Supplementary Information for

Microscopic Structural Features of Water in Aqueous-Reline Mixture of Varying Composition

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1. System information

System Identifier	No. of water molecules	No. of urea molecules	No. of choline ions	No. of chloride ions	Simulation length (ns)
W	1636	--	--	--	50
W-UC (2:1)	1211	60	30	30	100
W-UC (4:2)	794	120	60	60	100
W-UC (6:3)	444	180	90	90	100
W-UC (8:4)	166	240	120	120	100

Table S1: Details of the composition of solvent/co-solvent in different systems and their simulation Length.

Experimental		Simulation				
Reline (wt%)	Density (gm/cc)	System Identifier	Reline (wt%)	Density (gm/cc)	Pressure (Bar)	Temperature (K)
34.86	1.0652	W-UC (2:1)	26.3	1.05	1.0281	310.006
54.63	1.1047	W-UC (4:2)	52.5	1.11	1.0199	310.041
76.26	1.1492	W-UC (6:3)	74.8	1.16	0.9955	310.039
91.84	1.1817	W-UC (8:4)	91.4	1.19	0.9912	310.029

Table S2: Comparison of the simulated densities of the investigated solutions along with the experimental densities (at 313.15 K).

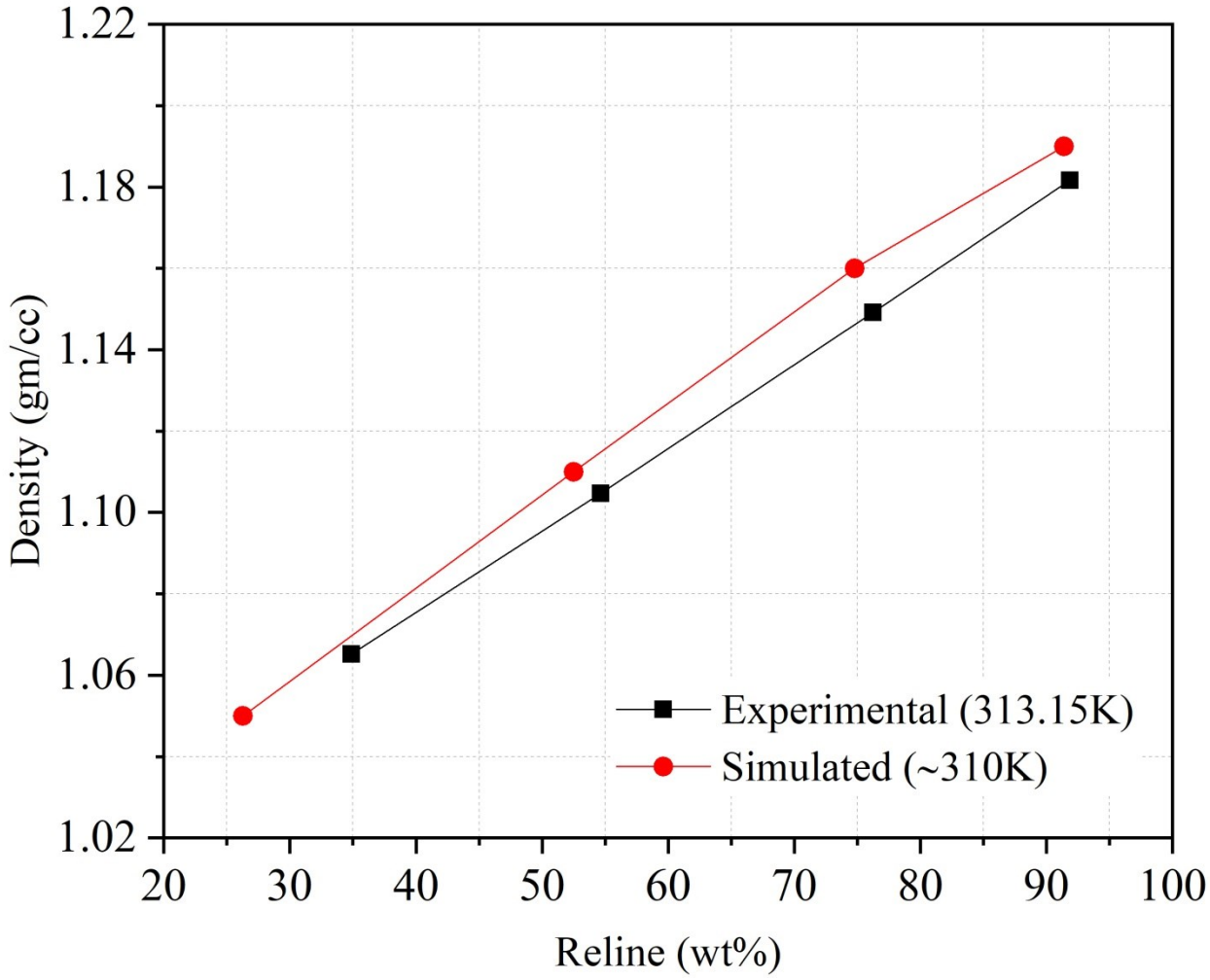

Fig S1: Comparison of the simulated densities of the investigated solutions with the experimental densities as a function of reline wt%.

2. Radial Distribution Function

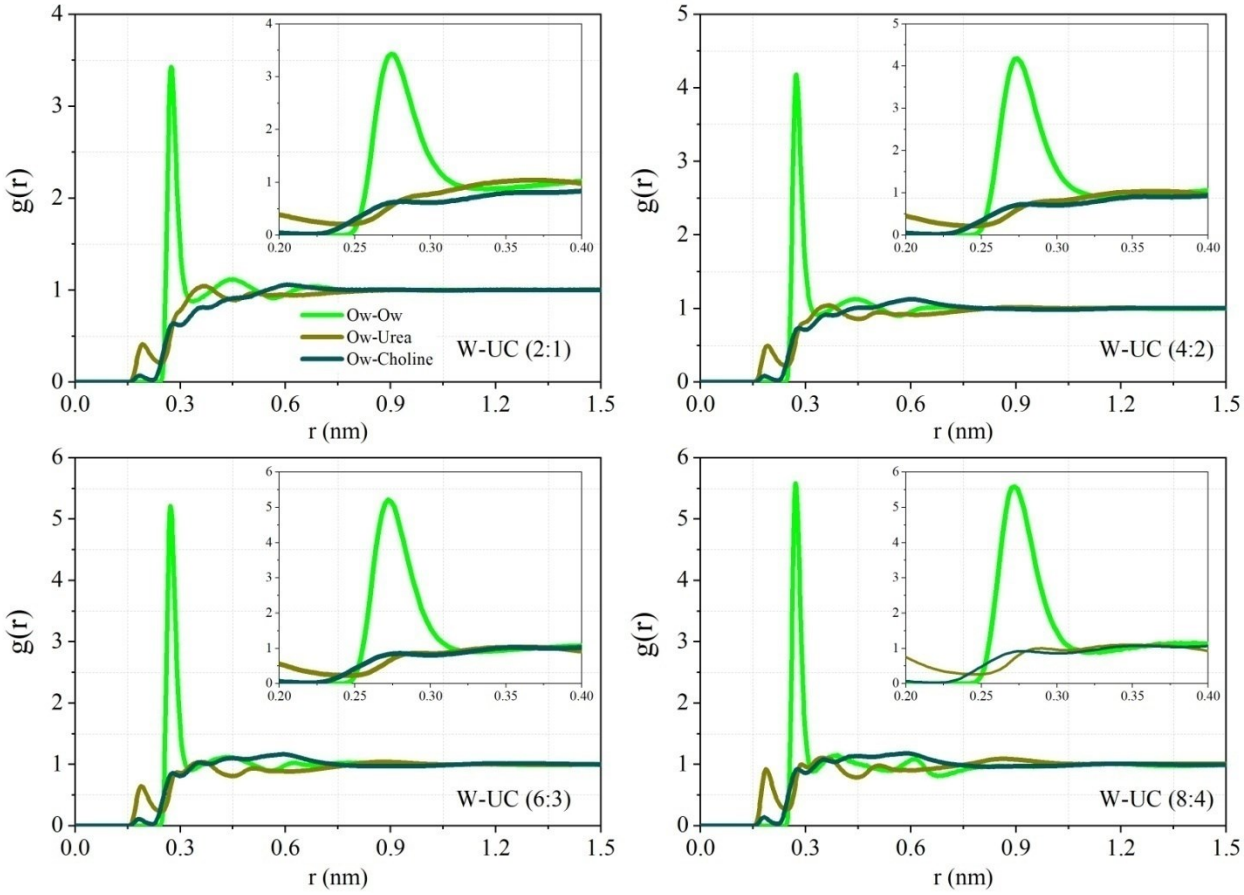

Fig S2: Radial distribution functions (g(r)) of Ow/Urea/Choline around water-oxygen (Ow) in different systems.

3. Tetrahedral order Parameter (q_{tet})

3.1. Probability Distribution (P(q_{tet}))

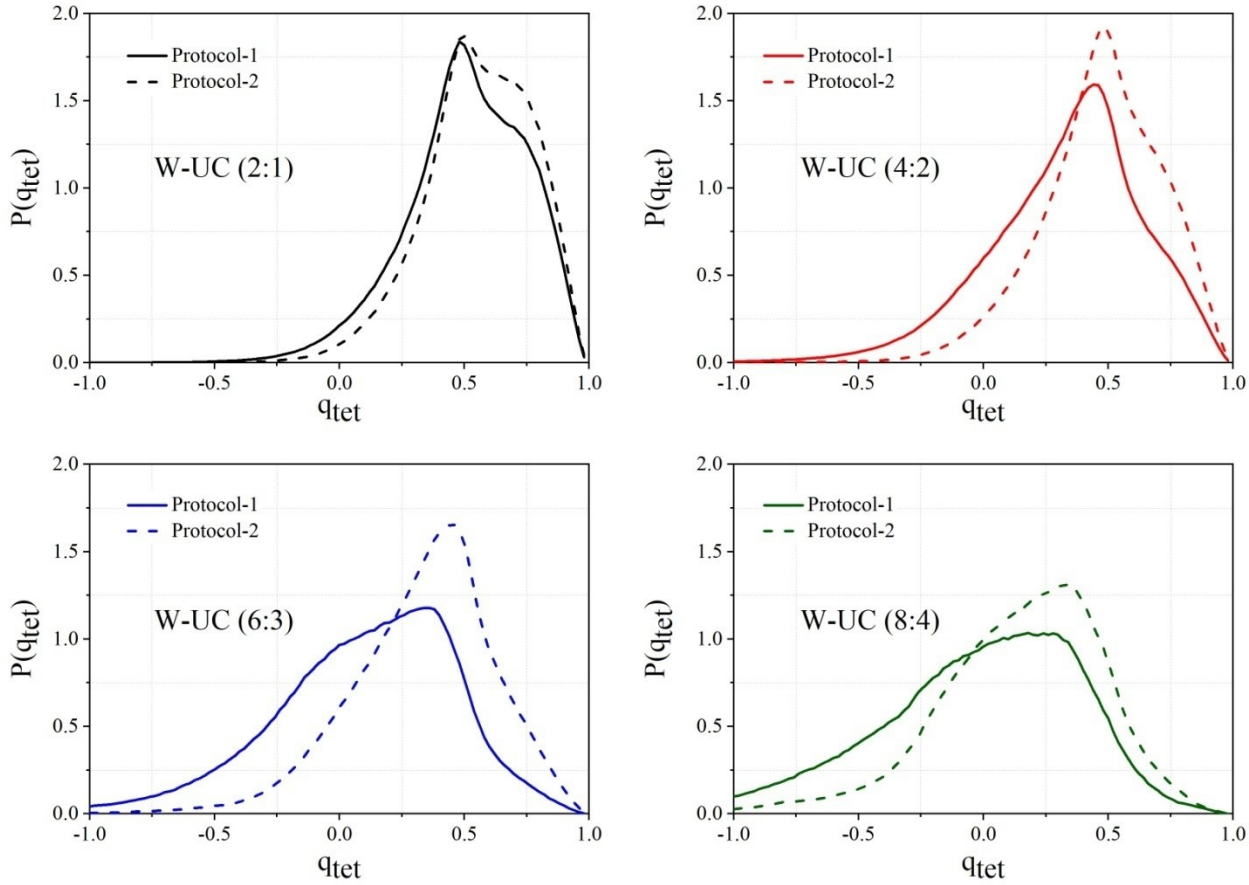

Fig S3: Comparison of the probability distributions of TOP ($P(q_{tet})$) calculated using Protocol-1 (solid line) and Protocol-2 (dashed line) for different systems under investigation.

3.2. Distance distribution of the neighbor

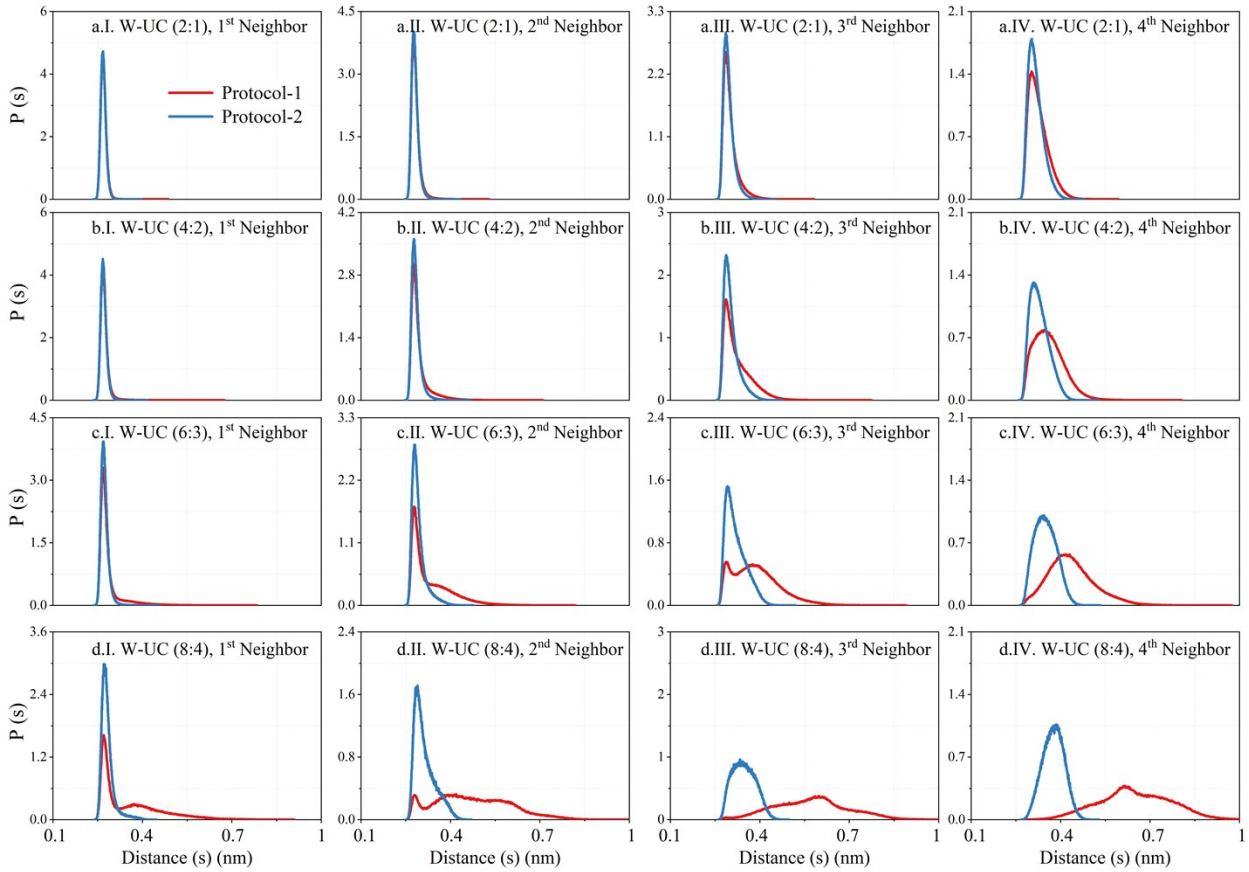

Fig S4: Probability distribution of the distance $(P(s))$ between the central water-oxygen atom (Ow) and the neighboring partner, for different protocols, followed. Along the row from left to right neighbors are varied and along the column from top to bottom systems are varied.

As can be seen from Fig S4, red curve represents Protocol-1 and blue curve represents Protocol-2. We can see, for systems with varying reline concentration considering all neighbors Protocol-2 ensures closer vicinity of the partners compared to Protocol-1. We find that for all cases considered in Fig S4, peak position of the probability distribution calculated from Protocol-2 resides within 0.4nm from the central water-oxygen atom while in case of Protocol-1, the distribution pattern is quite scattered. For the first neighbor we see that the peak position of the distribution for Protocol-1 and 2 almost coincide with each other and reside within 0.4nm while in case of W-UC (8:4) some contribution outside the 0.4nm sphere is accounted for. It sheds light on the fact that the first neighbor is not significantly disturbed on introducing co-solvents in the system. We have already witnessed a disorder in water structure in Fig 4 in terms of q_{tet} which could be justified by the plots provided under Fig S4. It is evident from Fig S4 that Protocol-1 has peak position around 0.7nm for the fourth neighbor for higher reline concentrations, which implies that in the presence of reline, water molecules are not even within the hydrogen-bonded donor-acceptor

distance which is 0.35nm. This ultimately ruptures the local water structure and helps it to deviate from tetrahedrality. The hydrogen-bonding distance criterion is fulfilled by the urea molecules and choline cations as they started contributing.

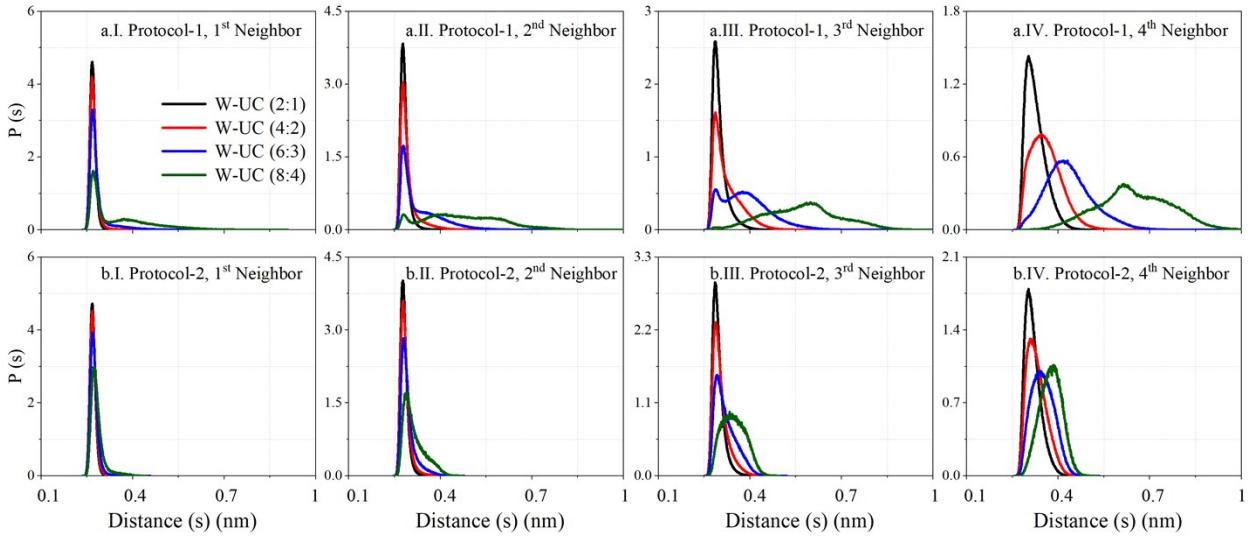

Fig S5: Probability distribution of the distance $(P(s))$ between the central water-oxygen atom (Ow) and the neighboring partner, for different systems. Along the row from left to right neighbors are varied and along the column from top to bottom protocols followed to consider the nearest neighbor are varied.

For a better understanding of the distance distribution $(P(s))$, we compare the systems for different protocols at four distinct neighboring positions (Fig S5). The plots shed light on the fact that an increase in reline wt% leads to the flattening of the curve and the peak position shifts to a larger distances, which is observed mainly in case of W-UC (6:3) and W-UC (8:4) systems. Specifically, W-UC (2:1) and W-UC (4:2) show peaks within 0.4nm but for other systems, the existence of the distribution peak is found beyond the 4Å sphere. The shift of the peak position with an increase in the reline wt% can be attributed to the highly crowded medium, where constituents are residing far from the central water molecule unlike in case of lower reline concentrations.

3.3. Probability Distribution of the subtended angle (P(θ_{jk})) and Free energy calculation

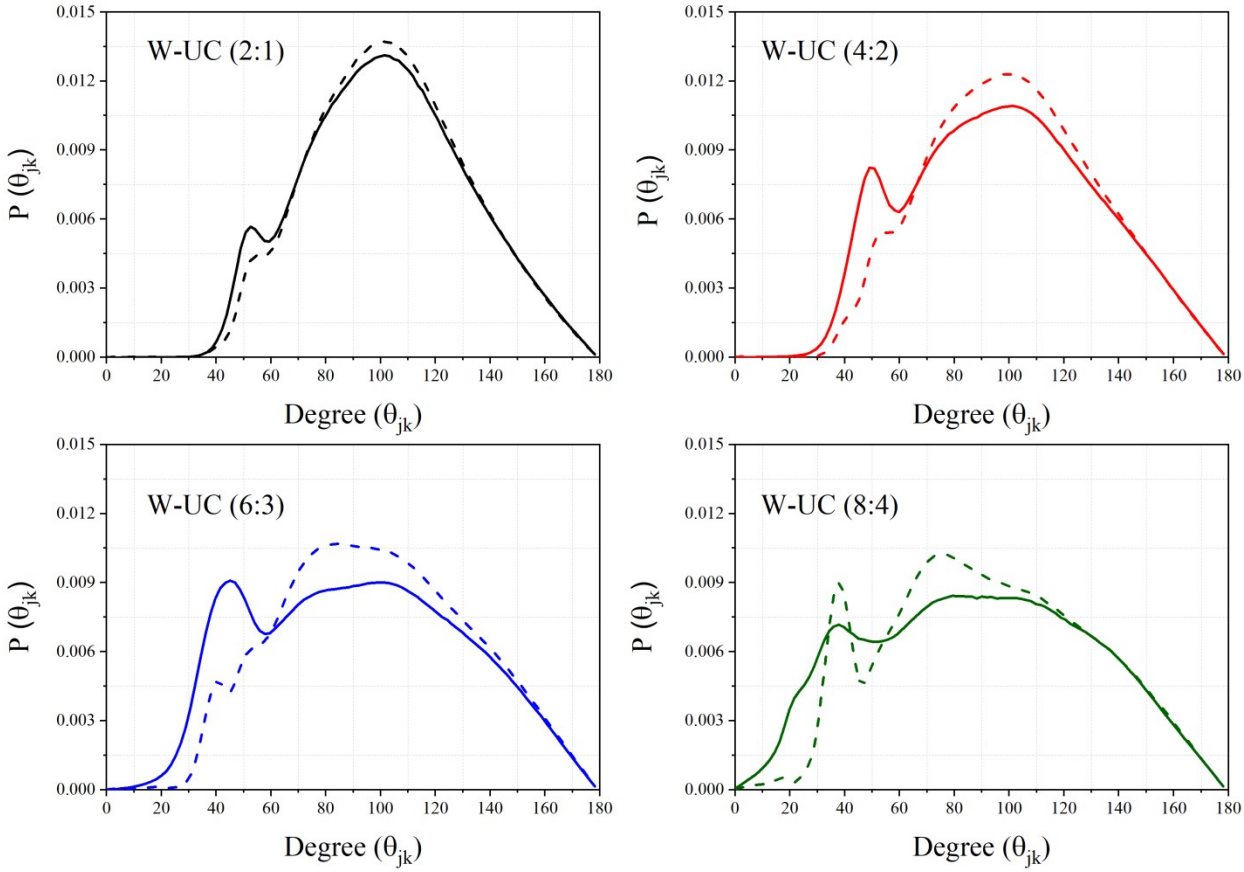

Fig S6: Comparison between the probability distributions of the subtended angle ($^{(P(\theta_{jk})}$) for different systems under investigation computed following Protocol-1 (solid line) and Protocol-2 (dashed line).

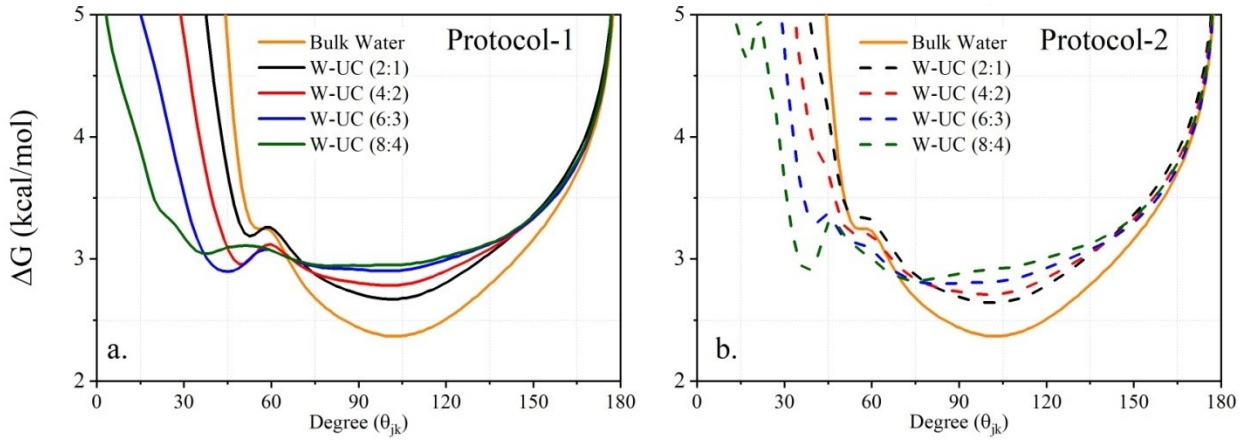

Fig S7: Free energy diagram derived from the probability distribution of the subtended angle (P(θ_{jk})) for Protocol-1 (left panel) and Protocol-2 (right panel), calculated for different systems under consideration.

In the bulk water system (orange solid representation), a prominent difference of 1kcal/mol is observed between the two minima, where the broad minimum is found at ~1.25kcal/mol and the minima

corresponding to the initial sharp rise is situated at ~2.25kcal/mol. The amount of stabilization is comparable to thermal fluctuation at normal room temperature. Considering protocol-1 and 2, the stability of the first minimum increases and the stability of the broad peak decreases as wt% of reline increases. For W-UC (8:4), the curve gets severely flattened that there is hardly any free energy difference between the first and the second minima. For all systems under investigation, Protocol-2 shows higher stability than that of Protocol-1, while the trend is similar in either of the cases.

4. Number of Hydrogen bonds

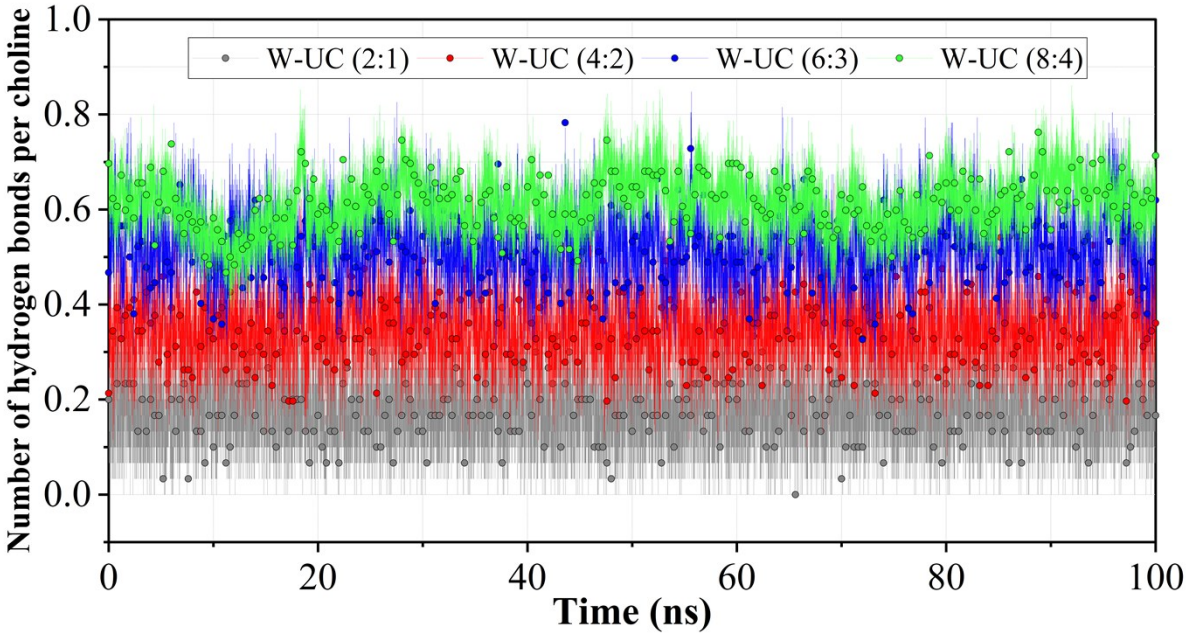

Fig S8: Numbers of hydrogen bonds between urea and choline per choline cation for different systems.

5. Modes of Hydrogen bond formation

Bonding statistics			**Identifier**
Mono coordinated water molecules			
Water	Urea	Choline	
1	0	0	1W-0U-0C
0	1	0	0W-1U-0C
0	0	1	0W-0U-1C
Bi coordinated water molecules			
Water	Urea	Choline	
2	0	0	2W-0U-0C
0	2	0	0W-2U-0C
0	0	2	0W-0U-2C

1	1	0	1W-1U-0C
1	0	1	1W-0U-1C
0	1	1	0W-1U-1C
Tri coordinated water molecules			
Water	Urea	Choline	
3	0	0	3W-0U-0C
0	3	0	0W-3U-0C
0	0	3	0W-0U-3C
2	1	0	2W-1U-0C
1	2	0	1W-2U-0C
2	0	1	2W-0U-1C
1	0	2	1W-0U-2C
0	2	1	0W-2U-1C
0	1	2	0W-1U-2C
1	1	1	1W-1U-1C
Tetra coordinated water molecules			
Water	Urea	Choline	
4	0	0	4W-0U-0C
0	4	0	0W-4U-0C
0	0	4	0W-0U-4C
3	1	0	3W-1U-0C
1	3	0	1W-3U-0C
3	0	1	3W-0U-1C
1	0	3	1W-0U-3C
0	3	1	0W-3U-1C
0	1	3	0W-1U-3C
2	2	0	2W-2U-0C
2	0	2	2W-0U-2C
0	2	2	0W-2U-2C
2	1	1	2W-1U-1C
1	2	1	1W-2U-1C
1	1	2	1W-1U-2C

Table S3: Possible combinations of coordination of central water by water, urea, and choline for mono, bi, tri, and tetra coordinated water molecules. The coordination number indicates the number of successful hydrogen bonds with the central water molecule.