Dual-Host Ion Pair Extraction:

Selectivity Investigation of Anion Receptors combined with

Calix[4]arene-bis-(*t*-octylbenzo-crown)-6 Cs$^+$ Extractant in Nitrobenzene

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Introduction

Cesium separation from aqueous solutions is an important issue in nuclear waste treatment.[1-5] High-level tank wastes such as stored at the U.S. Department Of Energy Savannah River Site (SRS) and Hanford site, contain fission products and in particular ^{137}Cs which is responsible of most of the radioactivity of waste. A solvent extraction technology, called Caustic-Side Solvent Extraction (CSSX),[6] was developed recently at Oak Ridge National Laboratory (ORNL) and selected for the removal of cesium from SRS high-level waste. Cs' complexation by calix[4]arene-bis-(t-octylbenzo-crown-6) is the basis of the CSSX process. The structure of this macrocycle permits high Cs' extraction efficiency and selectivity against Na' that is very abundant in alkaline high-level salt wastes at SRS. Chemical, thermal, and radiolytic stability as well as good solubility in alkane diluents exhibited by this extractant made it suitable for high-scale nuclear waste treatment by solvent extraction.

Calixcrown compounds as complexing agents for alkali and alkali-earth metal ions have been widely studied.[7-24] Efficient and selective Cs$^+$ complexation by calix[4]arene-crown-6 ligands has been observed and utilized for cesium separations in liquid-liquid extraction systems.[25] Investigation of transport mechanism has demonstrated that calixcrown extractants exhibit ion pair extraction mechanism; and both targeted cation and anion are transported from aqueous to organic phase. As a result, cesium distribution behavior is strongly influenced by the nature of anion that accompanies Cs' transport into organic phase. This effect of counter-anion is well-documented;[27,29,34,60] however, only little effort has been made to attenuate anion distribution behavior. One way to improve anion partitioning into organic phase is to add anion receptor into extraction system. Only recently attention has been directed toward anion recognition; and properties of anion receptors have been reviewed.[26] Selective extraction of specific anions may be of interest in nuclear waste cleanup processes since various anion compositions are found in high-level liquid waste stored in the U.S. For instance, high concentration of nitrate in SRS tank waste suggests selective cesium nitrate separation, which would enhance the efficiency of cesium separation.[6]

Principal motivation of this work was to investigate how anion complexation by selective receptors can be applied to solvent extraction systems and whether synergistic effect could be achieved in dual-host distribution systems. Anion receptors of different classes were studied in combination with calix[4]arene-bis-(t-octylbenzo-crown-6) cesium ligand in solvent extraction. Cesium distribution in a water-nitrobenzene biphasic system was determined and extraction constants were obtained using the modeling program SXLSQI. The focus of our attention was directed toward two main features: synergistic behavior of the cation and the anion hosts in the extraction system was evaluated; and selectivity exhibited by the anion receptors was studied.

The study of anion effect in competitive extraction is a question that has not been addressed in the literature due to the difficulty of detection of mixed anions. However, direct analytical measurements of anions are useful to characterize the selectivity of the hosts. Ion chromatography is a suitable technique for this purpose. The second part of my work was devoted to the development of an ion chromatography method for anion analysis in single competitive extraction experiment.

1. Background information

7.7. Ion pair extraction

Ion distribution between two immiscible liquids involves equilibrium processes depicted in **Figure** 1. Ion partitioning depends on ion'characteristics and on the properties of each phase. Since alkali metal ions have a high affinity to water, their standard Gibbs energies of partitioning $\Delta G_p°(M^+)$ are'generally highly positive. When an extractant is introduced into organic phase, transport of a cation from aqueous phase into organic phase is enhanced due to negative value of the standard Gibbs energy of complex formation $\Delta G_f°(MB^+)$. Cationic complex may interact with the co-extracted anion in the organic phase; ion-pairing Ieads to the formation of a complex with no net charge. This interaction occurs when ionic strength in the organic phase is high and more pronounced in organic solvents with poor solvation abilities. The standard Gibbs energy of ion-pairing is also negative and favors ion pair extraction.

$$\overline{MBX}$$

$$\Delta G_f°(\text{MBX}) \; x \qquad -$$
$$1\;1$$

$$\overline{M^+} \;+\; \overline{B} \;\rightleftharpoons\; \cdot\; \overline{MB^+}$$

$$\Delta G_f°(\text{MB}^+)$$

Organic phase

$$\Delta G_p°(M^+) \qquad\qquad\qquad \Delta G_p°(X^-) \quad \textbf{Aqueous phase}$$
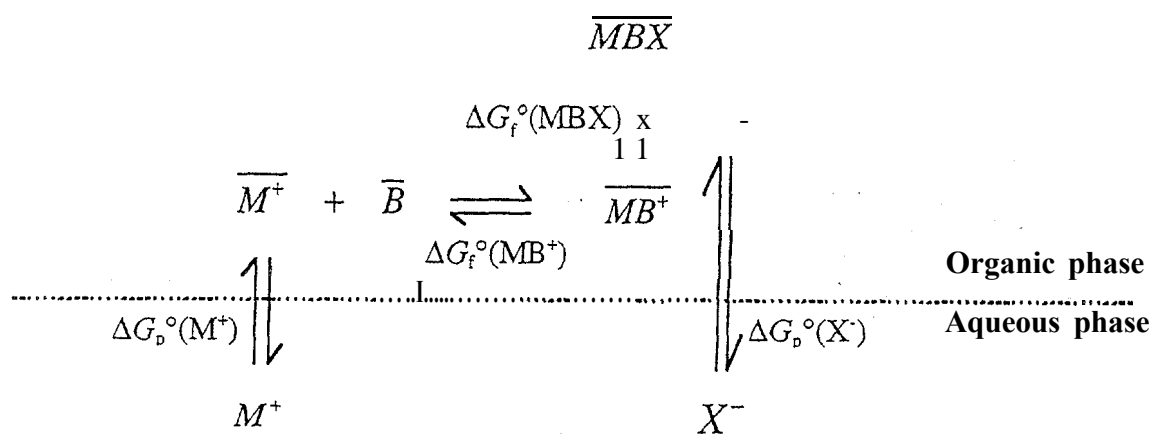
$$M^+ \qquad\qquad\qquad\qquad X^-$$

Figure 1. Equilibrium reactions in ion pair solvent extraction process. M^+, X^- and B refer to an alkali metal cation, an anion and a cation receptor, respectively, in the solvated form. Overbars indicate organic-phase species.
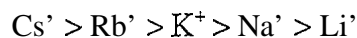
1.2. Partitioning

The first step in the extraction process **(Figure 1)** is solute partitioning between the two phases. Standard Gibbs energy of ion partitioning can be written as the difference between ion solvation and hydration energies in the organic and aqueous phases, respectively:

$$\Delta G_p^\circ = \Delta G_s^\circ - \Delta G_h^\circ \qquad (1)$$

According to the Born electrostatic model of ion solvation, the standard Gibbs energy of ion transfer (non mutually saturated phases) is related to the ionic radius of the solute, and to the dielectric constants of water and diluent..[27] Diluents with high dielectric constant are able to better stabilize ionic species and reduce their standard Gibbs energies of solvation. However, solvation also depends on hydrogen bond donor-acceptor properties of the diluent.

1.2.1. Alkali metal ion partitioning

Alkali metal cations are characterized by a single positive charge and a spherical shape since they possess electronic structures of inert gases. They are hard Lewis acids and strongly interact with the oxygens of water molecules. Hydration energy is higher for small, charge-dense cations. Cs' ion is the softest of the alkali metal series (not considering Fr^+) and exhibits the smallest hydration energy.[28] In organic solvents, large alkali metal cations are more easily solvated. In addition, solvation of cations depends on the diluent hydrogen bond'acceptance ability (β); coordination between the cation and diluent molecules is improved with strong hydrogen bond acceptor diluents. Transfer of alkali metal ions from water to a diluent is generally governed by the size of the cation, which gives the order:

$$Cs' > Rb' > K^+ > Na' > Li'$$

This size bias denotes that Cs' partitioning is the most favorable among the alkali metal series.

1.2.2. Anion partitioning

For a given cation, a large dependence of its partitioning between water and organic solvent on the nature of anion has been observed.[28] The hydration energy of the anion increases in order:

$$ClO_4^- \subset I^- < NO_3^- < Br^- < OH^- \leq Cl^- < F^-$$
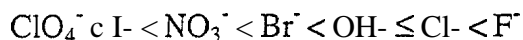
For small anions, salt partitioning generally becomes more unfavorable.[29-30] However, this order is no longer respected, and even reversed, for some protic diluents.[31] Simple electrostatic approach does not take into account specific interactions and cannot explain reversed trend. Diluent hydrogen bond donicity (a) significantly affects solvation of the anion by diluent molecules. Nevertheless, since water-immiscible diluents are needed for liquid-liquid extraction, aprotic diluents are more suitable. Some of these organic solvents possess weak hydrogen bond donicity and do not exhibit specific interactions with anions.

1.2.3. Choice of the diluent

As this survey focuses on anion complexation by anion hosts, any specific interaction of a diluent with anion via hydrogen bonds must be avoided. Nitrobenzene was chosen as a diluent since it possesses no hydrogen bonding donor properties ($\alpha=0$).[27] In addition, its high dielectric constant ($\varepsilon=34.8$) and non-negligible electron-pair donor ability ($\beta=0.39$)[27] promote good solvation of Cs^+, which increases its transport into nitrobenzene phase and helps distribution measurements.

7.3. Cs⁺ complexation

1.3.1. Cation receptors

Development of supramolecular chemistry has led to important achievements in selective separations of alkali metal ions based on host-guest interactions with the emergence of the concept of recognition.[32] Many cation receptors have been studied for applications in liquid-liquid extraction systems.[33-38] A breakthrough in selective solvent extraction of alkali metal ions was associated with discoveries of crown ethers by Pedersen in 1967,[39] and of polycyclic multidentate molecules, known as cryptands, by Lehn.[40-43] Such ligands are capable of

complexing small spherical cations thanks to their interactions with the multiple electron-donor atoms. Selectivity is based on spcecific interactions due to preorganization, namely "macrocyclic effects".[44-47]

More recently, it was discovered that alkali cations are recognized by other macrocyclic compounds such as calixcrown ligands.[7] Calixcrown ligands were introduced a decade ago. They are the combination of calixarene and polyethylene glycol chain. Examples of these molecules are shown in **Figure 2.**
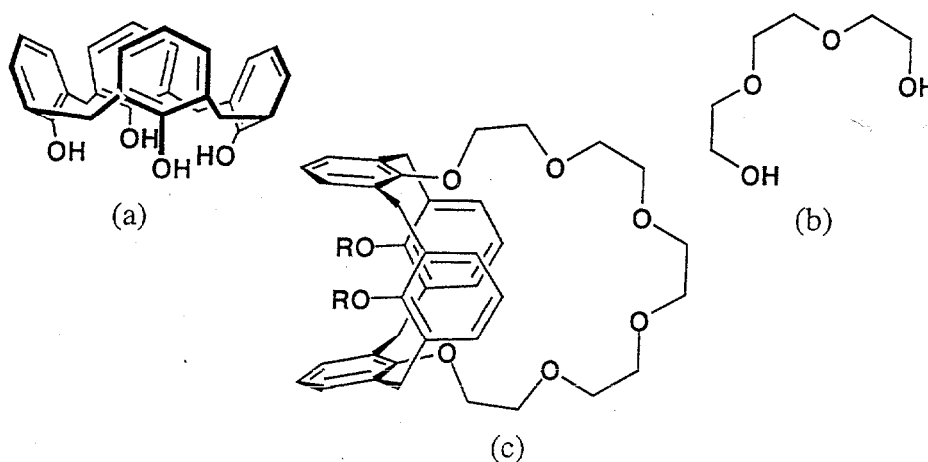

Figure 2. Examples of cation receptors: (a) calix[4]arene, (b) &ethylene glycol, and (c) 1,3-calix[4]arene-crown-6.

Calixarenes compounds are 'made of phenolic units connected by methylene bridges (numbers in square brackets indicate the number of phenolic units). They have the ability to bind cationic guests,[48] but their structural flexibility limits selectivity. Attachment of substituents to the upper rim or lower rim is synthetically possible. Preorganization of the receptor can be achieved by blocking the receptor in one conformation. It was observed that attachment of a polyether chain to a calixarene enhances the degree of preorganization, leading to a preferential binding of alkali metal ions. Calix[4]arene **(Figure 2(a))** can adopt four different conformations, and several of its calixcrown derivatives are selective alkali cation hosts. For instance, calix[4]arene-crown-4 and calix[4]arene-crown-5 selectively bind Na^+ and K^+ ions,

respectively.[49-52] Size complementarity between the ion guests and the cavity can explain cation recognition. Selective complexation of the larger Cs' ion was achieved with calix[4]arene-crown-6 **(Figure 2(b))** and calix[4]arene-biscrown-6 in the 1,3-alternate conformation.[53-55] Calix[4]arene-biscrown-6 receptors are especially of great interest for applications in high-level nuclear waste treatment thanks to synthetic availability and very high Cs^+/Na^+ selectivity factors (more than 10,000). The fixed 1,3-alternate conformation of the calixarene and the two complexation sites formed by crown ether chains define a preorganized structure that perfectly fits the size of the Cs^+ ion. In addition, the complex is stabilized by favorable interactions between Cs^+ and pi-clouds of two aromatic rings.[8,15]

1.3.2. BOBCalixC6 Cs' receptor

A calix[4]arene-biscrown-6 derivative, calix[4]arene-bis-(*t*-octylbenzo-crown-6) (BOBCalixC6) shown in **Figure** 3, exhibits optimized properties for Cs^+ liquid-liquid separations.[56-59] Benzo groups attached to crown ether moiety confer rigidity on the cavity. These substituents tend to enhance the selectivity of the receptor despite a slight decrease of extraction strength.[56] Alkyl substitution on the benzo groups improves solubility of the ligand in alkane diluent without strongly influencing their complexing properties. Direct measurements of BOBCalixC6 partitioning between water and organic solvent by ^{1}H NMR spectrometry confirmed that BOBCalixC6 partitioning to water is negligible.[58] A study of its speciation demonstrated that 1:1 cesium : ligand stoichiometry dominates. Due to these favorable attributes, BOBCalixC6 was the cation receptor of choice for the present work.
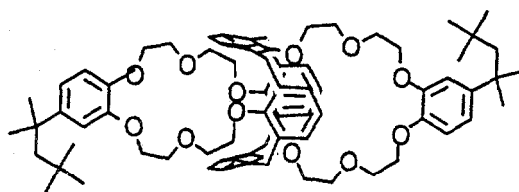
1

Figure 3. Calix[4]arene-bis-(*t*-octylbenzo-crown-6) **(BOBCalixC6).**

1.4. Effect of anion

1.4.1. Anion partitioning effect

From the equilibria shown in **Figure** 1, it may be seen that anion partitioning plays an important role in cesium extraction. Large, hydrophobic anions usually affect feebly extraction constants whereas the high affinity of small anions for water dramatically decreases extraction efficiency. Such electrostatic bias[60] is known as the Hofmeister selectivity'"" and acts as a baseline selectivity in aprotic diluents. This natural behavior makes it particularly challenging to extract efficiently Cs' accompanied by a small anion. Investigation of selectivity toward targeted anions using anion receptors is therefore of great interest.

1.4.2. Anions used in this survey

Selectivity of all anion hosts was assessed by extraction experiments involving five different anions. Nitrate was chosen since it is present in large quantities in nuclear waste tanks, especially at SRS. Perchlorate is a large, charge-diffuse anion and is generally not coordinated by anion receptors. Three halides were used as representative anions to depict a range of size. Their partitioning behavior in water/nitrobenzene biphasic liquid systems were characterized by their standard Gibbs energies of partitioning $\Delta G_p^\circ(X^-)$ **(Figure 1)**.[62]

1.5. Anion receptors

1.5.1. General considerations

Two different ion pair extraction approaches using an anion host can be distinguished. A dual-host approach refers to the combination of separated cation and anion receptors, which is the strategy adopted in this survey **(Figure** 4). Another approach is based on in binding of ion pairs with a bifunctional host, namely a ditopic receptor. Synergism in cation extraction as well as anion recognition may be achieved using dual-host systems, which are usually easier to design than ditopic receptors. Many anion hosts have been reported and their chemistry has been reviewed.[26] Depending on the type of interactions between the anion and the receptor, three classes of anion hosts appear. Positively charged receptors can interact strongly with anions;

however, this leads to non-directional interactions and anion selectivity generally entails a narrow complementarity of the sizes of the guest and a cavity. The two other classes encompass electroneutral hosts: Lewis acidic hosts that often possess one or multiple metal centers and coordinate the anion by covalent bonds; and hosts operating by hydrogen bonding. In the latter class, interactions may be weaker than the interactions between species bearing full charges and covalent interactions,. The directionality of hydrogen bonds however may leads to structural organization as well as specific interactions, as is observed with proteins for instance.

However, most of the studies of anion receptors are related to anion binding in homogeneous systems. The translation of binding abilities to heterogeneous systems is not immediate and needs to be investigated.

Figure 4 shows that formation of an anionic complex in the organic phase introduces an extra Gibbs energy term $\Delta G_f^{\circ}(AH \bullet X^-)$. The more negative the energy of anion complexation, the higher the enhancement of the overall ion pair extraction.

$$\overline{MB^+ \ AH \bullet X^-}$$

$$\Delta G_{\text{ion-pairing}}^{\circ}$$

$$\overline{M^+} \quad + \quad \overline{B} \xrightleftharpoons{\Delta G_f^{\circ}(MB^+)} \quad MB^+$$

$$+$$

$$X^- + \overline{AH} \xrightleftharpoons{\Delta G_f^{\circ}(AH \bullet X^-)} \quad \overline{AH \bullet X^-}$$

$$\Delta G_p^{\circ}(M^+) \qquad \Delta G_p^{\circ}(X^-)$$
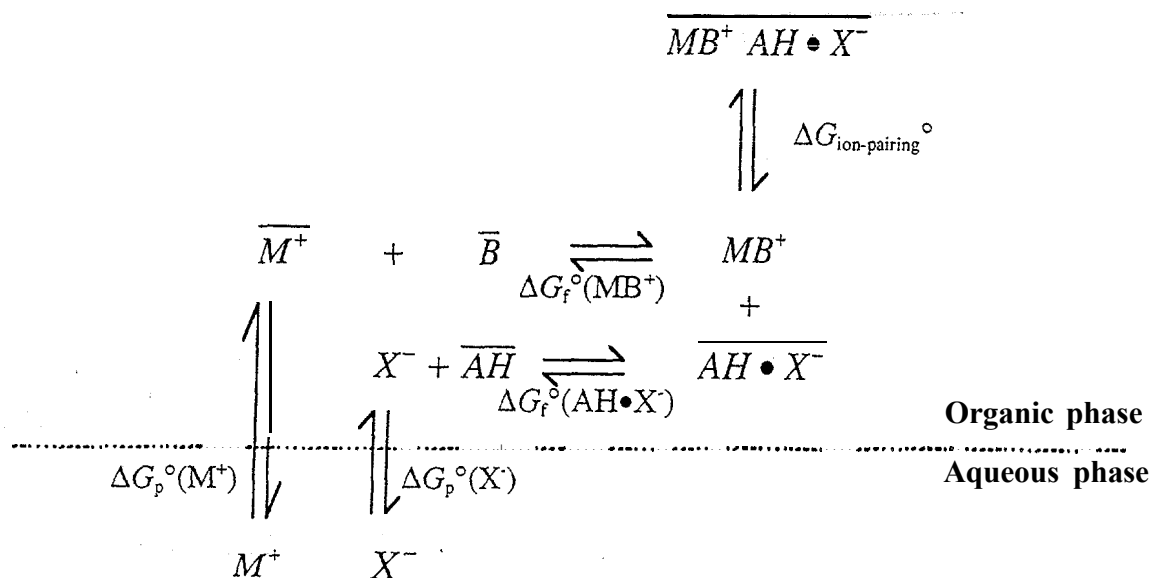
Organic phase

Aqueous phase

$$M^+ \qquad X^-$$

Figure 4. Equilibrium reactions in ion pair solvent extraction process, M^+, X^-, B, and AH refer to an alkali metal cation, a anion, a cation receptor, and an anion receptor, respectively, in the solvated form. Overbars indicate organic-phase species.

I.5.2. Receptors studied in this work

Herein, several anion receptors employing hydrogen bonding are investigated **(Figure 5).** These receptors can be classified into three families: pyrrole-based, phenol-based, and sulfonamide receptors.

1.5.2.1. Pyrrole-based receptors

Calix[4]pyrroles were found to act as receptors for anionic guests such as fluoride and chloride.[63-64] These macrocycles possess multiple hydrogen bond donor groups. Their structural flexibility[65-66] permits different conformations that are adopted depending on the nature of the guest. Sessler et al. reported that the fluorinated calix[4]pyrrole 3 binds fluoride, chloride, and dihydrogen phosphate with better affinity and enhanced selectivity than **2**.[67] The study of the conformation of the complexes of 3 by X-ray crystallography revealed that the fluoride complex adopts the cone conformation. The effect of fluorination was investigated through measurements of affinity constants for anionic guests in acetonitrile-d_3 by ^{1}H and ^{19}F NMR analyses. Significant enhancements were reported for 3 in comparison to 2, but less than one order of magnitude. The electron withdrawing effect of fluorine substituents in the β–pyrrolic positions increases the hydrogen bonding strength of the receptor, and thus the strength of binding,

1.5.2.2. Phenol-based receptors

As a comparison to calix[4]pyrroles, another macrocycle receptor, calix[4]arene (**5**), was studied. Four conformations are also possible.[48] However, a flat cone conformation is stabilized by strong intramolecular hydrogen-bonding interactions between the phenolic groups.[68-69] One can expect a different hydrogen bond donicity than calix[4]pyrroles. A mono-phenol (6) was used as a control receptor to point out preorganization and probable "pK_a" effects. Acid dissociation constants of calixarenes in nonaqueous solvents may be estimated from IR and ^{1}H NMR titration measurements.[70] The first pK_{app} of calixarenes is usually lowered compared to the corresponding phenol due to hydrogen-bond network.

In opposition to the previous macrocycles, disulfonamides are non-preorganized acyclic anion hosts. Strong halide and acetate complexation by isophthalamide receptors in organic solvents was reported.[71-72] In addition, it was observed that benzenedisulfonamides can complex anions using bidentate effect since the distance between the two amide groups is close to the size of some anions.[73] Recently, a study of two benzenedisulfonamides as anion receptors combined with calix[4]arene-bis-(benzo-crown-6) for cesium extraction in 1,2-dichloroethane revealed anti-Hofmeister (small anion favored) synergism, and extraction enhancement related to bidentate coordination of anions.[74] Here, the bidentate effect is investigated using disulfonamides 7 and 8, and mono-sulfonamide 9 combined with BOBCalixC6 in nitrobenzene. The effect of substituents of the amide moieties using benzyl and octyl groups is also studied.

1.6. Ion-pairing effect

Although ion pairing **(Figure 4)** is favorable to extraction,[27] this process depends on the nature of ionic species. As anions may influence the speciation due to interactions with positively charged species, it was necessary to keep the organic-phase ions in a dissociated state to compare the different anion receptors under the same conditions. We observed that ion pairing is totally hampered in nitrobenzene in the range of salt concentration used, which is not the case in the less polar 1,2-dichloroethane, for example.
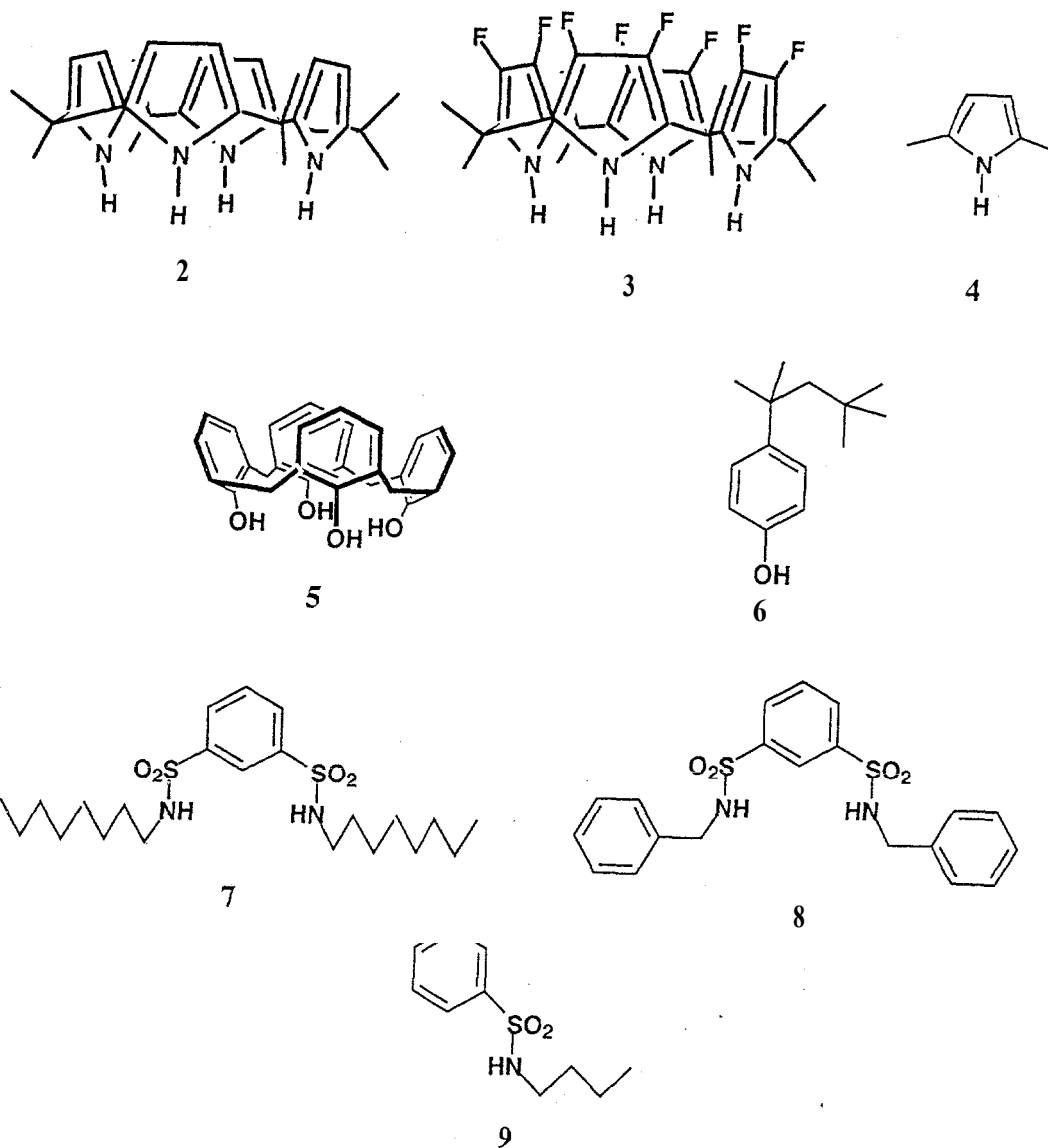
Figure 5. Anion receptors studied in this work: 2 octamethylcalix[4]pyrrole, 3 octamethyloctafluorocalix[4]pyrrole, 4 1,4-dimethylpyrrole, 5 calix[4]arene, 6 4-(*t*-octyl)phenol 7 N,N'-dioctyl-1,3-benzenedisulfonamide, 8 N,N'-dibenzyl-1,3-benzenedisulfonamide, 9 N-, butylbenzenesulfonamide.

2. Thermodynamic aspects

Considering a 1 : 1 metal : ligand stoichiometry[58] in a system containing only a cesium salt CsX and BOBCaIixC6, noted B, in a biphasic liquid system, one may expect two mechanisms of ion pair extraction:

- extraction of dissociated ion pairs
- extraction of ion pairs

which are described by the equilibrium reactions (2) and (3), respectively.

$$Cs^+ + X^- + \overline{B} \rightleftharpoons \overline{CsB^+} + \overline{X^-} \tag{2}$$

$$Cs^+ + X^- + \overline{B} \rightleftharpoons \overline{CsBX} \tag{3}$$

Overbars indicate species in the organic phase. Taking into account the molar activity coefficients y , the corresponding equilibrium constants can be expressed as

$$K_{ex,\pm}(\overline{CsB^+}) = \frac{\overline{y}_{CsB}[\overline{CsB^+}]\overline{y}_X[\overline{X^-}]}{y_{Cs}[Cs^+]y_X[X^-]\overline{y}_B[\overline{B}]} \tag{4}$$

$$K_{ex}(\overline{CsBX}) = \frac{\overline{y}_{CsBX}[\overline{CsBX}]}{y_{Cs}[Cs^+]y_X[X^-]\overline{y}_B[\overline{B}]} \tag{5}$$

All the concentrations expressed here are concentrations at equilibrium and the subscript ± indicates a completely dissociated system. The distribution ratio D of the Cs' ion is defined as the ratio of the cesium concentrations in the organic and aqueous phases at equilibrium:

$$D = \frac{[\overline{Cs^+}]}{[Cs^+]} \tag{6}$$

Since the aqueous phase contains only one cesium salt, electroneutrality in each phase implies $[\overline{CsB^+}] = [\overline{X^-}]$ and $[Cs^+] = [X^-]$. Then, using (4), (5), and (6), the equilibrium constants can be rewritten as

$$K_{ex,\pm}(\overline{CsB^+}) = \frac{\overline{y}_{CsB}\overline{y}_X}{y_{Cs}y_X\overline{y}_B} \times \frac{D^2}{[\overline{B}]} \qquad (7)$$

$$K_{ex}(\overline{CsBX}) = \frac{\overline{y}_{CsBX}}{y_{Cs}y_X\overline{y}_B} \times \frac{D}{[Cs^+][\overline{B}]} \qquad (8)$$

From these equations, we obtain two expressions of $\log D$ related to the mechanism based on dissociated ions and ion pairing, respectively:

$$\log D = \frac{1}{2}\log K_{ex,\pm}(\overline{CsB^+}) + \frac{1}{2}\log\left(\frac{y_{Cs}y_X\overline{y}_B}{\overline{y}_{CsB}\overline{y}_X}\right) + \frac{1}{2}\log[\overline{B}] \qquad (9)$$

$$\log D = \log K_{ex}(\overline{CsBX}) + \log\left(\frac{y_{Cs}y_X\overline{y}_B}{\overline{y}_{CsBX}}\right) + \log[\overline{B}] + \log[Cs^+] \qquad (10)$$

When complete dissociation is achieved, equation (9) shows that the distribution ratio of the Cs^+ ion does not depend on cesium concentration. On the other hand, ion pairing leads to a dependence of $\log D$ on cesium concentration in the aqueous phase at equilibrium as indicated by equation (10). In this case, plotting $\log D$ versus $\log[Cs^+]$ for a constant extractant concentration gives a slope of 1. When both mechanisms occur (partial ion pairing), the plotting of $\log D$ versus $\log[Cs^+]$ is no more linear and the slope of its tangent will be comprised between 0 and 1. It can be seen that a simple slope analysis [58] of $\log D$ versus $\log[Cs^+]$ plotting gives information about the mechanism involved.

True thermodynamic extraction constants can be calculated with the solvent extraction modeling program SXLSQI.[58,75-76] The Cs' distribution ratios and the speciation in both phases

are used as input by the program. The program takes into account non-linearity effects in aqueous and nonaqueous phases with adequate parameters. All constantsare corrected to infinite dilution.

Without anion host, extraction of dissociated ion pairs encompasses partitioning of the cation and the anion, and the formation of the cation complex **(Figure 1).** The logarithm of the extraction constant $K_{ex\,\pm}$ can be expressed with the constant of complex formation $K_{f,CsB}$ in the organic phase, and the standard Gibbs energies of Cs' and X^- partitioning in equation (11) according to the relationship between equilibrium constants and standard Gibbs energies (12).

$$\log K_{ex,\pm} = \log K_{f,CsB} - \frac{\Delta G_p \text{ "(C's')}}{2.303 \times RT} - \frac{\Delta G_p{}^{\circ}(X^-)}{2.303 \times RT} \tag{11}$$

$$\log K = -\frac{\Delta G^{\circ}}{2.303 \times RT} \tag{12}$$

The addition of an anion host AH to this system may modify the extraction constant due to interactions with the anion. As the speciation of anionic complexes is not known, we can only write the expression of an effective extraction constant $K_{ex,\pm}^{eff}$ in which the anion host effect is included in an effective standard Gibbs energy $\Delta G^{\circ,eff}(X^-)$ that takes into account anion complexation through the term $\Delta G_f{}^{\circ,eff}(X^- \bullet AH)$.

$$\log K_{ex,\pm}^{eff} = \log K_{f,CsB} - \frac{\Delta G_p \text{ "(C's')}}{2.303 \times RT} - \frac{\Delta G^{\circ,eff}(X^-)}{2.303 \times RT} \tag{13}$$

$$\Delta G^{\circ,eff}(X^-) = \Delta G_f{}^{\circ,eff}_{\text{□•□}} \bullet AH) + \Delta G_p{}^{\circ}(X^-) \tag{14}$$

Substituting (11) to (13) and replacing by (14), we obtain

$$\log K_{ex,\pm}^{eff} - \log K_{ex,\pm} = -\frac{\Delta G_f{}^{\circ,eff}(X^- . AH)}{2.303 \; x \; RT} \tag{15}$$

$$Synergistic\ factor = \frac{K_{ex,\pm}^{eff}}{K_{ex,\pm}} \qquad (16)$$

The difference of the logarithms of the calculated extraction constants with and without an anion host only depends on the interactions between the anion and the receptor. The interesting characteristic of the logarithm of the synergistic factor is that it does not depend on the standard Gibbs energy of anion partitioning, but only on the contribution of anion complexation.

3. Dual-host systems

3.1. Results and discussion

Single salt extraction experiments were performed at 25 °C by contacting equal volumes of aqueous and nitrobenzene phases. Aqueous solutions were made from five cesium salts, CsCl, CsBr, CsI, CsNO$_3$, or CsClO$_4$ in the 10^{-5} – 1 M concentration range with 10^{-4} M of acid using HCl, HBr, HI, HNO$_3$, or HClO$_4$, respectively. Organic phases were 10 mM of BOBCalixC6 with or without 10 mM of anion receptor in nitrobenzene. Cesium distribution ratios were calculated from direct activity measurements of ^{137}Cs tracer. The extraction data were treated using the modeling program SXLSQI as described above, and extraction constant values were calculated.

3.1.1. Cesium extraction by BOBCalixC6

Partition of cesium was tested with a nitrobenzene solvent without BOBCalixC6. No cesium was detected in the organic phase, but a small amount for the cesinm perchlorate salt. However, the cesium distribution ratio was about 4 orders of magnitude less than it is for extraction of cesium perchlorate by BOBCalixC6. Cesium was presumed to exist only in a complex form in the nitrobenzene phase.

Figure 5 shows extraction isotherms corresponding to each cesium salt. Significant differences of D values are observed between the five salts. Cesium extraction increases with the hydrophobicity of the anion in accord with the Hofmeister series. A flat behavior of $\log D$ versus $\log[\text{Cs}^+]$ is observed in widespread concentration ranges for all anions. According to equation (9), this characterizes complete dissociation of nitrobenzene-phase charged species. A decrease of $\log D$ inevitably occurs at high concentration of salt, which reflects the loading of BOBCalixC6; the variation of the concentration of free cation extractant is indeed no longer negligibie when the amount of extracted cesium is important. Equation (9) shows that a decrease of $[\bar{B}]$ due to its loading lowers the D value.
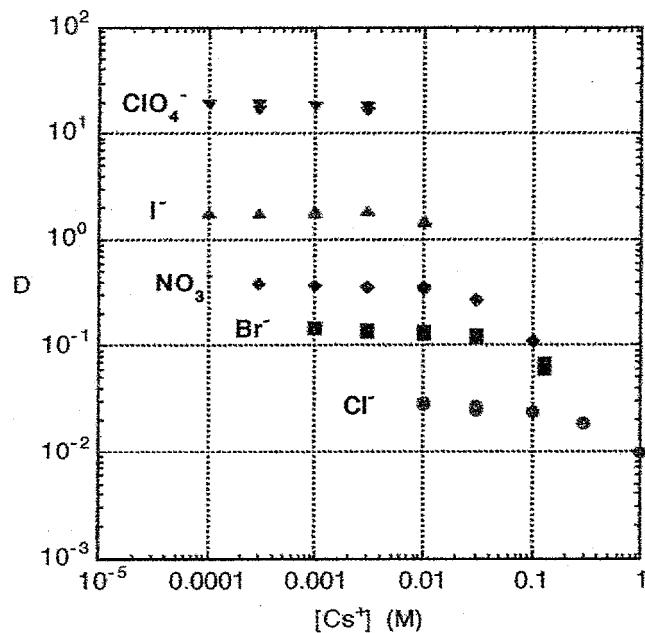
Figure 5. Cesium distribution ratios as a function of equilibrium aqueous-phase molarity of five cesium salts employing 10 mM BOBCalixC6 solutions in nitrobenzene at 25 "C.
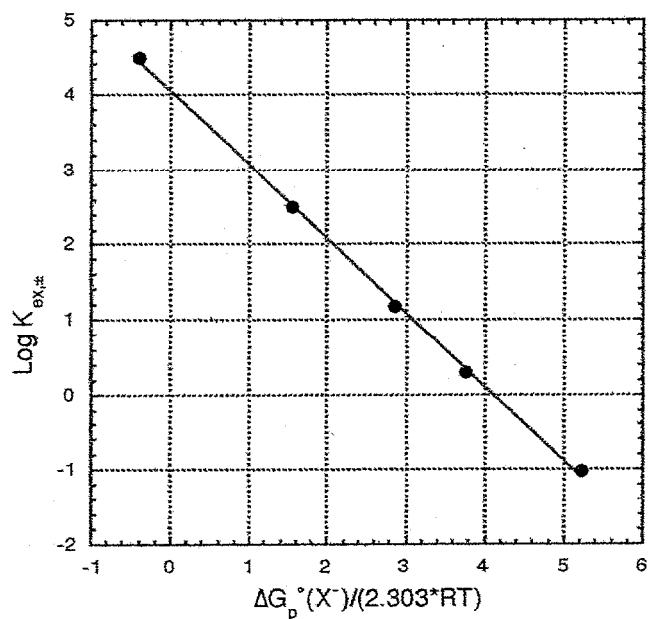

Figure 6. $\log K_{ex\,\pm}$ versus $\Delta G_p^{\circ}(X^-)$ for $X^- = ClO_4^-, I^-, NO_3^-, Br^-, and\ Cl^-$, employing 10 mM BOBCalixC6 solutions in nitrobenzene at 25 "C.

The calculation of extraction constants is based on speciation, and a 1 : 1 metal : ligand stoichiometry was assumed for each cesium salt according to a previous study in 1,2-dichloroethane.[58] Extraction isotherms were perfectly fit with this model, which confirms that this speciation dominates in the nitrobenzene phase.

The dependence of log $K_{ex,\pm}$ with the standard Gibbs energy of anion partitioning is shown in **Figure** 6. A Iinear regression of the five data points gives a slope of -0.984 ± 0.016 ($R^2 = 0.9992$). This is in very good agreement with the slope of -1 expected from equation (11) when complete dissociation of organic-phase ion pairs is achieved. The mechanism is thus the same for each cesium salt.
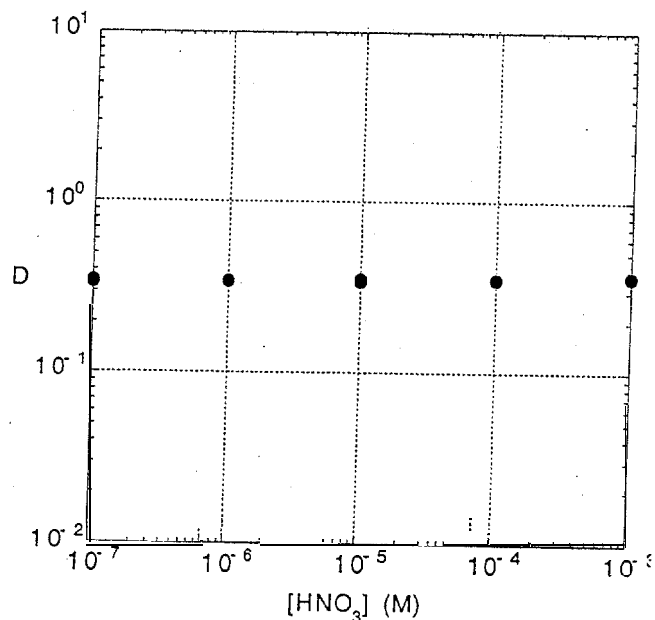

Figure 7. Cesium distribution ratios as a function of initial aqueous-phase molarity of HNO_3 employing 10 mM BOBCalixC6 solutions in nitrobenzene at 25 "C. Initial aqueous-phase $CsNO_3$ concentration was 10 mM.

The effect of pH on cesium nitrate extraction by BOBCalixC6 alone was investigated employing variable nitric acid concentration in the aqueous phase containing 10 mM of cesium nitrate **(Figure** 7). No pH effect is observed under these conditions of extraction since a constant D value was obtained. Extraction experiments were performed using aqueous phase with

variable cesium chloride and cesium nitrate concentration at neutral pH or with 10^{-4} M of the corresponding acid (**Figure 8**). The superimposition of the data points confirms that cesium extraction by BOBCalixC6 alone is not p&dependent in this range of cesium concentration and acidity.
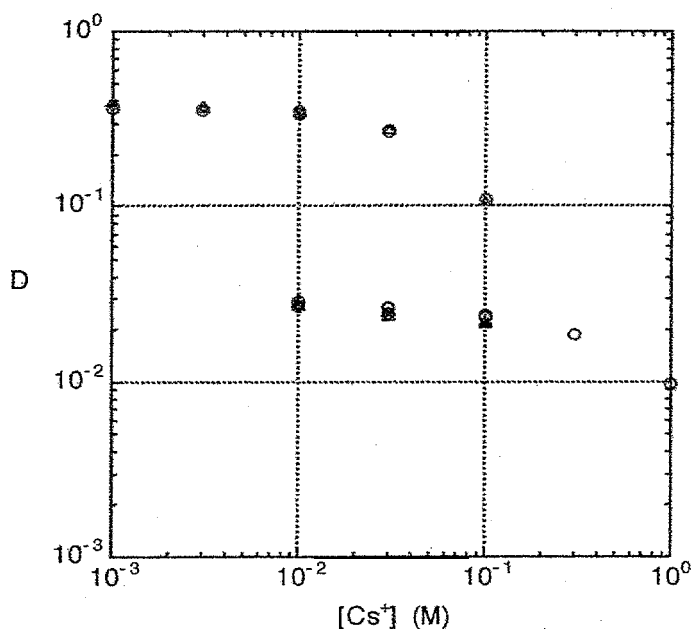

Figure 8. Cesium distribution ratios as a function of equilibrium aqueous-phase molarity of $CsNO_3$ (red plots) and $CsCl$ (green plots) (o) without acid and (A) with 10^{-4} M H NO_3 or HCl employing 10 mM BOBCalixC6 solutions in nitrobenzene at 25 "C.

3.1.2. Dual-host systems

Control experiments using nitrobenzene solution containing 10 mM of anion receptor and no BOBCalixC6 were performed. For every anion receptor, no cesium was detected in the organic phase, but the same amount as observed in the partition experiment for the cesium perchlorate salt. Cesium extraction by dual-host systems was studied using 10 mM of BOBCalixC6 and 10 mM of anion receptor solutions in nitrobenzene.

3.1.2.1. Pyrrole-based receptors

Figure 9 shows extraction results for BOBCalixC6 alone and the combination with calix[4]pyrrole 2 and with the mono-pyrrole 4 for cesium chloride, bromide, nitrate and iodide salts. The D values remain constant in every case, except when loading is significant at high cesium concentration. This observation indicates that addition of anion hosts 2 or 4 does not alter the extraction mechanism. Addition of 4 to the BOBCalixC6 solution gives no synergism for any cesium salt. However, addition of 2 leads to higher D values in cesium chloride and cesium bromide extractions, and weaker D values in cesium nitrate and cesium iodide extractions.

Synergism related to each pyrrole-based dual-host system is evaluated on the plotting of the logarithm of the synergistic factor versus the standard Gibbs energy of anion partitioning **(Figure 10)**. The data points corresponding to 4 almost fall on the horizontal line at zero. According to equation (15), this observation means that $\Delta G_f^{\circ, eff}(X^- \bullet AN)$ value is very low and no enhancement is thus obtained. The plotting shows significant synergism for both calix[4]pyrroles 2 and 3 considering cesium chloride extraction. The logarithm of the synergistic factor equals 1.2 and 3.8 for 2 and 3, respectively, suggesting a remarkable affinity of 3 for chloride. In both cases, the synergism decreases as the anion hydrophobicity increases and 2 gives increasing antagonism from nitrate to perchlorate. Interactions between the hydrogen atoms of the pyrrole groups of 2 and the oxygen atoms of the crowns of BOBCalixC6 could be responsible for aggregation between the two receptors. This effect would diminish the overall extraction, leading to antagonistic behavior. Aggregation is also likely to occur with 3 even if no antagonism is observed with this receptor. The effect on synergism would be a vertical offset of the data points for each anion receptor,
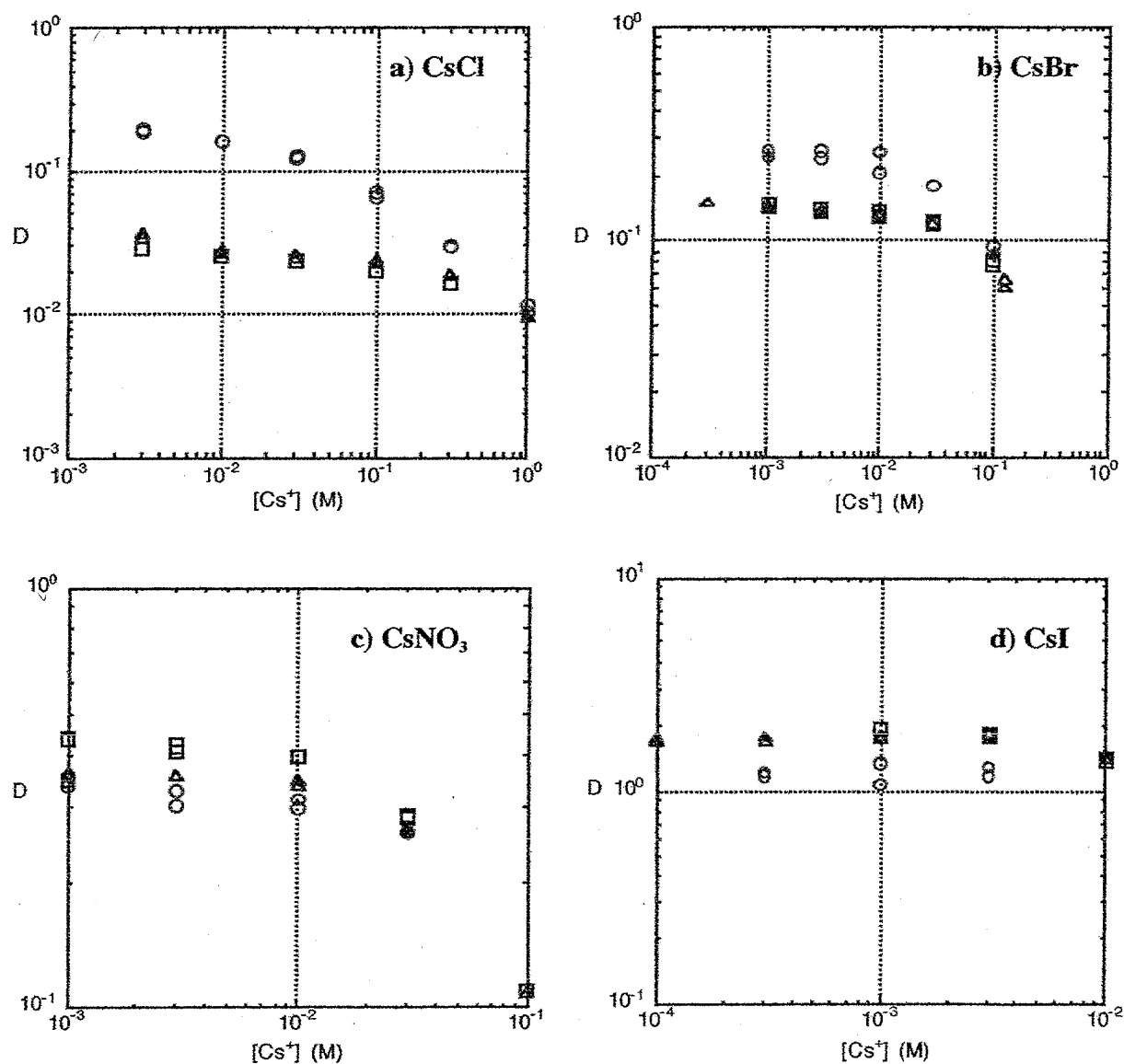
Figure 9. Cesium distribution ratios as a function of equilibrium aqueous-phase molarity of a) CsCl, b) CsBr, c) CsNO$_3$, or d) CsI, employing 10 mM BOBCalixC6 ($\triangle$) alone, (o) with 10 mM of 2, or ($\square$) with 10 mM of 4 in nitrobenzene at 25 °C.

Fluorine substituents in the β –pyrrolic positions of 3 lead to a dramatic increase of cesium extraction with small anions compared to that obtained with 2. The high electronegativity of fluorine strengthens the hydrogen bond donicity of the receptor and complexation of strong hydrogen bond acceptors such as chloride becomes much more favorable.

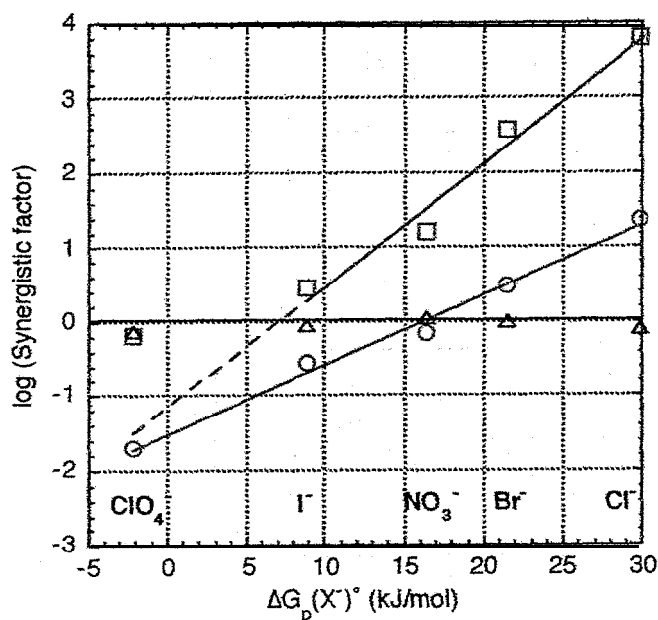**Figure 10.** Logarithm of synergistic factor $K^{eff}_{ex,\pm} / K_{ex,\pm}$ as a function of $\Delta G^{\circ}_{p}(X^{-})$ for $X^{-} = ClO_4^{-}, I^{-}, NO_3^{-}, Br^{-}, and\ Cl^{-}$, employing 10 mM BOBCalixC6 with (o) 10 mM of 2, (□) 10 mM of 3, or (Δ) 10 mM of 4 in nitrobenzene at 2.5 °C.

Interestingly, the dependence of the logarithm of the synergistic factor with the standard free energy of anion partitioning is linear for both anion receptors. This suggests an anti-Hofmeister bias selectivity since small anions are preferentially extracted to large ones. The enhanced extraction of cesium with small anions, especially with chloride, is in agreement with the binding abilities of 3 for fluoride and chloride reported by Sessler *et al.*[67] The slope of the straight line is approximately twice bigger with 3 than with 2, which indicates a stronger anti-Hofmeister bias selectivity for 3. **Figure** 11 shows the dependence of extraction constants for BOBCalixC6 alone and in combination with 3. Whereas a monotonic decrease of the extraction constant values is observed in cesium extraction by BOBCalixC6 alone, thk calculated constant corresponding to the addition of 3 is approximately constant. The opposite anion selectivity of 3 annihilates the natural behavior due to anion partitioning.
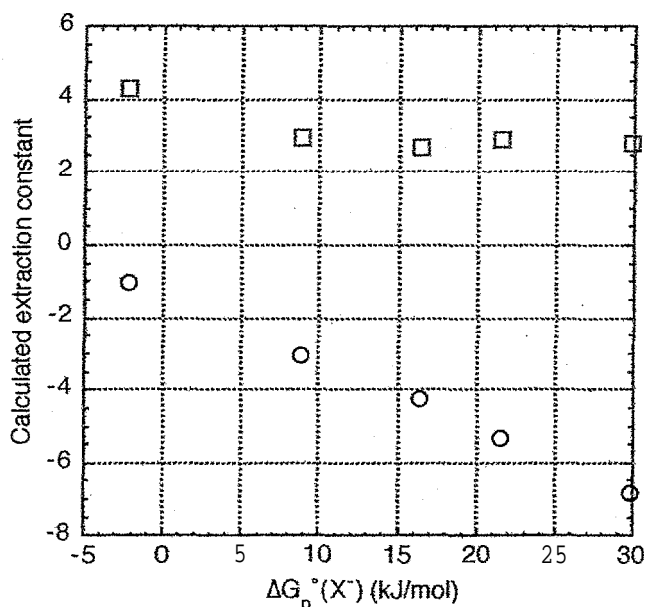
Figure 11. Calculated extraction constants as a function of $\Delta G_p^{\circ}(X^-)$ for

x- = ClO_4^-, I^-, NO_3^-, Br^-, and Cl^-, employing 10 mM BOBCalixC6 (o) alone, or (□) with 10 mM of 3 in nitrobenzene at 25 "C.

The fact that the datum point corresponding to cesium perchlorate falls off the trend line (Figure **10**) could point out an unexpected affinity of the fluorinated calix[4]pyrrole 3 for perchlorate. It was shown that the conformation adopted by **3•X⁻** complexes is related to the strength of hydrogen bond acceptance of the substrate.[67] Four different conformations of solid-state complexes were identified by X-ray crystallography analyses using three selected hydrogen bond acceptors (fluoride, DMSO-d_6, and methanol). Whereas the hard fluorine anion 'enforces a cone conformation of the calix[4]pyrrole, a weaker hydrogen bond acceptor, such as methanol, allows 1,3-alternate and. 1,2-alternate conformations. Since perchlorate has a weak electronic density, we can speculate that it would also allow an alternate conformation; in this case, the energy barrier corresponding to the change of conformation of 3 would be lower, which would facilitate anion binding. This effect could compensate probable aggregation of 3 with BOBCalixC6 leading to almost no change in cesium extraction. However, extraction experiments involving more hydrophobic anions would help to confirm this affinity.

3.122. Calix[4]arene

The logarithm of the synergistic factor versus the standard Gibbs energy of anion. partitioning is represented in **Figure** 12. It can be seen that the addition of either calix[4]arene 5 **or phenol 6** does not give any big effects on cesium extraction. Both receptors exhibit a similar behavior: little enhancement is obtained for nitrate, bromide and chloride leading to logarithms of synergistic factor approximately equal to 0.2. Reorganization of 5 in a cone conformation has no effect on extraction compared to mono-phenol 6. Speculatively, their hydrogen bonding properties are similar leading to no difference between their apparent pK_a values in this system. The small constant enhancement may be attributed to a change in the solvation properties.

Figure **12.** Logarithm of synergistic factor $K^{eff}_{ex,\pm} / K_{ex,\pm}$ as a function of $\Delta G_p^{\circ}(X^-)$ for $X^- = ClO_4^-, I^-, NO_3^-, Br^-, and\ Cl^-$, employing 10 mM BOBCalixC6 with (o) 10 mM of 5, or (□) 10 mM of 6 in nitrobenzene at 25 °C.

Weak antagonism also can be observed for cesium perchlorate extraction with 6, probably due to interactions between BOBCalixC6 and 6. These results do not demonstrate any selectivity of both dual-host systems.

3.1.2.3. Disulfonamides

The results corresponding to **7, 8**, and monosulfonamide 9 are given in **Figure 13**. Weak and constant enhancement (about 0.3) is obtained with the addition of 9 for nitrate, bromide and chloride. As for phenol-based receptors, no anion binding but a modification of the diluent properties may be involved here, principally affecting charge-dense anions.

Linear synergism less than one order of magnitude is observed for both disulfonamides and suggests anti-Hofmeister bias selectivity, as *it* was observed in a previous study using isophthalamide derivatives in 1,2-DCE.[77] Comparison of the slopes gives the order of selectivity strength 8 > 7. None of these receptors is apparently capable to complex perchlorate. Binding of smaller anions is a little more favorable when amide substituent is benzyl than octyl. This probably results from the difference of acidity of amide protons due to inductive effects.
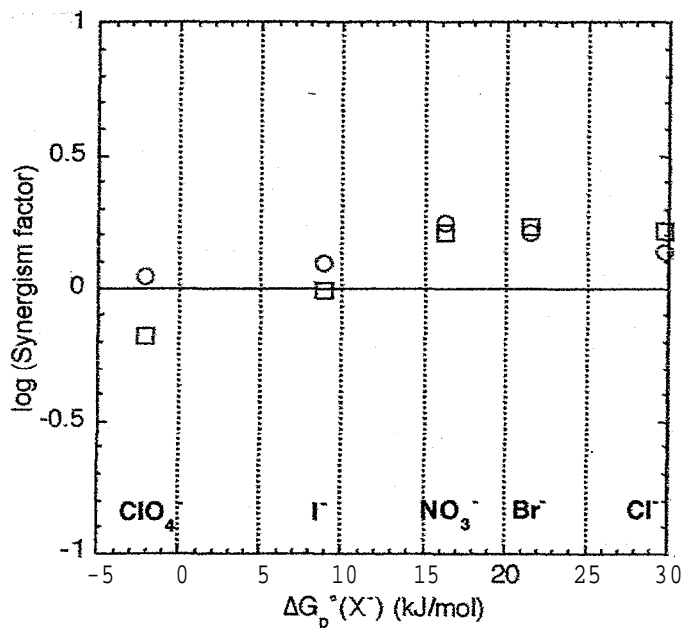

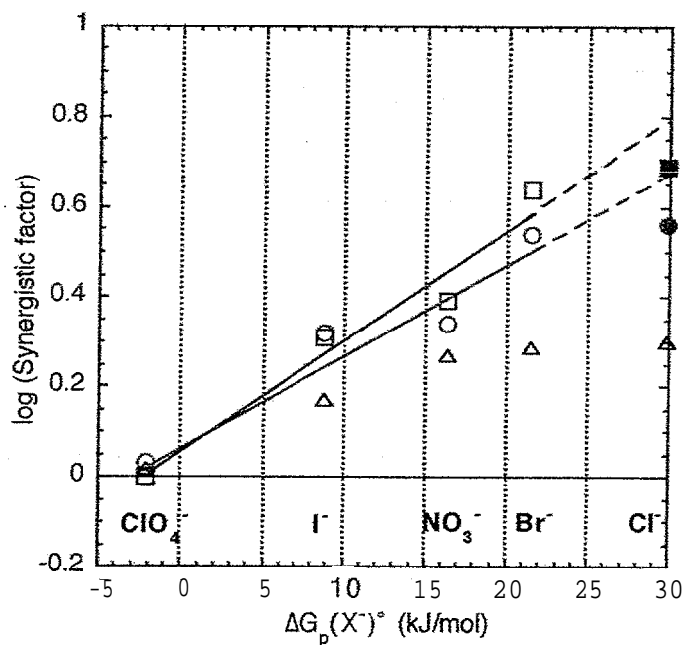**Figure 13.** Logarithm of synergistic factor $K_{ex,\pm}^{eff} / K_{ex,\pm}$ as a function of $\Delta G_p^{\circ}(X^-)$ for $X^- = ClO_4^-, I^-, NO_3^-, Br^-,$ *and* Cl^-, employing 10 mM BOBCalixC6 with (o) 10 mM of 7, (□) 10 mM of 8, or (Δ) 10 mM of 9 in nitrobenzene at 25 °C. Filled symbols indicate precipitation in the organic phase.

Equilibrium distribution ratios could not be obtained for cesium chloride extraction with 7 and **8** because of the formation of a precipitate in the organic phase under these experimental conditions. A way to avoid precipitation is to increase both concentrations of BOBCalixC6 and anion receptor in nitrobenzene, which have been demonstrated in this case using 50 mM of each. Some on-going experiments should yield to relevant extraction constant for cesium chloride,

Extraction results suggest that bidentate sulfonamide-based receptors are more likely to coordinate anions than monodentate. Moreover, the more acidic the protons involved in hydrogen-bonding, the stronger the binding and the selectivity. No surprising host-guest interaction or recognition was pointed out, but based on these considerations, one can expect that other designs or substituent properties would lead to stronger anion binding and possibly stronger selectivity.

3.2. Summary

Extraction of cesium salt into nitrobenzene using BOBCalixC6 was studied. From extraction isotherms and the use of the modeling program SXLSQI, we determined extraction constants $K_{ex,\pm}$ related to Cs^+ complexation by BOBCalixC6 in nitrobenzene at 25 °C for five cesium salts corresponding to a dissociated-state extraction mechanism. It was shown that nitrobenzene is an appropriate diluent to study synergism in a dual-host strategy as it provides with sufficient solvation of ionic species to avoid ion pairing.

Different anion receptors that all have hydrogen-bonding abilities were investigated in combination with BOBCalixC6 in nitrobenzene. A fluorinated calix[4]pyrrole demonstrated remarkable affinity to small anion according to the great synergism observed: cesium chloride extraction enhancement of almost 4 orders of magnitude was obtained. Unfortunately, no recognition of small anions was observed, but a possible specific interaction with perchlorate was suggested. Antagonism was observed with calix[4]pyrrole when larger anions were involved, and was attributed to aggregation with BOBCalixC6. Calix[4]pyrroles and disulfonamides demonstrated anti-Hofmeister bias selectivity. A simple calix[4]arene did not give any significant extraction enhancement. The selectivity of the fluorinated calix[4]pyrrole was very strong and could compensate the natural preference for large anion partitioning.

For future work, it is recommended to study the speciation of calix[4]pyrroles which is necessary to obtain anion binding constants and to confirm an aggregation with BOBCalixC6. Aggregation constants could be determined by ^{1}H NMR titration. Disulfonamides gave promising results for anion binding in nitrobenzene. Other disulfonamide-based receptors are currently being investigated.

4. Ion chromatography for anion analysis applied to ion pair extraction

Ion chromatography (IC) is a method of choice for anion quantitative analysis. This technique makes it possible to investigate competitive anion extraction in a single experiment. IC was applied to the analysis of organic phases in extraction systems involving a mixture of the five anions used in the study of dual-host systems.

4.1. Important issues

Samples for IC have to be aqueous solutions. A limited range of concentration, typically from 10" to 10^{-4} M, allows quantitative measurements and good resolution of peaks. Analysis of all anions simultaneously in organic phase requires adjustments of initial aqueous-phase salt concentrations in extraction systems to obtain organic phase concentrations in the desired range. However, direct measurements of ion concentrations in organic phases are not possible. The anions present in the organic phase of the extraction system must be removed into stripping aqueous phase. Stripping of extracted anions is thus a major issue: complete stripping has to be achieved in order to determine equilibrium anion concentration by IC analysis.

Perchlorate also brings the question of its detection. None of the standard methods for anion analysis provided by the supplier Dionex Corp. includes the perchlorate ion. Due to its high affinity to the column stationary phase, a strong eluent has to be used to reduce retention time. Characteristics of the detector limit the maximum strength of the eluent. A single method has to be designed for simultaneous detection of both hydrophilic and hydrophobic anions.

Although only five anions were investigated, a good separation of the peaks in the chromatograms is not immediate. Nitrate and bromide ions have close affinity for the column stationary phase, and only small differences between their retention times were observed. The determination of adequate eluents and the use of gradient elution are essential to separate the detection peaks, taking into account their broadening when anion concentration increases,

Quantitative measurements also imply the use of standard solutions for calibration and the achievement of good reproducibility. The assessment of the reproducibility of IC detection is essential to validate the method..

4.2. Development of a method for solvent-extracted anion analysis

4.2.1. Stripping a t elevated tempera ture

A stripping at elevated temperature was preferred to multiple stripping since a one-step process reduces the error on concentrations when stripping is incomplete. Water was used as the strip effluent and toluene was added to the system to decrease the polarity of the nitrobenzene diluent and improve ionic transport from the organic phase to the aqueous phase.

Extraction experiments were first performed. Organic phases were solutions of 10 mM of BOBCalixC6 in nitrobenzene and aqueous phases solutions of cesium perchlorate at variable concentration. The efficiency of the stripping at 25, 40 and 60 °C was determined by analyses of cesium distribution using ^{137}Cs tracer. A constant O/A ratio of 0.5 was employed [O/A = organic to aqueous volume ratio]. Stripping at 25 °C removed at most 87% of the cesium from the organic phase. More than 95% of the cesium was stripped at 40 and 60 °C for concentrations in the organic phase higher than 10^{-5} M. Only 86% of cesium was stripped at lower concentration in the organic phase, typically 3.2×10^{-6} M.

These results suggest that temperature of 40 °C is sufficient to strip more than 95% of cesium perchlorate with an O/A ratio equals to 0.5 in the range of concentration of interest. It was assumed that the stripping of less hydrophobic anions is even better under these conditions.

4.2.2. IC method

A method of detection of chloride, bromide, nitrate, iodide, and perchlorate by IC was set up using hydroxyde eluent only. Since large differences of affinity of these species for the column was observed, it was decided to use a non-isocratic method. Variation of the hydroxide concentration of the eluents during the run permits to reduce the time of the analysis and to obtain well-defined and resolved peaks. The method was set as shown in **Table 1.** A chromatogram of a mixture of the five anions is given in the Appendix.

Calibration of the peak areas was made using IC standards (chloride, bromide, nitrate, and iodide) and a recrystallised cesium perchlorate salt. Four standard solutions for calibration

were prepared by mixing the five salt solutions at the same concentration (5×10^{-6}, 8×10^{-6}, 10^{-5}, and 5×10"). Plotting of the peak area versus the concentration of perchlorate is shown in Figure 14 as an example of calibration curve. A linear dependence of peak areas versus concentrations was observed for all anions.

Time (min)	Eluent hydroxide concentration(mM)
Equilibration	
0 - 10	0.3
Analysis	
10 - 11	0.3
11 – 26	Gradient from 0.3 to 2
26 – 33	2
33 – 43	Gradient from 2 to 40
43 – 53	40

Table 1 Description of the IC method

A difficulty in the application of IC to extraction analysis is the contamination of the samples by impurities coming from extraction vessels and from the contact with the organic phase in the stripping process. Chloride and nitrate impurities from the equipment in contact with the solutions can be reduced by washing the vials prior to use. Polar impurities that are transferred from the organic phase to the aqueous phase also can perturb the detection and quantitative measurements. Elevated temperature favors contamination. For the five present anions, no overlapping of the peaks by impurity peaks was observed. However, those impurities could pose a problem for detection of hydrophilic anions such as fluoride and acetate.
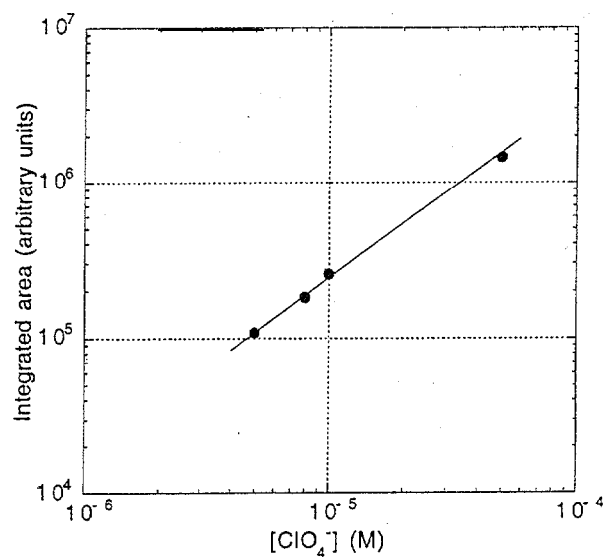
Figure 14. Calibration curve obtained for perchlorate anion

4.3. Preliminary results

IC analysis of extraction of 1 mM of cesium bromide by 10 mM of BOBCalixC6 in nitrobenzene was performed in four replicates, The organic phase was stripped at 25 "C. The average concentration of bromide in the organic phase was calculated:

$$[\overline{Br^-}] = 1.03 \pm 0.03 \text{ x } 10^{-4} M$$

The low standard deviation denotes that the four replicates provided consistent results, which suggests a good reproducibility of this analytical method. This value can be compared to the cesium concentration obtained under the same conditions of extraction from y-counting measurements:

$$[Cs^+] = 1.25 \pm 0.07 \text{ x } 10^{-4} \text{ A4}$$

The very good agreement between both concentrations helps to validate the relevance of the data obtained by IC.

A cesium extraction experiment involving a mixture of the five cesium salts was carried out to assess the direct competition between the different anions. Extraction was performed using 10 mM of BOBCalixC6 in nitrobenzene;, organic phase was stripped at 40 "C. The stripping solution was analyzed by IC. The concentrations of all the species in the organic phase at equilibrium were predicted using the modeling program SXFIT.[78] Unlike SXLSQI, this program permits user complete freedom to define the constituents of the system and is thus more suitable to predict equilibrium concentrations related to mixtures of species. The results are summarized in Table 2.

Anion	Initial aqueous concentration (M)	Measured concentration by IC in organic phase (xl 0^{-4} iv)	Predicted concentration in organic phase by SXFIT (X10^{-4} M)
Cl	1.23×10^{-2}	1.35 ± 0.02	1.74
Br$^-$	4.89×10^{-4}	1.11 ± 0.01	1.11
NO,-	3.40×10^{-4}	2.44 ± 0.01	2.36
I-	1.40×10^{-4}	1.19 ± 0.02	1.37
ClO$_4^-$	1.05×10^{-4}	0.722 ± 0.003	1.05
Cation		Sum of anion measured concentrations by IC ($\times 10^{-4}$ M)	Predicted concentration in organic phase by SXFIT ($\times 10^{-4}$ M)
Cs$^+$	1.34×10^{-2}	6.812 ± 0.03	7.63

Table 2 Comparison between measured anion concentrations by IC and predicted concentrations by SXFIT in a competitive extraction experiment involving CsCl, CsBr, CsNO3, CsI, and CsClO4.

The agreement between IC-measured and predicted values is remarkable. The mass balance is respected within 10% with regard to the sum of anion concentrations and the predicted cesium concentration. Since initial concentrations were determined using accurate distribution ratios, the agreement demonstrates the accuracy of IC and of the experimental protocol. These observations confirm the performance of IC as a suitable analytical method for investigations in competitive extraction.

4.4. Conclusion

The development of an IC method applied to extracted anion analysis required efficient stripping of organic phases to remove all anions. This was achieved by increasing the temperature to 40 "C. This result is of interest since stripping is a major issue in liquid-liquid extraction processes. The conditions of analysis were optimized to detect mixtures of five anions and measure their.concentrations with accuracy. In particular, detection and quantitative analysis of perchlorate was a challenging part of this study since perchlorate analysis does not exist in IC standard procedures. Goodreproducibility as well as good agreement with other measurements and predictions were demonstrated. Consequently, utilization of IC for extraction analysis allows one to expect new ways of investigation concerning determination of anion selectivity in extraction. IC appears to offer many benefits to studies of dual-host systems.

5. Experimental

5.1. Materials

All the solvents were purchased from EM Science unless otherwise stated. All inorganic salts and acid solutions were purchased from Aldrich Chemical Co. Standard solutions for-ion chromatography were purchased from EM Science.

The cesium chloride (99.9995%), cesium bromide (99.999%), and cesium nitrate (99.999%) salts were dried at 100 °C under vacuum for one day prior to use. The cesium iodide salt (99.99%) was dried at 60 °C under vacuum for one day prior to use. The cesium perchlorate salt (97%) was recrystallised and dried at 60 °C under vacuum for one day prior to use. Chloric, bromic, nitric, iodic and perchloric acids were titrated and used to prepare acidic solutions of their corresponding salts. The radiotracer ^{137}Cs was received as $^{137}CsCl$ in 1 M HCl (Amersham) and converted to a neutral aqueous solution of $^{137}CsCH_3SO_3$ by ion-exchange: All aqueous solutions were prepared with distilled deionized water (resistivity $\geq$ 18.0 MΩ).

Nitrobenzene (Aldrich, 99.99+%) was washed four times with a 0.1 M NaOH solution and five times with water using equal volumes of nitrobenzene and aqueous solution. It was then distilled under vacuum (P=36 torr, T=90 "C) and washed again once with a 0.1 M NaOH solution and five times with water. Its purity was checked by gas chromatography.

Calix[4]arene-bis-(t-octylbenzo-crown-6) (BOBCalixC6) was purchased from IBC Advanced Technologies. Filtration was carried out over Silica gel 40 μm (Baker) eluting with chloroform-ethyl acetate (9: 1). Three to four recrystallizations from acetone/heptane/1,2-dichloroethane (Sigma-Aldrich) of each collected fraction were made. All the fractions were combined after the purity was confirmed by TLC and another recrystallization from the same solvent mixture was carried out.

Octamethylcalix[4]pyrrole[44] and octamethyloctafl uorocalix[4]pyrrole[40] were obtained from the University of Texas at Austin and used without further purification.

Calix[4]arene (Aldrich), 2,5-dimethylpyrrole (Aldrich, 98%), 4-(t-octyl)phenol (Aldrich, 97%), and N-butylbenzenesulfonamide (Aldrich, 99%) were used as received.

N,N'-dioctyl-1,3-benzenedisulfonamide, and N,N'-dibenzyl-1,3-benzenedisulfonamide were prepared in our laboratory.

5.2. Extraction and stripping procedures

Solvent extraction experiments were carried out by contacting equal volumes (0.4 - 0.5 mL) of aqueous phase and organic phase in 2-mL cryogenic vials. After a small amount of $^{137}CsCH_3SO_3$ tracer was added, all samples were gently shaken by end-over-end rotation with a Glass-Co!@ laboratory rotator in a thermostated air box at 25.0 ± 0.2 °C for one hour. Complete phase separation was obtained by centrifugation at 3600 rpm for three to five minutes. An aliquot of each phase was removed to determine the cesium distribution by y-counting techniques. Duplicate experiments were performed for every data point.

Stripping was performed in 15-mL Nunc™ vials. One volume of the extraction organic phase, four volumes of distilled deionized water, and one volume of toluene (O/A = 0.5) were contacted by repeated inversion on a Glass-Col® laboratory rotator in a thermostated air box at 25.0 ± 0.2 °C, 40.0 ± 0.5 °C or 60.0 ± 0.5 °C for two hours. For stripping at ambient temperature, phase separation was obtained by centrifugation at 3600 rpm for three minutes at 25 °C; for stripping at 40 and 60 °C, decantation for thirty minutes inside the thermostated air box was applied. Stripping phases were directly analyzed by ion chromatography, Samples containing ^{137}Cs tracer were analyzed by y-counting techniques.

5.3. Analysis

The cesium distribution from aqueous solutions to nitrobenzene was determined by measuring the activity of ^{137}Cs in each phase by y-counting techniques using a 3" NaI(T1) crystal through-hole type detector (Packard Cobra Quantum Model 5003).

All instruments for ion chromatography were supplied by Dionex Corporation. Ion chromatography measurements were carried out using an IonPac® AS 11 Analytical Column (4 x 250 mm) and a ASRS-ULTRA 4-mm Anion MicroMembrane™ Suppressor. Each sample was analyzed by single injection of 1 µL using hydroxide eluents at a flow rate of 1.0 mL/min. Hydroxide concentration gradients were generated by combination of eluent solutions with a

GP50 Pump in Standard-Bore-Configuration. Anion detection was performed by conductivity measurements in a ED40 Conductivity Cell with DS3. Concentrations were calculated from the peak areas.

Appendix

Chromatogram of a mixture of chloride, bromide, nitrate, iodide, and perchlorate at 10^{-5} M each obtained by the method described in chapter V.B.

Standard 1, 10-5 M
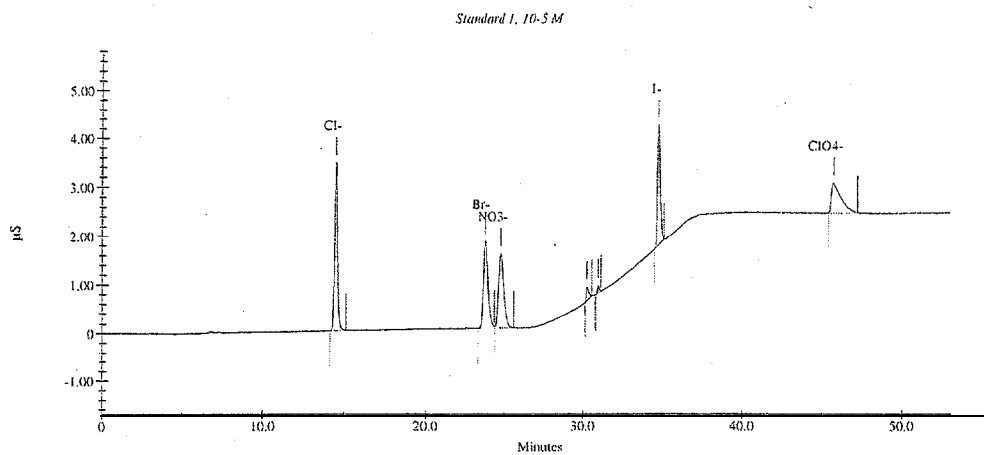
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