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The effect of an electric field on the association of uranyl in aqueous solutions

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ABSTRACT

In this contribution we study the role of electric field on the uranyl–uranyl association. For this purpose a set of molecular dynamics simulations has been performed for a series of uranyl aqueous solutions of different pH levels in an external electric field. The comparison of the association ratios with the corresponding no-field data reveals that, depending on the pH, the field can enhance or decrease the association. The fractions of uranyl in the associates are collected as well as the lifetimes of the associates. We also present a series of angular distributions characterizing the uranyl–uranyl mutual orientations within associates and the uranyl orientations with respect to the field direction.

1. Introduction

This study is inspired by a problem in the utilization of radioactive wastes. Besides their radiation effects these wastes pose a series of hazards due to the pollution of natural waters. It is known [1,2] that the hydration shell of uranyl, UO_2^{2+}, in aqueous solutions consists of five or six ligands (water molecules or OH^- ions [3]) in the equatorial (perpendicular to the O–U–O axis) plane. It is worthwhile to mention two recent DFT studies of uranium/uranyl complexation [4,5]. The results reported imply that the U(III) and U(IV) ions are hydrated by eight or nine waters, while the uranyls UO_2^{2+} form complexes with five or six ligands. Such a complexation leads to an increase of effective size of the uranyl and can be used in the extraction of contaminants from media. Among the effects due to this size variation one has to distinguish between phenomena of hydration [5–9], association between solutes [4,10–15], folding [16], fibrillization [17], etc. We mention the two latter ones since they can come into play for species with high molecular weights acting as uranyl ligands.

OH^- ions appear in the uranyl hydration shells as the result of the hydrolysis of water, while the remaining H^+ are pushed to the bulk [3] changing the solution's pH. Such a mediated change of pH is able to initiate highly mutagenic effects when human or animal tissues come into contact with contaminated water (see for example Refs. [18–22]). In Refs. [4,5] the authors also discuss the aspects of pH and hydrolysis in uranium solutions. Indeed, uranium ions are in solution a source of electrostatic fields strong enough to rupture protons from water molecules. A similar effect, proton jumps assisted by electric field, has been studied in water [23] and hydrogen-bonded [24] systems. Concerning the case of weaker fields without rupture effects one should mention a series of papers reporting investigations of the field assisted polarization and reorientation phenomena in aqueous solutions and ionic liquids [6–8,13,16,25–28]. The range of species involved in these studies varies from low-molecular and atomic ions to polymers and colloids, under static or alternating fields. Along with the reorientation processes several dynamic properties have been studied and special attention has often been paid to particle transport and mobility in the systems exposed to external fields [7–9,11,29–33].

In our earlier studies [34,35] we have investigated the influence of the pH level and temperature on the association ability of uranyls in aqueous solutions. We found that a low temperature and an alkaline environment favor the formation of polynuclear uranyl associates. In particular, while in a neutral environment uranyl ions are able to hydrolyze waters, the acidic environment prevents the hydrolysis and the uranyl hydration shells preferably consist of non-hydrolyzed water molecules. The picture changes in the alkaline case: extra OH^- ions from the bulk tend to replace uranyl hydrating waters. This screening of the uranyl ions by their hydration shells gives rise to uranyl association.

The focus of this contribution is the influence of an electric field on the association behavior of uranyl ions in aqueous solutions. The important feature is that the complex, consisting of uranyl and its hydration shell, has axial and planar symmetry. Our intention is to test whether

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a uniform electric field is able to influence the uranyl association and if the answer is "yes", to find the key mechanisms causing these changes. We are guided here by the polarization of the uranyl hydration structure in an electric field. Since the hydration structure of uranyl ions is strongly dependent on the pH one needs to model acidic, neutral, and alkaline solutions.

2. Model and simulation details

Following the course of our previous study [35] we have simulated three systems mimicking neutral, acidic, and alkaline uranyl solutions. The neutral solution consisted of 1600 water molecules and 16 uranyl ions. The concentration of uranyl was 0.55 mol/l. We modeled an acidic and an alkaline solution by adding 100 H^+ or 100 OH^- ions, respectively to the neutral system. For simplicity's sake we shall call these solutions acidic, neutral, and alkaline.

The model is the one used in our earlier studies [3,34,35]. The uranyl–uranyl and uranyl–water interactions were taken from Ref. [36] in the form:

$$E_{ij=}\frac{Z_iZ_j}{4\pi\epsilon_0 r}+\frac{A_iA_j}{r^{12}}-\frac{B_iB_j}{r^6} \tag{1}$$

where i and j are the sites listed in Table 1, where the corresponding parameters are collected.

The potential parameters for the uranyl ions were fitted by Guilbaud and Wipff [37,38] on the basis of the free energies of uranyl hydration. These parameters were optimized to yield a five-fold-coordination in the uranyl hydration shells, with ligands located in the equatorial plane and an average U–O_w distance of 2.5 Å. One has to mention that the uranyl–uranyl and uranyl–water interactions in real systems are more complex, including many-body interactions, charge transfer, and covalent bond effects. Recently, Benay and Wipff [39] studied the extraction of uranyl by amide ligands. Three different models were used in [39], one of them included the atomic polarizabilities on all atoms. However, despite the obvious advantages, the polarizable model was not the overall most successful one. Also consideration of the polarizable effects increases the computational costs. Moreover, the polarizable potentials for water in [39] were presented by the POL3 [40] model. The POL3 model, however, is unable to reproduce the water dissociation and therefore is inapplicable for the hydrolysis effect.

Greathouse and co-authors [36] described water with the SPC potentials [41]. In our study we used the central force model CF1 for water [42,43], in contrast with other simulation studies [37,38] of actinide solutions utilizing rigid models. Within the framework of the CF1 model the water is treated as a mixture of oxygens and hydrogens interacting via pairwise additive potentials. Due to this the water molecules can experience deformations and even hydrolysis, which is essential in the modeling of a hydration behavior of highly charged cations [3, 44]. For further model details we refer the reader to Ref. [3].

Since the CF1 is a flexible non-constrained model it also allows to include extra H^+ or OH^- ions into solutions. These extra ions are able to form $(H_3O)^+$, $(H_5O_2)^+$, or $(H_5O_3)^-$ charged complexes. An earlier study [44] of the structure of the $(H_3O)^+$, $(H_5O_2)^+$ complexes (within the CF1) has shown a reasonable agreement with ab initio MD results [45]. There is also a question about the transferability of the solute–solvent potentials due to the differences between the SPC and CF1 models. A comparison of the uranium–water radial distribution functions (RDFs) within these two models (Fig. 1 in Ref. [36] and Figs. 1, 2 in Ref. [35]) revealed, however, a good agreement between the locations of the RDF peaks, moreover, both models yielded a five-ligand hydration of the uranyl ions.

The molecular dynamics (MD) simulations were performed for the neutral, acidic, and alkaline solutions exposed to an external static electric field. The field, $E = 5 \times 10^8$ V/m, was uniformly directed along the Z axis in all three solutions. This rather moderate field is approximately the same as the one generated by a unit charge at the distance of 17 Å. Such a field is able to modify the uranyl hydration structure, but it is not strong enough to rupture water molecules (see for example Ref. [28] where the water properties were studied over the range of electric fields $E = 1.5 \times 10^8 - 15 \times 10^8$ V/m). The particles placed into a cubic MD box, $L_x = L_y = L_z \approx 37$ Å with periodic boundary conditions, were allowed to move freely. For the short-range interactions a cutoff radius of 15 Å was chosen. The electrostatic interactions were taken into account by the Ewald summation technique. One should note here that all the systems considered are physically non-neutral but still can be effectively treated since the charges are implicitly compensated by a neutralizing background in the Ewald formalism.

To reveal the field influence we used as a reference the corresponding "zero-field" solutions simulated before [35]. These earlier results were obtained in *NpT* simulations at a pressure of 1 bar and a temperature of 278 K and the parameters used in the current study. The conditions (temperature and pressure) during the simulations were controlled by means of Nose–Hoover barostat and thermostat in an isotropic *NpT* ensemble within the Melchionna realization [46,47]. We used the leapfrog integration algorithm with a time step of 0.2 fs. The length of the production runs ranged from 9 to 10 ns.

For a structural analysis the RDFs and a series of angular distributions are accumulated. Besides the structural details we also present distributions of lifetimes of the uranyl dimers and trimers.

3. Numerical results

3.1. Radial distribution functions

We begin with the analysis of the uranium–uranium RDFs. The comparison of the U–U correlations for the "field-on" and "zero-field" cases is shown in Fig. 1. With and without field the alkaline solution remains the most favorable environment for uranyl association. Most notably influenced by the field is the acidic RDF: one sees disappearance of the first pre-peak at 7 Å. A similar trend is observed for this pre-peak in the neutral case. In the alkaline case the first peak slightly decreases and sharpens at the top. In general the results indicate a weakening of the uranyl association in the external electric field. The uranium–uranium RDFs have a Debye–Hückel-like asymptote [48,49] at larger distances:

$$g^{\mathrm{asympt}}(r) = 1 - \frac{1}{kT}e^2 Z_{UO_2}^2 \frac{1}{4\pi\epsilon_0\epsilon r}\exp(-2\Gamma r) \tag{2}$$

where T is the temperature, k the Boltzmann constant, e the elementary electric charge, eZ_{UO2} the effective uranyl charge, ϵ_0 the vacuum permittivity, ϵ the solvent dielectric constant, and Γ the screening parameter.

Next in Fig. 2 we present the uranium–oxygen RDFs in the field. The highest first peak is found for the alkaline case, the other two peaks are lower with a slight shift of the maximum position toward larger distances. Negatively charged OH^- ions win the competition with neutral waters for the vacancies in the uranyl hydration shell and form more compact and stable complexes. This results in a higher uranium–oxygen peak in the alkaline case. This RDF coincides with the zero-field one, i.e. this RDF is, within our uncertainties, not sensitive to the electric field.

Table 1
Potential parameters for the uranyl–water interactions.

	Z	A (kcal Å^{12}/mol)$^{1/2}$	B (kcal Å^6/mol)$^{1/2}$
O in H_2O	−0.65966	793.322	25.010
H	0.32983	0.1	0.0
U	2.50	629.730	27.741
O in UO_2	−0.25	793.322	25.010

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