Desalination and Water Treatment
www.deswater.com

12 (2009) 93–99

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doi: 10.5004/dwt.2009.947

Conformational effect on the preferential binding of alkali metal cation with crown ether: A molecular level investigation

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Received 22 July 2008: Accepted 12 October 2009

ABSTRACT

We report density functional theory (DFT) based study to predict various conformation of free 12-crown-4 ether and its complexes with alkali metal cations. The optimized geometries, binding energies, and binding enthalpies of crown ether–cation complexes have been determined with a correlated hybrid density functional, namely Becke's three-parameter functional, B3LYP using split valence basis function, 6-311++G(d, p). Geometry optimizations for all the conformers of free 12-crown-4 ether and its metal cation complexes are carried out with several initial guess structures based on semi-empirical PM3 optimized results. The optimized structure for free 12-crown-4 ether and its metal cation complexes obtained from the present DFT calculation confirmed the experimentally reported structures. The calculated values of the gas phase binding energy for lithium ion is always found to be higher than that of the sodium ion for all the conformers of macrocyclic 12-crown-4 ethers reported in the present study. Expected preferential binding of Li^+ ion over Na^+ ion in case of a particular conformer of 12-crown-4 ligand is reversed due to micro-solvation effects reflecting its significant influence towards metal ion selectivity. The density functional theoretical calculated values of binding enthalpy are in fair agreement with the available reported experimental values.

Keywords: Crown ether; Alkali metal ion; Conformation; Extraction; Density functional theory; Molecular modeling

1. Introduction

Since the date of its discovery by Pederson, macrocyclic crown ethers [1,2] have been widely used for selective separation of various metal ions in different fields of applied nuclear science and technology. These cyclic polyethers display a wide range of selectivity for binding various metal cations depending not only on the size of the crown ether and type of the donor atom but also on the size of the metal cations, conformation of the crown ether and also on the micro-solvation of the metal cations. This highly specific and selective behavior has made it useful for various applications such as metal ion separation, isotope separations [3–6] and ion transport through membranes [7–10].

The metal ion/ether interaction is nothing but a simple charge–charge and charge–dipole electrostatic interaction. Earlier the matching of the metal ion diameter to the crown ether cavity was thought to be the most important criterion for the selectivity of the crown compounds. But extensive studies on these systems revealed that other factors like proper spatial orientation of the crown ether oxygen dipole in the direction of metal ion and micro-solvation of the metal cation are also of equal importance

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Presented at the Symposium on Emerging Trends in Separation Science and Technology (SESTEC-2008)
March 12–14, 2008, University of Delhi, Delhi, India

for this kind of interaction. Owing to its large structure and flexible nature, free macrocyclic crown ether can give rise to a large number of conformations in crystals and solution by changing the orientation of the O atoms present. Extraction of a metal ion will be favorable if there are suitable cavities inside the host ligand where a given metal ion can be attached, transported across the interface followed by easy recovery of the metal ion by other stripping reagents, mostly water as solvent.

Different conformers of crown ether with small energy gap and of low energy barriers enhance the extraction process greatly. In this context, all microscopic details of the host crown ether molecule, such as shape and dimensions of its cavity, sites for ion-pairing, ion-dipole and dipole–dipole interactions should be thoroughly studied for better understanding of the separation process [11]. But, these quantities are not experimentally available; therefore evaluations by other means are required for the necessary conformal analysis. Molecular modeling is being widely recognized as a powerful protocol for microscopic studies can be conveniently used to serve our purpose. Using present day computational methods [12–14] along with the high speed parallel computer, the properties of complex molecular systems can be confidently predicted, and thus designed and optimized, for specific applications.

In the above context, the structure and energetics of free 12-crown-4 (12C4) ether in gas phase has been reported earlier [15] using STO-3G minimal basis set. The structure and energetics of free 12-crown-4 and its Li^+ complex has been reported earlier at STO-3G minimal basis set level [16]. The conformation of free 12-crown-4 has also been reported at molecular mechanics level of calculation [17–19].

Ab initio calculations have been performed to study the proton affinity of 12C4 ether using RHF/6-31+G(d,p) optimized geometry followed by MP2/6-31+G(d,p) single point energy evaluation [20]. RHF and MP2 methods [21,22] have also been used to determine the structures and binding enthalpy of alkali metal ion and 12C4 ether complex using 6-31G(d,p) and aug.cc PVDZ bais set. The stability of the 12C4 ether-metal ion complexes has been studied using the semi-empirical CNDO/2 and *ab initio* method with minimal basis set [23,24]. *Ab initio* calculations have been carried out on a number of selected conformations of 12-crown-4 using molecular mechanics calculations (MM3) [25] at HF level for a range of basis sets varying from STO-3G, 3-21G and 6-31G up to 6-31G(d,p), 6-31++G(d,p) and 6-311++G(d,p). Recently, the conformational study of free 12-crown-4 and its metal ion complexes has been reported at the MM3 level and also at the B3LYP/6-31+G(d), MP2/6-31+G(d)//B3LYP/6-31+G(d) and MP2/6-31+G(d) level of computation [26–29] along with the data of vibrational spectra.

But a systematic density functional theoretical (DFT) based investigation using highest level of 6-311++G(d,p) basis function to study the preferential interaction of metal ion with different conformers of 12-crown-4 ether is still lacking, though it is well established that DFT based calculation can predict very reasonable structures at much less computational cost than others.

In the present work we have performed DFT based calculation to understand the microscopic interaction between alkali metal ions (M^+) and different conformers of macrocyclic 12-crown-4 ether (L). A hybrid density functional, namely Becke's three-parameter nonlocal hybrid exchange-correlation functional (B3LYP) has been applied using split valence 6-311++G(d,p) basis function in a very systematic way. Structures of fully relaxed geometry, binding energy and binding enthalpies for alkali metal ion-crown ether systems are presented. The present work will help in understanding the separation processes on the molecular level as well as in the synthesis of tailor-made new suitable solvent/extractant for better and selective separation of the metal ions. The outline of the paper is organized as follows. The computational protocols are described in section 2. In section 3, we discuss the calculated results and the present work is finally concluded in section 4.

2. Computational protocols

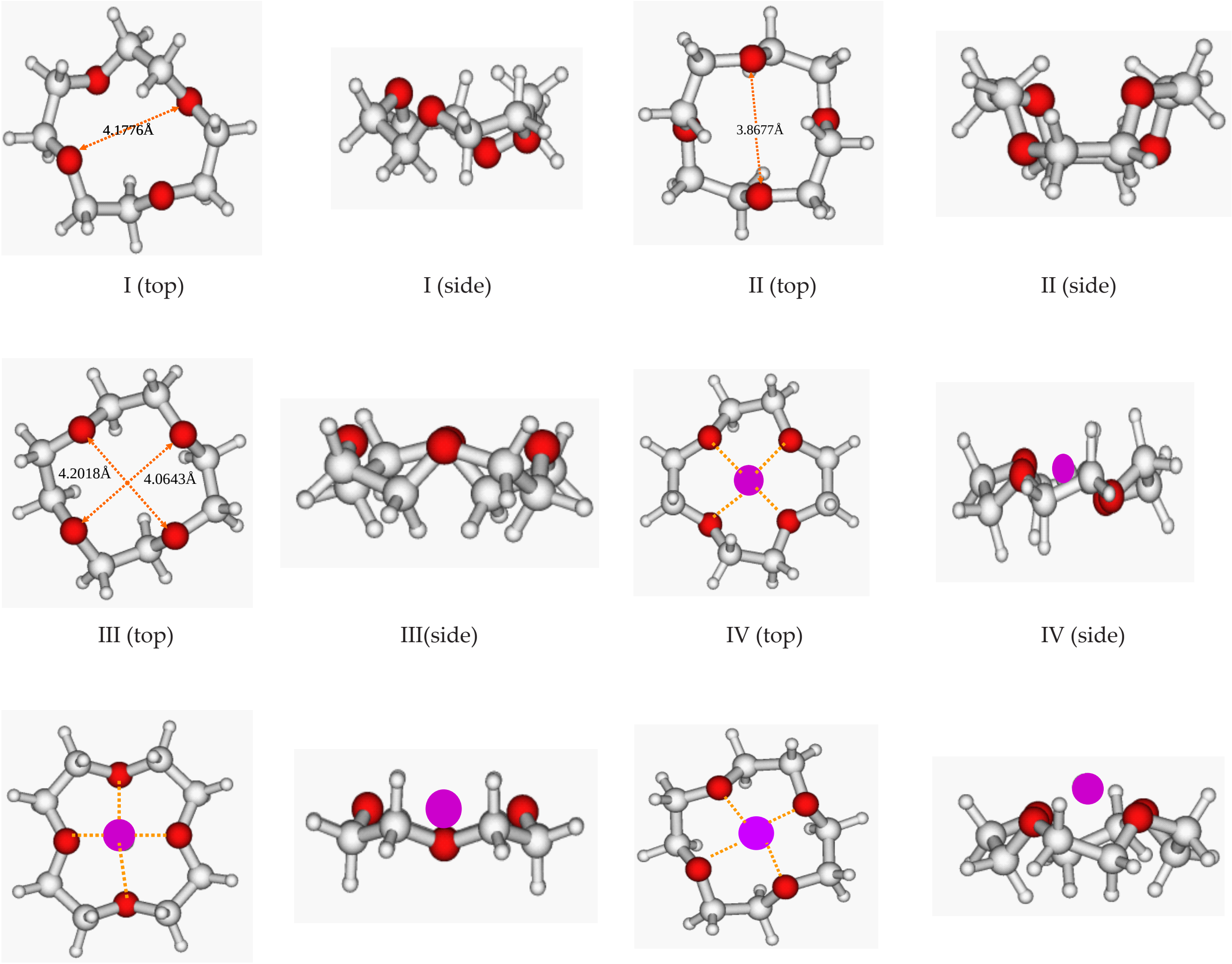
We have carried out a density functional theory based [30–32] study to predict various conformations of free crown ether and its complexes with metal cations and also the effect of micro-solvation on the binding of metal cations with different conformers of 12-crown-4 ether. We will present the optimized minimum energy structure of various conformers and various thermodynamic parameters for alkali metal cation–crown ether complexes. Density functional theory based electronic structure calculation is computationally less costly having a very good predictability power for various structural and thermodynamic properties of a molecular system [30]. Among the various density functional modules, the Becke's three-parameter nonlocal hybrid exchange-correlation functional (B3LYP) is the most popular one [33–36]. Density functional theory at 6-311++G (d, p) level using B3LYP functional has been used for the geometry optimizations of free crown ether and M^+-ether complexes based on Newton Rapson optimization procedure as implemented in GAMESS quantum chemistry code [37]. The initial guess structures are first calculated based on PM3 semi-empirical calculations and subsequently used for input in DFT calculation. We have used MOLDEN program [38] for the visualization of various molecular geometry.

3. Results and discussion

Fully relaxed structures, binding energy and binding enthalpies for free 12-crown-4 ether and its alkali metal complex systems with different conformers are calculated at B3LYP/6-311++G(d,p) level of theory. The representative metal ions considered for present DFT level calculations are Li^+ and Na^+ metal cations. Detailed calculated results are presented in the following paragraphs.

3.1. Structure

The fully relaxed equilibrated geometry for free 12-crown-4 ether is given in Fig. 1. We have shown three minimum energy conformers for 12-crown-4 (12C4) in Fig. 1 (I-III). The conformer of Fig. 1 (I) has the cavity size (centre to centre O–O diagonal distance as shown by dashed line in the figure) of the value of 4.1776 Å, the conformer (II) has the cavity size of 3.8677 Å and the conformer (III) has the average cavity size value of 4.1330 Å. The most stable conformer is one in which two O atoms, placed diagonally are at the top of the ring and two at the bottom of the ring (II) which has also been observed earlier at STO-3G and RHF/6-31+G* level of theory respectively [15,21]. This is due to the presence of 4 number of CH…O interaction within the crown ether ring, which in turn reduces the cavity size of the crown ring. Here the O–O repulsion is least. The least stable one

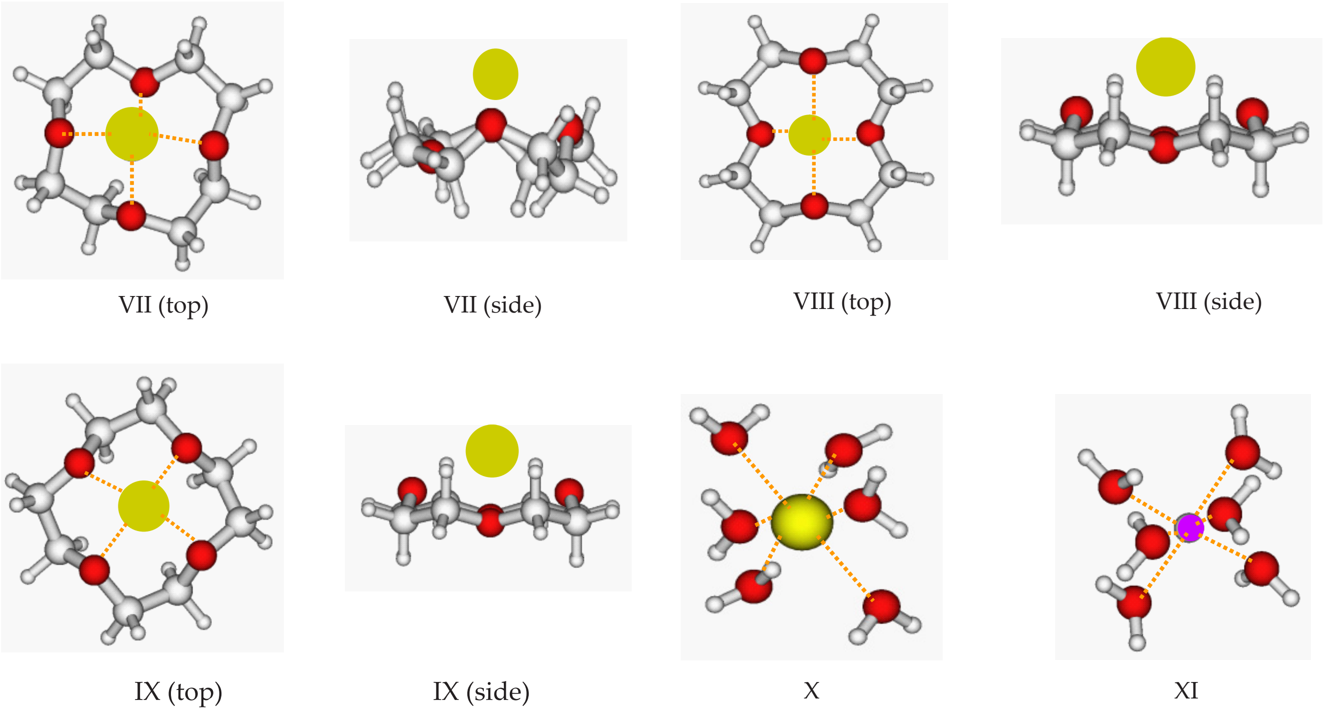


I (top) I (side) II (top) II (side)

III (top) III(side) IV (top) IV (side)

V (top) V (side) VI (top) VI (side)

Fig. 1. Optimized minimum energy structure at B3LYP level of theory using split valence 6-311++G(d,p) basis function for free 12-crown-4 and metal ion- crown ether complex. (I) free-12-crown-4 (top/side view), (II) free-12-crown-4 (top/side view), (III) free-12-crown-4 (top/side view), (IV) Li^+–12-crown-4 (top/side view), (V) Li^+–12-crown-4 (top/side view), (VI) Li^+–12-crown-4 (top/side view), (VII) Na^+–12-crown-4 (top/side view), (VIII) Na^+–12-crown-4 (top/side view), (IX) Na^+–12-crown-4 (top/side view), (X) Li^+–$(H_2O)_6$ (top view) and (XI) Na^+–$(H_2O)_6$ (top view). The largest red spheres, medium sized grey spheres and smallest grey spheres refer to O atom, C atom and H atom respectively. The violet and yellow sphere represents the Li^+ and Na^+ metal ions respectively.


VII (top) VII (side) VIII (top) VIII (side)

IX (top) IX (side) X XI

Fig. 1. Continued.

is that where all the O atoms are at the top of the ring and there is no CH…O interaction within the crown ether ring as clearly visible in Fig. 1 (III) and this effect is manifested in the comparatively large cavity size among all the three conformers. This may be due to the high electronic repulsion between four O atoms, which in turn makes the cavity elliptical in shape. The remaining conformer has two adjacent O atoms at the top of the ring and two at the bottom of the ring with two number of CH…O interaction within the crown ether ring (I). Hence this conformer lies in the intermediate level of stability as well as the cavity size is of the intermediate value between the other two conformers cavity size. The last two conformers have already been reported by the experiments [39].

The equilibrium geometries of the complex of Li^+ and Na^+ metal ion with 12-crown-4 ether calculated at B3LYP/6-311++G(d,p) level of theory are also given in Fig. 1 (IV-IX). The calculated values of the M^+–O bond distance are given in Table 1. Obviously the Li^+–O distance is shorter than the Na^+–O bond length due to the smaller cationic size of the Li^+ ion than Na^+ ion.

For both Li^+–12C4 complex (Fig. 1, IV–VI) and Na^+–12C4 complex (Fig. 1, VII–IX) ion, the most stable conformer is the one with all four oxygen atoms placed at the top of the ring and directly coordinated to the metal ion and has been reported earlier in solid state X-ray studies [40–42]. The least stable conformer, in the case of Li^+, has two O atoms placed diagonally at the top of the ring and other two are at the downside of the ring (Fig. 1, V). The Li^+–12C4 complex with intermediate stability has two adjacent O atoms at the top and other two at the bottom of the ether ring (Fig. 1, IV). One interesting point to be noted here is that the conformer of 12C4, which was least stable in free form has become most stable due to binding with the metal ion, whereas the most stable conformer in

Table 1
Calculated values of different structural parameters of free ligand (L) and metal–ligand (M+–L) system at B3LYP level of theory using 6-311++G(d,p) basis function for all the elements

System	C–C bond length (Å)	C–O bond length (Å)
Ligand (L)/M^+–L		
A		
I	1.5205	1.4242
II	1.5195	1.4223
III	1.5241	1.4151
M^+=Li^+		
IV	1.5251	1.4389
V	1.5296	1.4432
VI	1.5207	1.4342
M^+=Na^+		
VII	1.5213	1.4386
VIII	1.5214	1.4249
IX	1.5218	1.4346

free state with two diagonal O atoms up and other two down the ether ring (Fig. 1, IV) has become least stable after forming a complex with the metal ion. But in the case of Na^+–ether complex, the least stable conformer has two adjacent oxygen atoms at the top of the ring and two at the bottom of the ring (Fig. 1, VII). The conformer of the Na^+–ether complex with two diagonal O atoms up and other two down the ether ring (Fig. 1, VIII) stand at the intermediate energy level. In M^+–12C4 ether complex, two O atoms, placed diagonally are at the top of the crown ether ring and remaining two O atoms are at the bottom of the crown ether ring for both the metal ion has already been shown earlier at RHF and MP2 level of theory [21].

From the figure it is seen that the Li^+ metal ion fits nicely inside the cavity of 12C4 ether whereas sodium ion sits above the oxygen plane of 12C4 ether. The fact that the Na cation is found above and not inside within the crown ether cavity can be explained by both the actual size of the cavity and the preferred specific interactions of the cation with the lone pairs of the crown ether O atoms. The diagonal distance between the opposite crown O atoms across the crown ether ring is 3.8677–4.1776 Å, which means that the adjusted vander Walls diameter of the cavity is 1.2237–1.5336 Å after subtracting the diameter of oxygen atom as 2.644 Å [46]. The effective cavity size is therefore too small to accommodate the Na^+ cation within the plane of the four crown ether O atoms. From the above optimized structures it is seen that the matching of the cation size within the crown ether ring depends on the cavity size of the crown ether also. So this will help in screening and predicting the suitable extractants for selective separation of metal ions. These computational results of fitting trend of metal ion with different cavity size also will help in the synthesis of tailor made new suitable ligands by varying the structure of the crown ether with the addition of the substituent or adding extra ether linkage in the ring.

3.2. Binding energies and binding enthalpies

The most important property for cation selectivity with crown ether is the binding enthalpy (BE). The BE of M^+-ether complex is defined by the following general relation

$$BE = E_{M+\text{-ether}} - (E_{M+} + E_{\text{ether}}) \quad (1)$$

where $E_{M+\text{-ether},}$ E_{M+} and E_{ether} refer to the energy of the M^+–ether complex, M^+ ion and free ether system respectively. The values of $E_{M+\text{-ether}}$ and E_{ether} have been calculated at B3LYP/6-311++G(d, p) level of theory. The calculated binding enthalpy is given in Table 1. From Table 1 it is seen that the binding enthalpy of cation–ether complexes depends on the conformation also.

For both the Li^+ and Na^+ the highest binding enthalpy is obtained for that 12-crown-4 ether where all the four O atoms are at the top of the ring and there is no CH…O interaction within the crown ether ring. In the case of Li^+ the lowest binding enthalpy is obtained for the conformer having two O atoms, placed diagonally at the top of the ring and two at the downside of the ring whereas in case of Na+ the lowest binding enthalpy is obtained for the conformer with two adjacent O atoms at the top of the ring and two at the downside of the ring with two number of CH…O interaction within the crown ether ring. The binding enthalpy using standard statistical mechanical procedure [43] for Eq. (1) is calculated and listed in Table 2. The calculated values of binding enthalpy (T = 298 K) are different for different conformers of the crown ether.

It is seen from Table 2 that the calculated values of BE for Li^+ and Na^+ ions with 12-crown-4 are within the error bar of the experimental results [44,45]. The calculated values of BE indicate that all the conformers of the 12-crown-4 preferentially bind the Li^+ metal ions over Na metal ions. The present molecular level understanding of the metal ion crown ether systems will help in the

Table 2
Calculated geometry, energy and thermodynamics parameters of metal ion ligand (M+L) systems at B3LYP level of theory using 6-311++G(d,p) basis function

System (M^+L)	Bond length in Å (M^+–O)		Total electronic energy (a.u.)	Relative energy (kcal/mol)	Binding enthalpy (kcal/mol) (theory)	Binding enthalpy (kcal/mol) (experiment)
	Minimum	Maximum				
M^+=Li^+						
IV	1.8909	1.9516	–622.5577	6.19	–89.15	–90±12[†]
V	1.8736	1.8870	–622.5715	12.37	–82.91	–90±12[†]
VI	1.9595	2.1987	–622.5721	0	–95.41	–90±12[†]
M^+=Na^+						
VII	2.3710	2.3774	–777.2895	17.14	–55.85	–61±3[‡]
VIII	2.2370	2.5504	–777.2966	10.01	–62.46	–61±3[‡]
IX	2.3479	2.3575	–777.3076	0	–72.54	–61±3[‡]

[†]Ref. [44], [‡]Ref. [45]

synthesis of new suitable ligands for better and selective separation of the metal ions based on density functional theory based molecular modeling calculation.

The smaller the ion, the shorter the M^+–O bond length and the stronger the interaction which in turn increases the electrostatic binding energy. Earlier we have shown that for a given metal ion the binding energy increases with the increase in the number of donor oxygen atoms, i.e. with the increment of the ring size [32]. Here, we have shown that the binding enthalpy also depends on the spatial orientation of the donor oxygen atoms i.e. on the conformation of the crown ether structure.

3.3. Microsolvation

The selectivity of Li^+ ion is greater than Na^+ ion for all the conformers of 12-crown-4 ether ligands studied here as revealed from the following exchange reaction in gas phase as

$$Na^+–L + Li^+ = Li^+–L + Na^+ \qquad (2)$$

In the above exchange reaction the free energy change for the forward reaction for all the three conformers is always negative which means that the selectivity of Li^+ ions over Na^+ ions is always greater in the gas phase in the absence of any solvent water molecules.

In order to study the selectivity of metal ions in the presence of solvent water molecules, now we consider the same exchange reaction but in the presence of hydrated metal ion (Fig. 1 X and XI) by the following exchange reaction

$$Na^+–L + Li^+(H_2O)_6 = Li^+–L + Na^+–(H_2O)_6 \qquad (3)$$

Among the three isomers of 12C4 ligand, the one, which has two adjacent O atoms at the top of the ring and two below the ring (Fig. 1. I) favors the selection of Na^+ ion over Li^+ ions in the presence of solvent water. According to the cavity matching criteria, Li^+ ion (size 1.22 Å) is supposed to bind preferably with the crown ligand (cavity size 1.223–1.5336 Å) in comparison with Na^+ ion (size 1.9 Å). But the anomalous behavior of the particular conformer towards Na^+ reveals the importance of the micro-solvation in the ion exchange reaction.

4. Conclusions

The optimized geometries, binding energy and binding enthalpies for M^+–12C4 complexes (M^+= Li^+ and Na^+) along with the optimized structures of different conformers of free 12C4 ligand have been presented based on density functional theory at 6-311++G (d,p) level using B3LYP exchange functional in gas phase. It is noticed that Li^+ ion fits nicely inside the cavity of 12C4 ether leading to stronger electrostatic interaction with the ligand whereas Na^+ ion sits above the oxygen plane of 12C4 ether owing to its bigger size. Also, the binding enthalpy for Li^+–12C4 complexes is always higher than that of Na^+–12C4 complexes. From this study, it can be clearly stated that the preference of one conformer over others depends on the environment as well as the nature of the metal ion present as revealed from the change of the most stable conformer in free ligand during complex formation with the metal ion (Li^+ and Na^+). Preferential binding of Na^+ ion over Li^+ ion in case of a particular conformer of 12C4 ligand due to micro-solvation reflects its significant contribution towards metal ion selectivity. The calculated values of binding enthalpy (298 K) for Li^+ and Na^+ ions with 12C4 ether are in good agreement with the experimental results which means that the density functional theory can be suitably applied instead of computationally costly MP2 method for prediction of structures, binding energies and binding enthalpies of metal ion-crown ether complexes and hence can be used for the design of metal selective ligand.

Acknowledgements

We would like to acknowledge computer center BARC for the ANUPAM parallel computational facility. It is of great pleasure to acknowledge Dr. B.P. Sharma for his continuing support and encouragement.

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