

Hydrogen-Bond Network Collapse and Molecular Confinement in Ethanol–Water Mixtures at the Azeotrope

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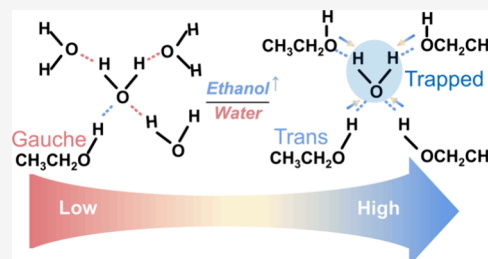


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Supporting Information

ABSTRACT: Azeotropic behavior in hydrogen-bonded mixtures raises the question of whether the azeotropic composition represents a unique microscopic structure or a continuous evolution of hydrogen bonding. Here, by integrating cavity-enhanced Raman spectroscopy with molecular dynamics (MD) simulations and density functional theory (DFT) calculations, we resolve the compositional evolution of ethanol–water mixtures with high sensitivity at the azeotropic concentration. We reveal two key signatures: the complete collapse of the tetrahedral water network with a high-frequency shift of the free OH stretch indicates dispersion of water as microclusters and isolated states, and ethanol spectra reveal a gauche-to-trans conformational change. MD simulations, supported by DFT calculations, indicate that these spectroscopic features reflect a microscopic reorganization of hydrogen-bond structure, characterized by the fragmentation of extended water–water connectivity and the spatial confinement of water molecules by surrounding ethanol. Our results provide direct experimental evidence of a structural transition in hydrogen-bond topology and molecular confinement occurring at the azeotropic composition.



Ethanol–water mixtures have long attracted attention due to their anomalous thermodynamic behavior, including azeotrope formation, which cannot be explained by simple compositional effects.^{1–5} These anomalies, observed in properties such as density, viscosity, and heat capacity, are widely attributed to the intricate hydrogen-bonding network involving water–water, alcohol–alcohol, and alcohol–water interactions.^{6–8} Although ethanol–water mixtures have been extensively studied, the structural interpretations reported in the literature often diverge or even contradict one another. For example, some studies proposed that the anomalous thermodynamic properties arise from incomplete mixing of alcohol and water rather than from the reorganization of water molecules.^{9,10} In contrast, Nishikawa and Iijima reported the absence of large clusters in ethanol–water solutions,¹¹ suggesting that the thermodynamic anomalies may not originate from nonideal mixing effects. Growing evidence suggests that hydrophobic hydration and self-organization lead to the reorganization of hydrogen bonds, giving rise to molecular structures such as clathrate-like,^{1,12–16} which may underlie the macroscopic thermodynamic anomalies, including azeotrope formation. Therefore, elucidating hydrogen-bonding interactions is critical for understanding the molecular mechanisms underlying the unique properties of alcohol–water systems.

Numerous studies have identified three critical ethanol mole fractions (0.07, 0.15, and 0.60 mol) where significant changes occur in the hydrogen-bond structure of ethanol–water mixtures.^{1,17–21} In dilute solutions, water molecules form clathrate-like cages around hydrophobic ethanol cores,²² while

at intermediate compositions, sandwich-like or percolated networks emerge.^{16,22–24} At high ethanol concentrations (0.6 mol), the water–water hydrogen-bond network is disrupted, and hydrogen bonding between water and ethanol becomes dominant, with water molecules mainly existing as small clusters.²⁵ However, the formation of azeotropes in ultraconcentrated ethanol–water mixtures represents a typical anomaly, while their molecular origin and hydrogen-bond structure remain unclear. This regime is dominated by ethanol, with water molecules sparsely distributed, posing major challenges for resolving their spatial structures and interaction patterns. Despite numerous theoretical studies on cluster structures and hydrogen-bonding networks in azeotropes,^{26–29} direct experimental confirmation of their molecular origin is still lacking.

To address these challenges, we introduce integrating cavity-enhanced Raman spectroscopy (ICRS), a sensitive spectroscopic technique capable of probing subtle molecular structures in ethanol-rich mixtures. Combining ICRS with MD simulations and DFT calculations, we reveal the hydrogen-bond structure of ultraconcentrated ethanol–water solutions. Our results show that water molecules exist as

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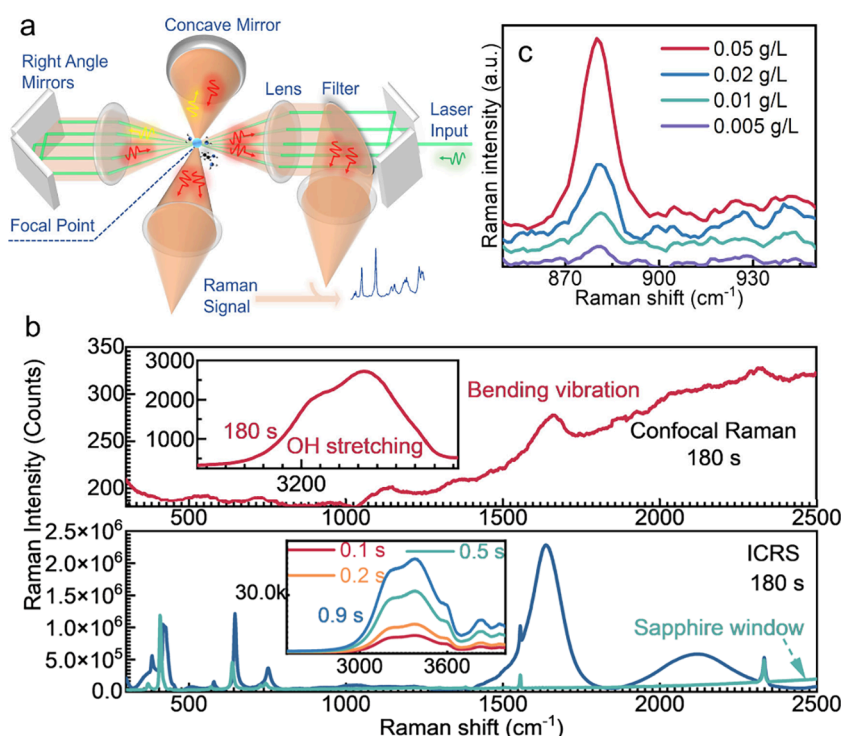


Figure 1. Schematic diagram of the experimental setup. (a) Optical path diagram of the multiple reflection cavity in a liquid. (b) Comparison of Raman spectra measured by ICRS and confocal Raman. (c) Detection limit of this experimental technique in an ethanol–water solution.

monomers (greater than 60%) or dimers, dispersed within the ethanol network to form clathrate-like structure or act as linkers among ethanol chains. This nanoscale reorganization suppresses the expansion of water–water connectivity, increases the configurational entropy, and imposes microstructural constraints on the emergence of azeotropic behavior.

EXPERIMENTAL METHODS

Ethanol–water mixtures (volume fractions of 0.7, 0.8, 0.9, 0.94, and 0.98) were prepared using three-times-distilled water and anhydrous ethanol. During Raman measurements, the samples were continuously circulated through a quartz or sapphire cell using a peristaltic pump to ensure a constant refreshment of the irradiated volume, thereby minimizing laser-induced local heating and cumulative thermal effects arising from repeated laser excitation. The optical setup for ICRS was shown in Figure 1a. A dual right-angle mirror system was first employed to achieve multiple reflections of the incident beam. In this configuration, the incident beam skims the first right-angle mirror, undergoes multiple reflections between two opposing right-angle mirrors, enabling repeated excitation of the sample. To further enhance the signal collection efficiency, a confocal cavity system with a focal length of 5 cm was introduced along the laser propagation direction, collecting both forward and backward Raman scattered signals along the optical axis. Simultaneously, a concave mirror was employed to collect side scattered Raman signals from the lateral directions around the focal point, thereby extending the collection solid angle, significantly improving the overall signal collection efficiency. The Raman detection limit is significantly improved by combining a multireflection excitation scheme with multidirectional signal collection. In addition, an off-axis parabolic mirror is used to replace the focusing lens, eliminating the aberration effects associated with focusing.

ICRS was employed to experimentally probe molecular aggregation in ethanol–water mixtures. As illustrated in Figure 1b, the signal-to-noise ratio obtained with ICRS is enhanced by 3–4 orders of magnitude relative to confocal Raman spectroscopy, enabling detection of trace vibrational features in mixed solutions. The high frequency region (3600–3800 cm^{-1}) of the OH stretching vibration band in Figure 1b contains oscillation like artifacts, originating from the sapphire cell. To eliminate this instrumental background, a reference spectrum of the empty sapphire cell was recorded under identical experimental conditions and subtracted from all measured spectra during data processing. In particular, the detection limit of ethanol–water solutions can reach as low as 0.005 g/L (Figure 1c), which confirmed that ICRS can effectively resolve vibrational information on relevant species in ethanol rich solutions.

Figure 2a presents the CH vibrational Raman spectra of mixed solutions at different ethanol concentrations. Two spectral features are observed: First, a weak band appears near 2893 cm^{-1} . The second-order derivative spectrum analysis clearly distinguishes this band, which disappears when the ethanol concentration is 0.94 (Figure 2b). The disappearance of this peak is consistent with a conformational change of ethanol molecules from gauche to trans,³⁰ reflecting a reorganization within the hydrogen-bond network in the mixed solution. Second, the CH vibrational bands display a systematic red shift in the range 0.7–0.9. Strikingly, once the ethanol concentration exceeds 0.94, the CH spectra of the mixtures become indistinguishable from those of ethanol. This convergence is confirmed by the second-order derivative spectrum (see Figure S1 in the Supporting Information). To further test the generality of this behavior, we analyze the CC and CCO vibrational modes, as shown in Figure S1 of the Supporting Information. These modes exhibit the same

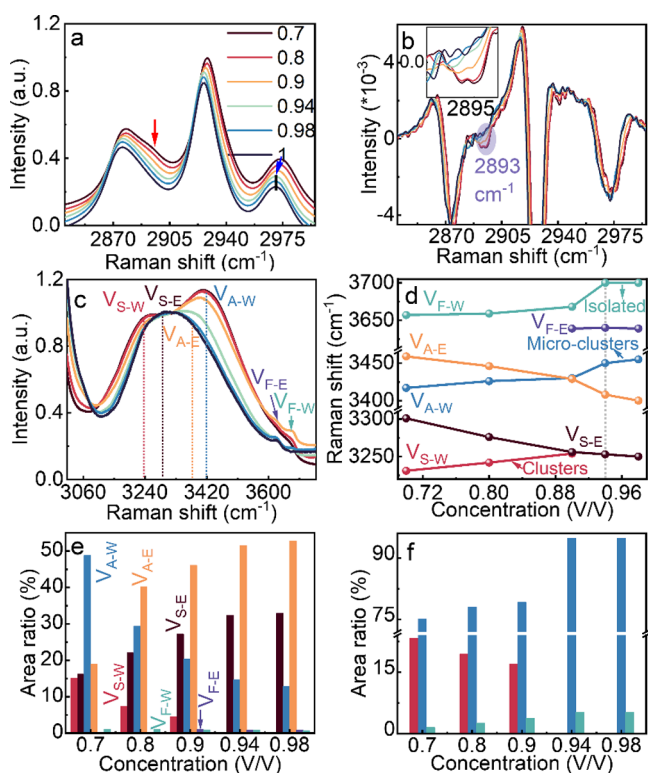


Figure 2. Raman spectra of ethanol–water solutions. (a) Raman spectra of CH vibration at different ethanol concentrations. Red arrows: weak vibrational peaks. Blue arrows: Raman peaks shifted to lower wavenumbers. Short black lines: unchanged peak positions. (b) Second-order derivative spectrum of CH. (c) Raman spectra of OH vibration at different ethanol concentrations. (V: vibration mode. W: water; E: ethanol. S: symmetrical stretching. A: Antisymmetric stretching. F: free. (d) Relationship between different Raman shifts of the OH vibration band and concentration. (e) Area ratios of different Raman modes in the OH vibration band. (f) Relative area ratios for Raman modes of water molecules in the OH vibration band.

concentration-dependent trends as the CH vibrations, indicating that the mixture at high ethanol concentration acquires a structural character indistinguishable from pure ethanol, thereby revealing a concentration-dependent structural reorganization. Therefore, the ethanol vibrational spectra reveal a reorganization of the hydrogen-bond network at the azeotropic point, which may be the triggering factor for the azeotropic composition.

The OH vibrational spectra are analyzed in Figure 2c, providing key evidence for changes in the hydrogen-bond structure of water. When the ethanol concentration reaches 0.94, the low-frequency part of the OH band overlaps with that of ethanol, leaving only a small shoulder at higher frequencies. Notably, the spectral evolution is not monotonic: the OH bands shift gradually from 0.7 to 0.9 but exhibit abrupt changes at 0.94, including the loss of the low-frequency component and a sudden shift in Raman position. Simultaneously, first-order derivative spectra confirm these features: the low-frequency water band disappears while the high-frequency component weakens at 0.94 (Figure S1 in the Supporting Information). These nonlinear spectral changes cannot be explained by a simple dilution effect but instead indicate an abrupt restructuring, or collapse, of the tetrahedral hydrogen-bond network of water. To resolve the spectral components, we perform peak fitting on the OH bands, as shown in Figure S2

in Supporting Information and Figure 2d. In the concentration range 0.7–0.9, three characteristic water peaks (V_{S-W} , V_{A-W} , V_{F-W}) shift toward higher frequency, whereas the two ethanol OH peaks move toward lower frequency (V_{S-E} , V_{A-E}). This opposite trend reflects a progressive shift from water–water hydrogen bonding toward mixed hydrogen-bonding configurations involving ethanol. At 0.94, the V_{S-W} vanishes, which is consistent with the disappearance of liquid water clusters, and the V_{A-W} component undergoes an abrupt red shift of 20 cm^{-1} , reflecting further breaking of residual water–water hydrogen bonds.³² Concomitantly, the free OH of water displays a blue shift of 30 to 3700 cm^{-1} , a position typically associated with interfacial or gas-phase OH and indicative of extremely weak or nonexistent hydrogen bonding (a locally isolated water-like environment).^{33,34} To quantify these spectral changes, we calculate the areas ratio of each Raman component (Figure 2e,f). With increasing ethanol concentration, the contributions associated with ethanol vibrations progressively dominate, while those of water diminish or vanish. Notably, the free OH of water increases gradually with concentration. At 0.94, however, the relative fractions corresponding to incomplete hydrogen bonds and free OH of water increases sharply (Figure 2f). The OH spectral evolution suggests that a percolation-like transition of the hydrogen-bond network occurs below 0.9, whereas the changes at 0.94 are more consistent with a transition from water nanoclusters to isolated monomers or microclusters confined by ethanol. Combined with the CH results, the OH spectra provide consistent experimental evidence for concentration-driven hydrogen-bond reorganization associated with the azeotropic composition.

MD simulations are performed for ethanol volume fractions of 0.7, 0.9, 0.94, and 0.98 (Figure 3a). The results illustrate

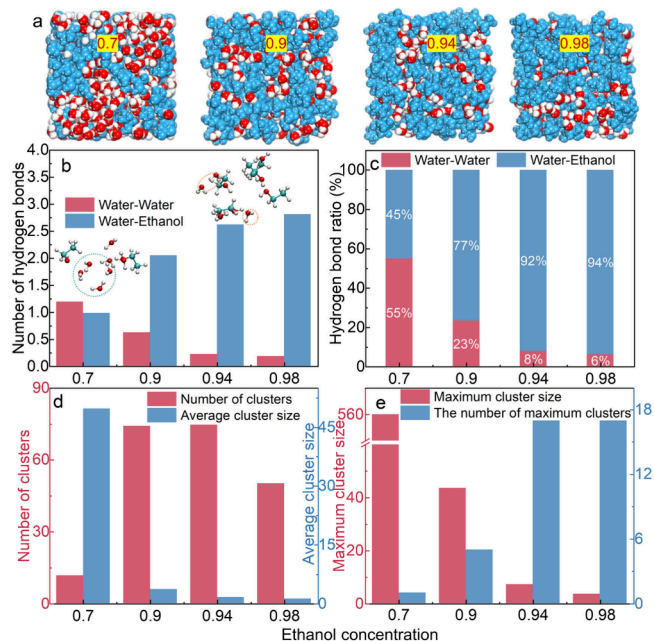


Figure 3. Hydrogen bonding and water cluster characteristics by MD simulations. (a) Structure snapshot. (b) Number and (c) proportion of hydrogen bonds formed by a water molecule with water and ethanol molecules. (d) Number and average size of water clusters in mixed solutions. (e) Maximum cluster size and number of water molecules in mixed solutions.

that water and ethanol molecules undergo incomplete mixing at a volume fraction of 0.7, forming large clusters independently. When the concentration is 0.94, the water molecules are increasingly separated by ethanol molecules, forming microclusters and isolated states. RDF and RDG analyses (Figures S4 and S5 in the Supporting Information) indicate that the microscopic structural transformation arises from a shift in hydrogen bonding: strong hydrogen bonds form between water molecules at a concentration of 0.7, whereas they form predominantly between water and ethanol molecules at 0.94 hydrogen bonds. Quantitatively (Figure 3b), each water molecule forms 1.2 hydrogen bonds with other water molecules and 0.9 with ethanol at 0.7, whereas at 0.94 water–water bonds drop to 0.25 and water–ethanol bonds rise to 2.6, accounting for over 92% of all hydrogen bonds (Figure 3c). These results indicate that even at high ethanol concentrations, water molecules remain predominantly hydrogen-bonded to ethanol rather than being fully isolated, which is consistent with the experimental observations in Figure 1f. This shift fragments the water network into microclusters with an average size of 1.5 molecules (Figure 3d). The maximum cluster size (Figure 3e) further illustrates the transition from a single large cluster at 0.7 to multiple microclusters at 0.94, reflecting a more homogeneous water distribution.

To further characterize these microclusters, statistical analyses based on the MD hydrogen-bond definition are performed, with DFT-based Raman spectra providing supplementary support (Figure 4a,b). The statistical results show that the microclusters at 0.94 are monomers, dimers, and trimers, with monomers being dominant. Further structural analysis at the DFT level (Figure S8) suggests that most trimers can be decomposed into a combination of dimer and monomer, rather than existing as fully independent trimeric

species. On the basis of this structural insight, a calibration procedure is applied in which trimers are approximately redistributed into equivalent populations of dimers and monomers. Following this correction, the fraction of monomers is estimated to exceed 60% (Figure 4c,d). Importantly, structural visualization (Figure 4e) shows that water molecules form cage-like structures with ethanol molecules through hydrogen bonding or serve as bridges connecting ethanol chains. Such structural characteristics disrupt extended water–water networks, promote a uniform distribution of water, and establish the microscopic basis for azeotrope formation.

As established by combined Raman spectroscopy and theoretical simulations and summarized in Figure 4f, the azeotropic composition corresponds to a distinct microscopic structural state in which water no longer forms an extended, percolating hydrogen-bonding network. Instead, water appears in two coexisting populations: hydrogen-bonded microclusters that are spatially confined within ethanol-rich regions, and locally isolated water species characterized by weak or incomplete hydrogen bonding. Meanwhile, ethanol molecules exhibit a conformational ordering, tending toward a more extended trans geometry, reflecting a collective reorganization of molecular packing and hydrogen-bond geometry. This heterogeneous structural arrangement signifies a transition in hydrogen-bond topology and local packing constraints, reshaping the energetic and entropic contributions during mixing at the microscopic level. While additional thermodynamic factors may also contribute to the macroscopic manifestation of azeotropic behavior, the observed collapse of the water hydrogen-bond network and the emergence of molecular confinement provide a plausible microscopic pathway for azeotropic composition.

By integrating ICRS, MD simulations, and DFT calculations, we identify a distinct microscopic structural state of ethanol–water mixtures at the azeotropic composition. ICRS exhibits two signatures: the tetrahedral water peak disappears while incomplete and free O–H stretches shift abruptly to higher frequency, reflecting the collapse of extended water–water hydrogen-bond networks and the dispersion of water into microclusters or isolated molecules. And the disappearance of the 2893 cm^{-1} ethanol band signals a gauche $\rightarrow$ trans conformational switch, which extends ethanol's geometry, making ethanol–water hydrogen bonds more favorable. MD and DFT corroborate these spectroscopic signatures by showing that water molecules lose extended connectivity and are confined by surrounding ethanol. This cooperative structural reorganization reshapes the balance of energetic and entropic contributions during mixing at the microscopic level and is closely associated with the emergence of azeotropic behavior. Beyond the ethanol–water system, our results establish a transferable experimental-theoretical framework for resolving hydrogen-bond topology and molecular confinement in complex liquid mixtures, offering new insight into how local structural transitions can govern macroscopic thermodynamic anomalies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpclett.6c01906>.

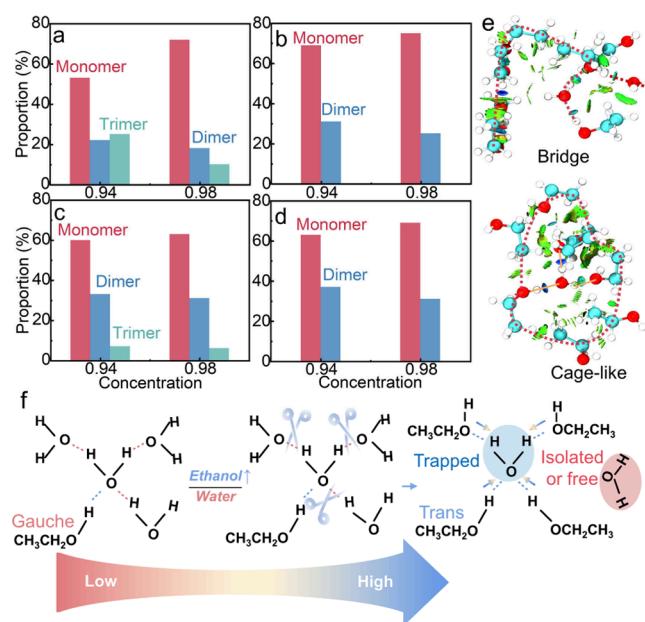


Figure 4. Microscopic aggregation of water and azeotrope mechanism in ethanol mixtures. Populations of water molecular aggregates from (a) MD and (c) DFT calculations statistics. Proportions of monomers and dimers after calibration of water trimers from (b) MD and (d) DFT calculations statistics. (e) Water–ethanol hydrogen-bonded structure at ethanol volume fraction 0.94. (f) Microscopic structural picture of ethanol–water mixtures at the azeotropic composition.

Experimental instrument parameters, MD simulation method and corresponding calculation results, DFT calculation and corresponding calculation results, Raman spectra of ethanol-aqueous solutions, peak deconvolution, MD and DFT calculation results, RDG map, hydrogen-bond analysis, and maximum clusters in mixed solutions (PDF)

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Author Contributions

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Notes

The authors declare no competing financial interest.

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