5th International Conference on Advances in Energy Research, ICAER 2015, 15-17 December 2015, Mumbai, India

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⁺NO₃⁻ 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.

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

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.

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

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$_2$N]-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

of $Cs^+NO_3^-$ were randomly introduced into the biphasic systems. The insertion was performed using PACKMOL [14] by randomly inserting the 12 molecules in the same system. The subsequent dynamics, pursued for 40 ns, and snapshots taken at regular intervals, are presented in Fig. 1. During the simulation, liquids separated into two clean bulk phases after 40 ns with the free crown ether moieties migrating to the IL phase and $Cs^+NO_3^-$ ions to the water+methanol phase. As expected some methanol molecules also migrate into the IL phase because of its partial solubility. It should be noted that methanol, has been added so as to reduce the dipole moment of the aqueous phase which results in lesser electrostatic interactions. The complexation of Cs^+ ion with DB18C6 was observed during the13[th] ns run only. Since the constituent solvents are immiscible in nature, the system is expected to form a flat interface in the process to minimize its interfacial energy.
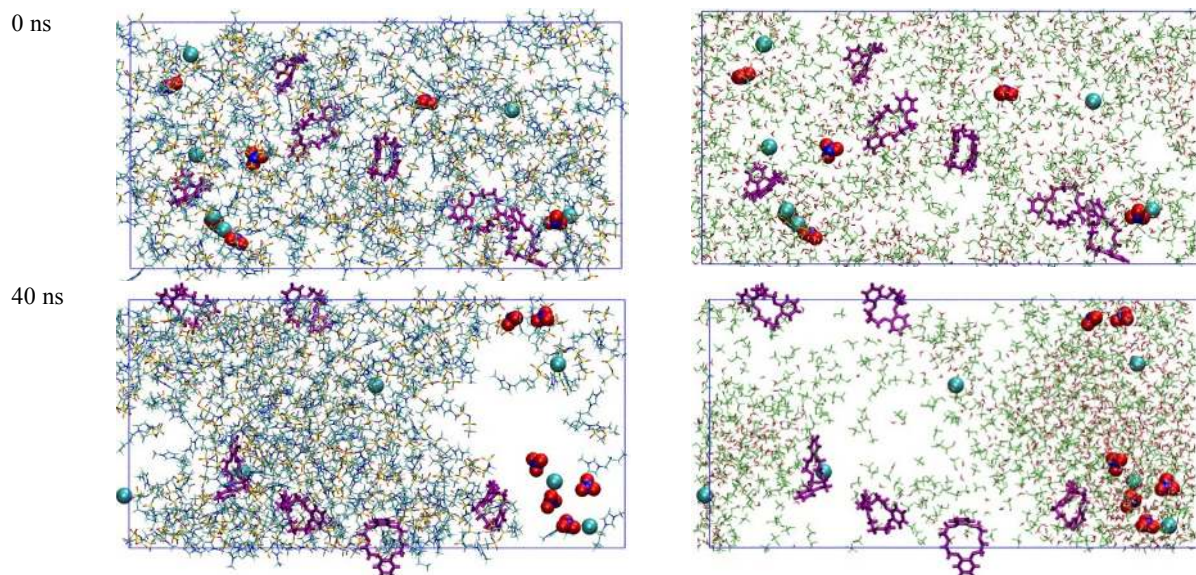
0 ns

40 ns

Fig.1. Snapshots of configurations at 0 and 40 ns for cesium nitrate as $Cs^+NO_3^-$and DCH18C6 inserted in the [BMIM][Tf$_2$N]-Water/Methanol system.

3.2. Solvated structure of Cs^+–DB18C6 complex

The structure of the solvent molecules around an ion is described by the radial distribution function (RDF)**.** The formation of Cs^+–DB18C6 complex was confirmed from the RDF of the Cs atom and one of the ether oxygen atoms in the crown ether, calculated over the final 10 ns (i.e. from 30 ns to 40 ns). The optimized distance of 3.14 Å is closely reciprocated by the equilibrium RDF (Fig. 2) with the first peak value of 3.94 Å. This suggests that the complexation indeed took place and the entity remained physically stable till the end of the simulation. Fig. 2(a) shows the molecular structure of the Cs^+–DB18C6 complex optimized at the same DFT level of theory by using the SDD basis set. Fig. 2(b) is the RDF plot of the same Cs–O interaction calculated over a trajectory from 30-40 ns of the simulation. The peak position at 3.94 Å is close to the optimal distance suggesting the formation of complex, and its large magnitude reinforces the stability of the complex. The large magnitude of the RDF peak between cesium and oxygen is similar to that obtained by Pooja *et al.* [15] for their study on liquid–liquid extraction of Li^+ ion using crown ether.
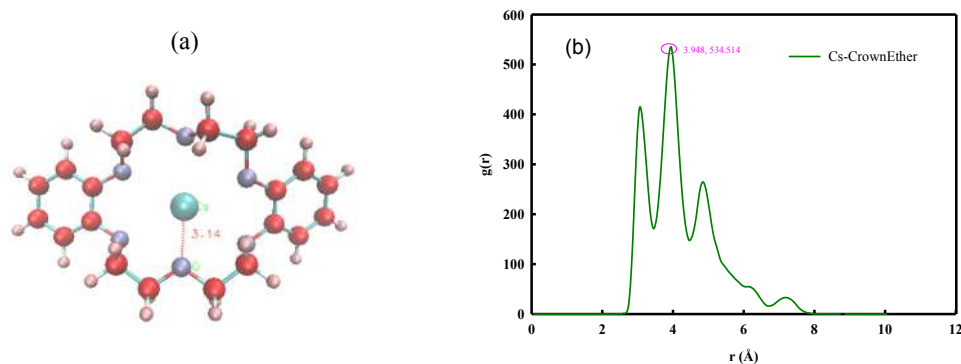
Fig. 2. (a) Optimized geometry of Cs$^+$–DB18C6 complex (b) RDF of Cs-O over the trajectory run from 30 to 40 ns.

Fig. 3 shows the RDF plot of Cs$^+$ with water, methanol and IL calculated over a trajectory from 30-40 ns of the simulation. It is observed that the RDF value of Cs$^+$-IL is zero for the first solvation shell when compared to ∼1.72 Å in bulk solution (Cs$^+$- water, Cs$^+$-methanol). In other words, the value of Cs$^+$- IL in the first solvation shell is observed at ∼2.2 Å, and is equivalent to the second solvation shell (∼4.4 Å) in bulk water (Fig. 3). Also, the peak height of the RDF in the IL is lower than that of bulk water and methanol. This indicates weaker coordination of Cs$^+$ with IL molecules in comparison to Cs$^+$ with water and methanol. The interaction between Cs$^+$ with water is much higher than that of IL and methanol. This is evident because the formation of the complex takes place at the interface (Fig.1), which is again confirmed by a RDF value ∼500 for the captured cesium ion (Fig. 2b).
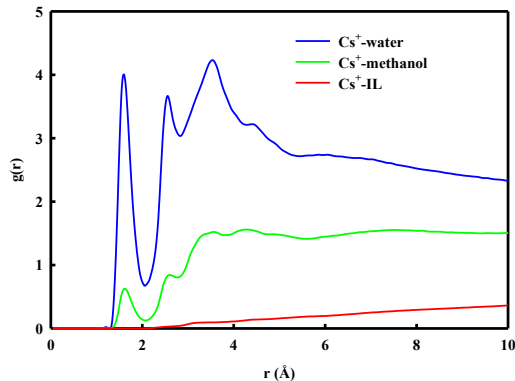

Fig. 3. Comparison of RDF of Cs$^+$ with bulk water ,methanol and IL

3.3. Interaction Energies of Cs$^+$–DB18C6 Complex

The interaction energies between Cs$^+$–Crown ether complex (Fig. 4a), Cs$^+$-Bulk water (Fig. 4b), Cs$^+$-IL (Fig. 4c) and Cs$^+$ -Methanol (Fig. 4d) have been plotted for 0–40 ns of the trajectory. Values of negative interaction energies imply stronger attraction for the desired ion. These values are negative throughout for Cs$^+$-IL (Fig. 4c), implying a strong affinity in the IL medium. The interaction energies during initial stages of the simulation have values close to zero suggesting that the Cs$^+$ cation is not present in the sphere of influence of the crown ether (Fig. 4a) . It is interesting to

observe that the capture of the ion takes place at the point where its interaction with the crown ether starts ~13 ns (Fig. 4a). A contrary transition is observed for both water (Fig. 4b) and methanol (Fig. 4d) where the values change to positive at 13 ns.

The attractive interactions between Cs^+-bulk water are suddenly found to rise by an order of 200 kcal/mol as shown in Fig. 4(b). This rise is much higher than what the BPC6 crown ether can offer through its binding energies (i.e. 53.4 kcal/mol). The interaction energies between Cs^+–DB18C6 Complex and IL were also around 150-200 kcal/mol, as shown in Fig. 4(c). The interaction energies between Cs^+–DB18C6 Complex and methanol were around 200-350 kcal/mol, as shown in Fig. 4(d) which is much higher than that of others. It is thus confirmed that the addition of methanol to the aqueous phase enhances the stability and extraction efficiency of the complex.
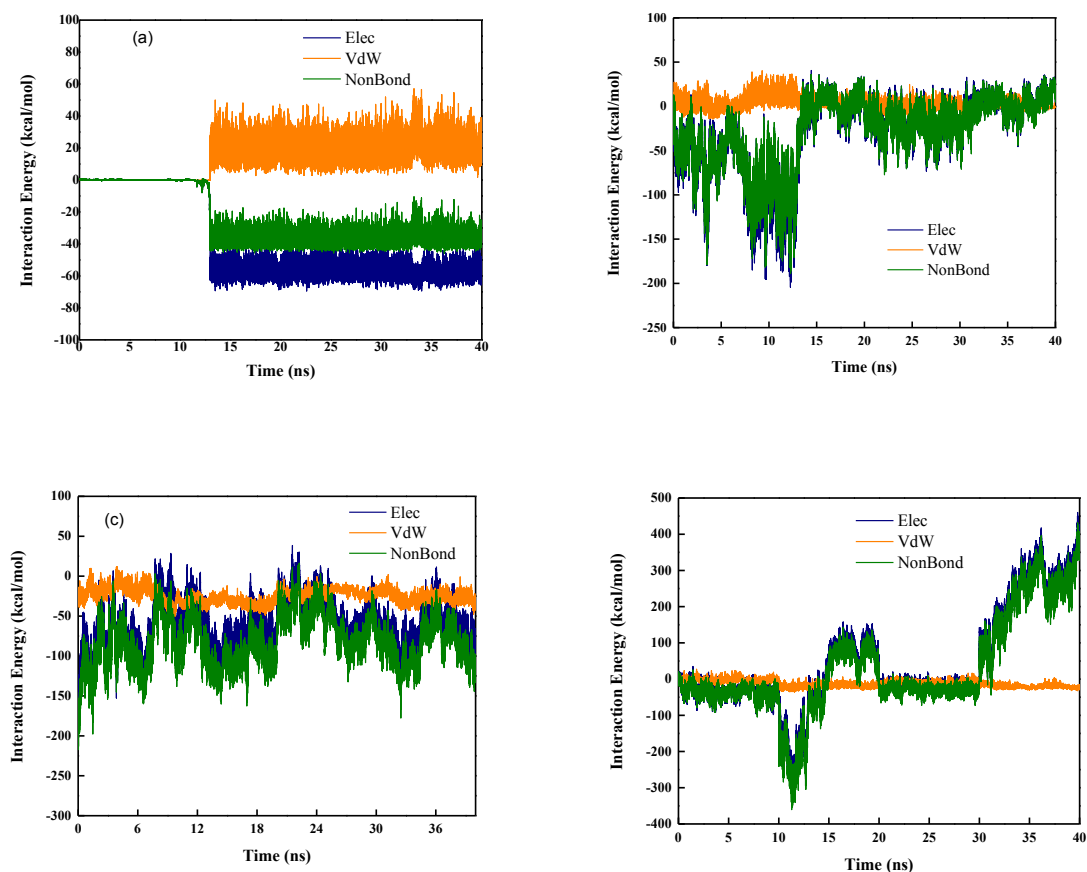

Fig. 4. Interaction energies of (a) Cs^+–DB18C6, (b) Cs^+–water and, (c) Cs^+–[BMIM][Tf$_2$N] (d) Cs^+-Methanol with time.

4. Conclusions

The MD simulations were carried out for the extraction of cesium ions using dibenzo-18-crown-6 (DB18C6) with ionic liquids .The complexation took place well before the phase separation, and the complexing entities were found to be in good contact with both IL, water and methanol. It is observed that the addition of a modifier with low dipole moment such as methanol to the aqueous phase has enhanced the stability and extraction efficiency of the complex.

Acknowledgements

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