

Dipolar Solvation Dynamics

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The dynamics of solvation of newly created dipoles is discussed. Developments of standard continuum models to include non-Debye dielectric response and saturation effects are described. Equilibrium and non-equilibrium molecular-dynamics simulations of ST2 model water are described. The simulations predict non-exponential solvation dynamics as a result of the radial dependence of the solvent response. Experimental data on time-resolved fluorescence Stokes shifts for a number of probe molecules in a variety of polar solvents are discussed in the context of the theoretical results.

1. Introduction

The influence of solvent dynamics on chemical reactions is a topic that has generated a good deal of experimental and theoretical study over the past decade. Solvent friction, which may often determine the frequency factor for the reaction, may be divided into two kinds, collisional (*i.e.* momentum and energy exchange) and dielectric. At the simplest level, both types of friction can be characterized by macroscopic quantities, the viscosity and the longitudinal relaxation time, τ_L . Recent theories suggest that for adiabatic electron transfer reactions the rate of reaction is proportional to $\tau_L^{-1,1-5}$. Although viscosity can be measured directly, τ_L is derived *via* a theoretical relation from experimental values of the dielectric relaxation time τ_D . (For a solvent with a single Debye response, *vide infra*, $\tau_L = [(2\epsilon_\infty + 1)/(2\epsilon_0 + 1)]\tau_D$, where ϵ_0 and ϵ_∞ are the zero and infinite frequency dielectric constants, respectively.) Thus, even at this level there is more uncertainty about the dielectric behaviour than about the normal friction.[‡]

To gain more insight into the timescales and mechanism of polar solvation we have been studying time-resolved fluorescence Stokes shifts of polar solutes in polar solution. The relaxation of the solvent around the newly formed excited state dipole leads to a red shift of the fluorescence spectrum. This shift may be represented by a correlation function $C(t)$ where

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

Here $\bar{\nu}(t)$ is the mean fluorescence frequency at time t . The technical details of determining $C(t)$ experimentally have been discussed elsewhere.⁷⁻¹² $C(t)$ may also be

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[‡]By this remark we do not intend to imply that viscosity is the appropriate measure of collisional friction on a molecular scale. See ref. (6) for a discussion of this point.

calculated; for a continuum model with a single Debye relaxation time, $C(t)$ decays exponentially with time constant τ_L . The strength and directionality of polar interactions suggest that the molecular nature of the solvent may be revealed more directly in polar solvation than in studies of friction between nonpolar molecules, where Stokes law often works surprisingly well.

In 1977 Onsager suggested that solvation (of electrons) proceeded on a range of timescales, with the near-neighbour solvent molecules reaching equilibrium last.¹³ Several theoretical models have been developed that support Onsager's suggestion. Wolynes¹⁴ applied the mean spherical approximation (MSA) to solvation dynamics and found that solvation could be roughly described by two times, τ_L and a longer time constant, τ_G , associated with the rearrangement of the solvation layer(s). A more detailed MSA calculation was carried out by Rips *et al.*¹⁵ For a single Debye response, non-exponential solvation was found with short-time response close to τ_L and long time response close to τ_D . Loring and Mukamel have also derived a microscopic expression for the dielectric response as a function of frequency and wavevector k and applied it to a lattice model of a polar fluid. Again a range of timescales is found for the relaxation. Both theories only predict exponential decay behaviour in the limit $\epsilon_{\text{bulk}} \rightarrow 1$ since here $\tau_L = \tau_D = \tau_{\text{or}}$, where τ_{or} is the rotational reorientation time. This limit is approached for a very dilute solution of dipolar molecules in a non-polar solvent. Loring and Mukamel point out that in the presence of interaction between dipoles no simple relation exists between τ_D and τ_L , and it may be inappropriate to apply the Debye model to pure polar liquids. Current theoretical models rest on two basic assumptions: (a) a continuum model for the solvent and (b) linear response theory. As noted by Rips *et al.*¹⁵ most discussions have concentrated on aspect (a), because the validity of linear response is by no means obvious. In section 3 we present molecular-dynamics simulations aimed at addressing this question. By 'continuum model' most authors mean a single or possibly a sum of Debye responses. From extensive studies of dielectric relaxation, it is well known that many solvents, particularly associating or highly polar solvents, do not have dielectric responses well characterized by the Debye equation.¹⁷ In addition, the experimental data generally relate to molecules with complex shapes, rather than the simple spheres assumed in the theories. Finally, the continuum models are based on the Onsager reaction field¹³ which 'turns on' the solvent dielectric response with a step function at the cavity radius. This is unlikely to be realistic in high dielectric constant solvents (such as propylene carbonate and *N*-methyl amides) and it may be necessary to consider a dielectric response with both frequency and spatial dependence. Before ruling out 'continuum model' descriptions of solvation dynamics it seems necessary to consider the following more general forms of the theory.

2. Continuum Models of Solvation Dynamics

A straightforward approach to the calculation of the Stokes shift correlation function [eqn (1)] is to use a dielectric continuum model.¹⁹⁻²⁴ The essential result of these studies is that the experimentally obtained correlation function $C(t)$ should decay exponentially with lifetime τ_L .

The basic premises of the previous continuum models are: (i) that the solute probe molecule may be represented by a point dipole at the centre of a spherical cavity, as in the Onsager approach, and that the point dipole is instantaneously changed in magnitude and/or orientation on absorption of a photon by the solute, and (ii) that the solvent may be described as a homogeneous, isotropic and frequency-dependent dielectric medium with the frequency dependence given by the Debye equation²⁵

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_0 - \epsilon_{\infty}}{1 + i\omega\tau_D} \quad (2)$$

where ϵ_0 and ϵ_∞ are the static and optical frequency dielectric constants, and τ_D is the dielectric relaxation time constant.

Recently we have generalized this approach in several ways. In particular, we have examined the behaviour of the $C(t)$ obtained when the solute cavity is described by an arbitrary ellipsoid instead of a sphere. The effect of non-Debye forms for $\epsilon(\omega)$ on the $C(t)$ has been studied. The dielectric response functions used here, the Davidson-Cole and Cole-Cole forms, adequately describe many solvents of experimental interest. Lastly, the requirement of homogeneity of the dielectric medium has been generalized to allow use of a radially and frequency-dependent dielectric response. This allows us to include dielectric saturation effects that may become important as μ_c (the excited state solute dipole moment), and ϵ_0 become large within the framework of a continuum model for the solvent relaxation.

We discuss here the substitution of a non-Debye dielectric response in the model, and the inclusion of dielectric saturation effects. By dielectric saturation, we mean the local reduction of the dielectric constant near the solute probe dipole from its bulk value ϵ_0 , to some reduced value that may be as low as ϵ_∞ . The third portion of this work, on the effects of non-spherical solute shapes on the predicted solvation dynamics, has been described previously.²⁶

Non-Debye Dielectric Response

The simplest form of the dielectric frequency-dependent permittivity, the Debye equation, $\epsilon(\omega)$ is given in the Debye equation, eqn (2). The single dielectric relaxation time τ_D is related to the single particle reorientation time τ_{or} in a given solvent. Here we will discuss results obtained using two of the most widely used dielectric response functions given by Davidson and Cole (DC)²⁷ and Cole and Cole (CC),²⁸ which involve distributions of relaxation times. The Davidson-Cole equation for $\epsilon(\omega)$ is

$$\epsilon_{DC}(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + i\omega\tau_0)^\beta}, \quad 0 < \beta \leq 1. \quad (3)$$

The Cole-Cole equation is given by

$$\epsilon_{CC}(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^\delta}, \quad 0 < \delta \leq 1. \quad (4)$$

The distribution of relaxation times τ_0 is symmetric for the CC function, with the distribution becoming broader as δ is decreased from unity. The DC distribution is truncated at τ_0 , with no relaxation times greater than τ_0 .

Following the procedure described in ref. (26), we have calculated the $C(t)$ assuming a CC dielectric response. Fig. 1 displays these results, along with the previous results obtained assuming a DC response. The prediction for a Debye response²²⁻²⁴ is the straight line decaying as τ_L in fig. 1. As the exponents β and δ (of the DC and CC response functions, respectively) are decreased from unity (within the physically realistic range of 0.4 to unity), the calculated solvation response function $C(t)$ deviates more strongly from the $C(t)$ obtained for the Debye response. The $C(t)$ curves are markedly non-exponential with both DC and CC results fitting well to the Kohlrausch-Williams-Watt (KWW)^{29,30} function, given by

$$C(t) = \exp[-(t/\tau)^\alpha], \quad 0 < \alpha < 1. \quad (5)$$

In all cases the CC curve decays more rapidly than the DC curve, with the discrepancy between the results becoming larger as the exponents β and δ are decreased.

It is clear from fig. 1 that the $C(t)$ curves are very sensitive to the form of the dielectric response chosen for the model. Small deviations from Debye type dielectric

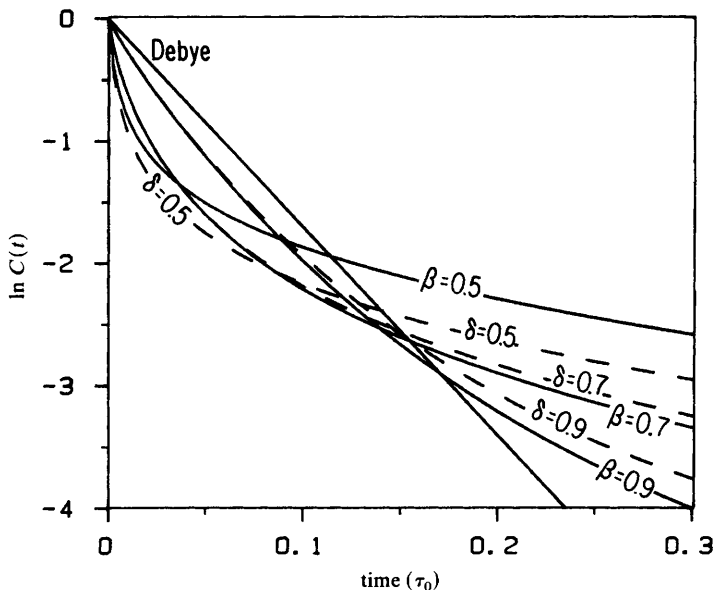


Fig. 1. The natural log of $C(t)$ is plotted *versus* the reduced time in units of τ_0 . For the curves shown here, $\epsilon_0 = 25.0$ and $\epsilon_\infty = 1.0$. $C(t)$ curves calculated for Davidson-Cole exponent values of 0.5, 0.7 and 0.9 are labelled β ; curves calculated for the same Cole-Cole exponent values are labelled δ .

response lead to highly non-exponential behaviour of the $C(t)$. Furthermore, these results suggest that experiments on the femtosecond timescale will be required to resolve the solvation dynamics in some solvents, and that the earliest time dynamics may not be resolvable with fluorescence techniques. Femtosecond absorption hole-burning experiments may prove to be a useful probe of solvation dynamics.³¹

Dielectric Saturation Effects

Our modified continuum model, including dielectric saturation effects, is based on only a few assumptions beyond those of the earlier models.²²⁻²⁴ We assume that the position dependent dielectric tensor $\epsilon(\mathbf{r}, \omega)$ is diagonal in \mathbf{r} , and is a scalar function of \mathbf{r} . We assume that the local reduction of $\epsilon(\mathbf{r}, \omega)$ near the solute, which is caused by polarization of the solvent molecules by the field of the solute dipole, is manifested only by a reduction of the static dielectric constant ϵ_0 . Further, it is assumed that aside from the newly introduced radial dependence, the dielectric response is of the Debye type in the frequency domain, *i.e.*

$$\epsilon_{\text{eff}}(\mathbf{r}, \omega) = \epsilon_\infty + \frac{\epsilon_0(\mathbf{r}) - \epsilon_\infty}{1 + i\omega\tau_D}. \quad (6)$$

We have chosen functional forms for $\epsilon_0(\mathbf{r})$ with two parameters. The results presented here were obtained using

$$\epsilon_0(\mathbf{r}) = \epsilon_0(a) + [\epsilon_{\text{bulk}} - \epsilon_0(a)] \tanh [(r - a)/\lambda] \quad (7)$$

where the parameter $\epsilon_0(a)$ is the reduced value of the static dielectric constant at the solute radius, and λ is the length scale of the solvent region over which saturation is important. Saturation effects are expected to be most important for small solutes (small a), large dielectric constant ($\epsilon_0 > 50$), and large solute dipoles μ_c .

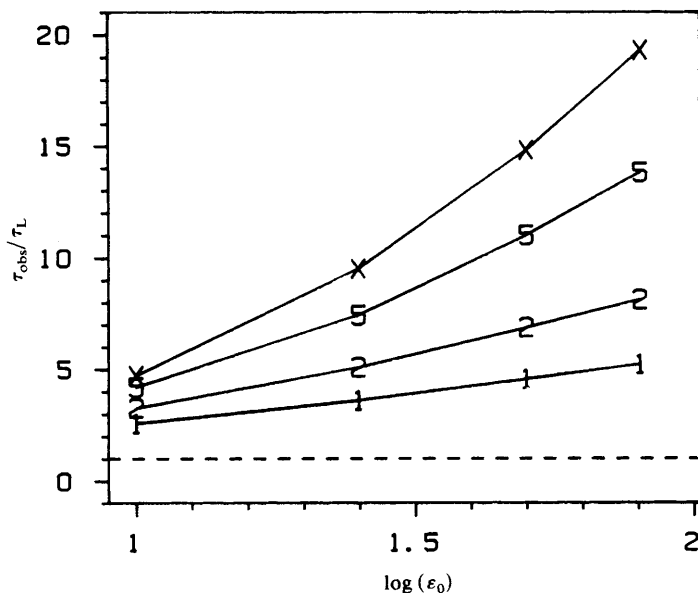


Fig. 2. Summary of results from saturation effect continuum model calculations. The ratio of the calculated solvation time τ_{obs} to τ_L versus the \log_{10} of ϵ_0 , the static dielectric constant, is plotted for four values of the parameter λ . Points labelled by 1, 2, 5 and \times are for values of λ/a equal to 1, 2, 5 and 10.

The time-dependent reaction field $R(t)$ is proportional to the solvation energy in a linear response theory.²²⁻²⁴ When normalized by $R(0)$, $R(t)$ is equivalent to the $C(t)$ obtained experimentally. To obtain the time-dependent reaction field, we calculate the frequency dependent reaction field $R(\omega)$ and do a numerical inverse Fourier transform. $R(\omega)$ has been obtained by solution of the quasi-static boundary value problem for the electric field potential ϕ .³² The potential ϕ has been found in turn by solving the Laplace equation for the electric field displacement D . We have carried out about one hundred simulations for values of ϵ_0 between 10 and 250, for values of the saturation length scale λ between one and ten times the solute radius a . The results are shown in fig. 2. For all the data shown, the value of $\epsilon_0(a)$ (the static dielectric constant at the solute cavity boundary) was set equal to ϵ_∞ (i.e. we assume complete dielectric saturation). This will likely be a reasonable assumption for a small solute having a giant solute dipole, μ_c . For small μ_c and large solute size, $\epsilon_0(a)$ approaches the bulk solvent dielectric constant ϵ_{bulk} . Most Stokes shift experiments performed to date have been done on moderate sized probe fluorophores that are 1.5 to 3 times the size of the solvent. The magnitude of the excited-state probe dipoles used have been moderate to large, ca. 5-15 D† greater than the ground state. Therefore we expect that $\epsilon_0(a)$ should have a value intermediate between ϵ_∞ and ϵ_{bulk} to model the experiments accurately. The length scale λ will become greater as the solvent dipole moment is increased. The $C(t)$ curves obtained with this modified continuum theory are presented elsewhere.³³ For complete saturation, i.e. $\epsilon_0(a) = \epsilon_\infty$, the calculated $C(t)$ values are highly non-exponential.

3. Molecular Dynamics Simulations

Molecular dynamics (MD) simulations offer another approach to understanding the experimentally observed behaviour. Simulations focus specifically on the molecular

†1 D = 3.33564×10^{-30} C m.

aspects of the solvation process and thus afford a very different perspective than do continuum models.

Since the main features of the experimental results are largely probe independent, we have concentrated on simulations of idealized probe solutes in more realistic model solvents. Model systems studied to date have involved spherical solutes in spherical clusters of ST2³⁴ water. The solutes considered are ions with varying size and charge that interact with the water *via* centred Lennard-Jones (LJ) and Coulomb terms. Simulations were carried out with the solute fixed at the centre of a free cluster of water molecules rather than using the more typical periodic boundary conditions. This method has the advantage of allowing dipolar interactions to be calculated exactly for a truly isolated solute in spherical surroundings. The price of having such a well defined system is that one must accept the presence of non-bulk waters near the cluster edges. For clusters of between 256 and 512 solvent molecules we have found that the solvation properties are negligibly altered by edge effects, so that we are therefore observing the solvation behaviour in bulk water.

Both equilibrium and non-equilibrium molecular dynamics have been employed in studying the above model systems. Information about the time-dependent solvation response can be obtained from the fluctuations of appropriate quantities in the equilibrium system.³⁵ Thus how the solvation energy relaxes after (small) step changes in the solute's charge, dipole moment, or quadrupole moment are respectively related to time correlation functions of fluctuations in the electric potential, field, and field gradient at the solute centre calculated under equilibrium conditions. Obtaining dynamics this way rests on the assumption of there being a linear response of the solvent to the (small) perturbation caused by time-dependent changes in the solute. The validity of such an assumption is not obvious. We are therefore also beginning non-equilibrium simulations to explore the conditions under which a non-linear response should be expected.

The solvation structures that exist about atomic species in water have been extensively discussed in the MD literature.³⁶ As a function of increasing charge to size ratio of the solute first solvation shell waters go from a fairly ordered state characteristic of 'hydrophobic' hydration, through an intermediate, disordered regime of 'negative' hydration, to a strongly ordered state of hydrophilic hydration.^{36a,37} We have examined two types of solutes.³⁴ The hydrophobic (type I) solutes are large, and their Lennard-Jones parameters (radius 3.5 Å, $\epsilon = 2660$ K) are chosen to represent the aromatic probes used experimentally. Solvents in the first solvation shell of such solutes tend to straddle the solute, pointing three of their four hydrogen-bonding groups tangentially to the solute surface and the fourth radially outward, to preserve all four hydrogen bonds to neighbouring solvent molecules. Placing a single charge at the centre of one of these large solutes changes the hydrophobic solvation structure only slightly.³⁸ Hydrophilic (type II) solutes are small and have their LJ parameters chosen equal to those of the ST2 oxygen (radius 1.55 Å, $\epsilon = 38$ K). Such solutes are intended to model effects that might arise when a molecular solute has small, highly charged pendant groups that are accessible to the solvent. For charges of $0.5e^-$ or greater, the first coordination waters tend to bond directly to type II solutes and give up one of their interwater hydrogen bonds in the process. The solvation energetics differ between the two types of solutes. For the large hydrophobic solutes the energies are in a linear regime. Thus the energy of solvation of a singly charged type I solute can be predicted from the first-order fluctuations observed in the uncharged solute and *vice versa*. We might therefore expect the dynamics to also be linear. The same is not true for the hydrophilic solutes.

Fig. 3 and 4 illustrate several aspects of the solvation dynamics observed in equilibrium simulations of a type I solute (+1 charge). Fig. 3 shows time correlation functions (TCF) of the electric field at the solute centre produced by the equilibrium fluctuations of the solvent. Assuming a linear response, this time dependence is what will occur after a step change in a centred point dipole. The bottom curve is the total response

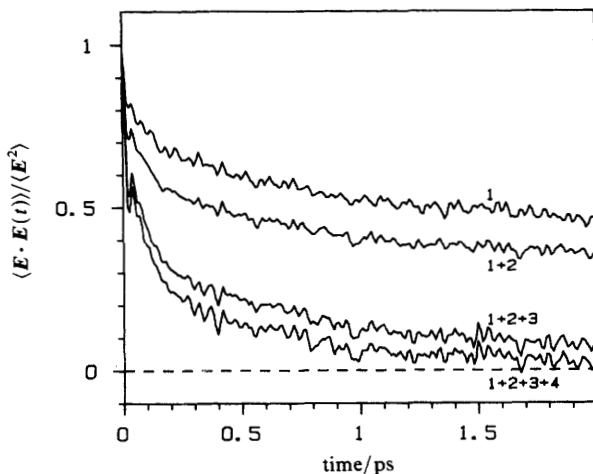


Fig. 3. Equilibrium time correlation functions of the electric field (\mathbf{E}) at the solute centre, $\langle \mathbf{E} \cdot \mathbf{E}(t) \rangle / \langle E^2 \rangle$, calculated from a 50 ps simulation of large LJ solute with +1 centred charge in a cluster of 512 waters. The bottom curve shows the total \mathbf{E} field TCF. The top curve is the contribution to the TCF due to only first solvation shell waters. The other two curves (from the top down) illustrate how the addition of further shells results in the total response. Shells 1–4 contain 40, 106, 192 and 157 water molecules, respectively.

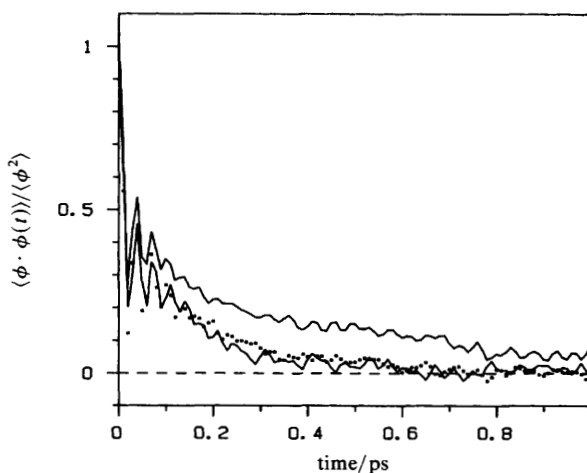


Fig. 4. Electrical potential (ϕ) decays. The top curve is the normalized potential TCF $\langle \phi \cdot \phi(t) \rangle / \langle \phi^2 \rangle$ obtained from an equilibrium simulation of a large LJ solute containing a centred +1 charge. The solid of the two lower curves is this same TCF obtained from an equilibrium simulation of the corresponding uncharged solute. The dotted curve is the normalized $\phi(t)$ response observed after instantaneously placing a +1 charge in the uncharged solute (average of a series of 36 non-equilibrium simulations). This latter curve should be identical to the former equilibrium curves in the linear response limit.

from all solvent molecules. Two time regimes are apparent: first, a large portion of the relaxation is very rapid, occurring within 10–20 fs, and results from librational motions of first coordination shell waters. The presence of such a fast component may be of prime importance in understanding reactions having high reactive frequencies (or sharp barriers). In water at least, sizeable dynamical effects may be operative even for reactive timescales much faster than the longitudinal relaxation time of the primary dispersion regime. It is worth remarking that although the librational component is weak relative to the primary Debye relaxation in the dielectric response, it has substantial weight in the solvation dynamics, *ca.* 40% here.

Contributions to the energy relaxation associated with the primary dielectric response are seen as the longer time component of the curves in fig. 3. It is this latter component that is most relevant for comparison to our experimental data (because of limited time resolution) and to theoretical treatments that assume that the solvent has a single Debye dielectric response. This longer time behaviour is non-exponential. The average time constant of the bottom curve in fig. 3 is roughly 350 fs. To put these observations in perspective we need to know the dielectric properties of the ST2 water model. Preliminary simulation results show that the main dielectric dispersion of ST2 water is Debye-like with a longitudinal relaxation time of *ca.* 150 fs. Thus the observed features of the simulated dynamics deviate from the simplest continuum model predictions in the same way as do both the experimental results and the more complete theoretical treatments.

The simulations lend insight into the reasons for the multiexponential relaxation. The remaining curves in fig. 3 show a decomposition of the total E field TCF into contributions from different regions in the solvent. The topmost curve is the contribution from only the first solvation shell waters. The second and third curves result from successively adding on contributions from radial shells further removed from the solute. Fig. 3 shows that the part of the response from waters in the first solvation shell is slow, being about equal to the single-molecule reorientation time (5 ps). The solvation response achieves its 'supermolecular' speed only through the correlated dynamics of many molecules. Thus as further shells are included in the response it becomes much faster than any single-molecule reorientation time of the solvent and approaches the limiting longitudinal relaxation time. The appearance of multiple relaxation times in the overall response reflects that for a molecular sized probe the molecularity of the surroundings renders the cooperativity of the solvent response incomplete. A large fraction of the energy of solvation comes from the first solvation shell and here the dynamics is slower than in the outer (continuum-like) solvent regions. For example, with the solute of fig. 3 we observed that fluctuations in the polarization become progressively faster as one moves away from the solute. This observation is in accord with the now famous 'snowball' comment of Onsager,¹³ and recent theoretical results.^{3,14,16} Since the dielectric constant gauges the cooperativity of electric interactions, the above features can be viewed as reflecting an effective dielectric constant near the solute that is much smaller than the bulk value. Thus a continuum model employing a radially dependent dielectric constant as discussed above is a simple way to account for the effects of solvent molecularity.

Time correlation functions of other properties such as the electrical potential and field gradient tensor components are similar to the electrical field TCF (fig. 3) for all type I solutes. The top curve of fig. 4 shows an electrical potential TCF for the same solute as in fig. 3. The potential TCF decays slightly faster and shows more inertial oscillations (fig. 4) than the others. However, the differences are small, and assuming a linear response is valid, the time-dependent responses to step changes in a point charge, dipole or quadrupole in these solutes are essentially the same.

Fig. 4 also illustrates that there is some difference between the TCFs (especially those for the electrical potential) observed with different type I solutes. The topmost curve in fig. 4 is for a large solute with a +1 charge whereas the lower curves are for

the corresponding uncharged solute. The time dependence of solvation in the uncharged solute is reproducibly faster than in the charged case. Such a difference is surprising given the similarity between solvation structures about these two solutes. This observation implies that even in this large a solute, the dynamics accompanying full charge jump involve non-linear effects. That is, the solvent is sufficiently different about these two solutes that the dynamics depend on which end one starts from in making the charge jump. (As already noted, the overall solvation energies do not exhibit this non-linearity.) In light of the above, one must question the relevance of equilibrium MD calculations in studying solvation dynamics because in real situations a substantial fractional charge separation may be produced.

We have begun to examine this question by using non-equilibrium MD. One can record the full response including any non-linear effects by simply starting with the uncharged large solute, instantaneously putting a +1 charge at its centre, and then watching how the solvation energy at the charge site subsequently relaxes. The dynamics in this case are very similar to those predicted by a linear response calculation using TCFs collected from the equilibrium MD of the uncharged solute. In fact, one of the two more rapidly decaying curves that are nearly indistinguishable in fig. 4 is the result of the non-equilibrium simulation just described. Thus, at least in this example, the linear response prediction does reproduce the actual dynamics of even a large charge jump accurately if the correct starting point is used for the equilibrium simulation. Our interpretation of these results is that there must be some subtle difference in the ordering that is present about the uncharged and charge solutes that causes the difference in their dynamics. Whatever the structural difference is, it does not influence the solvation energetics appreciably as is evidenced by the linearity of the total energy. Assuming then that this structure relaxes slowly, the observed solvation energy relaxation is just what is predicted based on the equilibrium solvent dynamics about the initial solute. Thus a linear response approach is valid in this case. The solvation dynamics of the hydrophilic or type II solutes is much more complex than for the type I solutes and will be discussed elsewhere.³⁹

4. Experimental Results

It is possible to probe dipolar solvation dynamics by measuring the time-resolved emission spectrum using ultra-short laser pulses. Time resolution of the fluorescence from a dye probe molecule is obtained using time correlated single photon counting,⁸ fluorescence upconversion,^{7,12} and streak camera¹¹ detection.

The experimental data are used to construct the correlation function $C(t)$, eqn (1). $C(t)$ is obtained in one of two ways. It may be obtained by reconstruction of the fluorescence spectrum from several time decays at any time delay after laser excitation. Barbara and coworkers^{9,12} have used an approach by which the solvation process may be resolved by measurement of only a single fluorescence decay at a fixed wavelength. The latter method is notable for its experimental efficiency, while obtaining $C(t)$ via spectral reconstruction yields more information. While the solvation rate would be expected to be affected by probe parameters such as size, formal charge (and associated counterions) and specific solute-solvent interactions, e.g. hydrogen bonding, at the current level of precision the data for different probes in the same solvents agree to within experimental error.

Measurements of $C(t)$ have been made for a wide variety of dipolar solute-solvent systems.⁷⁻¹² Smaller uncharged rigid probe molecules such as 1-aminonaphthalene, 4-aminonaphthalamide, Coumarins 153,⁸ 102 and 311¹² have been employed as well as larger molecules with more complex photophysics, e.g. LDS 750,⁷ bianthryl^{9,12} and bis-(4-aminophenyl)sulphone.¹¹ Among the solvents studied are the alcohols, *N*-methyl

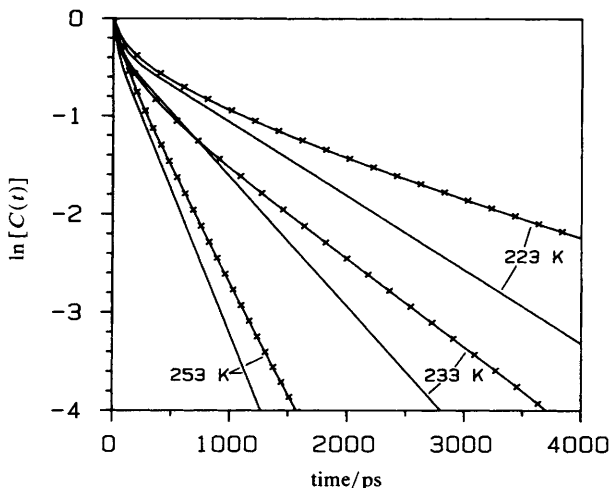


Fig. 5. Comparison of observed (\times) and calculated (—) correlation functions in *n*-propanol. The calculated curves were obtained using the continuum theory expressions [ref. (23)] and approximating the *n*-propanol dielectric response by a two-Debye form. The dielectric parameters used in these calculations were for 253, 233 and 223 K, respectively: $\epsilon_{01} = 27.81, 31.43$ and 33.80 ; $\epsilon_{\infty 1} = 3.94, 4.10$ and 4.20 ; $\epsilon_{\infty 2} = 3.10, 3.14$ and 3.16 ; $\tau_{D1} = 2140, 5190$ and 9600 ps; and $\tau_{D2} = 12.3, 19.7$ and 28.3 ps.

amides, alkyl nitriles, alkyl acetates, and such polar aprotics as DMSO, nitrobenzene and propylene carbonate.⁷⁻¹²

At the crudest level, for non-associating solvents of low to moderate polarity ($\epsilon_0 < 50$) the simple continuum models are qualitatively correct. In general, however, these continuum models do not accurately describe the experimental results. For the more complicated solvents such as associating liquids (alcohols and polyalcohols, amides *etc.*) and highly polar liquids (propylene carbonate, *N*-alkyl amides), the experiments deviate from the Debye/Onsager continuum model predictions in two ways. First, the experimental $C(t)$ curves are generally non-exponential. Secondly, the τ_{obs} obtained from these $C(t)$ values are often greater than τ_L . Fig. 5 compares experimental and calculated $C(t)$ curves for Coumarin 153 in *n*-propanol at three different temperatures. The calculated curves used a two-Debye dielectric response following ref. (23). It is clear that the measured $C(t)$ curves are non-exponential in a way quite different from the calculated curves. Comparing fig. 2 and 5 leads us to suggest that the long-time behaviour in the experimental data does not result from a DC distribution in *n*-propanol. Instead, we suggest that a radial dependence of the dielectric constant (see section 3) is responsible for the curvature and longer duration of the experimental $C(t)$ in fig. 5. The deviation of τ_{obs} from τ_L increases sharply with increasing ϵ_0 . To date, the τ_{obs} values always lie in the range $\tau_L \leq \tau_{\text{obs}} < \tau_D$.

Fig. 6 shows the dependence of τ_{obs}/τ_L on ϵ_0 for all the systems we have studied, plus several from the literature.¹¹ For $\epsilon_0 > 50$ the relaxation times are much slower than predicted by the Debye/Onsager continuum model. In the region where τ_{obs} is roughly equivalent to τ_L , the τ_{obs} values vary by a factor of 3×10^3 . For the high dielectric constant solvents, propylene carbonate and *N*-methyl propionamide, the τ_{obs} values lie in the middle of the full range of τ_{obs} values, and the magnitude of the spectral shift conforms to expectations. Thus the stabilization energy in the high dielectric constant solvents conforms to our expectations, but the dynamical process occurs much more slowly than predicted by the Debye type continuum model.

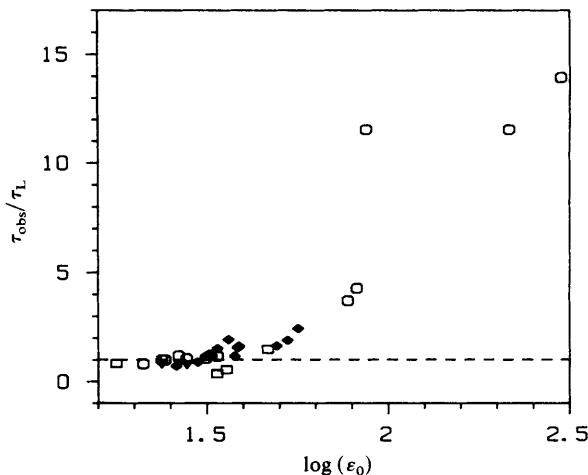


Fig. 6. Summary of observed solvation times compared with the solvent longitudinal relaxation time. Plots are of τ_{obs}/τ_L versus \log_{10} of ϵ_0 for the solutes LDS 750 (open squares), Coumarin 153 (open circles), 1-aminonaphthalene (filled triangles) and bis-(4-dimethylaminophenyl)sulphone (filled diamonds). The data for the sulphone compound was provided by John Simon.

5. Concluding Remarks

The solvation of polar molecules is, in general, expected to proceed over a range of timescales rather than with the single time constant τ_L predicted by Onsager continuum theories based on a Debye response. Fluorescence measurements on several probe systems confirm this expectation. There are several possible origins for this non-exponential behaviour. In continuum models non-exponentiality may arise from non-spherical solute shape, distributions of dielectric relaxation times (*i.e.* non-Debye dielectric response), or from a radial dependence of the dielectric response. Molecular dynamics simulations of ST2 model water suggest that the timescale of solvent relaxation decreases as the distance from the solute increases. Since the first shell molecules contribute significantly to the total stabilization energy, the relatively slow response of these molecules gives an intrinsic non-exponentiality to the solvation process. A major component of the relaxation caused by the librational motion of the first shell solvent molecules was observed in the simulations. This inertial response may be important in electron transfer reactions that involve high (sharp) barriers.

All current theoretical models are based on a linear response assumption. The molecular dynamics simulations suggest that non-linear response could be important in realistic experimental situations. A larger experimental data base and further theoretical work are clearly required to clarify this issue.

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