Dynamic Solvation in Phosphonium Ionic Liquids: Comparison of Bulk and Micellar Systems and Considerations for the Construction of the Solvation Correlation Function, C(t)

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Abstract
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Keywords
Correlation methods, fluids, ionization of liquids, solvation, Coumarin 153, micellar system

Disciplines
Biochemistry | Chemistry

Comments

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Dynamic Solvation in Phosphonium Ionic Liquids: Comparison of Bulk and Micellar Systems and Considerations for the Construction of the Solvation Correlation Function, C(t)

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Dynamic solvation of the dye coumarin 153 is studied in a phosphonium ionic liquid: hexadecyltributylphosphonium bromide, \([\text{[(C}_4\text{)}_3\text{C}_{16}\text{P}^+][\text{Br}^-]]\). It forms micelles in water, and the bulk also exists as a liquid under our experimental conditions. This system permits a comparison with an imidazolium ionic liquid studied earlier, which also formed micelles in water (J. Phys. Chem. A 2006, 110, 10725–10730). We conclude that our analysis of the comparable situation in a phosphonium liquid is not as definitive as we had proposed earlier; i.e., that the majority of the early-time solvation arises from the organic cation. Part of the difficulty in performing this analysis is most likely due to the amount of water that is associated with the micelle. In the course of this work, we have focused on the calculation of the solvation correlation function, \(C(t)\), and investigated how it depends upon the methods with which the “zero-time” spectrum is constructed.

Introduction

Room-temperature ionic liquids, most commonly comprised of organic cations and inorganic anions, are receiving an increasing amount of attention because of their utility as environmentally friendly, “green” solvents and because of a host of practical applications to which they are amenable.1–4 The importance of ionic liquids has consequently stimulated considerable interest in their dynamic solvation properties.5–34

A special issue of The Journal of Physical Chemistry has recently been devoted to ionic liquids.35 Major questions regarding dynamic solvation by ionic liquids deal with whether the organic cation or the inorganic anion solvates preferentially on different time scales, the role of the correlated motion of the ion pairs and their lifetime, and the importance of translational motion of the ions relative to dipolar relaxation.23–25 Previously, we attempted to address some of these questions by studying the solvation of the dye coumarin 153 in a bulk imidazolium ionic liquid, 1-cetyl-3-vinylimidazolium bromide ([(CVIM⁺][Br⁻]), and its corresponding micelle in water.36 (There is a growing body of work on the subject of ionic liquids in micelles, and related systems.37–43) Because coumarin 153 is only sparingly soluble and weakly fluorescent in water, a clear distinction can be made between its fluorescent properties in the bulk ionic liquid and those in the micelles formed from the ionic liquid. We concluded from this study that the same entity is responsible for the majority of the solvation in both the bulk and micellar [(CVIM⁺][Br⁻] ionic liquid, namely, as we have suggested elsewhere,23–25 that it is the imidazolium cation. This study was, however, limited: first, because bulk [(CVIM⁺][Br⁻] could only be studied as an opaque solid at the temperatures at which we investigated the micelle; second, because the study only considered ionic liquids based upon imidazolium. In this work, we investigate a phosphonium ionic liquid (Figure 1), which forms micelles in water and for which

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Figure 1. Structures of the solvation probe (a) coumarin 153 (C153) and the two ionic liquids studied in this work: (b) hexadecyltributylphosphonium bromide, \([(\text{C}_4\text{)}_3\text{C}_{16}\text{P}^+][\text{Br}^-]\) (liquid at room temperature). \([(\text{C}_4\text{)}_3\text{C}_{16}\text{P}^+][\text{Br}^-]\) forms micelles in water.

the bulk also exists as a liquid under our experimental conditions: hexadecyltributylphosphonium bromide, \([(\text{C}_4\text{)}_3\text{C}_{16}\text{P}^+][\text{Br}^-]\) (melting point of 58–60 °C). As a result of this study, our earlier conclusions have been tempered, and most importantly, we present conclusions dealing with the construction of the solvation correlation function, \(C(t)\).

Materials and Methods

Preparation and Purification/Decolorization of Low-Melting-Point Phosphonium Halide Organic Salts. Phosphonium halide ionic liquids (ILs) were donated by Cytect Inc. and were decolorized according to the procedure described elsewhere.44 A conventional column used for flash chromatography was packed with the following compounds: Celite on the bottom to trap charcoal particles, flash chromatographic silica gel and alumina in the middle for decolorization and removal of polar and inorganic impurities, and charcoal on the top for decolorizing. The column was treated with dichloromethane (CH2Cl2)
Dynamic Solvation in Phosphonium Ionic Liquids


The results obtained from both bands were determined by the same procedure we have employed elsewhere. Calculations can be performed using the method described by Turro and Yekta and later modified by De Schryver and co-workers. As before, we employ the latter method, where the micellar aggregation number is obtained by exploiting the vibronic fine structure of pyrene emission. Pyrene was recrystallized several times from absolute ethanol before use. Three stock solutions were prepared of pyrene in ethanol, cetylpyridinium chloride in water, and (C6H13)3N+ [Br−] in water at concentrations of 2 × 10−4, 10 × 10−3, and 5 × 10−2 M. For all measurements, pyrene and surfactant concentrations were kept constant at ~2 × 10−6 and ~2 × 10−2 M. Six solutions were prepared with increasing quencher concentration from 0 to 0.5 × 10−3 M. Samples were excited at 337 nm. The aggregation number was determined by the same procedure we have employed elsewhere. Calculations can be performed using the intensity of either band I or band III of pyrene emission.

Preparation of Micellar Solutions. The critical micelle concentration (CMC) was found by plotting surface tension (dyn/cm) vs concentration (M). Surface tension measurements were taken using a Fischer model 20 surface tensiometer. All glassware used was cleaned by chromic acid, rinsed with deionized water, and dried in an oven. Concentrations of hexadecyltributylphosphonium bromide between 0 and 0.1 M were prepared in aqueous solution at room temperature. An average of three measurements was taken to represent the surface tension at each concentration of IL. The CMC value of the [(C4)3C16P][Br−] micelle was found to be 2 × 10−3 M at room temperature. For all experiments in micellar systems, the C153 concentration was kept at 0.1 M.

Preparation of Micellar Solutions for Stern–Volmer Quenching Experiments. We initially attempted to perform quenching experiments with iodide anion, as we did in our previous work. We were not able to attain concentrations of I− higher than 3 mM due to solubility problems and consequently were not able to obtain enough data to determine quenching constants. We thus opted for N,N-dimethylaniline (DMA) to quench C153 fluorescence in this system. For quenching of C153 in bulk solvent, a stock solution of 2 × 10−4 M C153 in acetonitrile was used. The corresponding quenching experiment in micellar environment was performed by preparing two stock solutions: 2 × 10−3 M C153 in acetonitrile and 5 × 10−2 M [(C4)3C16P][Br−] in water. For all measurements, the C153 and surfactant concentrations were kept constant at ~2 × 10−6 and ~5 × 10−3 M (2.5(CMC)), and an 830:1 surfactant-to-C153 ratio was maintained. Under these conditions there is one C153 molecule for every 18 micelles, thus minimizing the possibility of aggregation. Seven solutions were prepared with increasing quencher concentration from 0 to 10 × 10−3 M. We could not increase the quencher concentration above 10 × 10−3 M due to precipitation of the surfactant at higher DMA concentration.

Emission spectra were obtained using an excitation wavelength of 420 nm. The control experiment was performed in acetonitrile rather than in bulk [(C4)3C16P][Br−] owing to the difficulties imposed in preparing solutions by the high viscosity of the bulk and the rather small quantities available to us of the purified material.

The apparatus for the time-correlated single-photon counting measurements is described in detail elsewhere. The instrument response function had a full width at half-maximum (fwhm) of ≤ 100 ps. A 1 cm path length quartz cuvette was used for the measurements. During spectroscopic measurements, the quartz cuvettes were kept tightly sealed to prevent moisture from being absorbed by the ionic liquids. The steady-state spectra can be used to compute the reorganization energy, λ,

\[
\lambda = \hbar \int_0^\infty \frac{d\nu}{\nu} \left[ \sigma_s(\nu) - \sigma_t(\nu) \right] \nu 
\]

σs,t are the absorption (or excitation) and emission spectral line-shapes, respectively.

Figure 2. Stern–Volmer quenching plots of C153 by DMA in acetonitrile (solid circles) and [(C4)3C16P][Br−] micelles (open circles). KSV values were found to be 60 M−1 for C153 in acetonitrile and 390 M−1 for [(C4)3C16P][Br−] micelle. All experiments were done at room temperature. DMA is negligibly soluble in water, and on the basis of NMR67 and fluorescence68 measurements in CTAB micelles, it has been concluded that DMA resides in the head group region of the micelles. We expect the same location of DMA in [(C4)3C16P][Br−] micelles. The very efficient quenching of C153 fluorescence by DMA (most likely by electron transfer from DMA to C153)36 indicates that the probe molecules are accessible to the quencher.
to a maximum of three exponentials. Transient spectra were typically from 470 to 610 nm at 10 nm intervals. They were fit using the method of Fee and Maroncelli.\(^4^7\) \(v(\infty)\) is the frequency at “infinite time”, which may be taken as the maximum of the steady-state fluorescence spectrum if solvation is more rapid than the population decay of the probe. \(v(t)\) is determined by taking the maxima from the log—normal fits as the emission maximum. In most of the cases, however, the spectra are broad, so there is some uncertainty in the exact position of the emission maxima. Thus, we have considered the 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 have determined the typical uncertainties as follows: zero-time \(\approx \pm 100 \text{ cm}^{-1}\) \(<\text{time-resolved} \approx 200 \text{ cm}^{-1}\) emission. We use these uncertainties to compute error bars for \(C(t)\). Finally, in generating \(C(t)\), the first point was obtained from the zero-time spectrum. The second point was taken at the maximum of the instrument response function, which, having a full width at half-maximum of \(\pm 100\) ps, was taken to be \(\approx 100\) ps. Fractional solvation at 100 ps was calculated using \(f(t = 100\) ps\) = 1.\(^{-}\)\(C(t = 100\) ps\).)

**Results**

C153 is sparingly soluble in water and hence must be located in the micelles formed by [(C₄)₃C₁₆P][Br⁻]. To characterize its location therein, we constructed Stern—Volmer plots using DMA as a quencher. Figure 2 presents the Stern—Volmer plots of C153 quenched by DMA in acetonitrile and micelles formed by [(C₄)₃C₁₆P][Br⁻]. \(K_{SV}\) values were 60 M⁻¹ for C153 in acetonitrile and 390 M⁻¹ for the [(C₄)₃C₁₆P][Br⁻] micelle. The greater \(K_{SV}\) value in the micelle compared to that in the bulk might be attributed to greater accessibility of C153 to the quencher in the micelle. We suppose this is due to the close proximity of C153 and DMA, the latter being preferentially located in the Stern layer of the micelle. This situation is comparable to that of [CVIM⁺][Br⁻], where C153 is quenched more efficiently in the micelle than in the bulk reference solvent.\(^3^6\) In both cases, C153 is interpreted to be located in...
TABLE 1: Solvation of Coumarin 153 in Bulk and Micellar Phosphonium Ionic Liquid Systems

<table>
<thead>
<tr>
<th>System</th>
<th>η (cP)</th>
<th>H₂O (wt %)</th>
<th>λₐ=λₐ⁰ (cm⁻¹)</th>
<th>λₑₜ (cm⁻¹)</th>
<th>f₁₀₀⁰ₚₜ (ns)</th>
<th>(ω) (cm⁻¹)</th>
<th>f₁₀₀⁰ₚₜ (ns)</th>
<th>(ω) (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] bulk (66 °C)</td>
<td>268 ± 2</td>
<td>0.2</td>
<td>1920</td>
<td>2480</td>
<td>0.44 ± 0.06</td>
<td>0.77</td>
<td>1910</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] micelle (room temp)</td>
<td>1.11 ± 0.01</td>
<td></td>
<td>1980</td>
<td>2740</td>
<td>0.59 ± 0.04</td>
<td>0.45</td>
<td>18080</td>
<td>0.55 ± 0.04</td>
</tr>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] micelle (66 °C)</td>
<td>0.44 ± 0.01</td>
<td></td>
<td>2000</td>
<td>2450</td>
<td>0.67 ± 0.04</td>
<td>0.12</td>
<td>18130</td>
<td>0.66 ± 0.04</td>
</tr>
<tr>
<td>[(C₅)₆Cl₆][Cl⁻] bulk (purified) (58 °C)</td>
<td>80 ± 1</td>
<td>0.3</td>
<td>1970</td>
<td>2660</td>
<td>0.41 ± 0.05</td>
<td>0.70</td>
<td>19160</td>
<td>0.33 ± 0.04</td>
</tr>
<tr>
<td>[(C₅)₆Cl₆][Cl⁻] bulk (unpurified) (58 °C)</td>
<td>234 ± 2</td>
<td>0.3</td>
<td>1960</td>
<td>2460</td>
<td>0.34 ± 0.05</td>
<td>4.9</td>
<td>18900</td>
<td>0.03</td>
</tr>
</tbody>
</table>

TABLE 2: Fluorescence Anisotropy of C153 in Bulk Solvent and Micellar Systems

<table>
<thead>
<tr>
<th>System</th>
<th>r₀</th>
<th>r₁</th>
<th>r(t)</th>
<th>τ₀⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] bulk (66 °C)</td>
<td>0.22 ± 0.02</td>
<td>0.09 ± 0.01</td>
<td>260 ± 70</td>
<td>0.13 ± 0.02</td>
</tr>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] micelle (room temperature)</td>
<td>0.35 ± 0.03</td>
<td>0.15 ± 0.02</td>
<td>200 ± 80</td>
<td>0.20 ± 0.02</td>
</tr>
<tr>
<td>[(C₄)₃C₁₆P][Br⁻] micelle (66 °C)</td>
<td>0.25 ± 0.04</td>
<td>0.25 ± 0.04</td>
<td>360 ± 80</td>
<td>0.40 ± 0.00</td>
</tr>
</tbody>
</table>

Discussion

**Bulk Solvent versus Micellar System.** As indicated directly above, there are significant differences between the fractional solvation at early times for the bulk and micellar forms of [(C₄)₃C₁₆P][Br⁻]. In addition, the average solvation time of the bulk at 66 °C is at least 3 times as long as that in the micellar environment at room temperature on the 20 ns time scale (Table 1). The enhanced f₁₀₀⁰ₚₜ in micelles is most likely a result of aqueous solvation. As in the case of the imidazolium ionic liquid, quenching experiments indicate that it is likely that C153 resides in the Stern layer of the [(C₄)₃C₁₆P][Br⁻] micelle. Such a probe location can also explain why the average solvation time is considerably longer in bulk [(C₄)₃C₁₆P][Br⁻] compared to that of the micelle. In bulk water, solvation is essentially complete after 1 ps, but water in confined environments gives rise to slower solvation response, which has been argued to arise from a dynamic equilibrium between bound and free water molecules. We do not, however, subscribe to the idea of “biological water”, which some of these latter references argue for. Consequently, we suggest that the water responsible for the relatively rapid solvation response in the micelles is colocalized in the Stern layer with C153.

It is well to note that temperature can have rather profound effects on the structure of micelles and, consequently, the solvation dynamics at their interfaces. The temperature dependence of the structure and hydration number of Triton X-100 (TX-100) micelles was demonstrated by Streletzky and Phillips, who reported an increase in the hydration number of the micelle with an increase in temperature. The temperature dependence of the solvation dynamics in micelles was studied in TX-100 using 4-aminophthalimide (4-AP) as a fluorescent probe, where an increase in temperature from 283 to 323 K results in a ~8-fold decrease in the average solvation time. From this study the authors also concluded that a temperature-dependent change of the structure and hydration number in the TX-100 micelle appears to play a minor role in their measurements of solvation dynamics. Finally, the temperature-dependent effects on the solvation dynamics of C153 and C151 are significant in TX-100 micelles and moderate in Brij-35.
that at least some of the observed differences could be attributed to the presence of water, most likely owing to its hydrophobic character. In any case, the amount of water present was determined to be less than 1% by weight, and this was found to have a negligible effect on C153, on the basis of the work of Ito et al.\(^{10}\)

Excitation spectra in our laboratory were collected at an emission wavelength of 600 nm. Unless otherwise indicated, the data were obtained with the purified phosphonium liquid.\(^{6}\) Nonpolar solvent employed to obtain the excitation or absorption spectra used for the construction of the zero-time spectrum. The \(v_{ex}\) and \(v_{em}\) values for a long-chain phosphonium halide ionic liquid is contrary to the hydrophobic character of these systems. Our anisotropic solvation dynamics, however, are not drastically different from those obtained with the unpurified liquid.

We have seen a lengthening in the longer solvation component of C153 when excited at 420 nm at room temperature. The solvation dynamics, however, are not drastically different from those obtained with the unpurified liquid. We can have a lengthening in the longer solvation component in the unpurified solvent compared to that in the purified one (see the caption to Figure 6 and Table 1), which is in accordance with the higher viscosity of the unpurified solvent.

While it is possible that some of these minor differences that we observe result from solvent purity and viscosity, there are, however, other more general factors that may explain the contrast between our results and those of Maroncelli and co-workers: namely, how \(C(t)\) is computed. How accurately the solvation correlation function, \(C(t)\), is constructed depends critically upon the quantities used in the denominator of eq 2. We have already indicated how sensitive the results can be to the choice of the time window used to collect the data, namely, the effect upon \(\nu(0)\) or, more precisely, \(\nu(0^+)\), but the determination of \(\nu(0^-)\) has its own idiosyncrasies. \(\nu(0^-)\) is the maximum of the estimated zero-time spectrum of the fluorescent probe after it has undergone intramolecular events contributing to its relaxation and before it has been altered by interactions with the solvent. The construction of the zero-time spectrum, which thus assumes such a time-scale separation of events, has been described by Fee and Maroncelli,\(^{47}\) and we...
have shown that it is consistent with an independent method we have proposed, which compares the experimentally and theoretically determined reorganization energies in solvents over a wide range of polarities and indicates that 2068 cm\(^{-1}\) of "solvation" in coumarin 153 is intramolecular.\(^{24}\) This value is consistent with the reorganization energies obtained from the zero-time spectra cited in Table 1, which are \(\sim 1950\) cm\(^{-1}\).

To gain insight into the apparent discrepancy between our results and those of Maroncelli and co-workers,\(^{11}\) we again considered the solvation of C153 in [\(\text{C}_6\text{H}_5\text{P}^+\text{Cl}^-\)] bulk, 66 °C. The required inputs for the calculation of the zero-time spectrum are the absorption (or excitation) spectrum of C153 in a nonpolar solvent, and the corresponding spectrum in the polar solvent under investigation—in this case, the phosphonium ionic liquid. Also required is the emission spectrum of C153 in the nonpolar solvent, and even the fitting procedure used.

The literature is often the zero-time spectrum in polar solvents, while Maroncelli and co-workers used 2-methylbutane. Calculated zero-time peak frequencies using different spectra from different sources and obtained under different conditions are presented in Table 3. As indicated, the value of \(ν(0)\) is subject to the differences in the polar absorption/excitation spectra, the excitation wavelength, the nonpolar solvent, and even the fitting procedure used to obtain the spectral maximum. The data indicate that these factors can produce a difference of up to 350 cm\(^{-1}\) in the position of the zero-time spectrum, which can represent \(\sim 20\%\) of the total Stokes shift at 20 ns. Such factors must be taken into consideration when data are analyzed or results from different laboratories are compared. Ideally, the reorganization energy, \(λ\), may be the best parameter to use for the computation of \(C(t)\) because it is an integrated measure of the solvation dynamics (eq 1). The construction of \(λ\), however, requires high-quality spectra, which are typically not provided by the traditional methods of spectral construction of 10–20 wavelength-resolved transients such as those illustrated in Figure 3.

We note, notwithstanding all the considerations enumerated above, that if the \(C(t)\) of Maroncelli and co-workers is normalized to begin at the end of the rapid component we observe, then their \(C(t)\) is within experimental error very similar to ours for both the purified and unpurified phosphonium liquid (Figure 6b and caption).

Finally, taking into consideration all of these issues, we believe that the full method of Fee and Maroncelli for obtaining the zero-time spectrum is the soundest available. The details of this method are clearly described in their paper,\(^{47}\) are briefly alluded to above, and provide the basis for the construction of an entire emission spectrum. In this paper, Fee and Maroncelli provide a simple equation for approximating the position of the zero-time spectrum:

\[
ν_\text{em}(0) = ν_\text{abs} - (ν_\text{abs}^\text{P} - ν_\text{em}^\text{P}) \tag{3}
\]

where \(P\) and \(nP\) refer to polar and nonpolar solvents, respectively. This approximate method has been employed by some workers, but we find that if it is successful in predicting the position of the zero-time spectrum, this success lies in using midpoint (rather than peak) frequencies in eq 3: \(ν_\text{mid} = (ν_+ + ν_-)/2\), where \(ν_+\) and \(ν_-\) are the midpoint frequencies at the blue and red edges of the spectrum, respectively. Also, to be consistent, this procedure recommends the use of midpoint frequencies in the construction of \(C(t)\). The literature is often murky on these important details. We find that if midpoint frequencies are not employed, the approximation always provides a lower value (by at least a few hundred wavenumbers) for the peak maximum of the zero-time spectrum than the full method. We have illustrated this for the systems investigated here in Table 4, which provides a comparison of the positions of the zero-time spectrum for the solvents studied here using the rigorous method and the approximate method with peak and midpoint frequencies. Equation 3 is a quick and useful way of estimating the position of the zero-time spectrum,\(^{37,63}\) but we suggest that it is no substitute for using the full method—especially when quantitative interpretations of \(C(t)\) are required.

For completeness, it has been suggested that the zero-time and steady-state frequencies could be obtained by rearranging eq 2 to

\[
ν(t) = C(t)[ν(0) - ν(∞)] + ν(∞) \tag{4}
\]

expressing \(C(t)\) in terms of some function such as a sum of exponentials, using a curve-fitting procedure to extract the required parameters.\(^{64,65}\) We find that this procedure yields unphysical results (such as negative steady-state frequencies) if all parameters are permitted to vary. It always yields severely red-shifted zero-time spectra. We suggest that such a fitting procedure will not produce an accurate result unless the time resolution of the experiment is adequate for resolving most of the solvation response in the first place.

**Conclusions**

In studying a phosphonium ionic liquid that can form micelles in water, we conclude that our analysis of the comparable situation in an imidazolium liquid\(^{36}\) is not as definitive as we had proposed: namely, that the majority of the early-time
solvation arises from the organic cation. Part of the difficulty in performing this analysis is most likely due to the amount of water that is associated with the micelle.

In the course of this work, we have found that the calculation of solvation correlation function, $C(t)$, is surprisingly dependent upon the methods with which the zero-time spectrum is constructed. An interesting means of validating such spectral construction may ultimately be based upon computing $C(t)$ using dielectric spectra, as we have done elsewhere. Finally, we have noted in another context, that of solvation by a protein environment, how important an accurate computation of $C(t)$ is for the interpretation of the experimental results.

Acknowledgment. We thank Professor Mark Maroncelli for sharing his data for coumarin 153 in 2-methylbutane and in the phosphonium chloride and for helpful comments. We thank Professor Xueyu Song for helpful comments.

References and Notes

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