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Cs Extraction from Chloride Media by Calixarene Crown-Ethers

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Abstract: Asse II salt mine, in Germany, contains low and intermediate-level radioactive waste that must be retrieved in the upcoming years. Potentially contaminated salts and brines will require treatment, with ^{137}Cs being the main contaminant. Cs^+ is problematic to selectively recover due to its chemical similarity with Na^+ and K^+ which are present in high quantities in a salt mine. This paper offers a novel solution for Cs^+ separation from concentrated chloride salt media by solvent extraction with calixarene-crown-ether extractants in an alcoholic diluent. The proposed solvent extracts Cs^+ at elevated chloride concentrations (3–4 M) while back-extraction is achieved by contacting the solvent with dilute (0.01 M) hydrochloric acid.

Keywords: Asse II salt mine; radioactive waste; cesium; chloride media; decontamination; extraction; calixarene-crown-ether

1. Introduction

The Asse II salt mine [1], Germany, contains low and intermediate-level radioactive wastes that have been emplaced from 1967 to 1978 and stored since then. The Federal Government of Germany ordered the retrieval of these wastes. Contaminated salts and brines may accrue from the retrieval, requiring an efficient method for their decontamination. One of the expected contaminants is ^{137}Cs, especially problematic to selectively recover due to its chemical similarity with sodium and potassium, found in high quantities in a salt mine.

Within the past years, several techniques have been investigated to recover radiocesium from contaminated aqueous media, such as adsorption on various inorganic and organic materials, membrane-based processes, precipitation, and solvent extraction [2,3]. Separation of radiocesium plays a role in the treatment of Fukushima-contaminated soil [4–8]. Furthermore, radiocesium separation might be part of advanced nuclear fuel reprocessing schemes [9–18] to decrease the heat load of the waste to be finally disposed of.

Amongst the different possibilities, solvent extraction is a convenient choice when large volumes need to be treated. Basically, an ionic solute in an aqueous phase forms a complex with a complexing agent (i.e., the extracting agent) present in an immiscible organic phase (the *solvent*). The complex is preferentially soluble in the organic phase—the solute is extracted. This way, the solute is separated from other solutes not forming complexes with the extracting agent. Contacting the organic phase with an aqueous phase of different composition allows for back extracting the solute; the organic phase can be recycled in a continuous manner. With its inherently low consumption of energy and chemicals, solvent extraction is advantageous over e.g., membrane processes and precipitation. Solvent extraction is widely used for separating and purifying ionic species. It is applied on an industrial level e.g., for the reprocessing of spent nuclear fuels by the PUREX process and for the large-scale copper production by the SX/EW (solvent extraction, electrowinning) technique.

The calix [4]crown-ether family has been extensively studied as extracting agents for alkali metal ions [10,12,15,19–23], as the number of ether groups in the crown-ether allows

tuning the extractant selectivity by adjusting the size of the ring from four ether functions for the smaller ions (Li^+, Na^+) to six for the larger ions (Rb^+, Cs^+). Their main drawback is their insolubility in aliphatic diluents and low solubility in most common diluents [10,15]. Still, some diluents with intermediate polarities such as long-chain alcohols can solubilize these ligands up to 30 mM, which is sufficient for the extraction of micro-amounts of Cs^+.

Most of these processes are extracting Cs^+ from high nitric acid concentrations, as it is the usual medium for nuclear reprocessing. However, other media need to be considered in the case of environmental contamination, such as chlorides and/or sulphates. Although usually overlooked, the nature of the aqueous medium can greatly impact the extraction efficiency, as shown by a recent publication [24], where it was found that the anionic order for Cs^+ extraction efficiency almost followed the Hoffmeister series [25], whereas the presence of competitive cations (Al^{3+}, Mg^{2+}, Ca^{2+}, Na^+, Li^+, H^+) had a lesser effect.

We have studied the extraction of Cs^+ by calixarene crown ethers from highly concentrated solutions of NaCl, KCl, $CaCl_2$, and $MgCl_2$. The choice of this aqueous medium is related to the composition of the brines of the Asse II mine. Several calixarene crown-ether ligands with different structures were compared (Figure 1). Three different structural parameters of the extractant were investigated: bis-or mono-crown ethers, where alkyloxy chains replace the second crown, the number of benzene rings attached to the crown-ether rim, and the size of the alkyl chain (Table 1). The chosen extractants were thus the in-lab synthesized mono-crown-ethers di-octyloxy-calix[4]crown-ether-6 (DOC[4]C6), di-octyloxy-calix[4]benzo-crown-ether-6 (DOC[4]BC6), di-dodecyloxy-calix[4]crown-ether-6 (DDC[4]C6), di-dodecyloxy-calix[4]benzo-crown-ether-6 (DDC[4]BC6) and di-dodecyloxy-calix[4]dibenzo-crown-ether-6 (DDC[4]DBC6), the commercially available mono-crown-ether di-(3,7-methyl)octyloxycalix[4]benzo-crown-6 (MAXCalix) and the commercially available bis-crown-ether calix[4]arene-bis(tert-octylbenzo-crown-6) (BOBCalix) represented in Figure 1. These latter two ligands were originally designed at Oak Ridge National Laboratory, USA, for the CSSX (Caustic-Side Solvent Extraction) process and the Next-Generation CSSX process [26–30] and were used for the decontamination of the alkaline high-level waste at the U.S. Department of Energy Savannah River Site (SRS).
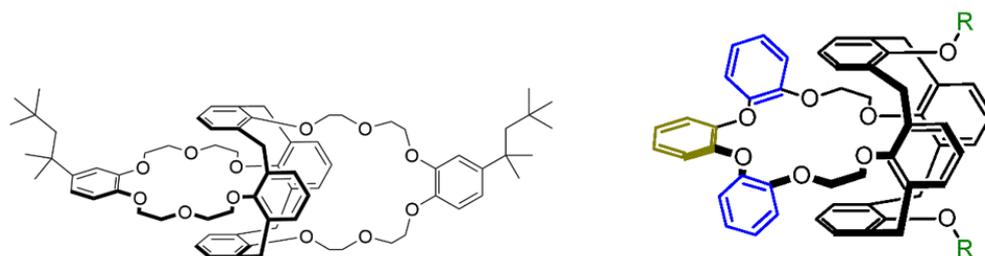

Figure 1. BOBCalix (**left**) and mono-crown-ether compounds representation (**right**): blue, dibenzo crown; light brown, benzo crown.

Table 1. Calixarene mono-crown-ethers corresponding to Figure 1 (right).

Number of Benzene Rings Chain Length R	0 (crown-6)	1 (benzo-crown-6)	2 (dibenzo-crown-6)
di-octyloxy (8 C)	DOC[4]C6	DOC[4]BC6	–
di-dodecyloxy (12 C)	DDC[4]C6	DDC[4]BC6	DDC[4]DBC6
di-(3,7-methyl)octyloxy (10 C)	–	MAXCalix	–

In addition to the extractant efficiency, several other parameters were studied, including finding an efficient diluent and investigating the effect of the concentrations of aqueous ions, including H^+, to determine the feasibility of Cs^+ recovery from saline chloride media by solvent extraction with calixarene crown-ethers.

2. Materials and Methods

2.1. Chemicals

BOBCalix and MAXCalix have been purchased from Marshallton Research Laboratories (USA) and used without further purification. The other five calixarene crown-ether extractants were provided by Dr. Yuji Miyazaki (JAEA). Diluents were purchased from Sigma-Aldrich. Aqueous phases were prepared by dissolving MCl (M = Na, K, Cs, Ca, Mg) salts in water and adding HCl to a concentration of 0.001 M.

2.2. Extraction

The extraction experiments have been conducted using stable CsCl or ^{137}Cs radiotracer. In both cases, aqueous and organic phases were prepared separately by adjusting the desired salts and extractant concentrations.

In the case of using stable CsCl, both phases (500 µL each) were then mixed at room temperature for 30 min (kinetics results provided in Figure S1) and centrifuged for 5 min. The organic phase was withdrawn for back-extraction into 0.01 M HCl (Table S2) at a 1:1 organic to aqueous volume ratio for 30 min. The aqueous phases of both the extraction and back-extraction experiments were then measured by ICP-AES (Optima 8300, Perkin Elmer, Waltham, MA, USA) and atomic emission spectroscopy F-AES (PinAAcle 500, PerkinElmer), along with the initial concentrations to check the mass balance. The organic phase concentration is then estimated either by the difference between the initial and the extracted concentrations or by considering the back-extracted concentration equal to the organic concentration. Overall uncertainties are considered as 15%.

In the case of using the ^{137}Cs radiotracer, spikes of ^{137}Cs (5 kBq) were added to 500 µL of a previously prepared aqueous phase containing the desired salts. The solution was then mixed with the same volume of organic phase for 30 min at 20 °C. After 2 min of centrifugation, both aqueous and organic phases were sampled for gamma counting (NaI scintillator Packard Cobra Auto-Gamma 5003) or gamma spectroscopy (Ge detector ORTEC GWL-90-10-S, Oak Ridge, TN, USA). Uncertainties are mainly due to the pipetting errors, except for very high or very low distribution ratios for which one of the phases has a low count rate.

The distribution ratio of a solute is the ratio of the solute's concentration in the organic phase over its concentration in the aqueous phase, $D_A = c(A)_{org}/c(A)_{aq}$.

3. Results

3.1. Study of the Organic Phase

3.1.1. Diluent Study

Unlike the NG-CSSX process [26,30] that uses a fluoride-based phenol as a modifier, only CHON diluents were considered in this study, as they can be directly incinerated after their final usage instead of forming additional radioactive waste requiring further specific treatment. Several alcohols and their mixture with kerosene were tested. The addition of kerosene allows for improved hydrodynamic properties such as viscosity.

Cs^+ extraction by the diluent 1-octanol itself has been checked as a reference (Figure 2). Very low distribution ratios were found, even at high chloride concentrations, confirming its inability to extract Cs^+.
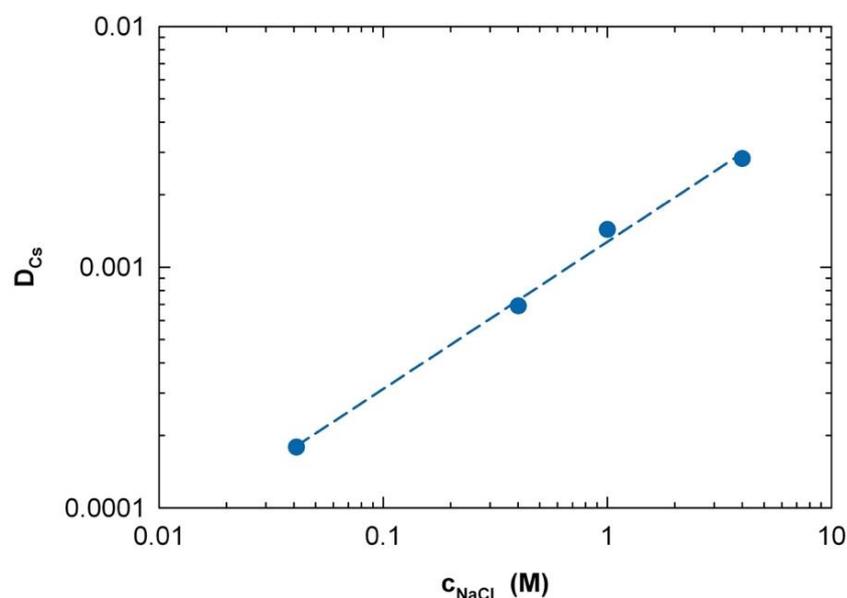
Figure 2. Cs$^+$ extraction by 1-octanol as a function of NaCl concentration. Organic phase, 1-octanol. Aqueous phase, NaCl + 0.001 M HCl + ^{137}Cs (10 kBq/mL).

When studying Cs$^+$ extraction by BOBCalix or MAXCalix in alcohol diluents, both the position of the alcoholic function (1-octanol vs. 2-octanol) and the branching of the alkyl chain (1-octanol vs. 2-ethyl-hexan-1-ol) were found to influence Cs$^+$ distribution ratios (Figure 3 and Table 2). Almost one order of magnitude is observed between the distribution ratios obtained with BOBCalix in 1-octanol and 2-octanol. This result is similar to other systems studied in the literature [15,31]. However, the ratios of D$_{Cs}$ at high to low chloride concentrations are similar for all three alcohol diluents.
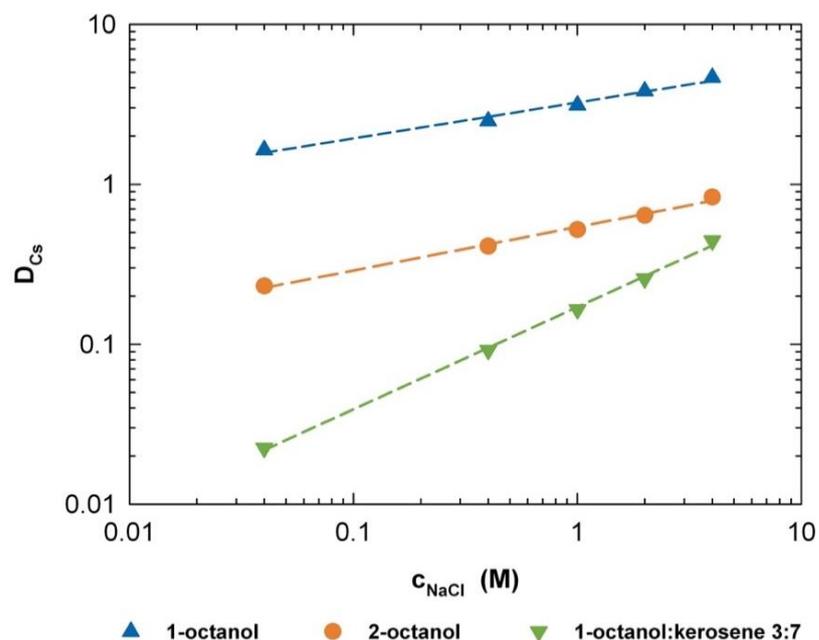

Figure 3. Cs$^+$ extraction as a function of NaCl concentration. Organic phase, 0.01 M BOBCalix in 1-octanol, 2-octanol, or 1-octanol/kerosene 3:7. Aqueous phase, NaCl + 0.001 M HCl + ^{137}Cs (10 kBq/mL).

Table 2. Cs^{+} distribution ratios for the extraction from 4 M NaCl or 0.4 M NaCl by BOBCalix and MAXCalix in several diluents. Organic phase, 0.01 M BOBCalix or MAXCalix. Aqueous phase, (4 M or 0.04 M) NaCl + 0.001 M HCl + [137]Cs (10 kBq/mL).

	BOBCalix	**MAXCalix**
1-octanol	4.6–1.6	3.3–1.2
1-octanol/kerosene 3:7	0.44–0.022	0.25–0.034
2-octanol	0.83–0.23	0.38–0.13
2-ethyl-hexan-1-ol	n/a	0.62–0.22

In the case of the addition of kerosene, a sharp decrease in extraction ability is observed, as expected from its low dielectric constant. However, a higher difference between high and low chloride concentrations is obtained, which is especially interesting from a process point of view.

3.1.2. Extractant Comparison

Cs^{+} extraction with BOBCalix (bis-crown representative) and MAXCalix (mono-crown representative) in several alcohol diluents has been studied (Table 2). Two different NaCl concentrations, 4 M and 0.04 M, have been used as representatives for extraction and stripping conditions; 0.001 M HCl was added to avoid any precipitation. In all systems, higher extraction was obtained at high NaCl concentration (4 M) than at low NaCl concentration (0.04 M). BOBCalix allows for higher Cs distribution ratios. However, it was found to be less soluble than MAXCalix in all tested diluents, with a maximum solubility of ≈0.01 M versus ≥ 0.03 M for MAXCalix. Consequently, MAXCalix is more suitable for an application.

The ability of the different mono-crown-ethers to extract Cs^{+} from NaCl media has been evaluated. Results are displayed in Figure 4. All ligands present about the same trend of extraction, with rather similar distribution ratios. The two ligands without any benzene ring, DOC[4]C6, and DDC[4]C6, present the lowest extractability, the dodecyl chain yielding higher D_{Cs}. At high NaCl concentrations, DDC[4]C6, MAXCalix, and DDC[4]DBC6 show similar distribution ratios. DDC[4]BC6 and DOC[4]BC6 are the ligands allowing the highest D_{Cs}, about 1.5 times that of MAXCalix, despite having the same benzo-crown-ether ring. The alkyl chain length thus has some influence, maybe because it modifies the solubility of the ligand in the diluent.
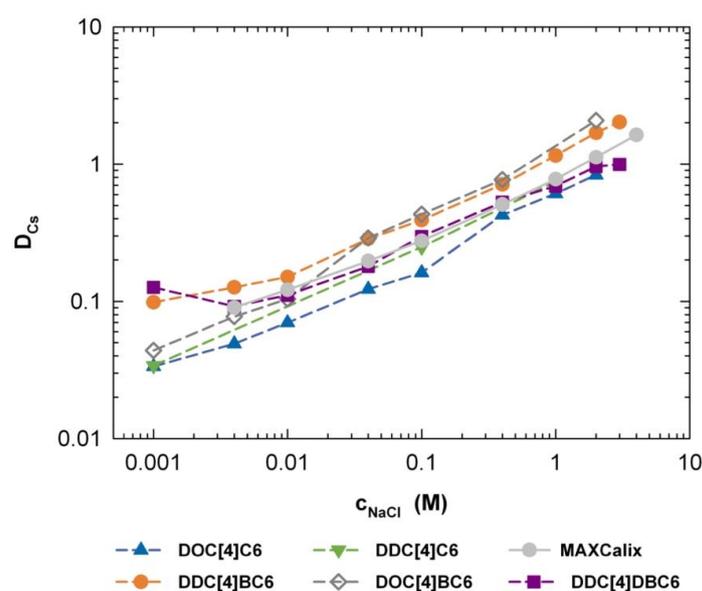

Figure 4. Cs^{+} extraction by various mono-crown ethers. Organic phase, 0.02 M mono-crown ether in 1-octanol/n-dodecane 75/25. Aqueous phase, NaCl + 0.001 M HCl + [137]Cs (10 kBq/mL).

Due to its commercial availability and suitable properties, most of the following experiments were conducted with MAXCalix.

3.1.3. Complex Stoichiometry

As reported in the literature [10,15,20], the formation of a 1:1 complex is expected between Cs^+ and the calixarene crown-ethers, according to below equation:

$$Cs^+{}_{aq} + Cl^-{}_{aq} + n\,L_{org} \rightleftharpoons CsClL_{n,org}$$
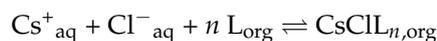
By plotting Cs(I) distribution ratios, D_{Cs}, obtained at a constant chloride concentration versus the extractant concentration on a double logarithmic scale, the number of extractant molecules involved, n, is obtained. Figure 5 shows D_{Cs} versus the MAXCalix concentration at two different NaCl concentrations. Slopes are 0.92 and 0.89 for 4 M NaCl and 0.4 M NaCl, respectively. The values being close to 1 proves the formation of a 1:1 complex.
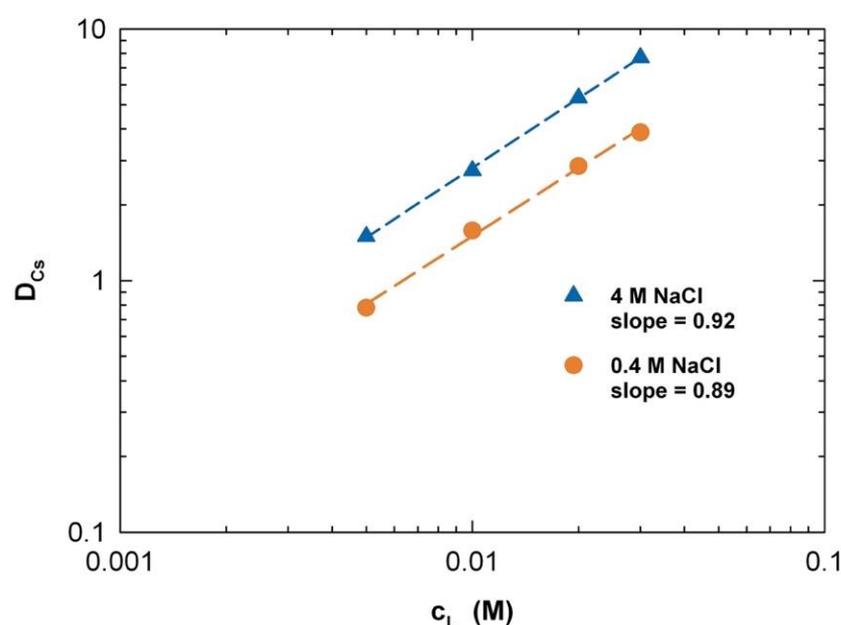

Figure 5. Cs^+ distribution ratios as a function of MAXCalix concentration. Organic phase, MAXCalix in 1-octanol. Aqueous phase, 4 M or 0.4 M NaCl + 0.001 M HCl + ^{137}Cs (10 kBq/mL).

3.2. *Study of the Aqueous Phase*
3.2.1. NaCl and HCl Effects

Figure 6 presents distribution data for the extraction of Cs^+ with MAXCalix in 1- and 2-octanol versus the initial concentrations of HCl or NaCl (HCl was investigated as a possible medium for back-extraction). As already reported in the literature for the nitrate systems [10,15], D_{Cs} shows a minimum. This effect, despite being important for process management, has not been fully explained yet, as the actual cesium speciation in the organic phase at low ionic strength is neither described in the literature nor could be determined by our experiments. Comparison between NaCl and HCl shows a different extraction behaviour, with the NaCl system showing less extraction at high chloride concentrations and more extraction at low concentrations as compared to the HCl system.

For further extraction studies, 3 M NaCl + 0.001 M HCl was selected as the reference aqueous phase composition.
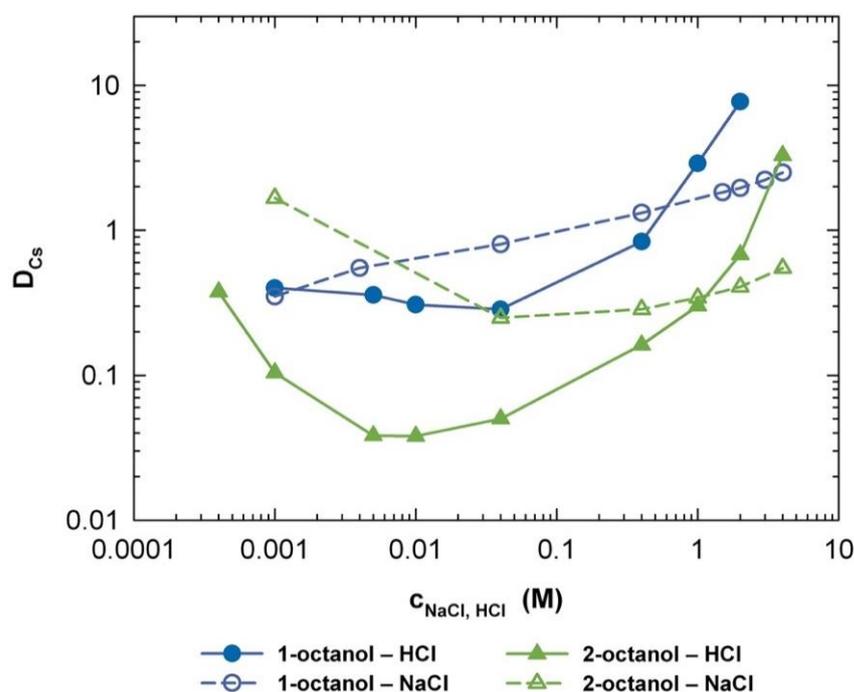
Figure 6. D_{Cs} versus initial NaCl or HCl concentration. Organic phase, 0.01 M MAXCalix in 1-octanol or 2-octanol. Aqueous phase, (NaCl + 0.001 M HCl) or HCl + ^{137}Cs (10 kBq/mL).

3.2.2. Effect of Other Cations

Other salts present may interfere with Cs$^+$ extraction. Focusing on the Asse II salt mine, KCl, CaCl$_2$, and MgCl$_2$ were considered. Very low extraction of Ca^{2+} was observed (with Ca^{2+} concentrations in the organic phase too close to the detection limit to yield reliable data). Table 3 shows the distribution ratios of several cations when extracted all together by MAXCalix 0.02 M dissolved in 75% 1-octanol/25% kerosene. Mg^{2+} and Na$^+$ distribution ratios are rather low. However, K$^+$ was found to be extractable to some extent, as previously reported [15,20].

Table 3. Mg^{2+}, Na$^+$, K$^+$ and Cs$^+$ co-extraction. Organic phase, 0.02 M MAXCalix in 1-octanol/kerosene 75:25. Aqueous phase, 1.9 M MgCl$_2$, 0.87 M NaCl, 0.28 M KCl, 1.5 mM CsCl + 0.001 M HCl.

Cation	Mg^{2+}	Na$^+$	K$^+$	Cs$^+$
D	$7.8 \times 10^{-4} \pm 150\%$	$1.9 \times 10^{-3} \pm 100\%$	$2.3 \times 10^{-2} \pm 25\%$	$1.44 \pm 15\%$

Even though the K$^+$ distribution ratio is rather low, a high K$^+$ concentration in the aqueous phase yields a drastic decrease in Cs$^+$ distribution ratio (Figure 7). At K$^+$ concentrations lower or equal to 2 M, which is the maximum concentration expected, this decrease remains sufficiently small to keep a distribution ratio over 1 (D_{Cs} = 1.17 at 2 M KCl + 1 M NaCl). This proves the feasibility of such a process.

Table 4 gathers Cs$^+$ distribution ratios obtained from a simulate of an Asse II mine brine (composition, see Table 4). Due to the very low D_{Cs} obtained in the conditions previously studied, 0.02 M MAXCalix in 75% 1-octanol/25% kerosene was used. Attempts were made at improving those results by further increasing the ligand concentration to 0.025 M and by adding a modifier, nitrophenyloctylether (NPOE). The increase in MAXCalix concentration showed no effect, most probably due to an increase in K$^+$ extraction that prevents any additional Cs$^+$ extraction. However, a low concentration of NPOE is able to increase D_{Cs}.
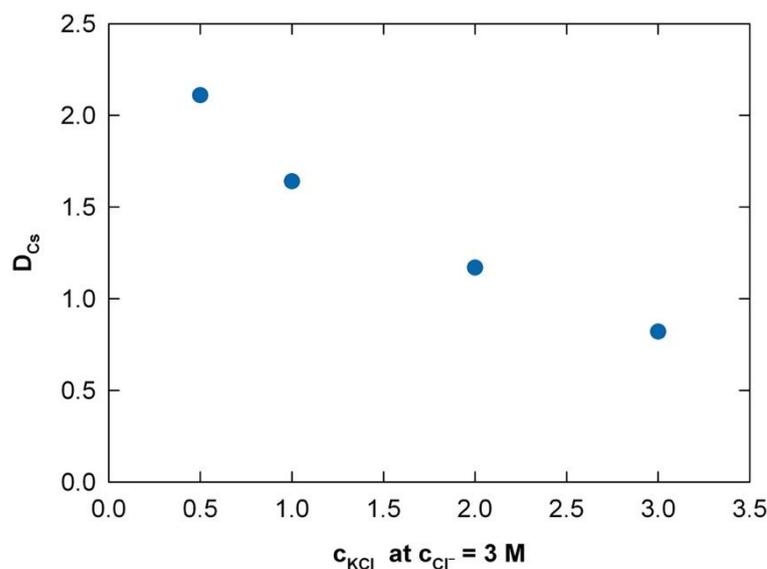
Figure 7. Cs$^+$ distribution ratios as a function of KCl concentration at a fixed chloride concentration. Organic phase, 0.025 M MAXCalix in 1-octanol/kerosene 75/25. Aqueous phase, 3 M (K, Na)Cl + 0.001 M HCl + ^{137}Cs (10 kBq/mL).

Table 4. Cs$^+$ extraction and stripping distribution ratios for 3 different organic phases. Aqueous phase (extraction), 4 M MgCl$_2$, 1 M KCl, 0.3 M NaCl, 0.2 M MgSO$_4$, 1 mM CsCl + 0.001 M HCl. Aqueous phase (stripping), 0.01 M HCl.

Diluent	25% Kerosene 75% 1-Octanol	25% Kerosene 75% 1-Octanol	25% Kerosene 5% NPO 70% 1-Octanol
MAXCalix Concentration	0.02 M	0.025 M	0.025 M
D$_{Cs}$ extraction	1.23	1.22	1.45
D$_{Cs}$ stripping	0.10	0.12	0.15

4. Conclusions

A novel system to separate Cs$^+$ from chloride brines by solvent extraction using calixarene crown ethers is proposed. Only CHON diluents have been used, namely octanol and kerosene-octanol mixtures. Several calixarene crown ethers have been screened. Due to its properties, solubility, and commercial availability, MAXCalix was chosen as a suitable candidate for an application.

A solvent comprising 0.025 M MAXCalix in 75% 1-octanol/25% kerosene allows for the extraction of Cs$^+$ from concentrated (3–4 M) chloride solutions. Cs$^+$ is readily back extracted from the organic phase into 0.01 M hydrochloric acid. K$^+$ suppresses Cs$^+$ extraction as it was found to be co-extracted to a small extent. Nevertheless, the system can cope with K$^+$ concentrations lower or equal to 2 M.

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