

## Solvation dynamics in imidazolium and phosphonium ionic liquids: Effects of solute motion

Hemant K Kashyap & Ranjit Biswas\*

Department of Chemical, Biological and Macromolecular Sciences, S N Bose National Centre for Basic Sciences,  
Block-JD, Sector-III, Salt Lake City, Kolkata 700 098, India  
Email: ranjit@bose.res.in

*Received 2 February 2010; revised and accepted 11 March 2010*

Experimental and simulation results of solvation dynamics in ionic liquids have so far been explained in terms of translational motion of the ions constituting the ionic liquids under investigation. A recent theoretical study [Kashyap & Biswas, *J Phys Chem B*, 114 (2010) 254] has indicated that while translational motion of the constituent ions is indeed responsible for Stokes' shift dynamics of a polar solute probe in non-dipolar ionic liquids (such as phosphonium ionic liquids), fast orientational relaxation of dipolar ions significantly affects the spectral dynamics in imidazolium ionic liquids. Herein, we investigate the effects of rotational and translational motions of a dissolved dipolar probe on the Stokes' shift dynamics in these representative non-dipolar and dipolar ionic liquids. Theoretical results presented here suggest that while the probe-motion accelerates the solvation-rate in non-dipolar ionic liquids twice over the fixed solute values, it plays a secondary role in dipolar ionic solvents. The sensitivity to the solute's self-motion of the rate of solvation has been found to be linked to the solute-cation size ratio and is decoupled from the initial ultrafast response in dipolar ionic liquids. This work also explains the reasons for not observing the effects of solute motion in simulation study of solvation dynamics in the imidazolium ionic liquid considered herein. Careful analyses of the effects of solute motion further support the fact that rotation of dipolar solvent species, like in conventional polar solvents, dictates the initial phase of solvation of a dipolar probe in imidazolium and other dipolar ionic liquids. In addition, probe size dependence is predicted in non-dipolar ionic liquids, such as phosphonium ionic liquids.

**Keywords:** Theoretical chemistry, Ionic liquids, Solvation dynamics, Solute motion, Phosphonium ionic liquids, Imidazolium ionic liquids, Dipolar cations

Ionic liquids, which remain molten at or near room temperatures, are usually composed of large organic cations and relatively smaller inorganic anions.<sup>1-4</sup> The presence of long-ranged electrostatic interaction among the constituent ions lead to several interesting and sometimes unusual solvent properties such as high solvating power, very low vapor pressure, large viscosity, variable miscibility and high thermal stability. These properties together with large electrochemical window, high electrical conductivity and ionic mobility have made these liquids a better option for use in chemical industry and other technological applications. While structural frustration due to the size disparity between the ions and the strength of the interionic interactions are responsible for the 'fluidity' of these liquids,<sup>5-7</sup> high solvating power seems to originate from the shielding of interactions<sup>8-9</sup> and stronger interaction between the solute and anion of a given ionic liquid.<sup>10</sup> According to the requirement for a reaction, therefore, both solvating power and fluidity of this class of liquids

can be tuned. However, a crucial ingredient – the knowledge about the motion of the constituent ions in response to the formation of an activated complex and the subsequent stabilization of this and the product – is required to design and tailor an ionic liquid for a desired product from a chemical reaction. This and the basic scientific aspect of how different these liquids are from the conventional polar solvents have provided the much needed motivation for studying the dynamical solvent response in these systems.<sup>11-25</sup>

Even though experiments<sup>11-15</sup> and simulations<sup>16-20</sup> have reported biphasic solvation response to an instantaneously altered charge distribution of a dipolar solute dissolved in imidazolium ionic liquids, the time constants and amplitudes of the solvation components are found to be considerably different from each other. Apart from the magnitude of the dynamic Stokes' shift of a dissolved dipolar solute being very large in these liquids of low dielectric constant ( $\epsilon_0$ )<sup>26</sup>, the dynamics in phosphonium ionic liquids has been found to be a stretched exponential

with only one solvation time constant.<sup>27</sup> This then naturally raises the following questions: what determines such a large Stokes' shift in these liquids of low  $\epsilon_0$  and why the observed dynamics in imidazolium ionic liquids is biphasic but a stretched exponential in phosphonium counter parts? The role of ion-solute interaction in producing large Stokes' shift was probably anticipated in earlier works<sup>11-15</sup> but it is difficult for conventional experiments to separate out the various interaction contributions to the measured shift. Interestingly, the importance of cation for producing the biphasic dynamics in imidazolium ionic liquids was hinted at in one of the earliest experiments<sup>28</sup>. Subsequent experimental<sup>15,27-30</sup> and simulation studies<sup>16-20, 31-32</sup> repeatedly stressed upon the translational motion of ions as the "mechanism" for solvation where the collective inertial translation of the lighter ion was linked to the ultrafast response at the early stage of solvation and the diffusive transport for the later part. None of the above studies, however, suggested any link between the dipolar rotation of the cations in imidazolium and other dipolar ionic liquids and solvation of a dipolar solute probe in them. Based upon the knowledge gained in solvation of polar solute molecules in common dipolar solvents, the neglect of the dipolar solvent rotation is particularly striking and, more so, because of the proven relationship between the initial ultrafast solvation energy relaxation and collective low frequency ( $\leq 100 \text{ cm}^{-1}$ ) intermolecular libration modes in many dipolar solvents.<sup>33-39</sup> What is even more interesting is that simulation study<sup>20</sup> of solvation dynamics of C153 (a dipolar solute probe) in 1-butyl-3-methylimidazolium hexafluorophosphate reported a negligible role of cation (imidazolium ion) rotation in the fast initial solvation response and no effect of solute motion on the rate of its own solvation.

Recently we have investigated the solvation dynamics in several dipolar and non-dipolar ionic liquids by modelling them as effective electrolyte solutions where the relationship between the experimentally measured frequency dependent dielectric function,  $\epsilon(z)$ , and dynamic Stokes' shift has been established.<sup>24-25</sup> According to this model, the total solute-solvent interaction energy in a dipolar ionic liquid is composed of contributions from two distinct interactions: (i) the dipole-dipole interaction between the dipolar solute and the dipolar cations, and, (ii) dipole-ion interaction between the solute and

the constituent ions. The solvent-solvent interactions which sets the natural dynamics of the medium then couples with solute-solvent interactions to finally determine the time scale for solvation of a solute dissolved in it. These studies have shown that a significant portion of the spectral dynamics is carried out by the orientational relaxation of the dipolar cations in these liquids and, similar to that in common dipolar solvents, the fast initial response is dominated by the collective orientational motion of the dipolar species. Since these theoretical studies<sup>24,25</sup> use as inputs the most recent experimental dielectric relaxation data<sup>26</sup> of ionic liquids measured over a frequency range of 0.1 GHz to  $\sim 3$  THz, and since dielectric relaxation signal is sensitive primarily to the time dependent change in dipole moment auto-correlation function,<sup>40</sup> the role of low frequency intermolecular librational modes in producing initial fast solvation response has been clearly reflected in these works.<sup>24,25</sup> As a result, the dipolar part of the solvation energy relaxation in imidazolium and other dipolar cation based ionic liquids has been found to be quite similar to that already known for common polar solvents and hence describable by the existing dielectric relaxation based theories of polar solvation dynamics. As expected, the interaction between the solute and the solvent ions has also been found to contribute significantly to the total Stokes' shift and also to the later stage of its dynamics. However, the effects of the solute's self-motion (both rotation and translation) which have not been analyzed in these earlier works<sup>24,25</sup> have been addressed in the present studies.

Herein we analyze the effects of solute motions on its own rate of solvation in two ionic liquids, viz., 1-N-butyl-3-N-methylimidazolium hexafluorophosphate ([bmim][PF<sub>6</sub>]) and trihexyl(tetradecyl)-phosphonium bromide ([P<sub>14,666</sub>][Br]). These two solvents represent two different classes of ionic liquids – dipolar and non-dipolar. The solute considered is a well-characterized and extensively studied solvatochromic probe, coumarin 153 (C153).<sup>41</sup> The choice of these ionic liquids and probe is motivated by the presence of experimental results for these systems which would enable a direct comparison between theoretical predictions and experimental data. Also, the experimental dielectric relaxation data for the dipolar ionic liquid and other parameters for calculations involving these liquids and C153 are known. The results presented here show that both translational and rotational motion of a dissolved dipolar solute play a very important role in

its fluorescence Stokes' shift dynamics in [P<sub>14,666</sub>][Br]. For [bmim][PF<sub>6</sub>], however, effects of solute motions have been found to be insignificant which is in accordance with what has been found in the most realistic simulation study of solvation dynamics involving imidazolium ionic liquids.<sup>20</sup> The present calculations also suggest that the size ratio between the solute and the cation is crucial for the solute motion to be important in Stokes' shift dynamics. This also corroborates well with earlier results for solvation dynamics of dipolar solutes in solvents composed of relatively larger molecules.<sup>42</sup>

### Theoretical Formulation and Calculations

As already mentioned above and elaborated elsewhere,<sup>24-25,43</sup> the present microscopic theory approximates the dipolar ionic liquids as electrolyte solutions of polar solvents where the dipolar interactions among the ions possessing permanent dipole moments produce the effective average polarity of the medium. For such a system it is possible to use the classical density functional theory<sup>44-45</sup> for the expression for the interaction part of the free energy functional ( $\Delta\beta F_{\text{int}}$ , with  $\beta = 1/k_B T$ ) in terms of position ( $r$ ) and orientation ( $\Omega$ ) dependent densities of dipolar cation, dipolar solute and position dependent anion in the solution. Then, equating the functional derivative of  $\Delta\beta F_{\text{int}}$  with respect to the solute density to zero (equilibrium property), provides the expression for the average interaction experienced by a dipolar solute molecule immersed in such a solution.<sup>24-25,33</sup> Subsequent extension into the time domain (logic explained in ref. 33) allows one to derive the following expression (Eq. 1) for the time ( $t$ ), position and orientation dependent average solvation energy for a mobile dipolar solute,<sup>24,25,33,43</sup>

$$\begin{aligned} \Delta E_{\text{total}}(r, \Omega; t) &= \\ & -k_B T \rho_s(r, \Omega; t) \left[ \int dr' d\Omega' c_{sd}(r, \Omega; r', \Omega') \delta \rho_d(r', \Omega'; t) \right. \\ & \quad \left. + \sum_{\alpha=1}^2 \int dr' c_{s\alpha}(r, \Omega; r') \delta n_{\alpha}(r'; t) \right] \\ & = \Delta E_{sd}(r, \Omega; t) + \Delta E_{si}(r, \Omega; t) \quad \dots (1) \end{aligned}$$

where  $\rho_s(r, \Omega; t)$  is solute density at position  $r$  with orientation  $\Omega$  at any time  $t$ .  $c_{sd}(r, \Omega; r', \Omega')$  and  $c_{s\alpha}(r, \Omega; r')$  are respectively the position and orientation dependent dipolar solute-dipolar ion and dipolar solute-ion direct correlation functions and  $\alpha$  denotes the type of ions (cation and anion). The

fluctuations in dipolar density ( $\delta \rho_d$ ) and ion density ( $\delta n_{\alpha}$ ) from the corresponding bulk values are defined as follows:  $\delta \rho_d(r, \Omega) = \rho_d(r, \Omega) - \rho_d^0 / 4\pi$  and  $\delta n_{\alpha}(r) = n_{\alpha}(r) - n_{\alpha}^0$ . Equation 1 expresses the total solvation energy  $\Delta E_{\text{total}}(r, \Omega; t)$  as a sum-total of two distinct contributions: one due to the dipole-dipole interaction,  $\Delta E_{sd}(r, \Omega; t)$  and other due to the dipole-ion interaction,  $\Delta E_{si}(r, \Omega; t)$ . Such a clear separation is not expected to exist in real electrolyte solutions as equilibrium ion-density fluctuation is coupled to dipolar density fluctuation. However, owing to orientational polarization density relaxation being much faster for several polar solvents, the time scales associated with the fluctuations in the dipolar ion density and spherical ion density may be significantly different from each other. Even though an indication of separation of the above sort has been found in the Stokes' shift measurements of electrolyte solutions where the ion dynamics was found to contribute to the later stage of the total relaxation,<sup>46</sup> the separation is only semi-quantitative as ion motion would always entail solvent motion and vice-versa.<sup>46-47</sup>

The expression for the time dependent fluctuating total solvation energy (fluctuation from the equilibrium value) auto-correlation function can then be written as follows<sup>24</sup> (Eq. 2),

$$\begin{aligned} \langle \Delta E_{\text{total}}(t) \Delta E_{\text{total}}(t') \rangle &= \\ & \langle \Delta E_{sd}(t) \Delta E_{sd}(t') \rangle + \langle \Delta E_{si}(t) \Delta E_{si}(t') \rangle \\ & \dots (2) \end{aligned}$$

where the cross-correlations have been neglected on the basis of the arguments (difference of time scales) discussed above. Within such an approximation, Eq. (2) expresses the total solvation energy auto-correlation function as a sum of dipole-dipole and dipole-ion interaction contributions.

The time dependence of the solvation energy relaxation is then followed in terms of the normalized solvation energy auto-correlation function (Eq. 3),

$$\begin{aligned} S_E(t) &= \frac{\langle |\Delta E_{sd}(0)|^2 \rangle S_{sd}(t)}{\langle |\Delta E_{sd}(0)|^2 \rangle + \langle |\Delta E_{si}(0)|^2 \rangle} \\ & \quad + \frac{\langle |\Delta E_{si}(0)|^2 \rangle S_{si}(t)}{\langle |\Delta E_{sd}(0)|^2 \rangle + \langle |\Delta E_{si}(0)|^2 \rangle} \\ & \dots (3) \end{aligned}$$

where  $S_{sx}(t)$  terms ( $x = d$  or  $i$ ) denote the normalized solvation energy auto-correlation functions due to solute-medium dipolar interaction ( $S_{sd}(t)$ ) and solute-ion (dipole-ion) interaction ( $S_{si}(t)$ ). Note that  $S_E(t)$  can decay via two separate channels where even though the channel which is inherently fast will dominate the total decay, the average rate of the decay would be determined by the slower of these two. In the limit of linear solvent response,  $S_E(t)$  becomes equivalent to the experimentally measured spectral or solvation response function,  $S(t)$ .<sup>24,33</sup> Since the normalized solvation energy auto-correlation function due to the dipole-dipole interaction ( $S_{sd}(t)$ ) has already been calculated and discussed in detail elsewhere<sup>24-25</sup>, we write down only the relevant expression here (Eq. 4),

$$S_{sd}(t) = \frac{\langle \Delta E_{sd}(t) \Delta E_{sd}(0) \rangle}{\langle |\Delta E_{sd}(0)|^2 \rangle}$$

$$= \frac{P \int_0^\infty dk k^2 S_{solute}^{10}(k, t) |c_{sd}^{10}(k)|^2 S_{solvent}^{10}(k, t) + 2P \int_0^\infty dk k^2 S_{solute}^{11}(k, t) |c_{sd}^{11}(k)|^2 S_{solvent}^{11}(k, t)}{P \int_0^\infty dk k^2 S_{solute}^{10}(k) |c_{sd}^{10}(k)|^2 S_{solvent}^{10}(k) + 2P \int_0^\infty dk k^2 S_{solute}^{11}(k) |c_{sd}^{11}(k)|^2 S_{solvent}^{11}(k)} \quad \dots (4)$$

where P denotes the prefactor,  $2\rho_d^0 \left( \frac{k_B T}{2\pi} \right)^2$ . In the above equation,  $c_{sd}^{lm}(k)$  represents the Fourier transform of the ( $l, m$ ) component of the static correlation function between the solute and dipolar ionic liquid species, and  $S_{solvent}^{lm}(k, t)$  is the same component of the orientational dynamic structure factor of the dipolar ionic liquid.  $S_{solvent}^{lm}(k, t)$  for these liquids has been calculated from the dielectric relaxation data following the method used for common polar solvents<sup>33</sup> (see also ref. 24 for detailed discussion). This also requires, as inputs, the orientational static structure factor, isotropic dynamic structure factor and translational diffusion coefficient of the dipolar RTIL. The orientational static structure

factor for the dipolar ILs is obtained from the MSA model<sup>48a</sup> with proper corrections at both  $k \rightarrow 0$  and  $k \rightarrow \infty$  limits. The isotropic dynamic structure factor has been approximated by its diffusive limit.<sup>24,33</sup> For the phosphonium ionic liquid studied here, the dipole-dipole contribution is assumed to originate from the interaction between the undissociated ion-pairs (IP)<sup>50</sup> and the solute molecule where the rotational dynamics, in the absence of any dielectric measurements, is approximated by its diffusive limit. Note that since the contribution of the solute-IP interaction is calculated in the diffusive limit, the time scale for relaxation of this part is expected to be not too different from the relaxation of the solute-ion interaction part. As a result, solute-IP interaction has very little relevance to the calculations presented here, even though in reality it may have some definite role to play.

$S_{solute}^{lm}(k, t)$  in Eq. 4 denotes the ( $l, m$ ) component of the solute self-dynamic structure factor which, for a single dipolar solute, is assumed to be given by Eq. (5),<sup>34</sup>

$$S_{solute}^{lm}(k, t) = \frac{1}{4\pi} \exp \left[ - \left( l(l+1) D_R^s + k^2 D_T^s \right) t \right] \quad \dots (5)$$

The rotational ( $D_R^s$ ) and translational ( $D_T^s$ ) diffusion coefficients of the solute are obtained from liquid viscosity using the stick boundary condition for rotation and slip for translation.<sup>49</sup> Note that use of Eq. 5 allows one to investigate separately the effects of rotational and translational motions of the solute on its own rate of solvation by making one of the diffusion coefficients equal to zero. Allowing the solute to both rotate and translate (non-zero values for  $D_R^s$  and  $D_T^s$ ) during the course of solvation, corresponds to solvation of a mobile dipolar solute in a given medium. Equating both to zero at the same time then describes the solvation of a fixed solute.

The expression for the normalized dipole-ion solvation energy auto-correlation function has been shown to be<sup>24</sup> as given in Eq. (6),

$$S_{si}(t) = \frac{\langle E_{si}(t) E_{si}(0) \rangle}{\langle |E_{si}(0)|^2 \rangle}$$

$$= \frac{2 \left( \frac{k_B T}{2\pi} \right)^2 \sum_{\alpha, \beta} \sqrt{n_\alpha^0 n_\beta^0} \int_0^\infty dk k^2 S_{solute}^{10}(k; t) \times c_{s\alpha}^{10}(k) c_{s\beta}^{10}(-k) S_{\alpha\beta}^{ion}(k; t)}{2 \left( \frac{k_B T}{2\pi} \right)^2 \sum_{\alpha, \beta} \sqrt{n_\alpha^0 n_\beta^0} \int_0^\infty dk k^2 S_{solute}^{10}(k) \times c_{s\alpha}^{10}(k) c_{s\beta}^{10}(-k) S_{\alpha\beta}^{ion}(k)} \quad \dots (6)$$

Here  $S_{\alpha\beta}^{ion}(k,t)$  is the isotropic ion dynamic structure factors and is assumed to be given by Eq. (7),<sup>49</sup>

$$S_{\alpha\beta}^{ion}(k;t) = S_{\alpha\beta}^{ion}(k) \exp[-D_{\alpha} k^2 t / S_{\alpha\alpha}(k)] \quad \dots (7)$$

where  $D_{\alpha}$ , the diffusion coefficient of an ion of type  $\alpha$  is experimental values from literature<sup>30,48b</sup>. For liquids for which experimental data are not available, Stokes-Einstein relation with slip boundary condition is used to obtain  $D_{\alpha}$ .  $S_{\alpha\alpha}(k)$  denotes the partial structure factor for the homogeneous binary mixture of ions and is calculated using Percus-Yevick (PY) solutions for hard sphere mixtures.<sup>49</sup> We have approximated each of the ions as hard sphere possessing unit charge at the centre with no size dissymmetry and used the expressions derived elsewhere<sup>51,52</sup> for the calculation of ion static structure factor,  $S_{\alpha\beta}^{ion}(k)$ . The longitudinal component of the wave number dependent direct correlation function between the dipolar solute and ions,  $c_{s\alpha}^{10}(k)$  is taken as  $-\sqrt{\frac{4\pi}{3}} \left( \frac{4\pi i \mu_1 q_{\alpha}}{k_B T \epsilon_0 k} \right) \frac{\sin(kr_c)}{kr_c}$ , where  $\mu_1$  is the dipole moment of the dipolar solute in the excited state,  $q_{\alpha}$  the charge of  $\alpha^{\text{th}}$  type ion,  $r_c$  is the distance of the closest approach between the solute dipole and the ionic species. Densities and viscosities required in the

calculation have been taken from literature and are provided in Table 1. The dipole moment of the effective liquid was estimated according to experimental static dielectric constant using the MSA formalism<sup>48a</sup>. Note that even though such a calculation provides a dipole moment ( $\sim 4$  D) for the cation quite close to that obtained via electronic structure calculations,<sup>48b</sup> it deviates ( $\sim 2.5$  D) from that estimated by an *ab initio* molecular dynamics simulation study<sup>48c</sup>. The excited state dipole moment ( $\mu_1$ ) of C153 was taken as 14 D<sup>39,41</sup>. The average solvation times ( $\langle \tau_s \rangle$ ) are then obtained by time-integrating the respective normalized solvation energy auto-correlation functions as follows:  $\langle \tau_s \rangle = \int_0^{\infty} dt S_x(t)$ , where  $x$  denotes the identity of the function ('E', 'sd' or 'si' to represent Eqs 3, 4 and 6).

## Results and Discussion

We next present the theoretical results of solvation dynamics for C153 in [P<sub>14,666</sub>][Br] and [bmim][PF<sub>6</sub>]. First we show the predicted decays of solute-solvent dipole-dipole ( $S_{sd}$ ) and dipole-ion ( $S_{si}$ ) interaction contributions, calculated by using Eq. 4 and Eq. 6, respectively. Figure 1 displays the calculated decays of dipole-dipole contribution ( $S_{sd}$ ) for C153 in these two ionic liquids. Note that while the calculations for [P<sub>14,666</sub>][Br] have been done at 343 K, those for [bmim][PF<sub>6</sub>] correspond to room temperature. The

Table 1 — Essential parameters required in the calculations<sup>a</sup>

| Ionic liquid          | [P <sub>14,666</sub> ][Br] | [bmim][PF <sub>6</sub> ] |
|-----------------------|----------------------------|--------------------------|
| M. wt. (g/mol)        | 564                        | 284                      |
| Cation dia. (Å)       | 10.68                      | 6.78                     |
| Anion dia. (Å)        | 4.56                       | 5.44                     |
| Viscosity (Poise)     | 1.2                        | 3.1                      |
| Density (g/ml)        | 0.925                      | 1.370                    |
| Dipole moment (Debye) | 5.6 (ion-pair)             | 4.4 (cation)             |

<sup>a</sup> The diameter of C153 is 7.8 Å (ref. 41).

<sup>b</sup> From ref. 30.

<sup>c</sup> Since the calculation is performed at 343 K for the phosphonium liquid, the parameters reported for this liquid are those at 343 K.

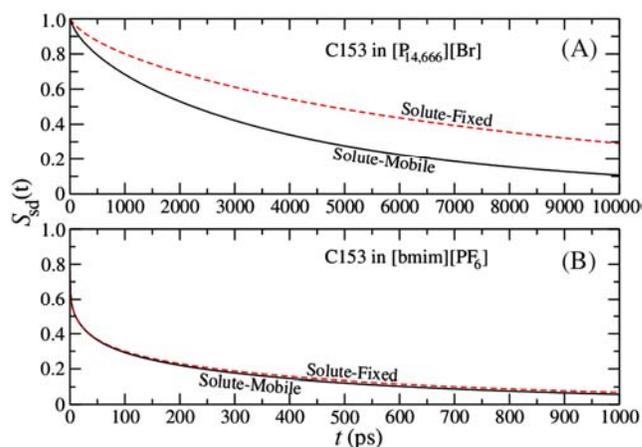


Fig. 1 — The solute-solvent dipole-dipole interaction part of the solvation response function,  $S_{sd}(t)$ , for C153 in (A) [P<sub>14,666</sub>][Br] and (B) [bmim][PF<sub>6</sub>]. The solid line represents the response function when the solute is both rotationally and translationally mobile and the dashed line represents the response function when all the motions of solute molecule are frozen.

results in this figure clearly demonstrate that while solute motion plays an important role for solvation energy relaxation in the phosphonium ionic liquid considered here, its solvation is much less affected by its own motion in [bmim][PF<sub>6</sub>]. In fact, similar results have also been found for the calculated decays of the dipole-

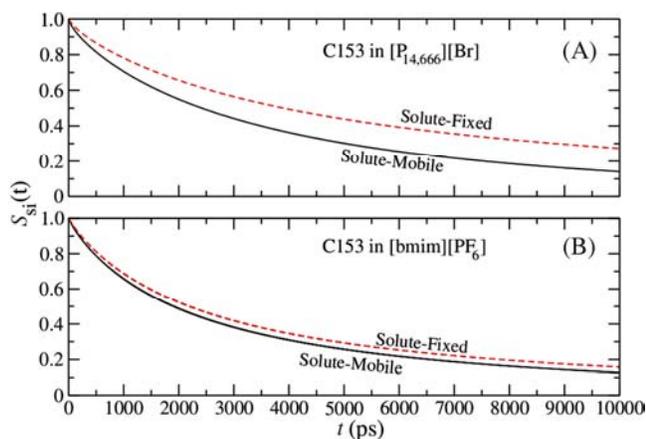


Fig. 2 — The solute-solvent dipole-ion interaction part of the solvation response function,  $S_{si}(t)$ , for C153 in (A) [P<sub>14,666</sub>][Br] and (B) [bmim][PF<sub>6</sub>]. Other representations remain the same as in Fig. 1.

ion contribution ( $S_{si}$ ) which are shown in Fig. 2. Note that dynamic Stokes' shift measurements in fauzasite zeolite have already hinted at the contributions of both, the solute's self motion and ion-solute interaction, on the solvation energy relaxation of a dipolar dye encapsulated in such supercaged solid structures.<sup>53</sup>

In order to reflect more on the effects of solute motion on solvation energy relaxation, the calculated decays of individual solvation response functions have been fitted to the following normalized function,  $S(t) = a_1 \exp[-t/\tau_1] + a_2 \exp[-(t/\tau_2)^\beta]$ , where  $a_i$ s denote the amplitude ( $a_1 + a_2 = 1$ ) and  $\tau_i$ s the time constants associated with each of the decay components ( $a_i$ ).  $\beta$  in the above fit-function represents an exponent, for which a value of unity corresponds to bi-exponential decay of the solvation response function. Parameters obtained from fit to the above equation are summarized in Table 2 where experimental numbers are also tabulated for comparison. In addition, fit parameters describing the decay of the total normalized solvation energy autocorrelation function ( $S_E$ ) obtained from Eq. 3

Table 2 — Solvation dynamics of C153 in imidazolium and phosphonium ionic liquids

| Solvent response function                              | $a_1$ | $\tau_1$ (ps) | $a_2$ | $\tau_2$ (ps) | $\beta$   | $\langle \tau_s \rangle$ (ns) |
|--|-------|---------------|-------|---------------|-----------|-------------------------------|
| <i>C153 in [P<sub>14,666</sub>][Br]: Fixed solute</i>  |       |               |       |               |           |                               |
| $S_{si}(t)$  | 0.46  | 2193          | 0.54  | 14604         | 1         | 8.90                          |
| $S_{sd}(t)$ (ion pair)                                 | 0.22  | 1253          | 0.78  | 10300         | 1         | 8.30                          |
| $S_E(t)$   | 0.44  | 2169          | 0.56  | 14126         | 1         | 8.86                          |
| Expt.  | 1     | 1310±70       | -     | -             | 0.38±0.05 | 5.05±0.43                     |
| <i>C153 in [P<sub>14,666</sub>][Br]: Mobile solute</i> |       |               |       |               |           |                               |
| $S_{si}(t)$  | 0.38  | 1289          | 0.62  | 6774          | 1         | 4.69                          |
| $S_{sd}(t)$ (ion pair)                                 | 0.25  | 708           | 0.75  | 5081          | 1         | 3.99                          |
| $S_E(t)$   | 0.37  | 1275          | 0.63  | 6634          | 1         | 4.65                          |
| Expt.  | 1     | 1310±70       | -     | -             | 0.38±0.05 | 5.05±0.43                     |
| <i>C153 in [bmim][PF<sub>6</sub>]: Fixed solute</i>    |       |               |       |               |           |                               |
| $S_{si}(t)$  | 0.27  | 846           | 0.73  | 5281          | 1         | 4.08                          |
| $S_{sd}(t)$  | 0.30  | 0.26          | 0.70  | 158           | 0.46      | 0.26                          |
| $S_E(t)$   | 0.14  | 0.47          | 0.86  | 2508          | 0.59      | 3.32                          |
| $0.85S_{sd}(t) + 0.15S_{si}(t)$                        | 0.21  | 0.24          | 0.79  | 293           | 0.37      | 0.97                          |
| Expt.  | -     | -             | 1.00  | 500           | 0.49±0.1  | 1.0±0.20                      |
| <i>C153 in [bmim][PF<sub>6</sub>]: Mobile solute</i>   |       |               |       |               |           |                               |
| $S_{si}(t)$  | 0.27  | 732           | 0.73  | 4604          | 1         | 3.56                          |
| $S_{sd}(t)$  | 0.30  | 0.25          | 0.70  | 145           | 0.8       | 0.22                          |
| $S_E(t)$   | 0.14  | 0.45          | 0.86  | 2160          | 0.59      | 2.86                          |
| $0.85S_{sd}(t) + 0.15S_{si}(t)$                        | 0.20  | 0.22          | 0.80  | 254           | 0.38      | 0.78                          |
| Expt.  | -     | -             | 1.00  | 500           | 0.49±0.1  | 1.0±0.20                      |

are also presented in Table 2 to stress the importance of solvent orientational relaxation in solvation dynamics of polar probes in imidazolium and other dipolar ionic liquids. Note that the present theory predicts  $\beta = 1$  for decay of both the contributions ( $S_{sd}$  and  $S_{si}$ ) in  $[P_{14,666}][Br]$  and of  $S_{si}$  in  $[bmim][PF_6]$ . While the neglect of static structural heterogeneity of these ionic liquids in the present theory is responsible for the predicted bi-exponential decay of these components,<sup>24</sup> use of experimental dielectric relaxation data for the calculation of  $S_{sd}$  in  $[bmim][PF_6]$  leads to  $\beta \approx 0.4$  which is quite close to experimental value<sup>15</sup> ( $\sim 0.5$ ) for this liquid. Calculated  $\beta$  is found to be independent of solute motion as the effects of solute motion enters through the macroscopic (that is,  $k \rightarrow 0$  limit) experimental values of diffusion coefficients which averages out the contributions due to the structural distribution around the moving solute.

Fit parameters summarized in Table 1 make it abundantly clear that the effects of solute motion is much more pronounced in  $[P_{14,666}][Br]$  than in  $[bmim][PF_6]$ . For the phosphonium ionic liquid, the solute motion reduces the average solvation time,  $\langle \tau_s \rangle$ , by a factor of  $\sim 2$  for each of the components ( $S_{sd}$ ,  $S_{si}$  and  $S_E$ ) in  $[P_{14,666}][Br]$ . In comparison, the solute-motion accelerates the decay rates in  $[bmim][PF_6]$  by only  $\sim 10$ - $20$  % over the fixed-solute results. The origin of this difference lies in the nature of the molecular interactions that are involved in the solvation of the dipolar solute in these ionic liquids. Since the cation,  $[bmim]^+$ , is dipolar and able to participate in librational motions collectively with many of its nearest neighbors,<sup>26,40</sup> the solvation energy relaxation of C153 in  $[bmim][PF_6]$  is principally guided by the solute-solvent polar interactions where collective ( $k \rightarrow 0$ ) modes of solvent polarization density fluctuation are known to dominate.<sup>33</sup> In such a situation it is therefore natural that the effects of variation in shape or size of the solute will be insignificant. Consequently, the solute motion, which is more local and thus couples to polar solvation energy relaxation only at later times, is not expected to affect the Stokes' shift dynamics for the most part of its duration. However, at later times when the solvent translational modes become operative, the solute-solvent short range correlations become important and the spectral shift begins to be affected

by the solute (shape and size) and its motions. The time scale in this part is guided by the structural relaxation of the solvent cage. This indicates that in systems where collective orientational solvent response is absent, effects of both the solute size and self-motion can be more pronounced and thus should be observable.

The cation,  $[P_{14,666}]^+$  in  $[P_{14,666}][Br]$  being non-dipolar in nature, the role of solvent orientational polarization density relaxation is much less important. As a result, the relaxation of the ion dynamic structure factor dictates the time scale of solvation in these non-dipolar ionic liquids. In this sense, the solvation dynamics in phosphonium ionic liquids is more akin to that in non-polar solvents where the rate of breakage and reformation of solvent cage around the solute determines the solvation time scale.<sup>41,54,55</sup> In such cases where the dynamics is more strongly coupled to the shorter-ranged interactions, solute-motion provides another important channel for solvation energy relaxation. This is the reason that solvation energy relaxation is significantly enhanced by the motion of the solute, particularly when the solute-solvent size ratio becomes less than unity. The size ratio between the phosphonium cation and C153 is  $\sim 1.4$  and that between the bromide and C153 is  $\sim 0.6$ . In comparison, the cation-solute size ratio in  $[bmim][PF_6]$  is  $\sim 0.9$  and the anion-solute size ratio is  $\sim 0.7$ . Therefore, the solute being  $\sim 40$  % smaller in size relative to the cation in  $[P_{14,666}][Br]$  allows more contributions from the nearest neighbor modes in the present theory and thus the effects of solute motion are realized. Another important factor to note in Table 2 is that the theoretical prediction for average solvation time becomes comparable to experimental values only when the solute motion is incorporated into the calculation. This indicates that for solvation in more non-polar like situation as in  $[P_{14,666}][Br]$ , the experimentally measured dynamics may derive contributions from both the solute motion and heterogeneity of the medium. The much less sensitivity of  $\langle \tau_s \rangle$  in  $[bmim][PF_6]$  to solute-motion and its strong bias towards the dipolar interaction contribution (for mobile solute,  $\langle \tau_s \rangle^{si} / \langle \tau_s \rangle^{sd} \approx 16$  and  $\langle \tau_s \rangle^{\text{experiment}} / \langle \tau_s \rangle^{sd} \approx 5$ ), on the other hand, suggests the dominance of solvent rotation for solvation energy relaxation in these dipolar ionic liquids.

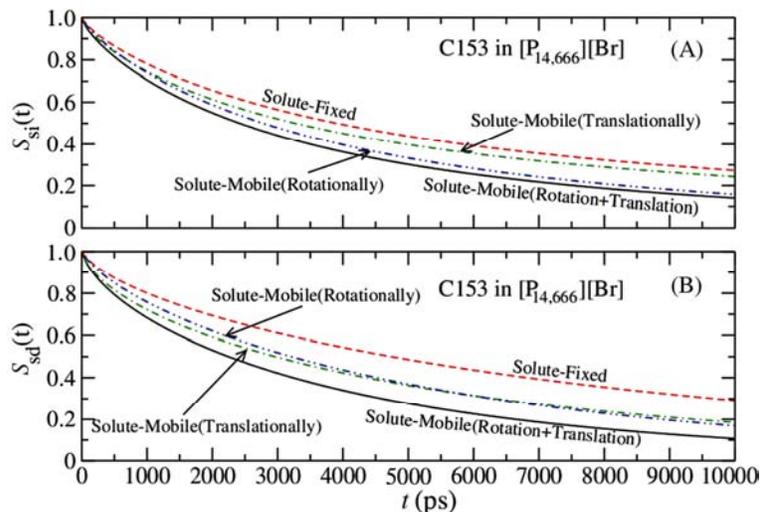


Fig. 3 — Individual effects of solute (C153) translation and rotation on the interaction contributions; (A)  $S_{si}(t)$  and (B)  $S_{sd}(t)$ , in  $[P_{14,666}][Br]$ . The results presented here suggest that rotation of the solute is more important than its translation for solvation in this liquid. For further details, see text.

It has already been explained elsewhere that the approximation of the solvent structure by its homogeneous picture has led to the bi-exponential decay of the ion-dipole interaction contribution ( $S_{si}$ ) in these liquids and of both  $S_{si}$  and  $S_{sd}$  in phosphonium liquids<sup>24</sup>. Even though the slowest of these two time scales have not been detected in the dynamic Stokes' shift measurements involving these liquids, prediction of such a slow component ( $4 \leq \tau/ns \leq 15$ ) in these liquids may not be completely an artifact of the theory. Recent experiments on solvation and rotation dynamics of C153 in a number of ionic liquids reports multi-exponential decay with slowest solvation time constants in this range at lower temperatures.<sup>56</sup> These slow time scales have been explained in terms of solute partitioning in the longer-lived local solvent structures in these strongly heterogeneous liquids.<sup>56</sup> The effects of solute-solvent short-range interactions in the distributed environments in such inhomogeneous liquids may be partially mapped by the wavenumber ( $k$ ) dependence of its homogeneous counter-part. Therefore, the similarity between the slowest time constants in these calculations and the recent experiments only signals the real existence of such slow time scales for fluorescence dynamics in these liquids. However, this is a conjecture which warrants further study.

We have so far studied the difference in solvation energy relaxations between two scenarios: a

Table 3 — Effect of solute translation and rotation separately on the solvation dynamics in phosphonium ionic liquids

| Solvent response function  | $a_1$ | $\tau_1$ (ps) | $a_2$ | $\tau_2$ (ps) | $\beta$ | $\langle \tau_s \rangle$ (ns) |
|--|-------|---------------|-------|---------------|---------|-------------------------------|
| <i>C153 in <math>[P_{14,666}][Br]</math>: Mobile solute (only translationally)</i> |       |               |       |               |         |                               |
| $S_{si}(t)$  | 0.42  | 1564          | 0.58  | 11602         | 1       | 7.39                          |
| $S_{sd}(t)$ (ion pair)   | 0.27  | 878           | 0.73  | 7335          | 1       | 5.59                          |
| $S_E(t)$   | 0.41  | 1542          | 0.59  | 11185         | 1       | 7.23                          |
| <i>C153 in <math>[P_{14,666}][Br]</math>: Mobile solute (only rotationally)</i>    |       |               |       |               |         |                               |
| $S_{si}(t)$  | 0.36  | 1538          | 0.64  | 7170          | 1       | 5.14                          |
| $S_{sd}(t)$ (ion pair)   | 0.18  | 872           | 0.82  | 6314          | 1       | 5.33                          |
| $S_E(t)$   | 0.34  | 1523          | 0.66  | 7092          | 1       | 5.20                          |

completely fixed solute (both rotation and translation of the solute frozen) and a completely mobile solute. We would like now to investigate what happens when the solute is allowed to rotate but not translate and then the solute is allowed to translate but not rotate. This has been done for solvation of C153 in  $[P_{14,666}][Br]$  as the effects of solute motion has been more pronounced for this solvent. The numerical results are shown in Fig. 3 and the fit parameters summarized in Table 3. These results indicate that the effects of solute rotation are much stronger on solvation energy relaxation in solvents where the relaxation of isotropic solvent structure controls the dynamics. In fact, one recovers the experimental average solvation time in  $[P_{14,666}][Br]$  by considering only the solute rotation (solute

translation frozen) in the calculated total solvation response function.

### Conclusions

In summary, the present microscopic theory predicts a strong role for solute rotation in determining the time scale of solvation energy relaxation of a dissolved dipolar dye in non-dipolar ionic liquids, such as the phosphonium ionic liquid studied here. Moreover, the solute rotation rather than the translation has been found to be more effective in accelerating the dynamics in such liquids. The theory also explains the absence of any solute-motion effects for solvation in dipolar ionic liquids such as the one studied here and thus corroborates with the simulation study solvation dynamics in this system. A better agreement to experimental average solvation time for  $[P_{14,666}][Br]$  has been obtained only after the incorporation of the solute motions. The present theory also predicted that a solute size dependence of solvation dynamics is more likely to be observed for solvation in non-dipolar ionic liquids where solvent orientational polarization density relaxation plays an insignificant role. This prediction can be tested in experiments with varying solute size, from substantially smaller to considerably larger than the cation size. A similar study may also be repeated by varying the anion-solute size ratio which will help understand more the role of different types of ions for fluorescence dynamics in these new class of solvents.

The demerits of the present formalism is as follows: (i) the constituting ions are assumed to be spherical which, in reality, is a oversimplification of the varied shapes in which they exist; (ii) the spatial correlations among various species have been obtained from the either MSA or Percus-Yevick<sup>49</sup> solutions for homogeneous liquids and thus the micro-heterogeneity of these liquids is ignored; (iii) ion-dipole and dipole-dipole interactions are approximated to be separable quantities; (iv) contribution of solute-IP interaction has been ignored. While these approximations may not be severe for dipolar ionic liquids, such as the imidazolium ones, because of the dominance of the collective polarization mode over the polar solvation energy relaxation in these liquids, their validity needs to be scrutinized for non-dipolar ionic liquids. In fact, the importance of the local solvent structure as well as the solute-IP interaction contributions has already been recognized in our earlier work<sup>24</sup> where a test

calculation indicates moderate contribution to the dynamic Stokes' shift in phosphonium ionic liquids. Since the solute-IP contribution to dynamics in these liquids is calculated in the diffusive regime, the time scale remains more or less the same for this contribution and the solute-ion interaction contribution. This is evident if one compares Figs 1A and 2A of the present article, and Fig. 4 of ref. 24. For imidazolium ionic liquids, no similar study has been attempted, although contribution from the solute-IP interaction enters indirectly in the calculations as the experimental dielectric relaxation data are used as input. Therefore, a better theory which removes the above approximations but still retains analytical simplicity and appeal as the present one would be a welcome development.

### Acknowledgement

Partial financial assistances from the Council of Scientific and Industrial Research (CSIR), India, (01/1958/04/EMR II), and the Department of Science and Technology (DST), India, (SR/S1/PC-03/2005) are gratefully acknowledged.

### References

- 1 Rogers R D & Seddon K R, *Ionic Liquids: Industrial Application for Green Chemistry*, (American Chemical Society Symposium Series), 2002, p. 818.
- 2 Wasserscheid P & Welton T, *Ionic Liquids in Synthesis*, (Wiley-VCH, Weinheim) 2003.
- 3 Welton T, *Chem Rev*, 99 (1999) 2071.
- 4 Dupont J, de Souza R F & Suarez P A Z, *Chem Rev*, 102 (2002) 3667.
- 5 Krossing I, Slattery J M, Dagueuet C, Dyson P J, Oleinikova A & Weingartner H, *J Am Chem Soc*, 128 (2006) 13427.
- 6 Shirota H & Castner Jr E W, *J Phys Chem B*, 109 (2005) 21576.
- 7 Hunt P A, *J Phys Chem B*, 111 (2007) 4844.
- 8 Aerov A A, Khokhlov A R & Potemkin I I, *J Phys Chem B*, 110 (2006) 16205.
- 9 Wang J, Chu H & Li Y, *ACS Nano*, 2 (2008) 2540.
- 10 Cadena C, Anthony J L, Shah, J K, Morrow T I, Brennecke J F & Maginn E J, *J Am Chem Soc*, 126 (2004) 5300.
- 11 Karamkar R & Samanta A, *J Phys Chem A*, 106 (2002) 4447.
- 12 Karamkar R, Samanta A, *J Phys Chem A*, 106 (2002) 6670.
- 13 Samanta A, *J Phys Chem B*, 110 (2006) 13704.
- 14 Ingram J A, Moog R S, Ito N, Biswas R & Maroncelli M, *J Phys Chem B*, 107 (2003) 5926.
- 15 Arzhantsev S, Jin H, Baker G A & Maroncelli M *J Phys Chem B*, 111 (2007) 4978.
- 16 Shim Y, Duan J, Choi M Y & Kim H J, *J Chem Phys*, 119 (2003) 6411.
- 17 Shim Y, Duan J, Choi M Y & Kim H J, *J Chem Phys*, 122 (2005) 044511.
- 18 Znamenskiy V & Kobrak M N, *J Phys Chem B*, 108 (2004) 1072.
- 19 Kobrak M N & Znamenskiy V, *Chem Phys Lett*, 395 (2004) 127.

- 20 Kobrak M N, *J Chem Phys*, 125 (2006) 064502.  
21 Margulis C J, *Mol Phys*, 102 (2004) 829.  
22 Hu Z & Margulis C J, *J Phys Chem B*, 102 (2006) 11025.  
23 Bhargava B L & Balasubramanian S, *J Chem Phys*, 123 (2005) 144505.  
24 Kashyap H K & Biswas R, *J Phys Chem B*, 114 (2010) 254.  
25 Kashyap H K & Biswas R, *J Phys Chem B*, 112 (2008) 12431.  
26 Stoppa A, Hunger J, Buchner R, Hefter G, Thoman A & Helm H, *J Phys Chem B*, 112 (2008) 4854.  
27 Ito N, Arzhantsev S, Heitz M & Maroncelli M, *J Phys Chem B*, 108 (2004) 5771.  
28 Arzhantsev S, Ito N, Heitz M & Maroncelli M, *Chem Phys Lett*, 381 (2003) 278.  
29 Mandal, P K & Samanta A, *J Phys Chem B*, 109 (2005) 15172.  
30 Jin H, Baker G A, Arzhantsev S, Dong J & Maroncelli M, *J Phys Chem B*, 111 (2007) 7291.  
31 Schroder C, Haberler M & Steinhauser O, *J Chem Phys*, 128 (2008) 134501.  
32 Schroder C & Steinhauser O, *J Chem Phys*, 131 (2009) 114504.  
33 Bagchi B & Biswas R, *Adv Chem Phys*, 109 (1999) 207.  
34 Bagchi B & Chandra A, *Adv Chem Phys*, 80 (1991) 1.  
35 Roy S & Bagchi B, *J Chem Phys*, 99 (1993) 9938.  
36 Roy S & Bagchi B, *J Chem Phys*, 99 (1993) 1310.  
37 Nandi N, Roy S & Bagchi B, *J Chem Phys*, 102 (1995) 1390.  
38 Biswas R & Bagchi B, *J Phys Chem B*, 100 (1996) 1238.  
39 Horng M L, Gardecki J A, Papazyan A & Maroncelli M, *J Phys Chem*, 99 (1995) 17311.  
40 Turton D A, Hunger J, Stoppa A, Hefter G, Thoman A, Walther M, Buchner R & Wynne K, *J Am Chem Soc*, 131 (2009) 11140.  
41 Reynolds L, Gardecki J, Frankland S J, Horng M L & Maroncelli M, *J Phys Chem*, 100 (1996) 10337.  
42 Biswas R & Bagchi B, *J Phys Chem*, 100 (1996) 4261.  
43 Guchhait B, Gazi H A R, Kashyap H K & Biswas R, *J Phys Chem B*, 114 (2010) 5066.  
44 Hohenberg P C & Halperin B I, *Rev Mod Phys*, 49 (1977) 435.  
45 Bagchi B, *Ann Rev Phys Chem*, 40 (1989) 115.  
46 Chapman C F & Maroncelli M, *J Phys Chem*, 95 (1991) 9095.  
47 (a) Chandra A & Patey G N, *J Chem Phys*, 100 (1994) 1552; (b) Chandra A, *Chem Phys Lett*, 244 (1995) 314; (c) Chandra A, Jana D & Bhattacharjee S, *J Chem Phys*, 104 (1996) 8662; (d) Mahajan K & Chandra A, *J Chem Phys*, 106 (1997) 2360.  
48 (a) Gray C G & Gubbins K E, *Theory of Molecular Fluids*, Vol I, (Clarendon, Oxford) 1984; (b) Jin H, O'Hare B, Arzhantsev S, Baker G, Wishart J F, Binesi A J & Maroncelli M, *J Phys Chem B*, 112 (2008) 81; (c) Bhargava B L & Balasubramanian S, *J Phys Chem B* 111 (2007) 4477.  
49 Hansen J P & McDonald I R, *Theory of Simple Liquids*, (Academic Press, London) 1986.  
50 (a) Fraser K J, Izgorodina E I, Forsyth M, Scott J L & MacFarlane D R, *Chem Commun*, 37 (2007) 3817; (b) Tokuda H, Tsuzuki S, Susan M A B H, Hayamizu K & Watanabe M, *J Phys Chem B*, 110 (2006) 19593; (c) Tokuda H, Tsuzuki S, Hayamizu K & Watanabe M, *J Phys Chem B*, 109 (2005) 16474.  
51 Attard P, *Phys Rev E*, 48 (1993) 3604.  
52 Chandra A & Bagchi B, *J Chem Phys*, 110 (1999) 10024.  
53 Das K, Sarkar N, Das S, Datta A & Bhattacharyya K, *Chem Phys Lett*, 249 (1996) 323.  
54 Bagchi B, *J Chem Phys*, 100 (1994) 6658.  
55 Fourkas J T, Benigno A & Berg M, *J Chem Phys*, 99 (1993) 8552.  
56 Funston A M, Fadeeva T A, Wishart J F & Castner Jr E W, *J Phys Chem B*, 111 (2007) 4963.