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

Understanding Alcohol Aggregates and Water Hydrogen Bond Network Towards Miscibility in Alcohol Solutions: Graph Theoretical Analysis

Seungeui Choi,▽ Saravanan Parameswaran▽ and Jun-Ho Choi*

Department of Chemistry, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju 61005, Republic of Korea

SUPPORTING INFORMATION

∗Author for correspondence: e-mail: junhochoi@gist.ac.kr

Author Contributions

▽ S.C. and S.P. contributed equally to this work.

Table S1: Population fraction of eigenvalue spectra for alcohol (above) and water (below) network. Non-integer value is associated with the presence of large alcohol (water) aggregates.

Mole fraction		Pure Water	0.09	0.29	0.41	0.5	Pure Alcohol
Alcohol Network							
Methanol	0	-	0.87964	0.6715	0.5622	0.49033	0.15222
	±1		0.10824	0.23228	0.26264	0.268	0.11351
	Non-integer		0.01212	0.09622	0.17516	0.24167	0.73427
Ethanol	0		0.85833	0.60301	0.52929	0.46269	0.16891
	±1		0.1235	0.23258	0.25235	0.25243	0.11753
	Non-integer		0.01817	0.16441	0.21836	0.28488	0.71356
Butanol	0		0.70957	0.49111	0.427	0.39323	0.21441
	±1		0.18506	0.21374	0.21458	0.21307	0.13431
	Non-integer		0.10537	0.29515	0.35842	0.3937	0.65128
Water Network							
Methanol	0	0.01067	0.01915	0.06203	0.11262	0.16183	-
	±1	0.002177	0.0383	0.12406	0.22524	0.32366	
	Non-integer	0.987153	0.94255	0.81391	0.66214	0.51451	
Ethanol	0	0.01067	0.02007	0.06004	0.10564	0.14909	
	±1	0.002177	0.00505	0.02221	0.0443	0.06906	
	Non-integer	0.987153	0.97488	0.91775	0.85006	0.78185	
Butanol	0	0.01067	0.01873	0.04074	0.07671	0.1047	
	±1	0.002177	0.00544	0.01539	0.03121	0.04551	
	Non-integer	0.987153	0.97583	0.94387	0.89208	0.84979	

Table S2: Comparison of density, the ensemble average degree and *lev* of alcohol and water aggregate for the box size effect from TIP3P water model.

		Methanol	Ethanol	Butanol
Number of molecules		700 Alcohol + 1000 Water (1400 Alcohol + 2000 Water)		
Box size (Å^3)		42.31 × 42.31 × 42.36 (53.36 × 53.45 × 53.36)	45.90 × 45.88 × 45.93 (57.86 × 57.86 × 57.80)	51.79 × 51.67 × 51.83 (65.15 × 65.42 × 65.35)
Density (g/cm^3)		0.89 (0.88)	0.86 (0.86)	0.84 (0.83)
Degree	Alcohol Aggregate	0.60 (0.63)	0.67 (0.74)	0.92 (1.01)
	Water Aggregate	2.18 (2.22)	2.29 (2.37)	2.73 (2.91)
lev	Alcohol Aggregate	2.14 (2.09)	2.15 (2.29)	2.31 (2.42)
	Water Aggregate	3.39 (3.47)	3.54 (3.66)	3.82 (3.94)

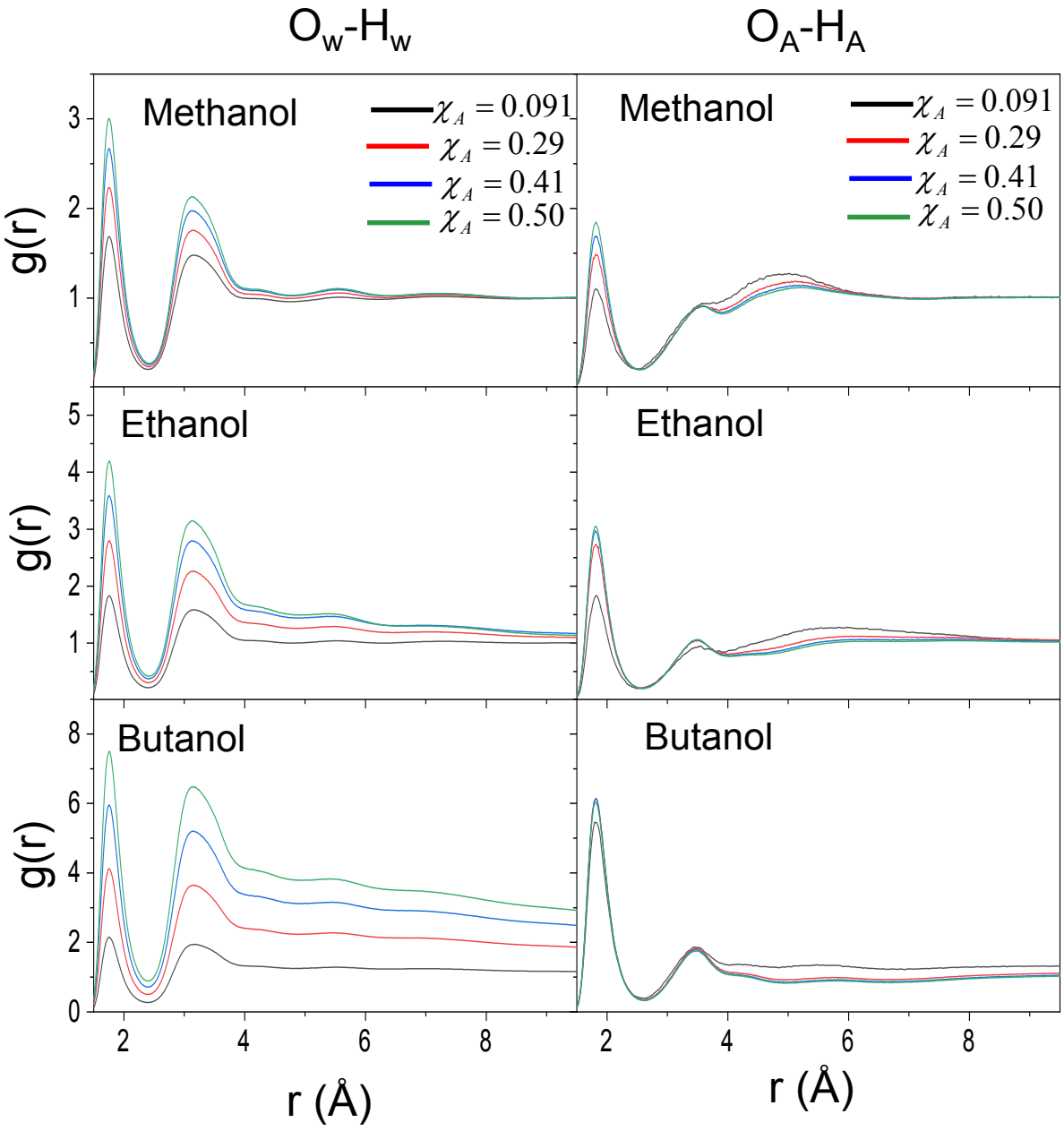

Figure S1. Radial distribution functions of water-water (between O-atom [Ow] and H-atom [Hw]) and alcohol-alcohol (between O-atom [O_A] and H-atom [H_A] of hydroxyl group) for methanol, ethanol, and butanol solutions with SPC/E water model. These functions are used for the construction of edges for graph theoretical analysis.

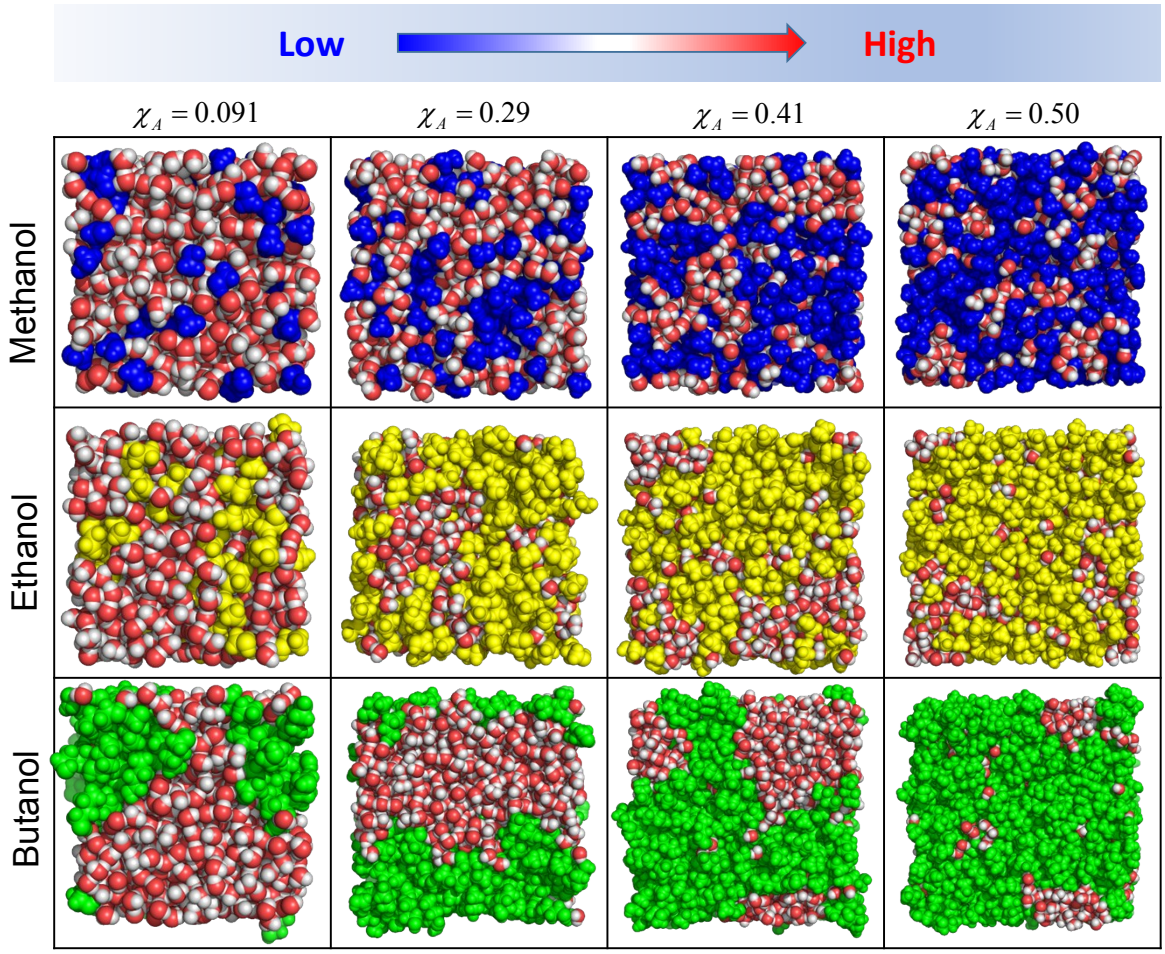

Figure S2. Snapshot structures of the three alcohol solutions with SPC/E water model provided structural insights in the formation of alcohol aggregates and the disruption of water H-bond network as the alcohol concentration increases. The methanol, ethanol, and butanol molecules in water-alcohol mixtures are represented by blue, yellow, and green color spheres, respectively. The oxygen and hydrogen atoms in water molecule are represented by red and white spheres, respectively.

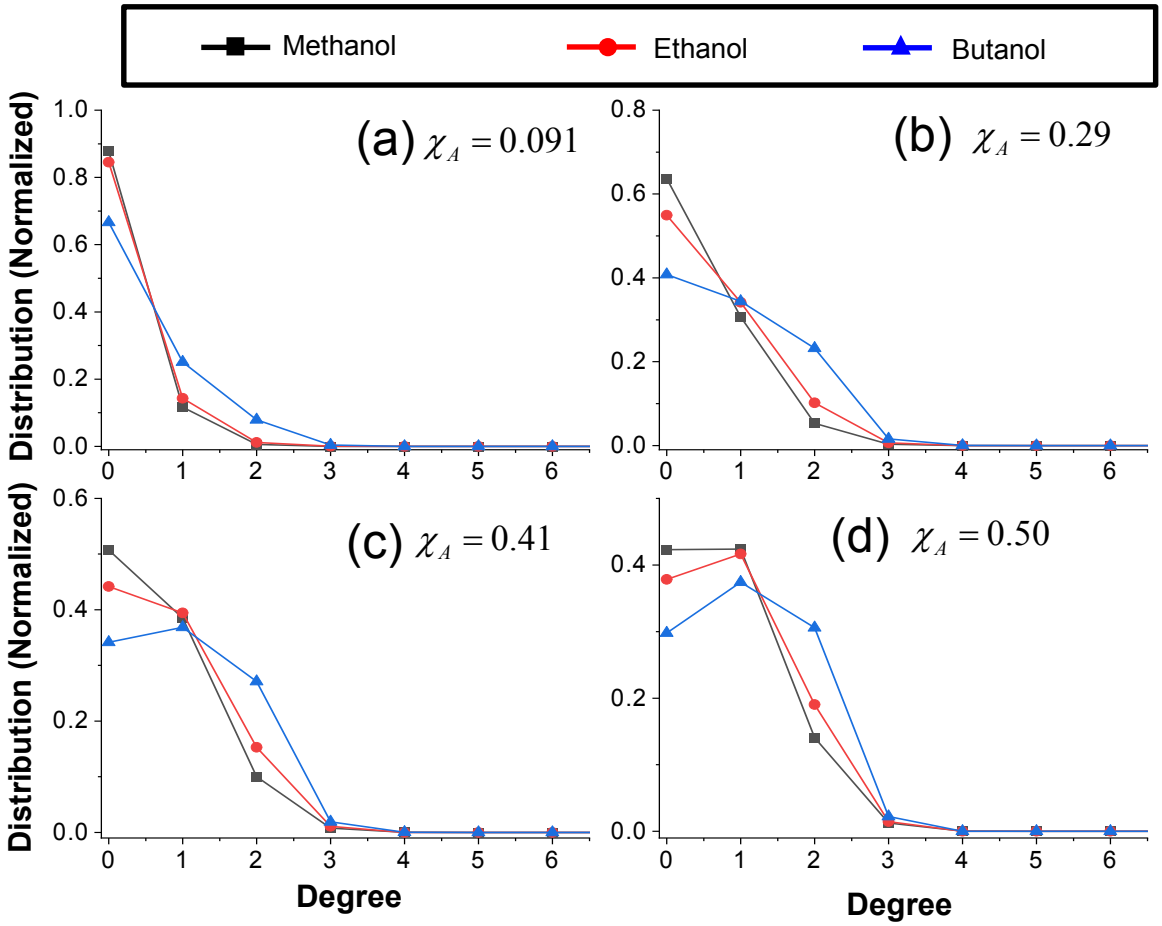

Figure S3. Normalized average degree distributions of alcohol aggregates for the three alcohol solutions with SPC/E water model confirm the formation of large alcohol aggregates, while the partially-miscible butanol aggregates have relatively slow decay pattern and segmented from water, as observed in TIP3P water model.

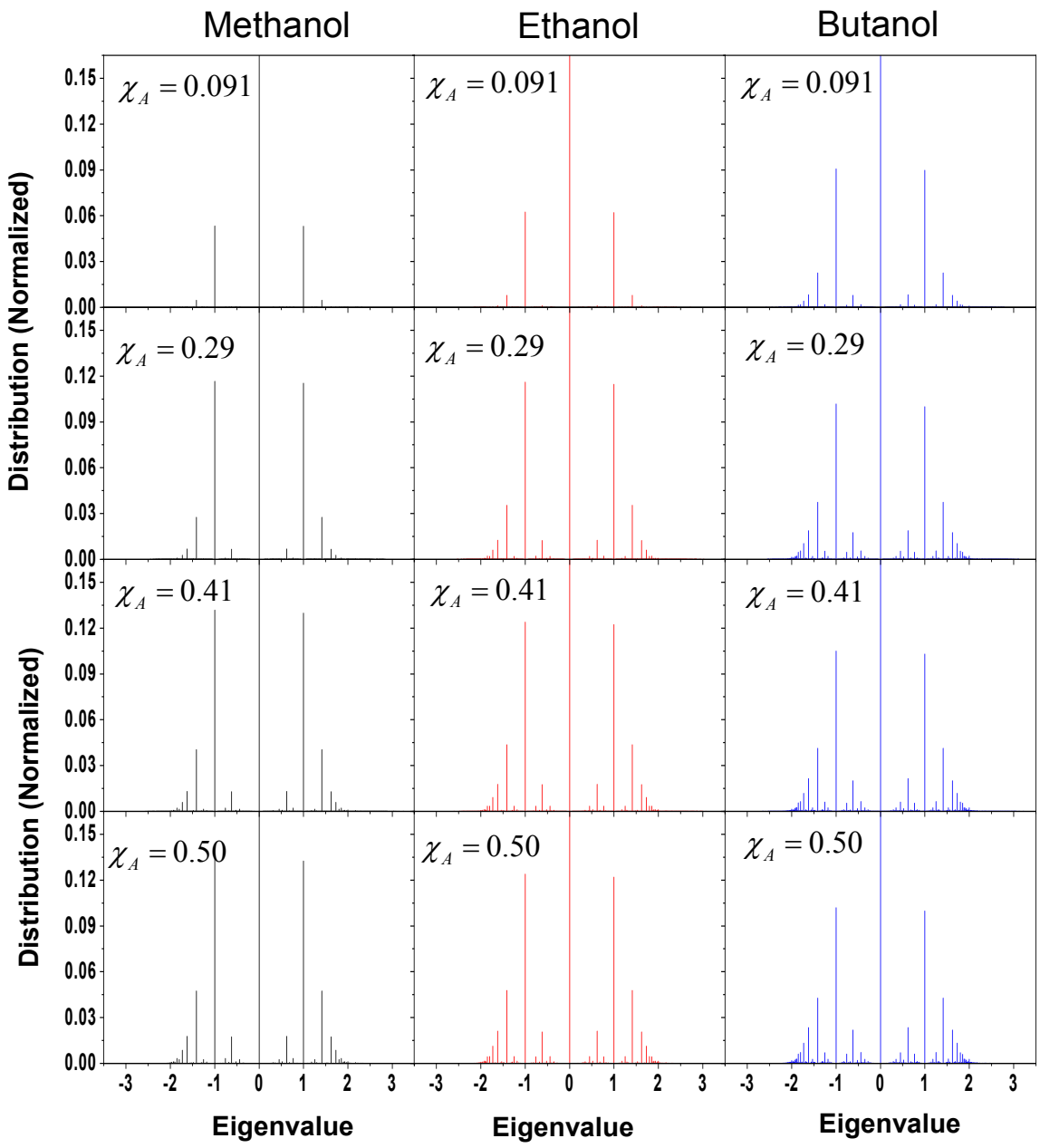

Figure S4. Normalized eigenvalue spectra are plotted for methanol, ethanol, and butanol solutions of mole fractions 0.091, 0.29, 0.41, and 0.50 with SPC/E water model. The eigenvalue spectra of alcohol aggregates indicated the growth of alcohol H-bond aggregates, while the spectral density of butanol is much denser, revealing the presence of comparatively larger aggregates.

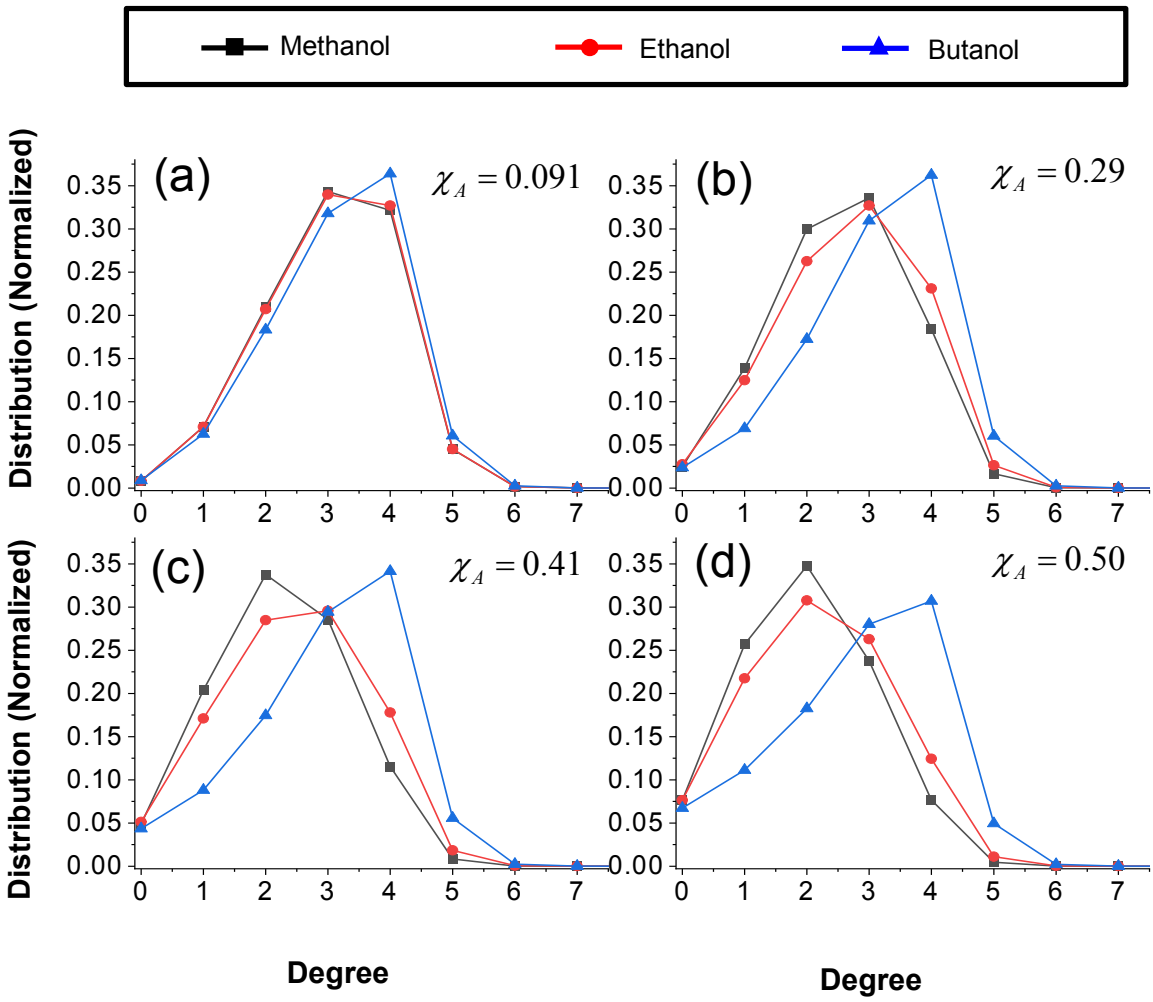

Figure S5. Normalized average degree distributions of water H-bond networks for the three alcohol solutions with SPC/E water model. The pattern observed in butanol solution is similar in both the water models, showing that the H-bond networks of butanol are not entangled with water H-bond network.

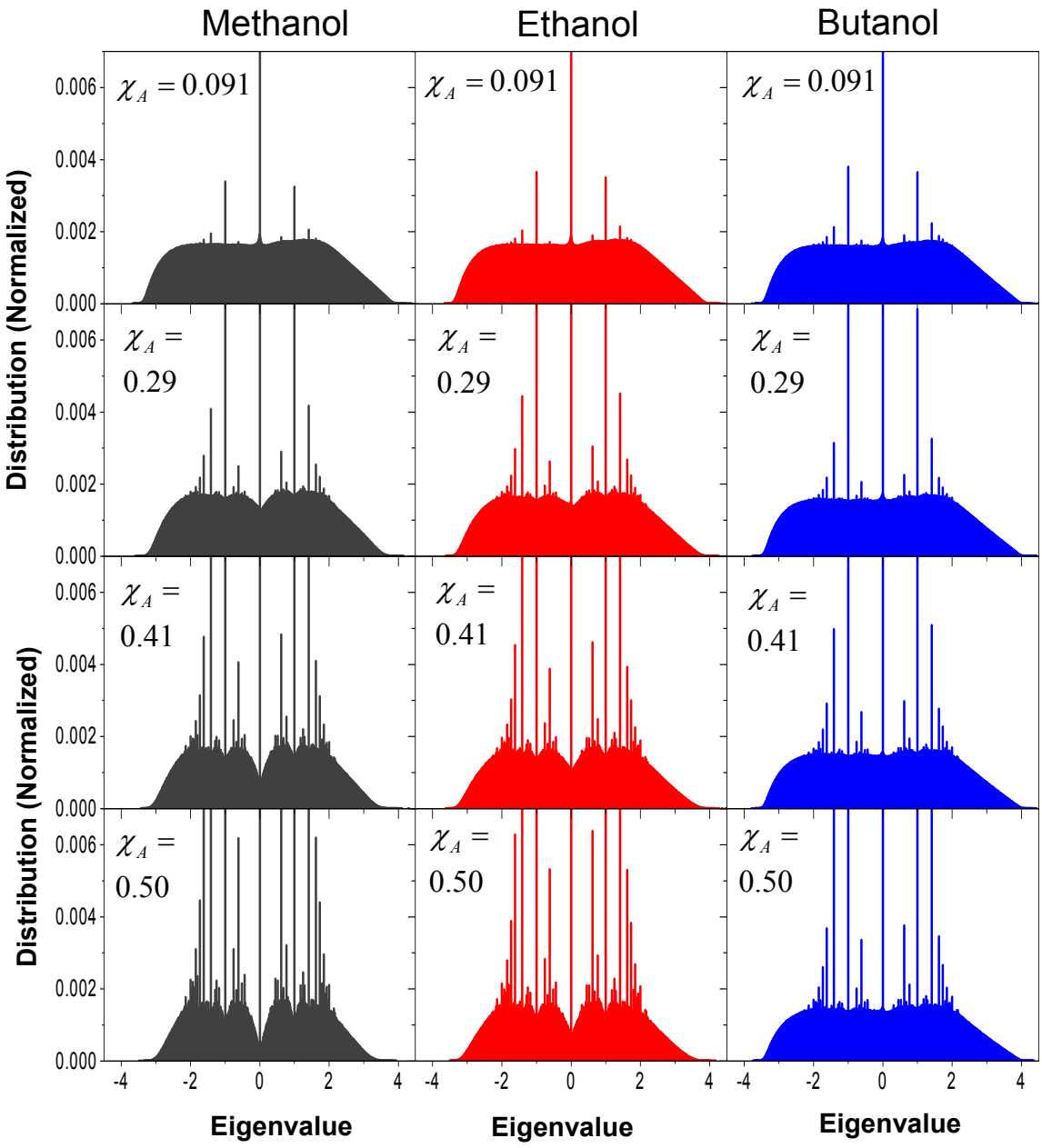

Figure S6. Normalized eigenvalue spectra of water H-bond networks in methanol, ethanol, and butanol solutions with SPC/E water model showed a serious disruption of water H-bond network in the miscible alcohol solutions, whereas the eigenvalue spectrum of butanol solution demonstrating that the butanol aggregates does not disrupt the water H-bond structure significantly. For the four mole fractions of 0.091, 0.29, 0.41, and 0.50, the eigenvalue spectra are plotted for each alcohol solution.