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Designing of ligands for solvent extraction of Cs^+ using molecular modeling approach

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ABSTRACT

A molecular modelling (MM) approach has been adopted for designing new ligands for the extraction of Cs^+. The structures of the metal ion-ligand complexes were initially optimized using FORCITE molecular mechanics module of Materials Studio 3.2. The ab initio DMol^3 DFT calculations were further conducted on the MM optimized structures. The selectivity of designed ligands for Cs^+ was ascertained by interaction, strain and hydration energies.

Keywords: Molecular modeling; Extraction; DFT calculations; Crown ethers; Complexation; Cs^+ ion

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1. Introduction

Crown ethers have gained immense popularity and importance over the years in every field of chemistry owing to their applications in a variety of fields that include organic synthesis, polymer synthesis, separation of metal ions, ion-selective electrode and chemical analysis. The use of optically active crown compounds for the resolution of (D-L) amino acids, enzyme models and biological fields have also been demonstrated by various research groups [1]. The ability of crown ethers to form complexes, in particular with metal ions, because of their hydrophilic core and an outer hydrophobic ring structure has been the basis of their many applications. The crown ether compounds have appreciable complexing capacities and selectivities toward alkali and alkaline earth metal ions, lanthanides and actinides, and neutral or ionic organic species in the solutions because of matching cavity sizes and respective metal ion diameters [2]. Crown ethers, in general, have found newer applications as components of supramolecular systems as well [3–5].

Cesium and strontium are high-heat-emitting fission products in the spent nuclear fuel streams which need to be separated and handled independently. The total heat output of the fission product solutions is essentially due to these two isotopes. Removal of these fission products reduces the radiation fields in subsequent fuel cycle reprocessing streams. If Cs-137 and Sr-90 are removed from the fission product solutions, then the solution need not be cooled and the vitrified waste need not be stored for 50 years. On the other hand, they are an excellent source for gamma irradiation and are used for the environmental pollution control, food preservation and sterilization of medical accessories, etc [6].

Several methods have been employed to remove Cs^+ and Sr^{2+} from the nuclear waste solutions. For the extraction of Sr^{2+}, di-cyclohexano-18-crown-6 extractant dissolved in 1-octanol was one of the first crown

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compounds to be tested [7]. One of the major concerns in the use of crown ethers as extractant is their significant solubility in aqueous solutions and therefore their loss during their use. Modification to the extractant structure, therefore, has been suggested to reduce the solubility of the complexes in the aqueous solutions. 4,4′(5′)-Di-*t*-butyl-cyclohexano-18-crown-6 in 1-octanol and later tributyl phosphate as diluents has been reported for strontium extraction [8]. 4,4′(5′)-di-[(l-hydroxy-2-ethylhexyl)benzo]-18-crown-6, derivative of dibenzo-18-crown-6 showed a good Cs^+ distribution coefficient and high selectivity but the extractant was not stable in the nitric acid media of high concentration from where Cs^+ is extracted [9].

Due to the similarity in the cavity size and the cation diameter, dibenzo-21-crown-7 extractant is suggested for Cs^+. In order to understand the mechanism of extraction of metal ions at molecular level, molecular modeling is increasingly employed as a tool. Molecular modeling helps in understanding a system with a better insight to implement the knowledge into practical applications and avoids a trial & error approach. In an attempt to design novel crown ether based ligands for the selective extraction of metal ions, molecular modeling concepts have been employed considering the practical requirements of the metal ions for efficient extraction. Theoretical calculations on various cation-ether complexes have been reported in literature [10]. There are reports about the gas phase calculations for the energies of 12-C-4 ether using STO-3G minimal basis set [11]. *Ab initio* calculations have been performed using RHF/6-31+G(d,p) optimized geometry to study the affinity of 12-C-4, 15-C-5, 18-C-6 ethers with the proton, followed by MP2/6-31+G(d,p) for single point energy evaluation [12]. The semi-empirical CNDO/2 and *ab initio* method with a minimal basis set have also been reported for the 12-C-4 ether–metal ion complexes [13,14]. The structures, binding energies and binding enthalpies of free 18-C-6 ether and its metal ion complexes have been studied at the RHF and MP2 levels using 3-21G and 6-31+G(d) basis sets [15,16].

As crown ethers are known to form stable complexes with the alkali metal ions, alkaline earth metals and some of the lanthanides and transition metal ions, the primary objective of the present work was to develop a suitable macrocyclic crown compounds based on the molecular modeling approach for the selective separation of Cs^+ and Sr^{2+} ions. In the present work, we have first carried out a DFT based study to understand the interaction between alkali metal ions and macrocyclic crown ethers with different ring sizes. Some novel molecules have been designed further for selective separation of Cs^+ and Sr^{2+} ions.

2. Materials and methods

The FORCITE module of Material Studio (MS) Version 3.2, Accelrys, Inc., USA was employed for molecular mechanics simulations using Universal Force Field (UFF) [17–19]. The partial charges on the atoms were calculated using QEq method [20]. Initially, the structures of the crown ethers were optimized independently in vacuum for their energies. The UFF force field parameters are not statistically orthogonal, so optimized values can be modified by coupling with other parameters. UFF has 126 atom types and it attempts to reduce almost all the parameters to being derivable from a fairly small set of atomic parameters. Most of the properties like torsion angles, polarisability, are well taken care of in this force field. But heavy metals, lanthanides and actinides are not represented well using UFF. The properties of alkali and alkaline earth metals which are used in the present study are precisely explained using UFF.

The DFT calculations were therefore conducted further on the MM optimized structures using $DMol^3$ module of MS 3.2. A double numerical plus polarization (DNP), numerical basis set, was used for all the DFT calculations in which a polarization *p*-function has been provided on all hydrogen atoms for the accurate measurements of energy values incorporating the hydrogen bonding in the system. Hybrid methods which mix exact exchange energy with density functional approximations to exchange and correlation have become a standard tool in quantum chemistry. Becke [21] noticed that utilizing a portion of the exact exchange energy together with density functional exchange and correlation, significantly improves the accuracy of energy values. But the Becke–Lee–Yang–Parr correlation (BLYP) functional does not only depend on the charge density and its gradient but also on the kinetic energy density [22]. So, the exchange correlation energy was calculated using (BLYP) functional [23–25]. A metal ion was appropriately placed inside the cavity of the optimized crown ether structure and the entire structure was further optimized.

3. Results and discussions

The size of the cation and that of the crown ether cavity are important factors in the formation of stable complexes between the metal ion and the crown ether. It has been well documented in the literature that there exists a correlation between the cavity radii of the crown ethers and the ionic radii of the alkali metal ions as shown in Table 1 [26]. Since the cavity radius (1.7–2.1 Å) of dibenzo-21-crown-7 (DB-21-C-7) is very close to the ionic radius of Cs^+ ion (1.67 Å), in order to design a novel extractant for the extraction of Cs^+ ion, a few derivatives

Table 1
Relative sizes of cations and crown ether cavities [26]

Cation	Ionic radius, Å	Crown ether	Cavity radius, Å
Li^+	0.76	12-Crown-4	0.60–0.75
Na^+	1.02	15-Crown-5	0.86–0.92
K^+	1.38	18-Crown-6	1.34–1.43
Rb^+	1.52	21-Crown-7	1.7–2.1
Cs^+	1.67		

of DB-21-C-7 were modeled to determine if the compounds selectively distinguish between different metal ions (Figs. 1–4). It was hypothesized that if DB-21-C-7 could be derivatised on the benzene rings with *e*-releasing and *e*-withdrawing groups, then the electron density inside the cavity of the crown ether molecule can affect the selective complexation with certain metals with the compounds. For instance, *t*-butyl and -NH_2 groups, being *e*-releasing groups, tend to push the electrons towards the cavity increasing the electron density on the oxygen atoms of the crown ether cavity and the –$CONH_2$ being *e*-withdrawing group would decrease the electron -density around the cavity. The charges on the oxygen atoms of the DB-21-C-7 molecule are given in Table 2 which confirm the above conjecture. The encapsulation of a metal ion in the crown cavity is based on the size of the cavity and electron density in the cavity which in turn is decided by electronegativity of oxygen

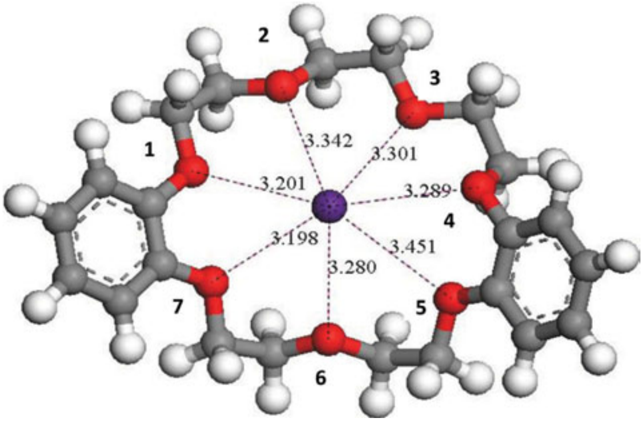

Fig. 1. Di-benzo-21-crown-7 with Cs^+ ion.

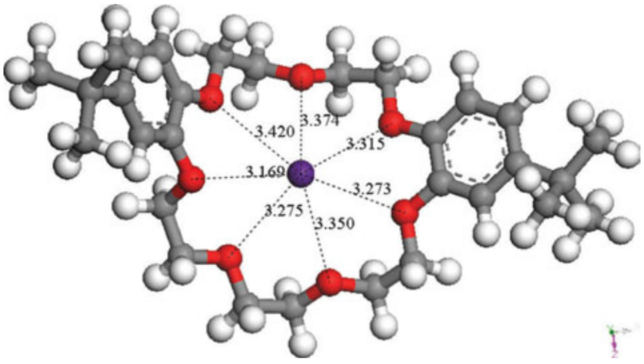

Fig. 2. Di-*tertiary* butyl -DB 21-C-7 with Cs^+ ion.

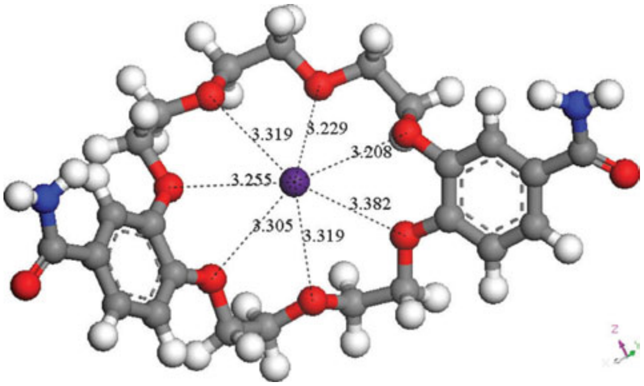

Fig. 3. Di-amido DB 21-C-7 with Cs^+ ion.

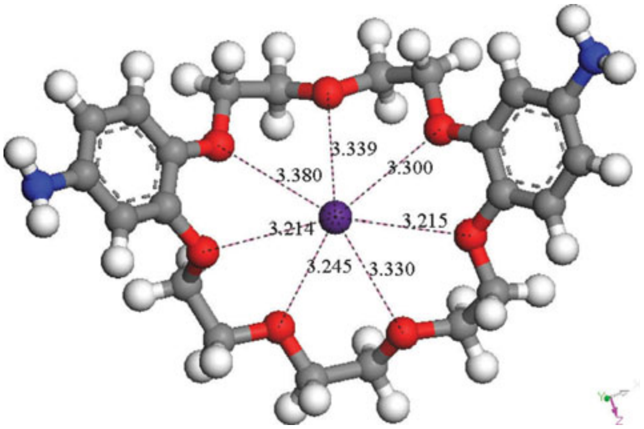

Fig. 4. Di-amino DB 21-C-7 with Cs^+ ion.

Table 2
Charges on the oxygen atoms of DB-21-C-7 and the derivatised DB-21-C-7 compounds

Oxygen atoms (as per Fig. 1)	DB21C7	Di-tertiary butyl DB21C7	Diamino DB21C7	Diamido DB21C7
O1	−0.4627	−0.5367	−0.5277	−0.4976
O2	−0.4335	−0.5135	−0.5028	−0.4726
O3	−0.4284	−0.5086	−0.4969	−0.4783
O4	−0.4597	−0.5186	−0.5014	−0.4868
O5	−0.4525	−0.5249	−0.5088	−0.4696
O6	−0.4199	−0.5012	−0.4987	−0.4707
O7	−0.4493	−0.5287	−0.5036	−0.4771

atoms. The selectivity of the designed ligands was analysed by comparing the interaction energies on complexation with the metal ions. The interaction energy of a metal ion with the crown compound was calculated as follows.

$$\text{Interaction energy} = E_{\text{metal-compound complex}} - (E_{\text{compound}} + {}_{\text{Emetal ion}}) \quad (1)$$

The interaction energy is indicative of the complex stability. The more stable is the complex, higher is the magnitude of the interaction energy of the system.

The electrostatic potential surface of DB-21-C-7, DB-21-C-7 + Cs^+ and DB-21-C-7 + Sr^{2+} are shown in Figs. 5–7, respectively. The blue region in the centre suggests high electron density inside the cavity of the crown compound and the reddish region on the metal ion depicts the electropositive nature of the metal ion. The reddish region around the periphery of the complex suggests low electron density around that area. Electrostatic charges on the system are computed from the electrostatic potential (ESP) which is a measure of charge distribution that also provides other useful information [27,28]. The electrostatic potential can be thought of as a measure of how positive or negative the molecule is at a point on the surface. A positive value at the point means that the net effect experienced by the probe charge as it was brought from infinity was repulsion, while a negative value means that the probe charge was attracted to the point, i.e. energy was released as it fell from infinity to P. The ESP at a point is the net result of the effect of the positive nuclei and the negative electrons. The shape of the surface shows the distribution of the electron density. The potential surface for a compound gives the details of the electron density on various atoms of the complex from which one can identify electropositive and electronegative sites.

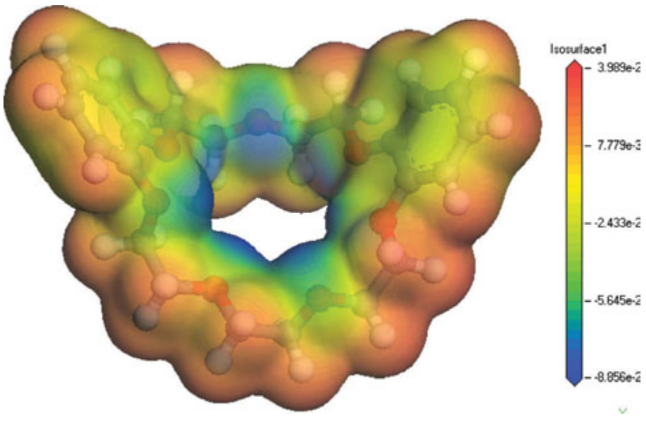

Fig. 5. ESP of DB-21-C-7.

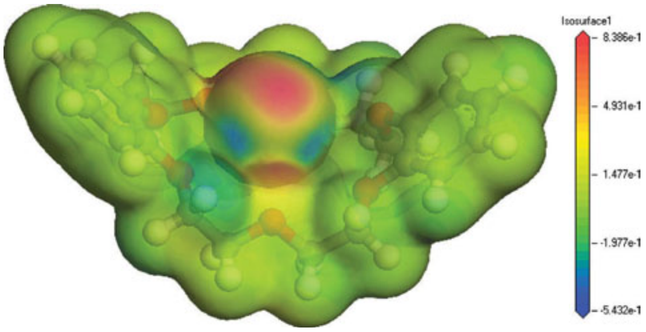

Fig. 6. ESP of DB-21-C-7 with Cs^+ ion.

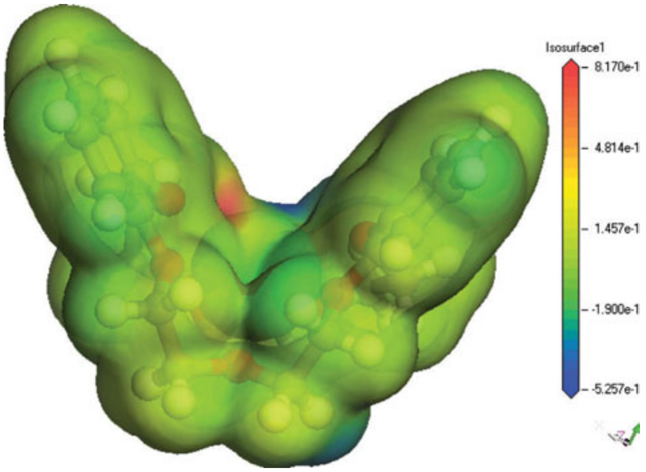

Fig. 7. ESP of DB-21-C-7 with Sr^{2+} ion.

The selectivity of ligands towards metal ions can be explained by two factors, namely, strain energy and hydration energy.

a) *Strain energy*: The ligand shows selectivity for a metal ion for which it has the highest interaction energy. In order to form a complex with a metal ion, the ligand molecule rearranges itself to have the maximum interaction. But it may be achieved at the cost of stretching of some bond lengths, bond angles, torsion angles, etc. As a result, the ligand molecule gets strained after the complex formation. This strain energy associated with the complexation process is, therefore, calculated from difference in valence energy of the complex and that of the free ligand, both estimated from FORCITE MM calculations on the respective structures. The Valence Energy is the summation of energy contributions from bond stretching, angle bending, torsion angle and out of plane motion. Any change inflicted in the ligand due to the presence of a metal ion would be reflected in the valence energy term and for this reason, pre-organization of the designed ligand can be analysed from the strain energy values.

Among the three derivatives of DB-21-C-7 which have been designed for Cs^+ ion extraction, the di-*t*-butyl derivative of DB-21-C-7 forms a more stable complex with Cs^+, than di-amino and di-amido derivatives as indicated by the interaction energy values. The structures of the DB-21-C-7 complexes indicate that the ligand gets reorganized to accommodate Sr^{2+} ion. Table 3 shows the interaction energies of Cs^+ and Sr^{2+} ions with the designed ligand and the strain energy of the complexes due to the strain induced in the ligand after the complexation. It can be seen that although the interaction energy values of Sr^{2+} ion with all DB21C7 derivatives are higher than those with respective complexes with Cs^+ but the strain induced in the ligands after complex formation is higher indicating higher degrees of preorganization of the ligand and distortion in the geometries in the presence of Sr^{2+} ion. This indicates that the strain energies may compensate for the interaction energies and thus affect the selectivity in complexation in presence of other ions in the solutions.

b) *Hydration energy:* Hydration effect refers to the stabilization of the protonated cation by water molecules. The water molecules surround the metal ions in a coordination shell with an associated hydration energy. The selectivity of the ligands towards Cs^+ and Sr^{2+} ions can be explained by considering the hydration of the two ions in the solution. In order to understand the system, hydration of the metal ions were studied by simulating metal ion-water complexes with the addition of upto eight water molecules in a stepwise manner and calculation of their hydration energy using the following Eq. (2);

$$E_{\text{Hyd}} = E_{\text{(metal ion in nth hydration sphere)}} - [E_{\text{(metal ion)}} + nE_{\text{(water molecules)}}] \quad (2)$$

where $E_{\text{(metal ion in nth hydration sphere)}}$ is the energy of the metal ion and water complex with 'n' no of water molecules where $n = 1$ to 8, $E_{\text{(metal ion)}}$ is the energy of the metal ion and $E_{\text{(water molecules)}}$ is the energy of a single water molecule [29]. The E_{Hyd} of the metal ion and water complex increases with the increase in the number of water molecules accounting for ion-water interactions as well as intermolecular H-bonding interactions between the water molecules in the system. The hydration energies for both the metal ions with corresponding water molecules are compared in Table 4.

The hydration energy of Cs^+ is lower than that for Sr^{2+}. Cs^+ is a mono-cation with the coordination number of 6 while Sr^{2+} is a di-cation with the coordination number of 8. Therefore, comparatively, lesser number of water molecules surround Cs^+ as opposed to that in the hydration shell of Sr^{2+} ion. In other words, Sr^{2+} ion shows higher hydration energy than Cs^+, which will be extensively hydrated. Any extraction process, in general, involves removal of metal ion from an aqueous phase where it is surrounded by water molecules to the organic phase with the help of extractants like crown ether compounds. So if the hydration energy is higher, then the metal ion is extracted with the help of ligand with difficulty because higher energy will be required to cross the hydration energy barrier to pull the metal out of its hydration sphere. The structure of cesium surrounded by six water molecules in a trigonal prismatic geometry and structure of Sr^{2+} with eight coordination number surrounded by eight water molecules in square antiprismatic geometry are shown in Figs. 8 and 9, respectively. The partitioning behavior of the metal ions is therefore decided not only by the interaction between the metal ion and the ligand but also by strain energy associated with the reorganization of the ligand structure to accommodate the metal ion to have the best interaction and the environment of the metal ion in aqueous solutions from where it is extracted and transferred to the organic phase by the extractant.

Table 3
Interaction energies of the metal ions and the strain energy values with derivatised DB21C7 ligands

S.No	Ligand	I.E (Kcal/mol)	Strain energy (kcal/mol)
1	DB21C7 + Cs^+	–60.63	6.85
2	DB21C7 + Sr^{2+}	–219.935	78.5
3	Diamino-DB21C7 + Cs^+	–64.208	7.388
4	Diamido-DB21C7 + Cs^+	–54.703	7.839
5	Di-*t*-butyl-DB21C7 + Cs^+	–65.442	7.339
6	Diamino- DB21C7 + Sr^{2+}	–231.180	63.834
7	Diamido-DB21C7 + Sr^{2+}	–210.336	72.975
8	Di-*t*-butyl-DB21C7 +Sr^{2+}	–229.181	74.336

Table 4
Hydration energy of Cs^+ and Sr^{2+} ions

No of water molecules	Interaction energy, kcal/mol	
	With Cs^+	With Sr^{2+}
1	–0.02506	–0.08008
2	–0.04782	–0.01507
3	–0.06835	–0.2135
4	–0.08622	–0.27002
5	–0.10719	–0.31698
6	–0.12546	–0.35644
7	–0.15807	–0.39009
8	–0.21428	–0.41828

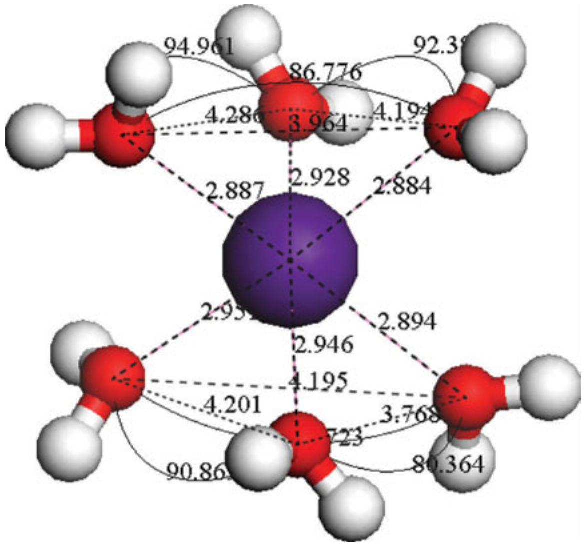

Fig. 8. Hydrated Structure of Cs^+ in water.

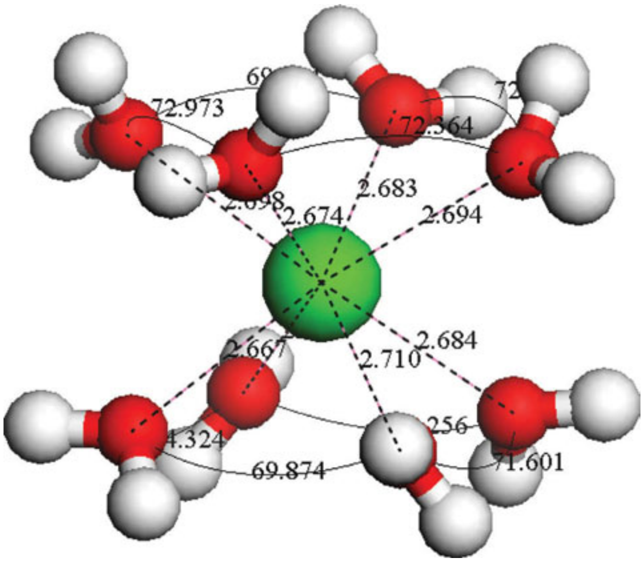

Fig. 9. Hydrated Structure of Sr^{2+} in water.

4. Conclusions

Crown ether compounds have proved to be excellent extractants for the extraction of various metal ions with significant selectivity and extraction efficiency. Molecular modeling potentially helps in understanding the properties of molecules and extending it to a larger spectrum of reactions. Molecular modeling performed on crown ethers have led to a better insight into the extraction process. Considering the possibility of derivatising crown ether compounds, different derivatives of DB-21-C-7 were modeled for the recovery of Cs^+ ion using DFT calculations. In order to estimate the selectivity of these derivatised crown ether compounds towards Cs^+, a comparative study was made using Sr^{2+} ion. Apart from interaction energy, which is a measure of stability of the complexes, strain energy and hydration energy were also computed for the crown compound complex with Cs^+ and Sr^{2+} which are the measures of geometric constraints and solvent effects. It can be construed from these observations that although, seemingly large interaction energy of Sr^{2+} ion with the DB21C7 derivatives might suggest these ligands to be better for Sr^{2+} ion extraction than for Cs^+ ion but the higher values of strain energy and hydration energy for Sr^{2+} ion demonstrate that these ligands are better suited for Cs^+ ion extraction.

Acknowledgements

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