

Femtosecond experiments on solvation dynamics of an anionic probe molecule in methanol

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Abstract

Fluorescence up-conversion measurements were conducted to investigate the solvation dynamics of a deprotonated coumarin 343 (C343) in a solution of $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$. In the presence of a base at an appropriate concentration, C343 exists in an anionic form. The observed relaxation kinetics of the solvent polarization exhibit behavior similar to those with a neutral probe molecule with an analogous structure, C152, although the average solvation time for the ionic probe is slightly longer. Theoretical calculations employing three different models for the solvation dynamics were performed: the dielectric continuum model, the mean spherical approximation (MSA) for ionic solvation, and the MSA for dipole solvation. Although the MSA for ionic solvation gives the best prediction for the average solvation time, none of the theories can explain the overall time profile of the solvation dynamics satisfactorily.

Keywords: Solvation dynamics; Anionic probe molecule; methanol

1. Introduction

Recent studies of polar solvation have focused on its dynamical aspects, and its role in chemical processes such as electron and proton transfer [1–6]. Critical comparisons between experimental results and theoretical predictions allow us to treat solvation dynamics beyond simple dielectric continuum models. Experimental [7–17] and theoretical [18–22] developments in this field have been reviewed by Barbara and Jarzeba [1], and by others [2–6].

The time-dependent fluorescence Stokes shift (TDFSS) measurements provide a powerful ultrafast method for elucidating the relaxation dynamics of polar liquids [7–17]. In this experiment a fluorescent probe molecule embedded in a polar solvent is electronically excited, and the solvent polarization relaxation around the newly created solute dipole is examined by monitoring the fluorescence spectrum shift as a function of time.

Although dynamical features of solvation for many liquids have been studied by the TDFSS techniques, there are important unresolved questions concerning the molecular detail of the solvation process [1,2]. One of them concerns the role of probes in determining solvation dynamics. Within simple dielectric continuum theories, solvent properties are the only important determinant of the dynamics. However, experiments show that time scales of the solvation dynamics of a liquid vary with the probe molecule. One property of the solute which should affect the dynamics is the nature of the charge distribution on the probe molecule. Several theoretical treatments where molecularity of the solvent is considered predict different dynamical behaviors of solvation depending on the nature of the charge on the probe.

The purpose of this work is to investigate the effect of permanent probe molecule charge on the solvation dynamics. We have chosen coumarin 343 (C343) (Fig. 1) and methanol as the solvation probe molecule and solvent respectively and studied the solvation dynamics of deprotonated C343 in methanol using TDFSS. Under our experimental conditions, C343 exists in an ionic form C343^- with a negative permanent charge. We compare these new results with previous studies of C152 (Fig. 1) [9], a neutral analogue of C343 with a

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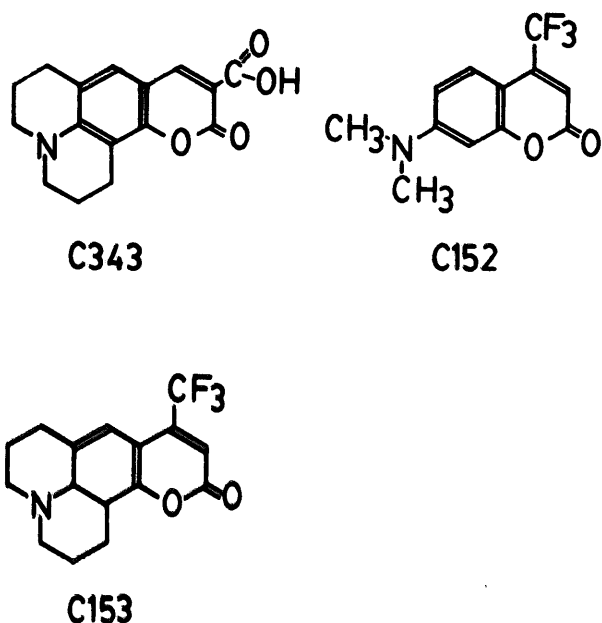


Fig. 1. Solvation probe molecules.

similar structure, in the same solvent. Kahlow et al. calculated solvation dynamics in methanol using several theoretical models and reported dielectric relaxation data [9,23]. Recently, Barthel et al. [24] measured the dielectric relaxation of methanol in the high frequency region with high accuracy.

We first describe static absorption and emission spectra of C343 in a solution of $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ as a function of CH_3ONa concentration. Fluorescence up-conversion data are reported in the next section. Finally, theoretical calculations are performed for the methanol solvation by employing several models and newly reported dielectric data from Barthel et al.

2. Experimental details

The apparatus for the femtosecond up-conversion has been described elsewhere [25]. Briefly, the second harmonic of a continuous-wave mode-locked (76 MHz) neodymium-doped yttrium aluminum garnet laser synchronously pumped a two-jet dye (HITCI, saturable absorber; styryl 8, gain jet) laser which produced 70 fs full width at half-maximum (FWHM) pulses centered at 792 nm. The pulses were amplified through a gain dye jet (styryl 8) pumped by a copper vapor laser operating at a repetition rate of 8.2 kHz, and the second harmonic produced in a 1 mm potassium dihydrogen phosphate crystal excited the sample in a quartz cell with an optical path length of 1 mm. A transient fluorescence signal was monitored by detecting the light at the sum frequency produced by mixing the residual fundamental laser with the fluorescence. Sample concentrations were adjusted so that the optical density

at excitation wavelength was around 1. An instrument response function had roughly a 260 fs FWHM.

The C343 and methanol were purchased from Eastman Kodak and Aldrich respectively and used without further purification. Small pieces of metal sodium were embedded in pure methanol to make a base solution of $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$.

Static absorption and fluorescence spectra were recorded on Shimadzu UV160 and Spex Fluorolog instruments, respectively. All the measurements were made at ambient temperature (22 °C).

3. Results and discussion

3.1. Static absorption spectroscopy and static emission spectroscopy

The absorption spectrum of C343 in methanol shifts to a higher energy when a base solution is added, as shown in Fig. 2. The concentration of C343 is 2.3×10^{-4} M. The base is a solution of CH_3ONa in methanol, which is fully dissociated into Na^+ and CH_3O^- , and concentrations of the solution in Fig. 2 range from 0 to 2.3×10^{-4} M. In the absence of the base, the spectrum is peaked at 445 nm. With increasing base concentration, the spectrum shifts to blue, showing an isosbestic point at 420 nm. No significant change in the spectrum is observed when the base concentration is increased beyond 2.3×10^{-4} M. The same process with a weaker basic solution such as $\text{CH}_3\text{COONa}-\text{CH}_3\text{OH}$ and C343 exhibits a similar spectrum change, a blue shift with an isosbestic point. For a weak base, the base concentration necessary to shift the spectrum completely is much higher than for a strong base. All the observations indicate that the protonated C343 is in equilibrium with the deprotonated C343, and the absorption

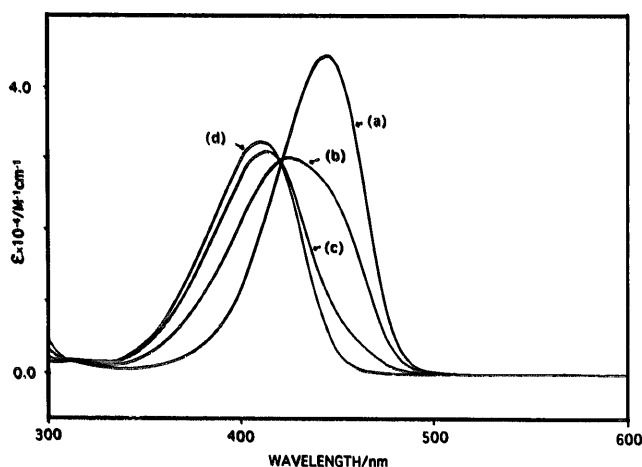


Fig. 2. Steady-state absorption spectra of C343 in CH_3ONa -methanol solutions as a function of CH_3ONa concentration: curve (a), 0 M; curve (b), 0.74×10^{-4} M; curve (c), 1.5×10^{-4} M; curve (d), 2.3×10^{-4} M. The concentration of C343 is 2.3×10^{-4} M.

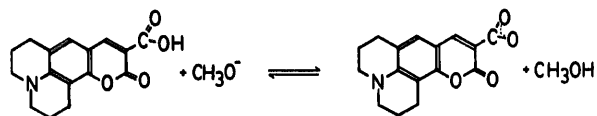
spectrum peaked at 410 nm is due to the ionic species (Scheme 1).

The spectral changes of C343 in the presence of base have already been reported for ethanol [26] and water [27] solvents and attributed to the acid-base reactions of C343.

Similarly, the fluorescence spectrum of C343 shows a blue shift on addition of the base solution of $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$. Fig. 3 shows a change in the normalized fluorescence spectra excited at 396 nm, as a function of base concentration. Spectrum (d) in Fig. 3 is a fully shifted spectrum. Since we observed no change in the fluorescence spectrum by changing the excitation wavelength, we conclude that the solute was totally ionized in the presence of the base of this concentration. We also investigated the effect of excessive base, and no significant change in the static fluorescence spectra was observed.

3.2. Time-resolved spectroscopy

Fig. 4 shows two examples of the fluorescence up-conversion signals at the red and blue sides of the emission spectrum of C343 in a $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solution. The base concentration was adjusted so that the ionic form of C343 exists predominantly over the neutral species. This was verified by observing the insensitivity of the static emission spectrum to the excitation wavelength. The rapid decay and rise in the



Scheme 1.

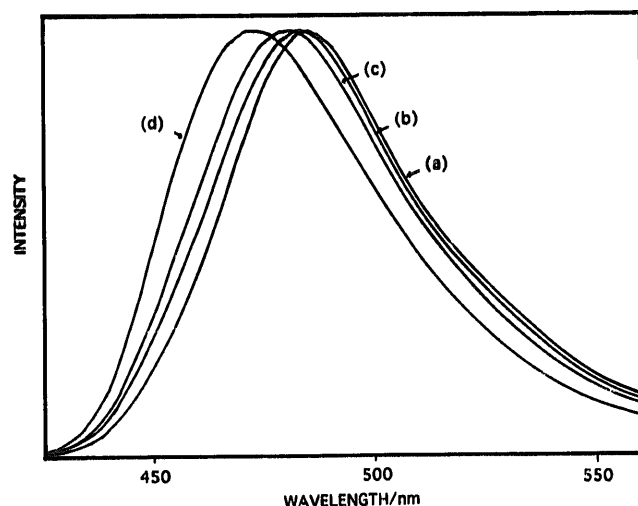


Fig. 3. Steady-state fluorescence spectra of C343 in $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solutions as a function of CH_3ONa concentration: curve (a), 0 M; curve (b), 3.8×10^{-7} M; curve (c), 1.5×10^{-6} M; curve (d), 3.8×10^{-5} M. The excitation wavelength is 396 nm. The concentration of C343 is 4.7×10^{-6} M. The fluorescence intensities are normalized.

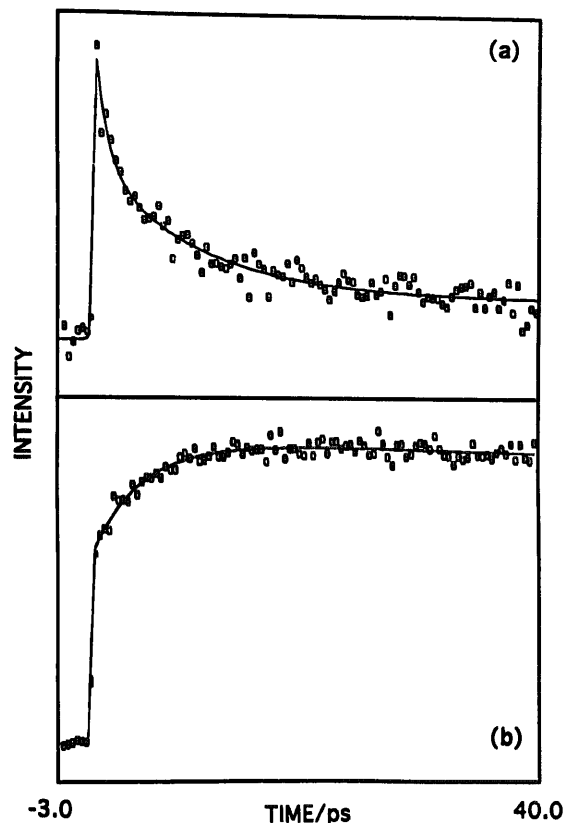


Fig. 4. Transient fluorescence dynamics at (a) 433 nm and (b) 483 nm of C343 in a $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solution. The concentrations of C343 and CH_3ONa are about 3.0×10^{-4} M and 4.5×10^{-4} M respectively. The excitation wavelength is 396 nm. The curves through the experimental data are the best fits with a three-exponential function $I(t) = \sum_i A_i \exp(-t/\tau_i)$, where the slowest component ($\tau_3 = 10$ ns) corresponds to the population depletion of the excited state. The two faster components represent the transient fluorescence dynamics.

fluorescence intensity at the wavelengths on the blue and red edges respectively reflect a red shift of the spectrum as a function of time owing to the solvent polarization relaxation. The fluorescence up-conversion measurements were done at nine different wavelengths to obtain time-resolved emission spectra.

In Fig. 5 a transient emission spectrum at 0.4 ps after the laser excitation is shown, which is reconstructed by fitting the fluorescence intensities at the various wavelengths, using a log-normal function [28]. Fig. 6 portrays time-dependent fluorescence spectra of the deprotonated C343 in methanol in the time range of 0.2 to 20 ps. The spectral dynamics in Fig. 6 exhibit a continuous evolution of the emission maximum, as observed in other dipolar solvation dynamics experiments [7-17]. We investigate the base concentration dependence on the up-conversion signals from 3.0×10^{-4} to 1.5×10^{-3} M with a C343 concentration of 3.0×10^{-4} M, and no significant change is observed. The deprotonated C343 may exist in an ion-pairing form with the cation Na^+ because of the Coulomb

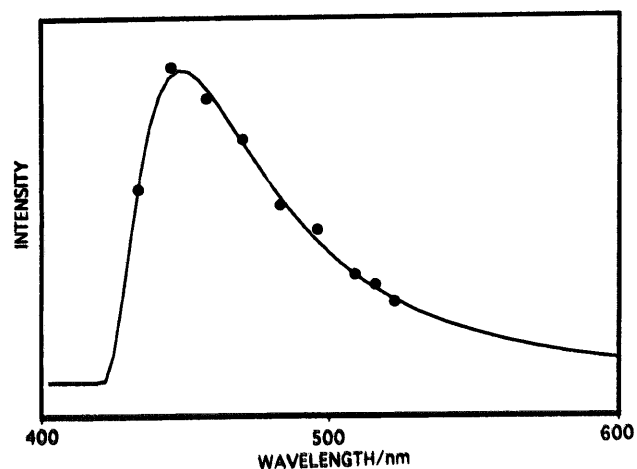


Fig. 5. Time-resolved spectrum of C343 in a $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solution at 0.4 ps after the laser pulse. ●, experimental data; —, log-normal function fit to the data. The concentrations of C343 and CH_3ONa are about 3.0×10^{-4} M and 4.5×10^{-4} M respectively. The excitation wavelength is 396 nm.

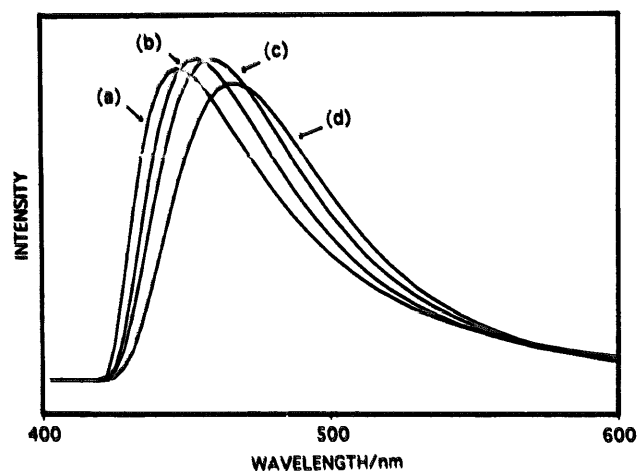


Fig. 6. Time-resolved spectra of C343 in a $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solution at 0.2 ps (curve (a)), 2.0 ps (curve (b)), 6.0 ps (curve (c)), 20.0 ps (curve (d)) after the laser excitation. The concentrations of C343 and CH_3ONa were about 3.0×10^{-4} M and 4.5×10^{-4} M respectively. The excitation wavelength was 396 nm. The curves are log-normal fits to the data (see Fig. 5).

attractive force. However, since the excess amount of the base does not affect the static absorption or emission spectra or the time-resolved emission spectra, we conclude that the effect of ion pairing on the solvation dynamics of C343^- in methanol is negligible.

The small effect of the ion pairing is also supported by some values of an association constant K_A for ion-pair formation [29]. K_A is defined as

$$K_A = \frac{c_{\text{IP}}}{c_{\text{M}^+} + c_{\text{A}^-}} \quad (1)$$

where c_{IP} , c_{M^+} and c_{A^-} are the concentrations of the ion pair, free cation and free anion respectively. The value of K_A was calculated for several systems of salts

in polar solvents and is normally around 10^2 M^{-1} . For example, the value of K_A of CsCl in ethanol is estimated to be $1.51 \times 10^2 \text{ M}^{-1}$. Considering that the concentrations of C343^- and Na^+ of our system are of the order of 10^{-4} M, the fraction is roughly estimated to be 0.01; about 1% of the free ions associate to form an ion pair.

Traditionally, solvent polarization relaxation is related to the relaxation function $C(t)$ defined by

$$C(t) = \frac{\nu_{\text{max}}(t) - \nu_{\text{max}}(\infty)}{\nu_{\text{max}}(0) - \nu_{\text{max}}(\infty)} \quad (2)$$

where $\nu_{\text{max}}(t)$ is the frequency of the fluorescence maximum at a time t . The fluorescence data yield the experimental $C(t)$ shown in Fig. 7. $C(t)$ shows a non-exponential behavior and can be fitted well by a double-exponential function $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$, where the sum of the A_i values is normalized to unity. The values obtained for A_i and τ_i are summarized in Table 1, together with an average solvation time defined by

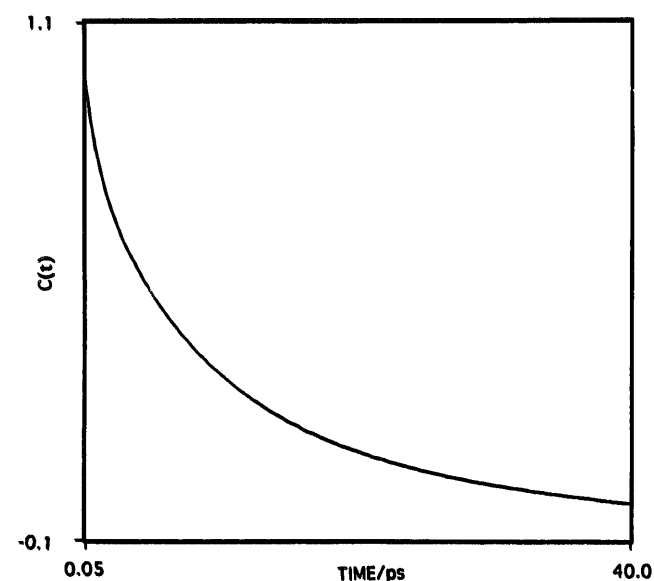


Fig. 7. Spectral response function $C(t)$ of C343 in a $\text{CH}_3\text{ONa}-\text{CH}_3\text{OH}$ solution. The concentrations of C343 and CH_3ONa were about 3.0×10^{-4} M and 4.5×10^{-4} M respectively.

Table 1
Transient solvation parameters for methanol solutions obtained experimentally (C152 [9] and C343^-) and theoretically

	τ_1 (ps)	A_1	τ_2 (ps)	A_2	$\langle \tau \rangle$ (ps)
C152	1.2	0.40	9.6	0.60	6.2
C343	1.0	0.21	10.3	0.79	8.3
DC	0.60	0.58	6.8	0.43	4.0
MSA, ion	0.73	0.54	10.3	0.46	6.3
MSA, dipole	1.1	0.33	17.7	0.67	16.2

$$\begin{aligned} \langle \tau \rangle &= \int dt C(t) \\ &= A_1 \tau_1 + A_2 \tau_2 \end{aligned} \quad (3)$$

The results for the solvation dynamics of C152, a neutral probe molecule, are also shown in Table 1 [9]. The dynamics are generally similar. Both can be described well by a double-exponential function with quite similar time constants of about 1 and 10 ps. This leads to one of the main conclusions of this work, namely that the permanent charge on the probe molecule does not affect the solvation dynamics in methanol.

Recently Rosenthal et al. [30] studied solvation dynamics in methanol by both the up-conversion technique and the molecular dynamics simulation. Because of their high instrument resolution of about 115 fs FWHM, they could observe very fast dynamics due to inertial motion of the solvent molecules [15]. For the system where C153 (Fig. 1) was used as a probe, the response function $C(t)$ was analyzed by a function which is a sum of one gaussian and two exponential terms. The gaussian term with a time constant of 80 fs and an amplitude of 22% describes the fast inertial response, which is not observed in our experiment owing to the limited time resolution. The remaining two exponential terms with time constants of 0.56 ps (23%) and 8.1 ps (34%), giving an average time of 5.1 ps, concerns the diffusive part of the solvation dynamics which we are observing in this work. This average time is quite similar to that of C152, which shows the structural effect of the 7-amino group on the solvation dynamics is minor.

On closer examination of the $C(t)$ functions, one can find that the average solvation time of C343⁻ is slightly longer than those of C152 or C153. Here we briefly consider possible origins of the slight difference between the dynamics of the ionic and neutral probe molecules. First, the negative charge on the ionic C343, not present in C153 or C152, creates a large reaction field, which affects the solvent polarization relaxation. Detailed theoretical studies are required to clarify this question. The second candidate for the different dynamics is associated with recent work of Huppert and coworkers [31,32] and Chapman and Maroncelli [33], who studied the effect of added salt on the solvation dynamics for various solutions. They noted that the spectral evolution due to dynamics of ionic atmosphere created by the salt takes place on a time scale of 1–10 ns for acetonitrile. In the case of methanol, however, Chapman and Maroncelli [33] concluded that no ionic contribution to the dynamics is observable by their apparatus with time resolution of 50 ps. The slow dynamics of the ionic probe in our work may come from the dynamical effect of the ionic environment caused by the counter-ion of Na⁺.

3.3. Comparison with theoretical calculations

We employ three different solvation dynamics models to compare the experimental results to theoretical predictions: a dielectric continuum (DC) model [18], the mean spherical approximation (MSA) for ionic solvation, and the MSA for dipolar solvation [19]. Detailed explanations of the theories are well described in the literature. Below, we shall outline the approaches for the calculations very briefly.

Kahlow et al. [9] made a thorough comparison of their experimental data on solvation dynamics in methanol with the same three theoretical models using dielectric data reported by Barthel et al. [23]. They found that the experimental $C(t)$ decay was in excellent agreement with the DC predictions, and both the MSA theories tended to give longer decays than the experiments. Experimental results for other alcohol solvation dynamics were well described in terms of the DC model [12], and methanol seemed to follow the behavior of other alcohols.

However, as often pointed out in the literature [1,2], the theoretical predictions strongly depend on the reliance on experimental $\epsilon(\omega)$ dielectric relaxation data. In particular, information on $\epsilon(\omega)$ in the high frequency regime must be extrapolated because of the difficulty in the experimental technique. Recently, Barthel et al. [23] obtained dielectric data for methanol using an apparatus which has been improved to obtain the data in the microwave region. We use these newly reported data for the comparison of the experiments to theoretical predictions.

The DC model treats the solute as a cavity of radius a , with a point dipole at the center. The cavity is assumed to be filled with a dielectric material having a dielectric constant ϵ_c . The solvent is treated as a uniform dielectric medium. A quantity associated with $C(t)$ is the time-dependent reaction field $R(t)$:

$$C(t) = \frac{R(t)}{R(0)} \quad (4)$$

The frequency-dependent reaction field $R(\omega)$, the Fourier transform of $R(t)$, can be expressed as

$$R(\omega) = r(\omega) \mu(\omega) \quad (5)$$

where

$$r(\omega) = \frac{2}{a^3} \frac{\epsilon(\omega) - \epsilon_c}{\epsilon_c [2\epsilon(\omega) + \epsilon_c]} \frac{\epsilon_c + 2}{3} \quad (6)$$

and $\mu(\omega)$ is the Fourier transform of the time-dependent dipole moment of the solute.

In contrast with the DC model the MSA treatment explicitly considers the molecularity of the solvent environment. In the MSA model for ion solvation, one considers a neutral hard sphere of radius λ_1 embedded

in a polar solvent consisting of hard polarizable spheres of radius r_s . The solvent polarization relaxation, followed by an instant ionization of the neutral sphere at time $t=0$, is described by the solvation correlation function $S(t)$ which is equal to $C(t)$. The Laplace transform of $S(t)$ is given by

$$S(p) = \frac{\chi(p) - \chi(0)}{p[\chi(\infty) - \chi(0)]} \quad (7)$$

Within the MSA, $\chi(p)$ is expressed as

$$\chi(p) = \frac{1}{2R_i} \frac{1 - 1/\epsilon(p)}{1 + \Delta(p)} \quad (8)$$

and $\Delta(p)$ can be well approximated by

$$\Delta(p) = \frac{3r_s}{R_i} \{108^{1/3} [\epsilon(p)]^{1/6} - 2\}^{-1} \quad (9)$$

In the calculation we assume the value of R_i/r_s to be 3.

The MSA model for dipole solvation is similar to that for ion solvation. The problem can be solved only for the special case where $r_s = R_i$. The Laplace transform of $S(t)$ is given by

$$S(p) = \frac{\xi(p) - \xi(0)}{p[\xi(\infty) - \xi(0)]} \quad (10)$$

where

$$\xi(p) = \frac{1 - 9/[h(p) + 4]}{2} \quad (11)$$

and

$$h(p) = 108^{1/3} [\epsilon(\omega)]^{1/6} \quad (12)$$

Necessary knowledge of the dielectric function $\epsilon(\omega)$ can be obtained from the recent report by Barthel et al. [24] on the dielectric dispersion and loss experiments on methanol [34]. They fitted the dielectric relaxation spectra of methanol with a multi-Debye form

$$\epsilon(\omega) = \epsilon_\infty + \sum_j \frac{(\epsilon_j - \epsilon_{\infty j})}{(1 + i\omega\tau_j)} \quad (13)$$

Barthel et al. [24] observed three different dispersion regions ($N=3$). The parameters for the dielectric function $\epsilon(\omega)$ used in the present calculation are summarized in Table 2.

The solvation dynamics calculated by the three models are shown in Fig. 8 together with double-exponential

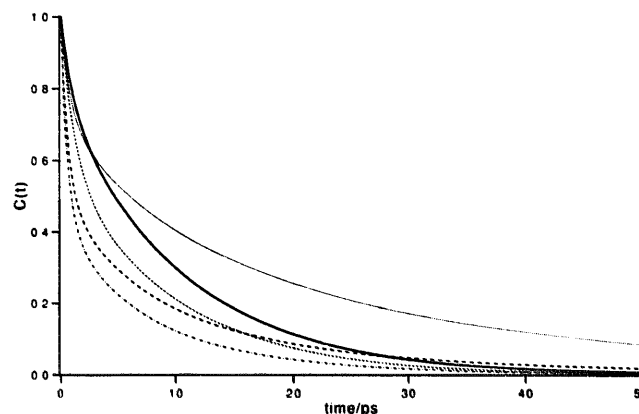


Fig. 8. Spectral response functions $C(t)$ for methanol and deprotonated C343 (—) and C152 [9] (---) with DC (-·-·), MSA ion (- - -) and MSA dipole (·····) calculations. Dielectric relaxation data from [24] were used.

functions which are the best fit for the experimentally obtained $C(t)$ for C152 and the ionic C343⁻. The three theoretical predictions show non-exponential behaviors and are approximated well by a double-exponential function. Parameters obtained for the decay by numerical fits are listed in Table 2, together with average solvation times obtained by integrating $C(t)$ over time t . As seen from Fig. 8 and Table 2, the DC model and MSA for ionic solvation predict fast initial responses which account for about 50% of the total relaxation. These fast decays are due to a dielectric dispersion regime of the highest frequency region ($\tau_3 = 1.12$ ps), showing the importance of reliable dielectric relaxation data for these calculations. The MSA for ionic solvation gives a better prediction for the average solvation time than does the DC model. However, it should be noted that none of the theories can predict the overall dynamical behavior reasonably well. It is interesting to see that the experimental decays lie between the predictions by the MSA treatments for ion and dipole. Since the dipole in this model is assumed to be a point dipole and the ion can be considered as a part of a "dipole" with charges separated infinitely, it is reasonable that the experimental probes which have a finite-length dipole give dynamics between those of the two extreme cases.

4. Conclusion

We have employed the fluorescence up-conversion technique to investigate the solvation dynamics of deprotonated C343 as an ionic probe molecule in methanol. The observed kinetics of solvent polarization relaxation for the ionic probe are similar to that for C152, a neutral probe molecule, although the average solvation time for the ionic probe is slightly longer. Calculations of the solvation dynamics based on three different

Table 2
Dielectric relaxation parameters of methanol at 25 °C from [24]

ϵ_1	τ_1 (ps)	$\epsilon_{\infty 1} = \epsilon_2$	τ_2 (ps)	$\epsilon_{\infty 2} = \epsilon_3$	τ_3 (ps)	$\epsilon_{\infty 3} = \epsilon_\infty$
32.50	51.5	5.91	7.09	4.90	1.12	2.79

theoretical models, namely the dielectric continuum model, the MSA for ionic solvation, and the MSA for dipole solvation, were performed by making use of newly available dielectric relaxation data reported recently. Although the MSA model for ionic solvation predicts the average solvation time well, none of the theories can explain the overall dynamical behavior satisfactorily.

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