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Nuclear waste management with the use of calixcrowns in the aspect of cesium removal

Abstract: Examples of calixcrowns useful in cesium removal from nuclear waste are given along with their synthetic approaches and complexation properties. Cesium extraction procedure from alkali metal ions mixtures applying ionic liquids is also presented.

Keywords: cesium, complexation, extraction, ionic liquids

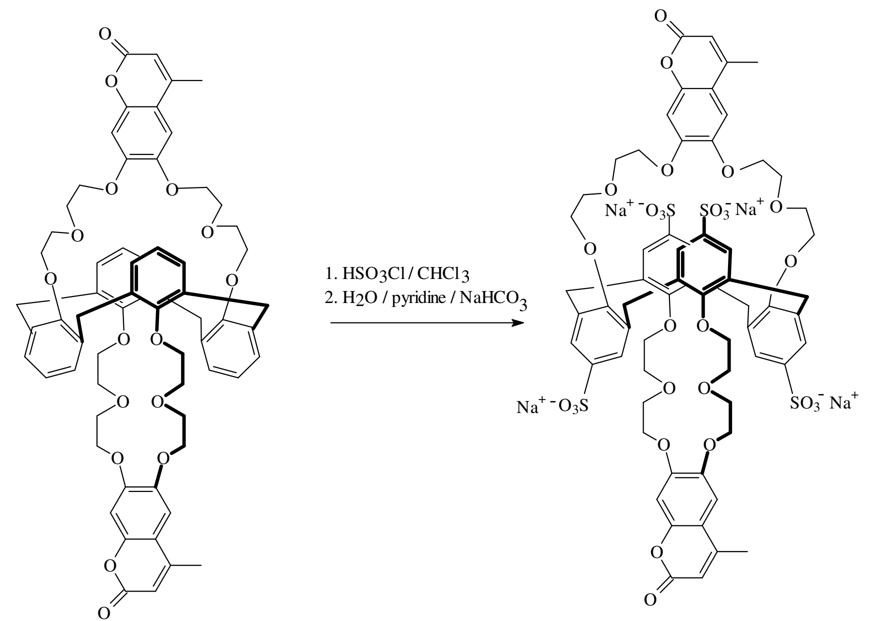
Introduction

Cesium ions are present in nuclear waste materials; it is a medium where sodium and potassium exist in a large excess. Nuclear waste materials are the major source of cesium. Cesium is toxic for humans since it replaces potassium in muscles and in red cells, therefore the removal of cesium from nuclear waste is now an important challenge [1].

Calixcrowns consist of calixarene and crown ether moieties; they show a high selectivity toward alkali metal ions [2]. Calixcrowns may bear one or two crown ether moieties. The number of benzene units in calixcrowns often is 4 or 6; such examples are shown in the present paper.

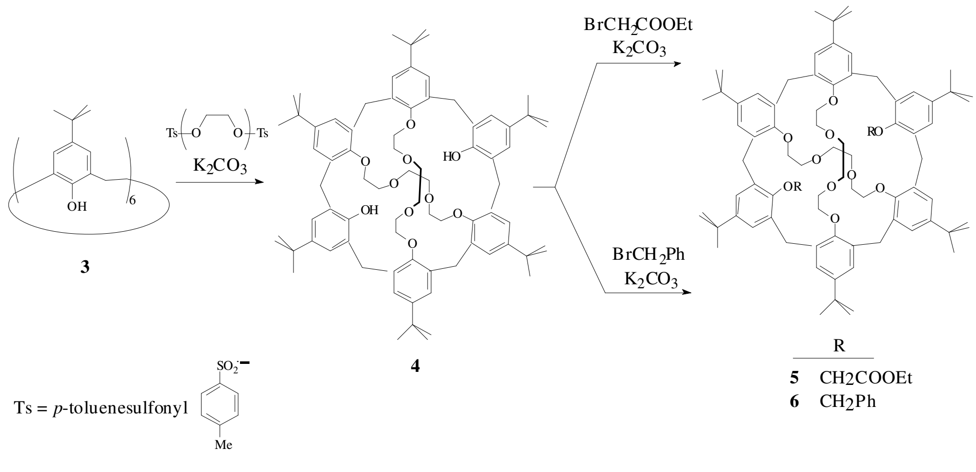
1. Extraction procedures with the use of conventional solvents

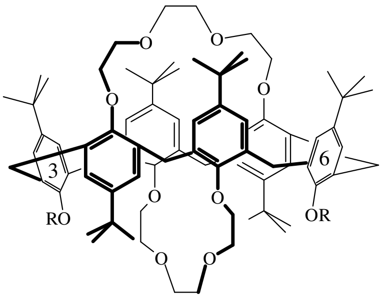
Cesium is found in nuclear waste together with sodium and potassium ions, therefore for its detection selective sensors are necessary. In the search for such species [3] the fluorescent molecular sensors **1** and **2** bearing two dioxycoumarin fluorophores have been synthesized [1]. Since **1** is insoluble in water, it was submitted to chlorosulfonylation followed by hydrolysis to give tetrasulfonated calixcrown **2**. One should point out that **2** is highly water soluble and can detect cesium ion in water very efficiently and selectively.



1 **2**

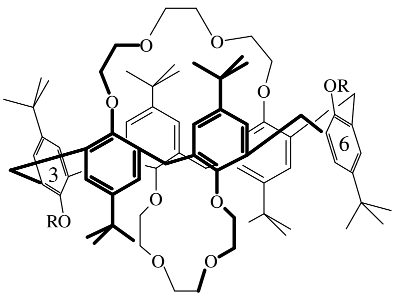
It is known that the complexation ability of calixarenes may be improved by presence of CH_2COOEt or CH_2CONMe_2 groups [2]. For this purpose calixarene **3** was treated with triethylene glycol ditosylate to give calixcrown **4**. The subsequent reaction of **4** with ethyl bromoacetate and benzyl bromide leads to substitution of two hydroxyl groups affording calixcrowns **5** and **6**, respectively, which exist as two pairs of stereoisomers: 3,6-*syn*(**a**) and 3,6-*anti*(**b**) [2].





3,6-*syn*

	R
5a	CH_2COOEt
6a	CH_2Ph



3,6-*anti*

	R
5b	CH_2COOEt
6b	CH_2Ph

The alkali metal complexing properties of **4**-**6** were studied by metal picrate extraction method, in which aqueous solutions of the picrate salts were shaken with chloroform solutions of **4**-**6**. The ESI-MS (electrospray ionization mass spectrometry) results indicate that the **5a**/Cs^+ complex has a 1:1 stoichiometry.

As it was expected, **5a,b** have higher extraction ability and selectivity towards cesium ions than the unsubstituted calixcrown **4**. The calixcrown **5a** shows a high complexation ability and high Cs/Na selectivity. It is worthnoting that the Cs^+/Na^+ selectivity of **5a**, (*i.e. syn*-isomer) is higher than that of **5b** (*i.e. anti*-isomer).

2. Extraction procedures with the use of ionic liquids

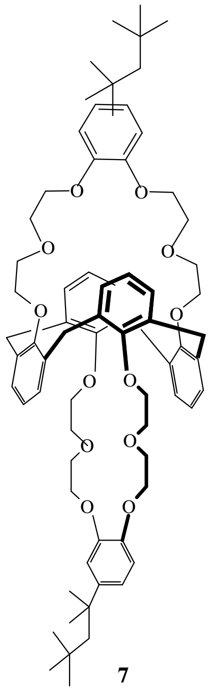
Ionic liquids, and especially room-temperature ionic liquids, ILs and RTILs, respectively, are „green" alternative [4,5] to conventional solvents; in contrast to the latter ones, the ionic liquids are nonvolatile, nonflammable and thermally stable.

ILs are salts XY where X are ammonium, imidazolium or pyridinium cations and Y are predominantly PF_6^- or Tf_2N^- hydrophobic anions (Tf = triflyl, trifluoromethanesulfonyl). ILs have lower melting points than molten salts (mostly below 100°C); RTILs have melting points at or below room temperature. The hygroscopic character and miscibility of ILs with water depend on the kind of Y. ILs which are the most used in liquid extraction are based on *n*-alkyl-methylimidazolium cations and PF_6^- or Tf_2N^- anions; they do not mix with water. It should be pointed out that ILs are more efficient extractants than classical organic solvents.

ILs form biphasic systems with water and can be used in liquid-liquid extraction processes [6]. Extractant compounds, generally used in classical liquid-liquid extraction, such as crown ethers [7] extract metal ions to ILs with higher efficiency than in the case of conventional organic solvents.

It was found that calixcrown **7** dissolved in imidazolium based ILs efficiently extracts cesium from aqueous solutions, with a high selectivity over Na^+ and Sr^{2+} ions [8]. It should be emphasized that the extraction efficiency with traditional solvents, such as 1,2-dichloroethane or chloroform is only negligible.

The molecular dynamics [9] study of cesium extraction by calixcrown **8** in [BMIM][Tf_2N] [10] and at classical water-oil interfaces [11] was made, along with the comparison of IL to a classical solvent (chloroform) serving as a receiving „oil" phase [12] ($BMIM^+$ = 1-butyl-3-methylimidazolium cation). Calixcrown **8** forms with cesium ion the 1:1 complex **9**.



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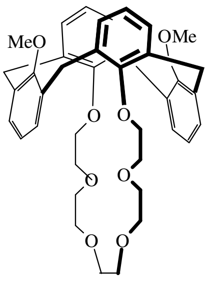
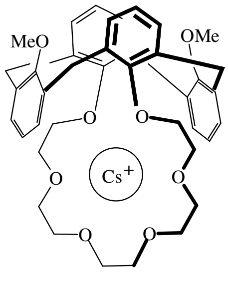


8



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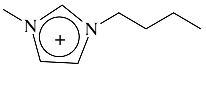
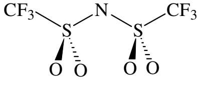


$BMIM^+$

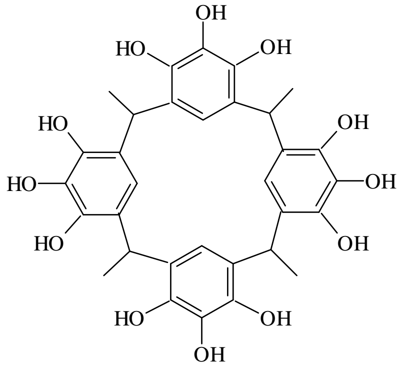


Tf_2N^-

Solvation of alkali metal ions Na^+, Rb^+ and Cs^+ and their complexation with calixcrown **8** has been studied in room-temperature ionic liquids in order to elucidate the effect of humidity of ILs on these processes [10]. For experiments [BMIM][PF_6] (A) and [BMIM][Tf_2N] (B) have been chosen; it was observed that A is more hygroscopic than B. Two models of A – dry and humid ones are considered. The dry model does not contain water molecules, the humid model however contains one water molecule per [BMIM][PF_6].

It was established that **8** selectively forms complexes with Cs^+ in considered ILs; the complexation selectivity Cs^+/Na^+ decreases in the order B>A dry>A humid. The Cs^+/Na^+ extraction selectivity by **8** in studied ILs is high, decreasing in the order A dry>B>A humid. The Cs^+/K^+ and Cs^+/Rb^+ extraction selectivities are lower [10].

One should also mention cesium receptors which do not bear crown ether moieties, as such compound may serve tetramethyl pyrogallolarene **10**.



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The results of investigation of X-ray crystal structure of complexes of **10** with K^+, Rb^+ and Cs^+ have shown strong cation-π-interactions in the complexation [13]. Cocrystallization of **10** with potassium bromide afforded the complex **10**·KBr, while with rubidium chloride and cesium bromide complexes **10**·RbCl and **10**·CsBr were formed.

Conclusion

Chemistry of calixarenes, mostly species containing four benzene moieties [14], as well as those composed of five [15], six [16] and eight [17] benzene moieties, along with calixcrowns [18, 19] is developing rapidly, this fact finding its reflection in a great number of works.

Due to their binding properties, calixarenes form numerous complexes with metal ions [20], *e.g.* with alkali [21] and alkaline earth metals [22], as well as with lead [23], nickel [24], molybdenum [25] and tungsten [26].

In investigations of metal complexation by calixarenes, the reports dealing with extractants for selective separation of lanthanides from actinides in the management of radioactive waste deserve a special attention in the aspect of environmental protection [27-29]. One should also point out importance of use of ionic liquids in these processes, having in view the principles of green chemistry [4,5,30].

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Zagospodarowanie odpadów nuklearnych w aspekcie usuwania cezu działaniem kaliksarenoeterów koronowych

Streszczenie: Podano przykłady kaliksarenoeterów koronowych stosowanych w usuwaniu jonów cezu z odpadów nuklearnych, omawiając ich syntezy i właściwości kompleksujące. Przedstawiono również procesy ekstrakcji cezu z mieszanin jonów litowców z użyciem cieczy jonowych.

Słowa kluczowe: cez, ciecze jonowe, ekstrakcja, kompleksowanie