Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Topological analyses and small-world patterns of hydrogen bond networks in water + *t*-butanol, water + *n*-butanol and water + ammonia mixtures

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Supplementary Information

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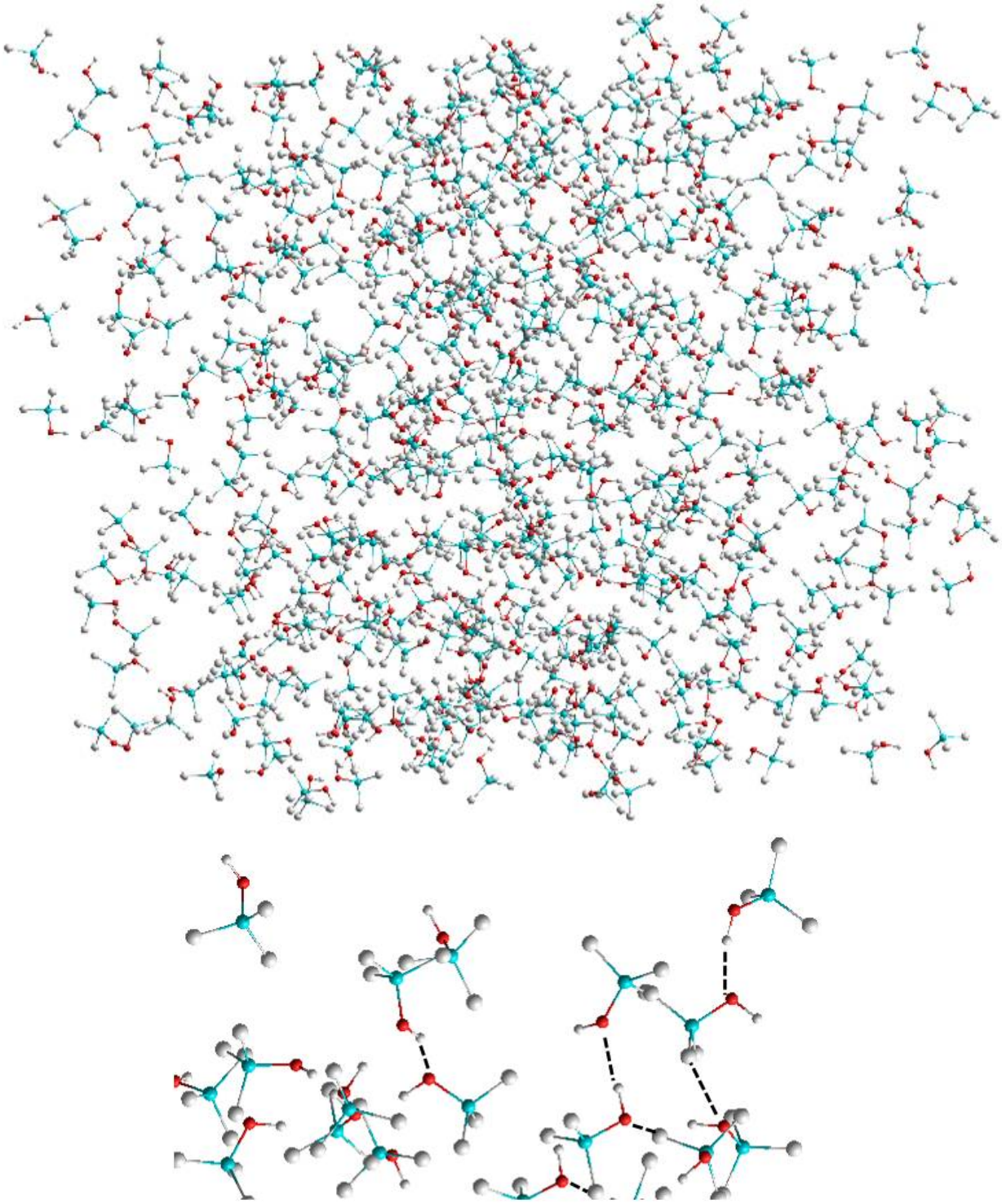
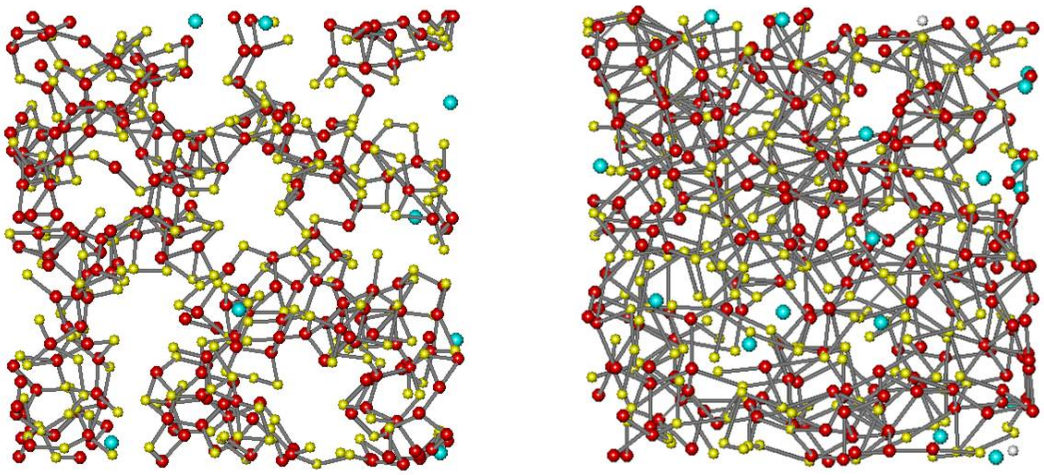


Figure S1. Top panel: atomistic snapshot showing the hydrogen bonds in *t*-butanol liquid at 298.15 K and lower panel: magnification of a region showing some molecules and their hydrogen bonds.



(a) **(b)**

Figure S2. Sphere-and-stick representation of the H-bond networks in (a) $x_{\text{t-but}} = 0.50$ and (b) $x_{\text{a}} = 0.50$. All results involving alcohols were obtained at 298.15 K and ammonia at 239.80 K. Each node (sphere) represents one molecule and the edges (sticks) the hydrogen bonds. The red and yellow balls represent H-bonded water and solute, respectively, whereas isolated (non-connected) nodes (molecules) are shown as white (water) and light blue (solute) spheres.

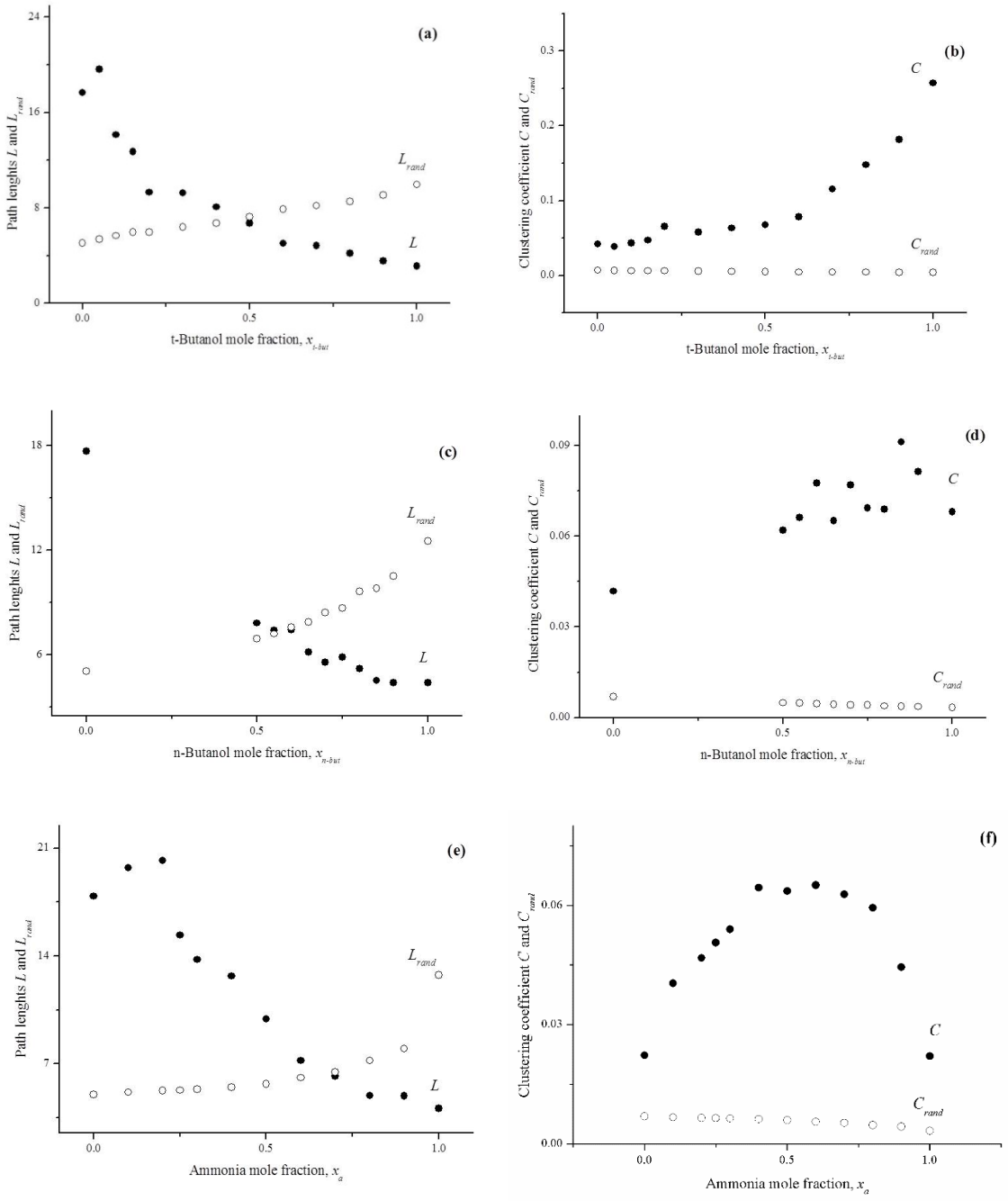


Figure S3. Path lengths (L): (a), (c), and (e), and clustering coefficients (C): (b), (d), and (f), for the H-bond networks as a function of mixture composition, x_s. (a) and (b) s = t-butanol at 298.15 K; (c) and (d) s = n-butanol at 298.15 K; (e) and (f) s = ammonia at 239.8 K. For comparison, the random network values are presented.

Comments on spectral density

The topological features of the network are also directly related to the spectral density. The eigenvalues of the network can be obtained from the adjacency matrix $\mathbf{A}(G)$ with $N \times N$ elements A_{ij} that represent the graph G with N nodes, where the elements satisfy the condition $A_{ij} = A_{ji} = 1$ if nodes i and j are connected and 0, otherwise. The diagonalization of the matrix $\mathbf{A}(G)$ produces a set of N eigenvalues, λ_j, which is the spectrum of the graph G and provides the following spectral density

$$\rho(\lambda) = \frac{1}{N}\sum_{j=1}^{N}\delta(\lambda - \lambda_j) \qquad \text{(S1)}$$

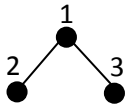
that approaches a continuous function when $N \to \infty$. The m-th momentum can be written as

$$\sum_{j=1}^{N}\rho(\lambda_j)^m\lambda_j^m = \frac{1}{N}\sum_{j=1}^{N}\lambda_j^m = \frac{1}{N}\sum_{i_1,i_2,\ldots,i_m} A_{i_1 i_2}A_{i_2 i_3}\ldots A_{i_m i_1}\ , \qquad \text{(S2)}$$

that is, this sum is the number of trajectories or paths that go to other nodes and return to the same node through m steps. For example, consider the aggregate that has connectivity or adjacency matrix given by equation S3 and represented by the graph of the first column of Table S1. The trajectories corresponding to m = 2, 3 and 4 steps are also shown in Table S1. It can be observed that odd momentum does not exist, i.e., there is no way to go back and forth to the same node through an odd number of steps.

$$\mathbf{A}(G) = \begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 1 & 0 & 1 \end{bmatrix} \qquad \text{(S3)}$$

Table S1. Cluster with 3 components and possible trajectories or paths with m = 2, 3 e 4 steps.

Cluster	$m = 2$	$m = 3$	$m = 4$
	1221	0	12211221
	1331		13311331
	2112		12211331
	3113		13311221

21133112
31122113
21122112
31133113

The diagonalization of the adjacency matrix of this example produces the eigenvalues $\lambda = 0, +\sqrt{2}, -\sqrt{2}$ and momentum corresponding to m = 2, 3 and 4, described respectively by

$$\begin{aligned} \frac{1}{3}\left(0+\left(\sqrt{2}\right)^{1}+\left(-\sqrt{2}\right)^{1}\right) &= \frac{4}{3}, \\ \frac{1}{3}\left(0+\left(\sqrt{2}\right)^{2}+\left(-\sqrt{2}\right)^{2}\right) &= 0, \\ \frac{1}{3}\left(0+\left(\sqrt{2}\right)^{3}+\left(-\sqrt{2}\right)^{3}\right) &= \frac{8}{3}. \end{aligned} \qquad \text{(S4)}$$

Thus, these three eigenvalues produce three peaks in the spectral density plot. In the case of random graphs there is almost a continuum of eigenvalues, which is attributed to the fact that there are many possibilities for these trajectories. The larger the number of similar clusters or with the same number of similar components and connectivity, the smaller the number of momenta that contribute to the spectral density. Graphs with large number of isolated sites or nodes have a high peak at $\lambda = 0$.

Often the spectral density is rescaled by,

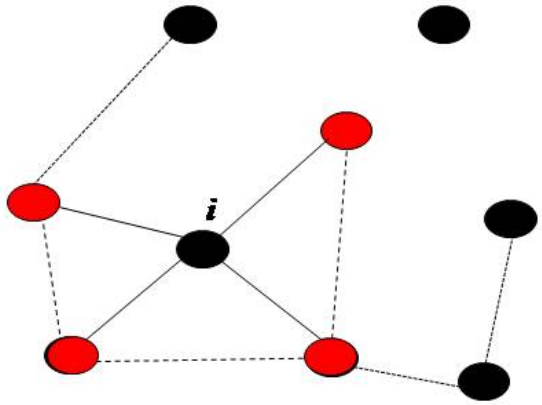
$$\begin{aligned} &\text{Ordinate rescaling:} \quad \rho\left[Np(1-p)\right]^{1/2} \\ &\text{Abscissa rescaling:} \quad \lambda/\left[Np(1-p)\right]^{1/2}, \end{aligned} \qquad \text{(S5)}$$

where $p = \frac{\bar{k}}{N}$ is obtained from random graphs theory and it is equivalent to the probability of connection, ρ is the density and λ is the eigenvalue, calculated for each sample and the average subsequently performed on all samples.

Illustration of clustering coefficient and degree calculations

Consider the example of a graph shown in Scheme S1. For example, if we wish calculate the clustering coefficient of site *i*, C_i, we need count the number of connections (dashed lines) *between* neighboring sites (in red) of *i*, in this case, are three:

C_i = 3. Whereas, the degree of site i (z_i) is the number of connections (solid lines) of i, in this case, four: z_i = 4. Thus, very different values for these properties are obtained mainly when there is a large number of connections (high degree value), but only a few connections between the neighbors (low clustering coefficient value), which usually occur when there are constraints to form new connections due to, for instance, steric hindrances.



Scheme S1. Graph with 9 sites. Nodes with connections to the site *i* are in red. The solid lines indicate connections with the site *i*, the dashed lines indicate connection between neighbors of the site *i*, and dotted lines connections between other nodes of the graph.