ESI

Structure and Dynamics of Dissociated and Un-dissociated Form of Nitric Acid and Its Implications at Interfacial Mass Transfer: Insights from Molecular Dynamics Simulations

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Text-S1

Bonded and Non bonded interaction

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

$$U_{BONDED} = \sum_{bonds} K_r(r_{ij} - r_{eq})^2 + \sum_{angles} K_\theta(\theta_{ijk} - \theta_{eq})^2 + \ ) \quad \text{(S1)}$$

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. 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.[43, 46-49]

The Non-bonded interaction between the atoms are calculated by Lennard-Jones potential and is represented as[43, 46-49]

$$U(r_{ij}) = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_o r_{ij}}. \quad \text{(S2)}$$

The first term represent the van der Waals interaction and the second term as electrostatic interaction between atoms i and j respectively.

$$U_{TOTAL} = U_{BONDED} + U_{NON\,BONDED} = \sum_{bonds} K_r(r_{ij} - r_{eq})^2 + \sum_{angles} K_\theta(\theta_{ijk} - \theta_{eq})^2 + \ ) - \varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} \quad \text{(S3)}$$

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:

$$\lim_{t\to\infty} < (r(t) - r(t_0))^2 > \ = 6Dt \quad \text{(S4)}$$

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.[54]

Text-S3

Hydrogen bond and tetrahedrality

Definition of hydrogen bonding:

In computer simulation the potential of interactions between molecules have been introduced without distinguishing hydrogen bonding presence in it. So, some additional criteria have to be used to identify between which molecules this H – bonding occurs. The important criterion is geometrical which differentiates between H – bonded and non H – bonded pairs of molecules. Let us assume the two molecules are to be hydrogen bonded if the following conditions are simultaneously satisfied,[60-64]

I. The oxygen-oxygen distance (R_{OO}) does not exceed some boundary value and it is less than 3.6 Å.

II. The distance between donor hydrogen and acceptor oxygen (R_{OH}) in neighbouring molecule also does not exceed some value and it 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◦.

So, the dynamics of hydrogen bonds among molecules present in the medium is investigated by calculating the intermittent hydrogen bond auto-correlation function. The time autocorrelation function relates the probability of the H-bond existing at a given starting point t = 0 will also exist at the next instant t, regardless whether the H – bond was broken or not in the interval [0 to t] and whether it will exist after the instant t.

$$C(t) = \frac{\langle h(0)\, h(t)\rangle}{\langle h(0)\, h(0)\rangle} \tag{S5}$$

where, h(t) measures the existence of H – bonds at any time t. The value of h(t) becomes unity, if the particular tagged pair of water molecules is hydrogen bonded at time t, according to adopted geometry criteria for H bond relation or zero if the H – bond is absent. 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 to enrich the present works. The tetrahedrality parameter following the prescription of Chau and Hardwick was determined for pure solvent and uranyl solution.

The tetrahedral order parameter is composed of two parts. One is angular part (S_g) and other is distance part (S_k). Orientational tetrahedral order (q) is the widely used parameter where the q varies from 0 (belongs to ideal gas) to 1 (for regular tetrahedron). The angular part can be expressed as

$$S_g = \frac{3}{8}\sum_{j=1}^{3}\sum_{k=j+1}^{4}\left(\cos\Psi_{jk} + \frac{1}{3}\right)^2 \tag{S6}$$

where, ψ_{jk} denotes angle between the lines joining the oxygen atom of the water molecule and its nearest neighbour oxygen atoms j and k. Then the orientational tetrahedral order can be written as

$$q = 1 - S_g \tag{S7}$$

where, q signifies the change in local structure of liquid water in the influence of solutes and surfaces. When the S_g increases, q decreases indicating deviation from regular tetrahedral structure of water.

Text-S4

Distribution coefficient:

The distribution constant has been calculated for various nitric acid models considering the interfacial zone where both the phases are present. Distribution constant describes the ratio between the numbers of molecules extracted by the organic phase and the numbers of molecules remained in the aqueous phase as reported recently by Sahu et al. [J Mol. Liq., 2021, **330**, 115621 (1-14)]. Therefore, the uranyl ions involved in the complex formation with TiAP may be considered as extracted by the organic phase and the rest of the uranyl ions are retained in the aqueous phase. The interfacial zone is considered here from 2 nm to 4 nm towards x-direction of the box length consists of blurred or rough interface to account the uranyl ions participated in the complex formation. Interfacial zone is decided normally from the die out region of each phase obtained from the density profile for Aqueous–organic system as shown in **Figure 6**. The value of the interfacial zone is chosen around 0.5 nm away from the die out position of each phase at both sides of the interface as shown in **Figure 7**. [J. Mol. Liq., 2021, **343**, 117599 (1-13)]

Text-S5

Methodology for determination of Total interface thickness from density profile:

The corresponding water–dodecane interface thickness has been calculated using water-dodecane density profile. The position of organic molecules at the aqueous edge and the water molecules at the organic edge are represented by the vertical lines and the distance between two vertical lines indicating the interface thickness (shown by green lines in **Figure 2**). [J. Mol. Liq., 2019, **277**, 217−232]

Text-S6

Equation for calculation of Total interface thickness:

The model equation relates the total interface thickness and the interfacial tension, γ, via the bulk correlation length as given below:

$$w_t^2 = C\frac{k_B T}{\gamma} ln\left(\frac{L_{II}}{L_b}\right) \quad (1)$$

$$C = \frac{(\sigma_{Water} + \sigma_{TiAP} + \sigma_{dodecane})}{1.4\,\sigma_{water}} \quad (2)$$

$$L_b = L_{W-T} * x_{TiAP} + L_{W-D} * x_{Dodecane} \quad (3)$$

where, w_t represents the total interface thickness, k_B is the Boltzmann constant, T is the temperature, L_{II} is the box dimension along the x or y direction and L_b provides the bulk correlation length in terms of the molecular length. Here the weighted average of bulk correlation length is used [see eqn. (3)] as discussed in our previous studies. [J. Mol. Liq., 2019, **277**, 217–232] The molecular diameters of TiAP, dodecane, water, UO_2^{2+}ion are calculated from the molecular volume using COSMOtherm package [Chem. Phys. Lett., 1989, **162**, 165–169] which are taken from our previous work. $Here, x_{TiAP}$ and $x_{Dodecane}$ represent the mole fraction of TiAP and dodecane molecule. [J. Mol. Liq., 2021, **343**, 117599 (1-13)]

The interfacial thickness using capillary wave theory (CWT) is written as[58]:

$$w_c^2 = \frac{k_B T}{2\pi\gamma} ln\left(\frac{L_{II}}{L_b}\right) \quad (4)$$

where, k_B and T are Boltzmann constant and temperature. L_{II} is the box size along the x or y direction and L_b denotes the bulk correlation length in terms of the molecular length. The L_b is computed using equation (3).

The intrinsic interface thickness (w_i) is related to the total interface thickness as,

$$w_i^2 = w_t^2 - w_c^2 \quad (5)$$

Table S1: **Bonded Forcefield Parameters**

Molecules	Bonds(i-j)	K_r ($kJmol^{-1}nm^{-1}$)	r_{eq} (nm)
H_3O^+	H-O	231154	0.096
NO_3^-	N-ON	125400	0.126
HNO_3	O-H	231154	0.103
	N-O	125400	0.126
Molecules	Angles(i-j-k)	K_θ ($kJmol^{-1}rad^{-2}$)	θ_{eq} (degree)
H_3O^+	H-O-H	418.2	104.5
NO_3^-	O-N-O	627.0	120.0
HNO_3	H-O-N	188.3	105.3
	O-N-O	627.0	120.0

Table S2: **Non bonded forcefield parameters**

Molecules	site	σ (nm)	ε (kJ/mol)
H_3O^+	H	0.100	0.000
	O	0.296	0.882
NO_3^-	N	0.315	0.711
	O	0.286	0.882
HNO_3	H	0.250	0.125
	N	0.325	0.711

	OH	0.312	0.711
	O1	0.296	0.879
	O2	0.296	0.879

Table S3: **Bonded Forcefield Parameters**

Molecules	Bond(i-j)	K_r ($kJmol^{-1}nm^{-1}$)	r_{eq} (nm)
TiAP	O2-P	219660	0.148
	P-Os	96232	0.161
	Os-C	133888	0.144
	C-C	112131.2	0.153
	C-H	142256	0.110
Dodecane	C-C	112131.2	0.153
	C-H	142256	0.110
UO_2^{2+}	U-OU	2090000	0.180
Molecules	Angle(i-j-k)	K_θ ($kJmol^{-1}rad^{-2}$)	θ_{eq} (degree)
TiAP	O2-P-Os	418.4	114.3
	P-Os-C	418.4	121.2
	Os-C-C	209.2	109.3
	Os-C-H	146.4	109.2
	Os-P-Os	188.3	102.7
	C-C-C	244.1	112.7
	C-C-H	156.9	110.7
	H-C-H	138.1	107.8
Dodecane	C-C-C	244.1	112.7
	C-C-H	156.9	110.7
	H-C-H	138.1	107.8
UO_2^{2+}	OU-U-OU	627.0	180.0

Table S4: Non bonded forcefield parameters

Molecules	site	σ (nm)	ε (kJ/mol)
TiAP	O2	0.315	0.8368
	P	0.374	0.8368
	Os	0.290	0.5857
	C	0.350	0.2761
	H	0.250	0.1255
Dodecane	C	0.350	0.2761
	H	0.250	0.1255
UO_2^{2+}	U	0.295	0.53
	OU	0.383	0.057

Table-S5: Dimensions of simulation box and composition

System	BOX Size	Composition
Undissociated	10.29 x 5.65 x 5.65	Water: 3000 nos., Uranyl ion: 70 nos., Nitrate ion: 140 nos., Nitric acid: 216 nos., TiAP: 150 nos. and Dodecane: 350 nos.
Dissociated	10.36 x 5.61 x 5.61	Water: 3000 nos., Uranyl ion: 70 nos., Nitrate ion: 356 nos., Hydronium ion: 216 nos., TiAP: 150 nos. and Dodecane: 350 nos.
Mixed	10.29 x 5.64 x 5.64	Water: 3000 nos., Uranyl ion: 70 nos., Nitrate ion: 248 nos., Hydronium ion: 108 nos., Nitric acid: 108 nos., TiAP: 150 nos. and Dodecane: 350 nos.

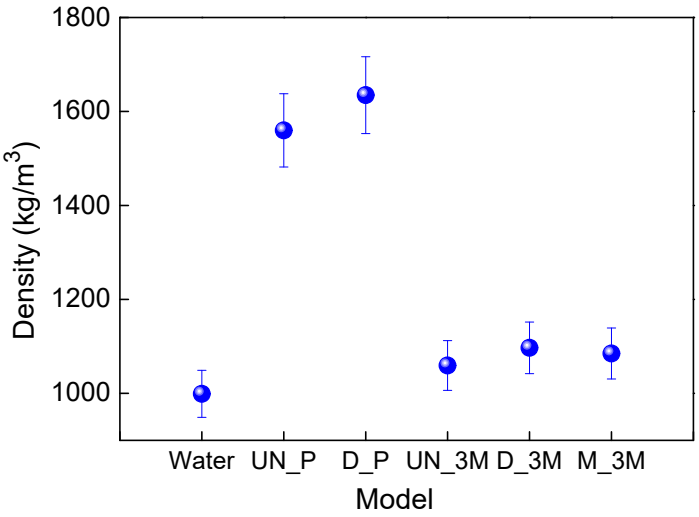

Figure S1. Ensemble averaged density vs composition

UN_P: Pure nitric acid with undissociated form.

D_P: Pure nitric acid with dissociated form.

UN_3M: 3M nitric acid with undissociated form.

D_3M: 3M nitric acid with dissociated form

M_3M: 3M nitric acid with mixed form

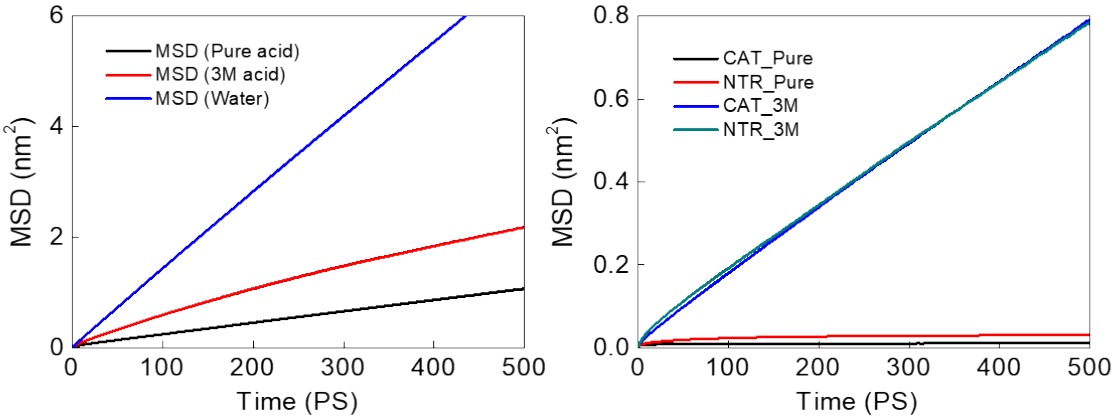

Figure S2. (a) MSD profiles of undissociated nitric acid in pure form and in solution form along with the water and **(b)** MSD profiles of dissociated nitric acid in pure form and in 3M solution form. (UN-Undissociated form, D-dissociated form and M-mixed form. NAC – undissociated nitric acid, CAT – hydronium ion and NTR – nitrate ion).