Supporting Information

Unraveling the Interplay of Temperature with Molecular Aggregation and Miscibility in TEA-Water Mixtures

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MD simulation detail

"The cross-interaction parameters of Lennard Jones potential are described by the Lorentz-Berthelot mixing rules.[1,2] No constraint in this simulation were implemented to restrict the motion of O-H in water or C-H bond in TEA. In NVT simulation process, the Berendsen thermostat[3] was employed to regulate the simulation temperature with a time constant of 2 ps. The time constants for the thermostat and barostat in NPT simulation process are set to be 2 ps to modulate the temperature and pressure of a given simulation. The velocity Verlet algorithm[4] was utilized to integrate Newton's equations of motions with a timestep of 1 fs."

The references are given as follows.

1   H. A. Lorentz, Ueber die Anwendung des Satzes vom Virial in der kinetischen Theorie der Gase, *Ann. Phys.*, 1881, **248**, 127–136.

2   Berthelot, D., and G. AMOREUX. Comptes Rendus Acad, 1898, 1703-1855.

3   H. J. C. Berendsen, J. P. M. Postma, W. F. Van Gunsteren, A. Dinola and J. R. Haak, Molecular dynamics with coupling to an external bath, *J. Chem. Phys.*, 1984, **81**, 3684–3690.

4   H. GrubmüLler, H. Heller, A. Windemuth and K. Schulten, Generalized verlet algorithm for efficient molecular dynamics simulations with long-range interactions, *Mol. Simul.*, 1991, **6**, 121–142.
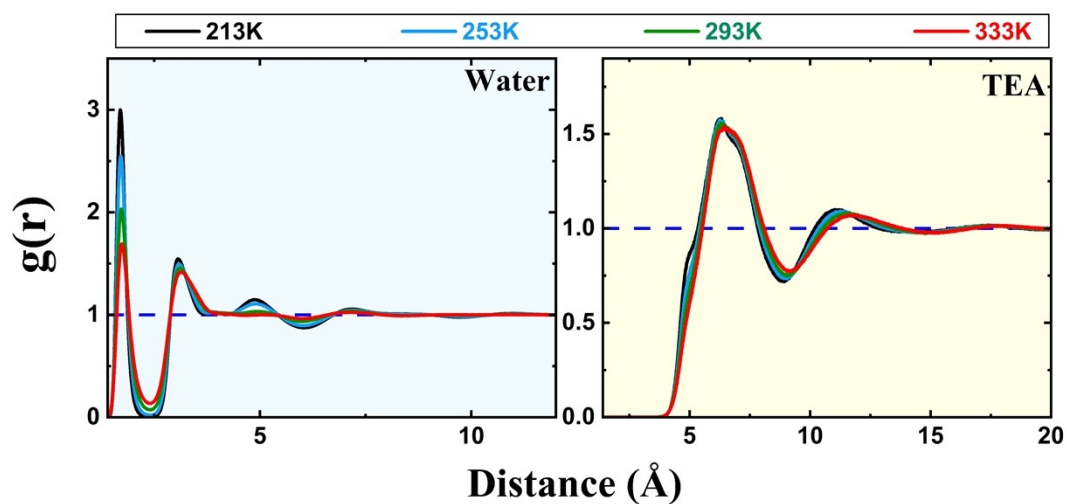
Figure S1. The radial distribution functions (RDF) of pure water (O_w-H_w) and pure TEA (N_{TEA}-N_{TEA}). The pure liquid systems exhibit little significant change in RDFs at the four temperatures except that the first peak height of water-water RDF is decreased as the temperature increases
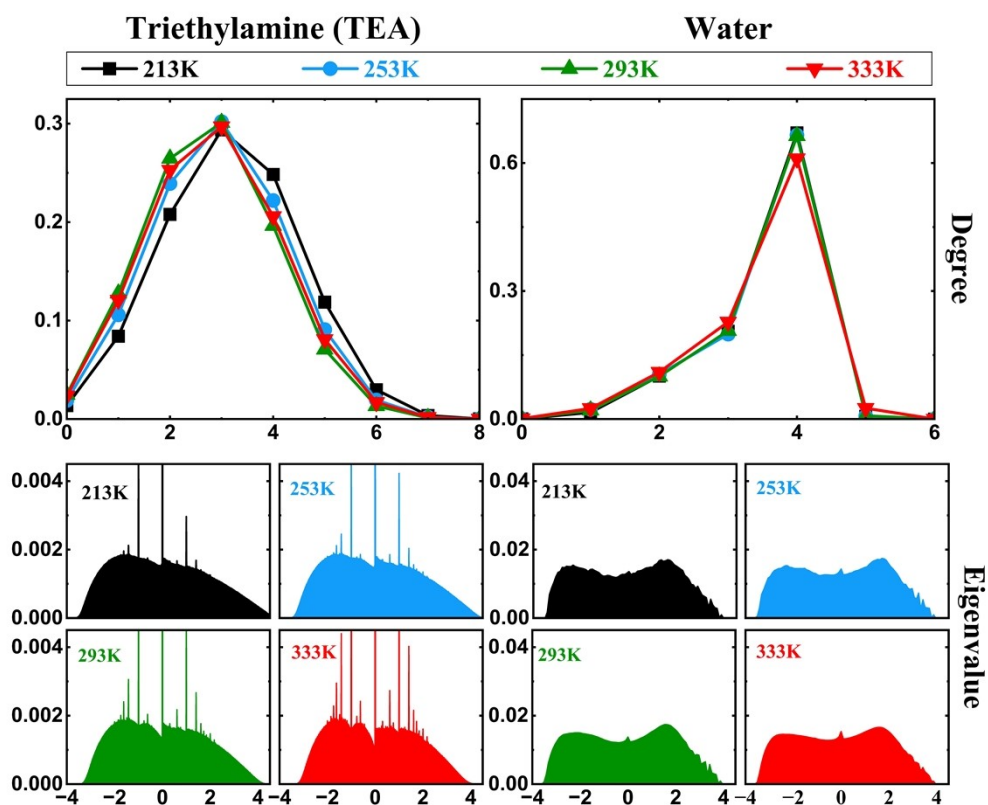
Figure S2. Graph theoretical analysis conducted on pure liquids of TEA and water with four distinct temperatures. The figure showcases the degree distribution of TEA and water in the top layer, eigenvalue spectrum in the bottom layer. Despite subjecting the liquids to varying temperatures, no notable heat induced alterations are observed in the graph theoretical properties of the pure liquids.
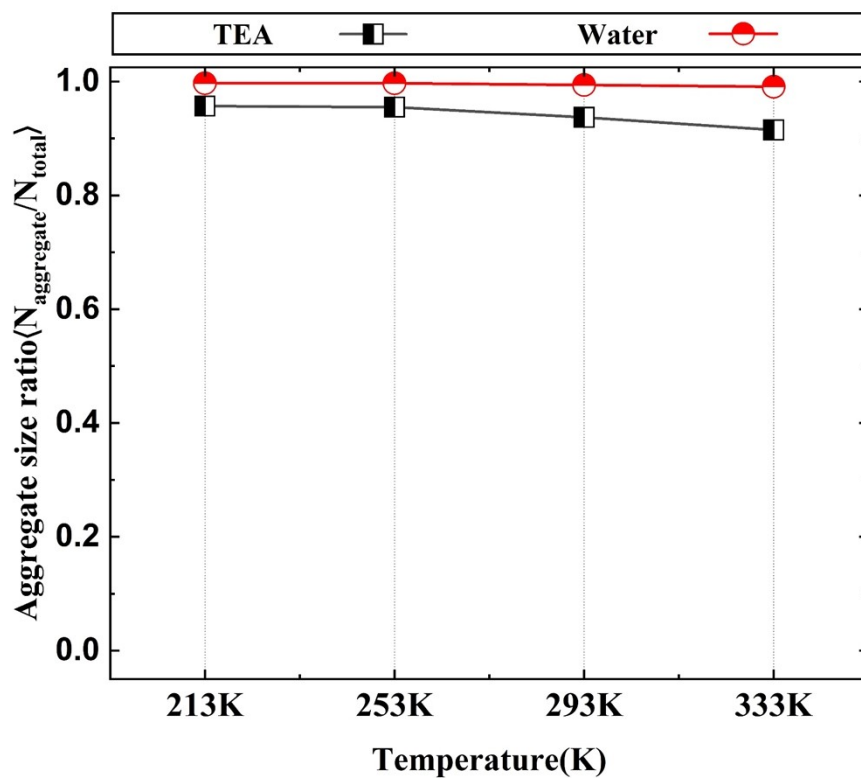
Figure S3. Aggregate size ratio, $\langle N_{aggregate} \rangle / N_{total}$, of the TEA aggregates and the water H-bonding network as a function of temperature. In the pure liquid system, the number of TEA and water molecules present is equivalent to 1,000 each. The normalized aggregate size ratio of water aggregate size indicates a tendency for the aggregates size to remain relatively constant, even when subjected with substantially higher temperatures. Similarly, the TEA aggregate size ratio as the temperature increases remains fairly consistent with a slight drop in the aggregate size ratio. It means that the TEA network is slighlty disrupted upon increase in temperature.
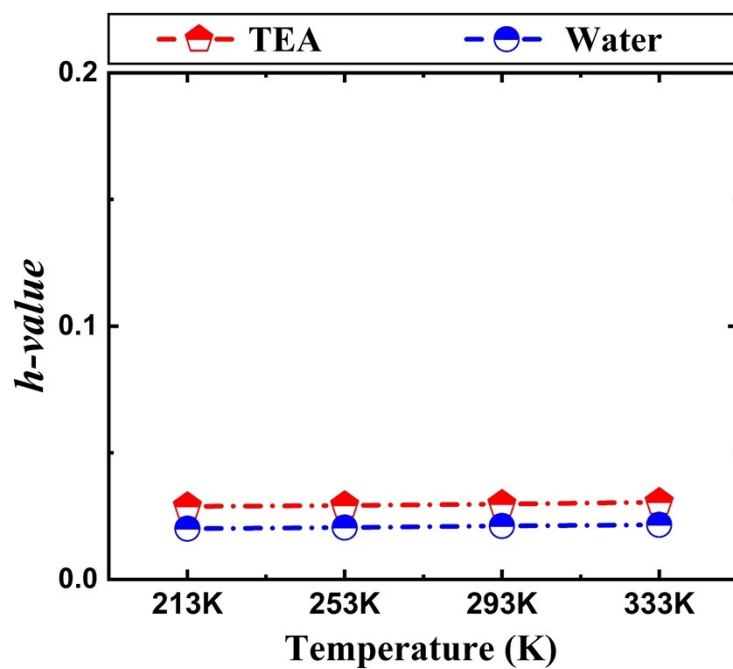
Figure S4. Average *h* value of two pure liquid systems spanning a temperature range of 213 to 333 K. The average *h* values have very small values close to zero, representing uniform distribution of component molecules throughout the systems.

MD simulations, graph theoretical analysis and spatial distribution analysis at 0.03 mole fraction of TEA-water mixture

We conducted MD simulations at a 0.03 mole fraction with the four representative temperatures. These simulations utilized a molecular system comprising 10,000 water and 300 TEA molecules, following the same simulation protocol detailed in our main manuscript.
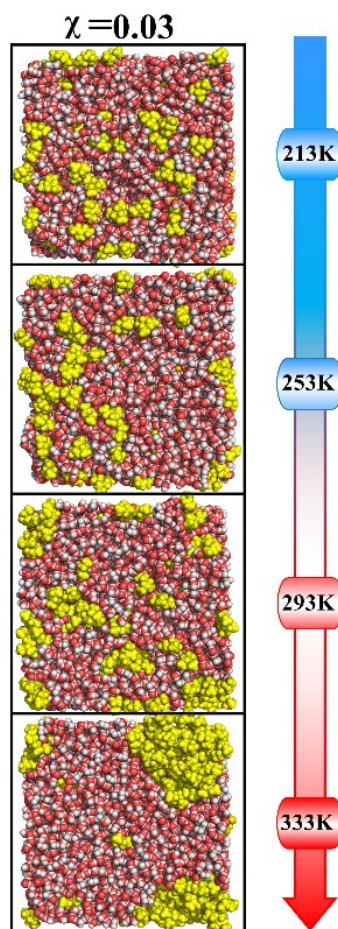

Figure S5: Illustrative snapshots extracted from MD simulations, capturing diverse temperatures within each binary liquid system. These simulations encompass 0.03 mole fractions of TEA-water mixture. Water molecules are denoted by red (oxygen) and white (hydrogen) spheres, and TEA molecules are represented by yellow at 0.03 mole fraction. Notably, the TEA-water mixtures exhibit a phase transition behavior from a single liquid phase to two separated phases as the temperature is raised.

The Figure S5 shows temperature-dependent phase separation behavior of aqueous TEA mixture, captured through the snapshots extracted from the MD simulations at four different temperatures of 213, 253, 293, and 333 K. The TEA aggregates at 213 K are evenly distributed making significant TEA-water interaction, but TEA molecule tends to form huge self-associated aggregates by avoiding interaction with water molecules, facilitating liquid-liquid phase separation in the binary liquid mixture.
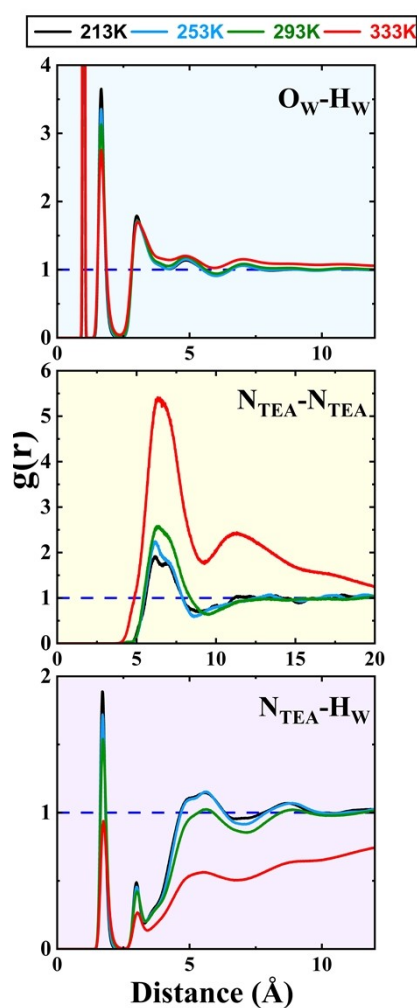

Figure S6: Illustrates the radial distribution functions (RDFs) of TEA-water binary mixtures, focusing on the interactions between oxygen (O) and hydrogen (H) atoms within water molecules (O_W-H_W), as

well as the nitrogen (N) atom within triethylamine (TEA) molecules (N_{TEA}-N_{TEA}) and between H atoms of water molecules and nitrogen of TEA.

At the lower concentration of the TEA-water mixture, the water-water RDFs does not show a sizable variation in the peak position and height, but the TEA-TEA and TEA-water RDF exhibit a distinct pattern with respect to the temperature. As shown in Figure S6, the g(r) tends to converge to the value 1 at the lower temperatures of 213, 253, and 293 K, indicating formation of homogeneous mixture, while two separate liquid phases appear in the higher temperature of 333 K, exhibiting a significant deviation from the value 1 in long-distance region.
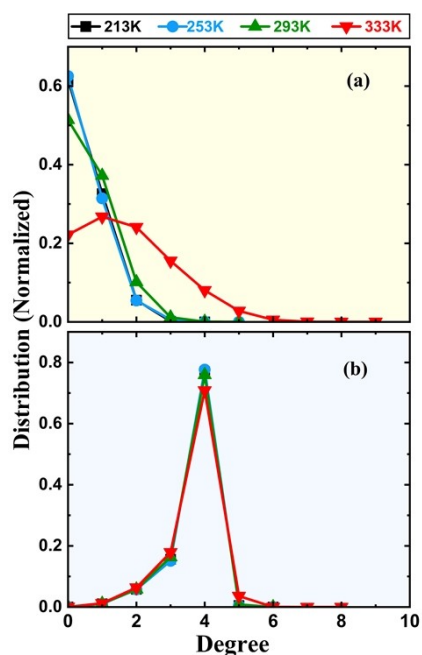

Figure S7: The normalized degree distribution of TEA and water in the TEA/water binary mixture depicted across four different temperatures and at a fixed mole fraction of 0.03. The upper panel illustrates the degree distribution of TEA while the bottom panel is that of water. Notable changes are absent in the degree distribution of water at all temperatures due to the low TEA concentration. TEA clearly exhibits a distinct pattern with a peak position of 0~1 at the lower temperatures compared to that

of 1~2 observed at the higher temperature of 333 K, implying a thermally induced change in TEA aggregation pattern.

In Figure S7, the degree distribution of water is overall similar regardless of the temperature at the 0.03 mole fraction, which indicates that the water H-bond network structure is not largely disrupted in the lower concentrated solution. To examine the effect of TEA aggregates on water H-bond structure, the interfacial waters around TEA are targeted, and the degree distribution of water around TEA is plotted in Figure S8.
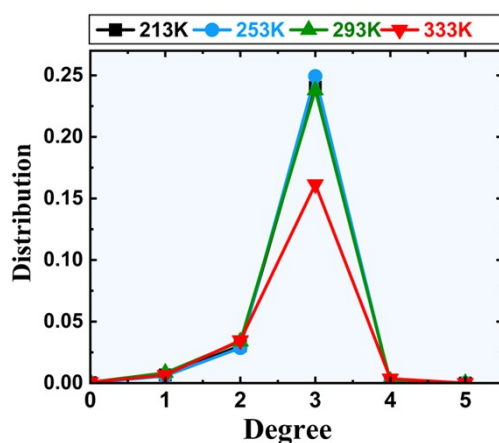

Figure. S8. The degree distribution of water at the TEA/water interface for 0.03 mole fraction at 213, 253, 293, 333K. The water H-bond networks in the interfacial region show clear differences according to the temperature. The peak intensity at 333 K is smaller than that of 213, 253, 293K, which reflects formation of two separated phases at 333 K while avoiding interaction with water.

The degree distribution of water molecule adjacent to water TEA at 333 K is clearly distinguished from those of lower temperatures of 213, 253, 293 K. It implies that the water-compatible aggregates with favorable interaction with water are altered into the water-incompatible aggregates with self-associated pattern as the temperature is elevated. This tendency is also manifested in the eigenvalue spectrum and aggregate size distribution of TEA and water.
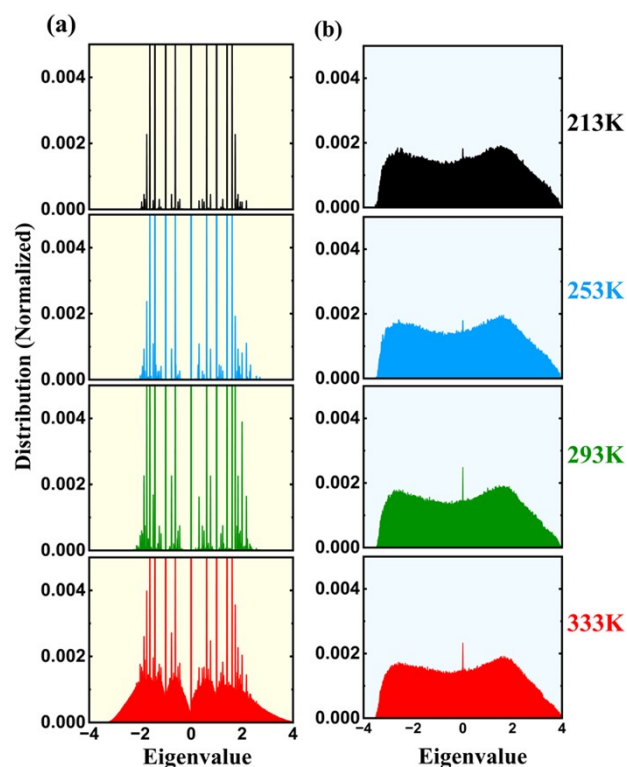
Figure S9: Normalized eigenvalue spectra of (a) TEA and (b) water H-bond networks are depicted at a 0.03 mole fraction of TEA/water mixture. Across all temperatures and concentrations water exhibits no considerable alterations in their eigenvalue spectrum. At 213, 253, and 293 K, the TEA spectrum appears to be discrete with various peaks, representing a significant disruption in the water H-bond network of the homogeneous mixture. At 333 K, the eigenvalue spectrum of TEA network in the TEA-water mixture becomes broad and continuous, indicating a phase transformation from single phase to biphasic state.
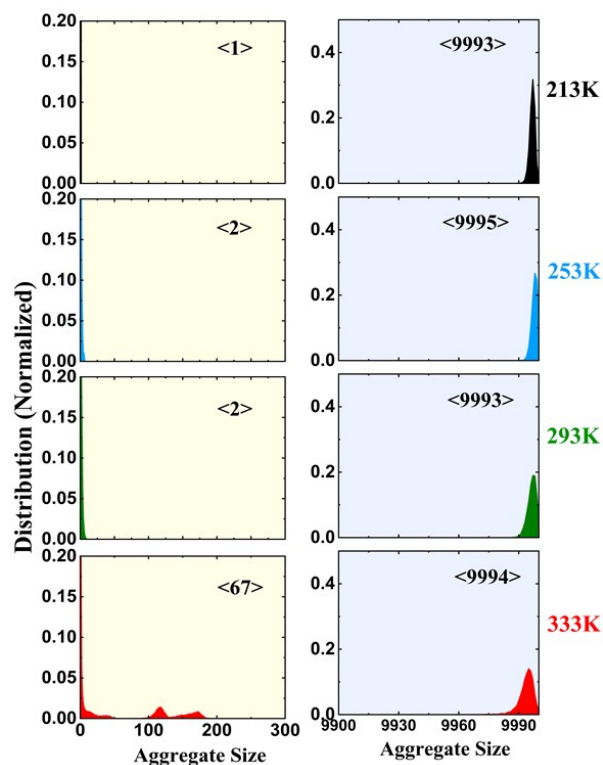
Figure S10: The Aggregate size distribution, of the TEA aggregates and the water H-bonding network in the 0.03 mole fractions as a function of temperature. The aggregate size of water tends to remain relatively consistent against the temperature. In the binary liquid mixture, the number of TEA and water molecules present is equivalent to 300 and 10,000. In the TEA-water mixture, the TEA aggregate size is suddenly increased at 333 K, which suggests that huge self-associated TEA aggregates are formed upon increase in temperature in the biphasic system.
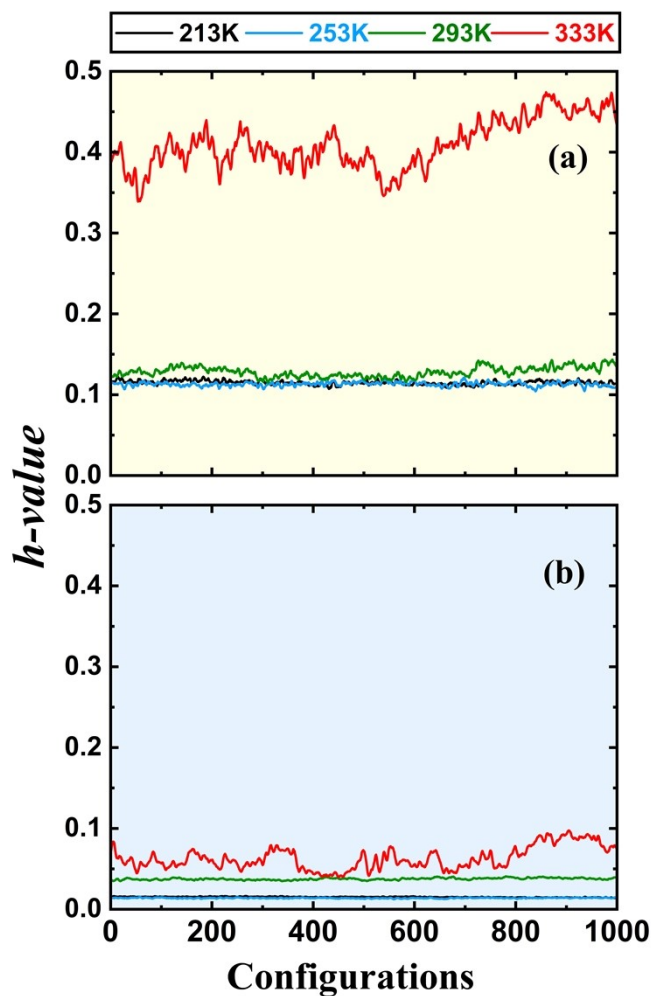
Figure S11: Time-varying *h*-value of (a) TEA and (b) water examined at a mole fraction of 0.03, spanning across four temperatures. Notably, the *h*-value of TEA in the 0.03 mole fraction of TEA-water mixture shows an evident increase at 333 K, which implies a phase transition from one to two phase. However, the *h*-value of water in the respective mixtures remains relatively unchanged to all temperatures.

As shown in Figure S11 in the two phase system which is obtained at 333K, the average *h*-value of TEA is close to 0.4, which is significantly higher than ~0.1 of 213, 253, and 293 K, representing phase transition from a single phase to two phases with temperature increase. In conclusion, the heat-induced aggregation pattern is evident even at the lower mole fraction of 0.03 as shown in the higher mole fraction of 0.5 and 0.67 of TEA-water mixtures.
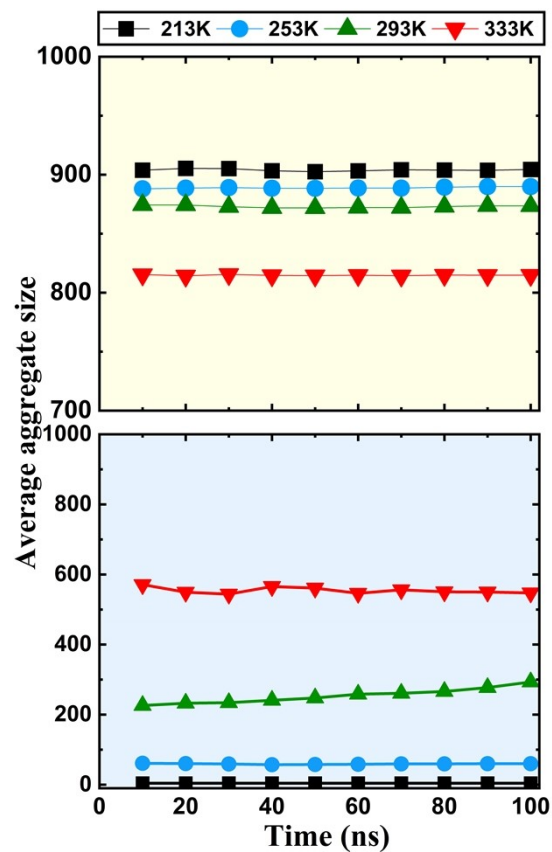
Figure S12: Time-varying average aggregate size of TEA-water mixture of 0.5 mole fraction at four temperatures. In the aggregate size of TEA (top) and water (bottom), the convergence behavior is shown with respect to the trajectory length.
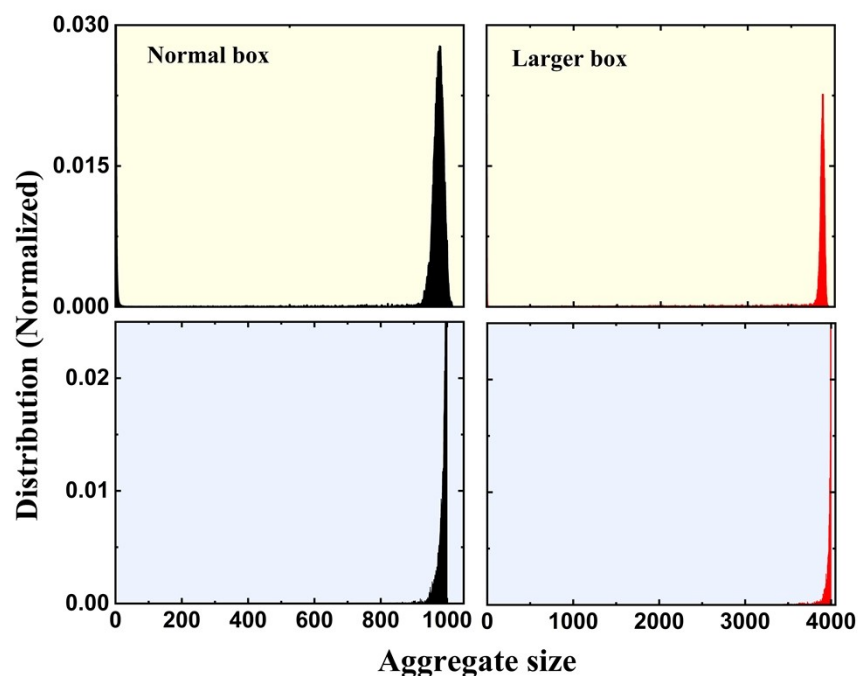
Figure S13. Normalized distribution of aggregate size of TEA and water for 0.5 mole fraction binary aqueous system at 333 K. The TEA (upper panel) and water (lower panel) form huge aggregates accompanying liquid-liquid phase separation, which most of constituent molecules participate in, at both molecular systems of aqueous mixture including 1000 TEA and 1000 water molecules and that including 4,000 TEA and 4000 water molecules. There is no significant box size dependence in aggregation pattern of TEA and water in the binary aqueous mixture.
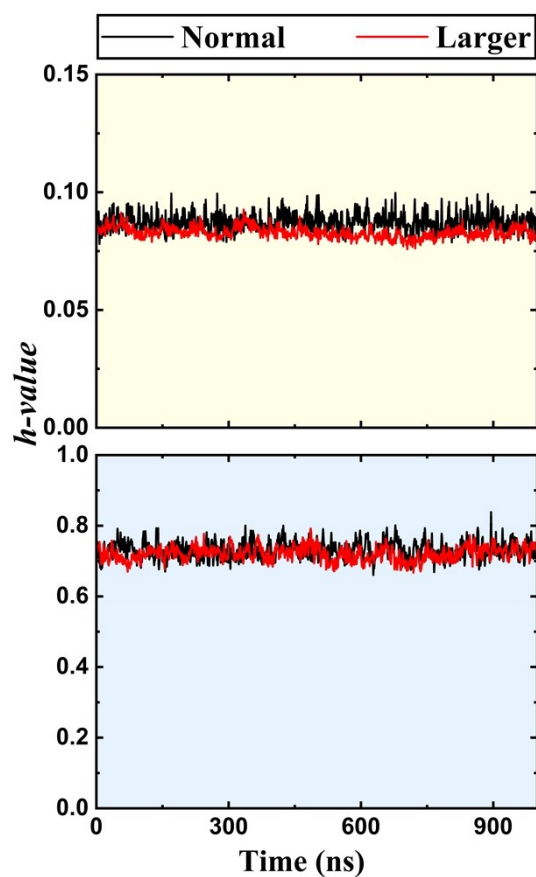
Figure S14. Time-varying *h*-value of TEA–water mixture at 333 K. The similar high *h*-values in water (lower panel) are obtained in both molecular systems of (1000 TEA and 1000 water) and (4000 TEA and 4000 water), indicating formation of two separated liquid phases. There is no significant box size dependence on the *h*-value in the binary liquid mixture.