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Molecular dynamics simulation study of hydration of uranyl nitrate in supercritical water: Dissecting the effect of uranyl ion concentration from solvent density

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ABSTRACT

All atom molecular dynamics simulations of uranyl ions in supercritical water are used to dissect the effects of concentration of uranyl ions and density of water on various structural and dynamic properties of the solutions. The analyses of radial distribution functions as a function of concentration of the uranyl ion and water density reveal that the effect of the former on the local structure is negligible as compared to the same of the later. The number of hydration water of the uranyl ion has been observed to increase with increasing density of the water, but it decreases with the increasing concentration of the uranyl ions. The orientational distributions are observed to be independent of variation in concentration of the uranyl ion, same as the case was with water density. The translational and rotational dynamics of the water molecules have been investigated from the respective mean squared displacements and time correlation functions. Although increase of both the concentration of the uranyl ions and the density of water reduces translational diffusivity of water as well as uranyl ions, the effect of changing water density is more than that of uranyl concentrations. However, orientational relaxation of various molecular vectors of the water molecule is practically unchanged with any variation in concentration of the uranyl ions and it changes only slightly with the change in water density. Unlike at ambient condition, orientational dynamics at supercritical conditions remains virtually unchanged with the change in uranyl ion concentration.

1. Introduction

A lot of industrial interest and importance have been imparted on dense fluids at temperatures slightly above the vapour liquid critical temperature i.e. supercritical fluids (SCFs) [1–5]. Considerable amount of recent research attention has been directed towards dilute supercritical (SC) solutions as solvents for separation processes and as reaction media, especially in nuclear fuel cycle [6]. The density of a SCF can be tuned between gas-like and liquid-like values in the near critical region even with a small change in pressure or temperature. Such a change can cause corresponding changes in solute solvation and dynamics. This feature makes SCFs attractive alternatives to liquid solvents for several uses [7]. The density variations can be utilized to study the root cause of different characteristics of solutions under supercritical conditions. Water is a unique liquid [8–10] due to its many anomalous properties and ability to act as solvent for a large class of materials used in different processes involved in chemical industries. Although extraction processes based on supercritical fluids have been developed for recovering actinyl ions from the waste generated during the various stages of nuclear fuel cycle [11–15], further improvements are required. Supercritical conditions are the backbone of heterogeneous reactions of aqueous uranyl solutions which depend strongly on the high pressure and temperature conditions [16]. The knowledge of distribution and dynamic properties of the actinyl ions in supercritical water is important to understand their interactions during the cooling process and to develop procedures for nuclear waste reprocessing. Moreover, understanding the behaviour of aqueous solutions of actinyl ions with varying solvent densities above critical temperatures of water would be of great interest for the scientific community. Due to radiological hazard of these actinyl ions as well as extreme thermodynamic conditions, experimental studies involving these ions have practical difficulties. In-silico method such as molecular

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dynamics (MD) simulation provides an efficient and useful alternative route for understanding the characteristics of these ions in extreme conditions. Moreover, atomistic MD simulation method has the added advantage of analyzing the results from atomistic details.

The MD simulations have been extensively used to study the behavior of bulk water [17–24] and that of simple ionic species in aqueous solutions [24–29] in supercritical state. Maginn and their group have investigated the characteristics of aqueous actinyl solutions by first developing the force fields and then carrying out analysis using MD simulations [31,32]. In recent studies [33,34], we have analyzed the changes in the distribution and dynamical aspects of solutions of uranyl ions under ambient conditions. Druchok et al. [35] have discussed hydrolysis reaction of water molecules in the first solvation shells of uranyl ions and reported a bi-pyramidal penta-coordinated structure $(UO_2)^{2+}(H_2O)_4(OH)^-$. Such hydrated-hydrolysed structure of hydration shell of uranyl is consistent with quantum-chemical investigations [36,37]. Moreover, such hydrated-hydrolyzed complexes can finally lead to condensation reaction creating polynuclear ions [38]. For instance, Druchok and Holovko [39] studied the association of uranyl ions in aqueous solutions based on varying pH in the presence of electric field. Although much literature on MD simulations of aqueous uranyl solutions is available under normal temperature and pressure [30–35,39–42], a very few simulations are reported on the same systems at extreme conditions of temperatures and pressures. Recently, we have reported the structural and dynamical characteristics of an infinitely dilute solution of uranyl ions in supercritical water at different densities [43]. It was observed that although the angular distribution remains unaffected, but the coordination number of uranyl ions increases, relaxation of various water vectors slows down slightly and diffusivity of various species in the solution reduces with increase in water density.

From our recent studies [33,34] related to aqueous uranyl solution at ambient condition, it is observed that the change in uranyl ion concentration significantly modify the transport characteristics of water and uranyl ions in solutions. This led to our curiosity to analyze the impact of uranyl ion concentration variation on these features of uranyl solutions at temperatures above the critical temperature of water and compare it with the effect of changing the density of the solvent. Here, we analyzed the distribution and transport characteristics of solutions of uranyl ions of different concentrations under supercritical conditions. The combined effect of water density and uranyl ion concentration in the solution on the behavior of various species is also analyzed by simulating systems of different densities. The structural characteristics are studied with respect to radial distribution of water molecules and orientational distributions calculated in terms of orientations of various molecular vectors of water with respect to uranyl orientation. The mean squared displacement (MSD) is used to analyze the translational motion of various species in the solutions and the power spectra of the collective vibrations of water molecules is used to corroborate the sequence of diffusion coefficients for various concentrations. The changes in the orientation of various molecular vectors of water molecules as a function of time are used as criteria to study their orientational dynamics. Comparison is also made between the features of uranyl solutions at ambient and supercritical temperatures [33,34].

2. Models and simulation details

In order to investigate the effect of varying uranyl ion concentration and density of water under supercritical conditions, different systems of aqueous solutions of uranyl ions are prepared by solvating different number of uranyl ions in specified number of water molecules within a cubical box with approximate dimensions 5.0 nm × 5.0 nm × 5.0 nm. Nine different sets of aqueous solutions of uranyl ions in supercritical water are simulated for different water densities and uranyl ion concentrations as given in Table 1. The Set No. 4 is same as that discussed in our previous study [43] and hence the results for this system are taken from Ref [43]. PACKMOL program [44] was employed to prepare various boxes of water molecules with specific bulk densities. The range of concentrations studied in this work are of the order of concentrations encountered generally in the back end of the nuclear fuel cycle, especially during reprocessing of uranium based spent fuel [45,46]. The electrical neutrality of the systems is maintained by introduction of nitrate (negative) ions. The systems are simulated under isothermal-isobaric (NPT) ensemble by making use of molecular dynamics (MD) method. Extended systems approach is used for maintaining the temperature and pressure of the system [47–51]. The values of box lengths and pressure of the systems at equilibrium are also given in Table 1. The equilibrium pressure values are of same order as recorded in some earlier experimental [52] and theoretical studies [43,53]. The uncertainties in densities and concentrations are estimated from the volume fluctuations in the NPT ensembles.

All atom models were employed both for uranyl ion, with one uranium atom and two oxygen sites bonded to it as well as nitrate ion, with one nitrogen atom bonded to three oxygen atoms [32,54]. The water molecule was simulated with standard three-site SPC/E model [55] in all the cases. The potential energy of the system is given as [33,34,43]:

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

where the symbols have their usual meaning. The electrostatic (Coulomb) and van der Waals [Lennard-Jones (LJ)] interactions are represented by the third term. The firsts and second harmonic potential terms simulate the intra-molecular movement of bonds and angles in case of uranyl and nitrate ions. The inter- and intramolecular potential parameter values were taken from the literature [32–34,43,54,55]. The bonded and non-bonded parameters as reported by Pomogaev et al. [32] for solvated uranyl ion and by Guilbaud et al. [54] for nitrate ion were used whereas those reported by Berendsen et al. [55] were used for SPC/E water molecules. The various parameter values used in this work are given in Table 2 of our recent publication [43]. The Lorentz–Berthelot mixing rule is made use of for calculating the cross-atom LJ parameters.

The critical temperature of water has been experimentally estimated to be 647 K whereas for SPC/E water, the value has been reported as 638.6 K [56]. We have used a temperature of 683 K for performing all our simulations under supercritical conditions. We have employed periodic boundary conditions and minimum image conventions in all the three directions. A time step of 1 fs is used in Velocity Verlet algorithm [51] to integrate the equations of motion, with saving of trajectories every 10 steps. The non-bonded interactions in real space are restricted within a cut-off distance of 1.2 nm. The OH bond lengths and the HH distance of the water molecules are constrained using RATTLE algorithm [51]. Ewald's summation method is used to evaluate the charge-charge interactions. The systems are equilibrated by simulating for a period of 2 ns. The results of further simulation of 2 ns after equilibration are used for analysis.

3. Results and discussion

The effect of variation in uranyl concentration and solvent density on the distribution and transport behavior of aqueous solution