Electronic Supplementary Information

Contents

Table S1: Dimension of the simulation cell for for water-ethanol mixtures at different compositions

Mole Fraction, x_{EtOH}	**Length of the simulation box (Å)**
0.1	15.42
0.2	16.31
0.3	17.11
0.4	17.84
0.5	18.51
0.6	19.14
0.7	19.74
0.8	20.29
0.9	20.82
1	21.32

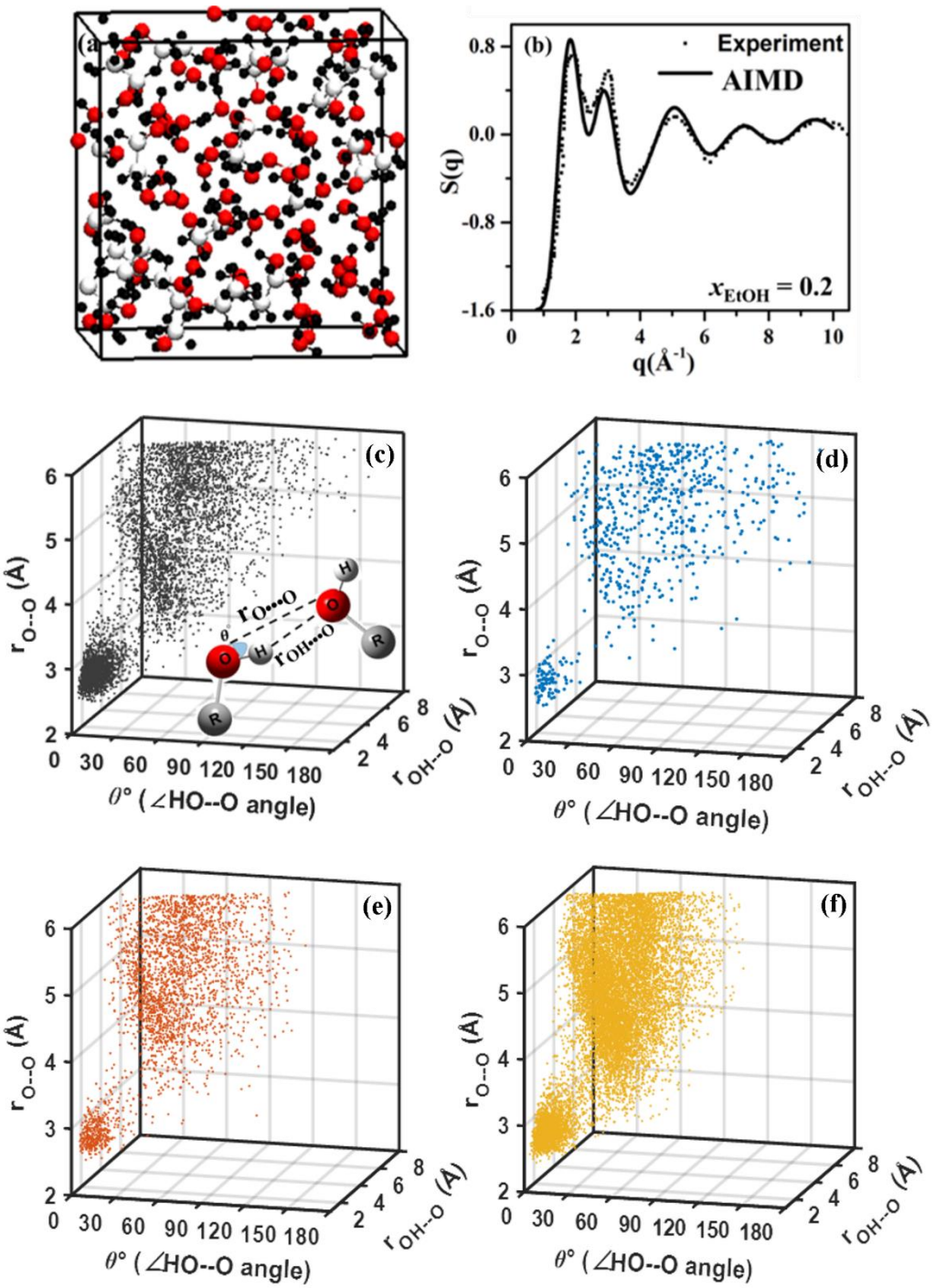

Figure S1: a) Snapshot of the post-equilibration simulation cell for an ethanol-water mixture, x_{EtOH} = 0.2 b) Comparison of the structure factor obtained from AIMD simulations with the X-ray scattering data for the x_{EtOH} = 0.2 water-ethanol mixture from Ref. 37. Scatter plot of the non-bonded $r_{OH\cdots O}$ and $r_{O\cdots O}$ distances and ∠HO–O angle (θ) for c) all possible pair of molecules in the ensemble, d) all EtOH-EtOH pairs, e) all EtOH-H_2O pairs of molecules and f**)** all H_2O-H_2O pairs, for a water-ethanol mixture with composition x_{EtOH}= 0.2.

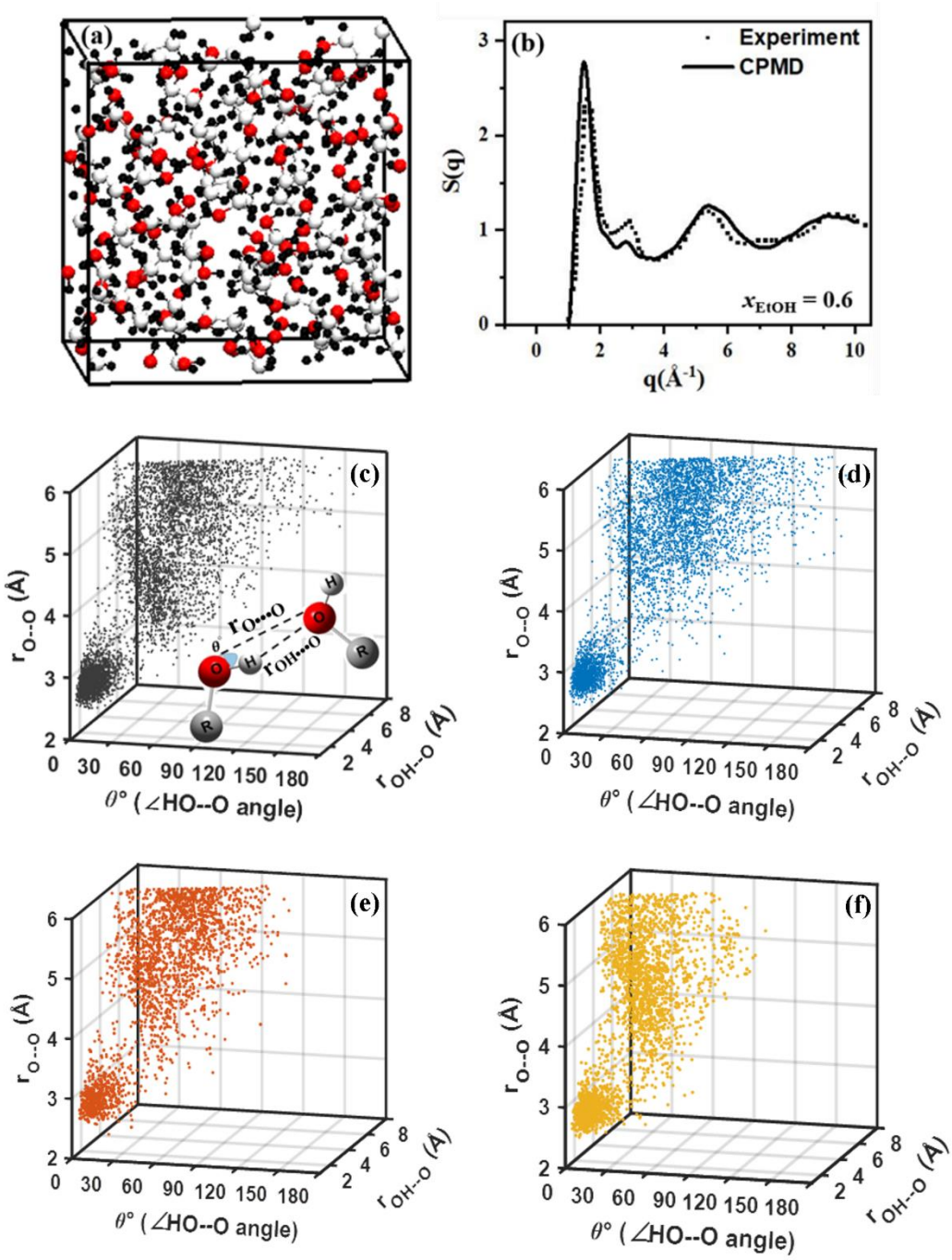

Figure S2: a) Snapshot of the post-equilibration simulation cell for an ethanol-water mixture, x_{EtOH} = 0.6 b) Comparison of the structure factor obtained from AIMD simulations with the X-ray scattering data for the x_{EtOH} = 0.6 water-ethanol mixture from Ref. 37. Scatter plot of the non-bonded $r_{OH\cdots O}$ and $r_{O\cdots O}$ distances and ∠HO–O angle (θ) for c) all possible pair of molecules in the ensemble, d) all EtOH-EtOH pairs, e) all EtOH-H_2O pairs of molecules and f**)** all H_2O-H_2O pairs for a water-ethanol mixture with composition x_{EtOH}= 0.6.

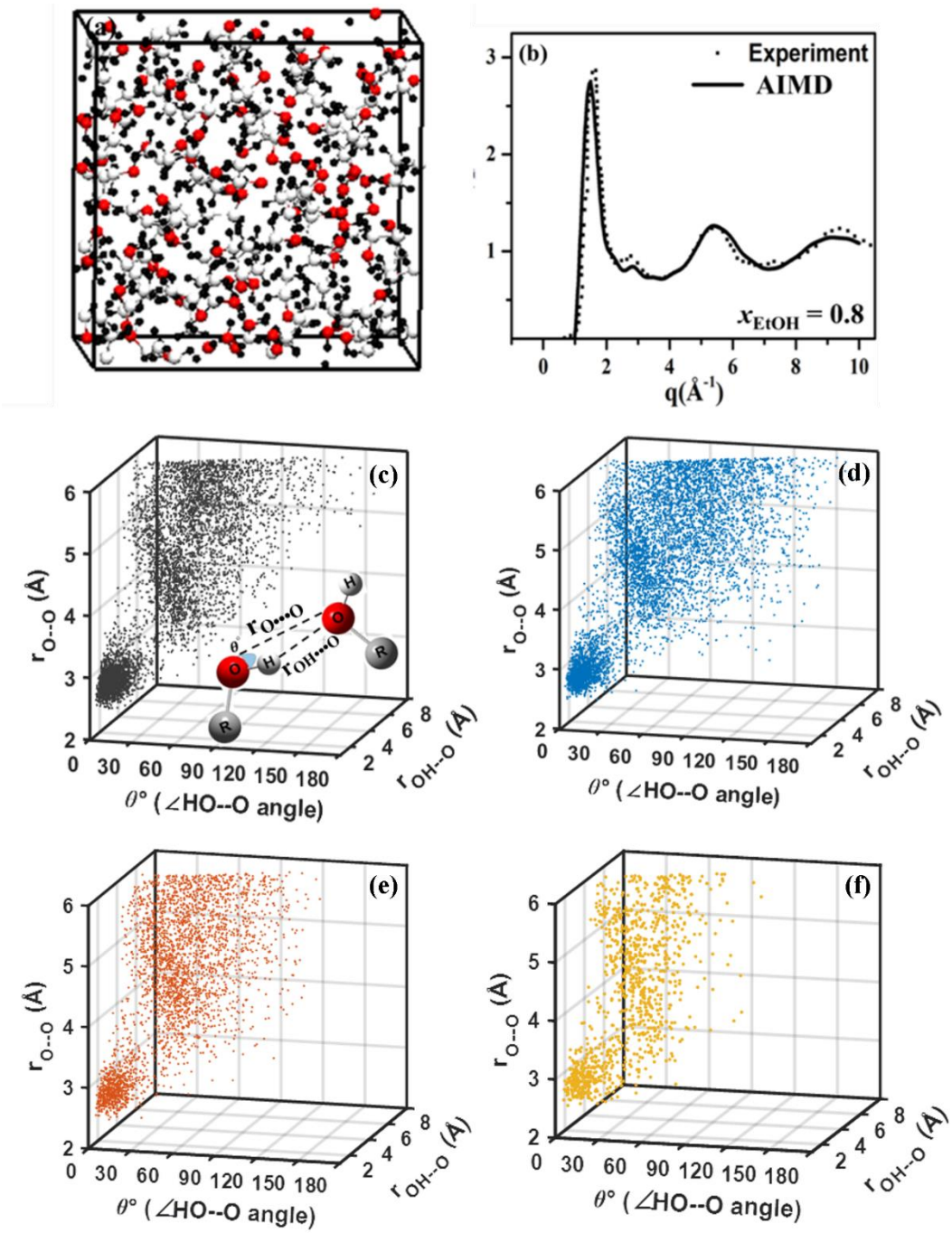

Figure S2: a) Snapshot of the post-equilibration simulation cell for an ethanol-water mixture, x_{EtOH} = 0.8 b) Comparison of the structure factor obtained from AIMD simulations with the X-ray scattering data for the x_{EtOH} = 0.8 water-ethanol mixture from Ref. 37. Scatter plot of the non-bonded $r_{OH\cdots O}$ and $r_{O\cdots O}$ distances and ∠HO–O angle (θ) for c) all possible pair of molecules in the ensemble, d) all EtOH-EtOH pairs, e) all EtOH-H_2O pairs of molecules and f**)** all H_2O-H_2O pairs for a water-ethanol mixture with composition x_{EtOH}= 0.8.

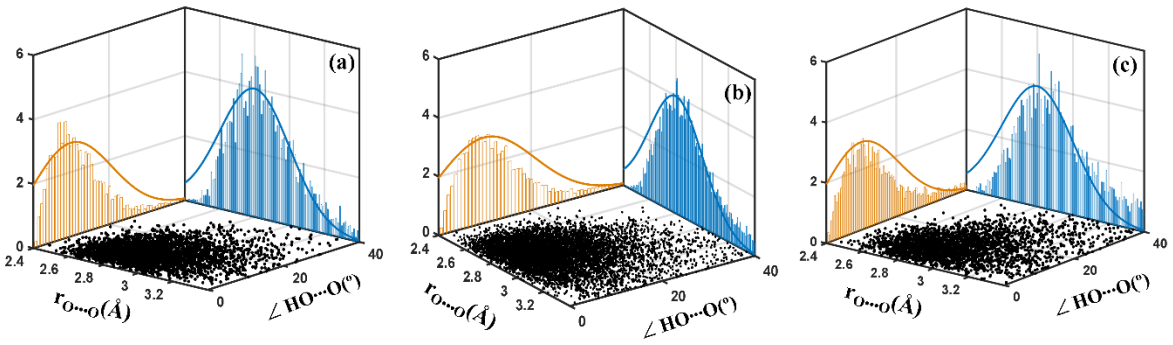

Figure S4: The distribution of non-bonded parameters, $r_{O\cdots O}$ (Å) and $\theta°$(∠HO⋯O), from the linear region in **Fig1 (a)** for ethanol pairs **(b)** for pairs of ethanol and water **(c)** for pairs of water. The orange and blue lines are the Gaussian profiles.

Table S2: The geometrical cut-off and centroid values for hydrogen bonding parameters for water-ethanol mixtures at different compositions

x_{EtOH}		$r_{OH\cdots O}$ (Å)	$\theta°$ (∠HO–O)	$r_{O\cdots O}$ (Å)	$r_{OH\cdots O}$ (Å)	$\theta°$ (∠HO–O)	$r_{OH\cdots O}$ (Å)
		Cut-off			**Centroid**		
0.1	EtOH:EtOH	2.3	25	3.3	1.9	11.8	2.9
	EtOH:H_2O	2.3	27.9	3.3	1.8	11.7	2.8
	H_2O:H_2O	2.4	27.6	3.3	1.8	11.4	2.8
0.2	EtOH:EtOH	2.3	24.1	3.3	1.8	9.9	2.8
	EtOH:H_2O	2.3	25.2	3.2	1.8	10.7	2.8
	H_2O:H_2O	2.4	27.3	3.3	1.8	11.3	2.8
0.3	EtOH:EtOH	2.3	26.2	3.2	1.9	11.6	2.8
	EtOH:H_2O	2.3	26.2	3.3	1.8	11.2	2.8
	H_2O:H_2O	2.3	27.9	3.3	1.9	12.3	2.8
0.4	EtOH:EtOH	2.3	26.5	3.3	1.8	11.7	2.8
	EtOH:H_2O	2.4	26.8	3.3	1.9	11.6	2.8
	H_2O:H_2O	2.3	27.6	3.3	1.9	12.1	2.8
0.5	EtOH:EtOH	2.3	27.2	3.2	1.8	11.0	2.8
	EtOH:H_2O	2.3	26.6	3.3	1.8	10.9	2.8
	H_2O:H_2O	2.3	27.9	3.3	1.9	11.8	2.8
0.6	EtOH:EtOH	2.3	26.3	3.2	1.8	10.6	2.8
	EtOH:H_2O	2.3	26.9	3.3	1.8	11.3	2.8
	H_2O:H_2O	2.3	26.9	3.3	1.8	11.3	2.8
0.7	EtOH:EtOH	2.3	25.3	3.2	1.8	10.5	2.8
	EtOH:H_2O	2.4	27.9	3.3	1.8	11.8	2.8
	H_2O:H_2O	2.4	27.9	3.3	1.9	12.7	2.8
0.8	EtOH:EtOH	2.4	27.7	3.3	1.8	12.0	2.8
	EtOH:H_2O	2.4	26.8	3.3	1.8	12.1	2.8
	H_2O:H_2O	2.3	27.9	3.3	1.9	12.6	2.8
0.9	EtOH:EtOH	2.4	27.3	3.3	1.8	11.1	2.8
	EtOH:H_2O	2.3	26.6	3.2	1.9	12.1	2.8
	H_2O:H_2O	2.3	27.9	3.2	1.8	12.2	2.8
1		2.3	27.4	3.3	1.9	11.4	2.8

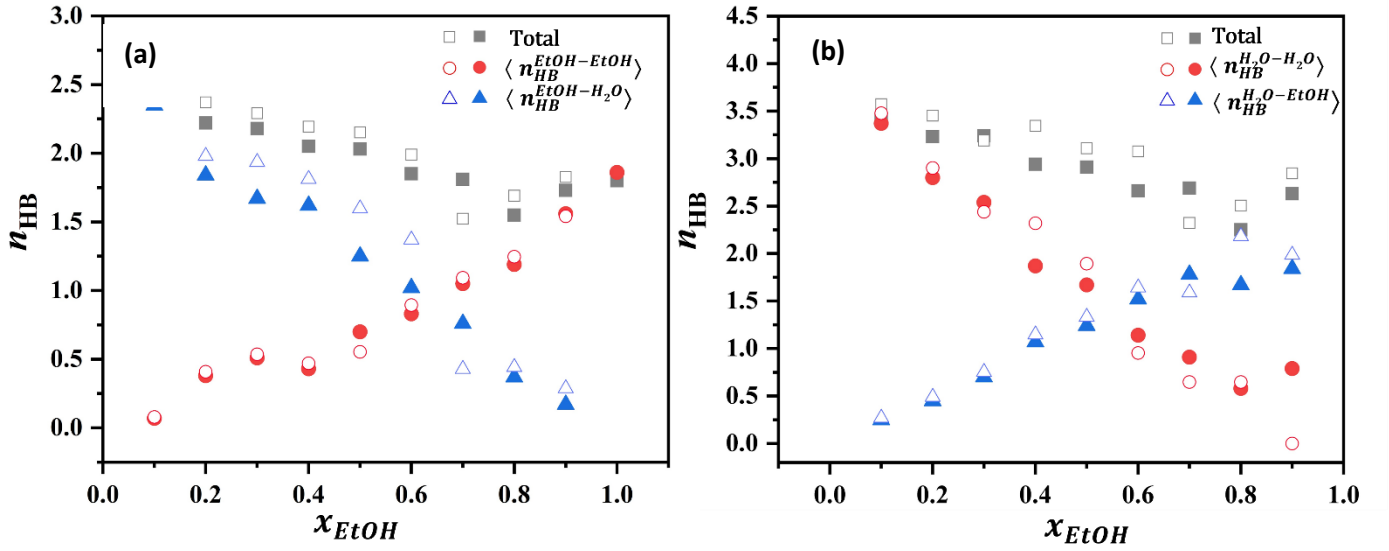

Figure S5. Average number of hydrogen bonds per molecule $\langle n_{HB} \rangle$ in the water-ethanol mixture at different compositions a) the average number of water, $\langle n_{HB}^{EtOH-H2O} \rangle$ and ethanol, $\langle n_{HB}^{EtOH-EtOH} \rangle$, molecules that are H- bonded to an ethanol molecule as a function of x_{EtOH}, and b) the average number of water, $\langle n_{HB}^{H2O-H2O} \rangle$, and ethanol, $\langle n_{HB}^{H2O-EtOH} \rangle$ molecules that are H-bonded to a water molecule as a function of x_{EtOH}. The filled data points were estimated using the cut-off parameters of Table S2 while the open data points using the empirical geometrical cut-off values , $r_{O\cdots O}$ <3.5Å and angle ∠HO···O < 30º from Reference 27.

Table S3: Average number of hydrogen bonds per molecule $\langle n_{HB} \rangle$ in the water-ethanol mixture at different compositions estimated using the cut-off parameters of Table S2. The values in parenthesis have been estimated using the empirical geometrical cut-off values , $r_{O\text{—}O}$ <3.5Å and angle ∠HO···O < 30⁰ from Reference 27,

	Ethanol, $\langle n_{HB} \rangle$			**Water, $\langle n_{HB} \rangle$**		
x_{EtOH}	**Total**	$\langle n_{HB}^{EtOH-EtOH} \rangle$	$\langle n_{HB}^{EtOH-H2O} \rangle$	**Total**	$\langle n_{HB}^{H2O-EtOH} \rangle$	$\langle n_{HB}^{H2O-H2O} \rangle$
0.1	2.42 (2.53)	0.07 (0.08)	2.35 (2.45)	3.42 (3.57)	3.37 (3.48)	0.25 (0.27)
0.2	2.22 (2.37)	0.38 (0.41)	1.84 (1.98)	3.23 (3.45)	2.8 (2.90)	0.45 (0.49)
0.3	2.18 (2.29)	0.51 (0.53)	1.67 (1.94)	3.24 (3.19)	2.54 (2.44)	0.7 (0.75)
0.4	2.05 (2.19)	0.43 (0.47)	1.62 (1.81)	2.94 (3.35)	1.87 (2.31)	1.07 (1.15)
0.5	2.03 (2.15)	0.7 (0.55)	1.25 (1.60)	2.91 (3.11)	1.67 (1.90)	1.24 (1.33)
0.6	1.85 (1.99)	0.83 (0.89)	1.02 (1.37)	2.66 (3.08)	1.14 (0.95)	1.52 (1.64)
0.7	1.81 (1.52)	1.05 (1.09)	0.76 (0.43)	2.69 (2.32)	0.91 (0.65)	1.78 (1.58)
0.8	1.55 (1.69)	1.19 (1.25)	0.37 (0.44)	2.25 (2.50)	0.58 (0.65)	1.67 (2.19)
0.9	1.73 (1.83)	1.56 (1.54)	0.17 (0.29)	2.63 (2.84)	0.79 (0)	1.84 (1.99)
1	1.8 (1.85)					