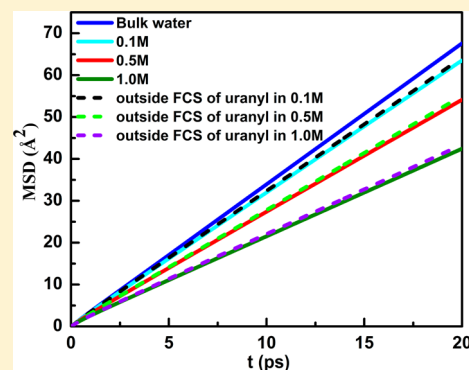


# Effect of Uranyl Ion Concentration on Structure and Dynamics of Aqueous Uranyl Solution: A Molecular Dynamics Simulation Study

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**ABSTRACT:** The effect of uranyl ion concentration on structure and dynamics of aqueous solutions of uranyl ions is investigated by molecular dynamics simulations. In order to get an idea about the effect of concentration of uranyl ions on local structural arrangements of water molecules around the uranyl ion, radial distribution functions of water molecules around the uranyl ion are analyzed for aqueous uranyl solutions of various concentrations. The concentration effect on translational dynamics has also been analyzed by calculating diffusion coefficients of uranyl ion, water, and nitrate ions in solution from their respective mean squared displacements. Mobility of water as well as uranyl ions has been found to decrease with increasing concentration of the uranyl ions. Orientational dynamics of water about different molecular axes of water have also been analyzed and decreasing orientational mobility of water with increasing uranyl concentration has been found. In order to get further insight into origin of slowing down of the translational mobility of water molecules with increasing uranyl ion concentration, two separate effects namely long-range effect of uranyl ions on the dynamics of water molecules beyond the solvation shell and short-range effect involving dynamics of solvation shell water have been analyzed. It is found that long-range effect is responsible for the slowing down of translational dynamics of water molecules in the presence of uranyl ions.



## 1. INTRODUCTION

Understanding the behavior of radiotoxic actinyl ions in aqueous solutions is of fundamental as well as technological importance due to its direct relevance to the nuclear fuel cycle. Knowledge of hydration and transport properties of these actinyl ions is essential for the development and improvement of the solvent extraction processes for recovering these ions from spent nuclear fuels or for understanding the migration characteristics of these radionuclides in hydrological conditions. As high level of radiotoxicity associated with these ions makes it difficult to study the properties of these ions experimentally, computational investigation based on molecular dynamics simulation has been proved to be a vital alternative for understanding the structural, dynamic, and thermodynamic behavior of these ions in clusters and in condensed phases.<sup>1–24</sup>

The pioneering work of Guilbaud and Wipff<sup>1–3</sup> on molecular dynamics simulation studies of aqueous solution of uranyl ions helps us to understand various aspects of uranyl hydration. On one hand, they have studied the complexation and hydration behavior of uranyl ions<sup>1,2</sup> and on the other hand they have generated force field parameters for uranyl ions from free energy calculations.<sup>3</sup> Wipff and co-workers<sup>5–11</sup> have carried forward their work on the behavior of uranyl and lanthanide ions in different solvation media. A detailed study on structure and free energy of uranyl hydration has also been presented recently by Rai et al.<sup>4</sup> and Kerisit et al.<sup>12</sup> On the basis of the free energy calculation, they have proposed modified force-fields for the uranyl-water system. These groups have also studied the bulk diffusion of uranyl ions at infinite dilution.<sup>13,23,24</sup>

There have been other researchers who have studied the characteristics of uranyl ion using first principle calculations or molecular dynamics simulations. For instance, Spencer et al.<sup>14</sup> have studied the hydration of the actinyl cations, uranyl ( $\text{UO}_2^{2+}$ ) and plutonyl ( $\text{PuO}_2^{2+}$ ), by performing Kohn–Sham density functional theory calculations. They have provided preliminary evidence that there will be no qualitative and very little quantitative difference between the uranium and plutonium species. Various other groups have also used quantum mechanical methods to understand uranyl–water interaction<sup>15</sup> and coordination environments.<sup>16</sup> Frick et al.<sup>17,18</sup> employed quantum mechanical charge field molecular dynamics (QMCF-MD) framework for simulating the behavior of uranyl(VI) ( $\text{UO}_2^{2+}$ ) and uranyl(V) ( $\text{UO}_2^+$ ) ions in aqueous solution. Apart from these investigations, several other investigations on structure and dynamics of the uranyl ion and its different complexes at various solid–liquid and liquid–liquid interfaces have been reported.<sup>19–22</sup>

In a series of investigations, Maginn and co-workers<sup>4,23</sup> have developed force fields for the different actinyl ions in their aqueous solution by taking into account the many-body solvation effects. Using this force field, Rai et al.<sup>4</sup> presented a detailed study on the radial and three-dimensional arrangements of water molecules in the solvation shell of the uranyl ions. In most of these studies structural arrangement of water

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molecules around the uranyl ions and free energy aspect of uranyl hydration have been investigated. Very recently, Maginn and co-workers<sup>24</sup> have studied translational dynamics and residence time of water in the solvation shell of different actinyl ions. In this study and most of the simulation studies, only one uranyl ion in a box of water is considered. Presence of the multiple ions in the solution may modify the properties of the aqueous uranyl solution. Water being a hydrogen-bonded network with tetrahedral structure, it is expected<sup>25</sup> that presence of a large number of uranyl ions in solution will perturb the tetrahedral structure and thereby modify the structure and dynamics of the aqueous uranyl solution. As far as we are aware, the effect of concentration of the uranyl ions on liquid structure and dynamics of different species in the solution has not been investigated in detail. Therefore, in the present study, we intend to investigate the effect of concentration of uranyl ions on structural and dynamical characteristics of water as well as uranyl and other co-ions using atomistic molecular dynamics (MD) simulations.<sup>26</sup> Proper understanding of the structure and dynamics of the ionic solution can be achieved from the knowledge of the behavior of water molecules in the solvation shells of ions. MD simulation has the advantage of probing the behavior of solvation water at the molecular length scale. Therefore, we use MD simulation here to understand the effect of concentration of the uranyl salt on the dynamics of solvation shell water too.

## 2. MODELS AND SIMULATION DETAILS

In the present investigation, we have prepared aqueous solutions of divalent uranyl ions,  $\text{UO}_2^{2+}$ , of different concentrations by solvating appropriate number of uranyl ions in a cubic box containing around 500 water molecules with a bulk water density of around  $0.98 \text{ g/cm}^3$ . The neutrality of the system was maintained by introducing required number of negative ions (nitrate) in the system. Three different systems are considered: (i) one uranyl ion (hereinafter, we call it system U1), (ii) five uranyl ions (hereinafter, we call it system U5), and (iii) 10 uranyl ions (hereinafter, we call it system U10). The total number of molecules, i.e., water plus uranyl nitrate in the system, is kept fixed at 513 molecules. The corresponding concentrations of the aqueous solutions of uranyl ions are 0.106 M for U1, 0.53 M for U5, and 1.06 M for U10 systems. The concentration range used here is relevant to the back end of the nuclear fuel cycle during the reprocessing of the spent fuel from uranium-based reactors.<sup>27,28</sup> It is also of academic interest to investigate the effect of concentration on the structural and dynamical aspects of the uranyl solution. Although in the computational study on uranyl solution generally bare uranyl ions are considered, it should be noted that the uranium speciation in aqueous solutions is not limited only to the isolated uranyl ion. Simulations were performed in canonical (NVT) ensemble with the molecular dynamics extended system approach of Nose.<sup>26</sup> All the simulations were carried out at a target temperature of 298 K using periodic boundary conditions and minimum image convention in all three directions. We have used atomistic model with one uranium and two oxygen sites for the uranyl ion and one nitrogen and three oxygen sites for the nitrate ion. Nonbonded site–site intermolecular interaction is modeled with Lennard–Jones plus Coulomb interactions and intramolecular interaction for uranyl and nitrate ions consist of bond and angle terms. Although the TIP3P model has been used in most of the calculation presented here, for comparison we have also used the SPC/E

water model, and the corresponding force field parameters for uranyl ion were taken from a recently published work.<sup>23</sup> The potential energy of the system is given by the equation

$$U = \sum_{\text{bonds}} 0.5K_r(r - r_{eq})^2 + \sum_{\text{angles}} 0.5K_\theta(\theta - \theta_{eq})^2 + \sum_{i < j} \left[ \frac{q_i q_j}{r} + 4\epsilon \left\{ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right\} \right] \quad (1)$$

where the symbols have their usual meaning. The first two terms are the intramolecular (bonded) potentials and the third term represents the nonbonded interaction, which involves the usual Lennard–Jones potential. The parameter sets for both inter- and intramolecular interactions are given in Table 1.<sup>1,4,29,30</sup> All cross parameters for the LJ potential were obtained by using the Lorentz–Berthelot mixing rule.

**Table 1. Force Field Parameters**

Nonbonded Parameters			
atom type	$\sigma$ (Å)	$\epsilon$ (kJ)	$q/e$
U	3.35	0.1145	+2.500
O <sub>U</sub> (uranyl oxygen)	2.85	1.8328	−0.250
N	3.12	0.6694	+0.626
O <sub>N</sub> (nitrate oxygen)	2.94	0.6276	−0.542
O <sub>W</sub> (TIP3P)	3.15	0.6364	−0.834
H <sub>W</sub> (TIP3P)	—	—	+0.417
Bonded Parameters			
bond type	$r_{eq}$ (Å)	$K_r$ (kJ mol <sup>−1</sup> nm <sup>−2</sup> )	
U–O <sub>U</sub>	1.80	418400	
N–O <sub>N</sub>	1.26	251040	
angle type	$\theta_{eq}$ (deg)	$K_\theta$ (kJ mol <sup>−1</sup> rad <sup>−2</sup> )	
O <sub>U</sub> –U–O <sub>U</sub>	180	1255.2	
O <sub>N</sub> –N–O <sub>N</sub>	120	1255.2	

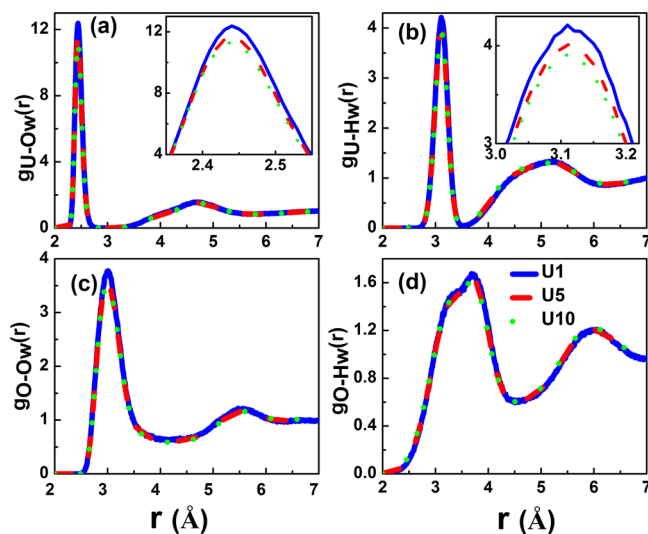
Electrostatic interactions were treated using Ewald's method.<sup>26</sup> During the simulation, the OH bond lengths and the HH distance of the water molecules were constrained using the RATTLE algorithm, and the velocity Verlet algorithm<sup>26</sup> was used for integrating equations of motion with a time step of 1 fs. For all nonbonding interactions, a cutoff distance of 12.0 Å in real space was used. For each system, the production run was for 8 ns after equilibration for 1 ns and the trajectories were saved at every 0.01 ps. For uncertainty in the calculated quantities, usual standard deviations were obtained from block averaging of eight independent simulations of 1 ns each.

## 3. RESULTS AND DISCUSSION

The structure and dynamics of aqueous solution of uranyl ions have been estimated using MD simulations. Our aim is to investigate the effect of uranyl ion concentration on the structure and dynamics of water and different ions present in the solution. The structural aspects are analyzed by calculating radial distribution functions (RDF) of water around different sites of the uranyl ion. Translational dynamics of different species including water has been investigated by analyzing mean squared displacement (MSD) of the corresponding species in solution. The orientational dynamics of water is also investigated by calculating orientational correlation functions around different molecular axes of the water molecules. In order to investigate the effect of uranyl ion concentration on

various properties, we have compared results obtained from U1, U5, and U10 systems containing one, five and ten uranyl ions respectively in around 500 water molecules. All these results pertaining to bulk uranyl solutions of different concentrations are presented in subsection 3(i). In order to get further insight, we have also analyzed uranyl concentration dependence on the dynamics of water in the solvation shells of uranyl ions and these results are presented in subsection 3(ii).

**(i). Structure and Dynamics of Different Species in the Bulk Aqueous Uranyl Solution.** In order to investigate the effect of increasing uranyl salt concentration on the structural aspects of the solution, we have calculated RDFs of two different water sites ( $O_w$  and  $H_w$ ) with respect to two uranyl sites (U and  $O_U$  of uranyl ion), and these are presented in Figure 1. The first hydration shell of the uranium atom of the



**Figure 1.** Radial distribution functions for (a)  $O_w$  around uranium, (b)  $H_w$  around uranium (c)  $O_w$  around uranyl-oxygen ( $O_U$ ) and (d)  $H_w$  around  $O_U$  for different concentrations of uranyl ions. In the insets of parts a and b, the first peak of the respective RDF is magnified.

uranyl ion as indicated by a sharp peak (see Figure 1a) is observed to be at a distance of 2.44 Å, whereas the first peak of  $H_w$  RDF (see Figure 1b) around U appears at 3.12 Å. Thus, the  $O_w$  atom of water is closer to the uranium of  $UO_2^{2+}$  as compared to  $H_w$  atom of water. Around the oxygen atom of the uranyl ion,  $O_w$  sites of water are distributed with first peak at around 3.0 Å (see Figure 1c), whereas RDF for hydrogen ( $H_w$ ) atoms of water shows a broad first peak with two small humps at around 3.2 and 3.7 Å (see Figure 1d). It is surprising to notice that water oxygen ( $O_w$ ) comes closer to  $O_U$  of the uranyl ion than  $H_w$  of water. This is probably because of the fact that large positive charge (+2.5) on U site overcompensates the negatively charged oxygen atoms leading to an overall positively charged environment around the uranyl ion as a whole. Similar RDFs have been reported in many previous investigations on uranyl ion.<sup>1,2,4,16,17,19,20,30</sup> The first minimum for distribution of  $O_w$  atoms around uranium atom of uranyl ion comes at around 3.0 and this value is used as the radius of the first coordination shell around uranium atom of uranyl ion for calculating coordination number and analyzing dynamical behavior of the solvation water. It is interesting to note that with the change in uranyl concentration, overall RDF and hence liquid structure does not change much, although there is

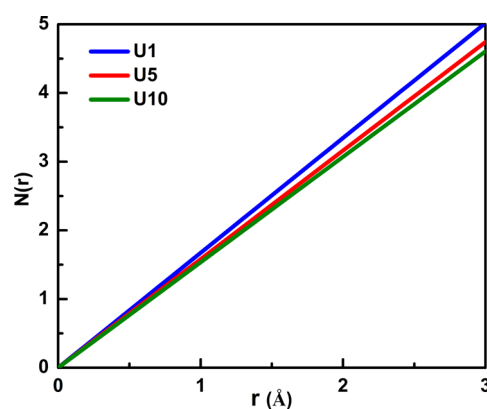
slight reduction in the peak of the RDF as we go from U1 to U10 system (see the insets of Figure 1, parts a and b).

We have also calculated the coordination number as defined by the number of water molecules in the first solvation shell (defined by the position of the first minimum in the RDF) around different species in the solution and tabulated in Table 2. The coordination number of water on an average was

**Table 2.** Average Number of Water Molecules in the First Coordination Shell

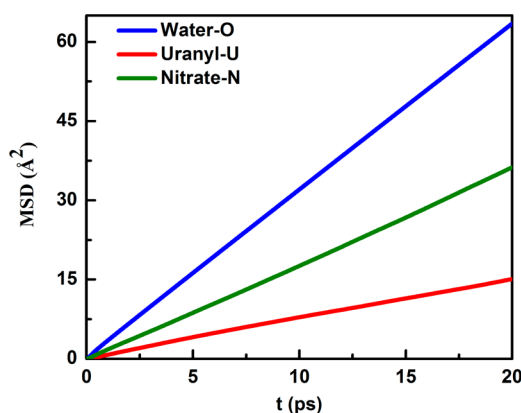
system	central atom	coordination number as defined by number of water molecules in the first shell
bulk–water (TIP3P)	water–oxygen	5.4
bulk–water (SPC/E)	water–oxygen	4.4
U1 (TIP3P)	uranium	5.0
U5 (TIP3P)	uranium	4.7
U10 (TIP3P)	uranium	4.6
U1 (uranyl nitrate–TIP3P)	nitrogen	10.2

observed to be around 5.4 for bulk TIP3P water whereas it is around 4.4 for bulk SPC/E water. In case of aqueous solution of uranyl ions, the coordination number of uranium with respect to water molecules comes out to be around 5 and is consistent with the reported value.<sup>1,3,4,10,14–17,20,21,23</sup> There is a slight reduction in the coordination number values as we move from U1 to U5 to U10, and this slight reduction is due to decrease in the peak height of RDF as shown in insets of Figure 1. The running coordination number  $N(r)$  as a function of radial distance from uranyl ions, defined as  $N(r) = 4\pi\rho_0 \int_0^r x^2 g(x) dx$ ,  $\rho_0$  being the bulk water density, is also calculated and shown in Figure 2. It is obvious that running coordination number  $N(r)$  decreases from U1 to U5 to U10 systems.



**Figure 2.** Running coordination number around U as a function of radial distance of water from uranyl ion.

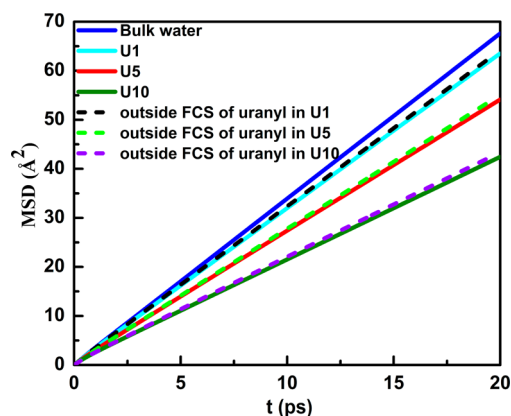
For dynamical aspects, first, we analyze the dynamical behavior of different species in the aqueous uranyl solution with only one uranyl ion (i.e., U1 system). The translational dynamics of the U1 system is analyzed in terms of MSD of uranium atom of the uranyl, nitrogen atom of the nitrate ions and oxygen atom of water molecules as shown in Figure 3. The mean squared displacements for different ions and water molecules reveal considerable difference in diffusivities of these species in U1 system. The sequence of decreasing diffusivities



**Figure 3.** MSD for oxygen of water (blue line), uranium of uranyl (red line) and nitrogen of nitrate (green line) for the U1 system.

as observed from the slopes of the MSD curves is oxygen (water) > nitrogen (nitrate) > uranium (uranyl) (see Figure 3). Water is the most mobile of all the species. It is not surprising that uranium being the heaviest atom in the system has the lowest diffusivity.<sup>30</sup> Nitrogen has diffusivity in between that of uranium and water oxygen.

The effect of increasing concentration of uranyl ion on the dynamics of water and uranyl ion is also investigated. Let us first analyze translational dynamics of the water molecules in the aqueous uranyl solutions of different concentrations. For comparison, the MSD of bulk water (as obtained from the simulation of neat bulk water) is also calculated. The MSD profiles for water oxygen in bulk water and in the aqueous solution of uranyl ions of different concentrations are compared in Figure 4. In case of the U1 system, diffusivity of water

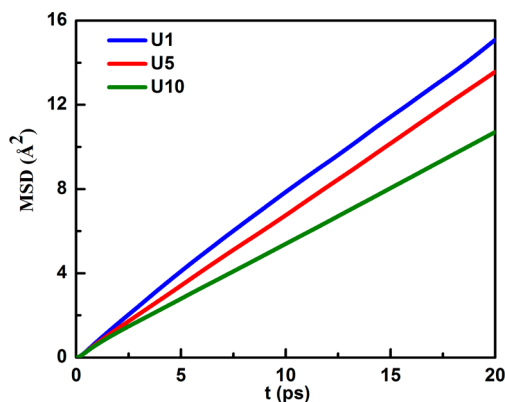


**Figure 4.** MSD profiles for water oxygen molecules in bulk water, U1 system, U5 system, and U10 system. The dashed lines represent MSD of only those water molecules that are outside the first coordination shell (FCS) of uranium in the U1, U5, and U10 systems.

molecules does not deviate much from that of the bulk water. In systems with higher uranyl concentrations, i.e., in the U5 and U10 systems, there is a prominent variation of the MSD line from that of the bulk water, indicating a considerable change in the dynamics of water. From the slopes of these MSD lines it is evident that average diffusivity of the water molecules in the concentrated uranyl solution decreases as compared to bulk water. It may be due to the fact that water molecules in the solvation shells of uranyl ions are probably diffusing slowly along with the slower moving uranyl ions. We shall try to get

further insight into this aspect by analyzing the dynamics of solvation water in the next subsection. Also, to confirm whether there is any long-range effect of the uranyl ions on the water dynamics, the MSD of water molecules outside the first coordination shell (FCS) of uranyl ions is estimated for U1, U5 and U10 systems (dashed lines in Figure 4). Since there is not much difference in the MSD of these water molecules (dashed lines) as compared to that calculated by taking all the water molecules in the system (solid lines) for all the three systems, it can be concluded that one of the reasons for the slowing down of the overall translational mobility of water is the long-range effects of the uranyl ions on the mobility of water outside the solvation shell.

Now, we turn our attention to the effect of increasing concentration on the diffusivity of uranyl ion. In Figure 5, we



**Figure 5.** MSD profiles for uranium atom in U1 (blue line), U5 (red line), and U10 (green line) systems.

have shown the MSD of U atom of the uranyl ion in three different systems with different uranyl ion concentrations. In this case also, the diffusivity of the uranyl ion is found to be reducing with increasing concentration of uranyl ions in aqueous solution (see Figure 5).

The mean square displacement is a good measure of translational mobility of a fluid in a given environment and therefore gives us information about the diffusion processes in the medium. In the long time limit, the MSD is related to the self-diffusion coefficient ( $D$ ) of the fluid through the well-known Einstein relation<sup>30–32</sup>

$$D = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle \Delta r^2 \rangle}{\Delta t} = \frac{1}{2d} \lim_{t \rightarrow \infty} \frac{\langle |\mathbf{r}(t) - \mathbf{r}(0)|^2 \rangle}{\Delta t} \quad (2)$$

where  $\mathbf{r}(t)$  is the position vector at time  $t$  and  $d$  is the dimensions of the system. The diffusion constant is obtained from the slope of a linear fit of the respective MSD data calculated from simulation trajectory as a function of time. The greater the slope of linear portion of MSD curve, the higher is the diffusivity. The diffusivity values along with the associated uncertainty (standard deviation) as estimated from the slopes of the MSD lines obtained from different simulation runs are given in Table 3. The diffusivity values tabulated in Table 3 suggest that there is concentration dependence of the diffusivity for all the three species namely, uranyl ions, nitrate ions and water molecules. The values of diffusion coefficients for bulk water, water in the U1 system, and uranium atom of uranyl ion in the U1 system are similar to those given by Tiwari et al. for the TIP3P model of water.<sup>24</sup> The self-diffusion coefficients for



**Table 3. Diffusion Coefficient Values for Different Systems**

serial no.	atom/group	system	diffusion coefficient ( $D_{PBC}$ ) from the slope of MSD curve ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	diffusion coefficient ( $D_0$ ) corrected for system size ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )
1	U of $\text{UO}_2$ (TIP3P water)	U1	$1.37 \pm 0.11$	$2.16 \pm 0.11$
2	U of $\text{UO}_2$ (TIP3P water)	U5	$1.09 \pm 0.05$	$1.88 \pm 0.05$
3	U of $\text{UO}_2$ (TIP3P water)	U10	$0.87 \pm 0.02$	$1.66 \pm 0.02$
4	U of $\text{UO}_2$ (SPC/E water)	U1	$0.60 \pm 0.04$	$0.94 \pm 0.04$
5	U of $\text{UO}_2$ (SPC/E water)	U5	$0.56 \pm 0.02$	$0.90 \pm 0.02$
6	U of $\text{UO}_2$ (SPC/E water)	U10	$0.46 \pm 0.01$	$0.80 \pm 0.01$
7	N of nitrate (TIP3P water)	U1	$2.88 \pm 0.16$	$3.67 \pm 0.16$
8	N of nitrate (TIP3P water)	U5	$2.33 \pm 0.13$	$3.12 \pm 0.13$
9	N of nitrate (TIP3P water)	U10	$1.82 \pm 0.06$	$2.61 \pm 0.06$
10	$\text{O}_W$ (TIP3P water)	bulk water	$5.60 \pm 0.12$	$6.39 \pm 0.12$
11	$\text{O}_W$ (TIP3P water)	U1	$5.28 \pm 0.02$	$6.07 \pm 0.02$
12	$\text{O}_W$ (TIP3P water)	U5	$4.50 \pm 0.02$	$5.29 \pm 0.02$
13	$\text{O}_W$ (TIP3P water)	U10	$3.58 \pm 0.02$	$4.37 \pm 0.02$
14	$\text{O}_W$ (SPC/E water)	bulk water	$2.76 \pm 0.08$	$3.1 \pm 0.08$
15	$\text{O}_W$ (SPC/E water)	U1	$2.52 \pm 0.01$	$2.86 \pm 0.01$
16	$\text{O}_W$ (SPC/E water)	U5	$2.20 \pm 0.02$	$2.54 \pm 0.02$
17	$\text{O}_W$ (SPC/E water)	U10	$1.80 \pm 0.02$	$2.14 \pm 0.02$

uranyl ion were observed to be lower for SPC/E water as compared to those for TIP3P water. The diffusivity values obtained for water molecules and uranyl ions in aqueous uranyl solution with SPC/E water model are in good agreement with those obtained earlier using molecular dynamic simulations.<sup>24</sup> At this point it is important to mention that the diffusion coefficients are dependent on the system size.<sup>13,33</sup> This was not considered in the work carried out by Tiwari et al.<sup>24</sup> The size dependence of the diffusivity ( $D_{PBC}$ ) can be corrected by using the method adopted by Yeh et al.<sup>33</sup> and Kerisit et al.<sup>13</sup> The corrected system size independent diffusivity ( $D_0$ ) can be obtained from the equation

$$D_0 = D_{PBC} + \frac{2.837297K_B T}{6\pi\eta L} \quad (3)$$

where  $\eta$  and  $L$  are shear viscosity of water and simulation box length, respectively. Using the shear viscosity values for TIP3P<sup>33</sup> and SPC/E<sup>13</sup> water models, the diffusion coefficient values have been corrected for system size dependence and are given in Table 3.

The un-normalized diffusivity of the uranyl ions for the concentration range of 0.1–0.5 M is in the range of  $(2.16\text{--}1.88) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in TIP3P water, whereas for SPC/E water it is in the range of  $(0.94\text{--}0.90) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ . Higher diffusivity of the uranyl ions in TIP3P water can be attributed to higher bulk water diffusivity ( $6.39 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) in this case. The experimental values of un-normalized diffusivities as given by Awakura et al.<sup>34</sup> are in the range of  $(0.47\text{--}0.39) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  for similar concentration range (0.1–0.5 M). It is to note that the experimental diffusivity value in 0.1 M uranyl solution as given by Awakura et al.<sup>34</sup> normalized with respect to water diffusivity<sup>13</sup> ( $2.3 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ ) is considerably lower as compared to the same obtained from other experimental and

simulation studies (see Table 4). The corrected, normalized diffusivity values of uranyl ions with respect to the respective

**Table 4. Comparison of Normalized Diffusion Coefficient Values for Uranyl Ions in the U1 System with Experimental and Theoretical Results Available in the Literature**

sample no.	source <sup>a</sup>	$D_{\text{UO}_2}/D_{\text{H}_2\text{O}}^a$
1	<sup>e</sup> Awakura et al., 1987 <sup>34</sup>	0.204
2	<sup>e</sup> Kern and Orlemann, 1949 <sup>35</sup>	0.296
3	<sup>e</sup> Brown et al., 1954 <sup>36</sup>	0.295
4	<sup>e</sup> Marx and Bischoff, 1976 <sup>37</sup>	0.330
5	<sup>t</sup> Kerisit and Liu, 2010 <sup>13</sup>	0.333
6	present study (TIP3P water), U1 system	$0.338 \pm 0.018$
7	present study (SPC/E water), U1 system	$0.303 \pm 0.015$

<sup>a</sup>Key: a = pure water, e = experimental value, t = theoretical value.

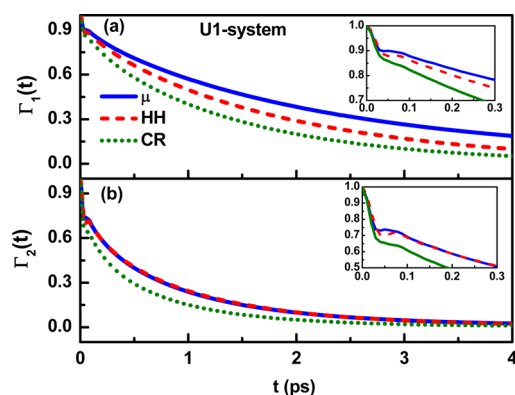
bulk water diffusivities in the U1 system are observed to be in overall good agreement with the diffusivity ratios obtained experimentally<sup>35–37</sup> or theoretically<sup>13</sup> (except the one given by Awakura et al.<sup>34</sup>) as shown in Table 4. Similar comparison of the normalized (with respect to water) diffusivity with the experimental one has been made by Kerisit et al.<sup>13</sup> and Maginn et al.<sup>24</sup> From the results obtained for TIP3P and SPC/E water models, it can be concluded that although the absolute values of diffusivities of uranyl ions are quite different for the two water models but the normalized diffusivity values compare fairly well. It is also observed that the normalized diffusivities of uranyl ion are comparable to those experimentally measured for other divalent positive ions such as  $\text{Mg}^{2+}$  (slightly lower),  $\text{Ca}^{2+}$ , and  $\text{Sr}^{2+}$  (both slightly higher) as given by Kerisit et al.<sup>13</sup>

Orientalional dynamics of water molecules can be obtained by analyzing orientational dynamics of various molecular

vectors of water. Here, we have considered three different unit vectors ( $u_\alpha$ ) along three different molecular axes, namely, (i) dipole moment vector ( $u_\alpha = \mu$ ) (ii) H–H vector ( $u_\alpha = \text{HH}$ ) (iii) a cross vector ( $u_\alpha = \text{CR}$ ), i.e., a vector perpendicular to the plane of water molecule. The time evolution of these three orientational vectors,  $u_\alpha$ , can be defined in terms of autocorrelation functions  $\Gamma_l^\alpha(t)$  of the form

$$\Gamma_l^\alpha(t) = \langle P_l(u_\alpha(t) \cdot u_\alpha(0)) \rangle \quad (4)$$

where  $P_l$  is the Legendre polynomial of order  $l$ . The angular brackets in the above equation represent average over time origins as well as the number of molecules.<sup>38</sup> The first ( $l=1$ ) and second ( $l=2$ ) order autocorrelation functions for the above-mentioned three unit vectors are given in Figure 6. As the figure



**Figure 6.** (a) First order and (b) second order orientational correlation functions of water molecules with respect to water dipole moment vector ( $\mu$ , blue solid line), water H–H vector (HH, red dashed line) and water cross vector (CR, green dotted line) for the U1 system.

suggests, there is a little anisotropy in case of  $\Gamma_1$ . Although not shown here, this anisotropy is also present in the rotational correlation function of bulk TIP3P water.

Visual inspection of the plots of the orientational correlation functions, as shown in the Figure 6 insets, indicates that there are two time scales in the relaxation of these functions: a very fast decay initially followed by a long-time relaxation. Therefore, in order to assess the two time scales, we have used a double exponential function  $S(t)$  of the form

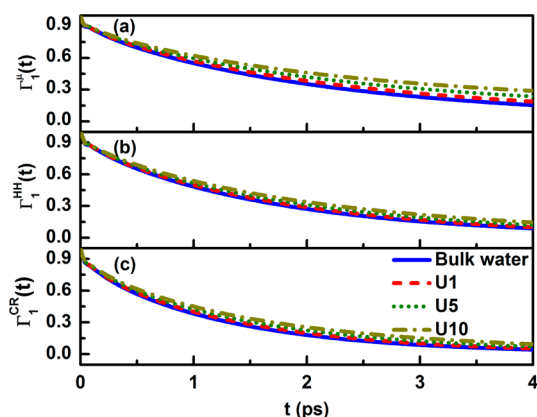
$$S(t) = A \exp\left(-\frac{t}{\tau_1}\right) + (1 - A) \exp\left(-\frac{t}{\tau_2}\right) \quad (5)$$

to fit the orientational time correlation functions. In the above equation,  $\tau_1$  and  $\tau_2$  represent, respectively, the time constants of longer and shorter time scales of the relaxation of  $S(t)$ , with  $A$  and  $(1 - A)$ , respectively, being their relative contributions.<sup>38</sup> The values of  $A$ ,  $\tau_1$ , and  $\tau_2$  for different systems as obtained from the fitting are given in Table 5. The effect of concentration of the uranyl ions on the rotational dynamics of water (all water molecules in solution) can be understood from plots in Figures 7 and 8. It is observed that for all the three different orientational correlation functions, the effect of increase in concentration of uranyl ions in aqueous solutions leads to a slight retardation of the rotational motion of water and this effect is more for the rotational motion of dipole moment vector as compared to other orientational vectors of water.

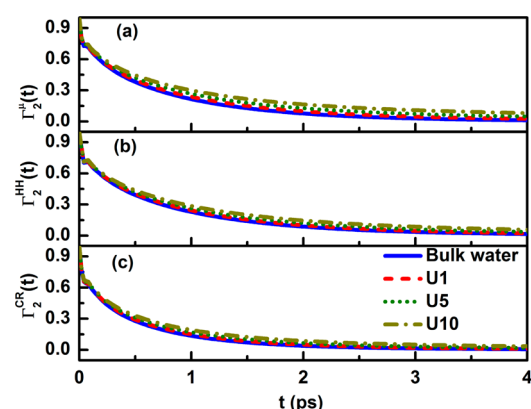
**(ii). Dynamics of Water in the Solvation Shell of Uranyl Ions.** In the previous subsection, we have shown that the translational dynamics of water (considering all the water molecules in the system) becomes slower with the increase in uranyl concentration. The reduced diffusivity of water in the concentrated solution may be due to solvation water. It is,

**Table 5. Values of Time Constants (in ps) of Longer ( $\tau_1$ ) and Shorter ( $\tau_2$ ) Time Scales of the Relaxation of  $S(t)$  and  $A$  (cf. eq 5) for Different Systems**

correlation function	bulk water	U1	U5	U10
$\Gamma_1^\mu$				
$A$	$0.83 \pm 0.004$	$0.75 \pm 0.01$	$0.57 \pm 0.008$	$0.54 \pm 0.004$
$\tau_1$	$2.37 \pm 0.01$	$2.93 \pm 0.08$	$4.55 \pm 0.09$	$6.32 \pm 0.17$
$\tau_2$	$0.20 \pm 0.01$	$0.4 \pm 0.04$	$0.82 \pm 0.02$	$0.91 \pm 0.006$
$\Gamma_1^{\text{HH}}$				
$A$	$0.86 \pm 0.02$	$0.861 \pm 0.003$	$0.85 \pm 0.004$	$0.83 \pm 0.006$
$\tau_1$	$1.75 \pm 0.02$	$1.85 \pm 0.02$	$2.02 \pm 0.02$	$2.28 \pm 0.03$
$\tau_2$	$0.07 \pm 0.004$	$0.092 \pm 0.004$	$0.13 \pm 0.01$	$0.18 \pm 0.01$
$\Gamma_1^{\text{CR}}$				
$A$	$0.835 \pm 0.001$	$0.82 \pm 0.004$	$0.8 \pm 0.007$	$0.76 \pm 0.008$
$\tau_1$	$1.31 \pm 0.004$	$1.42 \pm 0.01$	$1.61 \pm 0.02$	$1.88 \pm 0.04$
$\tau_2$	$0.07 \pm 0.004$	$0.09 \pm 0.004$	$0.13 \pm 0.006$	$0.19 \pm 0.01$
$\Gamma_2^\mu$				
$A$	$0.703 \pm 0.001$	$0.67 \pm 0.005$	$0.50 \pm 0.01$	$0.33 \pm 0.004$
$\tau_1$	$0.869 \pm 0.008$	$1.0 \pm 0.009$	$1.57 \pm 0.05$	$3.14 \pm 0.09$
$\tau_2$	$0.036 \pm 0.008$	$0.057 \pm 0.002$	$0.17 \pm 0.01$	$0.32 \pm 0.004$
$\Gamma_2^{\text{HH}}$				
$A$	$0.697 \pm 0.02$	$0.68 \pm 0.006$	$0.62 \pm 0.006$	$0.52 \pm 0.008$
$\tau_1$	$1.02 \pm 0.03$	$1.03 \pm 0.004$	$1.25 \pm 0.02$	$1.73 \pm 0.04$
$\tau_2$	$0.037 \pm 0.003$	$0.045 \pm 0.001$	$0.08 \pm 0.006$	$0.15 \pm 0.006$
$\Gamma_2^{\text{CR}}$				
$A$	$0.638 \pm 0.005$	$0.621 \pm 0.002$	$0.56 \pm 0.007$	$0.46 \pm 0.007$
$\tau_1$	$0.651 \pm 0.01$	$0.72 \pm 0.005$	$0.88 \pm 0.01$	$1.28 \pm 0.03$
$\tau_2$	$0.03 \pm 0.001$	$0.034 \pm 0.0005$	$0.058 \pm 0.001$	$0.11 \pm 0.006$

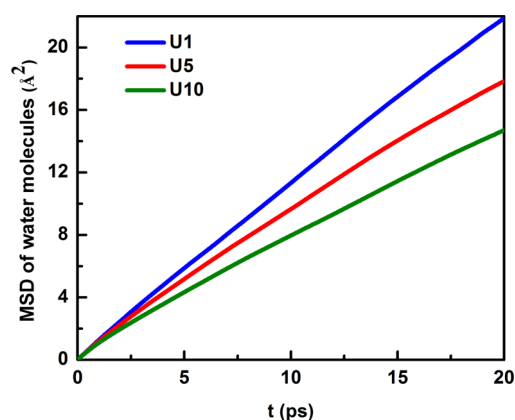


**Figure 7.** First order orientational correlation functions of water molecules with respect to (a) dipole moment vector ( $\mu$ ), (b) H–H vector (HH), and (c) a vector (CR) perpendicular to the plane of the water molecule for different systems of varying uranyl concentrations.



**Figure 8.** Second order orientational correlation functions of water molecules with respect to (a) water dipole moment vector ( $\mu$ ), (b) water H–H vector (HH), and (c) water cross vector (CR) for different systems of varying uranyl concentrations.

therefore, important to look into the dynamics of those water molecules residing in the first solvation shell of the uranium atom of the uranyl ion. In Figure 9, the MSD profiles of the water molecules in the solvation shell of the uranium atom in three different systems namely U1, U5, and U10 systems are



**Figure 9.** MSD profiles for water molecules within the first coordination shell of uranium atom of uranyl ion for U1 (blue line), U5 (red line), and U10 (green line) systems.

shown. The comparison of the MSDs of the coordination shell (of uranyl ion) water molecules in the system with that of bulk water as well as all water molecules in solution (see Figure 4) indicates a considerable decrease in diffusivity of solvation shell water as compared to the bulk water. Probably, the strong electrostatic interaction between the uranyl ion and water molecules in the solvation shell is responsible for the lower diffusivity of solvation water as compared to that of bulk water. It is to note that the effects of the hydration shell on diffusion coefficients have been previously discussed by Impey et al.<sup>39</sup> The diffusivity values as estimated using MSD along with the size independent diffusivities and their standard deviations for solvation water are given in Table 6. It may appear at this point

**Table 6. Diffusion Coefficient Values for Water Molecules within the First Coordination Shell of Uranium Atom of Uranyl Ions for Different Systems**

sample no.	system	diffusion coefficient of water from the slope of MSD curve ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )	diffusion coefficient of water corrected for system size ( $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ )
1	U1	$1.86 \pm 0.11$	$2.65 \pm 0.11$
2	U5	$1.35 \pm 0.01$	$2.26 \pm 0.01$
3	U10	$1.20 \pm 0.02$	$1.99 \pm 0.02$

that the reduction (see Figure 4 and Table 3) in overall diffusivity of water in the uranyl solution is due to these retarded solvation water. But, as the fraction of solvation water (around 1% in U1 system and around 9% in U10 system) is considerably small, contribution of the retarded solvation water to the overall diffusivity is negligibly small (see Figure 4). Thus, the reduction in overall water diffusivity is a consequence of the long-range effect (as shown in Figure 4) of the uranyl ions on the water beyond solvation shells.

#### 4. CONCLUSIONS

In summary, the behavior of aqueous solutions of uranyl ions is studied by analyzing both structural and dynamical aspects. In particular, we are interested in the effect of concentration of the uranyl nitrate on the structural and dynamical properties of the system. The radial distribution of water around the uranyl ion does not change appreciably with the concentration of the salt. A comparison of the diffusivities of uranyl ions, water and nitrate ions indicates uranyl ions diffuse slower than nitrate ions as well as water. It is expected as the uranyl ion is heavier than nitrate ion, which in turn is heavier than water. At very low concentrations, the presence of uranyl ions does not affect much the diffusion characteristics of different species in solution. However, significant changes in diffusivities of ions as well as water are observed at higher concentrations of uranyl ions. The diffusivity of the uranyl ion in the solution decreases considerably (by about 23% in TIP3P water and around 15% in SPC/E water) with the increase in uranyl ion concentration from 0.106 to 1.06 M. The rotational dynamics of water in terms of orientational time correlation functions have also been estimated and the results demonstrate that there is only slight retardation of the orientational motion of water at high concentration of uranyl ions in solution. The observed decrease in water diffusivity in the presence of uranyl ion/s may originate from (i) retardation of the solvation water and/or (ii) long-range effect of uranyl ion on the diffusion of water beyond FCS. We have therefore examined in detail translational dynamics of water in the solvation shell as well as outside the first

coordination shell of the uranyl ion. The analyses of the MSDs for water molecules within the first coordination shell of uranyl ions reveal that the motion of the water molecules in the hydration shell of uranyl ion is considerably retarded. The analyses of the MSD of the water molecules outside the FCS suggest (see Figure 4) that long-range effect of the uranyl ions on these water molecules also reduces water diffusivity. But, as the fraction of solvation water (around 1% in the U1 system and around 9% in the U10 system) is considerably small, contribution of the retarded solvation water to the overall diffusivity is negligibly small. Therefore, the decrease in overall diffusivity of water in the presence of uranyl ion is a consequence of long-range effect. The effect of finite concentration of the actinyl ions on the tetrahedral structure<sup>25</sup> of water is an interesting aspect to investigate, and work in this direction is in progress.

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### Notes

The authors declare no competing financial interest.

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