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Insights into the Interaction Energy for Cs$^+$–Crown Ether complex by Molecular Dynamics Simulations

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Abstract

Cesium is a major fission product in spent nuclear wastes. Crown ethers are used as extracting agent for the removal of cesium ions from aqueous media. We report the interaction energies between the individual complexing species i.e. crown ether and Cs$^+$ metal ion. In order to understand the mechanism of complexation and the behavior of crown ether ligand, crown ether (CE) molecules and Cs$^+$NO$_3^-$ ions were inserted randomly in the Ionic Liquid-water/methanol biphasic system, where Ionic Liquid is carrier solvent for CE. It was observed that the interaction energies which comprised of the non-bonded interaction during initial stages of the simulation have a value close to zero. This suggests that the Cs$^+$ cation is not present in the crown ether. After the formation of Cs$^+$–CE complex, it is very clear that the electrostatic interactions are particularly attractive in nature and are crucial in realizing complexation.

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Keywords: Crown Ether; Cs$^+$–CE complex; Interaction energies of Cs$^+$–CE complex

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1. Introduction

Cesium is a major fission product in spent nuclear wastes. Its removal from these wastes is a key part of waste remediation strategies. Cesium ion extraction using crown ethers has been investigated by McDowell [1] and Horwitz [2]. Removal of cesium ions from nuclear wastes is essentially safe and cost effective procedure for the removal of

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associated wastes. Macrocyclic crown ether [3] and calix[*n*] arene [4] compounds are being recently used for the removal of Cs^+ ion from the nuclear wastes solution. Recently, application of crown ethers has become very efficient for separation of metal ion especially cesium and strontium. The use of Ionic Liquids as an extracting agent for heavy metal ions has been reported earlier [4]. Ionic liquids (ILs) are generally salts of organic cations (such as imidazolium, pyridinium, etc.) and inorganic anions (such as $[BF_4]^-$, $[PF_6]^-$ and $[CF_3SO_3]^-$) exist in liquid state at relatively low temperatures. Extraction of various metal ions has been studied with imidazolium based ILs. The extraction of metal ions into the hydrophobic ILs phase was found to be irrelevant because metal ions which are to be extracted from the aqueous phase are strongly hydrated. Thus, an extractant should be used, which generally forms hydrophobic complexes with the metal ions and subsequently facilitates their transfer from aqueous to the ILs phase. Luo *et al.* [5] observed that BOBCalixC6 (calix [4]arene-bis(tert-octylbenzocrown- 6)) is an efficient extractant . Along with the imidazolium–based ILs it is able to extract higher amounts of Cs^+ ion from aqueous phase, as compared to other organic solvents like 1,2-dichloroethane or chloroform [6].

In this work, we have reported the extraction mechanism for ion selectivity of crown ethers in aqueous solutions. We have also attempted to study the interaction energies during complexation of Cs^+ cation with crown ether. The solvent extraction process were carried out for the extraction of Cs^+ ion from the [BMIM][Tf_2N] Ionic liquid-Water/Methanol binary system by DB18C6. To understand the mechanism of complexation and the behavior of crown ether ligand: dibenzo-18-crown-6 (DB18C6), $Cs^+NO_3^-$ ions were inserted in the IL–water methanol biphasic system.

2. Computational Methods

The MD simulation were performed with NAMD (version 2.9) [7] where the potential energy is described by a sum of bond, angle and dihedral deformation energies, and (electrostatic + van der Waals) interactions between nonbonded atoms.

$$U = \sum_{ij}^{\text{bonds}} \frac{k_{r,ij}}{2}\left(r_{ij} - r_{0,ij}\right)^2 + \sum_{ijk}^{\text{angles}} \frac{k_{\theta,ijk}}{2}\left(\theta_{ijk} - \theta_{0,ijk}\right)^2 + \sum_{ijkl}^{\text{dihedrals}} \sum_{m=1}^{4} \frac{v_{m,ijkl}}{2}\left[1 + \left(-1\right)^m \cos\left(m\varphi_{ijkl}\right)\right] + \\ \sum_i \sum_{j \neq i}' \left\{4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{1}{4\pi\varepsilon_0}\frac{q_i q_j}{r_{ij}}\right\} \qquad (1)$$

The parameters used for the ILs were taken from the OPLS force field [8] which were earlier used by Margulis *et al.* to simulate ILs [9]. Water was described by the TIP3P model [10]. Parameters of the Cs^+ cations were fitted on the hydration free energies by Aqvist [11]. The parameters for DB18C6 were taken from Weiner *et al.*[12]. The systems were represented with 3D periodic boundary conditions. The nonbonded interactions were calculated using a 12 Å atom-based cutoff correction for the long-range electrostatics using the Ewald summation method (PME approximation) [11]. The MD simulations were performed at 300 K starting with random velocities. The solutes (219 [BMIM][Tf_2N] molecules, 1200 H_2O molecules and 750 methanol molecules) were initially immersed in cubic boxes of 45 Å lengths. After 1000 steps of energy minimization, the systems were equilibrated in NVT ensemble. The temperature was monitored by Langevin thermostat, while the pressure was maintained by Langevin piston. All C-H and O-H bonds were constrained with SHAKE, using the Verlet algorithm with a time step of 2 fs to integrate the equations of motion. Typical snapshots were taken by VMD software [13].

3. Results and Discussion

3.1. Cs^+–DB18C6 Complex in [BMIM][Tf_2N]-Water Methanol Binary Systems

To understand the mechanism of complexation and the behavior of dibenzo-18-crown-6 (DB18C6), $Cs^+NO_3^-$ ions and DB18C6/Cs^+ were inserted in the IL–water biphasic system. Six molecules of DB18C6 crown ether and six molecules