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# Behind adhesion of uranyl onto montmorillonite surface: A molecular dynamics study

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## HIGHLIGHTS

- We investigated the adsorption of uranyl onto Montmorillonite surface.
- We studied the surface energy between layered Montmorillonite sheets.
- We studied the work of adhesion between radionuclide and charged Montmorillonite.

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## ABSTRACT

We have performed molecular dynamics simulations to investigate the adsorption of radionuclide elements species onto substituted Montmorillonite (001) surface in the presence of different counterions. The structure and the dynamics of uranyl ion as well as its aquo, chloride ion, and carbonate complexes are analyzed. In addition, we have studied the surface energy between layered Montmorillonite sheets and the work of adhesion between radionuclide and charged Montmorillonite. The clay model used here is a Wyoming-type Montmorillonite with 0.75e negative charge per unit cell resulting from substitutions in Octahedral and Tetrahedral sheets. The system model was constructed based on CLAYFF force field potential model. To evaluate the thermodynamic work of adhesion, each surface and clay layer regions are converted to a thin film model. One and two species of radionuclide elements ($UO_2(H_2O)_5$,$UO_2CO_3(H_2O)_5$, and $UO_2Cl_2(H_2O)_5$) were deposited near the clay surface in a pseudo-two-dimensional periodic cell. Analysis shows that the uranyl ion structure is preserved with two axial oxygen atoms detected at 1.8 Å. Radial distribution functions results indicate that average U—$O_w$ distances are 2.45–2.61 Å, and 2.29–2.40 Å for U—$O_c$ distance. Average U—Cl distances are 2.78–3.08 Å, which is relatively larger than that of Uranium atom-Oxygen atom because of electrostatic factors.

## 1. Introduction

In recent years, the study in actinide adsorption on clay mineral has greatly increased due to an ongoing concern in environmental research. Their interaction with clay mineral surface plays an important role to govern the migration of actinide in the environment. Knowledge of a description of how actinides interact with clay mineral surface is important for assessing the risk caused by the nuclear waste repositories [1]. Uranium is the predominant heavy metal content of the final waste in the nuclear fuel cycle (>95% $UO_2$). Also, uranium is a major contaminant in the soil, subsurface and groundwater as a result of human activity. Under standard environmental conditions, the most stable chemical form of U(VI) is the uranyl ion $UO_2^{2+}$, which is potentially very mobile and readily complexates with organic and inorganic matter. To assess the possibility of forming an adsorption complex of uranyl onto clay mineral, one has to analyze the energy change which concerned the adhesion strength between radionuclide and clay mineral. The thermodynamic concept quantifying the adsorption is the work of adhesion. However, only a few work of adsorption energy or interaction energy have been realized about clay [2–5]. In this work, the interaction between MMT sheets and the adsorption energy between the radionuclide and MMT surface will be discussed.

Numerous experimental studies of uranyl adsorption on various clay minerals surfaces have been published, e.g. montmorillonite, illite, and kaolinite [6–14]. X-ray adsorption fine structure (XAFS) spectroscopy has been used to study the structure details of surface complexes formed between uranyl and mineral surfaces [15–19]. Recent first-principles density functional theory (DFT) calculations show us a lot of possible inner- and outer-sphere adsorption complexes at kaolinite surface [2,3]. Although various experimental studies provide some measurement of attenuation capacity of clay minerals for uranyl [15,20–23], there is still much to be studied on

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the atomic scale about the structures details of uranyl adsorption onto mineral surfaces.

The remarkable development of molecular computer simulations is very helpful in demonstrating a chemical evolution on the structure and behavior of clay minerals on the atomic level. In this paper, Molecular Dynamics (MD) simulations methods [24] were employed to study the microscopic aspects of the interaction of uranyl with the Montmorillonite surface, followed by the methods used to obtain the interaction energy and work of adhesion.

## 2. Computational details

### 2.1. System parameters and MD simulation

We employed the CLAYFF [25], as implemented in DL-POLY code [26], for the potential parameter of Montmorillonite, water molecule and others counterions. All species were treated as rigid bodies. The partial charge CLAYFF model is used for its flexibility within clay lattice. The flexibility for all other counterions, including OH groups in the clay lattice, was realized with harmonic bond stretch and angle bend terms [27]. Parameters for the uranyl ion were taken from the work of Guilbaud and Wipff [28] where the angle bend force constant $k_2$ is 300 kcal.mol$^{-1}$.rad$^{-2}$, and the equilibrium angle for O—U—O is 180°. These parameters were used to model uranyl complexes with carbonate and chloride.For $UO_2{}^{2+}$, we used a partial charge of +2.5e, which change slightly compared with +2.8e obtained from ab initio results. Using these uranyl and Montmorillonite models, we have performed complexes simulations of uranyl with Montmorillonite surface in the presence of $Na^+$, $K^+$, $Cs^+$, $Ba^{2+}$, $Pb^{2+}$, $Ca^{2+}$, $Zn^{2+}$ interlayer cations, as well as carbonate and Chloride. The corresponding parameters are given in Table 1.

The total energy is expected to have contributions from the long ranged Electrostatic (Coulombic) interactions, the short ranged pair-body (van der Waals) interactions and the bond interaction which include the chemical bond stretch and valence angle bend terms:

$$U_{total} = U_{coul} + U_{pair} + U_{bond} + U_{angle} \tag{1}$$

In addition to the 4 terms involved in the Eq. (1), one can define dihedral angles and inversion angles potentials as intra-molecular interactions, three-body, Tersoff and four-body potentials as intermolecular interactions. However, during the simulation we ignore these terms to avoid time consuming. The corresponding equations for total energy calculation are represented in Table 1.

Montmorillonite is a 2:1 clay and a member of the smectite family, which has a strong adsorption and ion exchange capacity. The clay model used in our simulations is a Wyoming-type MMT [30] with the unit cell formula: $M_{0.75}(Si_{7.75}Al_{0.25})(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$ or $N_{0.325}(Si_{7.75}Al_{3.25})(Al_{3.5}Mg_{0.5})O_{20}(OH)_4$ where M represents a monovalent cation. In the present work $Na^+$, $K^+$, $Cs^+$ are considered. N represents a double valent cation such as $Ba^{2+}$, $Pb^{2+}$, $Ca^{2+}$, $Zn^{2+}$, etc. Negative charges resulted from isomorphic substitutions in the tetrahedral and octahedral sheets. In our MMT formula, the first and second bracketed terms refer to ions in the tetrahedral and octahedral layers. One out of eight Al atoms in octahedral sheet is replaced by Mg atom; likewise, one out of 32 Si atoms in tetrahedral sheet is replaced by an Al atom. The model system was expanded into a super cell of 21 Å × 36 Å in the *x* and *y* dimension, which contains 16 MMT unit cell (4 × 4 repeats in a and b dimension). The 4 × 4 unit cells of clay layer contain 640 atoms: 124 Si and 4 Al in the tetrahedral sheets, 56 Al and 8 Mg in the octahedral sheets, 384 O and 64 H centers; while 12e negative charge are contained in the clay layer. Different counterions were added to the surface and interlayer region to balance negative charge in the clay layers, one and two pairs of uranyl, carbonates ions and chlorine ions were added. For all adsorption simulations, 2D periodic boundary

**Table 1**
Force field parameters for radionuclide species and Montmorillonite [25,29].

| I. nonbond Species | Symbol | Charge (e) | $A_{ij}$ ((kcal. Å$^{12}$/mol)$^{1/2}$) | $B_{ij}$ ((kcal. Å$^6$/mol)$^{1/2}$) |
|---|---|---|---|---|
| Sodium ion | Na | +1.0 | 121.503 | 9.3622 |
| Potassium ion | K | +1.0 | 868.623 | 23.438 |
| Cesium ion | Cs | +1.0 | 1999.548 | 35.561 |
| Barium ion | Ba | +2.0 | 1340.126 | 24.105 |
| Plumbum ion | Pb | +2.0 | 2565.915 | 64.690 |
| Calcium ion | Ca | +2.0 | 354.91 | 14.982 |
| Zinc ion | Zn | +2.0 | 78.422 | 7.431 |
| Chloride ion | Cl | −1.0 | 4591.405 | 53.901 |
| Uranium | U | +2.5 | 713.840 | 31.759 |
| Uranyl oxygen | O | −0.25 | 793.310 | 25.009 |
| Carbonate carbon | C | +0.43 | 1338.021 | 22.989 |
| Carbonate oxygen | Oc | −0.81 | 522.393 | 22.336 |
| *Coulumbic potential* : $U_{r_{ij}} = \frac{1}{4\pi\varepsilon_0}\frac{q_iq_j}{r_{ij}}$; *Pair potential* : $U_{r_{ij}} = \left(\frac{A_iA_j}{r_{ij}^{12}}\right) - \left(\frac{B_iB_j}{r_{ij}^{6}}\right)$ | | | | |
| Potential energy U(kcal/mol), Atomic charge q(e), radius r(Å) | | | | |
| II. Bonds stretch | K1(kcal/mol.Å$^2$) | $r_o$(Å) | | |
| Species i | Species j | | | |
| U | O | 1000 | 1.8 | |
| C | Oc | 1312 | 1.25 | |
| *Bond potential* : $U_{ij} = \frac{1}{2}k_1(r_{ij} - r_0)^2$ | Potential energy U(kcal/mol), bond stretch force constant $k_1$,and equilibrium bond length $r_0$(Å) | | | |
| III.Angle bend | K2(kcal/mol .rad$^2$) | $\Theta_o$(deg) | | |
| Species i | Species j | Species k | | |
| O | U | O | 300.00 | 180.00 |
| $O_c$ | C | $O_c$ | 160.00 | 126.00 |
| *Angle potential* : $U_{ijk} = \frac{1}{2}k_2(\theta_{ijk} - \theta_0)^2$ | Potential energy U(kcal/mol), angle bend force constant $k_2$, and equilibrium angle $\theta_0$(deg) | | | |