

## Supporting Information Energetics of acid catalyzed biomass reactions: How and why does the solvent model matter?

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### 1. First principles DFT calculations – Implisolv method.

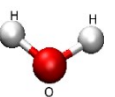
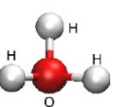
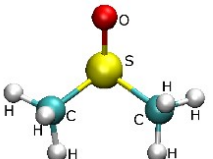
**Table 1 SI.** Free energy values for all the intermediate species and transition state for protonation of 5-HMF. Values are reported in kJ/mol.

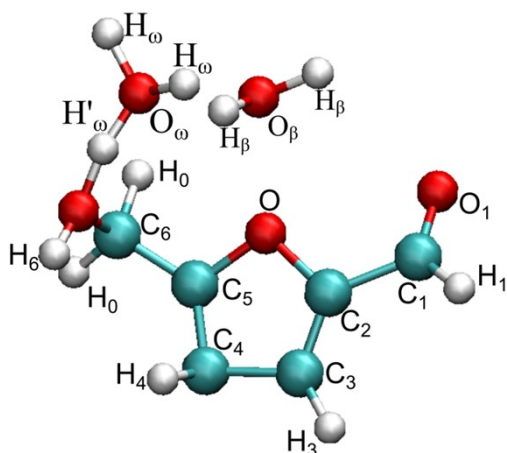
	Gas Phase	DMSO	water
<b>Reactant</b>	0	0	0
<b>TS</b>	92.8	94.5	93.9
<b>Product</b>	66.1	82.7	82.0

### 2. Explicit equilibrated solvation non polarizable without solvent dynamics - Resolv method.

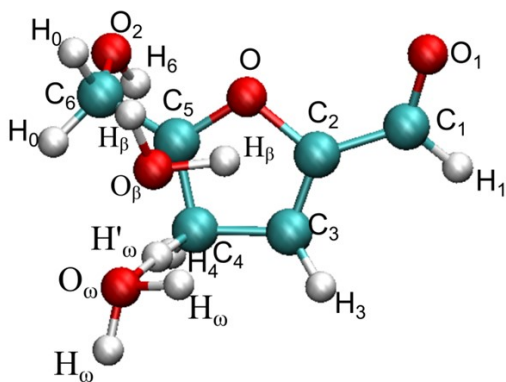
#### 2.1 Atomic charges and simulation parameters.

**Table 2 SI** Atomic charges and simulation parameters implemented in the present work for water, DMSO, 5-HMF and fructose. Blue balls indicate carbon atoms, red balls indicate oxygen atoms, white balls indicate hydrogen atoms and yellow ball indicates sulfur atom.

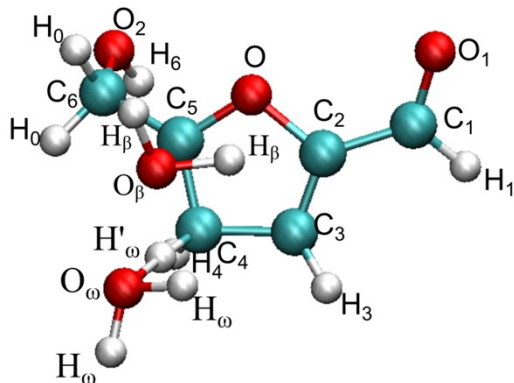
Molecule	Charges (in parentheses) and parameters, $\sigma/\text{\AA}$ , e/kJ mol <sup>-1</sup>
<b>Water</b> 	O (-0.834)-3.1,0.64 H(0.417)-0.0,0.00
<b>Hydronium ion</b> 	O(-0.626)- 3.1,0.64 H(0.542)-0.0,0.00
<b>DMSO</b> 	S(0.282)- 3.5,1.65 O(-0.515)-2.9,1.17 C(-0.406)- 3.8,0.27 H(0.174)- 2.5,0.21

**Reactant**

O<sub>1</sub>(-0.504)- 2.90,0.88  
 C<sub>1</sub>(0.412)- 3.70,0.44  
 H<sub>1</sub>(0.022)- 2.40,0.63  
 C<sub>2</sub>(0.020)- 3.50,0.32  
 O(-0.210)- 2.90,0.58  
 C<sub>5</sub>(0.210)- 3.50,0.32  
 C<sub>4</sub>(0.303)- 3.50,0.32  
 H<sub>4</sub>(0.196)- 2.40,0.13  
 C<sub>3</sub>(-0.086)- 3.50,0.32  
 H<sub>3</sub>(0.165)- 2.40,0.13  
 C<sub>6</sub>(0.096)- 3.90,0.49  
 H<sub>0</sub>(0.079)- 2.50,0.13  
 O<sub>β</sub>(-0.601)- 3.10,0.71  
 H<sub>6</sub>(0.416)-0.00,0.00  
 O<sub>ω</sub>(-0.834)-3.10,0.64  
 O<sub>β</sub>(-0.834)-3.10,0.64  
 H'<sub>ω</sub>(0.542)-3.10,0.64  
 H<sub>ω</sub>(0.542)-0.00,0.00  
 H<sub>β</sub>(0.417)- 0.00,0.00

**TS**

O<sub>1</sub>(-0.504)-2.90,0.88  
 C<sub>1</sub>(0.412)-3.70,0.44  
 H<sub>1</sub>(0.022)-2.40,0.69  
 C<sub>2</sub>(0.020)-3.50,0.32  
 O(-0.210)-2.90,0.58  
 C<sub>5</sub>(0.210)-3.50,0.32  
 C<sub>4</sub>(0.303)-3.50,0.32  
 H<sub>4</sub>(0.196)-2.40,0.13  
 C<sub>3</sub>(-0.086)-3.50,0.32  
 H<sub>3</sub>(0.165)-2.40,0.16  
 C<sub>6</sub>(0.096)-3.90,0.49  
 H<sub>0</sub>(0.079)-2.50,0.13  
 O<sub>β</sub>(-0.601)-3.10,0.71  
 H<sub>6</sub>(0.416)-0.00,0.00  
 O<sub>ω</sub>(-0.834)-3.10,0.64  
 O<sub>β</sub>(-0.834)-3.10,0.64  
 H'<sub>ω</sub>(0.542)-3.10,0.64  
 H<sub>ω</sub>(0.542)-0.00,0.00  
 H<sub>β</sub>(0.417)- 0.00,0.00

**Product**

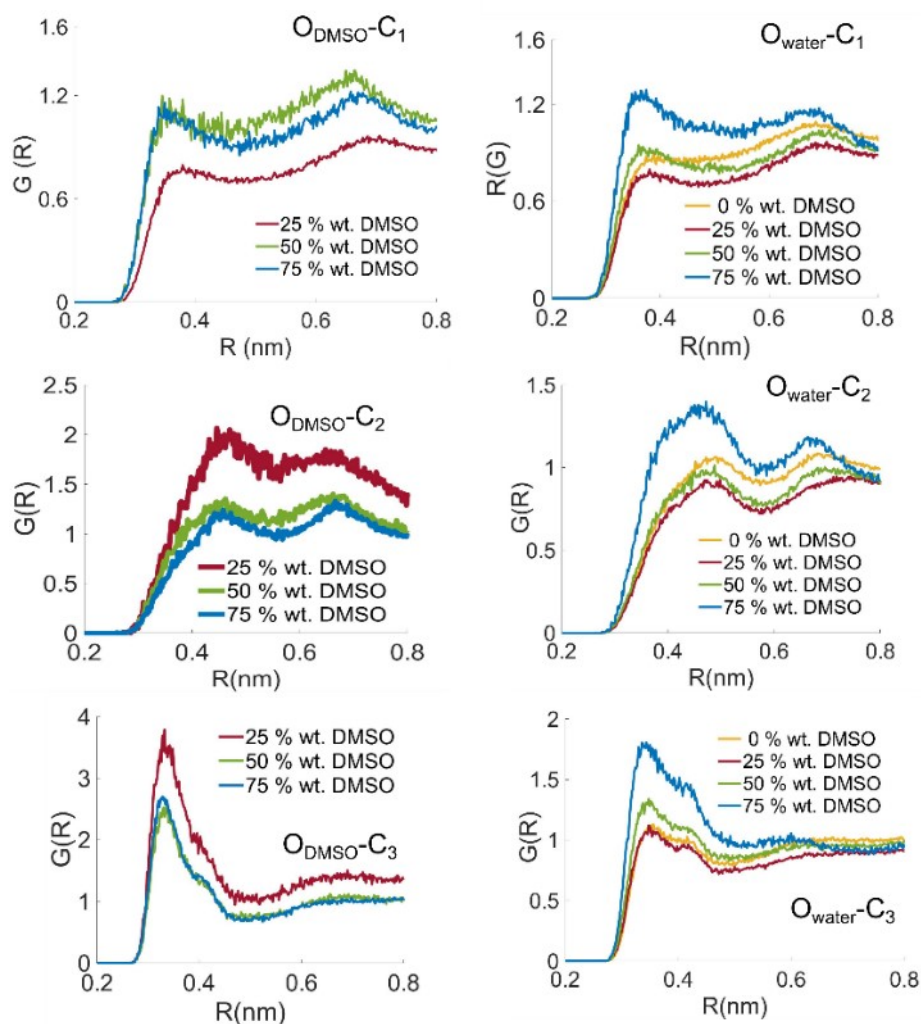
O<sub>1</sub>(-0.434)-2.9,0.88  
 C<sub>1</sub>(0.310)-3.7,0.44  
 H<sub>1</sub>(0.218)-2.4,0.69  
 C<sub>2</sub>(0.155)-3.5,0.32  
 O(-0.392)-2.9,0.58  
 C<sub>5</sub>(0.665)-3.5,0.32  
 C<sub>4</sub>(-626)-3.5,0.32  
 H<sub>4</sub>(0.350)-2.4,0.13  
 C<sub>3</sub>(-0.151)-3.5,0.32  
 H<sub>3</sub>(0.322)-2.4,0.13  
 C<sub>6</sub>(-0.299)-3.9,0.49  
 H<sub>0</sub>(0.288)-2.5,0.15  
 O<sub>2</sub>(-0.763)-3.1,0.71  
 H<sub>6</sub>(0.326)-0.0,0.00  
 O<sub>ω</sub>(-1.052)-3.1,0.64  
 O<sub>β</sub>(-1.033)-3.1,0.64  
 H'<sub>ω</sub>(0.382)-3.1,0.64  
 H<sub>ω</sub>(0.518)-0.0,0.00  
 H<sub>β</sub>(0.533)-0.0,0.00

**Table 3** SI Number of molecules and simulation cell size for reactant, TS, and product. at different concentrations of DMSO. For all systems, 1 hydronium ions.

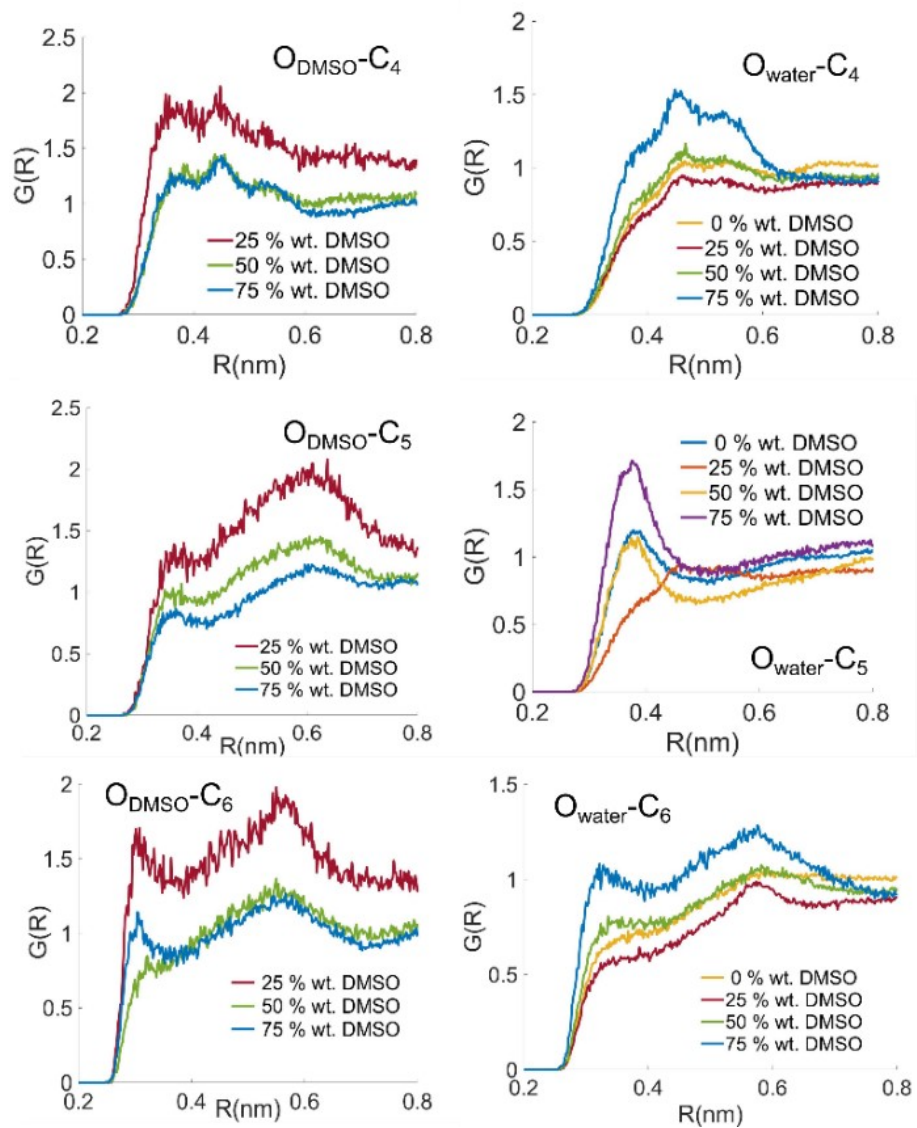
DMSO wt. %	No. water	No. DMSO	Cell size (length) nm
0	1400	0	3.711
25	1050	80	3.643
50	700	162	3.559
75	239	350	3.489

## 2.2 RDFs between reactant, TS, and product with solvent molecules.

### 2.2.1 Reactant

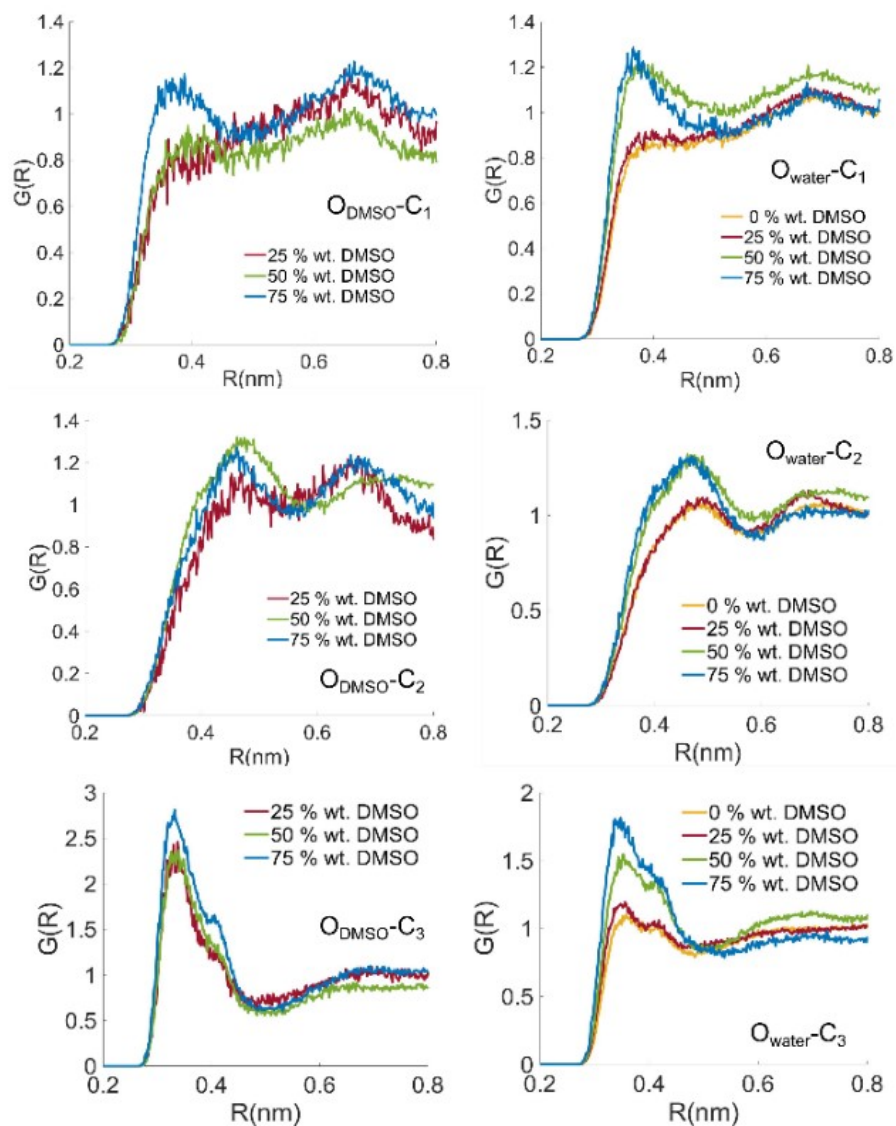


**Fig 1** SI Radial pair distribution Reactant -  $C_1$ ,  $C_2$ ,  $C_3$  with solvent oxygen atom pairs, at all DMSO concentration studied.

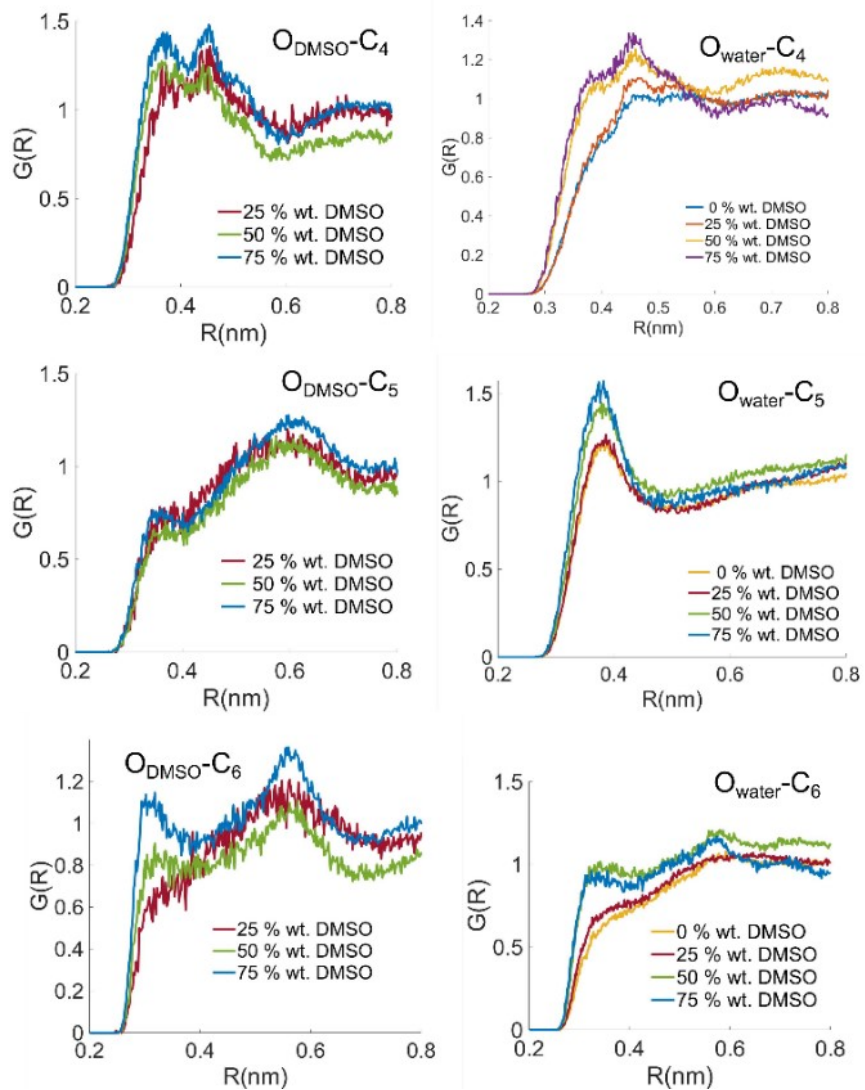


**Fig 2 SI** Radial pair distribution Reactant -  $C_4$ ,  $C_5$   $C_6$  with solvent oxygen atom pairs, at all DMSO concentration studied.

### 2.2.2. TS

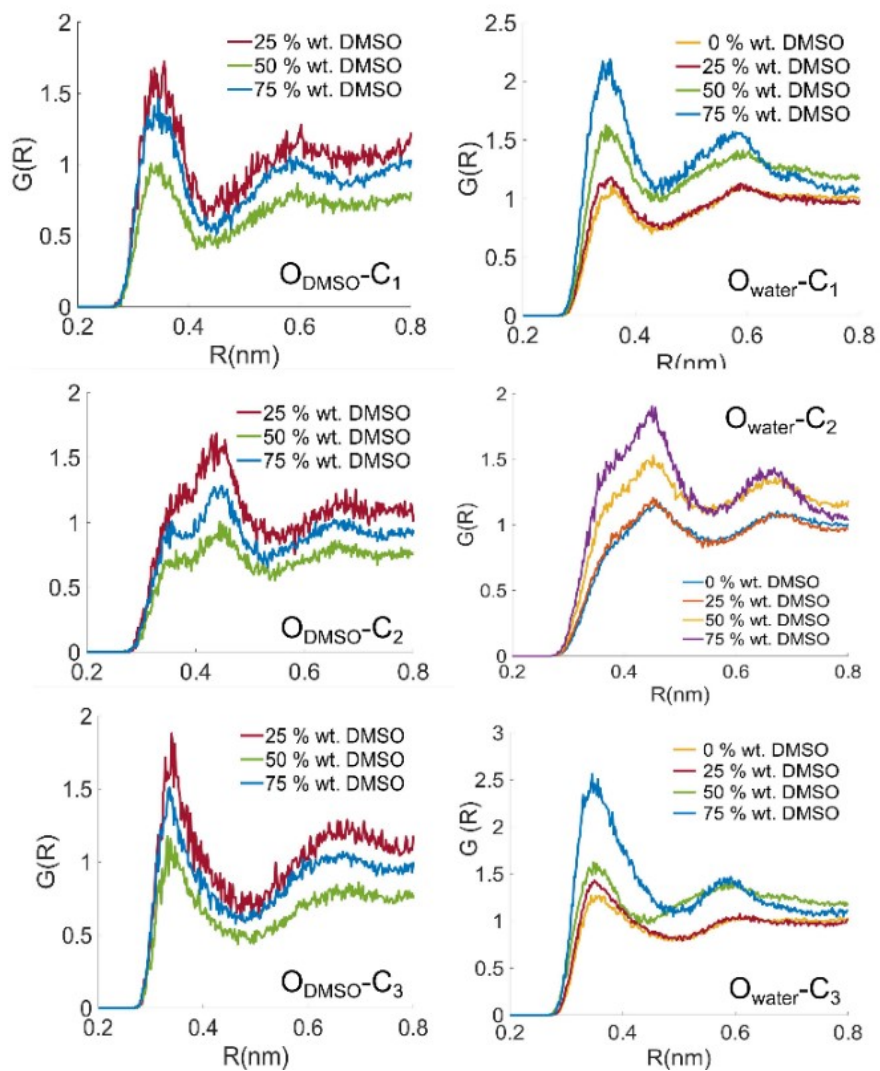


**Fig 3** SI Radial pair distribution TS -  $C_1, C_2, C_3$  with solvent oxygen atom pairs, at all DMSO concentration studied.

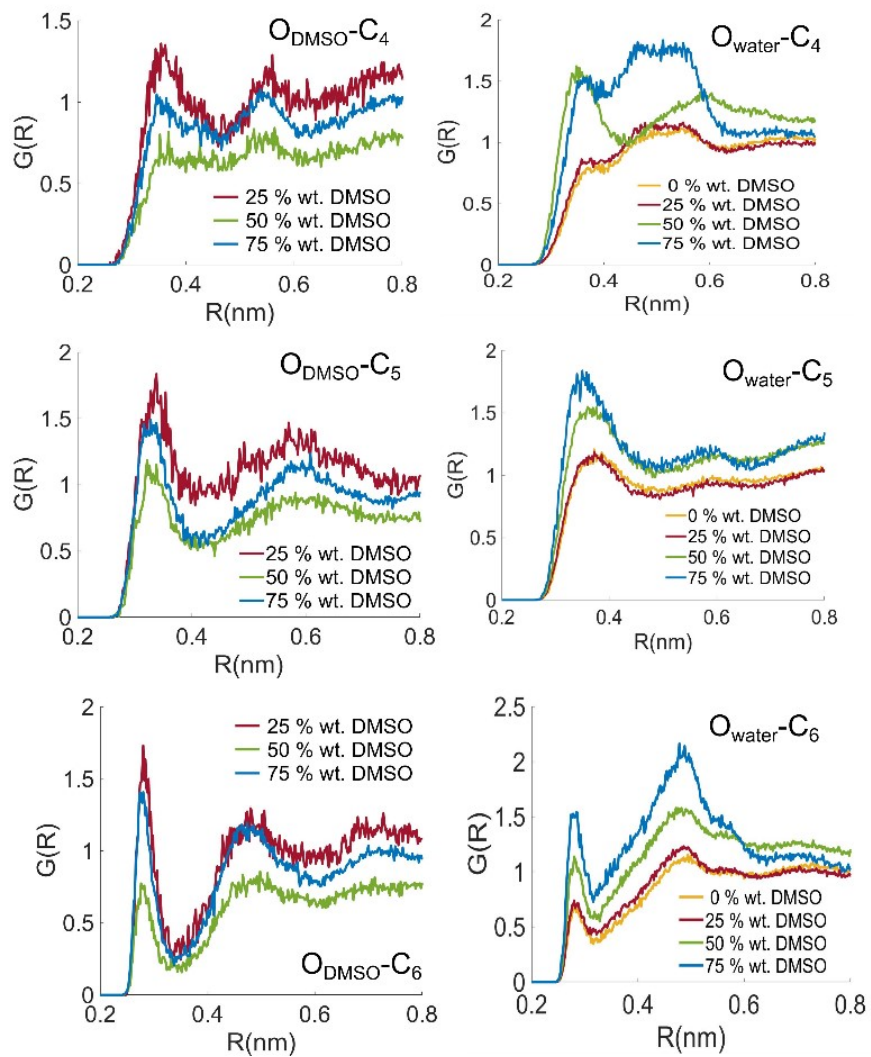


**Fig 4 SI** Radial pair distribution TS -  $C_4$ ,  $C_5$ ,  $C_6$  with solvent oxygen atom pairs, at all DMSO concentration studied.

### 2.2.3 Product



**Fig 5 SI** Radial pair distribution Product -  $C_1$ ,  $C_2$ ,  $C_3$  with solvent oxygen atom pairs, at all DMSO concentration studied.



**Fig 6 SI** Radial pair distribution Product -  $C_4$ ,  $C_5$ ,  $C_6$  with solvent oxygen atom pairs, at all DMSO concentration studied.

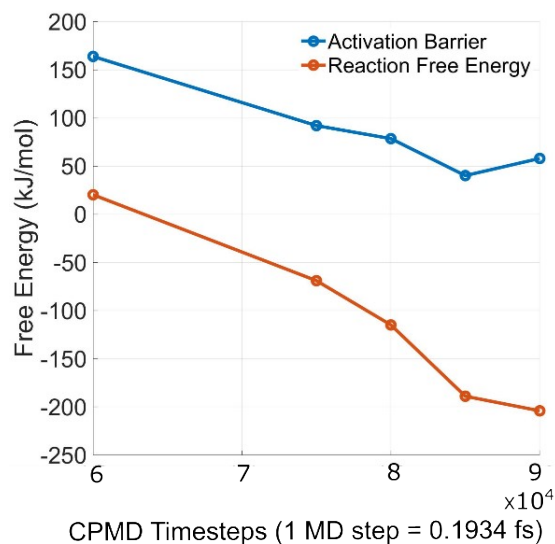


### 3. Ab initio molecular dynamics (CPMD scheme)-metadynamics implementation – converge criteria for Dynasolv method

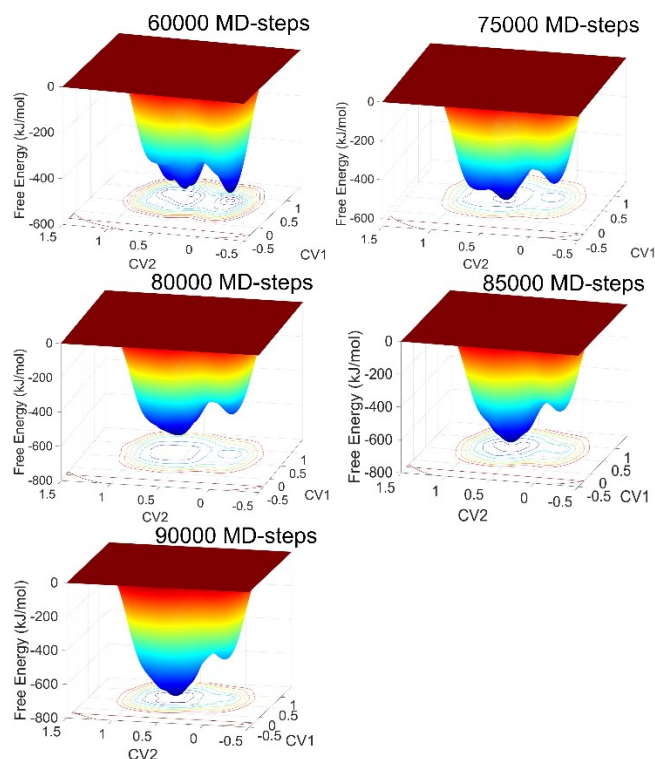
In this section, we present the converge criteria to determine the validity of the data reported using Dynasolv for 0, 25, and 50 % wt. DMSO proportions. This analysis determines until which simulation time the states of interest (5-HMF before and after protonation) converge. For each DMSO proportion, the following converge criteria are reported.

- (i) Activation and reaction-free energy values change as a function of simulation time.
- (ii) Free energy surfaces at different simulation times to compare their evolution and the possible exploration of other regions according to the collective variables specified.
- (iii) Key bond distances change as a function of simulation time.
- (iv) Time trajectories of CVs are also helpful in visualizing transitions between reactant and product states.

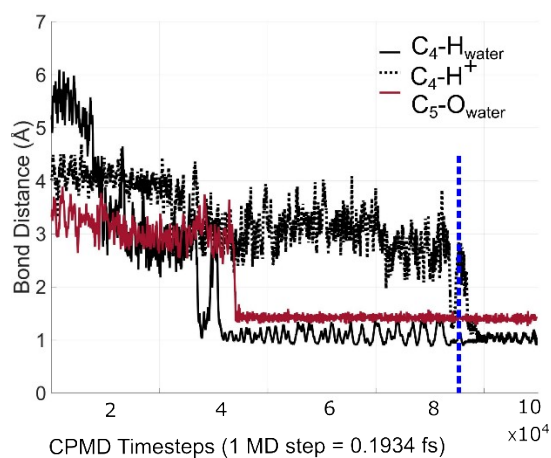
#### 3.1 System - 0 % wt. DMSO



**Fig 7 SI** Change of Activation Barrier and Reaction Free Energy in function of simulation time at 0 % wt. DMSO.



**Fig 8 SI** Evolution of Free Energy Surface as a function of simulation time at 0 % wt. DMSO.

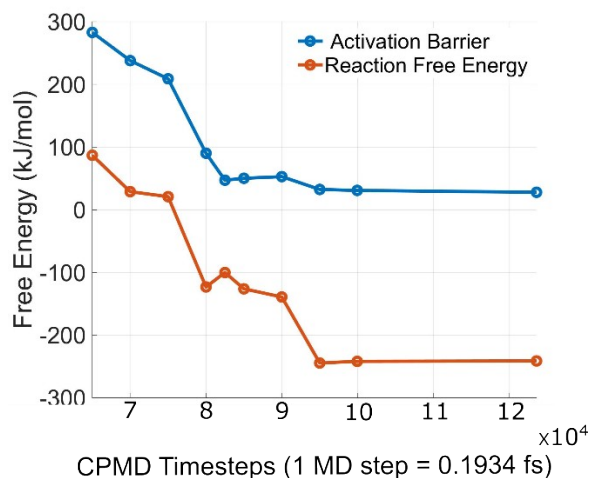


**Fig 9 SI** Variation in the bond distances during simulation time at 0 % wt. DMSO.

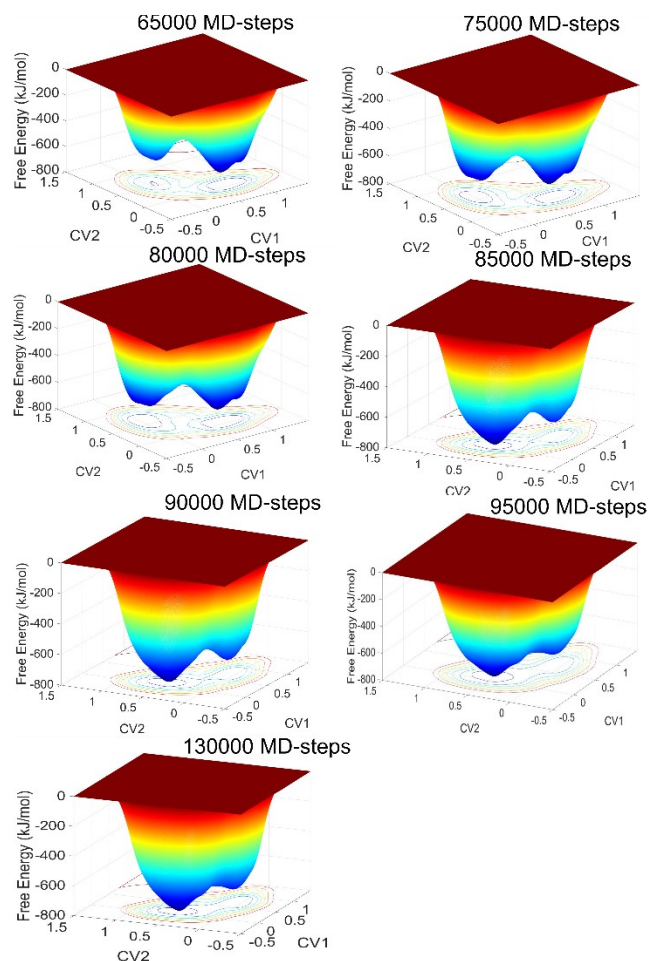
Activation barrier and reaction-free energy changes during the simulation time are reported in Fig 7 SI. It is observed that both the activation barrier and reaction-free energy converge over time. Additionally, Fig 8 SI shows how the wells within the FES evolve along the entire CPMD-metadynamics simulation. The first well is at  $CV1 \approx 1$  and  $CV2 \approx 0$  (5-HMF before protonation), and the second well is at  $CV1 \approx 1$  and  $CV2 \approx 1$  (5-HMF after protonation). Finally, the bond distance between  $C_4 - H^+$ ,  $C_4 - H_{water}$ , and  $C_4 - O_{water}$  is reported in Fig 9 SI. It is observed that the protonation occurs after 30 000 MD

steps (~6 ps), and  $O_{water}$  instantaneously stabilizes the electro deficient  $C_5$ . After 80 000 MD steps (~16 ps),  $H^+$  forms a bond with  $C_4$ , which is still bonded to  $H_{water}$ . This observation is enough to ensure that the two wells corresponding to 5-HMF before and after protonation have been filled with the potential added during the CPMD-metadynamics run allowing the system to explore new regions in the energy space bounded by the CVs.

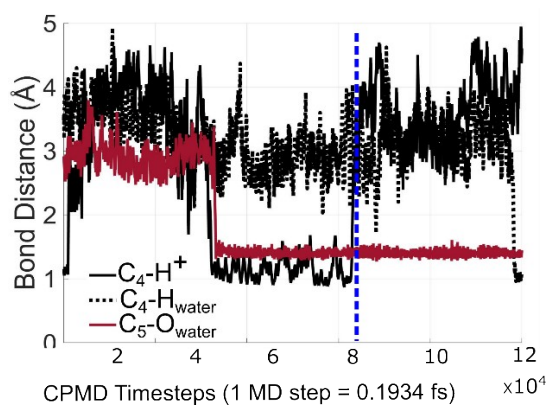
### 3.2 System - 25 % wt. DMSO



**Fig 10 SI** Change of Activation Barrier and Reaction Free Energy in function of simulation time at 25 % wt. DMSO.



**Fig 11 SI** Evolution of Free Energy Surface as a function of simulation time at 25 % wt. DMSO.

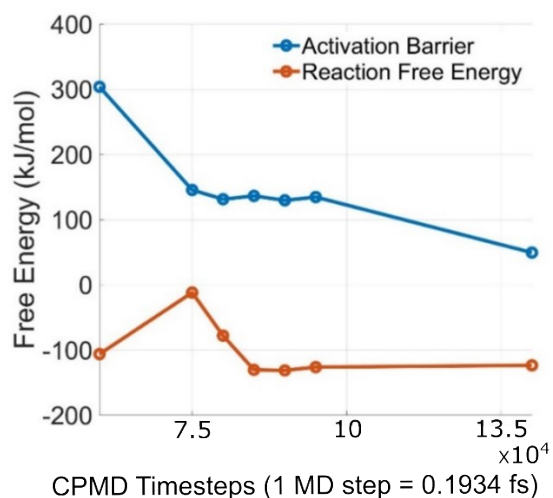


**Fig 12 SI** Variation in the bond distances during simulation time at 25 % wt. DMSO.

Activation barrier and  $\Delta G_R$  during the simulation time are reported in Fig 10 SI. It is observed that both the activation barrier and  $\Delta G_R$  converge after 80 000 MD steps (~16 ps). It is determined that the simulation converges at ~16 ps. According to Fig 12 SI, after 80 000 MD steps, bond  $C_4 - H^+$  is broken leading to the reactant state. Afterward, it

migrates to the product well and later it returns to the reactant state. This means that both the reactant and product wells have been filled with the potential added during the CPMD-metadynamics run. If the simulation continues, the FES may get deformed; therefore, the simulation stops after 16 ps. Similar to pure water,  $O_{water}$  stabilizes  $C_5^+$  after protonation occurs. In this case, as can be seen in Fig 11 SI, the first well corresponding to the reactant is at  $CV1 \approx 1$  and  $CV2 \approx 0$  (5-HMF before protonation), and the second well is at  $CV1 \approx 0$  and  $CV2 \approx 1$  (5-HMF after protonation).

### 3.3 System - 50 % wt. DMSO



**Fig 13 SI** Change of Activation Barrier and Reaction Free Energy in function of simulation time at 50 % wt. DMSO.

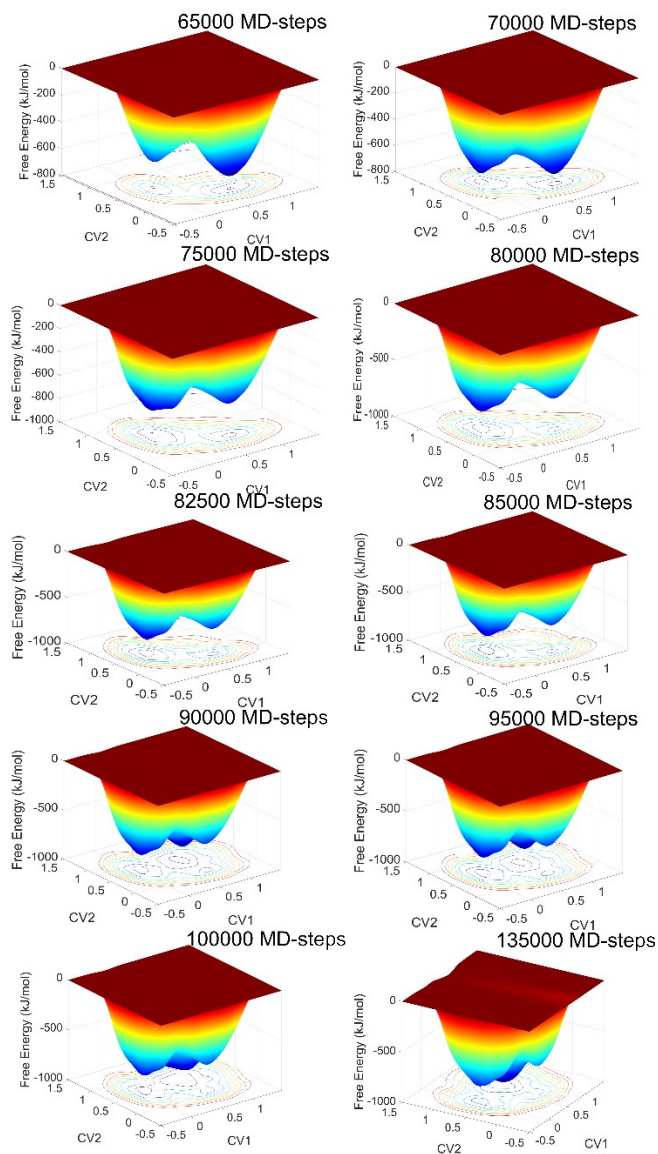


Fig 14 SI Evolution of Free Energy Surface as a function of simulation time at 50 % wt. DMSO.

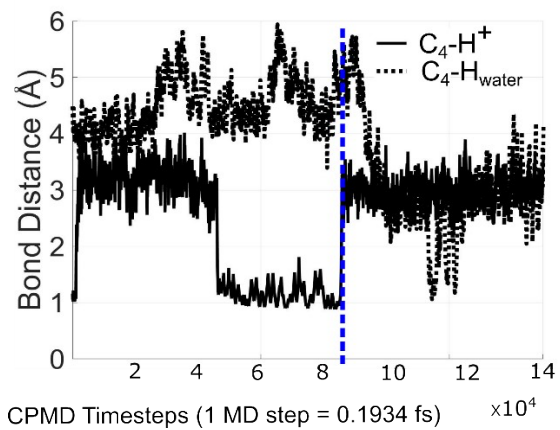


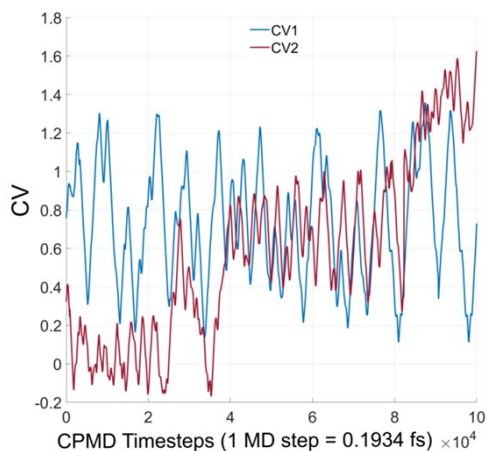
Fig 15 SI Variation in the bond distances during simulation time at 50 % wt. DMSO.

Finally, the activation barrier and reaction-free energy for 50 % wt. DMSO is shown in Fig 13 SI. It is observed how both the activation barrier and  $\Delta G_R$  converge after 80 000 (~16 ps). Fig 14 SI shows the FES evolution over time, like 25 % wt. DMSO, the first well corresponding to the reactant, is at  $CV1 \approx 1$  and  $CV2 \approx 0$  (5-HMF before protonation), and the second well is at  $CV1 \approx 0$  and  $CV2 \approx 1$  (5-HMF after protonation). It is also observed how a third well at 90 000 MD steps is formed. The well is at  $CV1 \approx 1$  and  $CV2 \approx 1$ , meaning  $H_{water}$  has replaced the proton to be bonded to  $C_4$ . The third well formation also suggests that the previous wells corresponding to reactant and product (before and after 5-HMF protonation) have been filled with the potential added during CPMD-metadynamics. In addition, Fig 15 SI shows that after 80 000, the bond between  $C_4 - H^+$  is broken, which that the system has moved from product to reactant, suggesting that both reactant and product wells have been successfully filled.

### 3.4 Collective variables as convergence criteria of metadynamics and reactant product transitions.

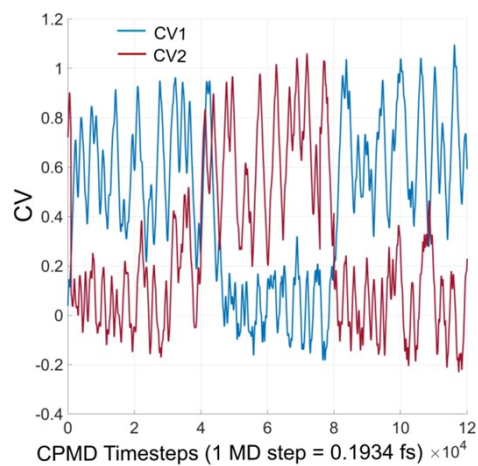
The time trajectories of CVs have been added in supporting information as the fourth convergence criteria for Dynasolv methodology. For each DMSO proportion, the CVs evolution over simulation time has been plotted and described in detailed, explaining and highlighting each transition of CVs values. The CVs values ensure convergence for all DMSO proportion in agreement with the other convergence parameters reported.

#### 0 % wt. DMSO



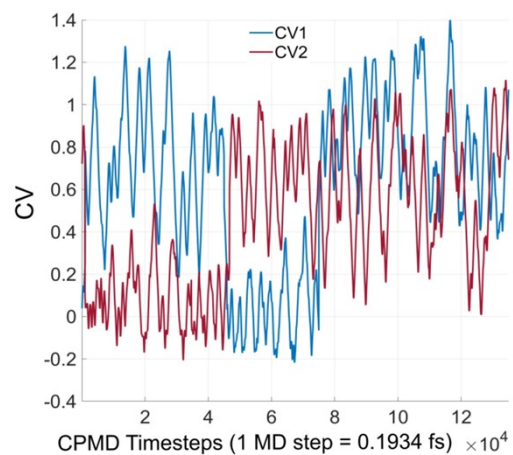
**Fig 16 SI** Time trajectories of CVs at 0 % wt. DMSO. CV1 - Coordination no. of  $H_\alpha$  and  $O_{water}$ , CV2 - Coordination no. of  $C_4$  with  $H_{water}$  &  $H_\alpha$ .

## 25 % wt. DMSO



**Fig 17 SI** Time trajectories of CVs at 25 % wt. DMSO. CV1 - Coordination no. of  $H_\alpha$  and  $O_{water}$ , CV2 - Coordination no. of  $C_4$  with  $H_{water}$  &  $H_\alpha$ .

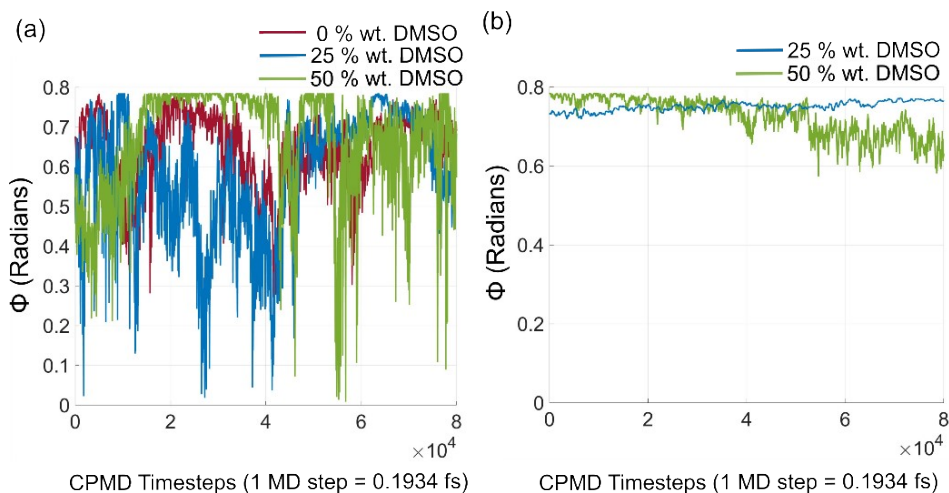
## 50% wt. DMSO



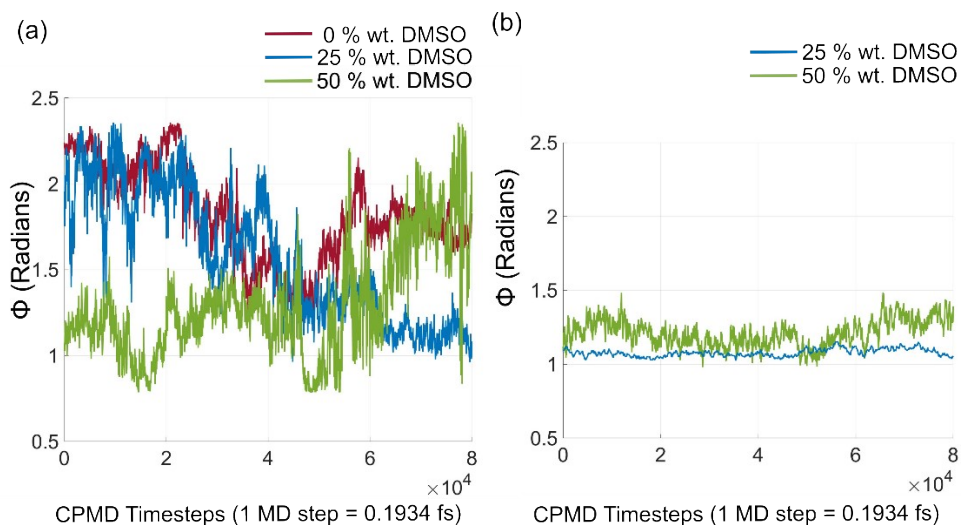
**Fig 18 SI** Time trajectories of CVs at 50 % wt. DMSO. CV1 - Coordination no. of  $H_\alpha$  and  $O_{water}$ , CV2 - Coordination no. of  $C_4$  with  $H_{water}$  &  $H_\alpha$ .



#### 4. Dipole orientational vectors for water and DMSO along the trajectory



**Fig 19 SI** Variation in the orientation of the solvent dipole vector for the water and DMSO molecules separately with respect to the **z-axis** (or the angle that the solvent dipole vector makes with the **z-axis** of the simulation cell) during the protonation step in the CPMD-metadynamics trajectory. (a) water molecules (b) DMSO molecules at different DMSO proportions.



**Fig 20 SI** Variation in the orientation of the solvent dipole vector for the water and DMSO molecules separately with respect to the **y-axis** (or the angle that the solvent dipole vector makes with the **y-axis** of the simulation cell) during the protonation step in the CPMD-metadynamics trajectory. (a) water molecules (b) DMSO molecules at different DMSO proportions.

