Supporting Information

Molecular Dynamics Simulation Studies on Structure, Dynamics and Thermodynamics of Uranyl Nitrate Solution at Various Acid Concentrations

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Text-S1

The total bonded interaction includes the bond stretching, bond angle bending and the dihedral deformation as

$$U_{TOTAL} = \sum_{bonds} K_r(r_{ij} - r_{eq})^2 + \sum_{angles} K_\theta(\theta_{ijk} - \theta_{eq})^2 +) + 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \sigma ijrij6 + qiqj4\pi\varepsilon 0rij \right. \quad \text{(S1)}$$

Where, U_{TOTAL} is the total energy including bonding and non-bonding energy. The various terms represent the bond length stretching between atoms i and j, bond angle bending between i, j and k and bond torsion between atoms i, j, k and l respectively.[25-29] The total non-bonded interactions coming from pair interaction between non-bonded atoms, includes both van der Walls and electrostatic interactions which are computed using Lennard – Jones potential.

Text-S2

Self-diffusion coefficient

Self-diffusion coefficient is a highly important dynamical quantity to build up an understanding of mobility of solute particles and is calculated from Einstein's equation using the mean square displacement (MSD) profile as:

$$\lim_{t\to\infty} < (r(t) - r(t_0))^2 > = 6Dt \quad \text{(S2)}$$

Where, r(t) and r(0) are positions of atom at any time t and at t=0 respectively. The left part of the equation indicates the ensemble average of squared displacement i.e. MSD. The diffusivity, D is then computed from the slope of MSD.

Text-S3

Hydrogen bond correlation function

The correlation between uranyl ions and water molecules is determined from HB correlation function, where the two molecules are to be hydrogen bonded was defined by the following conditions which simultaneously satisfied,[59-64]

I. The oxygen-oxygen distance ROO is less than 3.6 Å;

II. The distance ROH between donor hydrogen and acceptor oxygen is less than 2.4 Å;

III. The angle θ_{HB} between the vector connecting the two oxygen atoms and the vector connecting the donor oxygen and acceptor hydrogen atom is less than 30◦.

Then, the dynamics of hydrogen bonds among molecules present in the medium is investigated by calculating the intermittent hydrogen bond correlation function,

$$C(t) = \frac{\langle h(0)\, h(t)\rangle}{\langle h(0)\, h(0)\rangle}$$

where h(t) = 1, if the particular tagged pair of water molecules is hydrogen bonded at time t, according to adopted geometry criteria for H bond relation, 0 otherwise. C(t) represents the probability that H bond is intact at time t, given that it was intact at time 0, independent of possible breaking in the intervening time.

It will be really interesting to look into the local hydrogen bond topology [R1, R2, R3] to enrich the present works. The tetrahedrality parameter (q=1-Sg) following the prescription of P.L. Chau and A. J. Hardwick [R4] was determined for pure solvent and uranyl solution. The calculated results are presented in **Table S6**. From the results, it is seen that the tetrahedral order parameter (q) is reduced with increasing concentration of uranyl ions indicating the disruption of hydrogen bond.

Text-S4

Density measuring principle

A sample is prepared of which the density to be calculated. The sample is introduced into a U – shaped borosilicate glass tube that is being excited to variable at its characteristics frequency using DMA 5000 M, Anton Paar. The characteristics frequency changes depending on the density of the sample. Through the precise determination of the characteristic frequency and a mathematical conversion, the density of the sample can be measured.

The density is calculated from the quotient of the period of oscillations of the U – tube and the reference oscillator.

The uranyl nitrate solution is prepared in 3M nitric acid having a concentration range of 0.25 mole/lit to 4.65 mole/lit. The samples are named properly. Then the measuring cell is filled with sample before ensuring the measuring cell was clean and dry. Finally the result values are collected from the data memory.

Text-S5

Dynamic light scattering (DLS) experiments

In order to support the simulation findings, dynamic light scattering (DLS) experiment was conducted to explore the behaviour of aqueous mixture using a Malvern 4800 Autosizer employing a 7132 digital correlator. The scattering results (shown in **Figure 8**) depict that homogeneity of the aqueous mixture is maintained up to 4.0 moles/lit and after that the mixture becomes heterogeneous as the light fails to pass through the solution. The nonlinearity in the intensity curve is appeared at the same location where the nonlinearity in surface tension was observed.

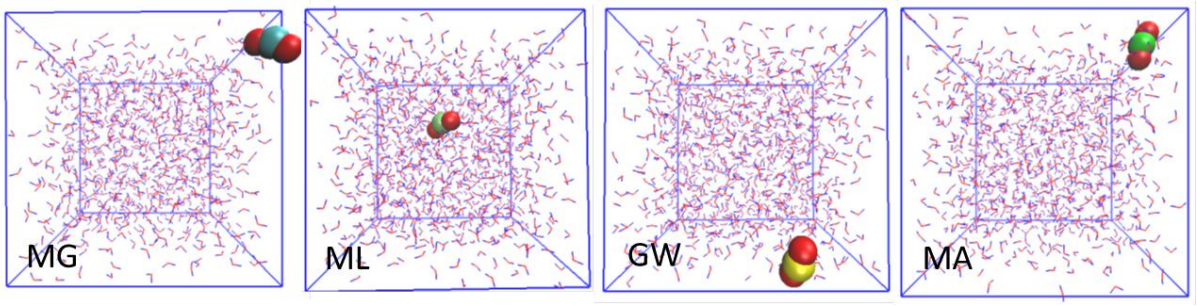

Figure S1. Liquid state structure of uranyl ion in water systems having different force field embedded with four types of partial atomic charges on uranium as well as on uranyl oxygen atom. Oxygen atom: Red, Uranium atom: Cyan, Light green, Yellow and Green and Water molecule: Pink.

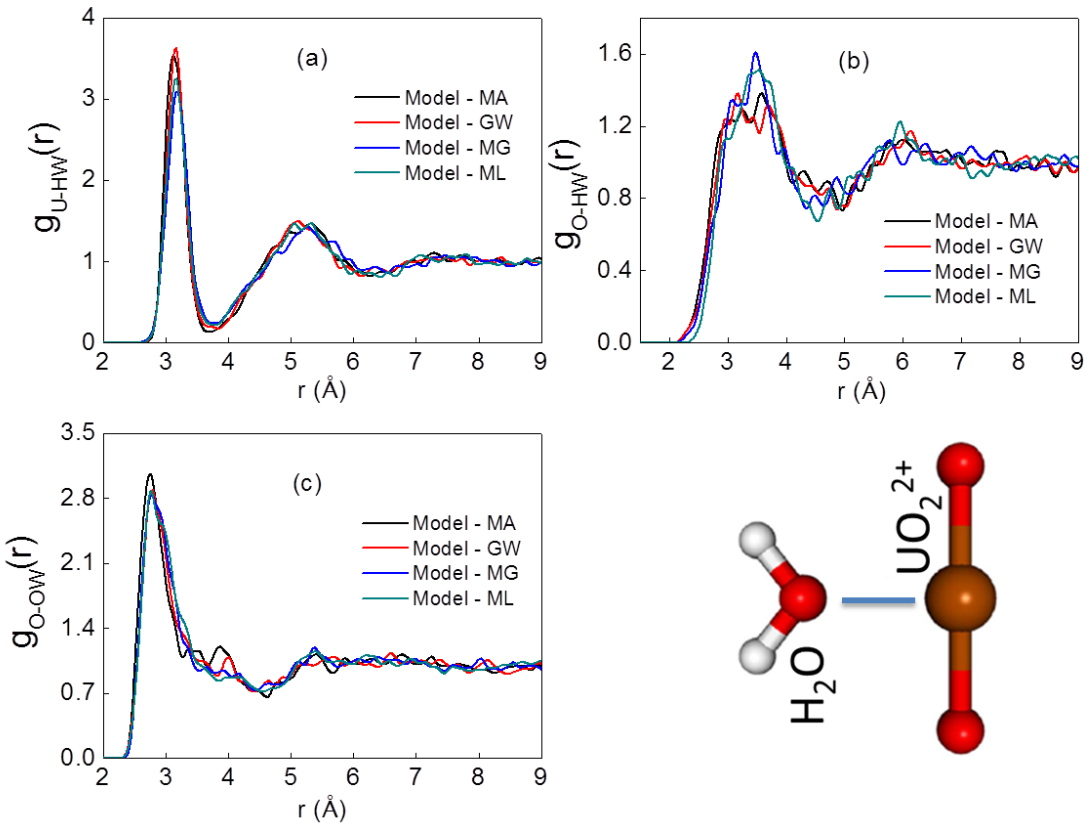

Figure S2. Pair correlation functions obtained from simulation of uranyl ion in water: (a) Water hydrogen (H_W) around U atom (U – H_W), (b) water hydrogen (H_W) around uranyl oxygen (O – H_W), (c) water oxygen (O_W) around uranyl oxygen (O – O_W) and (d) configuration of uranyl ion and water molecule. Red: Oxygen, White: Hydrogen and Brown: Uranium atom.

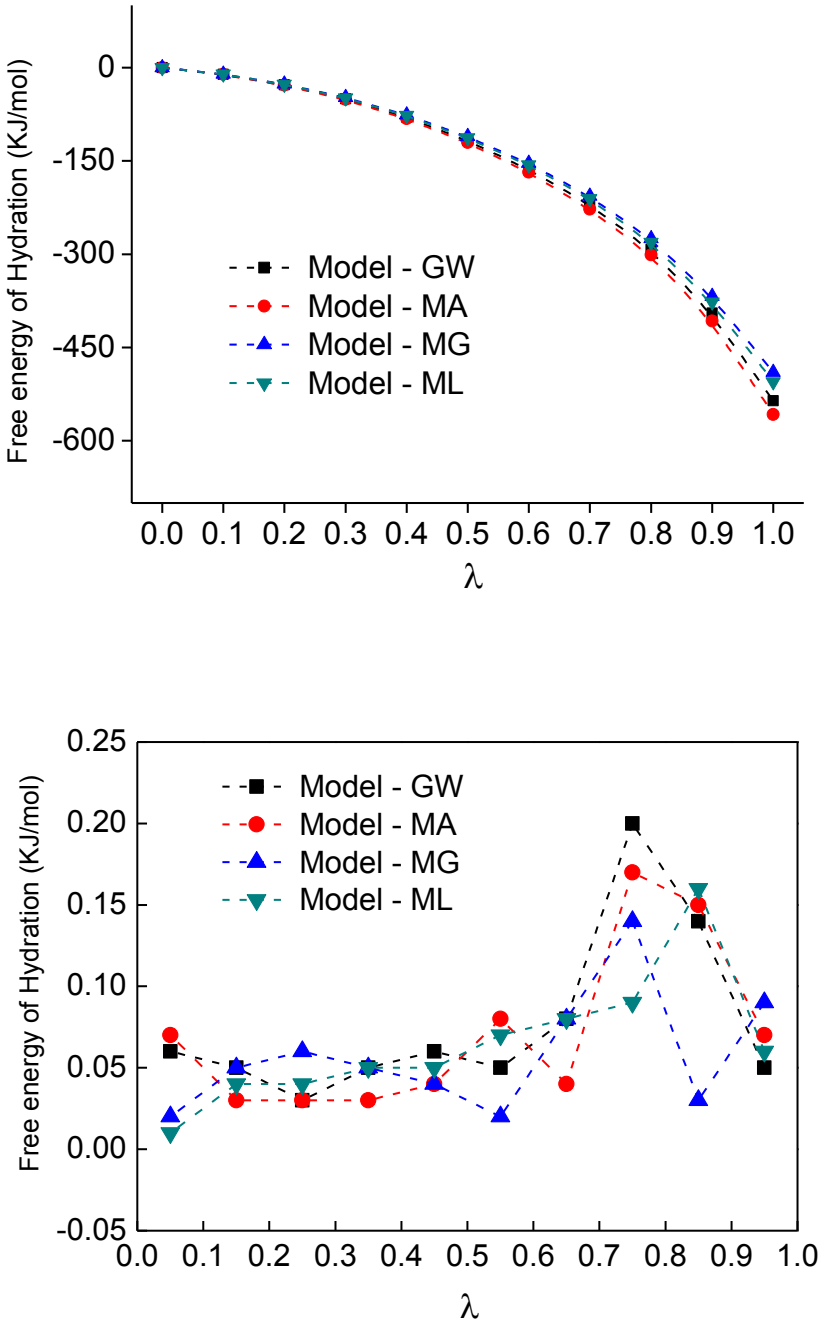

Figure S3. Change of free energy of hydration ($\Delta G_{Hydration}$) versus coupling parameter (λ) evaluated using thermodynamic integration

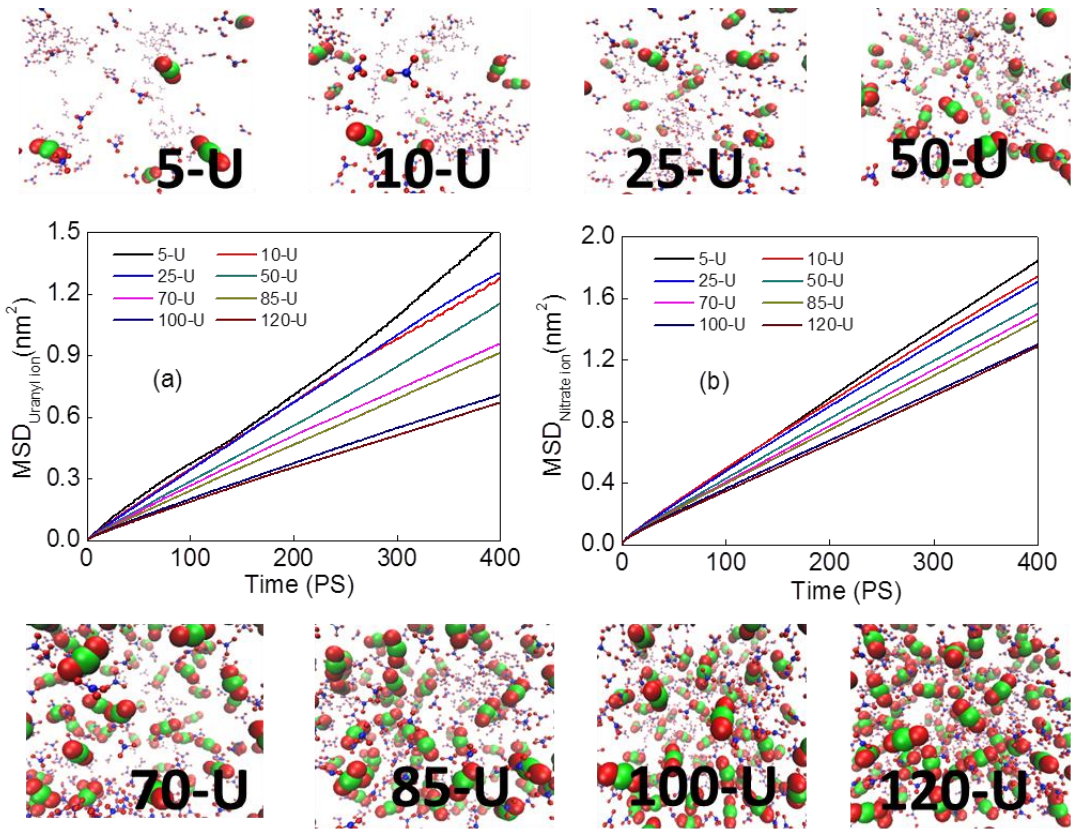

Figure S4.(a) MSD profiles of uranyl ions and **(b)** MSD profiles of nitrate ions in 3M acidic solution as a function of uranyl nitrate concentrations in that solution. The uranyl nitrate concentrations are represented as the numbers of uranyl ions present in the aqueous phase and denoted by respective system. The snapshots of respective liquid phase are illustrating the gathering of uranyl nitrate in the solution with concentrations. Colour code: Green-Uranium, Red-Oxygen, Blue-Nitrogen.

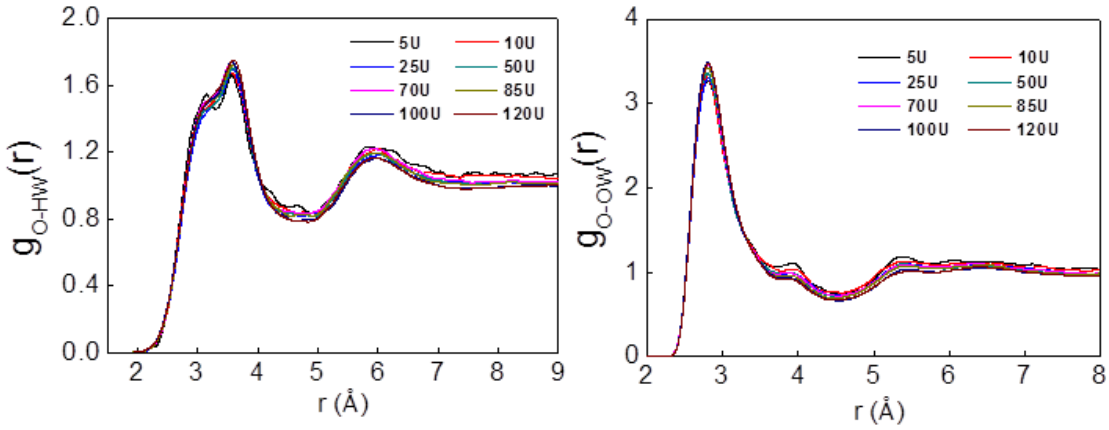

Figure S5. Pair correlation function between two interacting **(a)** oxygen atom of uranyl ion and hydrogen atom of water molecule and **(b)** oxygen atoms of uranyl ion and oxygen atom of water molecule at different uranyl nitrate concentration which represented by the numbers of uranyl ions present in 3M nitric acid.

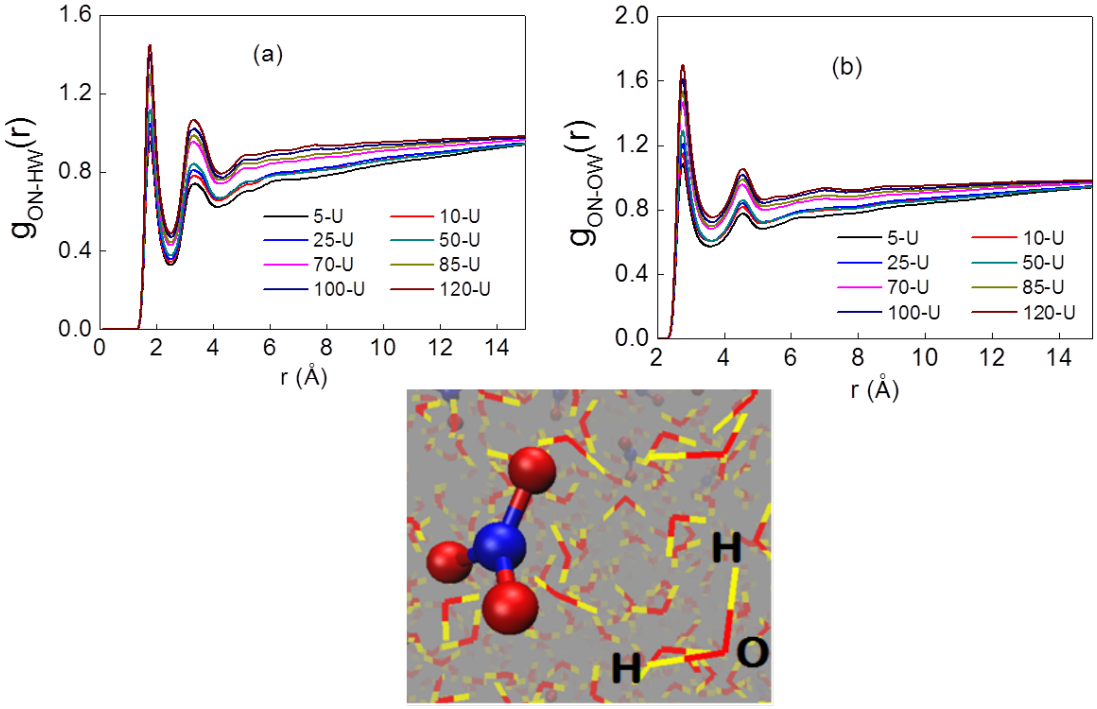

Figure S6. Pair correlation function between two interacting **(a)** oxygen atom of nitrate ion and hydrogen atoms of water and **(b)** oxygen atom of nitrate ion and oxygen atom water. Snap shot of orientation of water molecules around nitrate ions. Colour code: Red-Oxygen, Blue-Nitrogen and Yellow-Hydrogen.

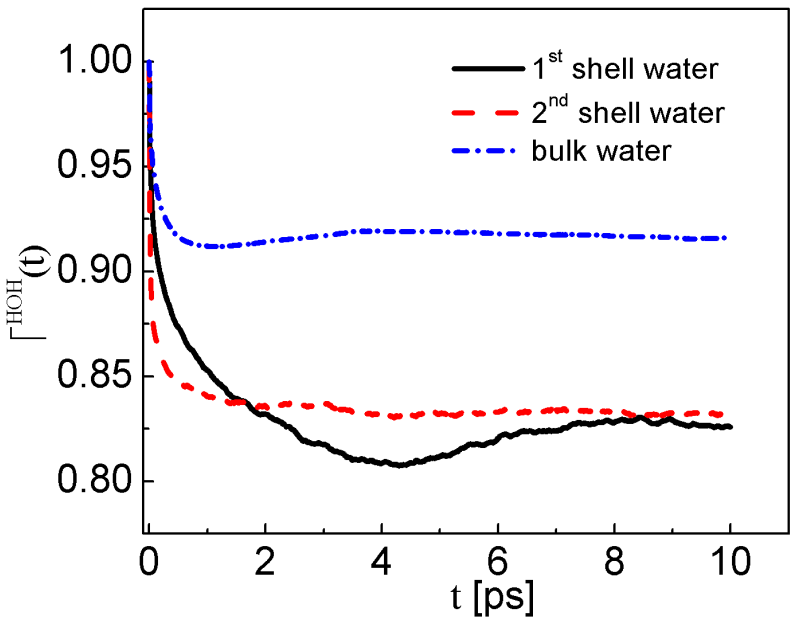

Figure S7. Plot of orientational correlation function versus time (t).

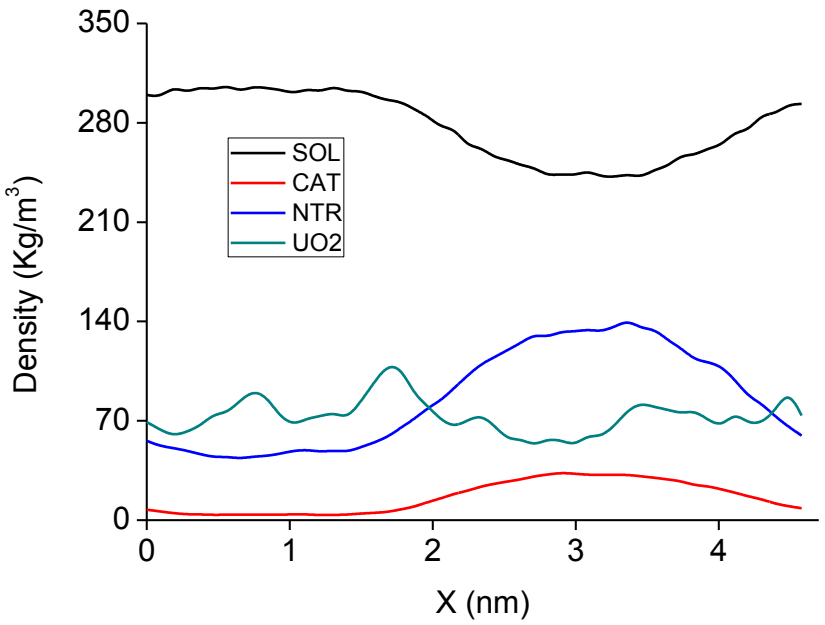

Figure S8. Plot of density of various chemical species along X-direction.

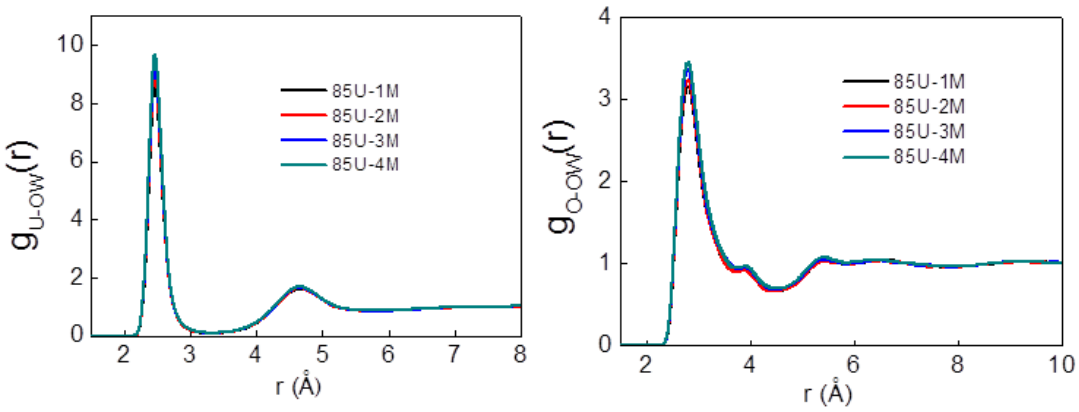

Figure S9. Pair correlation function between two interacting **(a)** U atom and O_W (water oxygen) atom and **(b)** oxygen atom (O) of uranyl ion and O_W (water oxygen) atom.

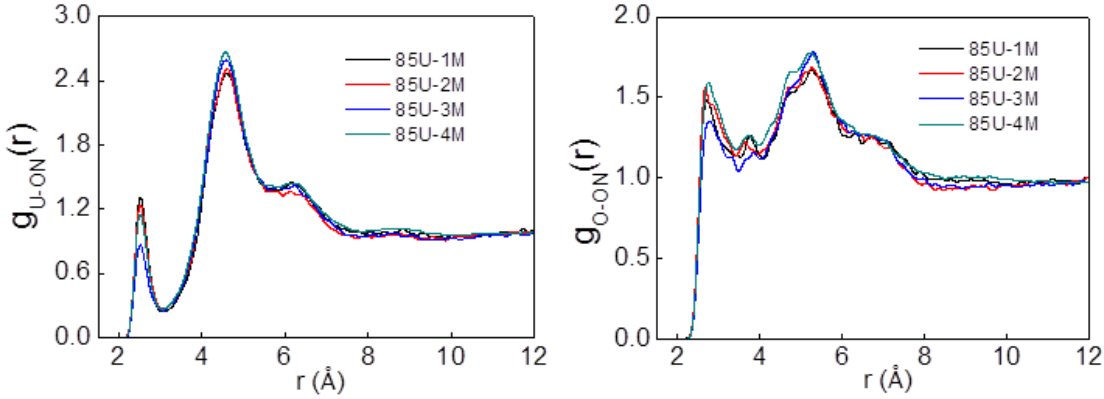

Figure S10. Pair correlation function between two interacting **(a)** U atom and O_N (oxygen atom of NO_3^-) atom and **(b)** oxygen atom (O) of uranyl ion and oxygen atom (O_N) of nitrate ion.

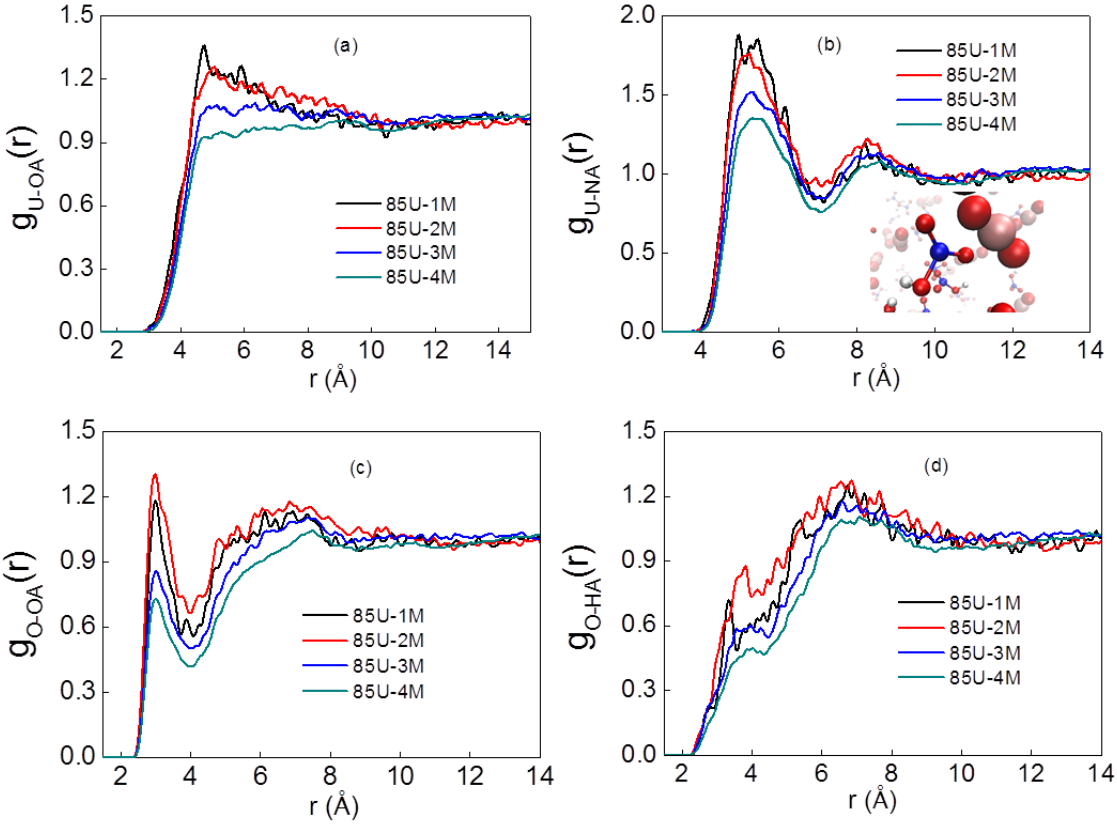

Figure S11. Pair correlation function between two interacting **(a)** U atom and O_A atom (oxygen atom of HNO_3), **(b)** U atom and nitrogen atom (N_A) of nitric acid, **(c)** uranyl oxygen (O) atom and oxygen atom (O_N) of nitric acid, **(d)** uranyl oxygen atom (O) and hydrogen atom (H_A) of HNO_3. Inset: Snap shot representing the orientation of nitric acid around uranyl ion. Colour code: White-Hydrogen, Red-Oxygen, Pink-Uranium, and Blue-Nitrogen.

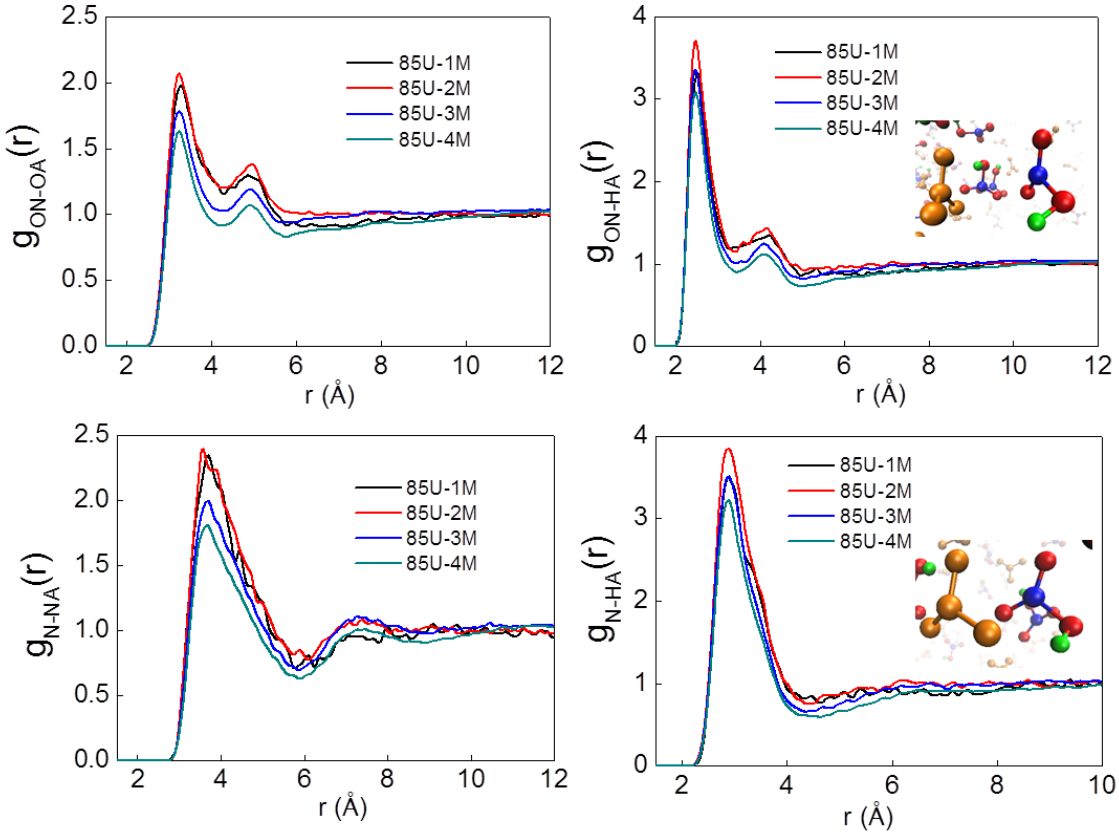

Figure S12. Pair correlation function between two interacting **(a)** oxygen atom (ON) of nitrate ion and oxygen atom (OA) of HNO_3 **(b)** ON atom of nitrate ion and hydrogen atom (HA) of HNO_3, **(c)** nitrogen atoms of nitrate ion and HNO_3, **(d)** nitrogen atom (N) of nitrate ion and hydrogen atom (HA) of HNO_3. Inset: Snap shot representing the orientation of nitrate ion around nitric acid. Colour code: Green-Hydrogen, Blue-Nitrogen, Red-Oxygen and Golden yellow-Nitrate ion.

Table S1. Density of uranyl ion in water system for different models computed from MD simulation. The self-diffusivity of uranyl ion in SPC/E water along with the self-diffusivity of water has been computed and the experimental values as well as the reported computational values available in the literature are listed.

System	Density(Kg/m^3)	Self-diffusivity (10^{-9}m^2/s)	
		UO_2^{2+}	Water
Model – MG	1013.05 ± 0.38	0.738 ± 0.05	2.154 ± 0.01
Model – ML	1013.40 ± 0.12	0.702 ± 0.03	2.283 ± 0.09
Model – GW	1013.44 ± 0.14	1.052± 0.38	2.432 ± 0.09
Model – MA	1013.10 ± 0.13	1.070 ± 0.02	2.312 ± 0.11

The experimental value for self-diffusion coefficient of uranyl ion was taken from 0.68 x 10^{-9} m^2/s as direct while 0.426 to 0.759 x 10^{-9} m^2/s as indirect[15]. The self-diffusion coefficients reported in the literature are 0.61 ± 0.09 x 10^{-9} m^2/s, 0.94 ± 0.03 x 10^{-9}m^2/s (using GW), 0.85 ± 0.04 x 10^{-9}m^2/s (using model-1) and 0.88 ± 0.03 x 10^{-9}m^2/s (using model-2)[9].The reported self-diffusivity of water is 2.52 ± 0.01 x 10^{-5} cm^2/s.[38]

Table S2. Comparison of structural parameter obtained from U – O_W PCFs for all the models. The reported experimental and calculated values computed from quantum mechanics calculation or molecular mechanics or CPMD/AIMD are also listed here to understand the geometrical parameters obtained from the present study.

System	1st peak location (Å)	1st peak height	1st Hydration shell radius (Å)	Coordination number
Model – MG	2.55	7.24	3.15	5.75
Model – ML	2.45	8.49	3.25	5.75
Model – GW	2.45	9.71	3.25	5.85
Model – MA	2.45	10.09	3.15	5.92

The experimental mean values for U – O_W distance of aqueous uranyl are 2.41Å[40-42] from X-ray absorption fine structure spectroscopy (XAFS) measurement and 2.42Å[43-44] from X-ray scattering data. The experimental values of coordination numbers varies from 4.5 to 5.3 obtained from XAFS data[41-43, 45,46] and 4.5, 5, 6 from EXAFS (extended X-ray absorption fine structure spectroscopy)[47].

Model	U⋯O_W (Å)	Model	U⋯O_W (Å)
GW, Model 1,Model 2	2.49, 2.36, 2.40[9]	CPMD	2.47[16]
QMCF – MD	2.49[12]	MM - MD	2.42[11]
MM – MD	2.40[21]	B3LYP	2.37 – 2.42[49]
MD	2.46[14]	CPMD	2.48[18]
MD	2.44[38]	MM – MD	2.40[10]
CPMD	2.44 – 2.46[48]	AIMD	2.47[16], 2.48[18]

Table S3. Self-diffusion coefficients of uranyl ion, nitrate ion and water molecule present in aqueous phase calculated from MD simulations for a wide range of uranyl nitrate concentrations.

System	Self-diffusion coefficient ($10^{-9}m^2/s$)		
	UO_2^{2+}	NO_3^-	H_2O
5-U	0.677± 0.09	0.676 ± 0.09	2.306 ± 0.01
10-U	0.557 ± 0.14	0.662 ± 0.08	2.239± 0.02
25-U	0.527 ± 0.11	0.656 ± 0.08	2.031 ± 0.04
50-U	0.457 ± 0.06	0.649 ± 0.04	1.748 ± 0.07
70-U	0.368 ± 0.05	0.588 ± 0.05	1.564 ± 0.05
85-U	0.333 ± 0.04	0.570 ± 0.03	1.466 ± 0.02
100-U	0.265 ± 0.01	0.548 ± 0.03	1.287 ± 0.02
120-U	0.260 ± 0.01	0.511 ± 0.04	1.168± 0.03

Table S4. Shear viscosity calculated from NEMD simulation for all the systems with the effect of concentrations of uranyl nitrate.

System	Shear Viscosity (mPa.s)	System	Shear Viscosity (mPa.s)
5-U	0.940	70-U	1.662
10-U	0.896	85-U	1.971
25-U	1.229	100-U	1.912
50-U	1.498	120-U	2.692

Table S5. Shear viscosity and surface tension computed from MD simulations with the effect of nitric acid molarities (associated form of HNO_3).

System	Shear Viscosity (mPa s)	Surface Tension (mN/m)
85U-1M	1.319 ± 0.01	115.31 ± 3.2
85U-2M	1.352 ± 0.01	112.01 ± 3.1
85U-3M	1.706 ± 0.02	116.21 ± 3.1
85U-4M	2.087 ± 0.01	114.99 ± 2.2

Table S6. Calculated tetrahedral order parameter (q) for various system.

System	S_g	Orientation Tetrahedral order ($q = 1 - S_g$)
SOL	0.0923	0.9077
5-UO2	0.1097	0.8903
10-UO2	0.1104	0.8896
25-UO2	0.1189	0.8811
50-UO2	0.1203	0.8797
70-UO2	0.1232	0.8768
85-UO2	0.1278	0.8722
100-UO2	0.1297	0.8703
120-UO2	0.1348	0.8652

References

R1. Gasparotto, P.; Hassanali, A.A.; Ceriotti, M. Probing defects and correlations in the hydrogen-bond network of ab initio water**,** J. Chem. Theory Comput., **2016**, 12, 1953–1964.

R2. Giberti, F.; Hassanali, A.A. The excess proton at the air-water interface: The role of instantaneous liquid interfaces**,** J. Chem. Phys. **2017**, 146, 244703.

R3. Ansari, N.; Dandekar, R.; Caravati, Sosso, G.C.; Hassanali, A.A. High and low density patches in simulated liquid water**,** J. Chem. Phys. **2018**, 149, 204507.

R4. Chau, P.L.; Hardwick, A.J. A new order parameter for tetrahedral configurations, Mol. Phys., **1998**, 93, 3, 511- 518.