Supporting Information

Structure and dynamics of aqueous $VOSO_4$ solution in conventional flow through cell design: a molecular dynamics simulation study

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1 Molecular dynamics simulation

All molecular dynamics simulation were performed within the periodic boundary condition to simulate the bulk and interface properties for system 1-9. The simulation boxes were made of the certain no of the ions and water molecules. Those numbers are already given in the manuscript. The box length for each simulation was determined using the experimental density of each solution. An energy minimization was run to remove the hard contacts. An isothermal-isobaric molecular dynamics simulation was performed to check the density of the system. After the minimization step additional $\sim$ 10 ns MD simulation was performed in isochoric-isothermal (NVT) ensemble. For each system, the isobaric-isothermal (NPT) simulation run was fixed except for the concentrated (system 3) and dilute (system 5) solution, the simulation run length was longer than the previous run to promote a better convergence in the bulk density. At last a production run for each system was performed in isochoric-isothermal (NVT) ensemble for $\sim$ 50 ns. Parrinello-Rahman[1] barostat and Nosè-Hoover thermostat[2,3] were used for the NPT and NVT simulations. The all bonds involving hydrogen atoms were constrained using the LINCS algorithm as available in GROMACS.[4] A timestep of 1 fs was used for all simulations. A radial cutoff at half box length was imposed to compute the non-bonded interactions in real space for system 1- 9. The particle mesh Ewald (PME) method[5,6] with an interpolation order 4 and a relative tolerance of 10^{-5} was used to calculate the electrostatic interactions above the half box length for each system. The tail corrections were added to potential energy and pressure. The Lorentz-Berthelot mixing rules were used to estimate the LJ parameters between the two different atom types.[7,8] The single precision GROMACS 2022 was used to run all the MD simulations. The force field parameters used for the simulations were given in table S1 and S2. The details about the group and designation of each atom in a group were shown in: (a) fig. S1 for the H_2O molecule, (b) fig. S2 for the HSO_4^- ion, (c) fig. S3 for the SO_4^{2-}, (d) fig. S4 for the H_3O^+ and, (e) fig. S5 for the VO^{2+} ion, respectively.

Bonded parameter

Group	Bond	l_0 (nm)	k_r (KJ.mol^{-1} nm^2)		
VO^{2+}	V4-OV	0.157	215159.7		
SO_4^{2-}	S1-OS1	0.157	215159.7		
	S1-OS2	0.1487	439740.0		
	S1-OS3	0.1487	439740.0		
	S1-OS4	0.1487	439740.0		
HSO_4^-	S2-O1	0.1487	439740.0		
	S2-O2	0.1487	439740.0		
	S2-O3	0.1487	439740.0		
	S2-O5	0.1633	178960.0		
	O5-H1	0.1000	418400.0		
H_3O^+	Oh1-Hh1	0.0973	345000.0		
	Oh1-Hh2	0.0973	345000.0		
	Oh1-Hh3	0.0973	345000.0		
H_2O	OW-HW1	0.1	345000.0		
	OW-HW2	0.1	345000.0		

Angle parameter

Group	Angle	θ (deg)	k_θ (KJ.mol^{-1} rad^2)		
SO_4^{2-}	OS1-S1-OS2	109.470	1171.60		
	OS1-S1-OS3	109.470	1171.60		
	OS1-S1-OS4	109.470	1171.60		
	OS2-S1-OS3	109.470	1171.60		
	OS2-S1-OS4	109.470	1171.60		
	OS3-S1-OS4	109.470	1171.60		
HSO_4^-	O1-S2-O2	114.000	969.000		
	O1-S2-O3	114.000	969.000		
	O1-S2-O5	103.500	1239.60		
	O2-S2-O3	114.000	969.000		
	O2-S2-O5	103.500	1239.60		
	O3-S2-OS5	103.500	1239.60		
	S2-O5-H1	109.500	1046.00		
H_3O^+	Hh1-Oh1-Hh2	111.600	383.00		
	Hh2-Oh1-Hh3	111.600	383.00		
	Hh1-Oh1-Hh3	111.600	383.00		

Dihedral angle parameter[9]

Group	Dihedral angle	i (KJ.mol^{-1})	j (KJ.mol^{-1})	k (KJ.mol^{-1})	l (KJ.mol^{-1})
HSO_4^-	H1-O5-S2-O1	1.8	-5.4	0.0	7.2
	H1-O5-S2-O1	1.8	-5.4	0.0	7.2
	H1-O5-S2-O1	1.8	-5.4	0.0	7.2

Table S 1: The bonded parameters for each atom used in the MD simulation.

Non bonded parameter				
Group	Atom	σ (nm)	ϵ (KJ.mol^{-1})	q (e$^-$)
VO^{2+}	V4	0.2602	0.123	2.062
	OV	2.253	2.9938	-0.062
SO_4^{2-}	S1	0.3555	0.837	0.8
	OS1	0.368	0.65	-0.70
	OS2	0.368	0.65	-0.70
	OS3	0.368	0.65	-0.70
	OS4	0.368	0.65	-0.70
HSO_4^-	S2	0.355	1.046	1.18
	O1	0.315	0.837	-0.65
	O2	0.315	0.837	-0.65
	O3	0.315	0.837	-0.65
	O5	0.290	0.586	-0.45
	H1	0.0	0.0	0.22
H_3O^+	Oh1	0.316557	0.650194	-0.248
	Hh1	0.0	0.0	0.416
	Hh2	0.0	0.0	0.416
	Hh3	0.0	0.0	0.416
H_2O	OW	0.316557	0.650194	-0.8476
	HW1	0.0	0.0	0.4238
	HW2	0.0	0.0	0.4238

Table S 2: The non-bonded parameters for each atom used in the MD simulation.

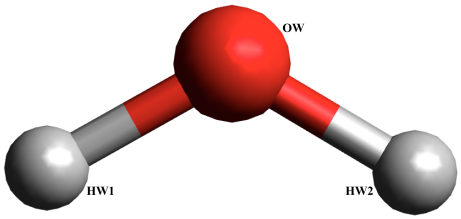

Figure. S 1

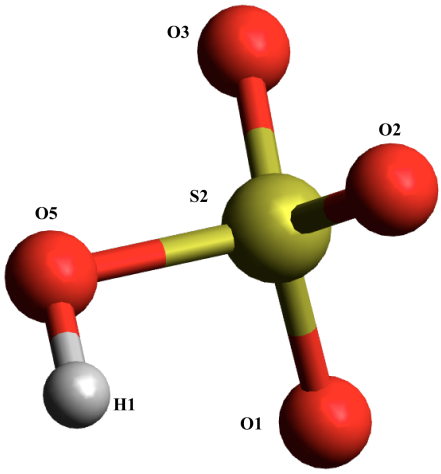

Figure. S 2

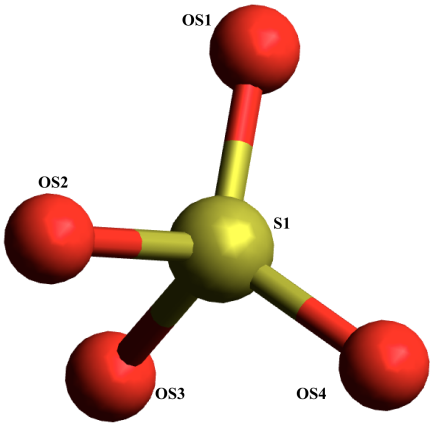

Figure. S 3

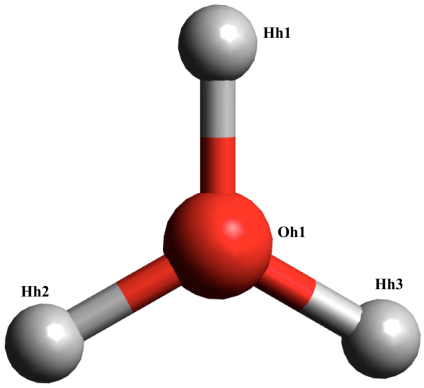

Figure. S 4

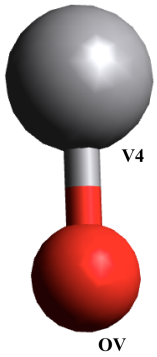

Figure. S 5

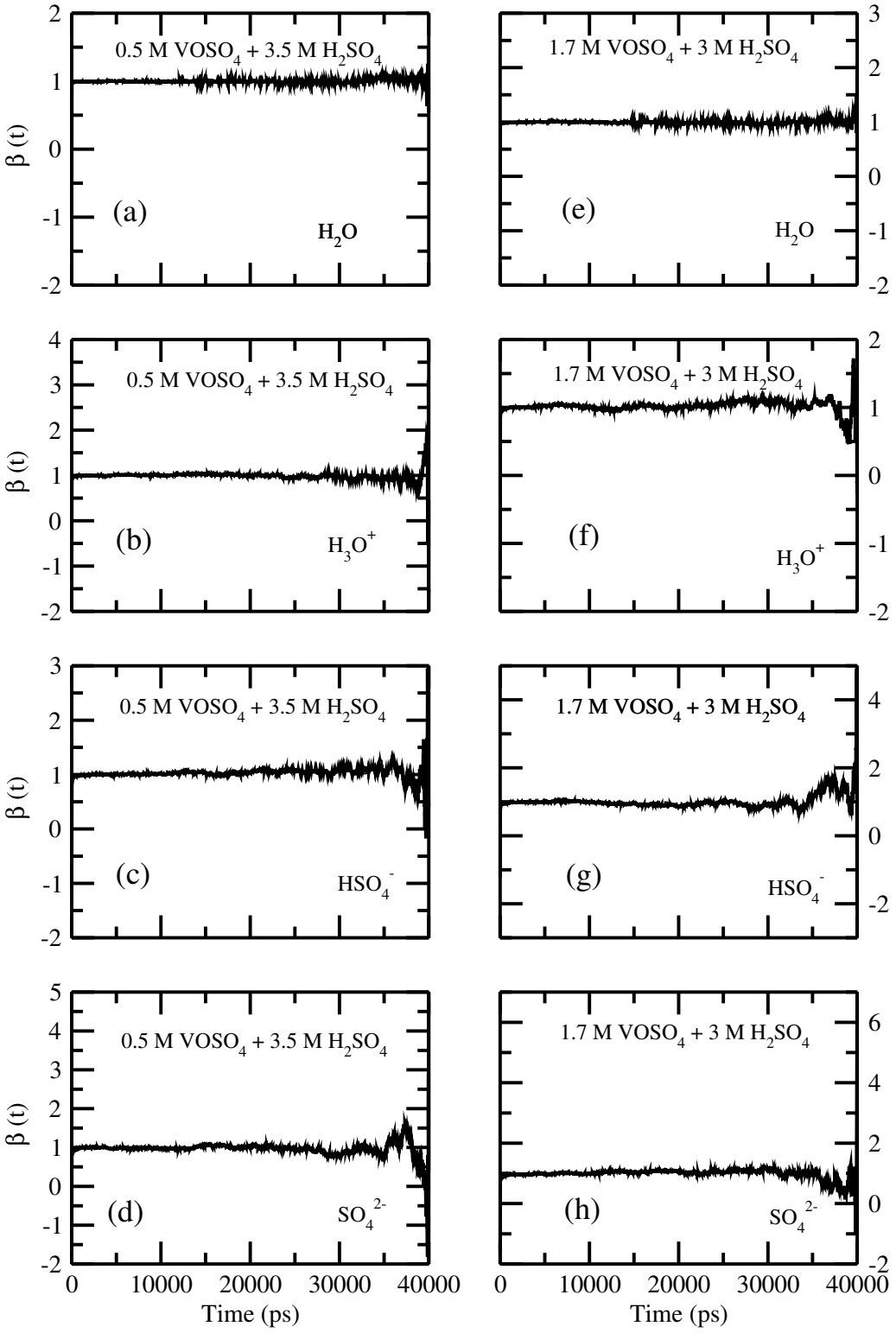

Figure. S 6: The β (t) versus time (t) plot for 0.5 M $VOSO_4$ + 3.5 M H_2SO_4 (system 1) and 1.7 M $VOSO_4$ + 3 M H_2SO_4 (system 3) solution at 25 °C.

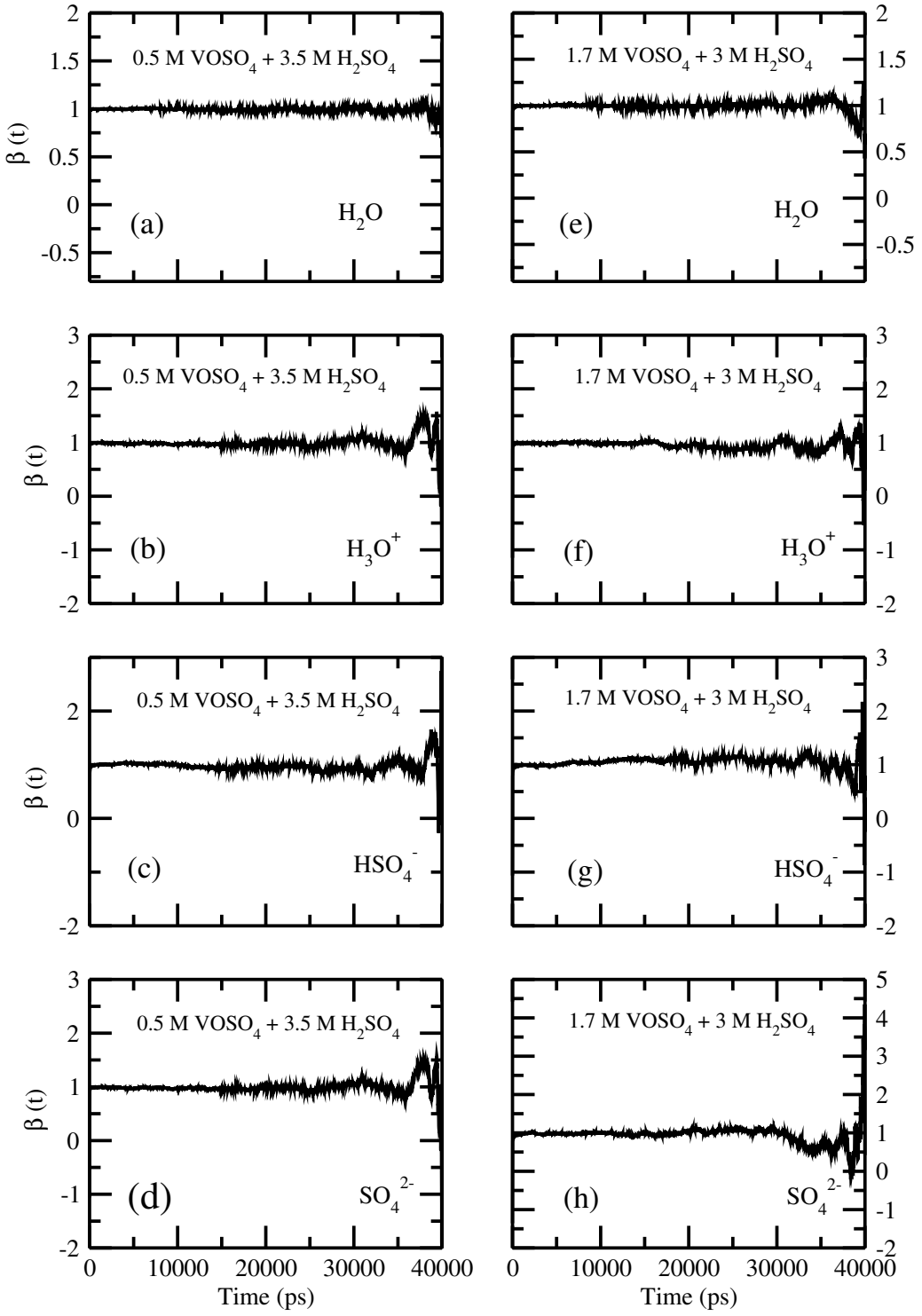

Figure. S 7: The β (t) versus time (t) plot for 0.5 M $VOSO_4$ + 3.5 M H_2SO_4 (system 2) and 1.7 M $VOSO_4$ + 3 M H_2SO_4 (system 4) solution at 50 °C.

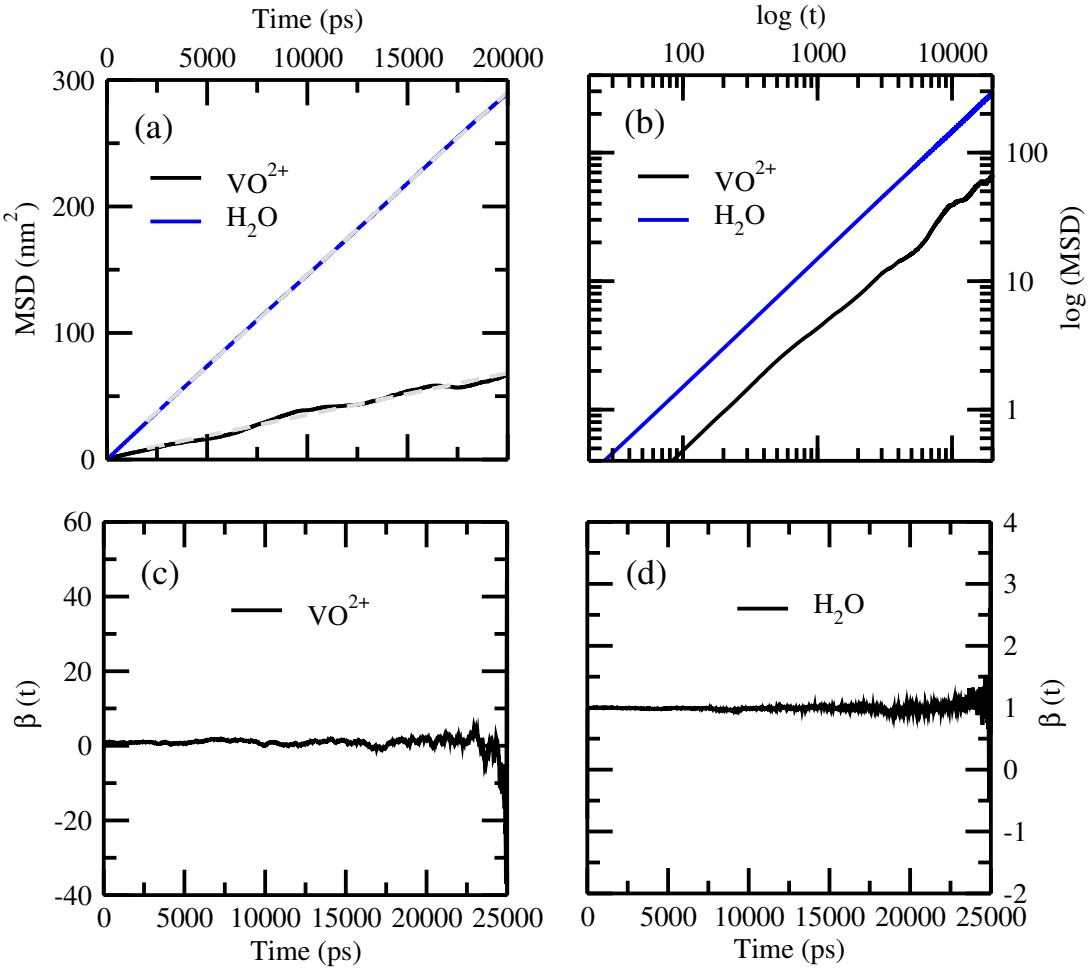

Figure. S 8: The diffusion for 1 VO^{2+} + 1000 H_2O system (system 5) at 25 °C.

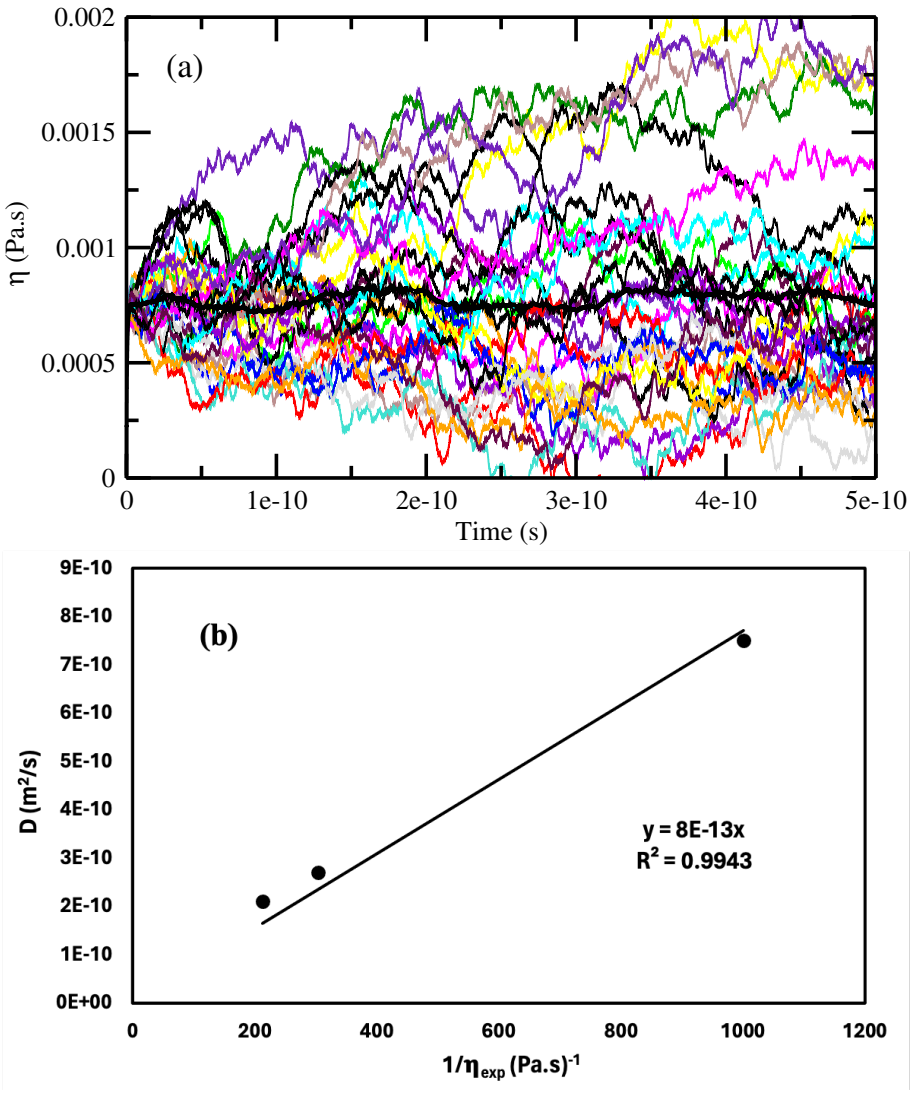

Figure. S 9: (a) The viscosity of the system 5. (b) The plot for Stokes - Einstein equation consisting the system 1, 3 and system 5.

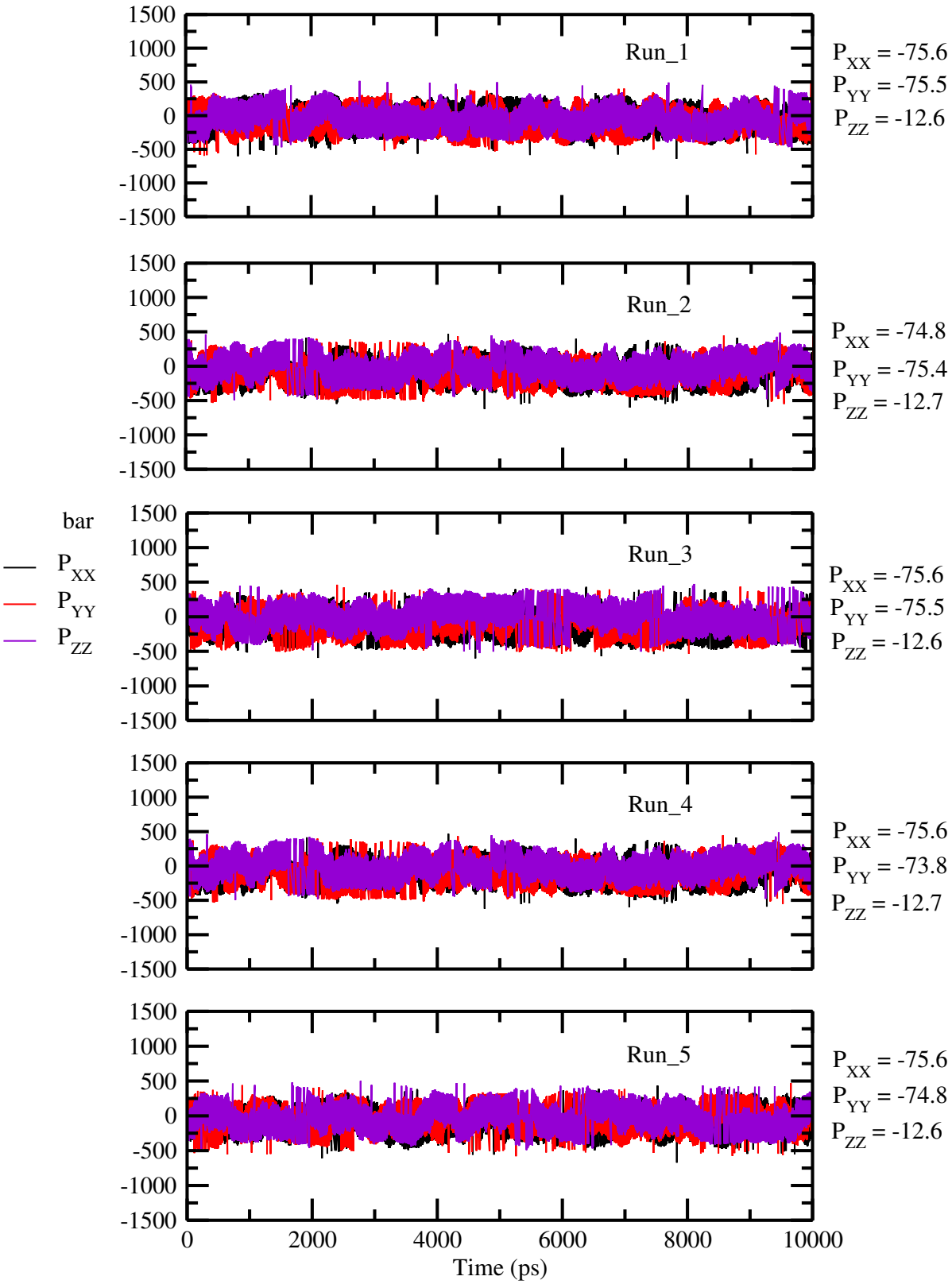

Figure. S 10: The calculated pressure tensor along x, y and z axis for system 1 has been shown.

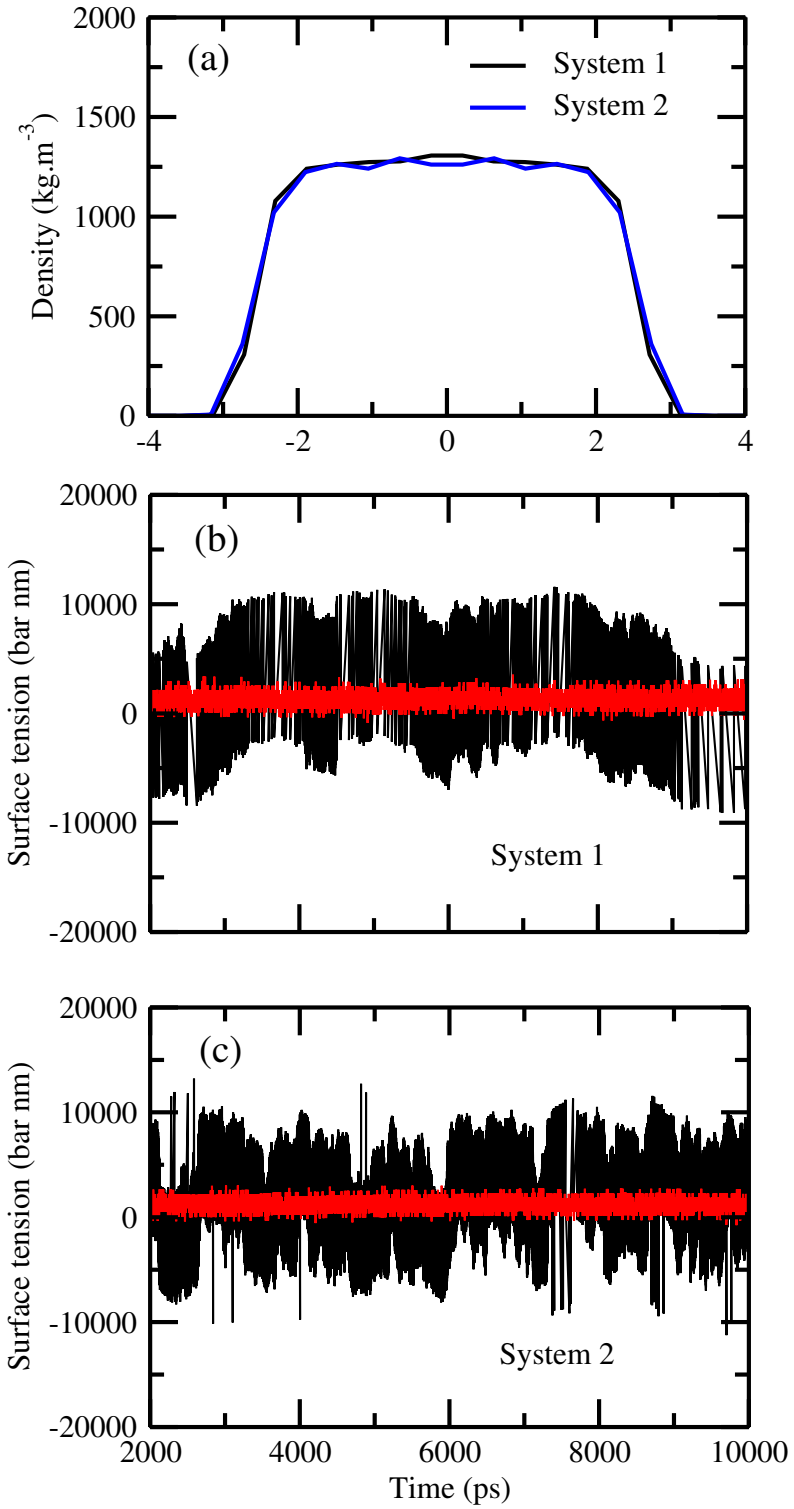

Figure. S 11: The calculated surface tension for system 1 and 2. The red line corresponds to the running average.

Systems	$f_{n=1}$	$f_{n=2}$	$f_{n=3}$	$f_{n=4}$	$f_{n=5}$	$f_{n=6}$	$f_{n=7}$	$f_{n=8}$	$f_{n=9}$	$f_{n=10}$	$< n_{HB} >$
1	0.59	19.02	31.23	36.28	10.12	2.02	0.41	0.09	0.01	0.00	3.44
2	0.73	19.52	32.80	33.77	10.18	2.14	0.44	0.09	0.02	0.00	3.41
3	0.73	19.51	29.71	34.70	11.47	2.74	0.64	0.15	0.03	0.01	3.48
4	0.81	19.67	30.95	33.02	11.48	2.88	0.69	0.16	0.03	0.01	3.46
5	0.00	0.80	22.18	67.61	9.25	0.16	0.00	0.00	0.00	0.00	3.86
6	0.57	17.96	31.33	36.77	10.55	2.07	0.42	0.08	0.02	0.00	3.46
7	0.71	18.59	32.91	34.33	10.41	2.21	0.45	0.09	0.02	0.00	3.43
8	13.94	24.17	25.52	19.84	8.53	3.21	1.10	0.35	0.10	0.02	2.92
9	0.75	15.40	31.55	35.18	12.62	3.22	0.77	0.18	0.04	0.01	3.57

Table S 3: The percentage of water molecules having n number of water-water hydrogen bonds and the average number of hydrogen bonds (n_{HB}) per water molecule.

Systems	$f_{n=1}$	$f_{n=2}$	$f_{n=3}$	$f_{n=4}$	$f_{n=5}$	$f_{n=6}$	$f_{n=7}$	$f_{n=8}$	$f_{n=9}$	$f_{n=10}$	$< n_{HB} >$
1	28.63	9.23	1.85	0.36	0.05	0.0	0.0	0.0	0.0	0.0	0.54
2	63.60	5.98	0.72	0.08	0.01	0.0	0.0	0.0	0.0	0.0	0.78
3	53.16	5.28	0.79	0.11	0.01	0.0	0.0	0.0	0.0	0.0	0.67
4	57.50	6.36	1.01	0.14	0.02	0.0	0.0	0.0	0.0	0.0	0.74
5	-	-	-	-	-	-	-	-	-	-	-
6	28.98	9.54	1.93	0.38	0.05	0.01	0.0	0.0	0.0	0.0	0.56
7	65.24	6.24	0.76	0.09	0.01	0.0	0.0	0.0	0.0	0.0	0.80
8	56.53	10.33	1.76	0.31	0.05	0.01	0.0	0.0	0.0	0.0	0.84
9	62.17	12.63	2.25	0.43	0.07	0.01	0.0	0.0	0.0	0.0	0.96

Table S 4: The percentage of water molecules having n number of water-hydronium ion hydrogen bonds and the average number of hydrogen bonds (n_{HB}) per hydronium ion.

Systems	$f_{n=1}$	$f_{n=2}$	$f_{n=3}$	$f_{n=4}$	$f_{n=5}$	$f_{n=6}$	$f_{n=7}$	$f_{n=8}$	$f_{n=9}$	$f_{n=10}$	$< n_{HB} >$
1	4.46	16.15	29.11	26.35	14.43	5.82	2.08	0.72	0.23	0.07	3.60
2	5.67	11.15	15.76	17.71	16.28	12.69	8.57	5.12	2.73	1.33	3.54
3	5.24	18.00	29.44	24.37	12.79	5.55	2.37	1.00	0.39	0.14	4.43
4	4.41	15.62	27.28	25.07	14.67	6.86	3.14	1.45	0.62	0.24	3.74
5	-	-	-	-	-	-	-	-	-	-	-
6	5.35	18.40	30.48	25.05	12.59	4.87	1.72	0.59	0.18	0.05	3.45
7	6.13	19.60	30.27	23.87	11.86	4.68	1.80	0.66	0.22	0.07	3.40
8	4.99	17.89	29.76	24.36	12.78	5.57	2.41	1.03	0.40	0.14	3.55
9	5.44	18.39	29.20	23.69	12.50	5.65	2.58	1.16	0.47	0.18	3.54

Table S 5: The percentage of water molecules having n number of water-bisulfate ion hydrogen bonds and the average number of hydrogen bonds (n_{HB}) per bisulfate ion.

Systems	$f_{n=1}$	$f_{n=2}$	$f_{n=3}$	$f_{n=4}$	$f_{n=5}$	$f_{n=6}$	$f_{n=7}$	$f_{n=8}$	$f_{n=9}$	$f_{n=10}$	$< n_{HB} >$
1	2.34	7.72	15.87	22.11	21.56	15.20	8.20	3.81	1.68	0.72	4.63
2	3.05	10.08	19.30	23.84	20.00	12.26	6.06	2.80	1.29	0.57	4.32
3	1.94	7.02	15.37	22.22	21.92	15.36	8.21	3.95	1.98	1.00	4.70
4	1.60	6.24	14.25	21.28	21.69	15.86	9.04	4.78	2.58	1.36	4.84
5	-	-	-	-	-	-	-	-	-	-	-
6	4.14	11.33	19.24	22.28	18.80	12.08	6.35	2.96	1.27	0.52	4.25
7	3.15	10.55	20.12	24.60	19.74	11.59	5.48	2.44	1.13	0.47	4.24
8	2.97	9.62	18.50	23.11	19.85	12.41	6.51	3.35	1.73	0.88	4.41
9	2.58	9.15	18.58	23.50	20.18	12.36	6.37	3.35	1.84	0.98	4.43

Table S 6: The percentage of water molecules having n number of water-sulfate ion hydrogen bonds and the average number of hydrogen bonds (n_{HB}) per sulfate ion.

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