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SELECTIVE EXTRACTION OF CESIUM AT TRACER LEVEL CONCENTRATION FROM A SODIUM NITRATE SOLUTION WITH CALIX-CROWNS. MOLECULAR MODELING STUDY OF THE Cs^+/Na^+ SELECTIVITY

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ABSTRACT

Calix[4]arene mono- and bis-crown6 in the 1,3 alternate conformation are highly selective extractants for cesium towards sodium in an acidic liquid waste. Extraction and selectivity are related to complexation properties which can be studied by Molecular Dynamics techniques. In this paper, we describe the results of Molecular Dynamics simulations in an explicit water phase for four complexes of 1,3-alternate mono- and bis-crown-calix[4]arenes. The structural features obtained are interpreted on the basis of cation/ligand complementarity and can explain the relative performances in Na^+ and Cs^+ extraction for the compounds simulated.
The relative free energy of binding can be computed and is in a semi-quantitative agreement with complexation data in an homogeneous medium.

INTRODUCTION

Nuclear reprocessing operations produce high and medium level activity liquid wastes (HLW/MLW) in which cesium is one of the major radionuclides. Great efforts have been devoted throughout the world to reduce the volume and to propose a safe storage of these wastes. For instance, MLWs can be treated by evaporation in order to concentrate their radioactivity into the smallest possible

volume (1). Nevertheless, the concentrated solutions obtained are mainly composed of inactive salts ($NaNO_3$ 4 $mol.L^{-1}$ and HNO_3 1 $mol.L^{-1}$ as a matrix) in which radionuclides, like cesium, are present at tracer level concentration. One major goal is to remove selectively these radionuclides from the salt matrix in order to reduce the volume of the long lived radioactive waste.

Calix[4]arenes-crown-6 in the 1,3-alternate conformation are powerful macrocyclic extractants (see liquid-liquid extraction results in TABLE 1) that are able to extract selectively cesium traces from these specific matrixes (2,3). Some compounds of this family are very efficient to transport cesium from a simulated MLW concentrate to demineralized water through a flat sheet supported liquid membrane (SLM) and lead to stable SLMs when diluted into a suitable solvent (4).

In order to deepen the knowledge concerning the structural data, extraction and complexation behaviour of these preceding compounds, studies are still performed. Molecular modeling is one of the tools used to gain insight into structural features and microscopic behaviour of these macrocyclic extractants. We have chosen Molecular Dynamics (MD), which is a widely used computational tool for studying macrocycles, ions, and their host:guest complexes in solution (5-12). In the field of calix[4]arenes, few papers have been published up to now concerning MD studies in a solvent phase (13-15). In a recent paper (16), Wipff *et al.* performed an extensive study about the conformationaly dependent stability of alkali complexes with calix[4]arene-monocrown-5 and -6 *in vacuo* and in water, as well as preliminary MD simulations to model the complexes at the water/chloroform interface.

In this work, we have studied by MD the relative stability and structural features of alkali cation complexes of four mono and bis crown calix[4]arenes in an explicit water phase (see compounds in FIGURE 1: 1,3-diisopropoxy-2,4-crown-6-calix[4]arene **DiiprC6** (2), bis-crown-6-calix[4]arene **BisC6**, bis-(1,2-benzo-crown-6)-calix[4]arene **Bisbz**, bis-crown-7-calix[4]arene **BisC7** (3)). The aim of these simulations was to correlate the extracting behaviour and Cs^+/Na^+ selectivity to molecular properties, considering that, with macrocyclic ligands, a

TABLE 1. LIQUID-LIQUID EXTRACTION RESULTS

Ligand	D_{Na}	D_{Cs}	$\alpha_{Cs/Na}$
1,3-Diisopropoxy-2,4-crown-6-calix[4]arene	$< 10^{-3}$	28.5	> 28500
1,3-Di(n-octyloxy)-2,4-crown-6-calix[4]arene	$< 10^{-3}$	33	> 33000
Bis-crown-5- calix[4]arene	2.3×10^{-3}	0.5	220
Bis-crown-6- calix[4]arene	1.3×10^{-3}	19.5	1500
Bis-(1,2-benzo-crown-6)-calix[4]arene	1.7×10^{-3}	32.5	19000
Bis-(1,2-naphtho-crown-6)-calix[4]arene	$< 10^{-3}$	29.5	> 49000
Bis-crown-7-calix[4]arene	$< 10^{-3}$	0.3	> 300
n-Decyl-benzo-21-crown-7 (crown-ether)	1.3×10^{-3}	0.3	250

Aqueous phase: $M^+NO_3^-$: 5×10^{-4} mol.L^{-1} in HNO_3: 1 mol.L^{-1}. Organic phase: extracting agent: 0.01 mol.L^{-1} in o-NPHE (4).

D_M : distribution coefficient of species M, $\alpha_{Cs/Na}$: selectivity expressed as the ratio of the distribution coefficients obtained separately for both cations.

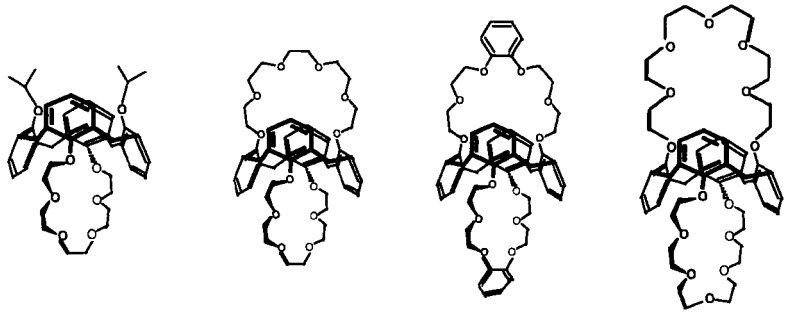


FIGURE 1. Calix[4]arenes mono- and bis-crown modeled

good extractant is first of all a good complexant that is lipophilic enough to stay in the organic phase. Water was chosen because, in solvent extraction experiments, the cations have to lose a part of their hydration shell to be complexed by the ligand located in an organic phase saturated with water. Furthermore, desolvation of the cation is known to be an important factor in the complexation selectivity which can be computed by means of Free Energy Perturbation (FEP) simulations (17, 18).

For these simulations in water, we considered that ions pairs were separated and we did not take into account the counter-ion. In this first approximation, we have focused on the structural complementarity between the cation and the ligand. Simulations with nitrate counter-ions will be reported in other papers (19, 20).

COMPUTATIONAL METHODS

All calculations were carried out on a SG INDIGO 2 R8000 workstation with the AMBER 4.0 software (21), using as a force field, the all-atom parameters and the following representation of the potential energy (22):

$$E_{pot} = \sum_{bonds} K_r(r - r_{eq})^2 + \sum_{angles} K_\theta(\theta - \theta_{eq})^2 + \sum_{dihedrals} \frac{V_n}{2}(1 + \cos(n\varphi - \eta)) +$$
$$\sum_{i<j}\left[\varepsilon_{ij}\left(\left(\frac{R^*}{R_{ij}}\right)^{12} - \left(\frac{R^*}{R_{ij}}\right)^{6}\right)\right] + \sum_{i<j}\left[\frac{q_i q_j}{\varepsilon R_{ij}}\right] + \sum_{H-bonds}\left[\varepsilon_{ij}\left(\left(\frac{R^*}{R_{ij}}\right)^{12} - \left(\frac{R^*}{R_{ij}}\right)^{10}\right)\right]$$

where r, θ and φ represent respectively, the bond length, the bond angle and the dihedral angle. R_{ij} is the distance between atoms i and j, q_i is the atomic charge on atom i and ε is the dielectric constant.

The atomic charges on the calixarenes were calculated with the MNDO semiempirical method and scaled up with a 1.26 scaling factor to allow a nice fit with 6-31G*/ESP values commonly used for crown-ether moieties (23). With these charges, the electrostatic term thus compensate the absence of an explicit polarization term in the force field equation. The ion parameters came from

Aqvist (24) and were adapted to the AMBER force field (TIP3P water model and periodic boundary conditions, PBC). The 1-4 non bounded contributions were scaled down by a factor of 0.5. The molecular dynamics simulations used a time step of 2.0 fs, a residue-based cut-off of 10 Å and a dielectric constant of 1.0. The SHAKE procedure (25) was used to constrain bonds involving hydrogen atoms. We used PBC with an isothermal/isobaric set of 300 K and 1 atm through coupling to a temperature and pressure baths.

As a starting point of our calculations we used cesium structures model built with SYBYL 6.0 software (26) and optimized by conformational sampling at 500 K and subsequent minimization *in vacuo*. The other complexes were generated by changing the parameters of the cations and equilibrating the structures by 50 ps of MD at 300 K and a final minimization *in vacuo*. All the starting structures were immersed in a TIP3P cubic box, removing water molecules within 2 Å of the solute. The number of water molecules is reported in the tables. These systems were energy minimized and submitted to, at least, 100 ps of MD in water. One conformation was saved on each picosecond calculation and the trajectories, constituted by the collection of these conformations, were visualized on a graphic screen by the MD/DRAW software and analyzed by the MDS software (27). The first ten picoseconds, corresponding to the system equilibration in temperature and pressure, were not taken into account in the structural and energetic analysis and averages were calculated over 90 ps of MD.

For free energy perturbations (FEP), the following thermodynamic cycle was considered (18).

$$\begin{array}{ccc} calix + M^+ & \xrightarrow{\Delta G_1} & calix : M^+ \\ \downarrow \Delta G_3 & & \downarrow \Delta G_4 \\ calix + N^+ & \xrightarrow{\Delta G_2} & calix : N^+ \end{array}$$

$\Delta G_{3\,exp}$: experimental relative desolvation energies of the cations (when computed according to the thermodynamic cycle, $\Delta G_{3\,calc}$ is the difference in free energy upon changing the free cation in the solvent, here water).

ΔG_4 : difference in free energy upon changing the cation when it is bound to the calixarene *in vacuo* or in water.

The relative binding selectivity is computed by the difference:

$$\Delta\Delta G = \Delta G_1 - \Delta G_2 = \Delta G_3 - \Delta G_4$$

The cation M^+ was mutated in the cation N^+ by dividing the calculation in a number of intermediate states (windows) defined by a coupling factor λ (λ =1 initial state, λ =0 final state). Each window was sampled by 5 ps of MD (1 ps equilibration and 4 ps data collection) and the calculation was performed by the thermodynamic perturbation method (18) in both directions $\lambda+\Delta\lambda$ (forward) and $\lambda-\Delta\lambda$ (reverse). The value reported was the average of forward and reverse calculations. When meaningful, we reported the average value between the two mutations $M^+ \rightarrow N^+$ and $N^+ \rightarrow M^+$. The starting point of a mutation was a structure equilibrated by MD in water at 300 K.

RESULTS

The first MD study was performed on Cs^+ and Na^+ BisCrown complexes, checking the influence of the crown size (Crown-6 and Crown-7) and of a structural change on the crown (benzoCrown-6). Crown-5 complexes were not modeled, as this crown size was obviously too small to fit Cs^+, and have been proved to be selective for K^+ cation (28).

Cesium Bis-Crown Complexes

When comparing the mean values <$dCs^+\_O_c$> reported in TABLE 2 , one can see that in the case of Bisbz:Cs^+, the cation is almost equidistant from the six oxygen atoms of the complexing crown. The distances $dCs^+\_O_c$ are more heterogeneous for the ligand BisC6, although remaining near the optimum, between 3.0 and 3.6 Å. On the contrary, the ligand BisC7 does not show a good

TABLE 2. ENERGETIC AND STRUCTURAL MEAN VALUES OVER 90 PS OF MD FOR CALIX[4]ARENE-BISCROWN Cs^+ AND Na^+ COMPLEXES

Complex	BisC6 Cs^+	Bisbz Cs^+	BisC7 Cs^+	BisC6 Na^+	Bisbz Na^+	BisC7 Na^+
Nb H_2O	868	1043	986	851	882	919
$E_{inter}^{M+/ligand}$	-54 (8)	-57 (4)	-37 (12)	-73 (4)	-81 (8)	-84 (4)
$E_{inter}^{M+/water}$	-41 (9)	-39 (7)	-69 (17)	-45 (6)	-26 (7)	-22 (6)
$<dM^+\_O_c>$	3.43 (0.26)	3.31 (0.09)	4.38 (0.40)	3.82 (1.01)	3.28 (0.82)	3.78 (1.24)
$<dM^+\_C_{Me}>$	4.83 (0.26)	4.86 (0.15)	6.38 (0.09)	3.94 (0.04)	4.18 (0.04)	4.17 (0.08)
dist Rdf M^+	3.1-3.6	3.0-3.6	3.1-4.0	2.4-2.7	-	-
N_{Ow}	1.09	0.94	3.85	1.00		

Nb H_2O : number of water molecules in the box, $E_{inter}^{M+/ligand}$ (kcal/mole): metal/ligand interaction energy. $E_{inter}^{M+/water}$ (kcal/mole): metal/water interaction energy. ( ) : fluctuations.
$<dCs^+\_O_c>$ (Å): average of the six or seven distances cation_oxygen atoms of the complexing crown computed during the duration of the dynamics.
$<dCs^+\_C_{Me}>$ (Å): average of the four distances cation_carbon atom of the methylene bridge computed during the duration of the dynamics.
Rdf: radial distribution function of the oxygen atoms of water around the cation during 90 ps of MD. dist (Å): distance cation_first shell of hydration. N_{Ow} : number of oxygen atoms of water related to the first hydration shell.

structural complementarity between the cation and the oxygen donors of the crown. The energetic analysis confirms this tendency: the interaction energy between the cesium and the ligand follows the preference Bisbz >BisC6 >BisC7 and evolves at the opposite from the interaction energy between the cesium and the surrounding water. By visualizing the MD trajectory (collection of the conformations saved during the MD), one can see the evolution of the complexes and their interactions with water molecules. Since the beginning of the simulation, only one water molecule, located out of the ligand, is coordinated to the cesium in

Crown-6 complexes. The BisC7 complex is coordinated to several water molecules. One of them enters into the crown under the cation after 40 ps and the cation decomplexes into the water phase after 75 ps of MD. A snapshot of cesium complexes equilibrated in water is reported in FIGURE 2.

These features are confirmed by the radial distribution function (rdf) data for the cation's hydration during these 90 ps: one separate peak, located between 3.1 and 3.6 Å from the cation appeared for crown-6 complexes, with a coordination number near 1.0, composing the first hydration shell of the cation. The rdf $Cs^+\_O_w$ for the BisC7 complex shows one broad peak with no return to the baseline whose integral, between 3.1 and 4.0 Å, corresponds to 3.85 water molecules. The rdf CM_O_w (CM: mass centre of the oxygen atoms of the crown) showed the hydration of the complexed crown in BisC7 where 1.44 water molecules ranged between 1.3 and 3.6 Å of the crown CM (see FIGURE 3). The free crown also, appears to be solvated in BisC7 and BisC6 cesium complexes after 80 ps of MD. No water molecules could be seen in either crown of the Bisbz complex during a 100 ps MD run.

Sodium Bis-Crown Complexes

The situation is very different for the Na^+ complexes. In the starting structures, the cation, much smaller than cesium, was located in the calixarene cavity with little interaction with the complexing crown. In complex BisC6:Na^+, a water molecule enters into the complexing crown during the first 10 ps of MD, and stays in this stable position, completing the coordination sites of the cation (rdf $Na^+\_O_w$: one peak with a coordination number equal to 1.00). This feature is not observed for Bisbz and BisC7 complexes during the first 100 ps of MD (see FIGURE 4), due to the best shielding effect of surrounding water by the crown. One must wait 120 ps to see the same solvation pattern of the cation in Bisbz:Na^+ complex (one H_2O at 0.4 Å of the Ocrown CM). The BisC7 complexing crown, completely folded above the cation, prevents this solvation and no structural changes can be seen during a 400 ps MD run. On the contrary, the free crown of

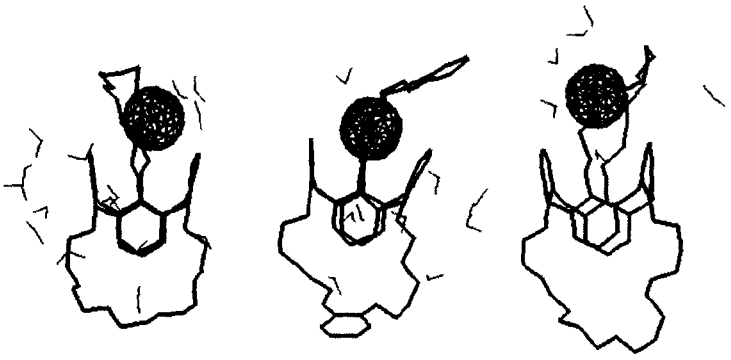


FIGURE 2. Cesium bis-crown complexes equilibrated in water

BisC7:Na^+ complex is well solvated with water present from 0.8 Å of the Ocrown CM*.

Whatever sodium complex studied, the mean values <$dNa^+\_O_c$> and their fluctuations reported in TABLE 2, indicate an important heterogeneity of the single distances $dNa^+\_O_C$. The complexing crowns are twisted and the cation is not coordinated to all their oxygen atoms. When calculating the averages from 120 to 150 ps for Bisbz:Na^+ complex, no more structural or energetic differences were seen for cation/ligand interactions between this complex and the BisC6:Na^+ complex.

* These simulations with the sodium cation are very sensitive to the starting structure of the complex. Other simulations were performed with a starting conformation non energy optimized *in vacuo*, where sodium was higher in the crown-7 with homogeneous single distances dNa_Oc. In this case, the crown shielding does not occur any more and, after 25 ps of MD, one can see one water molecule in the crown under the cation, here located very high in the crown. There was no more return to the baseline for the peak in the rdf Na_Ow curve, indicating interactions between the cation and bulk water.

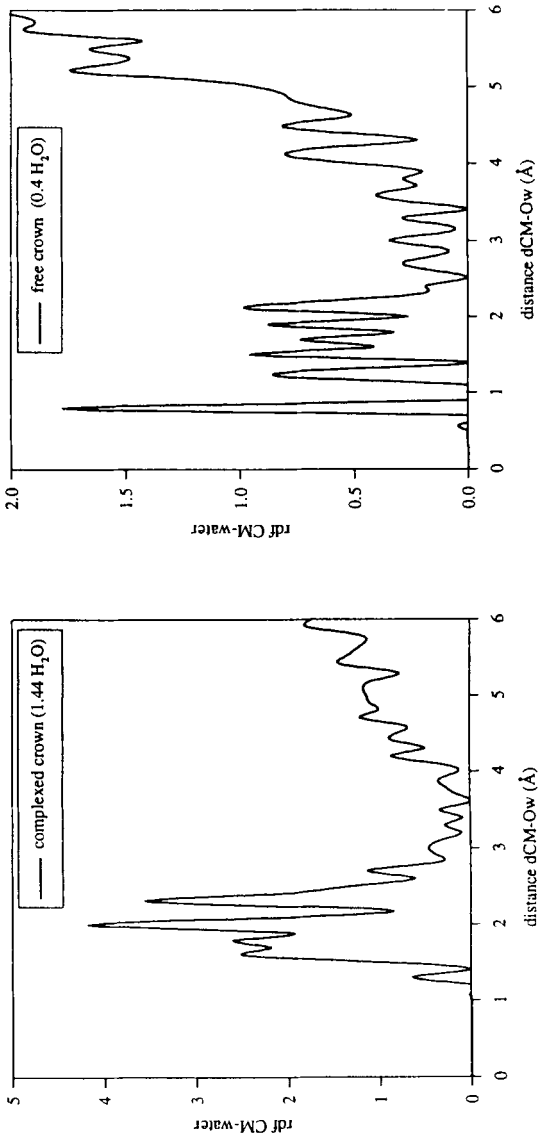
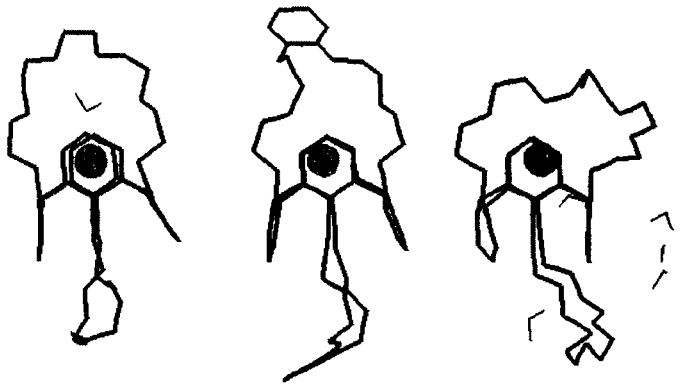


FIGURE 3. Rdf curves CM_O_w for complex BisC7:Cs^+ from 10 to 100 ps of MD



bisC6:Na^+ (100 ps) bisbz:Na^+ (100 ps) bisC7:Na^+ (100 ps)

only the closest water molecules are represented

FIGURE 4. Sodium bis-crown complexes equilibrated in water

Diisopropoxy-calix[4]arene-mono-crown Alkali Complexes

The first goal of this study is to compare Cs^+ and Na^+ complexes of mono- and bis-crown calix[4]arenes in the 1,3-alternate conformation. In a second time, one can estimate the selectivity of DiiprC6 towards alkali cations according to the FEP methodology, as it is possible to compare the results with the experimental complexation selectivity derived from stability constants measured in methanol (29).

For these reasons, MD averages and rdf data calculated over 90 ps were reported in TABLE 3, but we needed to further equilibrate some of the molecular systems to obtain stable solvation patterns in order to perform reliable FEP simulations.

MD study on alkali complexes. DiiprC6:Cs^+ complex had the same general behaviour as BisC6:Cs^+ with the best structural complementarity, similar to the Bisbz:Cs^+ one. The structural and energetic parameters of DiiprC6:Rb^+ complex are very similar to those of Cs^+ complex. The only difference is the presence of a water molecule in the cavity of the calixarene for Diipr:Rb^+.

TABLE 3. ENERGETIC AND STRUCTURAL MEAN VALUES OVER 90 PS OF MD FOR DIIPRC6 ALKALI COMPLEXES

Complex	Na^+	K^+	Rb^+	Cs^+
$Nb\ H_2O$	931	881	851	887
$E_{inter}^{M+/ligand}$	-76 (8)	-64 (7)	-65 (4)	-54 (4)
$E_{inter}^{M+/water}$	-25 (9)	-34 (9)	-40 (8)	-40 (10)
$<dM^+\_O_c>$	3.45 (0.76)	3.77 (0.71)	3.10 (0.10)	3.39 (0.09)
$<dM^+\_C_{Me}>$	4.21 (0.10)	4.04 (0.02)	4.87 (0.10)	4.89 (0.10)
dist Rdf M^+	2.3	2.6	2.8	3.1
N_{Ow}	0.05	0.71	1.00	1.03

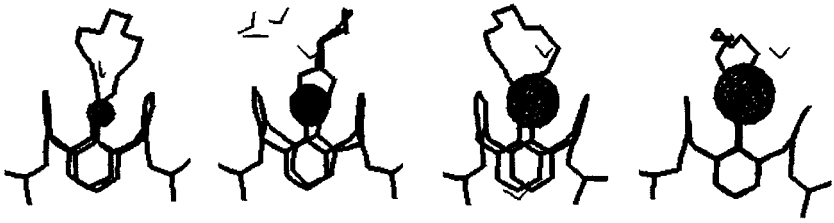
* for legend, see TABLE 2.

The Na^+ cation needs a long time to be coordinated with a water molecule in the crown of DiiprC6 (the first contact occurs at 93 ps and the equilibrated structure is obtained at 104 ps). The DiiprC6:K^+ complex shows a behaviour compared to Na^+ complex with a stable water molecule in the crown at 35 ps of MD.

A snapshot of these equilibrated structures is reported in FIGURE 5.

FEP simulations. When performing a mutation from M^+ to N^+, the N^+ complex must be compared to N^+ complex obtained by direct MD in water which is the departure point of the mutation from N^+ to M^+. The ΔG_4 values reported in TABLE 4 are averages of both independent mutations between M^+ and N^+ except for the mutation $Rb^+ \leftrightarrow Cs^+$, where the mutation $Cs^+ \rightarrow Rb^+$ was not taken into account because one could not obtain the solvation pattern of the Rb^+ structure at the end of cesium's mutation.

These quantitative results were very sensitive to cation's solvation. For instance, when performing a mutation $Na^+ \rightarrow K^+$ with a non hydrated Na^+



Na^+ (120 ps) K^+ (100 ps) Rb^+ (100 ps) Cs^+ (100 ps)

only the closest water molecules are represented

FIGURE 5. Alkali complexes of DiiprC6 equilibrated in water

TABLE 4. RESULTS OF FEP CALCULATIONS FOR DIIPRC6 COMPLEXES WITH ALKALI CATIONS

kcal/mole	Na^+ →	K^+ →	Rb^+ →	Cs^+
Departure conformation	120 ps	50 ps	150 ps	-
$\Delta G_{3\,calc}$	17.6 (0.1)	5.5 (0.1)	7.8 (0.0)	
$\Delta G_{4\,wat}$	15.3 (0.2)	5.2 (0.1)	7.35 (0.04)	
$\Delta G_{3\,calc} - \Delta G_{4\,wat}$	2.3 (0.3)	0.3 (0.2)	0.45 (0.05)	
$\Delta\Delta G_{MeOH}$	> 4	1.74	0.34	

structure (50 ps conformation), the corresponding ΔG_4 value is equal to 10.5 kcal/mole instead of 15.5 kcal/mole (120 ps conformation). In the same way, starting with a non hydrated Rb^+ structure in the calixarene cavity (50 ps conformation) leads to a ΔG_4 equal to -4.3 kcal/mole for the mutation from Rb^+ → K^+. These results were not retained because independent mutations $M^+ \leftrightarrow N^+$ do not converge to the same molecular system and subsequent ΔG_4 values. Nevertheless, in a quantitative point of view, the $\Delta\Delta G$ corresponding value were closer to the experimental selectivity in methanol. This points out the importance

of an accurate knowledge of the solvation of the complexes to validate the model and the necessity to perform simulations in an explicit solvent phase instead of a continuum representation of the solvent (15).

Anyway, we found the correct selectivity order $Cs^+ > Rb^+ > K^+ >> Na^+$ in agreement with the experimental data concerning both liquid-liquid extraction and complexation experiments.

DISCUSSION

An efficient complexant must provide coordination sites in replacement of the first hydration shell of the cation complexed, so that the best fit can be obtained between the cation and the ligand. In the simulations in water reported above, one could see that this condition is fulfilled for mono- and biscrown-6 cesium complexes with a light preference for Bisbz:Cs^+. These structural results were confirmed by the X-ray data available for DiiprC6:Cs^+:pic^- (30) and mononuclear or binuclear complexes BisC6:Cs^+:NO_3^- , BisC6:(Cs^+:NO_3^-)$_2$ and Bisbz:(Cs^+:NO_3^-)$_2$ (19, 31). In any case, the mean $dCs^+\_O_C$ values, calculated on a collection of 90 conformations generated in water without counter-ion, fit in the range centred on the corresponding mean values calculated from the preceding single solid structures. This means that the cesium fits so well the calixcrown that it is no more influenced by the surrounding medium (solid state, solvent phase, presence of a counter-ion). According to our simulations, we can retrieve the preference order for cesium extraction:

$$\text{Bisbz} \geq \text{DiiprC6} > \text{BisC6} >> \text{BisC7}.$$

One could expect a different behaviour for Na^+ complexes, as the ligands are too large for this cation, so that their structures will be greatly modified by the surrounding medium (water, counter-ion, calixcrown), and the simulations results greatly depend on the starting conformation or duration of the calculation (calculations with the nitrate counter-ion on BisC6:Na^+ complex are under investigation and will be reported in a following paper (20)). In liquid-liquid

extraction experiments of small cations, the presence of water in the complexing crown is possible because the cations coming from the water phase have no reason to loose their whole hydration shell when complexed in the calixcrown. Unfortunately, 1,3-alternate calix[4]arenes-Crown-6 being poor complexants for sodium, solvation and structural data are hardly available for these complexes. Nevertheless, it would be of interest to know the real solvation of Na^+ complexes to validate our model, mainly on a quantitative purpose, as selectivity calculations are very sensitive to the solvation of the cations.

CONCLUSION

Molecular Dynamics simulations in a water phase are able to take into account complexation properties of mono- and bis-crown calix[4]arenes with respect to the size or the presence of substituents on the crown, including solvation effects. Our results fit in a semi-quantitative way liquid-liquid extraction data and open the possibility to model unknown extractants of related families as far as complexation properties are concerned by the modification afforded to the new candidates.

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