

Molecular theory of ion solvation dynamics in water, acetonitrile and methanol: A unified microscopic description of collective dynamics in dipolar liquids

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Abstract. A recently developed microscopic theory of solvation dynamics in real dipolar liquids is used to calculate, for the first time, the solvation time correlation function in liquid acetonitrile, water and methanol. The calculated results are in excellent agreement with known experimental and computer simulation studies.

Keywords. Ion solvation dynamics; solvation time correlation function; dipolar liquids; microscopic theory of solvation dynamics.

1. Introduction

Our understanding of the solvation dynamics of charged species in dipolar liquids has undergone a renaissance in recent years (Bagchi 1989; Barbara and Jarzeka 1990; Maroncelli *et al* 1993; Roy and Bagchi 1993). Experiments (Rosenthal *et al* 1991) and computer simulations (Maroncelli and Fleming 1988) have shown that an ultrafast Gaussian component dominates the relaxation in both liquid acetonitrile and water. This ultrafast component seems to originate from the fast macroscopic relaxation mode of the solvent (Roy and Bagchi 1993a). In contrast, experimental (Kahlow *et al* 1989; Maroncelli *et al* 1993) and computer simulation (Fonseca and Ladanyi 1991; Maroncelli *et al* 1993) studies reveal methanol to be a rather different solvent, in not only being much slower, but also being nonlinear in its response to the sudden creation of an electrical charge in it. In this paper, a theoretical study of the solvation dynamics of a rigid ion in these three liquids is presented. Excellent agreement is obtained between theoretical prediction and the available experimental and simulation results in each case. Furthermore, the theory transparently explains the basic difference in behaviour between these structurally similar solvents.

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2. Theoretical formulation

Within the linear-response assumption, the time-dependent solvation energy, $E_{\text{sol}}(t)$, is given exactly by the following expression (Roy and Bagchi 1993a)

$$E_{\text{sol}}(t) \propto L^{-1} \int_0^\infty dk \left[\frac{\sin kr_c}{kr_c} \right]^2 \frac{1}{z} \left[\frac{1}{\varepsilon(k, z)} - \frac{1}{\varepsilon(k)} \right], \quad (1)$$

where L^{-1} denotes an inverse Laplace transformation with respect to the Laplace frequency, z ; r_c is the distance of closest approach between the ion and a solvent molecule; $\varepsilon(k, z)$ is the longitudinal dielectric function of the solvent, dependent on the wavevector (k) and frequency (z), and is related to the wavevector-dependent dielectric function $\varepsilon(k)$ by

$$1 - \frac{1}{\varepsilon(k, z)} = \left[1 - \frac{1}{\varepsilon(k)} \right] \left[1 - \frac{z}{z + \Sigma(k, z)} \right], \quad (2)$$

with the generalized rate $\Sigma(k, z)$ given by

$$\Sigma(k, z) = \frac{2f_L(k)}{\tau_I^2 [z + \Gamma_R(k, z)]} + \frac{pk^2 f_L(k)}{\tau_I^2 [z + \Gamma_T(k, z)]}. \quad (3)$$

Here, $f_L(k) = 1 - (\rho_0/4\pi)c(110, k)$ is a measure of the static structural correlation of the pure solvent as $c(llm, k)$ denotes the (llm) component of the direct correlation function in the intermolecular frame with k parallel to the z axis (Bagchi and Chandra 1991). ρ_0 is the average number density of the liquid. Note that $f_L(k)$ is related to $\varepsilon(k)$ by the following simple relation (Bagchi and Chandra 1991)

$$1 - (1/\varepsilon(k)) = 3Y/f_L(k), \quad (4)$$

where the polarity parameter $3Y = (4\pi/3) \beta \mu^2 \rho_0$ with μ as the dipole moment of the solvent molecules. $\beta = (k_B T)^{-1}$, k_B is the Boltzmann constant and T the absolute temperature. For a solvent molecule of effective moment of inertia I , $\tau_I = (I/k_B T)^{1/2}$ denotes the time constant for the free inertial motion of the solvent molecules. The natural dynamics of the liquid determines the rotational and translational dissipative kernels, $\Gamma_R(k, z)$ and $\Gamma_T(k, z)$.

It is clear from the above discussion that the intermolecular orientational (in this case, dipolar) correlation function and the dissipative kernels are the two crucial ingredients of the present theory. Fortunately, recent developments in the equilibrium theory of molecular liquids have made accurate calculation of the two particle orientational correlation functions possible (Raineri *et al* 1992). It is shown elsewhere (Roy and Bagchi 1993) that the rotational kernel can be obtained directly from dielectric and Kerr relaxation experiments by assuming that $\Gamma_R(k, z)$ can be replaced by its $k = 0$ limiting value. This is an inversion procedure where a microscopic relation between a correlation function and the relevant experimental observable is used to determine the dissipative kernel. For example, this procedure provides the following elegant relation with the dielectric relaxation, $\varepsilon(z)$ of the liquid (Roy and Bagchi 1993a)

$$\frac{1}{z + \Gamma_R(k=0, z)} = \frac{z\tau_I^2}{2f_L(k)} \frac{\varepsilon_0[\varepsilon(z) - n^2]}{n^2[\varepsilon_0 - \varepsilon(z)]}. \quad (5)$$

In the above equation, ϵ_0 and n^2 are the static and the optical dielectric constants of the pure solvent. Note that all the quantities appearing on the right-hand side of (5) are experimentally measurable. Similarly, for Kerr relaxation, the dissipative kernel is given by (Roy and Bagchi 1993b)

$$\frac{1}{z + \Gamma_R(k=0, z)} = \frac{\tau_I^2 [1 - zC_{20}(z)]}{6f_{220}(k=0)C_{20}(z)}, \quad (6)$$

where $C_{20}(z)$ is the Laplace transform of the correlation function $C_{20}(t)$ usually measured in the Kerr relaxation. $f_{220}(z) = 1 - (\rho_0/4\pi)c(220, k)$ and can be equated to 1 for spherical and nearly spherical molecules.

The translational dissipative kernel $\Gamma_T(k, z)$ is important only at intermediate to large k values where it can be approximated well by its single particle value, $\zeta_T(z)$. In liquid water, $\zeta_T(z)$ is calculated using its well-known memory function relation with the Laplace transform of the velocity time auto-correlation function. The latter is obtained from the simulations of Stillinger and Rahman (1971). For acetonitrile, the translational modes are found to be unimportant except at long time durations on account of its very fast rotational motion. Similar is the situation for methanol where the motion of the molecules is rather slow. In these solvents, we may approximate the frequency-dependent friction by its zero frequency value. It is then calculated using the known values of the translational diffusion coefficients via the Stokes–Einstein relation.

The experimental results of solvation dynamics is usually expressed in terms of the solvation time correlation function $S(t)$ defined as

$$S(t) = \frac{E_{\text{sol}}(t) - E_{\text{sol}}(\infty)}{E_{\text{sol}}(0) - E_{\text{sol}}(\infty)}. \quad (7)$$

The numerical results for all the three systems are presented next.

3. Numerical results

3.1 Liquid acetonitrile

Both the optical Kerr and the dielectric relaxation data have been used to calculate the rotational dissipative kernel. The normalized correlation function $C_{20}(t)$ was obtained using the Brownian oscillator representation of Cho *et al* (1992). The dielectric data (Barthel and Buchner 1991) consists of a Debye relaxation with $z = i\omega$ (ω is the Fourier frequency). The translational parameter $p = 0.07$. Since the dye molecule LDS-750 was used in the experimental study, we assume that the solute ion is a sphere of radius three times that of acetonitrile.

In figure 1 the theoretical and the experimental results are compared. The agreement is excellent for the case where the dissipative kernel is obtained from the Kerr relaxation, but is not satisfactory when it is calculated from the dielectric relaxation data. This is in accordance with the understanding that conventional dielectric relaxation measurements not only miss the contribution of the high frequency librational modes, but on extrapolation also lead to an underestimation of the underdamped dynamics. We have also compared the theoretical predictions with the

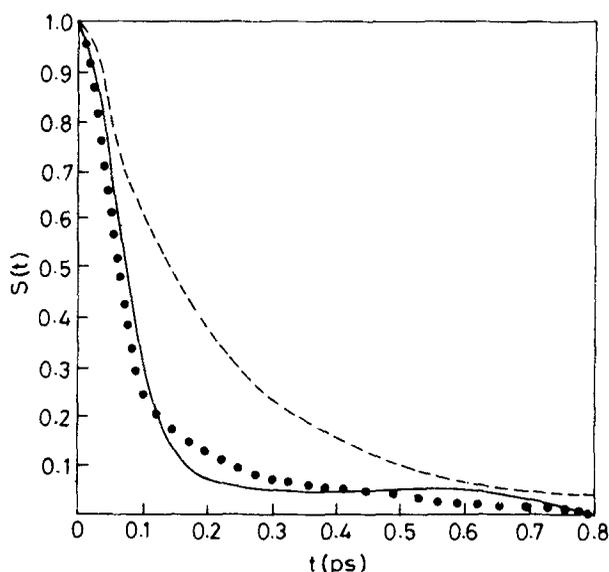


Figure 1. Comparison of the calculated solvation time correlation function, $S(t)$, with the experimental one for the solvation of LDS-750 in liquid acetonitrile. The solid and the dashed lines are the $S(t)$ calculated from the Kerr and the dielectric relaxations, respectively. The experimental result is shown by filled circles. The radius of the solute ion is three times that of an acetonitrile molecule.

computer simulations of Maroncelli (1991) where the solvent molecules are assumed to be non-polarizable. Again excellent agreement is obtained.

3.2 Water

For water, the correlation function, $c_{110}(k)$, and hence the $f_{110}(k)$, were calculated accurately by using the results of Raineri *et al* (1992). The experimental FIR absorption spectrum of water (Hasted *et al* 1985) shows a peak at 199 cm^{-1} which is believed to be mostly responsible for the high frequency dielectric relaxation. We used the following expression for $\epsilon(z)$

$$\epsilon(z) = n^2 + \frac{\epsilon_0 - \epsilon_\infty}{1 + z\tau_D} + (\epsilon_\infty - n^2)[1 - \Phi_{lib}(z)], \quad (8)$$

with $\tau_D = 9.33\text{ ps}$, $\epsilon_\infty = 4.86$ and $n = 1.33$ (Hasted *et al* 1985). Φ_{lib} is the librational moment correlation function. It is calculated using the damped oscillator model with the oscillation frequency equal to 199 cm^{-1} and the damping constant equal to 100 cm^{-1} (Hasted *et al* 1985). The translational parameter $p = 0.02$. As shown in figure 2, the calculated dynamics has a rich structure. The initial decay is Gaussian followed by exponential-like decay in the long time, with an oscillation in the intermediate time domain. This result, including the oscillation, is in good agreement with the computer simulations of Maroncelli and Fleming (1988). *The initial sharp Gaussian decay is primarily due to the librational mode whose contribution to solvation gets greatly enhanced (compared to dielectric relaxation) due to the large value of $f_{110}(k=0)$.* The initial decay can be fitted to a Gaussian form with a time constant

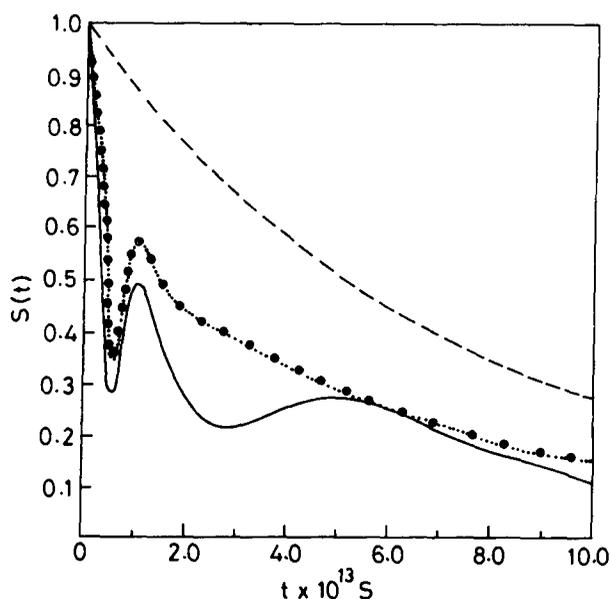


Figure 2. Calculated solvation time correlation function, $S(t)$, as a function of time for the solvation of a spherical ion in liquid water. The solid line includes both the rotational and the translational librations and the dotted line only the rotational libration. The dashed line shows the decay when only the Debye relaxation is accounted for. The solute to solvent size ratio is assumed to be 2:25.

(τ_G) equal to 42 fs and $\tau_G = 0.42 \tau_I$. This implies that the solvation is much faster than the free inertial decay. The slow exponential-like decay after the oscillation has two components with time constants approximately equal to 280 and 800 fs. *These are very close to the two components observed by Barbara and Jarzeba (1990a) who, however, missed the ultra-fast Gaussian component because of limited time resolution.* The slow 800 fs decay component is found to be due to the strong orientational correlations present at molecular length scales where $c_{110}(k)$ is positive and maximum so that $f_{110}(k)$ is small. This is essentially the orientational de Gennes narrowing. The translational librational modes of water play an important role in this regime.

3.3 Liquid methanol

Since experimental results are not yet fully available for liquid methanol, we compare our results with the simulations (Maroncelli *et al* 1993). As the molecules are not polarizable in the simulated system, the polarizability is ignored by setting the optical frequency equal to 1 and the $3Y$ parameter equal to 4.3276. Here, $p = 0.267$. The results are presented in figure 3 where the simulation results of Maroncelli *et al* (1993) are also shown for comparison. The solvation dynamics is found to be rather similar when $\Gamma_R(z)$ is obtained either from the dielectric (Guillot *et al* 1990) or from the Kerr relaxation (Cho *et al* 1993). In both the cases, the theoretical predictions for the initial decay are in perfect agreement with the simulated one. The dielectric model of the dissipative kernel provides slightly better agreement in the long time.

A comparison of the relaxation pattern obtained here with those for water and acetonitrile reveals two interesting features. First, both the fast (Gaussian) and the

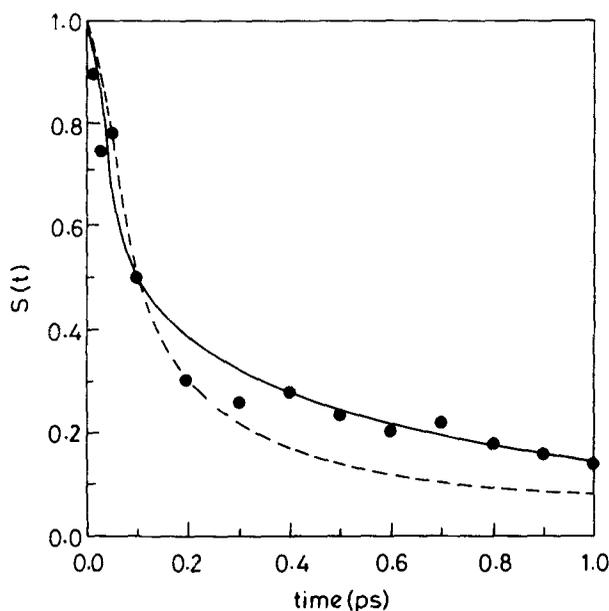


Figure 3. Solvation time correlation function, $S(t)$, calculated from the dielectric relaxation (solid line) and the Kerr relaxation (dashed line) for the solvation of a rigid ion in liquid methanol. The simulation results are shown by the solid circles. The solute is of the same size as coumarin.

slow (exponential-like) components are much slower in methanol than in the other two solvents. Second, the Gaussian component carries a smaller weight in methanol. The available experimental studies (Kahlow *et al* 1989; Maroncelli *et al* 1993) for solvation dynamics in methanol suffer from a limited temporal resolution. Comparison between theoretical calculations (now performed with polarizability effects included which makes solvation even faster) with experimental results suggests that the experiments have missed almost all of the fast Gaussian component that contributes about 40–50% of the total energy relaxation. Thus, we conclude that the *available experiments have detected only the last 50% of the decay*. This is also in agreement with the conclusion of Maroncelli *et al* (1993).

4. Conclusion

In this communication microscopic calculations of ion solvation dynamics in three common dipolar liquids are presented. The theory is sufficiently simple so that a detailed numerical calculation of the solvation time correlation function can be carried out for the common dipolar liquids. The agreement between theory and available experimental and computer simulation results is excellent in each case. It is found that while the librational modes and dipolar interaction induced effects are important in water, it is the single particle rotation that drives the ultrafast solvation in acetonitrile. Methanol exhibits markedly different dynamics because here the orientational motion is slow and the energy relaxation derives a significant contribution from the solvent translational modes. These factors also make the response of methanol nonlinear, as explained in more detail elsewhere (Roy *et al* 1993).

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