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1. Introduction

A significant amount of radioactivity in the high-level liquid waste obtained from the nuclear fuel recycling process is due to the presence of the ¹³⁷Cs radionuclide in the solution. Secure management of these nuclear waste solutions is one of the most significant technological and industrial challenges faced by the nuclear industry. The success and public acceptance of the nuclear power program are highly dependent on the successful removal of the harmful radionuclides from the radioactive nuclear waste. After separation of minor actinides, collectively, ~99% of the remaining radioactivity of the high-level waste (HLW) solution is mainly attributed to ¹³⁷Cs and ⁹⁰Sr present in the solution.¹ It is

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Achieving highly efficient and selective cesium extraction using 1,3-di-octyloxycalix[4]arenecrown-6 in *n*-octanol based solvent system: experimental and DFT investigation[†]

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Due to the long half-life of 137 Cs ($t_{1/2} \sim 30$ years), the selective extraction of cesium (Cs) from high level liquid waste is of paramount importance in the back end of the nuclear fuel cycle to avoid long term surveillance of high radiotoxic waste. As 1,3-di-octyloxycalix[4]arene-crown-6 (CC6) is suggested to be a promising candidate for selective Cs extraction, the improvement in the Cs extraction efficiency by CC6 has been investigated through the optimization of the effect of dielectric media on the extraction process. The effects of the feed acid (HNO₃, HCl, and HClO₄) and the composition of the diluents for the ligand in the organic phase on the extraction efficiency of Cs have been investigated systematically. In 100% n-octanol medium. Cs is found to form a 1:1 ion-pair complex with CC6 (0.03 M) providing a very high distribution ratio of $D_{Cs} \sim 22$, suggesting *n*-octanol as the most suitable diluent for Cs extraction. No significant interference of other relevant cations such as Na, Mg and Sr was observed on the D_{Cs} value in the optimized solvent system. Density functional theory (DFT) based calculations have been carried out to elucidate the reason of ionic selectivity and enhanced Cs extraction efficiency of CC6 in the studied diluent systems. In addition to the ionic size-based selectivity of the crown-6 cavity, the polarity of the organic solvent system, the hydration energy of the ion, and the relative reorganization of CC6 upon complexation with Cs are understood to have roles in achieving the enhanced efficiency for the extraction of Cs by the CC6 extractant in nitrobenzene medium.

well established that these two major radio nuclides, *i.e.* ¹³⁷Cs (half-life, $t_{1/2} = 30.1$ years) and ⁹⁰Sr (half-life, $t_{1/2} = 28.9$ years), are mainly responsible for the heat and radiation load of the HLW. Furthermore, due to high mobility of Cs, the radionuclide might pose a long-term unpleasant impact on the ecology.²⁻¹⁰

The main concept behind the separation of a metal ion into an organic phase through solvent extraction is the screening of the charge on the metal ion through suitable complexation followed by the mass transfer into the nonpolar organic phase. The lower ionic potential of Cs^+ makes it difficult to undergo complexation with conventional ligands and hence leaves us with the only choice of complexation based on the size selectivity of the macrocyclic cavities of the extractant molecules.

A variety of solid phase sorbents have been reported in literature for the effective separation of heavy metals from different aqueous streams.¹¹ Multiwall carbon nanotubes functionalized with thorium oxide (MWCNTs/ThO₂) was reported for effective adsorption of Pb²⁺ ions (sorption 93.8%) from aqueous system due to the removal of H⁺ ions.¹² Naushad *et al.* reported magnetic metal–organic framework for the removal of UO_2^{2+} and Th⁴⁺ with adsorption capacity of 227.3 and 285.7 mg g⁻¹, respectively.¹³ Iron based nanocomposite was

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reported to remove heavy metals including Cd^{2+} , Cr^{3+} and Co^{2+} effectively.¹⁴ Alqadami *et al.* reported Pb²⁺ sorption on nanocomposite using carboxylic and amino functionalities.¹⁵ Naushad *et al.*¹⁶ also reported curcumin based magnetic nanocomposite as highly efficient solid phase extractant for Hg²⁺ with a capacity of 144.9 mg g⁻¹. Khan *et al.* reported the utilization of hydrochar for the removal of heavy metals including Pb²⁺ and Cd²⁺.^{17,18}. Nanomagnetic copper ferrite/drumstick pod biomass (CuFe₂O₄/DC) composite has also been employed for removal of Pb²⁺ predominantly following Langmuir isotherm¹⁹ *Penicillium chrysogenum* and *Aspergillus ustus* were reported to separate Cd²⁺, Cu²⁺ and Pb²⁺ from aqueous medium.²⁰

The Cs-selective extractants, especially those in the calixarene-crown-6 and the calixarene-bis-(crown-6) families, have been known for decade now.21-30 Different extraction methods for the recovery of ¹³⁷Cs have been reported in the literature based on these crown based systems.³¹⁻³³ Calix crown ether have been introduced as a strong extracting agent for the alkali/alkaline earth metal cations, because of the presence of suitable pre-organised cavity in the structural frameworks of these ligands.³⁴⁻³⁷ The complexation selectivity for the metal ions by these ligands depends largely on the conformation adopted by the rigidified calix[4]arene moieties of these molecules. The partial cone isomer of 1-3-dimethoxy-p-terbutylcalix [4]arene-crown-5 has been established for the selective separation of potassium ion.38 Similarly, Casnati et al.25 synthesized and reported another calix-crown based ligand, namely 1,3-dioctyloxycalix[4]arene-crown-6 (CC6) which was found to be highly Cs selective. Further, Sharma et al.39 optimized the composition of the diluent system for the organic phase based on dodecane and iso-decyl alcohol to efficiently extract Cs⁺ using 0.03 M CC6 and obtained the D_{Cs} value as ~6.6.

Understanding the mechanistic aspects of the metal extraction processes is very essential in the nuclear waste management program. In this respect, the density functional theory (DFT) method is currently widely used^{40,41} which is an appropriate level of calculation can comprehensively provide molecular level insights of the experimentally obtained results on the selective extraction processes by different ligand systems. For instance, Ali and coworkers42 have reported an unusually high selectivity of Cs⁺ in a calix-crown based ligand using DFT calculations. Similarly, Boda et al. studied the selective binding of Cs⁺ over Na⁺ with a macrocyclic calix-bis-crown ether using DFT studies, whereby the calculated results correlate well with the experimental findings.43 Further, along with counter-ion influence, strong effect of different dielectric media on the solvent extraction process has also been reported in the literature based on the DFT calculations and experimental studies.

Apparently, besides the intrinsic metal binding property of the ligands, solvent polarity of the organic phase also plays a key role in the efficient extraction of the radionuclides from a solution. Thus, choice of proper diluent system for the ligand of consideration in the organic phase is of paramount importance to achieve the maximum efficiency in the extraction process. Moreover, from the environmental point of view, the chosen solvent/diluent system is required to be nontoxic and also should not produce any undesirable bi-products in the overall process. For instance, taking note to their toxicity, use of nitrobenzene and 1,2-dichloroethane is usually avoided in the back end nuclear fuel cycle.

Based on these understandings in the reported literature,^{25,38,39} in the present study we have explored the experimental conditions, especially through the use of varying dielectric media as the diluents for the ligand in the organic phase, aiming to achieve significantly enhanced distribution ratio (D_{Cs}) for the Cs extraction, employing the well-known CC6 ligand as the complexing agent. We have analysed the influences of several solvent systems of varying dielectric properties on the D_{Cs} values for Cs extraction using CC6 as the extractant. Based on our study, n-octanol is projected to be an appropriate dielectric medium for CC6 to provide maximum Cs extraction efficiency. Effects of different mineral acids and interference of relevant alkali and alkaline earth metal ions (Na^+, Mg^{2+}, Sr^{2+}) on the recovery of Cs⁺ have also been systematically investigated. Furthermore, to decipher the structures, binding motifs and energetics of the metal-CC6 complexes formed under different experimental conditions, the DFT based calculations have also been carried out to get a better insight of the studied systems.

2. Experimental

2.1 Materials

CC6 ligand was synthesized following the procedure reported by Casnati *et al.*,²⁵ which was further purified and characterized inhouse. Casnati *et al.* reported²⁵ 1,3-dialkoxycalix[4]arene-crown-6 ionophores are obtained in the fixed 1,3-alternate conformation in 63–85% yield, hence further purifications were carried out to avoid the side product interference to the reaction medium. At the same time to avoid the acidic impurity and to reduce the background noise. Chemical formula and geometry optimized structure of CC6 ligand are shown Fig. 1. The radiotracer ¹³⁷Cs was used in the present investigation and procured from Board of Radiation and Isotope Technology (BRIT), India. ¹³⁷Cs radiotracer was used throughout the experiment for evaluating extraction efficiency. During the



Fig. 1 Chemical formula (left panel) and geometry optimized structure (right panel) of 1,3-dioctyloxycalix[4]arene-crown-6 (CC6). In the optimized structure, the oxygen atoms of the crown cavity are presented in ball and stick model, other atoms are presented in wire frame (color code: C = tan; O = red; H = light grey).

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experiment proper personal protective equipment (PPE) and personal radiation monitoring instruments were used. Here, experiments were carried out with a suitable quantity of ¹³⁷Cs spiked into HNO₃ medium. We kept the solution activity less than 1 mCi L⁻¹ as well as gamma radiation field (as ¹³⁷Cs is a gamma emitter) less than 1 mR h⁻¹. The solvent *n*-octanol (99.9%) was purchased from S.D. Fine Chemicals, India. Suprapure HNO₃ and quartz double distilled water were used throughout the present investigation.

2.2 Distribution ratio measurement

To obtain the distribution ratio (D_M) , equal volume of organic phase containing CC6 in an appropriate solvent system (diluent) and aqueous phase containing ¹³⁷Cs tracer was equilibrated for 20 min. Then both the phases were separated by centrifugation. D_M of the radioactive metal ions was calculated as the ratio of the concentration (or radioactivity) of the radioactive metal ions in organic phase to that in aqueous phase. All the extraction experiments were carried out at the temperature of 25 ± 1 °C using the thermostated water bath. The activity of ¹³⁷Cs was determined by the gamma counting having an intrinsic Ge detector connected to 4 K MCA at 604.7 keV.

2.3 Computational protocol

All structures were geometrically optimized in the gas phase using a medium sized def2-SV(P) basis set44 with pure GGA functional BP86.45,46 Tight convergence criteria (10⁻⁸ hartree) were applied in all the calculations. Further, analytical frequency calculations were performed using the AOFORCE module as implemented in TURBOMOLE v6.6 (ref. 47) to verify the obtained structures at the corresponding minima of the potential energy surfaces. Most of the optimized structures were found to be free from any imaginary frequencies. In case of any imaginary frequency, structures were distorted using screwer utility and further structural optimizations were carried out. Finally, single point calculations were performed with hybrid B3LYP functional^{48,49} using large triple ζ-quality (TZVP) basis set^{50,51} in the presence of different solvents (dodecane, *n*-octanol and water) using ORCA 3.0.3 software package.52 Core electrons of Cs⁺ (replacing 46 electrons in core) and Sr²⁺ (replacing 28 electrons in core) were modelled using SD-ECP pseudo potential. Solvent effects were incorporated into the single point calculations via implicit COSMO solvation model.53 Dielectric constant values (ϵ) of 2, 10.3 and 78 were taken for dodecane, *n*octanol and water, respectively. In all optimizations as well as in single point calculations, Resolution of Identity (RI/RIJCOSX) approximation was invoked in conjugation with auxiliary basis set, in order to improve the speed of the calculation process. The above methodology was earlier reported to produce good correlation with the experimental results.54-56

Finally, binding free energy of the metal binding reactions was calculated using following reaction scheme:

CC6 (org) + M(H₂O)_n^{m+} (aq) = [CC6·M]^{m+} (org) + (H₂O)_n (aq)

where, M corresponds to Cs⁺ ions as well as different interfering metal ions (Na⁺, Mg²⁺ and Sr²⁺) considered in different cases. As noted earlier,^{54,57,69} hydration of these metal ions plays a vital role in determining the selectivity of the ions towards a given ligand. Thus, the hydrated model of the metal ions was chosen carefully from the previously reported studies.^{58-60,69} For Na⁺, Cs⁺ and Mg²⁺ ions, primary hydration shell of six water molecules was considered. While for Sr²⁺ ion, based on the previous QM and MD based studies,⁵⁹⁻⁶⁹ octa-hydrated solvation shell was considered in the present calculations.

Furthermore, the effect of nitrate coordination on the Cs⁺ binding affinity of CC6 ligand was calculated using the following reaction scheme.

$$CC6 (org) + Cs(H_2O)_6^+ (aq) + NO_3(H_2O)_6^- (aq) = [Cs \cdot NO_3 \cdot CC6] (org) + 2(H_2O)_6 (aq)$$

Mülliken population analysis (MPA)⁶¹ was also performed to quantify the ligand to metal charge transfer occurred in the complexes formed.

3. Results and discussion

The key idea for the effective separation of a metal ion into an organic phase through solvent extraction is the screening of the charge on the metal ion through suitable complexation followed by the mass transfer into the nonpolar organic phase. This complexation ability of a metal ion highly depends on its chemical potential. The chemical potential is nothing but charge to size ratio. More the charge of the metal ion, higher would be the chemical potential and higher would be the chance of getting coordinated by ligating atoms. Similarly, larger the size of metal ion, smaller would be the chemical potential and hence lesser would be the complexation ability. Cs⁺ is a mono positive charge metal ion with large size and hence lower is the chemical potential and consequently lower is the chance of getting coordinated. Therefore, for the mass transfer of Cs⁺ (and also Na⁺, K⁺ etc.) an alternative approach has been followed. A size selective pocket was created, where the Cs⁺ can comfortably sit. In that molecular cavity the metal ions fit by size selectivity and then get coordinated. In crown ether, the 'O' donors were the main source of coordination. The substitution in crown ether was utilized to fine tune the cavity size so that the metal ion binding selectivity can improve.

3.1 Effect of diluent phase composition on D_{Cs}

To assess the role of different diluents for CC6 in the organic phase on the extraction of Cs⁺ ion,⁶² corresponding $D_{\rm Cs}$ values were determined using different solvent systems. The choice of solvents was made based on prior reports.⁶³ To start with, $D_{\rm Cs}$ values were determined in different iso-decyl alcohol and dodecane mixtures by varying their volume fractions but keeping the CC6 concentration constant at 0.030 M. The typical $D_{\rm Cs}$ value as obtained in the 50 : 50 mixture of iso-decyl alcohol and dodecane ($D_{\rm Cs} = 7.43$) was interestingly found to be very similar to that reported by Sharma *et al.*³⁹ Noticeably, with the

Table 1 Extraction dependency of cesium ion on using different solvent composition as the diluent. Organic phase: 0.03 M CC6 in different solvent compositions; aqueous phase: 5 M HNO_3 spiked with 137 Cs

7.43
12.31
19.69
21.79

increasing polarity of the mixed solvent systems (*i.e.* with higher concentration of iso-decayl alcohol), the $D_{\rm Cs}$ value was noted to be increased systematically (Table 1). This observation prompted us to use a more polar environmentally safe *n*-octanol medium as the other diluent for the extraction of Cs by CC6 ligand. Indeed, we observed very high $D_{\rm Cs}$ value ($D_{\rm Cs} = 21.79$) with *n*-octanol as the solvent using 0.03 M CC6 ligand in the organic phase. Accordingly, all our subsequent studies were carried out in 100% *n*-octanol medium only, to understand the effect of varying concentration of CC6 or the effect of changing other experimental conditions.

3.2 Dependence of D_{Cs} on the nature of different acids (HNO₃, HCl, HCIO₄)

The extraction profiles for Cs^+ as a function of the concentration of different acids (HNO₃, HCl, HClO₄) were established by determining the D_{Cs} values using 0.015 M CC6 + 100% *n*-octanol in the solution [Fig. 2]. The obtained D_{Cs} values followed the trend HNO₃ > HClO₄ > HCl for the 3–4 M acidity range, which primarily suggest that the 'ion-pair' binding mechanism might be involved in the extraction process at this acidity range. In the presence of HCl, the extraction efficiency of Cs⁺ for CC6 ligand is found to be the least, possibly because of the lower proficiency of the Cs⁺-Cl⁻ ion-pair formation, understandably due to relatively higher hydration energy for the Cl⁻ ion.



Fig. 2 Extraction dependency of cesium on the different acids (HNO₃, HCl, HClO₄) concentration. Organic phase: 0.015 M CC6 in 100% *n*-octanol; aqueous phase: different concentration of acids (HNO₃, HCl, HClO₄) spiked with ¹³⁷Cs metal ions (triplicate measurements were done and the error is within ±5%).

In case of HNO₃, with an increase in the feed acidity, the $D_{\rm Cs}$ value was found to increase gradually, attending a kind of maximum in the concentration region of 4–5 M and subsequently reducing to a small extent. The initial increase in $D_{\rm Cs}$ values with feed HNO₃ acidity possibly revealed the gradual requirement of the NO₃⁻ ions for the formation of the Cs⁺–NO₃⁻ ion-pair complexes. At very high concentration of HNO₃, *i.e.* beyond about 5 M, the $D_{\rm Cs}$ value was decreased marginally, suggesting the competing reactions of H⁺ and Cs⁺ for the ion-pair formations with NO₃⁻ ions, which would become more prevalent at such high HNO₃ acidity (>5 M), the availability of large concentration of H⁺ ions compete largely with the Cs⁺ ions causing a decrease in the observed $D_{\rm Cs}$ value at the higher acid concentrations.

3.3 Determination of metal-ligand binding stoichiometry

In the presence of nitrate, reaction of Cs^+ with CC6 can be expressed *via* following reaction scheme.

$$Cs_{aq}^{+} + nCC6_{org} + NO_{3aq}^{-} = [Cs \cdot (CC6)_n]^{+} [NO_3]_{aq}^{-}$$
 (1)

Thus, the equilibrium constant or the extraction constant (k_{ex}) for Cs⁺ by CC6 can be expressed as,

$$k_{\rm ex} = \frac{\left[\left[{\rm Cs} \cdot ({\rm CC6})_n \right]^+ \left[{\rm NO}_3 \right]_{\rm aq}^- \right]}{\left[{\rm Cs}_{\rm aq}^+ \right]} \frac{1}{\left[{\rm CC6}_{\rm org} \right]^n} \frac{1}{\left[{\rm NO}_{\rm 3aq}^- \right]}$$
(2)

At a particular temperature and at a given HNO_3 concentration, nitrate ion concentration in the aqueous phase is constant. Therefore, eqn (2) can be simplified as

$$k'_{\rm ex} = \frac{D_{\rm Cs}}{\left[{\rm CC6}_{\rm org}\right]^n} \tag{3}$$

where k'_{ex} is the conditional extraction constant given as " k_{ex} [NO₃⁻]" and D_{Cs} is the distribution ratio of the Cs⁺ ion, *i.e.* $D_{Cs} = [Cs^+]_{org'}$ [Cs⁺]_{aq}. By taking logarithm on both the sides of eqn (3), as given by eqn (4), we can estimate the k'_{ex} value form the intercept of log D_{Cs} versus log[CC6]_{org} plot and subsequently we can evaluate the corresponding free energy change of the reaction (ΔG) using eqn (5).

1

$$\log D_{\rm Cs} = \log k'_{\rm ex} + n \log \left[\rm CC6_{\rm org} \right] \tag{4}$$

$$\Delta G = -2.303 RT \log k'_{\rm ex} \tag{5}$$

Plot of log $D_{\rm Cs}$ against log CC6 (shown in Fig. 3) gave a straight line with a slope of 0.998 \pm 0.014 which indicate the formation of 1 : 1 metal–ligand complex. From the intercept, the conditional extraction constant $k'_{\rm ex}$ and the change in Gibb's free energy change ΔG have been evaluated as 7.5 \times 10² and -3.93 kcal mol⁻¹, respectively. The negative ΔG value revealed that the extraction process is a thermodynamically favourable spontaneous process.

3.4 Interference of Na⁺, Mg²⁺ and Sr²⁺ ions on the extraction efficiency of Cs⁺

While processing a radioactive waste by an extractant in a solvent system, it is expected to encounter large amounts of



Fig. 3 Variation of D_{Cs} as a function of CC6 concentration. Organic phase: (0.003-0.03) M·CC6 + 100% n-octanol; aqueous phase: 5 M HNO₃ spiked with ¹³⁷Cs metal ions.



Fig. 4 Dependence of the distribution ratio of Cs^+ ion (D_{Cs}) on the interfering metal ion concentrations. Organic phase: 0.015 M CC6 in 100% n-octanol: aqueous phase: different concentration of metal ions (Na, Mg, Sr) from (0.1-3.0) M in 5 M HNO₃ spiked with ¹³⁷Cs metal ions. (Triplicate measurements were done and the error is within $\pm 5\%$.)

other metal ions, especially, Na⁺, Mg²⁺ and Sr²⁺. Therefore, it is required to have a systematic study on the interfering effects of these metal ions in the aqueous phase on the extraction property of Cs⁺ ions by the extractant used. Fig. 4 demonstrates the results on the interferences of Na⁺, Mg²⁺ and Sr²⁺ ions on the $D_{\rm Cs}$ values of Cs⁺ extraction by using CC6 ligand in 100% *n*-

octanol medium. Experimental data revealed that there was very minor interference of these ions on the extraction behaviour of CC6 for Cs⁺ ions. Insignificant interferences of Na⁺, Mg²⁺ and Sr²⁺ concentrations on the extraction property of CC6 for Cs⁺ was also observed in the corresponding extraction profiles.

Computational results 3.5

In order to investigate the reason behind the superior selectivity of Cs⁺ ion by CC6, DFT calculations were performed. Structural and thermodynamic parameters for the complexes formed by CC6 with various metal ions (M·CC6) are listed in Table 2. According to these results, we find the highest binding free energy for Cs^+ ($\Delta G =$ -15.11 kcal mol⁻¹). The Cs⁺ ion is seen to perfectly fit into the crown cavity to interact with all the six oxygen atoms of the crown ring through strong electrostatic interaction (Cs-O_{CC6}: 3.225-3.381 Å). Further, the Cs–C_{arene} bond distance (ortho carbon of benzene) of 3.443 Å and 3.470 Å probably indicate the presence of weak cation– π interaction between the Cs⁺ ion and the aromatic ring of the calix[4]arene moiety.

On the other hand, due to its smaller size, Na⁺ is seen to interact only with two oxygen atoms of the crown ring (2.430 Å, 2.447 Å), which subsequently resulted in a positive value for the free energy change. Owing to the high ionic potentials, Mg²⁺ and Sr²⁺ ions would have attracted stronger electrostatic interaction with the crown cavity as compared to Cs⁺ ions (see ESI, Fig. S1[†]). However, smaller ionic size allowed them to interact only with 3-4 oxygen atoms of the crown moiety, resulting in positive values for the free energy changes. Notably, formations of the metal CC6 complexes require removal of the primary hydration shells of the metal ions. Thus, least hydration energy of Cs⁺ facilitates its easy migration from aqueous phase to the organic phase. On the contrary, higher hydration free energy values of the divalent metal ions made their transfer from the aqueous to organic phase thermodynamically unfavorable. Partial charges derived from the Mülliken population analysis (MPA) depicted more ligand to metal charge transfer for divalent metal ions as compared to the monovalent metal ions (see ESI, Table S1[†]). Hence the MPA results failed to produce the actual ionic selectivity trend observed experimentally, suggesting that the metal-ligand charge transfer does not contribute much in the selectivity displayed by the host for the metal CC6 complex formations (Fig. 5).

Upon complexation, the ligand is also required to reorganize itself in order to capture the metal ion of interest. The energy involved in this reorganize process is known as the re-

Table 2 Optimized structural parameters and thermodynamic parameters of [M·CC6] complexes. ($M = Na^+$, Mg^{2+} , Sr^{2+} and Cs^+) ^{<i>a</i>}								
Complex	M–O _{CC6} (Å)	$M-C_{arene}^{b}(A)$	ΔH	$T\Delta S$	ΔG			
Na ⁺ ·CC6	2.430, 2.447, 3.537, 3.613, 4.331, 4.34	2.770, 2.914	-4.62(+45.76)	-6.08	+1.46 (+12.46)			
$Mg^{2+} \cdot CC6$	2.083, 2.114, 2.163, 2.215, 3.679, 4.06	52 2.408, 5.604	+31.24 (+86.57)	-3.58	+34.83 (+90.16)			
$\mathrm{Sr}^{\bar{2}^+} \cdot \mathrm{CC6}$	2.719, 2.628, 2.650, 2.698, 2.857, 4.86	59 3.119, 3.262	-5.34(+6.38)	-12.71	+7.36 (+58.47)			
$Cs^+ \cdot CC6$	3.225, 3.244, 3.283, 3.315, 3.325, 3.38	3.443, 3.470	-17.56(-6.53)	-2.45	-15.11(-4.07)			
$Cs^+ \cdot NO_3^- \cdot C$	C6 3.151, 3.185, 3.332, 3.335, 3.502, 3.58	3.366, 3.479	-22.21(-18.44)	+0.75	-22.97(-19.19)			

^a Values in bracket correspond to dodecane solvent (dielectric constant = 2), ^b Distance between Cs^+ and *ortho*-carbon of aromatic moiety.

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Fig. 5 Optimized structures of $[Cs^+, CC6]$ complex in the absence and presence of nitrate counter ion. Cs^+ coordinated oxygen atoms are presented in ball and stick model; other atoms are presented in wire frame.

organization energy of the ligand. In this regard, we also calculated the reorganization energy associated with all the metal CC6 complexes, as listed in Table S2.[†]

Expectedly, the highest reorganization energy is noted for Mg^{2+} (>+34 kcal mol⁻¹), which is followed by Sr^{2+} (>+22 kcal mol⁻¹) and Na⁺ (>+6 kcal mol⁻¹) ions. In line with the computed free energy trend, least reorganization energy is found for Cs⁺ ion. These results reiterate the importance of the size-fit concept of this ligand, suggesting that the divalent metal ions do not fit properly into the binding site of CC6 and hence

led to a large deformation of the host molecule and accordingly less efficient binding of these ions as compared to Cs^+ ion. Molecular descriptor like HOMO–LUMO gap (HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital) provide information on the stability of the formed metal·CC6 complexes. In line with the experimental selectivity trend, we have also noted the highest HOMO–LUMO gap for Cs^+ (-5.54 eV), which confirms the kinetic stability of the Cs^+ ·CC6 complex.

Our experimentally obtained metal-ligand stoichiometry for $Cs^+ \cdot CC6$ complex suggests the presence of NO_3^- in the periphery of Cs⁺ion to form 1 : 1 ion-pair complex. As reported earlier,64,65 the presence of counter anion near metal ion in host-guest complexes is expected to provide additional assistance for the metal binding through cooperative effect. In this regard, a set of calculations were also carried out in the presence of NO₃⁻ ion at the outer sphere of crown cavity. Here, apart from the coordination with the oxygen atoms of crown ring (Cs- O_{crown} : 3.151–3.585 Å), the Cs⁺ ion is also noticed to coordinate with the oxygen atoms of NO₃⁻ ion using a bidentate binding motif (Cs-Onitrate: 3.077-3.147 Å). This resulted in the more negative binding free energy for the $Cs^+ \cdot NO_3^- \cdot CC6$ complex $(\Delta G = -22.97 \text{ kcal mol}^{-1})$, confirming the formation of the Cs⁺-NO₃⁻ ion-pair complex in the studied system which is transferred favourably from the aqueous phase to the organic phase. To probe the effect of low dielectric media as a solvent in the concerned metal extraction process, we also performed a set of calculations with dodecane solvent ($\varepsilon = 2$). As evident from Table 2, the binding free energy values for all the metal CC6 complexes are noted to decrease significantly upon decreasing the dielectric constant of the solvent. This is in excellent correlation with our experimental finding (Table 1). Possibly,

Table 3 A comparative study on Cs⁺ extraction by crown ether in molecular diluents

Ligand	Solvent composition	Metal : ligand ratio	$D_{\rm Cs}$	Ref.
1,3-Dioctyloxycalix[4]arene-crown-6 (CC6)	<i>n</i> -Octanol	1:1	21.67	Present work
1,3-Dioctyloxycalix[4]arene-crown-6 (CC6)	Isodecyl alcohol/ <i>n</i> -dodecane	1:1	6.6	36
Calix[4]arene-bis(crown-6)	Nitrobenzene	1:1	5.20	63
Calix[4]arene-bis(crown-6)	1,2-Dichloroethane	1:1	3.90	
Calix[4]arene-bis(crown-6)	1-Octanol	1:1	2.9	
Calix[4]arene-bis(crown-6)	Chloroform	1:1	0.62	
Calix[4]arene-bis(crown-6)	Toluene	1:1	0.30	
Calix[4]arene-bis(crown-6)	2-Nitrophenyl octyl ether	1:1	1.01	
Calix[4]arene-bis(napthocrown-6)	Nitrobenzene	1:1	7.71	
Calix[4]arene-bis(napthocrown-6)	1,2-Dichloroethane	1:1	2.62	
Calix[4]arene-bis(napthocrown-6)	1-Octanol	1:1	0.15	
Calix[4]arene-bis(napthocrown-6)	Chloroform	1:1	0.09	
Calix[4]arene-bis(napthocrown-6)	Toluene	1:1	0.02	
Calix[4]arene-bis(napthocrown-6)	2-Nitrophenyl octyl ether	1:1	3.78	
Bis-(octyloxy)calix[4]arene-mono-crown-6	Nitrobenzene	1:1	0.91	66
Bis-(octyloxy)calix[4]arene-mono-crown-6	NPOE	1:1	1.42	
Bis-(octyloxy)calix[4]arene-mono-crown-6	1-Octanol	1:1	0.37	
Bis-(octyloxy)calix[4]arene-mono-crown-6	MIBK	1:1	0.74	
Bis-(octyloxy)calix[4]arene-mono-crown-6	Chloroform	1:1	0.05	
Bis-(octyloxy)calix[4]arene-mono-crown-6	PTMS	1:1	1.04	
<i>p-tert</i> -Butylsulfonylcalix[4]arene (SC4A)	Chloroform	1:1	25	67
D ^T BuB18C6	Nitrobenzene	1:1	5.2	68

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changing the diluent with a more polar solvent, such as *n*-octanol, as used in our present study, helps to satisfy the primary coordination shell of Cs^+ in the process of aqueous to organic phase transfer, facilitating the extraction of the metal ion by the CC6 ligand used in the present study.

3.6 Comparative evaluation of Cs⁺ extraction with crown ether

Table 3 is summarizing the results for Cs^+ extraction by different crown ether in different solvents that were reported in literature and their comparison with the present investigation. In all the cases they were reported to form 1:1 metal-ligand complex and the size selectivity was the main driving force for the mass transfer of metal ions to the organic phase. The maximum D value achieved in the present case was found to be significantly higher for all the solvent systems reported in the Table 3. However, for *p*-tertiary-butylsulfonylcalix[4]arene in chloroform the D value was reported to be 25, which was almost similar to that obtained in present investigation. The crown 6 ethers and its derivatives were found to form an appropriate size for Cs⁺ ion cooperation and hence were explored extensively. The effect of diluent on Cs^+ extraction using calix[4]arenebis(crown 6) ether and calix[4]arene-bis(naphthocrown-6) ether revealed that the extraction efficiency followed the order: nitrobenzene > 1,2-dichloromethane > 1-octanol > 2nitrophenyl octyl ether > chloroform > toluene. Such diluent dependent Cs⁺ extraction was also reported using bis-(octyloxy) calix[4]arene-mono-crown-6 ether. They have reported that, the D values followed the trend: NPOE > PTMS > nitrobenzene > MIBK > 1-octanol. Almost no extraction was reported for using chloroform as diluent. The di-tertiary-butylbicylo-18-crown-6 ether in nitrobenzene was reported to achieve the maximum D value of 5.2 for Cs⁺ ion. This comparative evaluation definitely indicated that, 1,3-dioctyloxycalix[4]arene-crown-6 ether in noctanol (present case) was a more efficient solvent system for extraction of Cs⁺.

4. Conclusions

In summary, we have investigated here the effect of different dielectric media on the selective cesium extraction behaviour of CC6 ligand. We report that 100% n-octanol can be used to enhance the distribution ratio (D_{Cs}) of Cs⁺ significantly as compared to iso-decyl alcohol-dodecane based mixed solvent systems used previously. Highly polar solvents tend to satisfy the primary coordination shell of Cs⁺ ion and thus facilitate efficient migration of the ion from aqueous to the organic phase. The effect of interfering cations (Na⁺, Mg²⁺ and Sr²⁺) was noted to be insignificant in Cs⁺ extraction by CC6. Metal-ligand stoichiometry analysis predicts the formation of the ion-pair complex with the involvement of the nitrate counter anion, which is further supported by the results from DFT calculation. Theoretical investigations on the structures and binding energies further confirm the thermodynamic and kinetic stability of the $Cs^+ \cdot CC6$ complex and also point out the importance of the metal hydration energy, the reorganization energy of the ligand

and the size fit concept to operate in a synergistic manner to provide the $\rm Cs^+$ selectivity inside the cavity of the CC6 host molecule.

Conflicts of interest

There are no conflicts to declare.

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References

- D. H. Meikrantz, T. A. Todd, C. L. Riddle, J. D. Law,
 D. R. Peterman, B. J. Mincher, C. A. McGrath, J. D. Baker, *US Pat.*, 10/808039, 2004.
- 2 *Radioactive Waste Management and Disposal*, ed. L. Cecille, Elsevier Science Publisher, London, New York, 1991.
- 3 X. Chao, J. Wang and J. Chen, *Solvent Extr. Ion Exch.*, 2012, **30**, 623–650.
- 4 Actinides and fission products partitioning and transmutation, in *Proceedings of the Fifth International Information Exchange Meeting, Mol, Belgium, 2527 November.* 1998, NEA/OECD, 1999.
- 5 H. Zhou, K. E. Connery, R. A. Bartsch, B. A. Moyer, T. J. Haverlock and L. H. Delmau, *Solvent Extr. Ion Exch.*, 2013, **31**, 683–696.
- 6 V. Kumar, J. N. Sharma, P. V. Achuthan and R. C. Hubli, *RSC Adv.*, 2014, **4**, 805–810.
- 7 V. Kumar, J. N. Sharma, P. V. Achuthan and R. C. Hubli, *J. Radioanal. Nucl. Chem.*, 2014, **299**, 1547–1553.
- 8 W. R. Wilmarth, G. J. Lumetta, M. E. Johnson, M. R. Poirier, M. C. Thompson, P. C. Suggs and N. P. Machara, *Solvent Extr. Ion Exch.*, 2011, 29, 1–4.
- 9 W. W. Schulz and L. A. Bray, *Sep. Sci. Technol.*, 1987, **22**, 191–214.
- 10 J. F. Dozol, M. Dozol and R. M. Macias, J. Inclusion Phenom. Macrocyclic Chem., 2000, 38, 1–22.
- 11 J. Wang and C. Chen, Biotechnol. Adv., 2009, 27, 195-226.
- 12 A. Mittal, M. Naushad, G. Sharma, Z. A. ALothman, S. M. Wabaidur and M. Alam, *Desalin. Water Treat.*, 2016, 57, 21863–21869.
- 13 A. A. Alqadami, M. Naushad, Z. A. Alothman and A. A. Ghfar, *ACS Appl. Mater. Interfaces*, 2017, **9**(41), 36026–36037.
- 14 A. A. Alqadami, M. Naushad, M. A. Abdalla, T. Ahamad,
 Z. A. ALOthman, S. M. Alsehri and A. A. Ghfar, *J. Cleaner Prod.*, 2017, 156, 426–436.
- 15 A. A. Alqadami, M. Naushad, Z. A. ALOthman, M. Alsuhybani and M. Algamdi, *J. Hazard. Mater.*, 2020, **389**, 121896– 121909.

- 16 M. Naushad, T. Ahamad, Z. A. AlOthman and A. H. Al-Muhtaseb, J. Mol. Liq., 2019, 279, 1–8.
- M. A. Khan, A. A. Alqadami, M. Otero, M. R. Siddiqui, Z. A. Alothman, I. Alsohaimi, M. Rafatullah and A. E. Hamedelniel, *Chemosphere*, 2019, 218, 1089–1099.
- 18 M. A. Khan, A. A. Alqadamia, S. M. Wabaidur, M. R. Siddiqui, B. Jeon, S. A. Alshareef, Z. A. Alothman and A. E. Hamedelniel, *J. Hazard. Mater.*, 2020, 400, 123247– 123259.
- 19 M. A. Khan, M. Otero, M. Kazi, A. A. Alqadami, S. M. Wabaidur, M. R. Siddiqui, Z. A. Alothman and S. Sumbul, *J. Hazard. Mater.*, 2019, 365, 759–770.
- Z. A. Alothman, A. H. Bahkali, M. A. Khiyami, S. M. Alfadul,
 S. M. Wabaidur, M. Alam and B. Z. Alfarhan, *Sep. Sci. Technol.*, 2020, 55(10), 1766–1775.
- 21 V. Bohmer, Angew. Chem., Int. Ed., 1995, 34, 713.
- 22 C. D. Gutsche, *Calixarenes: An Introduction*, The Royal Society of Chemistry, Cambridge, 2nd edn, 2008.
- 23 R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J. F. Dozol,
 C. Hill and H. Rouquette, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 1506–1509.
- A. Casnati, S. Barboso, H. Rouquette, M. J. Schwing-Weill,
 F. Arnaud-Neu, J. F. Dozol and R. Ungaro, *J. Am. Chem. Soc.*, 2001, 123, 12182–12190.
- 25 A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M. J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767–2777.
- 26 P. Thuéry, M. Nierlich, J. C. Bryan, V. Lamare, J. F. Dozol, Z. Asfari and J. Vicens, *Dalton Trans.*, 1997, 4191–4202.
- 27 Y. Deng, R. A. Sachleben and B. A. Moyer, *J. Chem. Soc., Faraday Trans.*, 1995, **91**, 4215–4222.
- 28 R. A. Sachleben, P. V. Bonnesen, T. Descazeaud, T. J. Haverlock, A. Urvoas and B. A. Moyer, *Solvent Extr. Ion Exch.*, 1999, 17, 1445–1459.
- 29 T. J. Haverlock, P. V. Bonnesen, R. A. Sachleben and B. A. Moyer, *J. Inclusion Phenom. Macrocyclic Chem.*, 2000, 36, 21–37.
- 30 M. P. Wintergerst, T. G. Levitskaia, B. A. Moyer, J. L. Sessler and L. H. Delmau, *J. Am. Chem. Soc.*, 2008, 130, 4129–4139.
- 31 A. Casnati, A. Pochini, R. Ungaro, F. Ugozzoli, F. Arnaud, S. Fanni, M. J. Schwing, R. J. M. Egberink, F. de Jong and D. N. Reinhoudt, *J. Am. Chem. Soc.*, 1995, **117**, 2767–2777.
- 32 W. W. Schulz and L. A. Bray, *Sep. Sci. Technol.*, 1987, **22**, 191–214.
- 33 R. L. Miller, A. B. Pinkerton, P. K. Hurlburt and K. D. Abney, *Solvent Extr. Ion Exch.*, 1995, **13**, 813–827.
- 34 L. H. Gerow, J. E. Smith and M. W. Davis, *Sep. Sci. Technol.*, 1981, **16**, 519.
- 35 J. Vicens and V. Bhomer, *Calixarenes, a versatile class of macrocyclic compounds*, Kluwer Academic Publishers, Dordrecht, The Nerherlands, 1991.
- 36 Z. Asfari, C. Bressot, J. Vicens, C. Hill, J. F. Dozol, H. Rouquette, S. Eymard, V. Lamare and B. Tou-mois, *Anal. Chem.*, 1995, 67, 3133–3139.
- 37 P. Thuery, M. Nierlich, V. Lamare, J. F. Dozol, Z. Asfari and J. Vicens, *J. Inclusion Phenom.*, 2000, 36, 375–408.

- 38 R. Ungaro, A. Casnati, F. Ugozzoli, A. Pochini, J. F. Dozol, C. Hill and H. Rouquette, *Angew. Chem., Int. Ed. Engl.*, 1994, 33, 1506–1509.
- 39 J. N. Sharma, A. Kumar, V. Kumar, S. Pathan, C. Janardahan, V. Tessi and P. K. Wattal, *Sep. Sci. Technol.*, 2014, 135, 176– 182.
- 40 B. Sadhu, M. Sundararajan, G. V. Elmurugan and P. Venuvanalingam, *Dalton Trans.*, 2015, 44, 15450–15462.
- 41 M. Sundararajan, V. Sinha, T. Bandyopadhyay and S. K. Ghosh, *J. Phys. Chem. A*, 2012, **116**(17), 4388–4395.
- 42 V. Kumar, J. N. Sharma, P. V. Achuthan, D. K. Singh and S. M. Ali, *RSC Adv.*, 2016, **6**(52), 47120–47129.
- 43 A. Boda and M. A. Sheikh, J. Phys. Chem. A, 2012, 116, 8615.
- 44 A. Schäfer, H. Horn and R. Ahlrichs, *J. Chem. Phys.*, 1992, **97**, 2571–2577.
- 45 A. D. Becke, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1988, **38**, 3098–3100.
- 46 J. P. Perdew, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1986, 33, 8822–8824.
- 47 R. Ahlrichs, M. Bar, H. P. Baron, R. Bauernschmitt, S. Bocker, M. Ehrig, K. Eichkorn, S. Elliot, F. Furche, F. Haase, M. Haser, H. Horn, C. Huber, U. Huniar, M. Kattannek, C. Kolmel, M. Koolwitz, K. May, C. Ochsenfeld, H. Ohm, A. Schafer, U. Schneider, O. Treutler, M. von Arnim, F. Weigend, P. Weis, and H. Weiss, *TURBOMOLE V6.3.1 2011*, A Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from, http://www.turbomole.com.
- 48 A. D. Becke, J. Chem. Phys., 1993, 98, 5648-5652.
- 49 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1988, 37, 785–789.
- 50 A. Schäfer, C. Huber and R. Ahlrichs, J. Chem. Phys., 1994, 100, 5829–5835.
- 51 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, 7, 3297–3305.
- 52 F. Neese, ORCA Version 3.0, an ab initio density functional and semiempirical program package, 2013.
- 53 A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans.* 2, 1993, 799–805.
- 54 B. Sadhu, M. Sundararajan, G. Velmurugan and P. Venuvanalingam, *Dalton Trans.*, 2015, 44, 15450–15462.
- 55 B. Sadhu, M. Sundararajan and T. Bandyopadhyay, *Inorg. Chem.*, 2016, **55**, 598–609.
- 56 B. G. Vats, D. Das, B. Sadhu, I. C. Pius, D. Noronha, S. Kannan and M. Sundararajan, *Dalton Trans.*, 2016, 45, 10319–10325.
- 57 A. Boda and M. A. Sheikh, J. Phys. Chem. A, 2012, 116, 8615.
- 58 B. Sadhu, M. Sundararajan and T. Bandyopadhyay, J. Phys. Chem. B, 2015, **119**, 12783–12797.
- 59 B. Sadhu, M. Sundararajan and T. Bandyopadhyay, *J. Phys. Chem. B*, 2015, **119**, 10989–10997.
- 60 M. Peschke, A. T. Blades and P. Kebarle, *J. Phys. Chem. A*, 1998, **102**, 9978–9985.
- 61 R. S. Mülliken, J. Chem. Phys., 1955, 23, 1833-1840.
- 62 E. Makrlik, P. Selucký and P. Vaňura, *Acta Chim. Slov.*, 2011, 58, 850.

- 63 D. R. Raut, P. K. Mohapatra, S. A. Ansari, A. Sarkar and V. K. Manchandda, *Desalination*, 2008, 232, 262–271.
- 64 B. Sadhu, M. Sundararajan, G. Velmurugan and P. Venuvanalingam, *Dalton Trans.*, 2015, 44, 15450–15462.
- 65 S. K. Kim, G. I. Vargas-Zúñiga, B. P. Hay, N. J. Young,
 L. H. Delmau, C. Masselin, C. H. Lee, J. S. Kim,
 V. M. Lynch, B. A. Moyer and J. L. Sessler, *J. Am. Chem.* Soc., 2012, 134, 1782–1792.
- 66 D. R. Raut, P. K. Mohapatra, M. K. Choudhary and S. K. Nayak, *J. Membr. Sci.*, 2013, **429**, 197–205.
- 67 C. Liu, D. Zhang, L. Zhao, P. Zhang, X. Lu and S. He, *Appl. Sci.*, 2016, 6, 212–219.
- 68 P. K. Mohapatra, S. A. Ansari, A. Sarkar, A. Bhattacharyya and V. K. Manchanda, *Anal. Chim. Acta*, 2006, 571, 308–314.
- 69 B. Sadhu, M. Sundararajan, A. Pillai, R. Singh and T. Bandyopadhyay, *Int. J. Quantum Chem.*, 2017, **117**, e25418.