Dynamic Heterogeneity Hot Paper

DOI: 10.1002/anie.201409136

Ionic Liquids: Not only Structurally but also Dynamically Heterogeneous**

*Zhuan-Ping Zheng, Wen-Hui Fan, Soham Roy, Kamila Mazur, Andreas Nazet, Richard Buchner, Mischa Bonn, and Johannes Hunger**

Abstract: *In recent years, the complex and heterogeneous structure of ionic liquids has been demonstrated; however, the consequences on the dynamics have remained elusive. Here, we use femtosecond IR spectroscopy to elucidate the local structural dynamics in protic alkylammonium-based ionic liquids. The structural relaxation after an ultrafast temperature increase, following vibrational excitation and subsequent relaxation of the N-D (or N-H) stretching vibration, is found to vary substantially between the ionic and hydrophobic subdomains. The dynamics in the ionic domains are virtually unaffected by the alkyl chain length and is, therefore, decoupled from viscosity. Equilibration within the hydrophobic subdomains, as evident from the dynamics of the C-H stretching vibration, is faster than that in the ionic domains and shows a remarkably low thermal activation.*

As a result of their unique properties,[1,2] such as high thermal stability, wide electrochemical window, and several other interesting features, room-temperature ionic liquids (RTILs) have found a wide range of applications,[3–5] such as in solar energy systems,[5] as heat-transfer media, and also as reaction media. Despite being macroscopically homogeneous, it has become apparent in recent years that RTILs are structurally heterogeneous, with ionic and hydrophobic domains.[6,7] This heterogeneity provides new opportunities for material science[8] and is thought to be the origin of the failure of macroscopic theories to predict reaction rates when RTILs are used as the solvent.[9] This failure is thought to arise from heterogeneity, as the local structural reorganization around a reactant and the ability to dissipate excess energy largely determine how a reaction medium influences the rate at which the reaction proceeds.[10] Despite the apparent importance of the local structural and energy dynamics in RTILs, surprisingly little is known about the impact of structural heterogeneity on such local dynamics.[9]

Herein, we use femtosecond infrared (fs-IR) spectroscopy to systematically study the effect of RTIL heterogeneity on heat dissipation and local structural reorganization in response to an ultrafast temperature jump.[11] By systematically varying the size of the hydrophobic alkyl chain in a series of alkylammonium formates and probing the thermal equilibration in the ionic and hydrophobic domains with molecular specificity, we have obtained detailed insight into the local dynamics of RTILs.

In the first set of experiments, we studied the N-D stretching vibration of isotopically labeled ethylammonium formate (EAF, $[C_2H_5NH_{3-3x}D_{3x}]^+[COOH]^-$) with different isotope exchange ratios, $x = D/(D+H)$. Using a frequency-tunable intense fs-IR pump pulse centered at 2260 cm^{-1}, we generated a population in the first vibrationally excited state ($v = 1$), which led to a reduced absorbance at the fundamental mode ($v = 1 \leftarrow 0$). This reduced absorbance, which we measured with a weak, temporally delayed laser pulse, can be seen in the isotropic transient spectra (i.e. the difference between the spectrum of the excited and the non-excited sample) at short times in Figure 1a: immediately after the excitation (0.2 ps, Figure 1a), the transient spectra are dominated by a bleaching signal ($\Delta\alpha_{iso} < 0$) at 2240 cm^{-1}. As can be seen from the temporal evolution of this bleaching signal in Figure 1b, this excitation is very short lived and has fully decayed at about 2 ps. As the excitation decays, the absorbed energy is dissipated to low-energy modes and eventually leads to an increase in temperature by a few Kelvin in the laser focus.[12] RTILs exhibit structural reorganization (e.g. thermal expansion) in response to fast "thermal" excitation.[13,14] Such structural changes go along with an increase in the intermolecular distances and thus lead to a blue-shift in the frequency of the molecular vibrations, which can thus be followed with ultrafast IR spectroscopy. This slow thermal equilibration occurs on a distinctively slower timescale (ca. 10 ps) than vibrational relaxation, which is evident from the slow increase in the magnitude of the transient spectra $\Delta\alpha_{iso}$ (see Figure 1a,b) at long delay times.

For quantitative analysis, we used a kinetic model to describe the experimental isotropic data (for details see the

[*] Z. Zheng, S. Roy, Dr. K. Mazur, Prof. M. Bonn, Dr. J. Hunger
Department for Molecular Spectroscopy
Max Planck Institute for Polymer Research
Ackermannweg 10, 55128 Mainz (Germany)
E-mail: hunger@mpip-mainz.mpg.de

Z. Zheng, Prof. W. Fan
State Key Laboratory of Transient Optics and Photonics
Xi'an Institute of Optics and Precision Mechanics
Chinese Academy of Sciences
Xi'an, Shaanxi, 710119 (China)

A. Nazet, Prof. R. Buchner
Institute of Physical and Theoretical Chemistry
University of Regensburg (Germany)

S. Roy
Graduate School Materials Science in Mainz (Germany)

[**] Z.Z. was supported by the MPG-CAS Joint Doctoral Promotion Programme (DPP). S.R. is a recipient of a DFG fellowship/DFG-funded position through the Excellence Initiative by the Graduate School Materials Science in Mainz (GSC 266). We thank Marc-Jan van Zadel for technical support and Martina Knecht for help with sample preparation.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201409136.

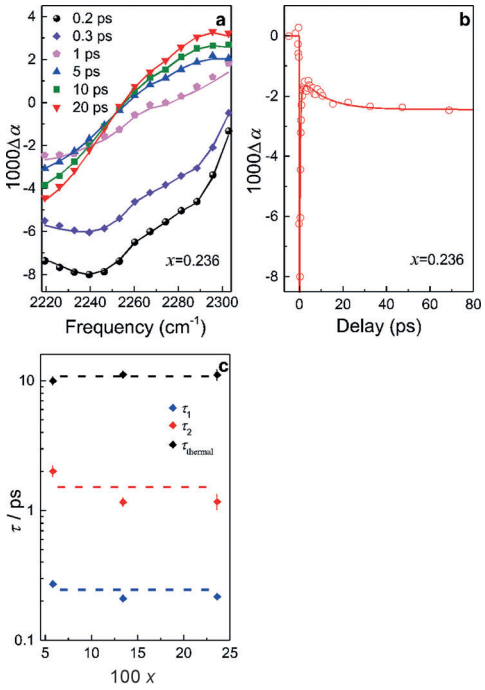

Figure 1. a) Isotropic transient spectra $\Delta\alpha_{iso}(\omega)$ at N-D stretching frequencies at different delay times and b) isotropic transient signal $\Delta\alpha_{iso}(\omega)$ at $\omega = 2240\ cm^{-1}$ for EAF (D fraction: $x = 0.236$). The symbols represent the experimental data and the solid lines show fits of the vibrational relaxation model to the data (see text). c) Extracted decay times for EAF at different isotopic exchange $x = 0.058$, 0.134, and 0.236. The error bars correspond to a 2% increase in the sum of the squared deviations of the fit from the data.

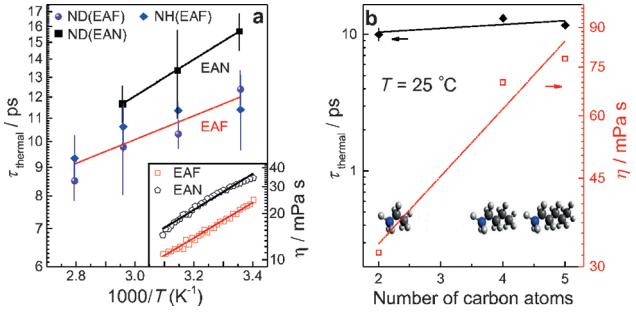

Figure 2. a) Thermal equilibration and viscosity (inset) for EAF and EAN. The symbols represent the experimental data and the solid lines show Arrhenius fits. b) Thermal equilibration and viscosity for different lengths of the hydrophobic side chain. The lines are visual aids. Error bars correspond to a 2% increase in the sum of the squared deviations of the fit from the data. Viscosities were taken from the literature.[18,20]

Supporting Information). As shown previously,[13] the initial vibrational relaxation is biexponential (τ_1 and τ_2 in our model, see the Supporting Information) followed by a slow thermal equilibration with time constant $\tau_{thermal}$. We found vibrational relaxation to be fast ($\tau_1 \approx 240$ fs, $\tau_2 \approx 1.5$ ps)—similar to that of ethylammonium nitrate (EAN)[13]—while thermal equilibration of EAF occurred on a timescale of $\tau_{thermal} \approx 11$ ps. To obtain further insight into the nature of the thermalization dynamics, we varied the isotopic composition, $x = D/(D+H)$ (i.e. we varied the average distance of the N-D oscillators in the sample). As can be seen from Figure 1c, τ_1 and τ_2 are virtually independent of the deuterium concentration, which indicates that the mechanism of vibrational relaxation only depends on the local environment of the excited N-D group. Furthermore, the subsequent thermal equilibration dynamics are independent of x, which suggests that the process associated with $\tau_{thermal}$ corresponds to a local structural equilibration which does not depend on the average distance between the N-D chromophores. This observation implies that the dynamics associated with $\tau_{thermal}$ correspond to structural relaxation in the vicinity of the excited N-D oscillator, and that thermal diffusion from initially excited N-D groups to non-excited ND oscillators does not contribute significantly.[15] We note that the dynamics for EAF at low isotopic exchange ($x = 0.05$) differ slightly from those measured at high deuterium content (Figure 1c). This deviation likely originates from a weak absorption band centered at 2160 cm^{-1} in EAF ($x = 0$, no D present; see Figure S1 in the Supporting Information), which contributes to the measured dynamics at low values of x. To avoid significant contribution of this background band, we focus on samples with high isotope exchange, where the contribution of the background band at 2160 cm^{-1} can be considered negligible (see Figure S2 in the Supporting Information). We further confirmed that the dynamics associated with $\tau_{thermal}$ reflect the local equilibration of the ionic ammonium group by studying the inverse system (excitation of the N-H stretching band at 3040 cm^{-1} for EAF at $x = 0.92$, see Figure S3 in the Supporting Information). As can be seen from Figure 2a, the equilibration dynamics measured for the N-D and N-H stretching vibrations in response to the ultrafast temperature change are in broad concordance.[16] This agreement is consistent with the dynamics associated with $\tau_{thermal}$ being due to thermal equilibration of the ionic ammonium group.

To glean insight into the underlying molecular mechanism of the thermal equilibration, we studied the temperature dependence of $\tau_{thermal}$. From an Arrhenius fit of the data (Figure 2a), we determined an activation energy of $E_A(\tau_{thermal}) = (4.7 \pm 1.0)$ kJ mol^{-1}.[17] As mentioned above, equilibration will only lead to spectral changes in the N-D (or N-H) stretching band if the intermolecular distance between the ammonium group and the anion is altered. Thus, on a molecular level, the equilibration is expected to be dominated by local translational motion of the ions. It is thus informative to compare our present results to the thermal activation of the viscosity (i.e. translation under shear; see inset in Figure 2a). Interestingly, the shear viscosity[18] exhibits a markedly higher activation energy (for EAF, $E_A = (22.1 \pm 0.5)$ kJ mol^{-1}) than the thermal equilibration $E_A(\tau_{thermal})$, thus indicating that the energy barrier for translation associated with the thermal equilibration is much lower than that under shear. The difference in activation energy is perhaps not surprising, given that the restructuring after thermal excitation corresponds to a rather local translation, as opposed to the long-range translation under shear. Such a reduced activation barrier is also observed for ethylammonium nitrate:[13] similar to our

findings for EAF, the activation energy for thermal equilibration of EAN ($E_A = (6.2 \pm 0.1)$ kJ mol^{-1})[13,17] is much smaller than for viscosity ($E_A = (22.8 \pm 0.6)$ kJ mol^{-1}).[18] We note that the absolute values of $\tau_{thermal}$ are larger for EAN, in line with its higher viscosity (compared to EAF). This implies that the nature of the anion critically influences the local intermolecular interaction and consequently the local dynamics.

In contrast to the marked change of $\tau_{thermal}$ (ca. 11 ps for EAF vs ca. 16 ps for EAN[13] at 25 °C) upon substitution of the anion, increasing the alkyl chain length of the cation from ethylammonium (EA) to pentylammonium (PeA)[19] (see Figures S4 and S5 in the Supporting Information) has little impact on the local dynamics of the ammonium group, with $\tau_{thermal}$ remaining virtually constant for all the studied alkylammonium formates (see Figure 2b). This is even more surprising given that the viscosity[20] increases by a factor of 2.5 upon changing the cation from EA to PeA (see Figure 2b). It also contrasts the finding for hydrogen-bonded alcohols, where the size of the alkyl group markedly affects the dynamics of the hydroxy group.[14] For alkylammonium formates, the increase in the size of the hydrophobic fragment goes along with a marked increase in the hydrophobic domain size, as evident from scattering experiments.[21] Our results show that the local dynamics in the ionic region of the RTILs are remarkably insensitive to the increase in the size of the hydrophobic domain.

Conversely, it is of interest how fast the hydrophobic domains can equilibrate after the ultrafast temperature rise. Accordingly, we performed experiments with the pump pulse centered at 3040 cm^{-1}, predominantly exciting the N-H stretching band for a sample of EAF at $x = 0.92$ and probed the dynamics of the C-H stretching vibration at 2985 cm^{-1}. We found thermal equilibration to be significantly faster for the C-H (alkyl) stretching vibration, with $\tau_{thermal} \approx 6$ ps at ambient temperature (see Figure 3 and Figure S6 in the Supporting Information). This time constant is only half that observed for the ammonium group embedded in the ionic domain (ca. 11 ps). Importantly, the values for $\tau_{thermal}$ at C-H stretching frequencies are nearly independent of temperature, decreasing from 6.4 ps at 25 °C to 6.1 ps at 85 °C, which corresponds to an Arrhenius activation energy of about (0.7 ± 0.1) kJ mol^{-1}.[17] The low value of E_A clearly indicates that the equilibration within the hydrophobic domain has a remarkably low activation barrier. It further suggests that the amphiphilic nature of the EA cation, which underlies the structural heterogeneity, also leads to substantial heterogeneity with respect to the dynamics. Our results suggest that the hydrophobic domains, where molecular interaction is dominated by van der Waals forces, are very flexible and can readily adapt to the dissipated energy. In contrast, the Coulombic and hydrogen-bonding interaction between the cationic ammonium group and the anions make the ionic substructure more rigid, as the breaking and reformation of these strong intermolecular forces require higher activation energy. The rigid structure is presumably a direct consequence of the highly anisotropic energy landscape around the ionic groups as a result of the reported directional hydrogen bonds.[22,23] Our results further indicate that, despite being correlated, the local dynamics are largely decoupled from the viscosity. This is consistent with the view that the viscosity is determined by the local interactions and dimensions of the hydrophilic and hydrophobic domains (which give RTILs their particular structure), while the liquid dynamics are determined primarily by local intermolecular interactions.

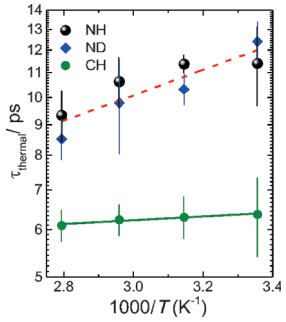

Figure 3. Thermal equilibration times $\tau_{thermal}$ of the ammonium group of EAF as determined from the dynamics of the N-D and N-H stretching vibrations together with the dynamics of the hydrophobic (C-H stretching vibration) domain at different temperatures. Error bars correspond to a 2% increase in the sum of the squared deviation of the fit from the data.

In summary, we studied structural equilibration in RTILs after a fast temperature jump, which was induced by vibrational excitation and subsequent relaxation. We find this structural relaxation is a rather local process. The relaxation of the ammonium entity within the ionic substructures markedly depends on the counterion, whereas the size of the alkyl group has little influence on these dynamics. This indicates that local dynamics within the ionic domains are not affected by the size of the hydrophobic aggregates. Interactions within the hydrophobic domains are much weaker and equilibration within these domains is accordingly faster. Thus, our results show that ionic liquids are not only structurally heterogeneous, but the dynamics vary considerable among the different substructures. This has implications for the performance of RTILs as reaction media, as the local structural dynamics and the ability to dissipate excess energy affect reaction rates and may provide a rationale as to why predictions of reaction rates based on macroscopic observations fail for RTILs. It may further help to understand the rather complex solvation dynamics[24] in these systems. Finally, the heterogeneous thermal dynamics are likely the origin of the anomalous heat transport in RTILs,[25] which is pertinent to their applications as electrolytes or heat-storage media.

Received: September 15, 2014
Published online: November 19, 2014

Keywords: ionic liquids · IR spectroscopy · thermal equilibration

[1] S. Zhang, N. Sun, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data* **2006**, *35*, 1475 – 1517.
[2] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2008**, *108*, 206 – 237.
[3] M. Petkovic, K. R. Seddon, L. P. N. Rebelo, C. S. Pereira, *Chem. Soc. Rev.* **2011**, *40*, 1383 – 1403.

[4] C. Giorgio, C. Chiappe, *Green Chem.* **2014**, *16*, 2375 – 2385.
[5] M. H. Chakrabarti, F. S. Mjalli, I. M. AiNashef, M. A. Hashim, M. A. Hussain, L. Bahadori, C. T. J. Low, *Renewable Sustainable Energy Rev.* **2014**, *30*, 254 – 270.
[6] E. J. Maginn, *J. Phys. Condens. Matter* **2009**, *21*, 373101.
[7] O. Russina, A. Triolo, L. Gontrani, R. Caminiti, *J. Phys. Chem. Lett.* **2012**, *3*, 27 – 33.
[8] C. C. Weber, A. F. Masters, T. Maschmeyer, *Green Chem.* **2013**, *15*, 2655 – 2679.
[9] E. W. Castner, C. J. Margulis, M. Maroncelli, J. F. Wishart, *Annu. Rev. Phys. Chem.* **2011**, *62*, 85 – 105.
[10] R. A. Marcus, *Rev. Mod. Phys.* **1993**, *65*, 599 – 610.
[11] H. J. Bakker, J. L. Skinner, *Chem. Rev.* **2010**, *110*, 1498 – 1517.
[12] D. J. Shaw, M. R. Panman, S. Woutersen, *Phys. Rev. Lett.* **2009**, *103*, 227401.
[13] J. Hunger, T. Sonnleitner, L. Liu, R. Buchner, M. Bonn, H. J. Bakker, *J. Phys. Chem. Lett.* **2012**, *3*, 3034 – 3038.
[14] A. J. Lock, S. Woutersen, H. J. Bakker, *J. Phys. Chem. A* **2001**, *105*, 1238 – 1243.
[15] Note that a decrease in the magnitude of $\Delta\alpha_{iso}$ with increasing time would be expected for thermal diffusion from excited N-D to non-excited N-D chromophores, as the dissipated energy will be distributed over all the ions and thus the energy within all N-D groups would decrease as time evolves. This is clearly not borne out by the experiment (see Figure 1 a).
[16] Note that the vibrational relaxation of the N-H stretching vibration ($\tau_1 \approx 160$ fs, $\tau_2 \approx 1.3$ ps) is similar to that of the N-D band.
[17] The error in the activation energy is obtained from a weighted fit of the mean values of $\tau_{thermal}$. From the maximum and minimum slopes, the uncertainty in the activation energy was determined to be ± 3 kJ mol^{-1}.
[18] J. A. Smith, G. B. Webber, G. G. Warr, R. Atkin, *J. Phys. Chem. B* **2013**, *117*, 13930 – 13935.
[19] Propylammonium formate is not included as it is solid at room temperature.
[20] T. L. Greaves, A. Weerawardena, C. Fong, I. Krodkiewska, C. J. Drummond, *J. Phys. Chem. B* **2006**, *110*, 22479 – 22487.
[21] T. L. Greaves, D. F. Kennedy, A. Weerawardena, N. M. K. Tse, N. Kirby, C. J. Drummond, *J. Phys. Chem. B* **2011**, *115*, 2055 – 2066.
[22] T. Peppel, C. Roth, K. Fumino, D. Paschek, M. Köckerling, R. Ludwig, *Angew. Chem. Int. Ed.* **2011**, *50*, 6661 – 6665; *Angew. Chem.* **2011**, *123*, 6791 – 6795.
[23] A. Stark, M. Brehm, M. Brüssel, S. B. Lehmann, A. S. Pensado, M. Schöppke, B. Kirchner, *Top. Curr. Chem.* **2013**, 1 – 39.
[24] A. Samanta, *J. Phys. Chem. Lett.* **2010**, *1*, 1557 – 1562.
[25] K. Yoshida, K. Iwata, Y. Nishiyama, Y. Kimura, H. Hamaguchi, *J. Chem. Phys.* **2012**, *136*, 104504.

