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PAPER

Picosecond dynamics of hydrogen bond rearrangements during phase separation of a triethylamine and water mixture†

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The earliest stages of phase separation in a liquid triethylamine (TEA)–water mixture were observed using a picosecond IR laser pulse to produce a temperature jump and ultrafast Raman spectroscopy. Raman spectral changes in the water OH stretching region showed that the temperature rise induced by IR pulses equilibrated within a few tens of picoseconds. Amplitude changes in the TEA CH-stretching region of difference Raman spectra consisted of an initial faster and a subsequent slower process. The faster process within 100 ps is attributed to hydrogen bond weakening caused by the temperature rise. The slower process attributed to phase separation was observed for several nanoseconds, showing the number of hydrogen bond between TEA and water gradually decreased with time. The kinetics of hydrogen bond scission during phase separation indicated a linear growth of the phase-separated component, as observed previously on the nanosecond time scale, rather than the more usual exponential growth. A peak blueshift was observed in the difference Raman spectra during phase separation. This shift implies that hydrogen bond scission of TEA–water aggregates involving very few water molecules took place in the initial stage of phase separation (up to 2 ns), and then was followed by the breaking of TEA–water pairs surrounded by water molecules. This effect may be a result from spatial inhomogeneities associated with the phase separation process: aggregates or clusters existing naturally in solution even below the lower critical soluble temperature.

Introduction

Some binary liquid mixtures, such as triethylamine (TEA) and water, have their own lower critical soluble temperatures (LCSTs) and split into two phases from a single phase with a temperature rise.[1] This phase splitting is one where small changes in intermolecular interactions and the cooperative motion of molecules lead to macroscopic changes. In a mixture having an LCST, hydrogen bonding between unlike molecules, which is enthalpically favored though unfavored by orientational entropy, plays an important role.[2–4] Below its LCST, unlike molecules mix with each other by forming stronger hydrogen bonds. Above the LCST, hydrogen bonds between unlike molecules are no longer dominant, and mixtures separate into two phases. Such changes in hydrogen bonds by changing temperature and components have been studied with

vibrational spectroscopy,[5–7] which implies that spectroscopic techniques are essential to understand phase separation from a molecular viewpoint. Spectroscopic and diffraction studies, such as Raman spectroscopy,[8] X-ray small angle scattering,[9,10] ultrasonic attenuation measurements[11–13] and fluorescence correlation spectroscopy,[14] have shown that concentration fluctuations and molecular aggregates exist even in a single-phase solution below its LCST. It is known that concentration fluctuations play an important role in phase separation dynamics, whereas the role of molecular aggregates remains unclear.

Time-resolved studies of phase separation have been also carried out by chemists and physicists,[15–19] with significantly lower time resolution than what is reported here. These previous studies were mainly concerned with morphological changes, such as the macroscopic growth of phase domain. Few spectroscopic studies have been carried out to investigate molecular-level changes during phase separation.[20] Phase separation is the result of a fine balance between molecular attractions and repulsions and the process should involve microscopic changes of the fine balance as well as the hydrodynamics and the energetics of the surface and the bulk. Therefore, a full picture of phase separation dynamics should involve molecular-level information that can be obtained from vibrational spectroscopy.

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In the last decade, the co-authors at Tohoku University have employed pump–probe methods with nanosecond temperature jump (T-jump) to investigate phase separation dynamics in TEA–water mixtures[21,22] and 2-butoxyethanol–water mixtures.[23,24] In these reports, 1.9 μm nanosecond pulses, which directly excited water molecules vibrationally and caused a nanosecond T-jump in the aqueous solutions,[25–27] were used to initiate phase separation. The dynamics of phase separation were observed by transient Raman spectroscopy and shadow graphic imaging of micron-scale phase-separated regions. Nano-/micro-phase regions in dynamically phase-separating media were also used as unique reaction fields for nanomaterial synthesis.[28,29] By photoreduction of aurate ions in dynamic phase separating media, size-controlled single crystalline gold square plates were obtained successfully. The result implies that the dynamic phase separating media has quite different properties from static solutions, which can affect nanoparticle synthesis. The microscopic nature of the dynamic phase separating media, however, is not yet fully understood.

In the case of TEA–water mixtures, nanosecond T-jump experiments revealed that molecular restructuring involving hydrogen bond scissions occurred within a few microseconds, and only after that did macroscopic phase-separated domains appear, as observed by optical microscopy. The hydrogen bond scission involved two stages: the faster (0 to ∼200 ns) and the subsequent slower changes (∼200 ns to 1 μs). We discussed these processes, connecting them to the early, intermediate and late stages of spinodal decomposition. However, with the nanosecond T-jump method, the time resolution was not fast enough to discuss the early-stage molecular view of phase separation dynamics. It is still not clear how molecules segregate and form their own phases and interfaces in the very initial stage of phase separation, and how the fluctuations and aggregates, which have been observed in static solution, affect the dynamics of phase separation.

In this paper, we used a mid-IR picosecond pulse to induce a rapid T-jump that initiates phase separation in TEA–water mixture and transient Raman spectra were observed. Based on the nanosecond experiments, we were certain that we were seeing the same phase separation process but with much greater time resolution.[21] From time-resolved Raman difference spectra, we observed hydrogen bond scission during the very initial stage of phase separation. This scission contains two stages and the kinetics were non-exponential in time. Furthermore we observed a frequency shift in the Raman difference spectra, indicating that the hydrogen bonds which broke away in the very initial stages of phase separation were different from those broke away in the later stages. From these results, we will discuss the molecular view of the very early stages of phase separation.

Experimental section

The sample was a mixture of triethylamine and water with 0.2 mole fraction of TEA. Triethylamine was purchased from
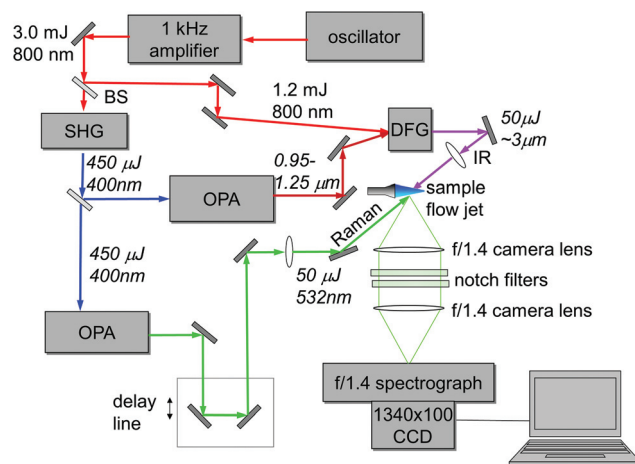

Fig. 1 A schematic experimental setup for a picosecond T-jump experiment. Phase separation was induced in triethylamine and water mixtures in a jet cell by the irradiation of an IR pulse, which was obtained with differential frequency generation (DFG). SHG: second harmonic generation, OPA: optical parametric amplifier, NF: notch filter, delay: optical delay line.

Acros Organics and used without additional purification. The laser apparatus used in this study has been described elsewhere.[30,31] Briefly, a kilohertz Ti-sapphire picosecond laser system (800 nm, 1.2 ps, 3.0 mJ per pulse) pumped two optical parametric amplifiers, one with a difference frequency generator which produced mid-IR pump pulses (3.28 μm (3050 cm^{-1}), 30 μJ per pulse) and optical-delayed 532 nm probe pulses (Fig. 1). A liquid jet of the sample solution was produced from a nozzle 60 μm thick. A temperature controller maintained the solution at 285 K at the output of the nozzle. Raman scattering from 532 nm probe pulses spatially overlapped with the IR T-jump pulses was collected by a spectrograph with a high quantum yield charge coupled array detector (CCD). At each delay time a spectrum was obtained by averaging for 5 min. Steady-state Raman and IR spectra were also measured for TEA water mixtures at a variety of compositions. The IR liquid cell had CaF_2 windows and a 6 μm spacer.

The CH str. region of each time-resolved difference Raman spectrum was fitted with a pair of positive and negative Gaussian peaks by using IGOR Pro software (Wavemetrics Inc.). Error bars of wavenumbers were obtained from conventional fitting errors (standard deviation). Error bars of the spectral amplitudes were calculated from the bandwidths of confidence bands showing the region within which measured data are expected to fall with 95% probability.

Results and discussion

Fig. 2 shows IR and Raman spectra of TEA–water mixtures with different compositions. As we already reported,[21] a peak shift was observed at the methylene C–H stretching region (∼2800 cm^{-1}) in Raman spectra. The peak redshift increases
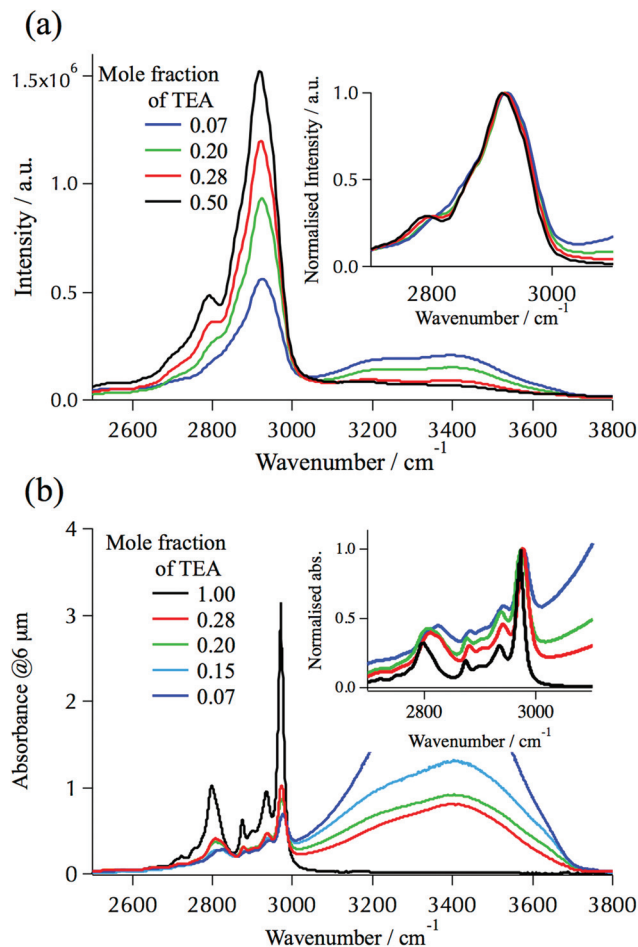
Fig. 2 Steady state Raman (a) and IR (b) spectra of TEA–water mixtures with different compositions. The insets show spectra normalized to the highest peak intensity of the CH₃ str. mode.

Fig. 3 Time resolved Raman (a) and difference Raman spectra (b) after a laser induced temperature jump. At each delay, the arrow indicates the peak position of a negative peak in the methylene CH str. region. The dashed line at 2830 cm^{-1} indicates the negative peak position after several nanoseconds.

with increasing TEA mole fraction. A similar shift was observed in IR absorption. According to a quantum chemical calculation,[32] these shifts can be ascribed to hydrogen bond formation between TEA and water molecules. This hydrogen bond formation induces a change in the electron density distribution in TEA, and as a result, the electron density on the methylene H atom decreases and the strength of the methylene CH bond of TEA increases. Furthermore, when the number of water molecules that participate in a TEA–water hydrogen bond complex increases, the CH bond strength becomes stronger and the peak blueshifts. Both the Raman and IR spectra qualitatively agreed with the results of the cited calculations. By monitoring the methylene CH-stretching peak shift during phase separation, hydrogen bond formation between TEA and water can be studied. According to the IR absorption spectrum of the 0.20 mole fraction mixture, the penetration depth in the mixture, of the 3.2 μm IR light used for the T-jump is ~8 μm. This means that the much thicker liquid jet was not heated homogeneously. We heated only the first ten or so microns of the sample whereas the visible probe interrogated the entire liquid jet. In this situation we had to
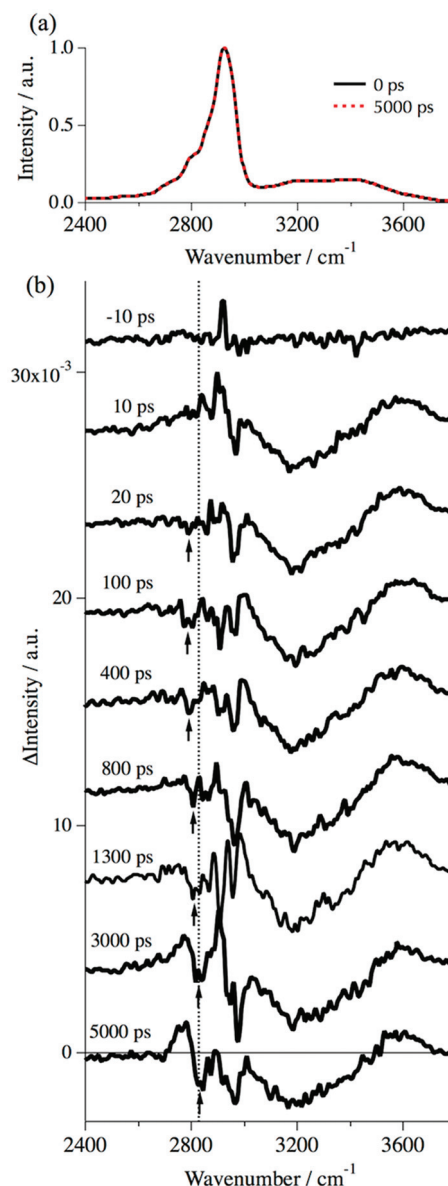
subtract away the effects of the liquid that was not subjected to a T-jump using difference Raman spectroscopy. The magnitude of the T-jump was estimated to be less than 40 K.

Fig. 3 shows Raman spectra of TEA–water mixture with 0.20 mole fraction of TEA at 0 ps and 5000 ps after the T-jump and the difference Raman spectra at each delay time. In order to account for the small variations in laser intensity with time, the intensity of each Raman spectrum was normalized to the intensity of the highest peak at ~2930 cm^{-1} whose intensity was not affected much by phase separation. The difference spectra were obtained by subtracting normalized Raman spectra with and without a T-jump induced by IR pump

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pulses. In difference Raman spectra, spectral changes caused by T-jump were observed in the C–H stretching (2700–3000 cm^{-1}) and also the O–H stretching (3000–3700 cm^{-1}) region. In the O–H region, a pair of broad negative and positive peaks was observed immediately after the T-jump. On the other hand, several negative and positive peaks were seen in the CH region, and the intensities of the peaks changed with time after the T-jump. These behaviors can be interpreted as following.

Changes in the water O–H str. region

There is a well-known relation between the OH frequency red-shift and the hydrogen bond strength. When temperature is increased, the hydrogen bonding weakens overall and the broad OH spectrum loses intensity on the red edge and gains intensity on the blue edge. The difference spectrum after T-jump is negative-going on the red edge and positive-going on the blue edge.[26,33–35] Based on this discussion, we obtained the intensity difference of the positive and negative peaks in the OH region, $\Delta\Delta I_{OH}$, to observe temperature change after picosecond pulse irradiation (for definition of $\Delta\Delta I_{OH}$, see ESI†).

Fig. 4(a) shows $\Delta\Delta I_{OH}$ plotted as a function of the delay time. $\Delta\Delta I_{OH}$ increased rapidly and then stayed constant for 5 ns, indicating the picosecond IR pumping process led to an equilibrium T-jump within a few tens of picoseconds. This result is consistent with previous results on temperature change in pure water,[35,36] and aqueous solutions[31] after ps laser irradiation observed by anti-Stokes Raman scattering. We also monitored the changes in the intensity of anti-Stokes Raman scattering after CH stretching pumping at 2840 cm^{-1} (see Fig. S2†). The result shows that nonequilibrium vibrational populations created in the pumped molecules thermalized within a few tens of picoseconds, and $\Delta\Delta I_{OH}$ is a direct monitor of the time dependence of the temperature jump in an aqueous solution.

Changes in the methylene C–H str. region

Even though the rapid spectral change in the OH-stretch region associated with thermalization of the IR pump pulses was essentially a step function, the amplitudes of peaks in the CH region in the difference spectra continued to change for nanoseconds after the T-jump. In difference spectrum such as the 5000 ps spectrum in Fig. 3, there is a clear derivative-shaped peak at ~2800 cm^{-1}, indicating a red shift of the methylene CH stretching peak. This derivative peak shape and position were similar to those observed after a nanosecond T-jump.[21] As described above and also in previous reports, this red shift is due to decrease of the number of hydrogen bond between TEA and water molecules. From the time evolution of the amplitude of the peak, $\Delta\Delta I_{CH}$, we obtained the dynamics of hydrogen bond evolution after ps laser irradiation (Fig. 4(b)). $\Delta\Delta I_{CH}$ increased rapidly after the T-jump, and then, $\Delta\Delta I_{CH}$, continued to slowly increase for nanoseconds. Fig. 4(b) shows that phase separation continued long after the T-jump,
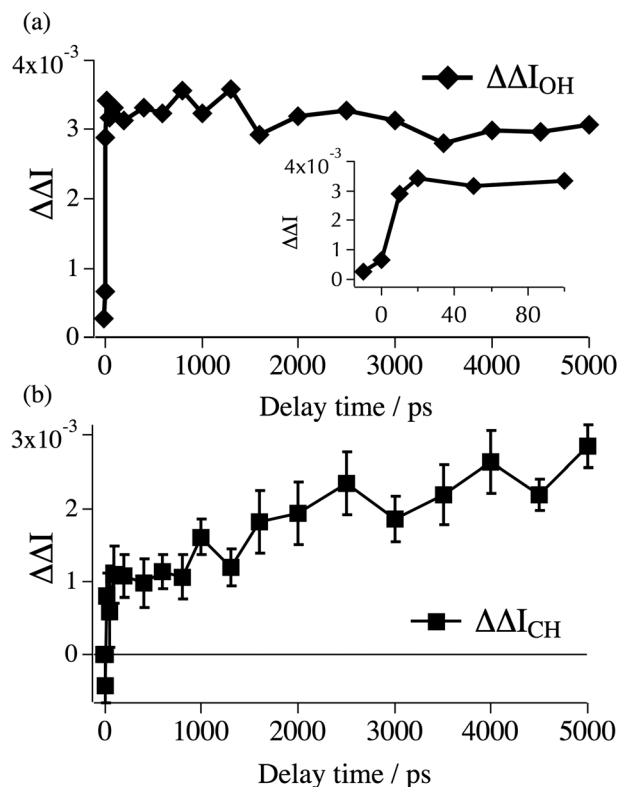

Fig. 4 Time evolution of the intensity of differential shaped peak, $\Delta\Delta I$, in difference Raman spectra in the OH region (a) and the methylene CH region (b). Each error bar was estimated from the band width of a confidence band obtained from the fitting analysis (see text).

and that the kinetics of the phase separation process were linear, as opposed to exponential in time. This unusual linear temporal behavior is similar to what was previously observed with nanosecond T-jump.[21] This linear change, that was much slower than the T-jump itself implies that the hydrogen bond restructuring continued to take place long after the T-jump.

In the case of ns laser induced phase separation, quasi-isosbestic points were observed in difference Raman spectra during phase separation, and those allowed us to propose a simple two-species model which involved H-bonded and non-H-bonded TEA molecules. In that model, we assumed that $\Delta\Delta I_{CH}$ was simply proportional to the number of hydrogen bond scissions. On the other hand, in the very initial stage of phase separation induced by ps laser irradiation, no isosbestic points were observed and the position of the negative peak in the methylene CH region shifted to higher frequency during phase separation, whereas the position of the positive peak stayed almost constant at ~2770 cm^{-1}. The negative peak is attributed to the decrease of H-bonded TEA; therefore, the amplitude and the peak position of the negative peak should represent the number of TEA molecules having reduced hydrogen bonding. For this reason, the blue shift of the negative peak indicates that the hydrogen bonds which broke away at the initial stage of phase separation can be different from those which broke at the later stage and the hydrogen bonds
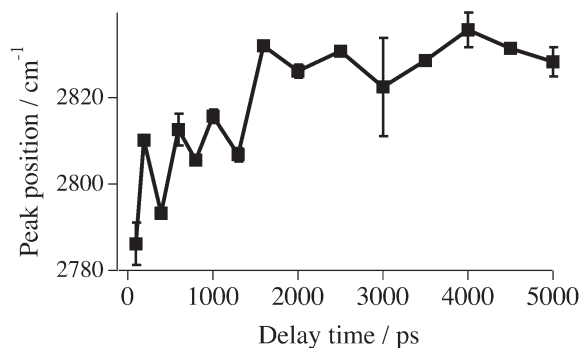
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Fig. 5 Time evolution of the peak position of a negative peak in the methylene CH region. Error bars were estimated from fitting errors.

where larger number of water molecules participate may break away at later stages.

In Fig. 5, the position of the negative-going peak was plotted as a function of delay time. Although the data were noisy, the figure clearly shows that the peak position shifted from 2810 cm⁻¹ to 2830 cm⁻¹ during the earliest stages of phase separation. According to density functional calculations,[32] the strength of CH bond and the position of the Raman peak of methylene CH stretching depend on not only whether a hydrogen bond was formed or not, but also on the number of water molecules which participate in hydrogen bonds with one TEA molecule. When the number of associated water molecules increases, the peak shifts to higher frequency region. Thereby, the negative peak at 2810 cm⁻¹ at the initial stage indicates that hydrogen bond between a TEA molecule and one or two water molecule(s) would break at the initial stage of phase separation. On the other hand, the negative peak at higher frequency region implies that hydrogen bonds between a TEA molecule and several surrounding water molecules started to break away at the later stage. This means that phase separation starts with hydrogen bond scissions of TEA–water aggregates involving a few water molecules just after a temperature rise, and then is followed by the breaking of TEA–water pairs surrounded by large number of water molecules. The difference between types of hydrogen bonds may come from the concentration fluctuation which naturally exists in the solution.

It is known that the TEA–water mixture is not totally homogenous and there is spatial and temporal concentration fluctuation even below the LCST. Thus, there are TEA-rich regions and water-rich regions in an instant and they decompose and form repeatedly. In the TEA-rich region, the number of water molecules is less such that hydrogen bond between TEA and a single/few water molecule(s) can be dominant. On the other hand, in the water-rich region, hydrogen bond between TEA and surrounding water molecules can be dominant. The experimental results imply that, when a mixture was T-jumped on the picosecond time scale, scissions of hydrogen bonds in TEA rich region occurred first, and then hydrogen bonds in water rich region started to break away with a delay of a few

nanoseconds. Namely, phase separation started in TEA rich regions after the rapid temperature rise.

Conclusion

In this study, we successfully initiated phase separation of a TEA–water mixture by an ultrafast T-jump produced by absorption of a picosecond IR pulse. The earliest stages of phase separation were observed with time-resolved Raman spectra. The Raman spectral changes in the O–H stretching region showed that the temperature of the mixture rose within a few tens of picoseconds after the T-jump pulse. Spectral changes in the TEA CH-stretching region showed that the number of hydrogen bond between TEA and water molecules continued to decrease for nanoseconds after the picosecond T-jump. The hydrogen bond scission process observed in the CH stretching region involved initial faster and subsequent slower stages. The faster stage is attributed to a simple temperature effect. The second slower change, continuing for nanoseconds, showed that the molecular-level phase separation process continued for nanoseconds. The kinetics of slow hydrogen bond scission showed linear rather than exponential behavior. In addition, a peak shift was found in the methylene CH region among difference Raman spectra during phase separation. The negative peak was initially observed at around 2810 cm⁻¹ in the Raman difference spectra, then the peak shifted to 2830 cm⁻¹. This shift suggests that, at the very initial stage of phase separation, the hydrogen bond scission starts from TEA–water aggregates existing in the TEA-rich region. After that, hydrogen bonds in water rich region started to break away with a delay of a few nanoseconds. Thus, molecular aggregates originated from inhomogeneity in solution, existing even below its LCST, are essential for the dynamics of phase separation. To our knowledge, this is the first report to observe molecular level dynamics of liquid–liquid phase separation in sub-nanosecond and nanosecond time region.

Acknowledgements

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