Dynamics of solvation of an ion in a dense dipolar liquid

A CHANDRA and B BAGCHI

Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India

Abstract. A molecular theory of the dynamics of solvation of an ion in a dense dipolar liquid is presented. The theory is based on an extended hydrodynamic approach that properly includes the interparticle correlations that are present at molecular length scales. The effects of the solvent inertial and viscoelastic responses are also included consistently. Numerical studies reveal rich relaxation behaviour such as short-time oscillations followed by a slow long-time decay. The results are in semi-quantitative agreement with recent computer simulation studies.

Keywords. Dipolar liquid; dynamics of solvation; molecular theory; computer simulation studies.

1. Introduction

An understanding of the dynamics of solvation of polar solute molecules in dipolar solvents is essential to understand the dynamic solvent effects on many liquid phase chemical reactions, such as the electron and the proton transfer reactions. This is a subject of tremendous current interest (Hynes 1985; Bagchi 1989; Maroncelli *et al* 1989; Barbara and Jarzeba 1990; Fleming and Wolynes 1990). In recent years, a large amount of theoretical (Calef and Wolynes 1983; Bagchi *et al* 1984; van der Zwan and Hynes 1985; Friedrich and Kivelson 1987; Loring and Mukamel 1987; Wolynes 1987; Bagchi and Chandra 1988, 1989; Chandra and Bagchi 1988, 1989, 1990a; Nichols and Calef 1988; Rips *et al* 1988; Fried and Mukamel 1990; Wei and Patey 1990; Raineri *et al* 1991) and experimental work (Castner *et al* 1987; Kahlow *et al* 1987; Maroncelli and Fleming 1987; Nagarajan *et al* 1987; Su and Simon 1987, 1989; Declemy and Rulliere 1988; Kinoshita and Nishi 1988; Chapman *et al* 1990) has been devoted to understanding the dynamics of polar solvation. Several computer simulation studies (Karim *et al* 1988; Maroncelli and Fleming 1988; Bader and Chandler 1989; Carter and Hynes 1991; Maroncelli 1991) have also been carried out to study the dynamics of solvation and its role in charge transfer reactions in real liquids like water and acetonitrile. As a result of this great effort, a microscopic understanding of the process of solvation is beginning to emerge.

It has become clear that the continuum model based theories (Bagchi *et al* 1984; van der Zwan and Hynes 1985) are inadequate to describe the complexities of the solvation phenomena. Recent studies have shown that the molecular aspects of relaxation are important and that solvation dynamics is non-exponential, in general. It has been pointed out that the translational modes of the solvent molecules can play an important role in the dynamics of solvation. The effects of the solvent inertial

response have also been explored (Chandra and Bagchi 1991). It has been shown that solvent inertial effects can play an important role in the short-time dynamics of solvation (Chandra and Bagchi 1991). During the initial relaxation in ultra-fast solvation, not only the inertial but also the solvent viscoelastic effects are expected to be important. In this paper, we present a theory which includes all these effects consistently.

The present study of the dynamics of solvation is based on a microscopic expression of the time-dependent solvation energy. We will consider the solvation of a stationary solute. In this limit, the dynamics of solvation depends on the time-dependence of the solvent polarization relaxation. The calculation of the solvent polarization relaxation is carried out by using a non-Markovian extended hydrodynamic approach which properly takes into account the intermolecular correlations that are present at molecular length scales. This approach has been used successfully to study the dynamics of various relaxation processes in dense liquids (Bagchi and Chandra 1991). We also find that the dynamics of solvation is in general, non-exponential. The solvent inertial and viscoelastic effects can give rise to rich dynamical behaviour of the solvation phenomena. The dynamics of solvation can become oscillatory in time when the solvent is in the underdamped limit and also when the viscoelastic response of the solvent is important, which is the case for slow complex liquids like hexanol. Although this oscillatory behaviour in solvation dynamics has recently been observed in the computer simulation of ionic solvation in acetonitrile (Maroncelli 1991), the direct experimental verification of this is yet to be made.

The organisation of the rest of the paper is as follows. In §2 we discuss the theory. The numerical results are presented in §3, in which brief discussion is also included.

2. Theory

The study of the dynamics of solvation is based on the following microscopic expression of the time-dependent solvation energy

$$E_{solv}(t) = -\tfrac{1}{2} \int d\mathbf{r}\, \mathbf{E}_0(\mathbf{r}) \cdot \mathbf{P}(\mathbf{r}, t),$$ (1)

where $\mathbf{E}_0(\mathbf{r})$ is the bare electric field and $\mathbf{P}(\mathbf{r}, t)$ is the time-dependent solvent polarization. It is convenient to work in the wavevector space. We write the solvation energy as an integration over the wavevector ($\mathbf{k}$) space in the following way

$$E_{solv}(t) = -\tfrac{1}{2}(2\pi)^{-3} \int d\mathbf{k}\, \mathbf{E}_0(\mathbf{k}) \cdot \mathbf{P}(\mathbf{k}, t),$$ (2)

where $\mathbf{E}_0(\mathbf{k})$ and $\mathbf{P}(\mathbf{k}, t)$ are the Fourier transforms of $\mathbf{E}_0(\mathbf{r})$ and $\mathbf{P}(\mathbf{r}, t)$, respectively. The Fourier transform of the bare field of the solute ion, $\mathbf{E}_0(\mathbf{k})$, is given by

$$E_0(k) = \frac{4\pi i q}{k} \frac{\sin k r_c}{k r_c},$$ (3)

where q is the charge of the solute ion, $r_c = a + \sigma/2$, a being the radius of the solute ion and σ the diameter of a solvent molecule and $i = \sqrt{-1}$. An accurate expression of the time-dependence of the solvent polarization, $P(\mathbf{k}, t)$, including the inertial and

the viscoelastic effects, can be derived from an extended hydrodynamic theory which has been discussed elsewhere (Chandra and Bagchi 1991). In the Laplace space, the frequency (s) dependent polarization, $P(\mathbf{k}, s)$, is given by

$$P(\mathbf{k}, s) = P(k, t = 0)(s + \tilde{B}(s))(s + AB\tilde{T}(s)/2p')$$

$$\times [s(s + \tilde{B}(s))(s + AB\tilde{T}(s)/2p') + ABk^2 f(k)(s + \tilde{B}(s))$$

$$+ 2Bf(k)(s + AB\tilde{T}(s)/2p')]^{-1}. \tag{4}$$

The different quantities in (4) are defined by the following expressions

$$f(k) = 1 - \frac{\rho_0}{4\pi} C(110; k), \qquad B = k_B T / I D_R^2,$$

$$A = I/m\sigma^2, \qquad p' = D_T/2D_R\sigma^2,$$

$$\tilde{B}(s) = B\tilde{\zeta}_R(s)/\tilde{\zeta}_R(s = 0), \qquad \tilde{T}(s) = \tilde{\zeta}_T(s)/\tilde{\zeta}_T(s = 0),$$

$$D_R = k_B T / \tilde{\zeta}_R(s = 0), \qquad D_T = k_B T / \tilde{\zeta}_T(s = 0), \tag{5}$$

where m and I are, respectively, the mass and moment of inertia of a solvent molecule. $\tilde{\zeta}_R(s)$ and $\tilde{\zeta}_T(s)$ are the frequency-dependent rotational and translational frictions, respectively. D_T and D_R are the translational and rotational diffusion coefficients of the liquids. $C(110; k)$ is the (110) component of the two-particle direct correlation function of the liquid (Hansen and McDonald 1986). The quantity p' is a measure of the relative importance of the translational modes of the solvent. The dynamics of solvation becomes faster with increasing p'. Note that the importance of the inertial effects is gauged by the parameters A and B and the effects of solvent viscoelasticity are included through the frequency-dependent frictions, $\tilde{\zeta}_R(s)$ and $\tilde{\zeta}_T(s)$. For the translational friction, $\tilde{\zeta}_T(s)$, we use the expression given by Zwanzig and Bixon (1970), and for the rotational friction, the expression derived by Montgomery and Berne (1977) has been used. Two important ingredients of these expressions are the frequency-dependent shear and the bulk viscosities, $\eta_s(s)$ and $\eta_v(s)$, which are assumed to be of the simple Maxwell forms,

$$\eta_s(s) = \eta_s(s = 0)/(1 + s\tau_s),$$

$$\eta_v(s) = \eta_s(s = 0)/(1 + s\tau_v), \tag{6}$$

where τ_s is the viscoelastic relaxation time and τ_v is the bulk relaxation time. The time-dependence of the solvent polarization can now be obtained in a straightforward manner by Laplace-inverting (4), and that of the solvation energy can then be obtained from (2). Next, we discuss the numerical results.

3. Numerical results and discussion

The results of the solvation dynamics are usually expressed in terms of a solvation time-correlation function, $C_s(t)$, defined

$$C_s(t) = \frac{E_{\text{solv}}(t) - E_{\text{solv}}(t = \infty)}{E_{\text{solv}}(t = 0) - E_{\text{solv}}(t = \infty)}, \tag{7}$$

where $E_{solv}(t)$ is the solvation energy at time t. For numerical calculations of $C_s(t)$ we require the values of the solvent two-particle direct correlation function. For this, we use the mean spherical approximation (MSA) for the dipolar hard spheres (Hansen and McDonald 1986). The reason for using MSA is that it provides simple analytic expression of the direct correlation function which is fairly accurate for not too strongly polar liquids.

In figure 1 we show the calculated time-dependence of the solvation time correlation function, $C_s(t)$, for two different values of the viscoelastic relaxation time, τ_s. The value of the inertial parameter, B, is 50. This value of B is small enough for inertial effects to be important. (The values of the other parameters are given in the caption to figure 1.) The bimodal character of the relaxation is clear from figure 1. There is a fast inertial decay in the short time period which is followed by a slow long-time decay. In the absence of any viscoelastic effects ($\tau_s = 0$) the solvation energy decays smoothly towards its equilibrium value. However, a small oscillation in the short time period is found in presence of viscoelastic responses ($\tau_s = 1\cdot0$). Such oscillations in the dynamics of solvation have also been found in recent computer simulation studies of ionic solvation (Maroncelli 1991). However, direct experimental detection of such oscillatory behaviour is yet to be made.

To summarize, we have presented a microscopic study of the dynamics of solvation in a dense dipolar liquid. The theory properly includes the interparticle correlations that are present in the solvent. The effects of the solvent inertial and viscoelastic responses are also included in the theory. It is found that the inertial and the viscoelastic responses can play an important role in the dynamics of solvation. They can give rise to an oscillatory decay of the solvation energy. The predictions are in semi-quantitative agreement with the results of computer simulation. It may be worthwhile to carry out experimental investigations to detect these predictions.
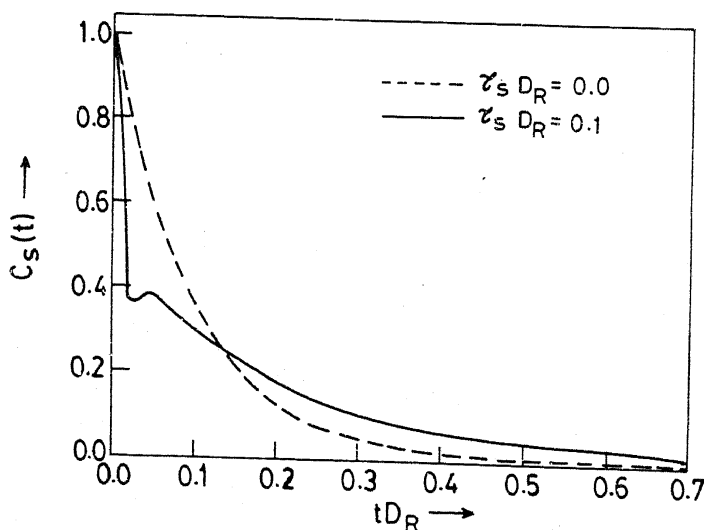

Figure 1. The time dependence of the solvation energy time correlation function, $C_s(t)$. $C_s(t)$ is plotted against time for two different values of the viscoelastic relaxation time, τ_s. The bulk relaxation time, τ_v, is assumed to be equal to τ_s. The value of both the zero frequency shear viscosity, η_s, and the bulk viscosity, η_v, is 1 cp. The values of the parameters B, A and p' are $50\cdot0$, $0\cdot05$ and $0\cdot05$, respectively. The value of the solute–solvent molecular size ratio, R, is $1\cdot0$. The values of the solvent dielectric constant, ε_0, and the reduced density, $\rho_0\sigma^3$ ($\sigma =$ solvent molecular diameter) are $18\cdot0$ and $0\cdot8$, respectively.

Acknowledgements

References

Bader J S and Chandler D 1989 *Chem. Phys. Lett.* **157** 501
Bagchi B 1989 *Annu. Rev. Phys. Chem.* **40** 115
Bagchi B and Chandra A 1988 *Proc. Indian Acad. Sci. (Chem. Sci.)* **100** 353
Bagchi B and Chandra A 1989 *J. Chem. Phys.* **90** 7338
Bagchi B and Chandra A 1991 *Adv. Chem. Phys.* **80** 1
Bagchi B, Oxtoby D W and Fleming G R 1984 *Chem. Phys.* **86** 257
Barbara P F and Jarzeba W 1990 *Adv. Photochem.* **15** 1
Calef D F and Wolynes P G 1983 *J. Chem. Phys.* **78** 4145
Carter E A and Hynes J T 1991 *J. Chem. Phys.* **94** 5961
Castner E W, Maroncelli M and Fleming G R 1987 *J. Chem. Phys.* **86** 1090
Chandra A and Bagchi B 1988 *Chem. Phys. Lett.* **151** 47
Chandra A and Bagchi B 1989a *J. Phys. Chem.* **93** 6996
Chandra A and Bagchi B 1989b *J. Chem. Phys.* **91** 2594
Chandra A and Bagchi B 1990 *J. Phys. Chem.* **94** 3152
Chandra A and Bagchi B 1991a *J. Chem. Phys.* **94** 3177
Chandra A and Bagchi B 1991b *Proc. Indian Acad. Sci. (Chem. Sci.)* **103** 77
Chapman C E, Fee R S and Maroncelli M 1990 *J. Phys. Chem.* **94** 4929
Declemy A and Rulliere C 1988 *Chem. Phys. Lett.* **146** 1
Fleming G R and Wolynes P G 1990 *Phys. Today* **43** 36
Fried I E and Mukamel S 1990 *J. Chem. Phys.* **93** 932
Friedrich V and Kivelson D 1987 *J. Chem. Phys.* **86** 6425
Hansen J P and McDonald I R 1986 *Theory of simple liquids* (London: Academic Press)
Hynes J T 1985 *Annu. Rev. Phys. Chem.* **36** 573
Kahlow A M, Kang T -J and Barbara P F 1987 *J. Chem. Phys.* **86** 3183
Karim O, Haymet A D J, Banet M J and Simon J D 1988 *J. Phys. Chem.* **92** 3391
Kinoshita S and Nishi N 1988 *J. Chem. Phys.* **89** 6612
Loring R F and Mukamel S 1987 *J. Chem. Phys.* **87** 1272
Maroncelli M 1991 *J. Chem. Phys.* **94** 2084
Maroncelli M and Fleming G R 1987 *J. Chem. Phys.* **86** 6221
Maroncelli M and Fleming G R 1988 *J. Chem. Phys.* **89** 5044
Maroncelli M, McInnis J and Fleming G R 1989 *Science* **243** 1674
Montgomery J A and Berne B 1977 *J. Chem. Phys.* **66** 2770
Nichols A III and Calef D F 1988 *J. Chem. Phys.* **89** 3783
Nagarajan V, Brearly A M, Kang T -J and Barbara P F 1987 *J. Chem. Phys.* **86** 3183
Raineri F, Zhou Y, Friedman H L and Stell G 1991 *Chem. Phys.* **152** 201
Rips I, Klafter J and Jortner J 1988 *J. Chem. Phys.* **88** 3246
Su S G and Simon J D 1987 *J. Phys. Chem.* **91** 2673
Su S G and Simon J D 1989 *J. Phys. Chem.* **93** 753
van der Zwan G and Hynes J T 1985 *J. Phys. Chem.* **89** 3783
Wei D and Patey G N 1990 *J. Chem. Phys.* **93** 1399
Wolynes P G 1987 *J. Chem. Phys.* **86** 5133
Zwanzig R and Bixon M 1970 *Phys. Rev.* **A2** 2005