Additivity in the Optical Kerr Effect Spectra of Binary Ionic Liquid Mixtures: Implications for Nanostructural Organization

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Low-frequency spectra of binary room-temperature ionic liquid (RTIL) mixtures of 1-pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide and 1-pentyl-3-methylimidazolium bromide in the 0–250 cm^{-1} region were studied as a function of mole fraction at 295 K. The spectra were obtained by use of optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES). The spectra of these binary mixtures are well described by the weighted sums of the spectra for the neat RTILs. This surprising result implies that the intermolecular modes giving rise to the spectra of the neat liquids must also produce the spectra of the mixtures. Additivity of the OKE spectra can be explained by a model in which locally ordered domains are assumed to exist in the neat liquid with the structures of these locally ordered domains preserved upon mixing. Recently published molecular dynamics simulations show that RTILs are nanostructurally organized with ionic networks and nonpolar regions. If ionic networks also exist in the mixture, the additivity of the OKE spectra implies that there are "blocks" along the network of the mixture that are ordered in the same way as in the neat liquids. These "block co-networks" would have a nanostructural organization resembling that of a block copolymer.

Introduction

Due to their negligible volatility and the ease with which their properties can be tuned through structural modification of the organic cation and variation of the anion, room-temperature ionic liquids (RTILs) have become promising candidates for "clean" solvents in green chemistry. RTILs have found wide usage as solvents in chemical reactions,[1–3] in analytical chemistry,[4–6] and in industrial applications.[7] To take advantage of RTILs as "designer solvents" in such applications, one must understand how the physicochemical properties of an RTIL depend on the nature of the cation and anion.

In chemical reactions, viscosity and polarity are two properties of a liquid that can significantly affect reaction rates and product yields. To this end, numerous studies have focused on the dependence of the viscosity or polarity of an RTIL on the nature of the cation or anion.[8–14] In addition to these physical properties, one must also understand the dynamics of an RTIL, in particular the intermolecular dynamics. At a molecular level, the intermolecular modes of a liquid and their couplings to solute molecules are what ultimately determine the outcome of a chemical process.

One way of obtaining information about the intermolecular modes of a liquid is to study its low-frequency spectrum. Because of its ease of use and the high quality of the resultant data, femtosecond optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) has recently become the most commonly used method for studying low-frequency intermolecular modes of a liquid.[15–17] OHD-RIKES is a nonlinear optical time-domain technique that measures the polarizability anisotropy dynamics of a liquid. Using a Fourier transform deconvolution procedure,[18,19] the OHD-RIKES time-domain data can be converted to a reduced spectral density (RSD) or optical Kerr effect (OKE) spectrum, which is directly related to the depolarized Rayleigh/Raman spectrum of the liquid.[20]

Several groups have recently measured the low-frequency OKE spectra of a number of RTILs.[21–26] The ultimate goal of these studies is to identify the molecular motions that give rise to the OKE spectra of RTILs. Because RTILs are so molecularly complex, their OKE spectra tend to have complicated line shapes that are more difficult to interpret than those of simple molecular liquids. The most widely investigated class of RTILs are those with imidazolium cations.[21–23,26] The studies to date have primarily focused on understanding how varying the alkyl substituents on the imidazolium ring or changing the anion affects the OKE spectra. In this letter, we report the OKE spectra of binary mixtures of 1-pentyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C$_5$mim][NTf$_2$]) and 1-pentyl-3-methylimidazolium bromide ([C$_5$mim]Br) in the 0–250 cm^{-1} region at 295 K. Such mixtures are of great importance because they are another way of expanding the range of RTILs.[27] To our knowledge, this is the first study of the OKE spectra of binary ionic liquid mixtures. We find the OKE spectra of RTILs to be additive. This additivity is explained by assuming the existence of locally ordered domains in the liquid mixture. These results are discussed in the context of the nanostructural organization that was recently predicted in molecular dynamics (MD) simulations of imidazolium ionic liquids.

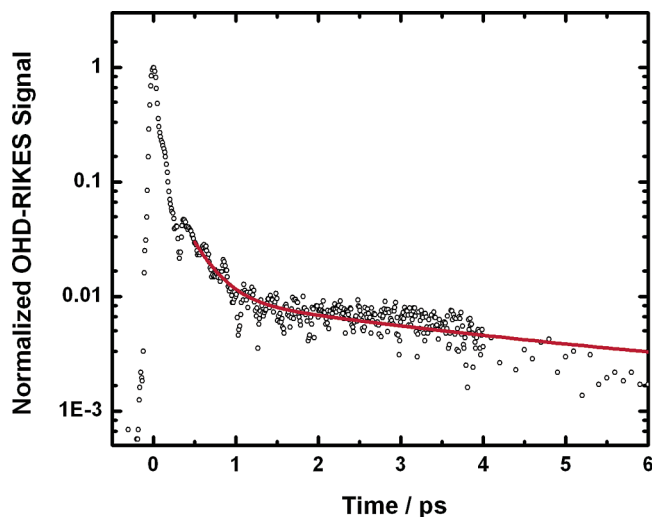* To whom correspondence may be addressed. E-mail: edward.quitevis@ttu.edu.

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Figure 1. Semilogarithmic plot of typical OHD-RIKES data for the $x_{NTf_2} = 0.75$ mixture between -0.2 and 6 ps at 295 K. The solid red curve is a fit of the data to a biexponential decay function (eq 1) for $0.5 < t < 6$ ps. See text for further details.

Experimental Section

The synthesis of [C$_5$mim][NTf$_2$] and [C$_5$mim]Br has been described previously.[9,28] The water content of the RTILs was determined by Karl-Fisher titration to be 40.1 μg/g for [C$_5$mim]-[NTf$_2$] and 7.3 μg/g for [C$_5$mim]Br. Mixtures of [C$_5$mim][NTf$_2$] and [C$_5$mim]Br were prepared with [C$_5$mim][NTf$_2$] mole fractions of $x_{NTf_2} = 0.25$, 0.50, and 0.75. The samples were contained in a sealed 2-mm path length, UV grade, fused silica cell (Hellma Cells). The sample cell was placed in a lab-built copper cell holder, whose temperature was regulated and controlled with a thermoelectric heater/cooler system.

The 45 fs titanium–sapphire laser, OHD-RIKES apparatus, and method of data acquisition have been described in detail previously.[21,29] The current version of the apparatus incorporates balanced detection with compensation for fluctuations in the laser intensity. To minimize the data collection time, scans were carried out in 10 fs steps for time delays between -1 and 4 ps and in 100 fs steps for time delays greater than 4 ps. The current apparatus and the analysis of typical OHD-RIKES data for the mixtures by the Fourier transform deconvolution procedure are described in detail in the Supporting Information.

Results and Discussion

Figure 1 shows a typical OHD-RIKES signal for the $x_{NTf_2} = 0.75$ mixture at 295 K between -0.2 and 6 ps. The OHD-RIKES signal is dominated by the electronic response (coherent spike) near zero delay. The nuclear response appears as a shoulder on the coherent spike that evolves into a nonexponential decay after 0.5 ps. The OHD-RIKES signal does not decay to zero within the time range of our measurements, indicating the presence of a much slower component in the diffusive response. Figure 1 reveals coherent oscillations due to the superposition of several intramolecular vibrational modes that are mainly associated with the NTf$_2^-$ ion (see below). The empirical decay function

$$r(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + B \qquad (1)$$

was fit to the data in the 0.5–6 ps range using nonlinear least-squares. The constant B accounts for the slower contributions to the diffusive response that exhibit negligible decay within the time range of our measurements. The parameters from the fits are given in Table 1. The value of the fast component τ_1,

TABLE 1: Fit Parameters for OHD-RIKES Response for $0.5 < t < 6$ ps[a]

RTIL system	A_1	τ_1/ps	A_2	τ_2/ps	B
[C$_5$mim]NTf$_2$	0.8811	0.115 ± 0.019	0.0915	2.62 ± 0.35	0.0275
[C$_5$mim]Br	0.9200	0.12 ± 0.06	0.0716	0.67 ± 0.07	0.0084
$x_{NTf_2} = 0.25$	0.9355	0.41 ± 0.06	0.0150	4.96 ± 0.41	0.0495
$x_{NTf_2} = 0.50$	0.9492	0.28 ± 0.02	0.0095	4.32 ± 0.77	0.0413
$x_{NTf_2} = 0.75$	0.9352	0.26 ± 0.03	0.0542	3.79 ± 0.23	0.0106

[a] See eq 1 for definition of parameters.
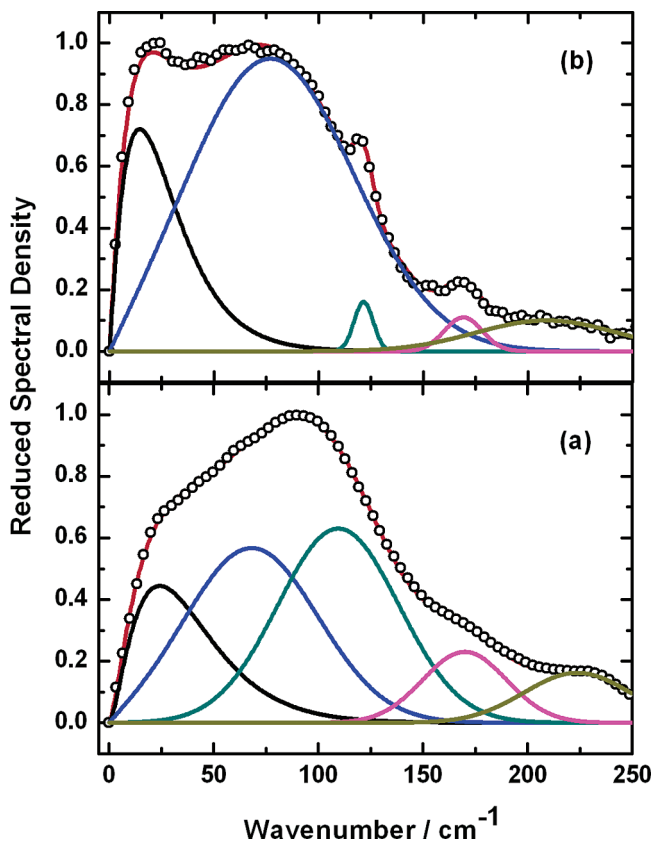
Figure 2. Reduced spectral densities (points) of (a) [C$_5$mim]Br and (b) [C$_5$mim][NTf$_2$] at 295 K. The solid red curves through the points are the multicomponent fits of the reduced spectral densities. Also shown are the component bands obtained in the multicomponent analysis of the reduced spectral densities. See text for details of the analysis.

which is associated with the nondiffusive dynamics, varies from $\sim$0.1 to 0.4 ps, whereas the value of the slow component τ_2, which is associated with diffusive dynamics, varies from $\sim$0.7 to 5 ps. Interestingly, the diffusive dynamics are slower in the mixtures than in the neat liquids.

Figure 2 shows the RSDs for neat [C$_5$mim][NTf$_2$] and [C$_5$mim]Br in the 0–250 cm^{-1} region. These RSDs are consistent with previously published RSDs for imidazolium RTILs.[21–26] The RSD of [C$_5$mim]Br (Figure 2a) is broad and featureless with a peak frequency of 89.6 cm^{-1} and a full-width-at-half-maximum (fwhm) of 124 cm^{-1}. The absence of sharp intramolecular peaks indicates that the RSD of [C$_5$mim]Br at low frequencies is mainly due the intermolecular dynamics of the liquid. In contrast, the RSD of [C$_5$mim][NTf$_2$] (Figure 2b) is highly structured with well-defined peaks. The sharp peaks at 121.5, and 169.2 cm^{-1} correspond to intramolecular vibrational modes of NTf$_2^-$. The broader part of the RSD, which is mainly due the intermolecular modes of the liquid, is clearly bimodal in character with a fwhm of 118 cm^{-1}. To provide a more quantitative description of the OKE data, multicomponent line-shape analysis was performed on the RSDs, with the lowest
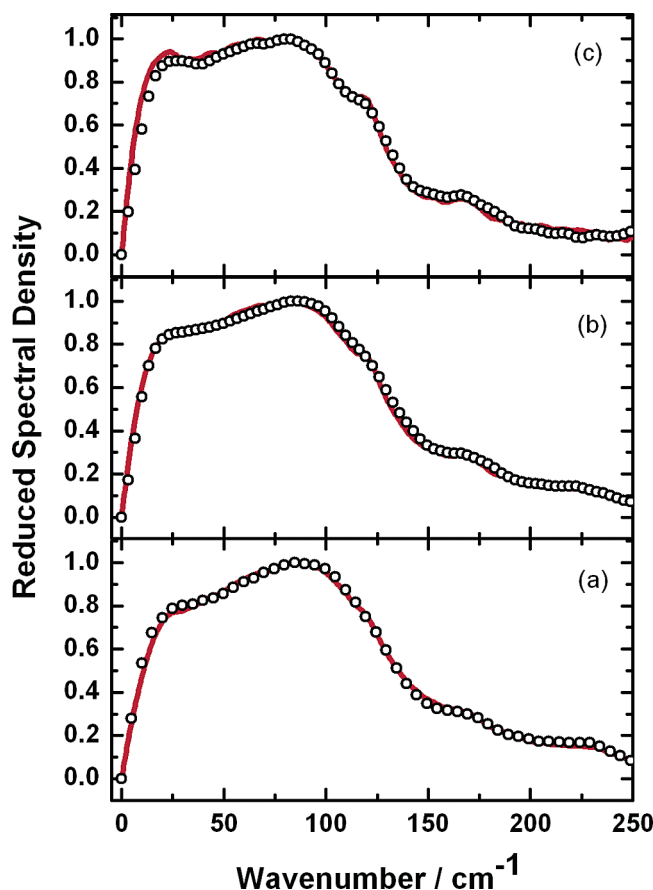
Figure 3. Experimentally measured (points) and calculated (lines) reduced spectral densities of binary mixtures of $[C_5mim][NTf_2]$ and $[C_5mim]Br$ corresponding to $x_{NTf_2} =$ (a) 0.25, (b) 0.50, and (c) 0.75. The calculated reduced spectral densities were obtained from the mole-fraction weighted sums of reduced spectral densities for the neat ionic liquids (eq 2).

frequency component being given by a Bucaro−Litovitz function and the other components given by anti-symmetrized Gaussian functions. The parameters from this analysis are tabulated in the Supporting Information.

The RSD of $[C_5mim]Br$ in the $0-200$ cm^{-1} region can be well fit by the sum of four components: a low-frequency component at 24.2 cm^{-1}, two intermediate-frequency components at 68.0 and 109.5 cm^{-1}, and a high-frequency component at 169.9 cm^{-1}. In contrast, the intermolecular part of the RSD of $[C_5mim][NTf_2]$ in the $0-200$ cm^{-1} region can simply be fit by the sum of a narrow low-frequency component at 14.6 cm^{-1} and a broad high-frequency component at 77.0 cm^{-1}.

Figure 3 shows the observed RSDs of binary mixtures of $[C_5mim][NTf_2]$ and $[C_5mim]Br$ at $x_{NTf_2} = 0.25$, 0.50, and 0.75. The intramolecular bands at ∼120 and ∼170 cm^{-1} are clearly evident in the RSD of the $x_{NTf_2} = 0.75$ mixture (Figure 3c), but are less noticeable in the RSD of the $x_{NTf_2} = 0.25$ and 0.50 mixtures (Figures 3a and 3b, respectively). The intramolecular band at ∼120 cm^{-1} appears in the RSDs of the $x_{NTf_2} = 0.25$ and 0.50 mixtures as a low intensity shoulder on the high-frequency side of the main band. We also present in Figure 3 calculated RSDs, which were obtained from the mole fraction weighted sum

$$I^0_{mix}(\omega) = N[x_{NTf_2}I_{NTf_2}(\omega) + (1 - x_{NTf_2})I_{Br}(\omega)] \quad (2)$$

In this equation, $I_{NTf_2}(\omega)$ and $I_{Br}(\omega)$ are, respectively, the normalized RSDs of neat $[C_5mim][NTf_2]$ and neat $[C_5mim]Br$,

and N is a normalization factor. (The use of normalized RSDs for the neat RTILs in eq 2 is justified because their polarizability anisotropy dynamics, as we will show below, are largely determined by the librational dynamics of the $[C_5mim]^+$ cation.) As can be seen in Figure 3, there is excellent agreement between the calculated and observed RSDs.

The additivity of the OKE spectra in these binary ionic liquid mixtures is quite remarkable. Additivity in physical properties is usually indicative of ideal behavior, where interspecies interactions are absent. Given their molecular complexity, RTILs however are far from being ideal systems. We would not have predicted the OKE spectrum of a binary ionic liquid mixture to be simply given by the sum of the OKE spectra of the neat ionic liquids. Reported OKE measurements on mixtures of molecular liquids have shown the OKE spectra to be nonadditive, even for nonassociating molecular liquids.[17,30,31] Clearly, the additivity of the OKE spectra in binary ionic liquid mixtures must be unique to RTILs. To explain this additivity of the OKE spectra, we first must understand the basic mechanism that gives rise to the OKE spectrum of a neat RTIL.

In principle, the OKE spectrum of a liquid will have contributions from a molecular term, an interaction-induced term, and a molecular interaction-induced cross term.[32] The OKE spectrum for most liquids tends to be dominated by the molecular term, which arises from the collective librational motion of the molecules in the liquid.[32] For RTILs consisting of an organic cation and an inorganic anion, only the librational motion of the cation contributes to the OKE spectrum. This clearly is the case for RTILs with spherical anions. To show this for RTILs with nonspherical inorganic anions, we make use of the dependence of the OKE spectrum on the square of the derivative of the polarizability anisotropy, $(\partial\alpha/\partial q)^2$, where q is a canonical coordinate associated with one of the modes of the liquid, to estimate the relative contributions of the various motions of the liquid to the OKE spectrum.[32] Giraud et al.[22] showed that the value of $(\partial\alpha/\partial q)^2$ for the imidazolium ring is a factor of ∼4×10^{13} times greater than that of the NTf_2^- ion. Because of this difference in the polarizability derivatives, the OKE spectrum of an RTIL is a reflection of the librational motion of the imidazolium ring.

At first glance one would expect additivity to hold for an AX + AY mixture where the A$^+$ cation dominates the OHD-RIKES response, if the librational (i.e., nondiffusive) dynamics are governed by single particle motions. It is reasonable to assume that this should also be the case for the diffusive dynamics. The diffusive response in mixtures must then be given by a biexponential decay function[33,34]

$$r(t) \propto \frac{x_A}{\tau_A}\exp(-t/\tau_A) + \frac{x_B}{\tau_B}\exp(-t/\tau_B) + B \quad (3)$$

with the amplitudes being proportional to the populations (i.e., mole fractions) of the A$^+$−X$^-$ and A$^+$−Y$^-$ ion pairs divided by their corresponding time constants. If additivity holds for the diffusive response as it does for the nondiffusive response, then the time constants in eq 3 should be equal to values of τ_2 for the neat liquids given in Table 1. The OHD-RIKES signals, however, reveal only a single-exponential decay for the short-time part of the diffusive response in mixtures. This discrepancy might be due to the signal-to-noise in the OHD-RIKES signals being such that a biexponential decay is indistinguishable from a single-exponential decay. If this is the case, a fit of the simulated response for a given mixture based on eq 3 to a single-exponential decay function

$$r(t) = A\exp(-t/\tau_{\text{eff}}) + B \qquad (4)$$

should then yield an effective relaxation time τ_{eff} that is approximately equal to the value of τ_2 for that mixture. When the simulated responses are analyzed this way, we find τ_{eff} to be equal to 0.77, 0.96, and 1.37 ps for the $x_{\text{NTf}_2} = 0.25$, 0.50, and 0.75 mixtures, respectively. These values of τ_{eff} clearly do not agree with the values of τ_2 in Table 1. In fact τ_{eff} and τ_2 vary with the composition in opposite directions. Therefore, there must be another explanation for additivity of the OKE spectra.

The OKE spectra of RTILs, as Giraud et al.[22] first noted, tend to be broader than those of nonpolar, weakly interacting molecular liquids, such as cyclohexane, but comparable in width to that of polar, strongly interacting molecular liquids, such as dimethyl sulfoxide. No doubt, the broadness of the OKE spectrum of an RTIL can partially be attributed to the presence of hydrogen-bonded clusters in the liquid.[35,36] Broad OKE spectra can also be indicative of increased order in the liquid. For example, Hyun et al.[29] showed that going from the isotropic phase to the more ordered smectic-A (Sm-A) phase of the liquid crystal, 4-octyl-4′-cyanobiphenyl, broadens and shifts the OKE spectrum to higher frequencies. These changes can be attributed to an increase in the density of states that occurs when the liquid crystal is cooled and becomes more "solid-like". Therefore, the width of the OKE spectra of RTILs might also reflect a high density of states due to solid-like local order. This would be consistent with the charge ordering in RTILs, as evidenced by the pronounced oscillations in cation–cation radial distribution functions (RDFs) and out-of-phase anion–cation RDFs derived from neutron diffraction measurements[37,38] and MD simulations.[39–44] Moreover, the RDFs indicate that charge ordering is limited to the first two to three cation shells around the central imidazolium ring. This would suggest then that the OKE spectrum of an RTIL arises from the collective modes of locally ordered domains. Indeed, the importance of collective cation and anion motion was recently demonstrated in MD simulations on the solvation response of an RTIL to photoexcitation of a chromophore.[45]

One expects there to be an ensemble of locally ordered domains in the liquid. Each domain will be characterized by a set of normal-mode frequencies corresponding to the collective translational and rotational motion of the ions within the domain. Because not all of the domains have the same size or same structure, the normal mode spectra will not necessarily be the same for all domains. The OKE spectrum of an imidazolium RTIL will be given by an ensemble average with

$$I_{\text{OKE}}(\omega) \propto \int I(\omega;\xi)g(\xi)\,d\xi \qquad (5)$$

where $I(\omega;\xi)$ is the polarizability-weighted part of the domain spectrum associated with the collective librational motions of the imidazolium rings within the domain and $g(\xi)$ is a distribution function, which accounts for different domain sizes and structures. This approach, which has been used previously to model the OKE spectra of liquid benzene,[46,47] is known as the "quasi-crystalline" approach. To explain the additivity of the OKE spectra, the locally ordered domains must also be present in the mixture and these domains must have same size and structure as in the neat RTILs. The OKE spectrum of the binary mixture will also be given by an ensemble average of the domain spectra, but with contributions coming from both RTILs.

Lopes and Padua[48] recently performed MD simulations on [C$_n$mim][PF$_6$] and [C$_n$mim][NTf$_2$] ionic liquids with $n = 2, 4, 6, 8$, and 12. By examining the long-range structure, they found

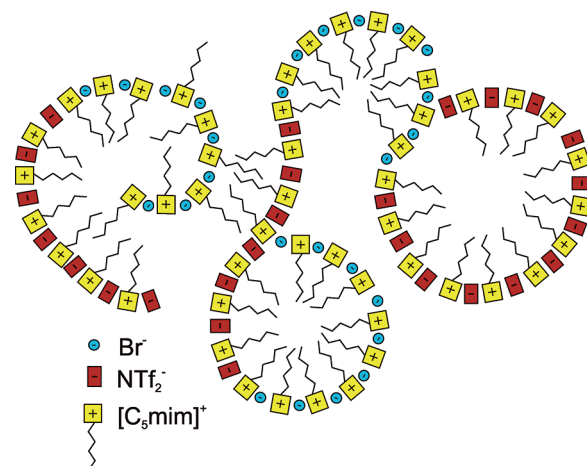**Figure 4.** Schematic illustration of the nanostructural organization in a binary mixture composed of [C$_5$mim][NTf$_2$] and [C$_5$mim]Br. See text for further details.

RTILs to be nanostructurally organized. That RTILs are nanostructurally organized is not surprising given that the interactions in RTILs involve both electrostatic and dispersion forces. By color coding the nonpolar and polar regions in the liquid, Lopes and Padua showed that for RTILs with alkyl chains of C$_4$ or longer the liquid separates into two types of regions: nonpolar regions arising from clustering of the alkyl chains and polar regions arising from charge ordering of the anions and imidazolium rings of the cations. Interestingly, the polar regions are not isolated but are interconnected in such a way as to form a three-dimensional ionic network permeated by nonpolar regions in a manner not unlike that of a swollen gel.

If RTILs are nanostructurally organized as predicted by the MD simulations of Lopes and Padua, then the OKE spectrum of the neat RTIL must correspond to the local modes of the ionic network associated with the collective librational motions of the imidazolium rings. Moreover, if our explanation for the additivity of the OKE spectra is correct and one assumes that the mixtures are nanostructurally organized as in neat RTILs, with three-dimensional ionic networks permeated by nonpolar regions, then one arrives at the intriguing prediction that the structure of an ionic network in the mixture is such that there are "blocks" along the network ordered in the same way as in the neat liquids with clustering of the alkyl groups into nonpolar domains. These "block co-networks" have a nanostructural organization resembling that of a block copolymer. In this scheme, the OKE spectrum of the mixture arises from collective modes of ordered domains within these blocks. Figure 4 schematically illustrates this nanostructural organization, where the cation is depicted as a polar headgroup (the imidazolium ring) with a nonpolar tail (the C$_5$ group). The ionic network in this figure is represented as a single-stranded chain of ions, which would imply a nearest neighbor coordination number of two. The structure of an ionic network no doubt is more complicated than this. Indeed, neutron diffraction measurements[37,38,49] and MD simulations[42–44] indicate that there are several anions in the first coordination shell around a given cation. The ionic network should therefore be thought of as a multistranded chain instead of a single-stranded chain of ions.

Partitioning of the ionic network in the mixture into blocks is not unreasonable given that Br$^-$ is smaller than NTf$_2^-$ (31.5 versus 153 Å^3, based on atomic increments). Because of this size difference, polar regions of [C$_5$mim]Br will be more closely packed than those of [C$_5$mim][NTf$_2$]. This in turn results in the cohesive energy density of [C$_5$mim]Br being greater than that of [C$_5$mim][NTf$_2$]. This reasoning is commonly used to rational-

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ize the lower viscosities and melting points of ionic liquids with NTf_2^- as the anion compared to ionic liquids with smaller inorganic anions. Formation of these blocks in a sense is analogous to the process of selective precipitation involving a common ion, with $[C_5mim]^+$ being the common ion and $[C_5mim]Br$ being the precipitate. The mixture can be thought of then as a dispersion of $[C_5mim]Br$ nanocrystallites in $[C_5mim][NTf_2]$. However, instead of being homogeneously distributed in the mixture, the dispersion will nanostructurally organized as $[C_5mim]Br$ and $[C_5mim][NTf_2]$ blocks in a three-dimensional ionic network facilitated by clustering of the alkyl chains into nonpolar regions.

Concluding Remarks

To summarize, additivity of the OKE spectra in the binary RTIL mixtures can be explained if we assume: (1) the existence of locally ordered domains in the neat RTILs and (2) the structures of these locally ordered domains are preserved upon mixing. When viewed in the context of the nanostructural organization observed in MD simulations of neat RTILs, this domain model predicts the formation of ionic networks in the mixtures consisting of blocks that are ordered in the same way as in the neat liquids. If the blocks are contiguously joined in the network, there should also be a set of modes associated with the collective motion of all three ions in the transition regions between blocks. Because of these "junction" modes, which obviously are not present in the neat liquids, the OKE spectra in the mixtures should be nonadditive. The fact that we see no evidence for nonadditivity suggests that these modes do not contribute to the OKE spectra of the mixtures. One possible reason is that the blocks are so large that the OKE spectrum is dominated by modes associated with locally ordered domains within the blocks. However, one expects the average block size to diminish with increasing temperature, leading to an increase in the number of transition regions or junctions in the network. Therefore, we predict a breakdown of additivity of the OKE spectra at higher temperatures, due to an increase in the relative contribution of these junction modes. Also, if packing effects drive the formation of blocks in mixtures, OKE spectra should be nonadditive for binary mixtures of imidazolium RTILs with anions of similar size. We are currently pursuing OHD-RIKES measurements on other binary ionic liquid mixtures, as well as temperature-dependent studies of the OKE spectra of these mixtures, to test these ideas. Another intriguing result is that the short-time part of the diffusive dynamics is slower in the mixtures than in the neat liquids. As we showed above, the behavior of the diffusive dynamics in mixtures in the time regime of our measurements is not what one would have predicted on the basis of single-particle dynamics. Clearly, further studies are needed to explain the behavior of the relaxation dynamics in mixtures. Finally, water is known to influence the solvation dynamics in RTILs.[50] If RTILs are nanostructurally organized as the MD simulations of Lopes and Padua suggest, the effects of water should be manifested in changes in the dynamics within the ionic networks.

Supporting Information Available: Description of the OHD-RIKES apparatus and data analysis and fit parameters for multicomponent line shape analysis. This material is available, free of charge via the Internet at http://pubs.acs.org.

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