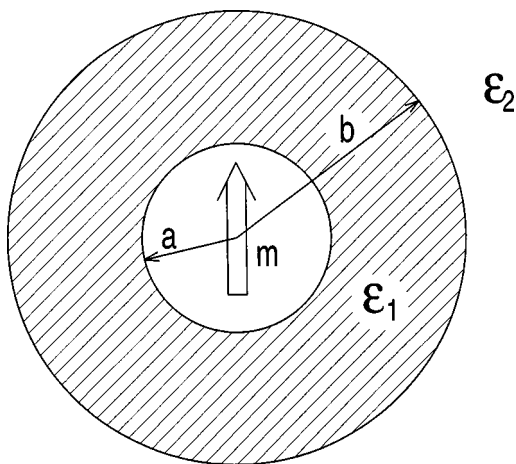
FIG. 1. A spherical polar microcluster (shaded region) around the dipole moment m placed in the cavity of a radius of a. The permittivity of the shaded region is ϵ_1 (i.e., that of a polar component of the mixture). The permittivity outside of the sphere of radius b is ϵ_2, and that in the cavity is unity.

a layer of polar molecules arises around a dipolar probe molecule owing to preferential solvation (see Fig. 1). Following Onsager's approach we consider a cavity surrounded by a polar layer with a dielectric permittivity of the polar component ϵ_1.

In the Laplace equation,

$$\Delta \varphi = 0, \tag{3}$$

φ is the electric potential. The solution can be expressed as follows:[8,9]

$$\varphi = \frac{m \cos \theta}{r^2} - R r \cos \theta, \quad (r < a),$$

$$\varphi = \frac{A \cos \theta}{\epsilon_1 r^2} - \frac{B r \cos \theta}{\epsilon_1}, \quad (a < r < b), \tag{4}$$

$$\varphi = \frac{C \cos \theta}{\epsilon_2 r^2}, \quad (r > b),$$

where θ is the angle between the dipolar moment and a radius vector; A, B, C are parameters that are determined from the boundary conditions, i.e., (i) φ should be continuous, and (ii) at interfaces $\epsilon_1 (\partial \varphi / \partial r) = \epsilon_2 (\partial \varphi / \partial r)$ and $(\partial \varphi / \partial r) = \epsilon_1 (\partial \varphi / \partial r)$. From the above solution of the Laplace equation, applying the boundary conditions and after necessary algebraic rearrangements, we then obtain for the reaction field of the binary spherical system (Fig. 1),

$$R = \frac{2m}{a^3} \frac{(\epsilon_1 - 1)}{(2\epsilon_1 + 1)} \frac{\left[1 + \left(\frac{\epsilon_1 + 2}{\epsilon_1 - 1} \right) \frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_1 + 2\epsilon_2)} \left(\frac{a}{b} \right)^3 \right]}{\left[1 + \frac{2(\epsilon_1 - 1)}{(1 + 2\epsilon_1)} \frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_1 + 2\epsilon_2)} \left(\frac{a}{b} \right)^3 \right]}. \tag{5}$$

The permittivity of a mixture, ϵ_2, can be determined by the capacity method, or alternatively, may be approximately calculated with the formula $\epsilon_2 = v_1 \epsilon_1 + v_0 \epsilon_0$,[4] where v_1 and v_0 are the volume fractions of polar and nonpolar components, respectively. It is worth noting that $(a/b) < 1$ by definition;

even if the cavity was surrounded by only a polar monolayer, and if the radius of the cavity and that of the polar molecules are equal, we have $(a/b)^3 \approx \frac{1}{27}$. In addition, the fact that the reaction field increases steeply as the radius of the polar microcluster increases, means that almost all changes in the energy of the excited dipole occurs after the dielectric enrichment of the first coordination shell is completed.

Taking a series expansion of Eq. (5) in terms of the parameter $(a/b)^3 \ll 1$, we obtain an expression for the reaction field in a more suitable form

$$R \approx \frac{2m}{a^3} \frac{(\epsilon_1 - 1)}{(2\epsilon_1 + 1)} \left[1 + \frac{(\epsilon_2 - \epsilon_1)}{(\epsilon_1 + 2\epsilon_2)} \frac{9\epsilon_1}{(\epsilon_1 - 1)(1 + 2\epsilon_1)} \left(\frac{a}{b} \right)^3 \right]. \tag{6}$$

In this expression the influence on the reaction field of a polar microcluster formed around the excited fluorescent molecule is considered as a small correction to Onsager's expression [Eq. (2)] where the excited dipole is immersed in a neat polar solvent. In the present case, however, $\epsilon_1 \approx 50$, $\epsilon_2 \approx 5$; therefore Eq. (6) can be reduced to

$$R \approx \frac{m}{a^3} \left[1 - \frac{9}{2\epsilon_1} \left(\frac{a}{b} \right)^3 \right]. \tag{7}$$

From the above, a maximum change in the dipole energy is approximately $(9/2\epsilon_1)(m^2/a^3)$. For $m \approx 15$ D, $a = 3.5$ Å, this gives the order of magnitude which is compatible with the data of the system investigated.[10]

Note that $(a/b)^3$ is actually the ratio of molecular volumes of the cavity and the polar microcluster, i.e., $b^3 = N\sigma^3 + a^3$, where N is the number of polar solvent molecules in the cluster, and σ is the radius of the polar molecules. If $a \approx \sigma$, then

$$(a/b)^3 \approx \frac{1}{N+1}. \tag{8}$$

Knowing $N = N(t)$, one can determine the time dependence of solvatochromic shift by means of Eq. (5) or Eq. (6). To that end we have to turn to the problem of the formation of the first solvation shell around the excited dipole.

B. Transport of polar molecules to the first coordination shell

We consider an immobile fluorescent probe molecule placed in a dilute solution of mobile polar molecules, e.g., dimethylsulfoxide (DMSO) in the inert solvent toluene. We propose that polar molecules obey the diffusion equation

$$\frac{\partial c}{\partial t} = D \Delta c, \tag{9}$$

which can be solved with appropriate boundary conditions. Here $c(r,t)$ is the concentration of diffusing polar molecules at distance r from the center of the fluorescent molecule at time t after its instantaneous excitation. Spherical symmetry is assumed as usual. We employ an initial condition $c(r,0) = c_0$ for $t = 0$, and $r \geq r_0$. Boundary conditions are determined at a sphere of radius r_0, the average distance of closest approach of two particles. It is worth noting that at $r = r_0$ the energy of dipole–dipole interaction between an ex-
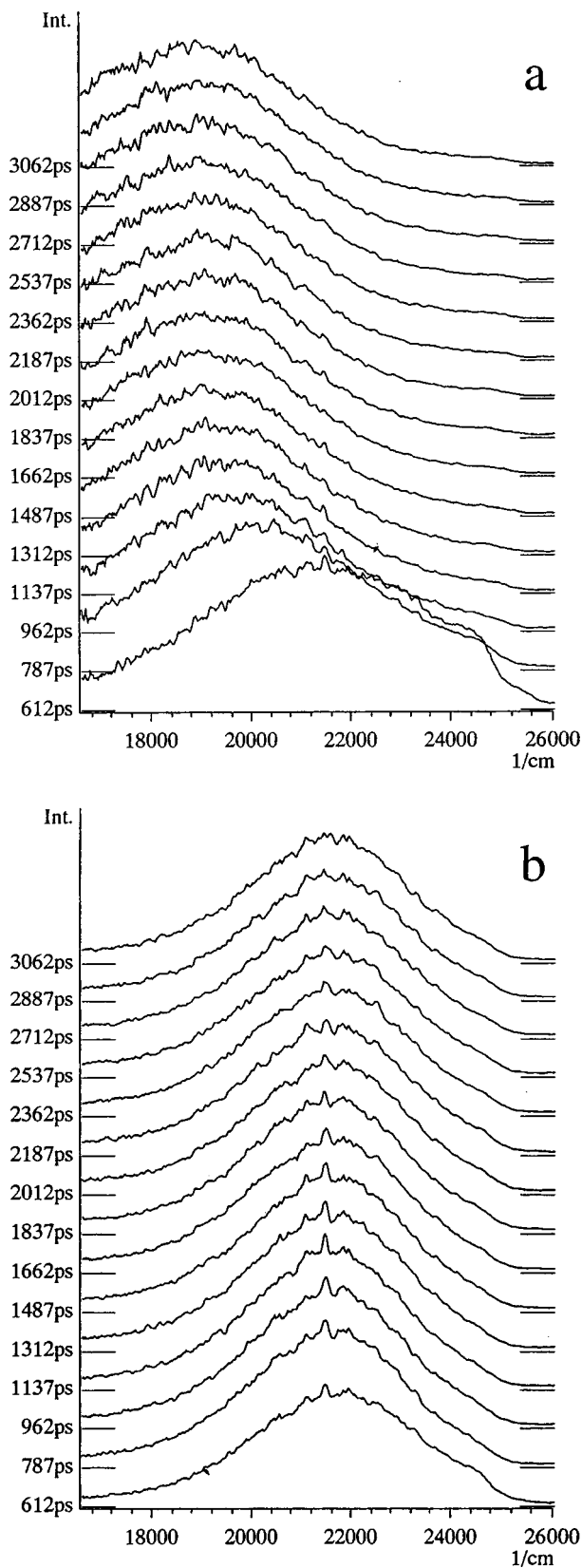
FIG. 2. Histogram of a typical spectro-streak measurement of excited Py(s) DMA spectra in a toluene/DMSO mixture (a) and for comparison in the neat solvent chlorobenzene (b), which has the same permittivity as the mixture of experiment (a).

cited fluorescent dipolar molecule and polar molecules might exceed the thermal energy significantly. Therefore, having reached the first coordination shell, molecules of the polar component become completely unable to diffuse. This problem is similar to the classical problem of colloid coagulation that was first considered by Smoluchowski on the basis of the diffusion equation subjected to the following boundary condition.[11]

$$c = 0, \quad \text{at } r = r_0. \tag{10}$$

This results in the following expression for the diffusion flux:

$$j = 4\pi r_0^2 D \left(\frac{\partial c}{\partial r} \right) \bigg|_{r_0} = 4\pi D r_0 c_0 \left(1 + \frac{r_0}{\sqrt{\pi D t}} \right), \tag{11}$$

where D is the diffusion coefficient, r_0 is the capture radius (in our case this is a radius of the first coordination shell). For times $t \gg r_0^2/D$ the second term within brackets can be neglected; this means that the process becomes steady state. The disturbing feature of Eq. (11) is that for $t \to 0$, $j \to \infty$. However, an integral $\int_0^t j(t')dt'$ exists for finite times and provides the net number of absorbed particles as

$$N(t) = \int_0^t j(t')dt' = 4\pi D r_0 c_0 \left(t + \frac{2r_0\sqrt{t}}{\sqrt{\pi D}} \right). \tag{12}$$

Obviously, the above singularity is a consequence of the chosen boundary condition used since a concentration of polar molecules in the vicinity of an excited fluorescent molecule cannot decrease to zero instantaneously from an initial concentration at the very beginning of the process. Nevertheless, for relatively long times the following expression might be a good approximation,

$$N(t) \approx 4\pi D r_0 c_0 t. \tag{13}$$

Here $4\pi D r_0 \equiv k_d$ is a bimolecular diffusion controlled rate constant.

Collins and Kimball[12] have suggested that within a small separation, $r_0 \approx r$ the rate of a bimolecular process is no longer diffusion controlled, but proceeds according to simple chemical kinetics, described by a constant k of the nature of a specific reaction rate. For large separations between reactants, the process is assumed to be controlled by diffusion. They employed the following boundary condition:

$$D \left(\frac{\partial c}{\partial r} \right) \bigg|_{r_0} = kc. \tag{14}$$

This is the so-called ''radiation boundary condition'' because this problem is similar to the radiation problem in heat-flow theory. However, for long times in the case of diffusion-controlled processes this boundary condition gives almost the same results as that of the Smoluchowski model.[13] In particular, Eq. (13) is valid if r_0 is replaced by r_{eff}, where $r_{\text{eff}} = r_0^2/(r_0 k + D)$. Note, that if $r_0 k \gg D$, then $r_{\text{eff}} \approx r_0$. Although the classic models might give a poor correlation with
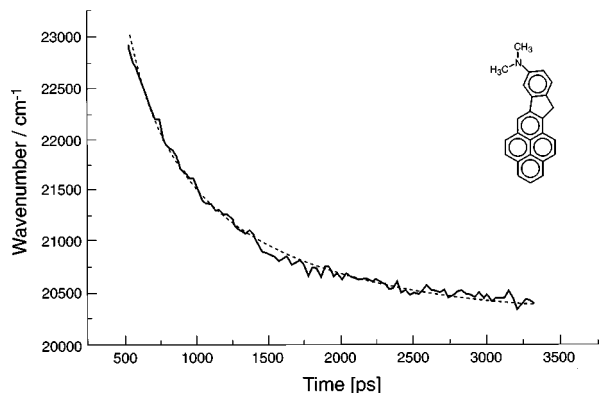
FIG. 3. A typical transient solvatochromic shift of the [corrected (Refs. 4,8)] CT fluorescence band maxima vs time for Py(s)DMA (insert) in a toluene/DMSO (0.4 mol/ℓ) mixture. The dotted line is obtained from fitting with the parameters $\tau = 355$ ps and $\Delta\tilde{\nu} = 3960$ cm^{-1}.

TABLE I. Solvation time τ as function of the DMSO concentration in the toluene solution. $\Delta\tilde{\nu}$ is the bathochromic shift of the charge transfer fluorescence band, $\tilde{\nu}$ indicates the band maximum at long times.

[DMSO] (mol/ℓ)	τ (ps)	$\Delta\tilde{\nu}$ (cm^{-1})	$\tilde{\nu}(\infty)$ (cm^{-1})
0.2	376	2110	22 200
0.4	355	3960	19 962
0.8	142	3517	19 015

experimental data on fast processes in solutions (see for example in Ref. 14), in the present case they are relevant for the ''long-time tail'' of the solvatochromic shift. Preliminary analysis[5] showed that the characteristic times of solvatochromic shift varies from 0.9 ns to 0.25 ns when the concentration of the polar component increases from 0.2 mol/ℓ to ~ 1 mol/ℓ. These values are larger than the characteristic time of establishing the steady state in the framework of the classical Smoluchowski model, $r_0^2/\pi D \approx 80$ ps, justifying its use.

III. EXPERIMENTAL DETAILS

As a fluorescent probe, we used 8-N,N-(dimethylamino)-11H-indeno[2,1-a]pyrene (Py(s)DMA) that contains an N,N-dimethylaniline moiety rigidly coupled to pyrenyl (see insert in Fig. 3).[10(a)] With the excitation of this compound, charge separation occurs, leading to a charge transfer (CT) state with a large dipole moment (15–20 D) and a long fluorescence lifetime of 25–29 ns. A typical concentration of Py(s)DMA in the ground state was 3 $\times 10^{-5}$ M.

In order to measure exciplex fluorescence intensity $I(t,\lambda)$ as a function of time and wavelength we used a spectro-streak photometer that consists of a picosecond Nd: glass laser (pulse width 7 ps) and a single-shot streak camera (Hamamatsu C1370-01) equipped with a grating objective.[4] The solvents used in this work, toluene and dimethylsulfoxide (DMSO), were of spectrograde (Uvasol, Merck). All experiments were carried out at room temperature. Samples were saturated with nitrogen before measurements. For more details, see Refs. 4 and 5.

IV. RESULTS

Typical time-resolved spectra are shown in Fig. 2. The position of the maximum $\tilde{\nu}(t)$ as a function of time is finally fitted to the following formula obtained from Eq. (1) by using Eqs. (7), (8), and (13),

$$\tilde{\nu}(t) = \tilde{\nu}(\infty) + \frac{\Delta\tilde{\nu}}{1 + (t - t_0)/\tau}. \qquad (15)$$

Here $\Delta\tilde{\nu} \equiv 9m^2/2\epsilon_1 a^3$, τ is the half-lifetime of solvatochromic shift, and t_0 is another adjusting parameter since the true zero point is uncertain under the experimental conditions used. Note that $\tilde{\nu}(\infty)$ is well determined experimentally. Moreover, these values obtained from steady-state fluorescence spectra are nearly coincident with those obtained from the corresponding time-resolved spectra averaged over a time interval of interest.[5]

An example of fitting curves is shown in Fig. 3 and the typical values of adjusting parameters obtained are presented in Table I. In the framework of the proposed model $\tau \approx 1/k_d c_0$ so that for a realistic value of $k_d \approx 10^{10}$ ℓ/mol s, and $c_0 = 0.8$ mol/ℓ, one can obtain $\tau \approx 125$ ps which is in good agreement with that obtained by fitting. The values of $\tilde{\nu}(\infty)$ from fitting corresponds well to that obtained from steady state fluorescence spectra. Values of $\Delta\tilde{\nu}$, obtained by fitting, are physically meaningful and give the right order of magnitude for $a = 3 - 3.5$ Å and $m = 15 - 20$ D. Note that in terms of this model the excited dipolar molecule is an unsaturable sink for diffusing polar solvent molecules [Eq. (10)]. In fact, its ''absorbing'' ability[13,15] should be determined by intermolecular interactions, in other words, by the polar-molecule capability of making aggregates. Obviously, the larger the concentration of polar molecules the larger their number in the solvation shell of an excited dipolar molecule. This is in agreement with the experimental fact that $\tilde{\nu}(\infty)$ decreases when the volume fraction of a polar component increases, $\tilde{\nu}(\infty)$ values being the same for stationary and time-resolved spectra.

Thus bearing in mind all simplifying assumptions on which the model is based, one may consider its agreement with experimental data to be satisfactory.

ACKNOWLEDGMENTS

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