Experimental and Theoretical Investigations of Solvation Dynamics of Ionic Fluids: Appropriateness of Dielectric Theory and the Role of DC Conductivity

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Received: May 13, 2006

An analysis is provided of the subnanosecond dynamic solvation of ionic liquids in particular and ionic solutions in general. It is our hypothesis that solvation relaxation in ionic fluids, in the nonglassy and nonsupercooled regimes, can be understood rather simply in terms of the dielectric spectra of the solvent. This idea is suggested by the comparison of imidazolium ionic liquids with their pure organic counterpart, butylimidazole (*J. Phys. Chem. B* **2004**, *108*, 10245−10255). It is borne out by a calculation of the solvation correlation time from frequency dependent dielectric data for the ionic liquid, ethylammonium nitrate, and for the electrolyte solution of methanol and sodium perchlorate. Very good agreement is obtained between these theoretically calculated solvation relaxation functions and those obtained from fluorescence upconversion spectroscopy. Our comparisons suggest that translational motion of ions may not be the predominant factor in short-time solvation of ionic fluids and that many tools and ideas about solvation dynamics in polar solvents can be adapted to ionic fluids.

Introduction

The problem of understanding solvation by room-temperature ionic liquids (RTILs) is a specific aspect of the more general problem of understanding solvation in ionic fluids. RTILs are becoming an increasingly rich area of study.[1−4] Their growing utility has stimulated studies to understand the fundamentals of their behavior. For our current investigation, particularly relevant experimental studies have been based upon fluorescence techniques[5−16] and those obtaining the dielectric spectrum.[17,18] In particular, Weingärtner et al.[17] have investigated the dielectric relaxation of ethylammonium nitrate (EAN) in the 3 MHz to 40 GHz range, and their data stimulated much of the work discussed here.

On the theoretical side, several simulations have been performed to study solvation dynamics in RTILs. The initial rapid solvation events have been the object of computer simulations: Shim et al.,[19] placing a dipolar excitation on a model diatomic solute in a RTIL, observe a fast initial relaxation and suggest that it arises from translations of the anions. Given the small size of the model solute and the large changes in net charge, the motions of the resulting concentrated anionic charges may dominate the relaxation. In the experimental solvation dynamics studies of organic dye molecules such as coumarin 153 (C153) in RTILs, the charge distribution change is scattered across the whole probe molecule, which is most likely well solvated by the bulky organic cations given the hydrophobic nature of C153 in the ground state. We have suggested, therefore, that the most possible scenario is that the cation motions dominate the contribution of the initial fast relaxation upon excitation.[20] To elucidate the nature of the fast relaxations, a realistic model of C153 in RTILs will be needed.

Znamenskiy and Kobrak have recently performed molecular dynamics simulations of the dye betaine-30 in [$BMIM^+$][PF_6^-].[21] They obtain radial distribution functions indicating the proximity of the 1-butyl-3-methylimidazolium ring to the dye, which is consistent with our experimental observations for coumarin. As in experimental studies, the nature of solvation relaxation is argued to be from the translation and diffusional motion of ions.

A fundamental problem, then, in the study of ionic liquids is assessing the relative importance of translational motion of ions,[15,16,22] which can roughly be identified with dc conductivity, and the dielectric relaxation of dipoles. More specifically, an alternative view of the origin of solvation by ionic fluids, which we propose, is that it arises from the dielectric relaxation of dipoles resulting from ion pairs due to local neutrality and permanent dipoles carried by the ions. As a clear separation of the ac conductivity and the dielectric function is not possible except at zero-frequency (the static case), we will view the total dielectric function arising from the static conductivity contribution, which is related to the translational motion of ions, and the rest of dielectric function, which is due to the polarization relaxation.[23] For the polarization relaxation, the major contribution is from the ion pairs, ion clusters, and the dipole moments carried by the cations and anions. The size of these dipole moments can be estimated by taking the geometric center of the ions as the origin. For electrolyte solutions and molten salts, this point of view has been used fruitfully to interpret the experimental dielectric spectra.[24−28] Our recent work on the dynamic aspects of solvation by RTILs using Stokes shift data of the fluorescent probe, coumarin 153, from the picosecond to the nanosecond time regimes[20] already suggested such a connection. In that work, we investigated four RTILs based on the 1-butyl-3-methylimidazolium cation, $BMIM^+$. A major conclusion was that the rapid initial phase of solvation arises from the cations, which are the major carriers of permanent dipoles. The conclusion is reasonable because it is unlikely that symmetrical nonpolar inorganic anions such as Cl^-, BF_4^-, and PF_6^- play a significant role in the solvation of the coumarin probe. We are cautious, however, to extend this conclusion to the NTf_2^- anion, which is polar, polarizable, large, and flexible.[29]

In this report the solvation relaxation measured from fluorescence upconversion experiments is compared with that calculated from the dielectric spectra of the neat ionic liquids.

10.1021/jp062936l CCC: $33.50 © 2006 American Chemical Society
Published on Web 06/20/2006

Our results suggest that the time dependent solvation relaxation from solvation dynamics experiments is indeed directly related to the dielectric spectra, $\epsilon(\omega)$, of the ionic liquids just as in the case of dipolar fluids. Furthermore, at least for one solvent studied, the agreement between theory and experiment is much better when dc conductivity is eliminated from the dielectric spectra. The justification for omitting the conductivity at times probed in our experiments is that there is a time scale separation between the dielectric relaxation processes and the conductive processes in an ionic fluid. The latter can be described by a contribution of $\sigma/i\omega$ to the total dielectric response function, where σ is the dc conductivity.[23] The former is given by the dielectric relaxation via much higher frequency processes (>1 GHz for the subnanosecond processes in solvation dynamics) as shown by a significant body of experimentally measured dielectric spectra of electrolyte solutions[24] and ionic liquids.[25]

Materials and Methods

Preparation of EAN. Ethylammonium nitrate (EAN, Et−$NH_3^+NO_3^-$) was made by adding a limiting amount of concentrated nitric acid dropwise to a solution of 70% ethylamine in water at 0 °C with constant stirring. The mixture was allowed to stir for 30 min to ensure complete consumption of the acid. Excess ethylamine and water were removed by rotary evaporation. To remove small traces of water, the ethylammonium nitrate was dried under vacuum at 323 K for 72 h, using P_2O_5 as a drying agent. After drying, the ethylammoninum nitrate was sealed in a desiccator under argon. Before use, the salt was passed through a microscale silica gel column to ensure dryness. The column was constructed using a glass pipet sealed with cotton, and the salt was passed through the silica under pressure from a pipet bulb. Although ionic liquids have been known to dissolve cellulose, using cotton in such a fashion is not a concern under our conditions. Ionic liquids containing halide anions (more notably, chloride anions) seem to be the efficient systems for breaking up the complicated hydrogen bonding network within cellulose.[30] Furthermore, even for these solvents, at room temperature (at which the purification is performed) no dissolution is expected. It should be noted that when Rogers and co-workers first described the dissolution of cellulose in 1-butyl-3-methylimidazolium chloride, they were working at elevated temperatures (∼100 °C) and found that ∼25% w/w of cellulose could be dissolved.[30] The role of water on the physical properties of ionic liquids is well-known, and an excellent study is provided by Bright and co-workers.[31] This work indicates that the solvation probe, PRODAN, is highly sensitive to water content. On the other hand, Ito et al.[13] have shown that coumarin 153 is fortuitously insensitive to the presence of water, most likely owing to its hydrophobic character.

Steady-State Measurements. Steady-state excitation and emission spectra were recorded with a SPEX Fluoromax with a 4 nm band-pass and were corrected for detector response. A 1 cm path length quartz cuvette was used for the measurements. The steady-state spectra can be used to compute the reorganization energy, λ, by means of[32]

$$\lambda = \hbar \frac{\int_0^\infty d\nu\, [\sigma_a(\nu) - \sigma_f(\nu)]\nu}{\int_0^\infty d\nu\, [\sigma_a(\nu) + \sigma_f(\nu)]} \tag{1}$$

the $\sigma_{a,f}(\nu)$ are the absorption (or excitation) and emission spectral line-shapes, respectively.

Fluorescence Upconversion Measurements. Fluorescence upconversion measurements were performed using a homemade unamplified Ti:sapphire laser system.[20,33,34] The cross-correlation functions of its pulses have a fwhm of ∼300 fs. Upconversion profiles were used to construct time-resolved emission spectra. They were typically collected over a range of wavelengths from 480 to 560 nm at intervals of 10 nm. Nine transients were used to construct the time-resolved emission spectra by normalizing to the steady-state spectra of refs 20 and 35. We have employed the traditional approach of fitting the time-dependent spectra to a log-normal line-shape function, from which we extract the peak frequency, $\nu(t)$. The solvation dynamics were described by the normalized correlation function:

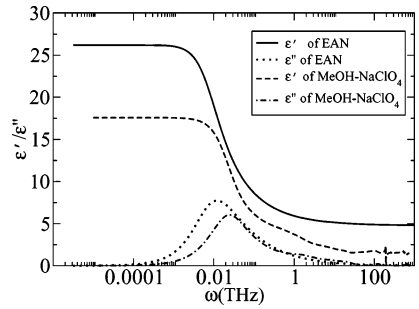

Figure 1. Dielectric spectra (without conductivity contributions) used to obtain the solvation energies, and ultimately the solvation relaxation functions, via eq 4.

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(\text{“}t{=}0\text{”}) - \nu(\infty)} \tag{2}$$

ν(“t=0”) is the frequency at zero time, calculated using the method described by Fee and Maroncelli.[36,37] $\nu(\infty)$ is the frequency at “infinite time”, the maximum of the steady-state fluorescence spectrum. $\nu(t)$ is determined by taking the maxima from the log-normal fits of the emission spectra. In most cases, however, the spectra are broad, so there is some uncertainty in the determination of the emission maxima. Thus, we took a range of the raw data points in the neighborhood of the maximum to estimate an error for the maximum obtained from the log-normal fit. Depending on the width of the spectrum (i.e., “zero-time”, steady-state, or time-resolved emission spectrum), we determined the uncertainties as follows: “zero-time” ∼ steady-state (∼±100 cm^{-1}) < time-resolved emission (∼±200 cm^{-1}).

Calculation of the Solvation Relaxation Function. The theoretical solvation spectral density was calculated using a dielectric continuum theory developed by one of us.[38,39] To model the solvation dynamics for C153, we used the geometry and charge distribution change that we employed elsewhere.[38] The frequency dependent dielectric function of the ionic fluid in question is obtained from experimental data. For EAN, the dielectric spectrum at frequencies below 90 GHz is from Weingärtner et al.;[17] higher frequencies are estimated by extending this spectrum via the Cole−Davison spectral function:[23]

$$\epsilon(\omega) = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + i\omega\tau_{CD})^\beta} \tag{3}$$

where $\epsilon_\infty = 4.8$, $\epsilon_s = 26.3$, $\beta = 0.52$, $\tau_{CD} = 160$ ps and ω is the angular frequency. The dielectric spectrum of methanol/$NaClO_4$ for frequencies lower than 90 GHz is from the tabulation by Barthel and Neueder;[40] the spectrum for higher frequencies is obtained from the data for pure methanol scaled at 90 GHz. Figure 1 gives the dielectric spectra used in our calculations. These data were used to calculate the total solvation energy $E(\omega)$ of C153 in an ionic fluid. A relationship between

TABLE 1: Spectral Parameters for Ionic Solvation of Coumarin 153[a]

solvent system	σ (S cm^{-1})	$\lambda_{t=0}$ (cm^{-1})	$\lambda_{t=\infty}$ (cm^{-1})	f_{300fs}[b]	$\langle\tau\rangle_{expt}$ (ps)[c]	$\langle\tau\rangle_{-\sigma}$ (ps)	$\langle\tau\rangle_{+\sigma}$ (ps)
EAN	0.028[d]	1845	2710 ± 20	0.33	26	17	33.2
1.05 M $NaClO_4$/MeOH	0.0387[e]	1955	2860 ± 15	0.30	9.8	7.5	27.6

[a] All the experiments were done at room temperature. For the steady-state data, the samples were excited at 420 nm. For the excitation spectra, the emission monochromator was set at 600 nm. The steady-state reorganization energies are based on the average of four measurements. [b] $f(t) = 1 - C(t)$, where $C(t)$ is obtained from eq 2. [c] $\langle\tau\rangle = \int_0^\infty C(t)_{fit}\, dt = \int_0^\infty \Sigma_i A_i \exp(-t/\tau_i)\, dt$. $C(t)$ are fit to sums of three exponentials. [d] From ref 17 at 298.15 K. [e] From ref 40 at 298.15 K.

the imaginary part of the solvation energy and the solvation correlation function, $C(t)$, can be derived

$$C(t) = \frac{\hbar}{\lambda}\int_0^\infty d\omega\, \frac{E(\omega)}{\omega}\cos(\omega t) \qquad (4)$$

where $E''(\omega)$ is the imaginary portion of the total solvation energy and λ is the reorganization energy, which is obtained from solving the Poisson equation with a complex dielectric function $\epsilon(\omega)$.[38]

Results and Discussion

Solvation data are compiled in Table 1. The experimentally obtained solvation relaxation functions for EAN and the 1.05 M $NaClO_4$/methanol solution are presented on 10 and 200 ps time scales in Figures 2 and 3, respectively, along with the corresponding theoretical relaxation functions obtained using eq 4, including and excluding the dc conductivity.

There are several important results. Approximately 30% of the solvation has already been accomplished in 300 fs for both systems. The $C(t)$'s are fit to a sum of exponentials, but we attribute no special significance to this functional form. The agreement between the experimental and theoretical curves is very good, especially when several points are taken into account.

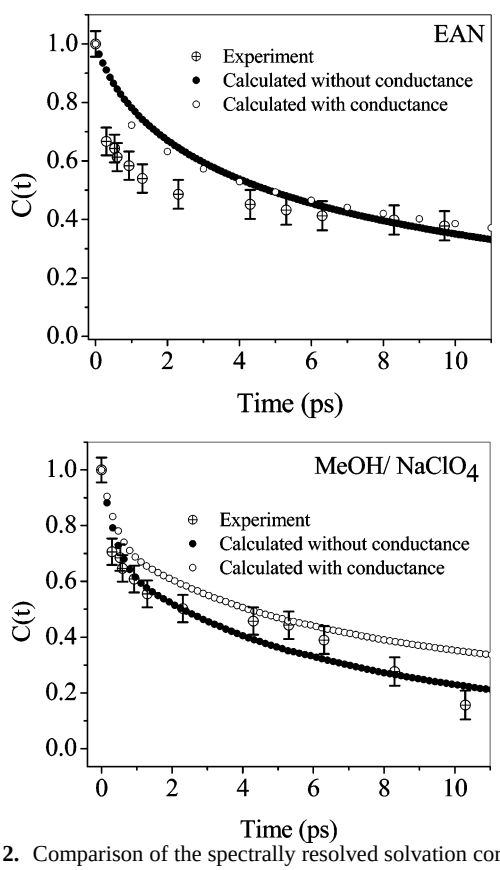

Figure 2. Comparison of the spectrally resolved solvation correlation function for EAN and MeOH/perchlorate, 10 ps full scale obtained from fluorescence upconversion experiments (⊕). The $C(t)$'s obtained from simulation are shown by solid circles (without conductance) and open circles (with conductance).

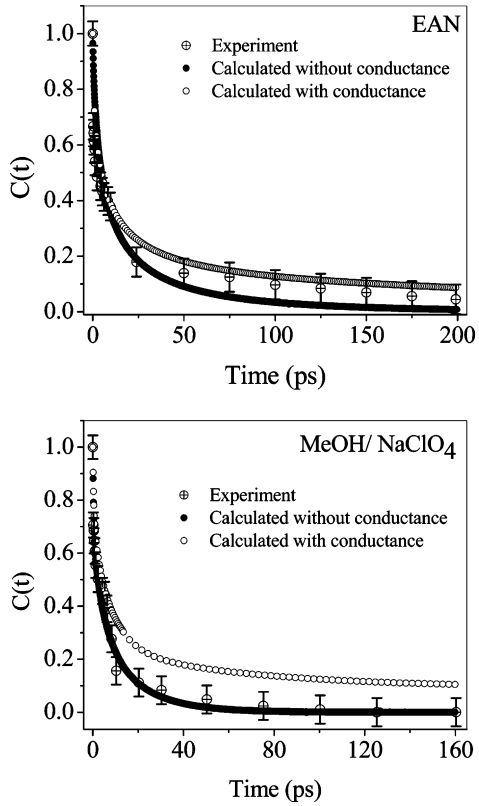

Figure 3. Comparison of the spectrally resolved solvation correlation function for EAN and MeOH/perchlorate, ~200 ps full scale obtained from fluorescence upconversion experiments (⊕). The $C(t)$'s obtained from simulation are shown by solid circles (without conductance) and open circles (with conductance).

At early times (10 ps time scale), the theoretical curve for MeOH/perchlorate corresponds very well with the experimental curve—especially when the dc conductivity has been eliminated. On the other hand, for EAN, the theoretical curves, both with and without conductivity though very similar to each other, deviate from the experimental curve. This divergence for EAN should not be surprising because the high-frequency portion of $\epsilon(\omega)$ is obtained by extrapolation. When the comparison is made on the 200 ps time scale, it is clear that for MeOH/perchlorate exclusion of the conductivity is required to superpose theory and experiment. On the other hand, for EAN, the two theoretical curves, both with and without conductivity, lie within the uncertainty of the measurement.

The good agreement between experiment and theoretical calculation clearly indicates that the solvation relaxation in ionic liquids comes from the dielectric relaxation of the fluid.

Conclusions

In summary, it is our hypothesis that solvation relaxation in ionic fluids, in the nonglassy and nonsupercooled regimes, can be understood rather simply in terms of the dielectric spectra of the solvent. This idea was initially suggested by our

comparison of imidazolium RTILs with their pure organic counterpart, butylimidazole.[20,37] It is supported by a calculation of the solvation relaxation function obtained from frequency dependent dielectric data for the RTIL, ethylammonium nitrate, and for the electrolyte solution of methanol and sodium perchlorate. Further experimental and theoretical work is required to understand ionic liquids. A larger spectrum of solvents needs to be studied to test the ideas presented here, detailed measurements of the higher frequency dielectric spectra may lead to better agreement between experiments and theoretical calculations, and more work needs to be done to understand the relative contributions to solvation relaxation from ion pairs and the permanent dipoles from the individual ions.

Acknowledgment. X.S. thanks the NSF for support from grant CHE0303758. We thank Professor Jared Anderson for helpful comments.

References and Notes

(1) Seddon, K. R. *Nature (Materials)* **2003**, *2*, 363.
(2) Anderson, J. L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.* **2002**, *124*, 14247.
(3) Poole, C. F. *J. Chromatogr. A* **2004**, *1037*, 49.
(4) Pandey, S. *Anal. Chim. Acta* **2006**, *556*, 38.
(5) Huppert, D.; Ittah, V.; Kosower, E. M. *Chem. Phys. Lett.* **1989**, *159*, 267.
(6) Ittah, V.; Huppert, D. *Chem. Phys. Lett.* **1990**, *173*, 496.
(7) Chapman, C. F.; Maroncelli, M. *J. Phys. Chem.* **1991**, *95*, 9095.
(8) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 6670.
(9) Karmakar, R.; Samanta, A. *J. Phys. Chem. A* **2002**, *106*, 4447.
(10) Karmakar, B.; Samanta, A. *J. Phys. Chem. A* **2003**, *107*, 7340.
(11) Ingram, J. A.; Moog, R. S.; Ito, N.; Biswas, R.; Maroncelli, M. *J. Phys. Chem. B* **2003**, *107*, 5926.
(12) Ito, N.; Arzhantsev, S.; Maroncelli, M. *Chem. Phys. Lett.* **2004**, *396*, 83.
(13) Ito, N.; Arzhantsev, S.; Heitz, M.; Maroncelli, M. *J. Phys. Chem. B* **2004**, *108*, 5771.
(14) Arzhantsev, S.; Ito, N.; Heitz, M.; Maroncelli, M. *Chem. Phys. Lett.* **2003**, *381*, 278.
(15) Arzhantsev, S.; Hui, J.; Naoki, I.; Maroncelli, M. *Chem. Phys. Lett.* **2006**, In press.
(16) Arzhantsev, S.; Hui, J.; Baker, G. A.; Naoki, I.; Maroncelli, M. Solvation dynamics in ionic liquids, results from ps and fs emission spectroscopy. Femtochemistry VII, 2005.
(17) Weingartner, H.; Knocks, A.; Schrader, E.; Kaatze, U. *J. Phys. Chem. A* **2001**, *105*, 8646.
(18) Ito, N.; Huang, W.; Richert, R. *J. Phys. Chem.*, Submitted for publication.
(19) Shim, Y.; Duan, J.; Choi, M. Y.; Kim, H. J. *J. Chem. Phys.* **2003**, *119*, 6411.
(20) Chowdhury, P. K.; Halder, M.; Sanders, L.; Calhoun, T.; Anderson, J.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. B* **2004**, *108*, 10245.
(21) Znamenskiy, V.; Kobrak, M. N. *J. Phys. Chem. B* **2004**, *108*, 1072.
(22) Kobrak, M. N.; Znamenskiy, V. *Chem. Phys. Lett.* **2004**, *395*, 127.
(23) Bottcher, C. J. F. *Theory of Electric Polarization*, 2nd ed.; Elsevier: Amsterdam, 1973; Vol. 2.
(24) Bruesch, P.; Pietronero, L.; Zeller, H. R. *J. Phys. C: Solid State Phys.* **1976**, *9*.
(25) Happ, H.; Boehm, H.; Kasemann, A.; Neuerbourg, R. *J. Phys. C: Solid State Phys.* **1987**, *20*, 5889.
(26) Barthel, J. M. G.; Krienke, H.; Kunz, W. *Top. Phys. Chem.* **1998**, *5*, 1.
(27) Kasemann, A.; Happ, H.; Wienpahl, U. *J. Phys.: Condens. Matter* **1989**, *1*, 5253.
(28) Wegdam, G. H.; Te Beek, J. B.; Van der Linden, H.; Van der Elsken, J. *J. Chem. Phys.* **1971**, *55*, 5207.
(29) Shirota, H.; Funston, A. M.; Wishart, J. F.; Castner, E. W., Jr. *J. Chem. Phys.* **2005**, *122*, 184512/1.
(30) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.* **2002**, *124*, 4974.
(31) Baker, S. N.; Baker, G. A.; Munson, C. A.; Chen, F.; Bukowski, E. J.; Cartwright, A. N.; Bright, F. V. *Ind. Eng. Chem. Res.* **2003**, *42*, 6457.
(32) Jordanides, X. J.; Lang, M. J.; Song, X. Y.; Fleming, G. R. *J. Phys. Chem. B* **1999**, *103*, 7995.
(33) Das, K.; Smirnov, A. V.; Wen, J.; Miskovsky, P.; Petrich, J. W. *Photochem. Photobiol.* **1999**, *69*, 633.
(34) Smirnov, A. V.; Das, K.; English, D. S.; Wan, Z.; Kraus, G. A.; Petrich, J. W. *J. Phys. Chem. A* **1999**, *103*, 7949.
(35) Maroncelli, M.; Fleming, G. R. *J. Chem. Phys.* **1987**, *86*, 6221.
(36) Fee, R. S.; Maroncelli, M. *Chem. Phys.* **1994**, *183*, 235.
(37) Headley, L. S.; Mukherjee, P.; Anderson, J. L.; Ding, R.; Halder, M.; Armstrong, D. W.; Song, X.; Petrich, J. W. *J. Phys. Chem. A* **2006**, Submitted.
(38) Song, X.; Chandler, D. *J. Chem. Phys.* **1998**, *108*, 2594.
(39) Song, X. *AIP Conf. Proc.* **1999**, *492*, 417.
(40) Barthel, J.; Neueder, R. *Electrolyte data collection: tables, diagrams, correlations, and literature survey*; DECHEMA: Frankfurt am Main, Germany, 1995.