To the Graduate Council:

I am submitting herewith a thesis written by Anil Kumar Batra entitled "Selective Extraction of Cesium using Crown Ethers". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Environmental Engineering.

R. Bruce Robinson, Major Professor

We have read this thesis and recommend its acceptance:

Accepted for the council:

Associate Vice Chancellor and
Dean of the Graduate School

SELECTIVE EXTRACTION OF CESIUM USING CROWN ETHERS

A Thesis

Presented for the

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Anil Kumar Batra

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ABSTRACT

The fission product cesium-137, represents an environmental concern to U. S. Department of Energy and nuclear industry. Cesium-137 though present in trace concentrations in various tanks, waste streams, soil and sediments, accounts for a major fraction of radioactivity. With regard to environmental, safety and, health issues, there is a need to remove cesium-137 isotope from various media. High concentrations of other metal ions especially sodium present in these waste often pose a problem in cesium removal.

The solvent extraction process has been previously used and is a suitable method for removal of metals from radioactive waste. Crown ethers, which are known to selectively form complexes with alkali and alkaline earth metals [Pedersen, 1967, 1970], are potential solvent extractants for metal removal. Crown ethers of 21-crown-7 family have been found previously to selectively form complexes with cesium [Deng et al., 1994,1995]. Three crown ethers of 21-crown-7 family viz., dibenzo-21-crown-7, bis(tert-butylbenzo)21-crown-7 and dicyclohexano-21-crown-7, were tested as cesium extractants in this research. Cesium was extracted from a nitrate solution also containing a high concentration of sodium. Cesium nitrate concentration was varied from $4.00X10^{-3}$ to $4.00X10^{-1}$ M and sodium nitrate concentration was fixed at 3.00 M for all the tests. Crown ether concentration was fixed at 0.025 M. Two diluents, n-octanol and 1,2-dichloroethane were tested.

Distribution coefficients in the range of $6.20X10^{-3}$ - $6.12X10^{-2}$, loadings in the range of 0.22 - 21.2% and selectivities in the range of 2.80 - 107.41 were exhibited by the crown ethers tested. The cesium distribution coefficients, loadings and selectivities were very low for practical applications. Distribution coefficients, loadings and selectivites were found to increase with decreasing initial aqueous cesium concentrations. Since real wastes have cesium concentration in the range of 10^{-5} - 10^{-3} M, lower than those tested in this research, these trends indicate better performance by the crown ethers for real waste.

Cesium and sodium extraction data were modeled by the computer program SXLSQI. Cesium and sodium were found to be extracted as 1:1 complexes (metal : crown ether molecule) with all the crown ethers tested. Using extraction equilibria found by the model, cesium extraction by crown ethers at initial aqueous phase other than those tested cesium concentrations can be estimated.

Since cesium extraction was low for practical applications, various synergistic combinations of organic acids and crown ethers were also tested to enhance cesium extraction. Organic phase consisted of 0.025 M of each extractant (crown ether and organic acid) . Initial cesium and sodium concentrations were fixed in the aqueous phase. Aqueous phases at three pHs, 10, 12 and, 14, were tested. These synergistic combinations were found to be pH dependent, exhibiting increasing extraction with increase in pH. Very little synergism was observed in most cases. Antagonism was also

observed in some cases. Dodecylphenol-crown ether combinations exhibited maximum synergism in cesium extraction in this research. Synergistic factors as high as 63.2 were obtained. With HMNA-crown ether combination in toluene cesium loadings as high as 114.23% was obtained (loadings in this case were calculated only on the basis of organic acid concentration only while total extractant concentration was 0.05M thus resulting greater than 100%). Cesium distribution coefficients, loadings and selectivites were still too low for practical applications.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF TABLES
(continued)

LIST OF FIGURES

LIST OF FIGURES
(continued)

LIST OF FIGURES
(continued)

I. INTRODUCTION

Cesium-137, a radioactive isotope, is a major concern to U.S. Department of Energy (DOE) and the nuclear industry with regard to the environment and waste management. Cesium-137 is present in various waste holding tanks and has also been found in the waste streams, ground water, soil and sediment of various DOE facilities. It is the third most common radionuclide found in soil/sediment of various DOE sites, the other two being uranium and plutonium [Riley et al., 1992]. Concentrations in groundwater range from 0.0027 - 1,830 pCi/L, and in soil/sediment from 0.02 - 46,900 pCi/Kg [Riley et al., 1992]. Though present in trace concentrations, Cs-137 accounts for the major fraction of the radioactivity [Shuler et al., 1985]. [Appendix I]

In view of the hazard to health and environment posed by this radionuclide and the cost associated with waste disposal, a need has arisen to develop technology to decontaminate various media. The separated cesium-137 can also potentially be used for many beneficial purposes. [see Appendix II]

Solvent extraction, which has been used previously by many workers [Schulz et al., 1987] for separation of radionuclides from high level radioactive waste, is potentially a suitable system for the separation of cesium from such wastes. Solvent extraction involves the transfer of a solute from one liquid phase to another

immiscible or partially miscible liquid phase which is in contact with the first phase.

Usually an organophillic extractant is added to an organic liquid called the diluent. The extractant is an active substance capable of combining with the aqueous metal ion to give extracted species which are soluble in the diluent.

There are a number of features which are essential for an extractant if it is to achieve the extraction of the desired metal [Blasius et al. I, 1984 & Hudson, 1982]. In general it must

(1) have the ability to extract the metal at the required pH.

(2) be selective for the required metal and should also have high extraction coefficient D (preferably D >10). [See below for definition]

(3) have acceptable rates of extraction and stripping.

(4) be soluble in the organic phase and have a very low solubility in the aqueous phase (i.e. minimum bleeding).

(5) have high chemical stability.

(6) have satisfactory stability to radiolysis.

(7) be easily regenerative.

(8) be cost effective.

Some of the above criteria are mutually incompatible, so it is important to find an extractant which has a balance of these.

Macrocyclic polyethers (crown ethers), which can selectively form complexes with alkali and alkaline earth metal ions, have been considered by many researchers as promising extractants for removal of these metals from radioactive wastes by solvent

extraction. Most of the common crown ethers meet the requirements for practical applications with regard to stability (both chemical and radiolytic), hydrophobicity, easy regeneration and low toxicity [Blasius et al. I, 1984].

Separation of cesium from sodium represents the primary issue concerning the usefulness of crown ether for decontamination of alkaline high level waste containing a high sodium nitrate concentration. Previous work in this area has indicated that the crown ethers of the 21-crown-7 (21C7) family have high selectivity for cesium cation over relatively smaller alkali metal cations such as sodium in solvent extraction [McDowell et al., 1989].

The objective of this study was to test candidate crown ethers which can be used for possible removal of cesium from the radioactive waste. Particularly, this work has aimed at determining the degree of selectivity for cesium over sodium that can be obtained in some simple systems. Several crown ethers of the 21C7 family were investigated for selective extraction of cesium from a solution containing high sodium concentration. Various synergistic systems have also been investigated in order to optimize solvent extraction with crown ethers.

II. LITERATURE REVIEW

As a background for the presentation of this work, relevant topics in the area of cesium extraction are discussed. Initially the theory and terminology of solvent extraction are discussed followed by the factors affecting solvent extraction by crown ethers. Finally the study of various extractants used for alkali metal extraction, particularly cesium, is presented.

Solvent Extraction

Introduction

Solvent extraction, also called liquid - liquid extraction, is the process of separation of the constituents of a liquid solution by contact with another immiscible liquid. Any substance which is soluble in both the solvents distributes between the two solvents, and in some cases the substance dissolved in one phase is nearly completely transferred to the other phase.

There are two principal stages of solvent extraction, namely extraction and stripping (Figure 1). In the extraction stage, the aqueous solution containing the metal is brought into contact with the organic solvent phase. The products of the extraction stage are the organic solvent loaded with the desired metal, and the aqueous extraction raffinate. Raffinate here means a residual aqueous phase after the extraction of some specified solute. The extraction

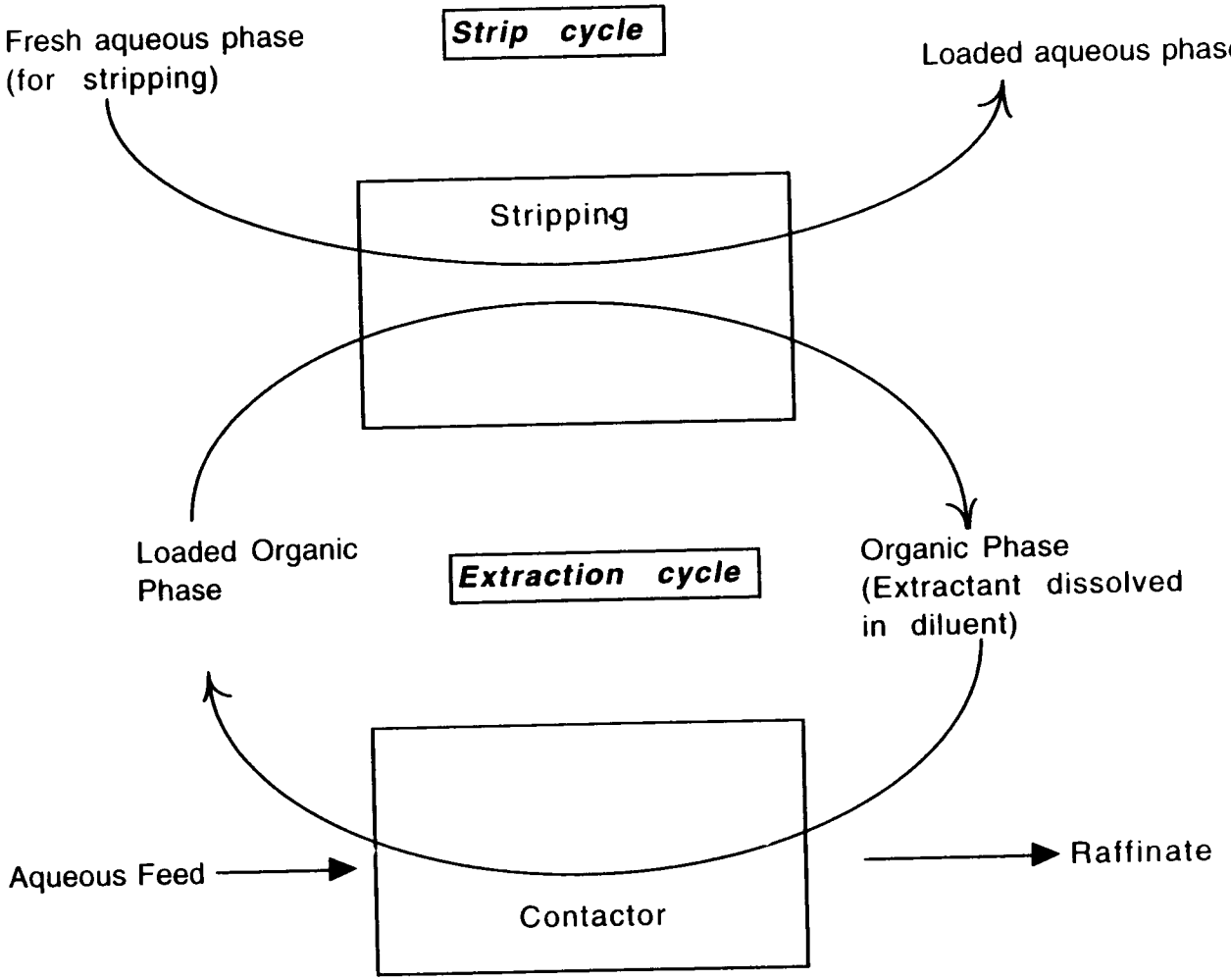


Figure 1. Flow Diagram of Solvent Extraction Process

raffinate could either go to waste or to further processing. The loaded organic solvent is then stripped by an aqueous phase in order to recover the desired solute. After stripping, the organic solvent is recirculated back into the extraction process.

In all solvent extraction processes, the solution from which a substance is to be extracted is called the feed, and the liquid with which the feed is contacted is called the solvent [Treybal, 1980].

Solvent extraction is now a familiar tool in heavy chemical industries such as metallurgy and in analytical chemistry, but it was not widely used before the 1940s. The initial extraction systems consisted of extractants (ethers, polyethers, ketones, phosphates etc.) which were normally used without dilution by any inert solvent and required a high aqueous anion concentration, usually nitrate or chloride [McDowell et al. 1992].

Recently-developed solvent extraction systems generally consist of an extractant dissolved in a diluent to promote the extraction process. The basic requirements of a diluent are that it should have low toxicity and low flammability [Morrison et al., 1966]. Both the diluent and the extractant should not distribute to the aqueous phase, and also the compound formed between the extractant and the metal must be highly organophilic.

Extractants can be classified in two broad categories; viz., neutral species extractant and cation exchangers [McDowell et al.,1992].

Neutral-Coordinating Extractants - These extractants coordinate directly with the metal cation and provide the coordination initially supplied by water in the aqueous phase. In this type of extraction, a stochiometrically required amount of aqueous phase anion must be transferred to the organic phase, along with the metal, to maintain the charge neutrality. This class of extractants includes, for example, water insoluble ketones, ethers, linear poly-ethers, and macrocyclic or crown ethers. The equation below represents a general extraction equilibrium by a neutral-coordinating extractant to form a neutral organic-phase complex:

$$mM^{q+}_{(aq)} + xX^{-}_{(aq)} + bB_{(org)} \rightleftharpoons M_mB_bX_{x(org)}$$

M^{q+} = metal ion

X^- = anion

B = extractant

$M_mB_bX_x$ = extracted complex

As evident from the equation above, the amount of metal extracted is dependent on the concentration of aqueous anion. A large degree of control over selectivity of the system is possible by varying the aqueous phase anion and acid concentration [McDowell et al., 1980]. The amount of metal ion extracted is also dependent on the amount of other species present in aqueous phase which may compete with the target metal ion for complexation by the extractant molecule.

Cation exchange extractants - These extractants combine with the metal through the simple cation exchange reaction thus producing an organophillic salt. The equation below illustrates simple cation exchange extraction.

$$M^{q+}(aq) + qHA(org) \rightleftharpoons MA_q(org) + qH^+(aq)$$

M^{q+} = metal ion

AH = cation exchange extractant

MA_q = extracted complex

Phenols, branched alkyl carboxylic acids, alkyl phosphoric acids, diketones, and alkyl-aryl sulfonic acids are examples of cation exchange extractants. ß-Diketones, alkyl phosphoric acids and carboxylic acids can provide both cation exchange and coordination functions.

Synergistic extraction system - When two extractants are mixed in a diluent and the combined extractive strength of the two extractants mixed is greater than the sum of their extractive strength when used separately, the extraction system is termed synergistic. Such synergistic systems usually consist of a cation exchange extractant and a neutral coordinative extractant. The coordinator either replaces water in the organic-phase complex thus making it more organophilic or adds to a coordinatively unsaturated organic-phase complex making it more stable. The cation exchanger combines with metal through simple cation exchange. It exchanges

hydrogen ion for metal ion thus extracting metal into the organic phase. A general equation for such a reaction is [McDowell et al., 1980]

$$M^{q+}_{(aq)} + qHA_{(org)} + bB_{(org)} \rightleftharpoons MA_q.bB_{(org)} + qH^+_{(aq)}$$

This equation accurately describes the extraction system only if 1) there is no interaction between the extractants, 2) there is only one metal ion complex formed in the organic phase, and 3) there is no extraction of the nitrates or the hydroxide anions [McDowell et al.,1989].

Back Extraction

The metal, after selective extraction into an organic solvent, is to be concentrated for final disposal or for other beneficial uses. For this purpose, the metal ion has to be transferred to a fresh aqueous phase from which it can be easily concentrated. The process of reversing the extraction equilibrium and transferring the extracted element from the loaded organic phase to a fresh aqueous phase is called stripping or back extraction. The usual procedure to achieve stripping is to contact the loaded solvent with a fresh aqueous phase (neutral or acidic) under conditions whereby the extractable complex is destroyed. This is followed by the transfer of metal ion in the organic phase to the aqueous phase [Morrison et al., 1966]. Water stripping is effective for some neutral

extractants. For cation exchange systems, acid stripping is effective since the metal ion has to exchanged for some other cation, which is H^+ provided by acid.

Solvent Extraction Relationships

In this section various terms used in analysis of extraction system are discussed.

Distribution coefficient - In solvent extraction systems, the distribution of metal, M, between the aqueous and organic phases at equilibrium is described by a distribution coefficient, $D_{(M)}$, where [M] represents the concentration of the metal in mole/L.

$$D_{(M)} = \frac{[M]_{org}}{[M]_{aq}}$$

This is true at any phase ratio, Vorg/Vaq. However $D_{(M)}$ is a concentration ratio, and the total amount of metal recovered depends also on the phase ratio.

The distribution coefficient is a function of the composition of both the organic and aqueous phases. If the composition of either phase is changed, the distribution coefficient can change [McDowell et al. , 1992].

Separation factor - The separation factor of a metal ion A^+ over the metal ion B^+ is defined as the ratio of distribution coefficients of A^+ and B^+. It is given by the following relationship

$$S_{A/B} = \frac{D_{(A)}}{D_{(B)}}$$

$S_{A/B}$ = Separation factor of A^+ over B^+

Loading - It is defined as the amount of metal extracted per unit amount of extractant.

$$\text{Loading \%} = \frac{[M]_{org}}{[EX]_{tot}} \text{ X } 100 \text{ \%}$$

$[M]_{org}$ = concentration of metal extracted

$[EX]_{tot}$ = total concentration of extractants

Synergistic factor [McDowell et al., 1983] - The synergistic factor, a measure of synergism, is calculated as below

$$Fsyn = \frac{D_{(mix)}}{D_{(\text{cation exchanger})} + D_{(\text{coordinator})}}$$

Fsyn = synergistic factor

$D_{(mix)}$ is the distribution coefficient of metal when extracted by a mixture of acid and a coordinator. $D_{(\text{cation exchanger})}$ and $D_{(\text{coordinator})}$

are the distribution coefficients of metal when extracted by cation exchanger or coordinator alone, respectively.

Factors Affecting Metal Extraction by Crown ethers

Initial solvent extraction studies by Pedersen and Frensdorff [Pedersen, 1970; Pedersen, 1967; Frensdorff, 1971] indicated that crown ether ring size or cavity is an important parameter in extraction of metal ions. When the polyether ring is large enough to accommodate the cation (Table 1), the cation is held in the center of the crown. The cation may be sandwiched between the two crown ether molecules when it is larger than the crown ring size. The crown ether may wrap around the cation, when the crown is much larger than the metal ion diameter [Gerow, 1979]. In many cases the metal is most easily extracted when there is a perfect match between the ring size and metal ion. This property of extraction by crown ethers is called size selective extraction.

The aqueous anion also plays a vital role in solvent extraction by crown ethers since the anion also has to be extracted along with cation to maintain the charge balance [McDowell, 1988].

The solubility of crown ethers in both aqueous and organic phases is also an important factor. The crown ether should have a high solubility in the organic phase and almost no solubility in the aqueous phase. If the crown ether has very high solubility in the aqueous phase, then the crown-metal complexation may take place in aqueous phase thus preventing metal extraction into the organic phase. On the other hand, crown ether having high organic solubility

Table 1. Comparison of Alkali Metal Cation and Crown Ether Cavity Diameters [Walkowiak et al., 1990]

Cation	Ionic diameter Å	Crown ether cavity	Cavity diameter Å
Li+	1.20	12-crown-4	1.2-1.5
Na+	1.90	14-crown-4	1.2-1.4
K+	2.66	15-crown-4	1.7-2.2
Rb+	2.96	16-crown-5	2.0-2.4
Cs+	3.38	18-crown-6	2.6-3.2
		19-crown-6	3.0-3.5
		21-crown-7	3.4-4.3
		24-crown-8	4.5-5.6

will facilitate the organic phase in extracting the metal. A substituent attachment to the crown ether main structure is also found to have an effect on crown ether selectivity in extracting a particular metal ion. Side rings can also make crown ethers more organophillic [McDowell et al., 1992].

The organic diluent should also be highly hydrophobic, so that no loss of diluent to aqueous phase occurs.

In summary, extraction of metal by crown ether is dependent on the following parameters.

(1) The cavity size or the polyether ring size.

(2) The anion associated with the metal.

(3) The solubility of crown ether in both phases.

(4) The chemical composition and nature of both phases including pH of aqueous phase.

(5) The effect of the nature of substituents fused to the main polyether ring.

Extractants For Alkali Metals

Various substituted phenols have been used since the 1960s by various workers for cesium extraction from radioactive waste. The alkali metal extraction by substituted phenols is a simple cation exchange reaction. The alkali metal extraction by phenols is found to be sensitive to pH changes; appreciable cesium extraction is obtained only from highly alkaline liquids [Horner et al., 1963].

Several phenols, 2-tert-butyl-4-(2-phenylpropyl)phenol (AO4), 2,6-di-tert-butyl-4-methylphenol(AO4K) and 2,2-methylene-bis-(4-methyl-6-tert-butyl)phenol (AO2246 or NOCRAC 2246) and 2,2-methylene-bis-(4-{2-phenylpropyl}-6-tert-butyl)phenol (AO301) were tested by Gulis [1989] using nitrobenzene, carbon tetrachloride (CCl_4), chloroform, benzene and cyclohexane as diluents. Of all these phenols NOCRAC in nitrobenzene and AO4K in cyclohexane were found to have appreciable cesium extraction. Cesium distribution coefficients of approximately 12 with NOCRAC and 0.19 with AO4K were observed. The distribution coefficient of cesium increased with increasing pH for both NOCRAC and AO4K. NOCRAC exhibited maximum efficiency of 92.3% at pH = 13.23 [Gulis, 1989]. These results were quite promising, but when these phenols were used for cesium extraction from intermediate level liquid waste (pH=11.35) results were very disappointing. AO4K had very low extraction efficiency and NOCRAC had a distribution coefficient of 0.0823 and efficiency of 7.606%. It was suggested that NOCRAC can be used with crown ether for cesium extraction, but to date to the knowledge of the author, no further work has been done in this direction.

Various other substituted phenols viz. p-dodecylphenol (PDO), o-phenylphenol (OPP), 4-chloro-2-phenylphenol (PCOPP), 4-sec-butyl-2-(α-methylbenzyl)-phenol (BAMBP) and 4-chloro-2-benzylphenol (santophen-1) were also found to be good extractants for cesium [Horner et al., 1963]. With OPP, PCOPP and santophen, the extraction coefficient increased with pH up to 12-12.3 and then

decreased. The decrease at higher pH was due to the loss of phenols from the solvent phase. At pH less than 12, PCOPP and santophen were better than BAMBP. BAMBP showed increasing extraction coefficient with increasing pH over the whole pH range tested and thus was the best for cesium recovery from solution at pH above 10.

Despite the fact that crown ethers have been known since 1937, interest in their ability to complex alkali and alkaline earth metals did not begin until 1967, when Nobel laureate Charles J. Pedersen of DuPont Company discovered that certain crown ethers, particularly those containing five to ten oxygen atoms, would form complexes with alkali and alkaline earth metal salts [Pedersen, 1970]. Pedersen did pioneering work in the synthesis and use of crown ethers as solvent extractants.

One of the first crown ethers made by Pedersen was called 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacycloocta-2,11-diene according to IUPAC nomenclature. Due to the cumbersomness of the nomenclature by IUPAC standards, Pedersen also developed a system of naming compounds based on: 1) substituents, 2) the number of atoms in the ring, 3) "crown"- which describes the crown shape of the ring, and 4) the number of oxygen atoms in the ring [Pedersen, 1967]. Pedersen's studies indicated that solvent extraction by crown ethers is dependent on various factors, which have already been discussed.

Most of the early work to investigate the crown ethers as potential extractants for alkali metals was done using organophillic anions such as picrate, tetraphenylborate, or dipicrylamine as

aqueous anions [Rais et al., 1971; Densei et al.,1975]. These anions were used because of the difficulty in transferring a mineral acid anion to the organic phase. However, for analytical or process applications the aqueous anion should be one of the more common mineral acid anions such as chloride, nitrate, or sulfate. The necessity of transferring the aqueous system containing mineral anions to one with organophillic anions makes this system impractical [Kinard et al., 1980].

Early work in metal extraction by crown ethers helped to establish the general behavior of crown ethers. Extraction of metal ions by crown ethers alone was not found high enough to be used for process applications [McDowell et al., 1977]. The probable reason was the difficulty in solvating common mineral acids into organic solutions. Several workers used alternative procedures to overcome this problem.

Marcus et. al. [1978] tried to solve the problem of anion transfer by using highly polar organic solvents to solvate the anion and thereby increase its solubility in the organic phase. The problem with this approach is that the polar solvent is appreciably soluble in the aqueous phase and hence is lost. Considering the cost and environmental concern, this loss is intolerable.

Synergism, as termed by Coleman [1963], has been a major breakthrough in the use of crown ethers for metal extraction. McDowell and Shoun theorized that a combination of an organophillic cation exchanger and crown ether in the organic phase can extract the metal ion by simple cation exchange, thus avoiding the anion

transfer [McDowell et al., 1977]. Since then, several workers have used the combination of organophillic macrocyclic ethers with organophillic cation exchangers to extract aqueous metal ions into an organic solution. This system takes advantage of both the size selective extraction of crown ether and cation exchange by organophillic cation exchangers. In this system the cation in the aqueous phase is exchanged at the interface for the hydrogen of the organic phase acid (cation exchanger). The metal then exists as an organic-phase-soluble salt with which the crown ether can easily coordinate. The crown ethers appear to promote the extraction of metal ions by providing oxygen coordination in the organic phase through the ether oxygen, such coordination having been supplied by the oxygen atoms from water molecules when the metal ions were in the aqueous phase [McDowell et al., 1989].

Since the extraction by crown ethers is size selective, McDowell et al. [unpublished results] tested a combination of crown ethers and a variety of extractants to demonstrate that synergistic extraction systems were also size selective. They tested a variety of compounds including tributylphosphate, trioctyphosphine oxide, a secondary and tertiary amine, a carboxylic acid, a sulphonic acid, and di-(2-ethylhexyl)phosphric acid (HDEHP), to demonstrate the size selective extraction of alkali metals by the synergistic extraction system. They reported that cation exchangers showed sizable synergistic effects when used with crown ethers while only slight synergism was observed with the amine and no synergism was seen with neutral phosphorus extractant. Alkali metals as nitrate

salts were used in these experiments. HDEHP-DC18C6 system in benzene was found to give separation factors very similar in trend, but more than 1000 times greater than those observed in extraction of picrates by crown ether alone for alkali metals tested. This system appeared to be size selective; K^+ and Rb^+ showed largest synergism with DC18C6-HDEPH as expected from their ionic diameter and crown ether cavity size [Kinard et al., 1980]. Cesium had a distribution coefficient which was approximately 5 times less than K^+ and Rb^+; probably this was due to the crown ether ring size being small for cesium extraction. Size selective synergism was also exhibited by a didoecylnaphthalene sulfonic acid (HDDNS)-crown ether mixture for extraction of alkali metal from the nitrate solution [McDowell et al., 1983]. K^+ and Na^+ were strongly synergized by 18C6 and 15C5 respectively combined with HDDNS in toluene. Synergized extraction coefficient for K^+ with this system was high enough to be useful in analytical or process separation. No data on cesium extraction was reported.

Synergistic adducts (an adduct is an unbound association of two molecules in which a molecule of component is either wholly or partly locked within the crystal lattice of the other) of DB21C7 with some cesium-selective adducts were used by Blasius et al. [I & II 1984] 12-Heteropolyacid, hexachloroantimonate(V), triiodomercurate, triphenylcyanoborates tetraphenylborate, tetraiodobismuthate, and biphenylcyanoborate acid or their metal(M^+) salts dissolved in appropriate solvents were used as cesium selective adducts. They used nitrobenzene, 1,2-

dichloroethane, and 1,1,2,2-tetrachloroethane as the diluents. When the salt forms of the liquid exchangers were used, the extraction coefficient was found to be dependent on the type of cation associated with these salts. The ability of Cs^+ to replace one of the initial cations decreased in the series $H^+ = Na^+ >= NH_4^+ > K^+ > Tl^+$. Na^+ concentration was found to have an effect on Cs^+ extraction, because as the Na^+ concentration increased, the extraction coefficient of Cs^+ decreased because DB21C7 extracted more and more Na^+. K^+ was not found to have any appreciable effect on Cs^+ extraction. However only adducts of 12-Heteropolyacid and hexachloroantimonate(V) were suitable for practical applications, since other adducts had insufficient stability to nitric acid solutions. The above mentioned two adducts were successfully applied for removal of cesium from simulated medium active waste solution [Blasius et. al., I & II 1984].

In an attempt to find a better crown ether for cesium extraction, McDowell et al. [1986] found that the difference in the constituent attached to the crown ether ring has a profound effect on extraction of alkali metals. It was indicated that bis(t-butylbenzo) substituted crown ethers were found to be better synergists than cyclohexano substituted crown ethers. The synergistic combination of D(tB)B21C7 and sulfonic acid (HDDNS) in toluene were very effective and selective for cesium extraction from acidic nitrate solution. Separation factors of 1.5 from rubidium, 6.4 from potassium and 192 from sodium were observed for competitive extraction of alkali metals by this system (0.025 M

HDDNS + 0.025 M B(tBB)21C7 in toluene), from an aqueous phase containing alkali metal nitrates (0.01 M each). The $D_{(Cs)}$ varied with the ratio of crown ether concentration to the total extractant concentration with maximum of about 22 at a ratio of 0.4-0.5 [McDowell et al., 1992]. It was also indicated that t-butylbenzo substituted crown ethers of the general structure (OCH 2CH 2-) n with n= 5-7 tend to be selective for alkali metals.

Vibhuthe et al. [1991] used 0.03 M DB24C8 at pH = 3.0 to extract cesium from 0.01 M picric acid in presence of 2 mL methanol. Cesium was successfully separated from alkali and alkaline metals and also from zirconium, hafnium, thorium, lead, bismuth, etc. This system achieved 100 % extraction.

Crown ethers bearing an attached proton ionizable site have also been used by many workers to enhance the extraction of metals. A sidearm which contains an acid group allows the crown ether to function both as a cation exchanger extractant and a coordinator. The biggest advantage of using proton ionizable groups for extraction of metals is that it obviates the need to transfer aqueous phase anions into the organic phase, thus making them a potential extractant for practical application where hard aqueous phase anions (chloride, nitrate and sulfates) are involved [Bartsch, 1989].

Several proton ionizable crown ethers have been synthesized, to study alkali metal extraction [Bartsch, 1989; Charewicz, I & II 1982]. Based on the extraction of alkali metals using these crown ethers, the following conclusions were drawn by Bartsch [1989].

1. Proton ionizable crown ethers are better than neutral crown ethers for metal extraction

2. Structural variations, which include ring size and rigidity, the nature and attachment site of lipophilic group and the sidearm length, affect the selectivity and efficiency of extraction.

3. Crown carboxylic acids are efficient only for metal extraction from neutral and basic aqueous solutions, while phosphonic acid are effective extractants of metal from all aqueous solution with pH > 5.

Benzo crown ether derivatives bearing a potential anionic site are known to form ion-pair complexes with alkali metal ions selectively under basic condition. 4-Picrylamino benzo-18-C-6 [McDowell et al., 1983] extracts alkali metal cations into chloroform forming complexes of 1:1 metal to crown ether ratio. The ease of extraction by this crown ether followed the order, $K^+ > Rb^+ > Cs^+ > Na^+ \geq Li^+$. Novel benzo-15-Crown-5 and 18-Crown-6 derivatives bearing an ionizable group were used by Sakamato et.al. [1992] to extract alkali metals. The selectivities for both crown ethers decreased in the order of K^+, Rb^+, Cs^+, Na^+ and Li^+.

Gerow et al. [1981] and Antaya et al. [1981] reported that bis-(4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6 was the most effective crown ether compound studied for recovery of cesium from 3M HNO_3 solution. They used crown ethers in an organic extraction solution consisting of the cation exchanger didodecylnaphthalene sulfonic acid (DNS) (5 vol%), TBP (27 vol%), and kerosene (68 vol%) to extract various fission products. The distribution coefficient of the fission products using the above crown ether solution tended to

increase with decreasing initial aqueous phase metal concentrations [Shuler et al., 1985]. Since the solubility of (4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6 in 50 vol% TBP, 50 vol% kerosene was equal to 0.0284 M [Antaya et al., 1981], bis-4,4'(5')-[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 was synthesized to improve organic phase solubility [Shuler et al., 1985]. (4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6 and bis-4,4'(5')-[1-hydrox-2-ethylhexyl]benzo-18-crown-6 were both tested at a concentration of 0.02 M. (4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6 appeared to be a better complexing agent, but bis-4,4'(5')-[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 exhibited greater solubility. For bis-4,4'(5')-[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 the distribution coefficient of cesium increased with increasing crown concentration. The distribution coefficient of cesium at high concentration of bis-4,4'(5')-[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 was much greater than that obtained using (4,4'(5')-[1-hydroxyheptyl]-benzo)-18-crown-6 at its solubility limit of about 0.02 M. It implied that bis-4,4'(5')-[1-hydroxy-2-ethylhexyl]benzo-18-crown-6 is a much more useful extractant for cesium recovery. A distribution coefficient of 5.64 was obtained by using 0.1 M crown ether solution [Shuler et al., 1985].

Several lipophilic crown ether carboxylic acids were used by Walkowaik et al. [1990] to competitively extract alkali metal ions. Selectivity with these crown ethers was found to be strongly influenced by the crown ether ring size and number of oxygen atoms. Lipophilic crown ether carboxylic acids with ring sizes of 12C4,

15C5, 18C6 and 21C7 exhibited extraction selectivities for Li^+, Na^+, K^+, and Cs^+ respectively, as would be predicted from the matching of the crown ether cavity size and metal ion diameters (Table 1 pp. 13). A Cs^+ : Na^+ selectivity coefficient of 15 was observed with a lipophilic 21C7 carboxylic acid. Lipophilic 24C8 carboxylic acid was also found to be Cs^+ selective, but selectivity was much less (Cs^+ : Na^+ = 1.5) than an analogous 21C7 compound. The separation factors of Cs^+ : Na^+ with these extractants were not high enough for practical applications.

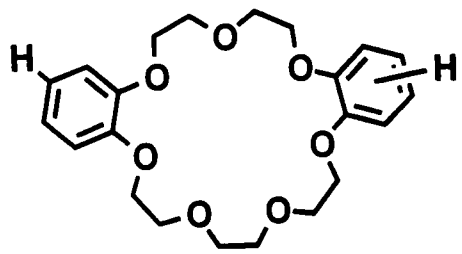
In the view of the previous work it can be concluded that not much has been achieved in competitive extraction of cesium from nitrate solutions containing high concentration of sodium. The main focus of the research presented here is to investigate alternative crown ether systems which can be used for selective extraction of cesium from alkaline high level waste in the presence of high sodium concentration. Some synergistic combinations are also investigated.

III. EXPERIMENTAL

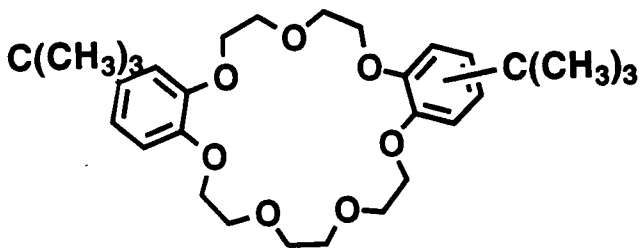
Apparatus And Chemicals

Metal concentration in the aqueous phase was determined by a Dionex model 2020i ion chromatograph. A Brinkmann potentiograph model E536 and, Orion 8103 ROSS electrode were used to determine the pH of the aqueous solutions. A Beckman model TJ-6 centrifuge was used to centrifuge and separate the organic and the aqueous phases after extraction and back extraction. Eppendorff and Pipetman pipeters were calibrated and used for all experiments.

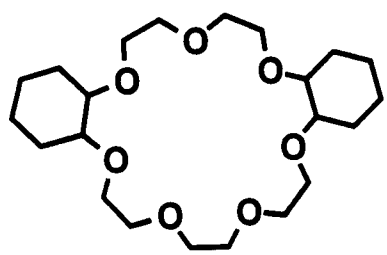
Three crown ethers of 21C7 family bearing different substituent ring attached to main polyether ring were tested to see the effect of substituent ring on metal extraction. The crown ethers used were dibenzo-21-crown-7 (DB21C7), bis(t-butyl)benzo-21-crown-7 (B(tBB)21C7, mixed isomers), and dicyclohexano-21-crown-7 (DC21C7, mixed isomers). These crown ethers are shown in Figure 2. DB21C7 was purchased from Parish Chemicals, and used as received. DC21C7 was also purchased from Parish Chemicals but it was purified by distillation under vacuum before use. B(tBB)21C7 was prepared by Dr. R. A. Sachleben in the Chemical Separation Group, Oak Ridge National Laboratory, Oak Ridge, TN, and used without any further purification. 1,3-diphenyl-1,3-propanedione was purchased from Eastman Organic Chemicals, dodecylphenol from Rohm-Haas Industries, and 2-heptyl-2-methyl-nonanic acid from Aldrich Chemicals; all these chemicals were used as received. NaOH



DB21C7



B(tBB)21C7



DC21C7

Figure 2. Crown ethers used in the study

solutions and $CsNO_3$ were purchased from J.T. Baker, Inc. and used without any purification.

Aqueous stock solutions of $NaNO_3$, $CsNO_3$, and NaOH were stored in polypropylene bottles to reduce the level of background contamination of sodium. Working aqueous phases were prepared by diluting these stock solutions. Distilled and deionized water was used for all experiments.

Organic phase stock solutions of 0.025 M crown ethers were prepared in two diluents, 1,2-dichloroethane (DCE) and n-octanol, and stored in highly chemical resistant Teflon containers. Since DB21C7 and B(tBB)21C7 were found to be insoluble in n-octanol, their solutions were prepared only in DCE.

For synergistic extraction tests, individual stock solutions of crown ether, dodecylphenol (DP), 2,6-di-tert-butyl-4-methylphenol (2,6DT4MP), 1,3-diphenyl-1,3-propanedione (1,3DP1,3PD), 2-heptyl-2-methyl-nonanic acid (HMNA) and 4-sec-butyl-2-(α-methylbenzyl)-phenol (BAMBP) were prepared in two diluents, DCE and toluene. Each solution was of 0.05 M concentration. Working organic solutions were prepared by mixing crown ether solution (0.05 M) and phenol (0.05 M) in 1:1 ratio by volume.

All the bottles and vials used for storage and experiments were acid washed before use.

Solvent Extraction

Crown Ethers Only

For each extraction test, equal volumes (0.5 mL each) of the aqueous phase and organic phase were mixed in a 1.5 mL polypropylene vial and rotated for 2 hours on a rotator at constant temperature (25.0 ± 0.5 ^{o}C) in an air box. 2 hours was sufficient to reach equilibrium [Deng et al, 1994]. The mixture was then centrifuged for 5-10 min. A portion (0.3 mL) of organic phase was removed and mixed with 3 mL of water in a 3.5 mL polypropylene vial for back extraction. This mixture was again rotated overnight (about 16 hours). It was then centrifuged, and 2 mL of aqueous phase was removed and further diluted to 7 mL by water in a sample vial; it was then ready to be analyzed by ion chromatography (IC).

Synergistic Extractions

The same method as above was used, except for back extraction, where 3 mL of 0.1 N HNO_3 was used instead of water. Also, 0.2 mL of solution in toluene was used in place of 0.3 mL due to the difficulty in transferring 0.3 mL volumes from glass vials used for extraction in toluene solutions.

Analysis

Three samples for each condition and 3 injections for each sample were taken, and the result was the average of these nine values. IC

conditions were column, CS12 cation exchange; eluent, 0.02 M methyl sulfonic acid (MSA); flow rate, 1.0 mL/min or 2.0 mL/min; detector, conductivity; calculation, external standard method. Three standard solutions of $CsNO_3$ and $NaNO_3$ of concentrations $8X10^{-5}$ M, $2X10^{-5}$ M, and $4X10^{-6}$ M were used; a linear relationship between concentrations and the peak area under the chromatograms was obtained and used for calibration. The concentrations thus obtained were multiplied by a dilution factor of 35 to give the final concentrations of Cs^+ and Na^+ in the organic phase. A dilution factor of 52.5 was used for all extraction in toluene because of the lesser amount of organic phase used in back extraction. The limits of detection for sodium and cesium in the organic phase were $1.0X0^{-5}$ and $1.0X10^{-6}$ respectively. Data obtained were usually precise within an error limit of ±10%. Precision estimates in tables were determined by taking the average of three samples for each condition and three injections for each sample.

IV. RESULTS AND DISCUSSION

Crown Ethers Used Alone

Crown ethers of the 21C7 family are good extractants for cesium due to in part to the match of their cavity size with the cesium ion diameter [McDowell et al., 1992] In the initial tests crown ethers alone were tested for their ability to selectively extract cesium from an aqueous solution also containing high sodium concentration. Nitrate was chosen as the aqueous anion for all the experiments. Two diluents DCE and n-octanol were used for these tests. Since DB21C7 and B(tBB)21C7 had low solubility in n-octanol, their solutions were prepared only in DCE. Figure 3 illustrates the extraction of cesium by crown ethers of 21C7 family.

Cesium and sodium concentration in the organic phase after extraction by DCE alone were below the limit of detection, $1.0X10^{-5}$ and $1.0X\ 10^{-6}$ M respectively. Table 2 shows the cesium and sodium extracted into the n-octanol i.e. organic phase as compared to the aqueous phase. The data for the cesium and sodium extractions by the crown ethers in the diluents were not adjusted to account for extractions by the diluents alone. Figures 4 and 5 summarize the effect of the initial aqueous phase cesium concentration on cesium and sodium extraction by crown ethers. It indicates that for all the crown ethers tested the amount of cesium extracted (Figure 4) increased with increasing initial aqueous phase cesium concentration. DC21C7 both in DCE and in n-octanol extracted a

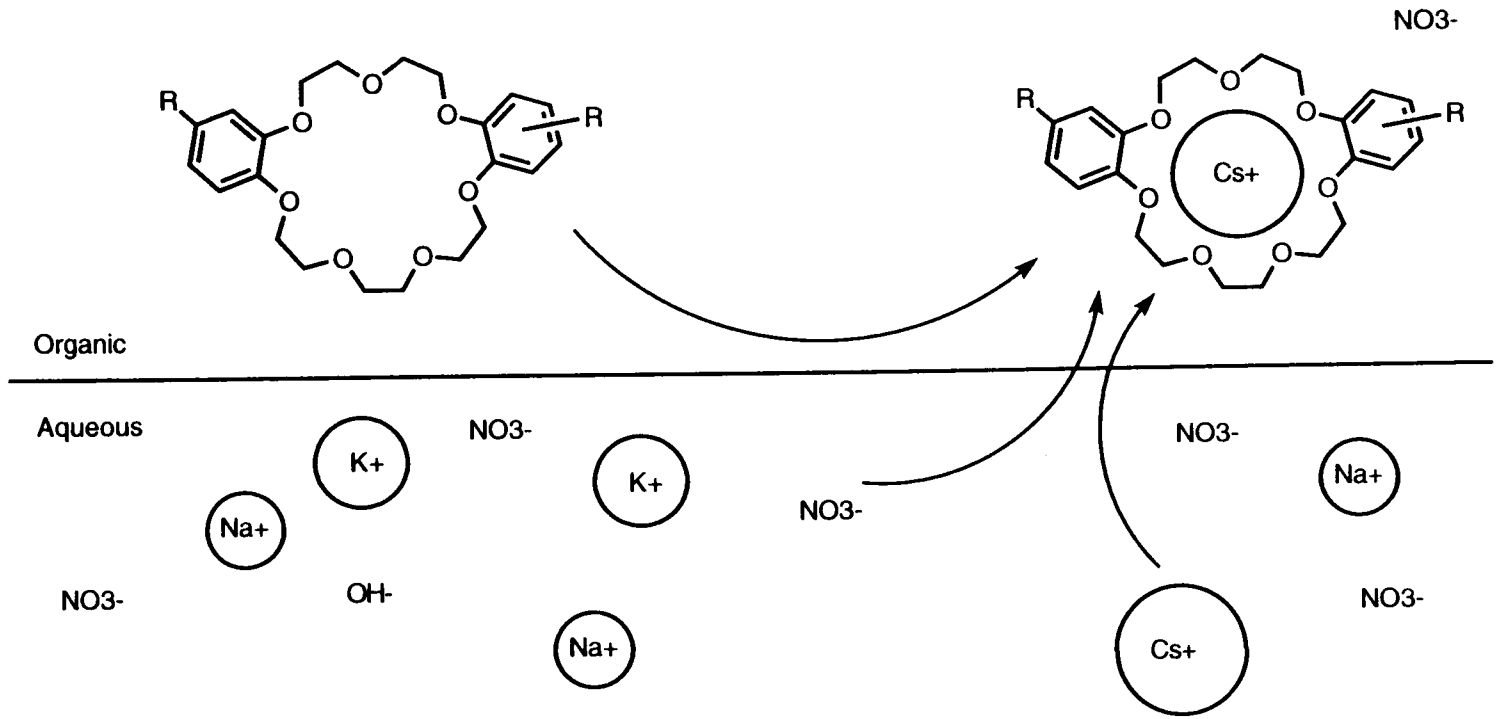


Figure 3. Cesium extraction by crown ethers of 21-crown-7 family

Table 2. Cesium and sodium extraction data for solvent extraction by n-octanol

[NaNO3]aq,o = 3.00 M					
[Cs+]aq,o (M)	[Na]org (M)	[Cs+]org (M)	D(Na+)	D(Cs+)	S
4.00E-01	2.33(±0.05)E-03	2.85(±0.01)E-04	7.77E-04	7.14E-04	0.92
2.00E-01	2.37(±0.01)E-03	1.95(±0.02)E-04	7.91E-04	9.75E-04	1.23
1.00E-01	2.55(±0.09)E-03	-	8.49E-04	-	-
4.00E-02	2.59(±0.02)E-03	2.73(±0.04)E-05	8.63E-04	6.82E-04	0.79
2.00E-02	2.54(±0.02)E-03	1.55(±0.00)E-05	8.46E-04	7.75E-04	0.92
1.00E-02	2.52(±0.06)E-03	-	8.40E-04	-	-
8.00E-03	2.50(±0.02)E-03	7.70(±0.39)E-06	8.33E-04	9.63E-04	1.16
4.00E-03	2.50(±0.01)E-05	-	8.32E-04	-	-

( ) contains the standard deviation for the observed data
[X]y,o is the initial concentration of X in y-phase
[X]y is the concentration of X in y-phase at equilibrium
(M) stands for molar concentration
"-" indicates data which could not be determined due to either experimental errors or the limit of detection
All the data are rounded off to three significant figures
D(Cs+) and D(Na+) stand for the distribution coefficients of cesium and sodium respectively
S is the selectivity of cesium over sodium

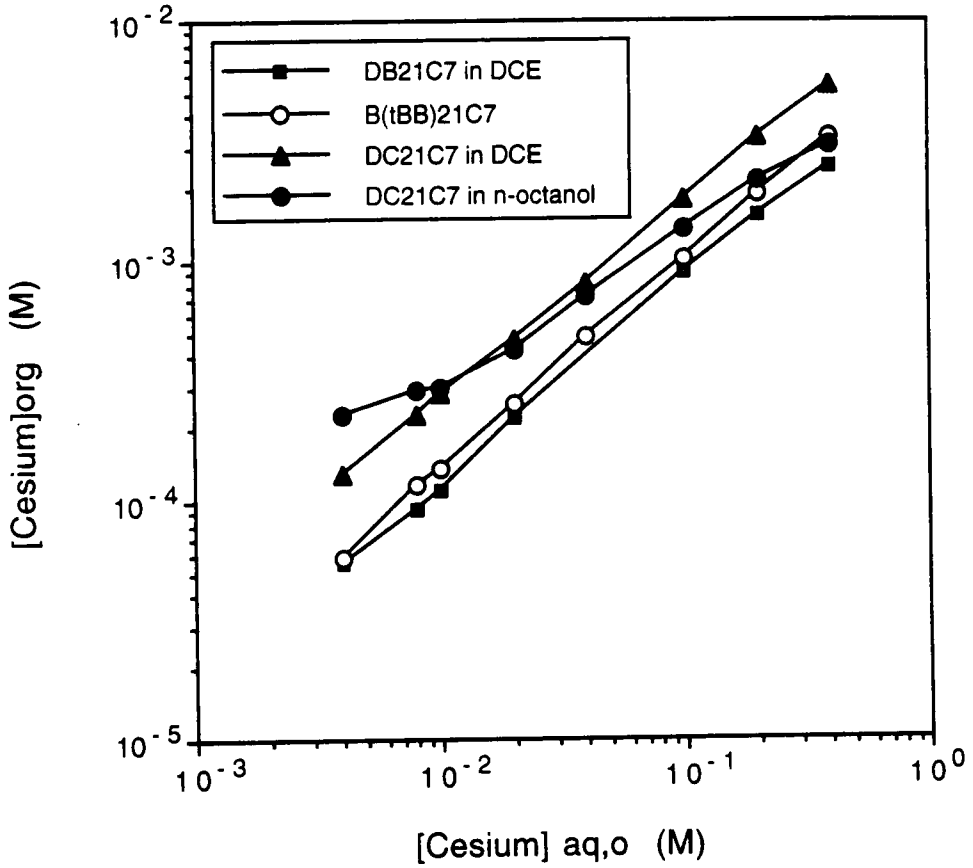


Figure 4. Plot of cesium ion concentration in the organic phase at equilibrium versus the initial aqueous phase cesium concentration for extraction by each of the crown ether solutions.

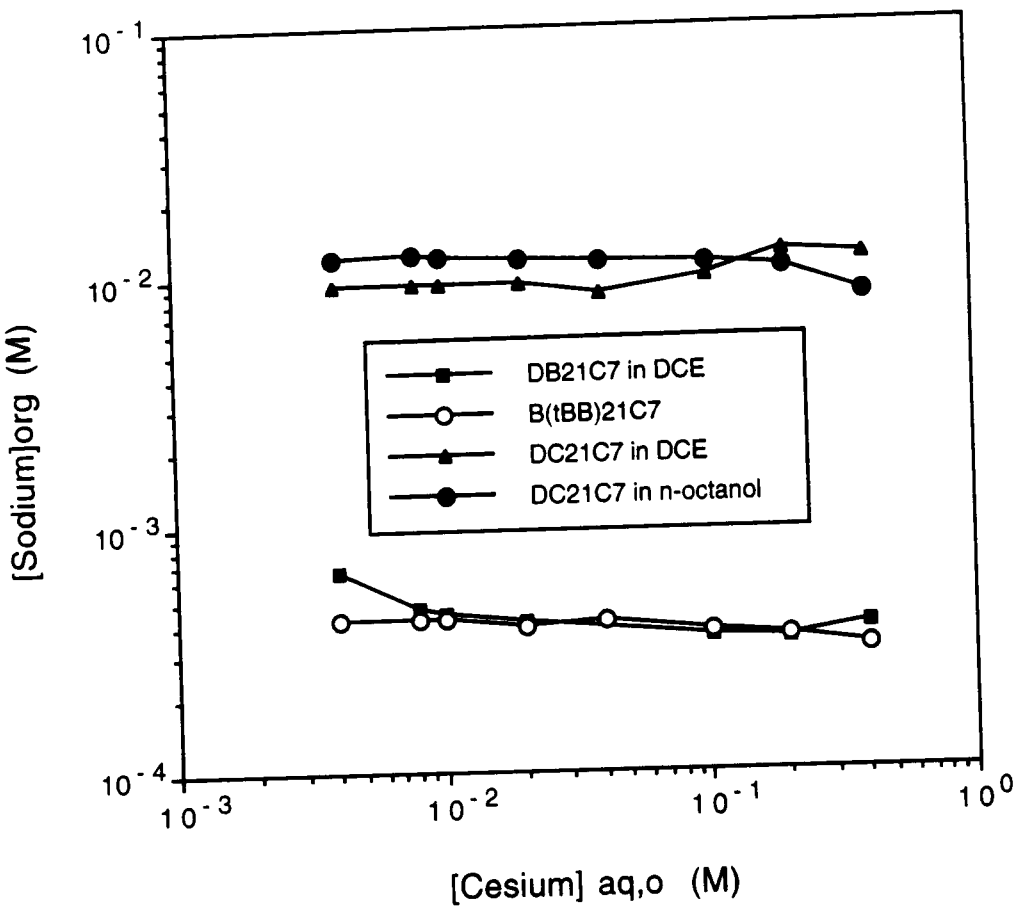


Figure 5. Plot of sodium ion concentration in the organic phase at equilibrium versus the initial aqueous phase cesium concentration for extraction by each of the crown ether solutions.

large amount of cesium as compared to DB21C7 andB(tBB)21C7 in DCE. DC21C7 in DCE extracted larger amount of cesium at higher concentrations of initial aqueous phase cesium concentration. For initial aqueous phase cesium concentrations less than 1.00×10^{-2} M, DC21C7 in n-octanol extracted more amount of cesium than the other crown ethers. No specific trend was observed in the amount of sodium extracted (Figure 5) by all the crown ethers. Maximum sodium extraction was observed with DC21C7 in n-octanol almost throughout the concentration tested. DB21C7 and B(tBB)21C7 extracted about an order of magnitude less sodium than DC21C7.

Distribution coefficients of cesium and sodium are plotted in Figure 6 and 7. Since the amount of cesium and sodium extracted was very low (about 1% or less of the original amount present in aqueous pahse), the distribution coefficient is approximately equal to the extraction efficiency (amount of metal extracted /initial metal present) per extraction cycle. Increasing the number of extraction cycles can increase the overall extraction efficiency. One interesting trend observed in all the systems was an increase in the cesium distribution coefficient (Figure 6) with decreasing initial aqueous phase cesium concentration, which means, a larger fraction of cesium is extracted at low initial aqueous phase cesium concentration. The distribution coefficient of sodium (Figure 7) did not exhibit any particular trend. Cesium to sodium separation factors are plotted in Figure 8. An increase in cesium selectivity (cesium to sodium separation factor) with decreasing initial cesium concentration was observed with DC21C7 in both DCE and n-octanal.

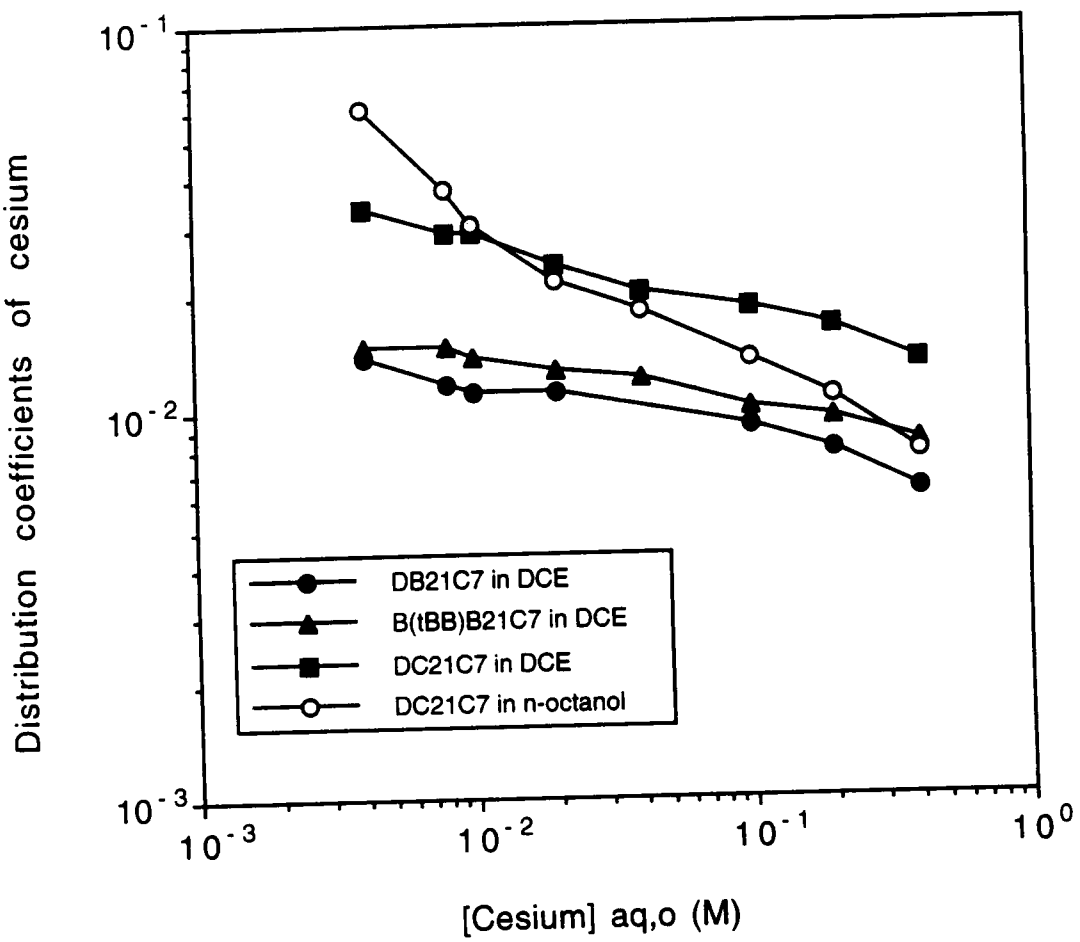


Figure 6. Plot of distribution coefficients of cesium for solvent extraction by each of the crown ether solutions.

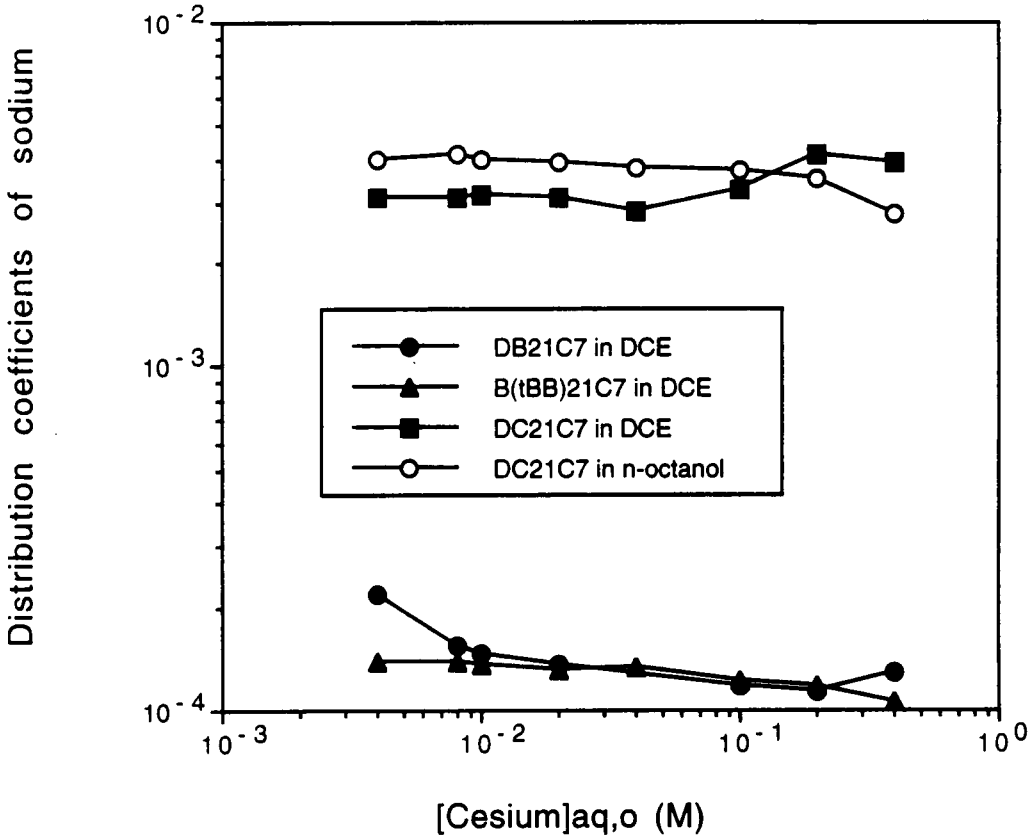


Figure 7. Plot of distribution coefficients of sodium for solvent extraction by each of the crown ether solutions.

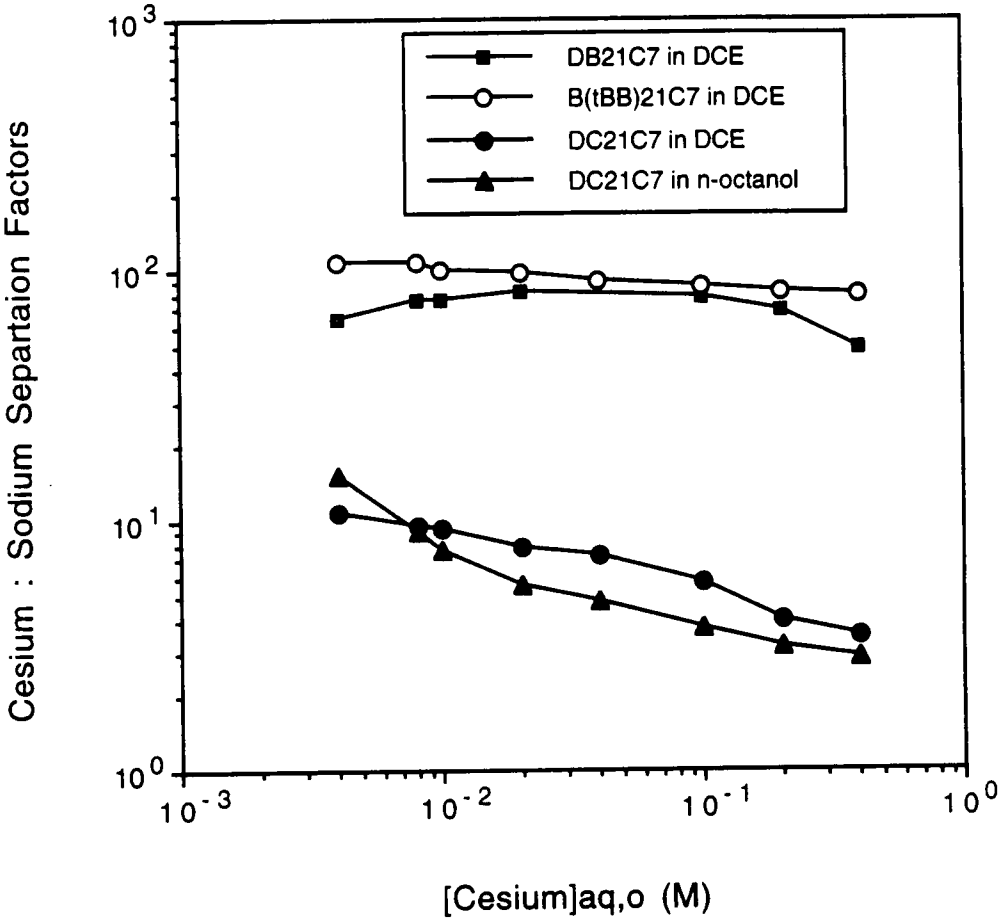


Figure 8. Plot of cesium to sodium separation factors versus the initial aqueous phase cesium concentration for extraction by each of the crown ether solutions.

A slight decrease in cesium selectivity was also observed for extraction by B(tBB)21C7. With DB21C7 selectivity, on an average, remained constant. The two benzo crowns exhibited cesium selectivites which were an order of magnitude higher than those exhibited by DC21C7 solutions in two diluents. Although DC21C7's extractability towards cesium is high it also extracts large amounts of sodium, resulting in low cesium selectivity. The loadings cesium, sodium, and total by the metal the crown ethers are plotted in Figures 9 - 11 respectively. As evident from the figures, DC21C7 in both the diluents on average exhibited higher cesium, sodium and total loadings as compared to DB21C7 and B(tBB)21C7. All the crown ethers exhibited decreasing cesium loading (Figure 9) with decreasing cesium concentration. Sodium loading (Figure 10) for these crown ethers was virtually constant or slightly decreasing. For all the practical applications, our main focus is to find an extractant which can effectively and selectively remove cesium from aqueous waste. In spite of the very high cesium extraction efficiency by DC21C7, low cesium selectivity poses a question for DC21C7 as a practical cesium extractant. Although DB21C7 and B(tBB)21C7 extracted approximately 50-90% less cesium than DC21C7 (Figure 4), they exhibited high cesium selectivity (Figure 8). However, one important point which goes in favor of DC21C7 is the increase in cesium selectivity at low initial aqueous cesium concentrations. In the case of DC21C7, there was a 5 to 7 fold increase in selectivity as initial aqueous phase cesium concentration decreased from $4X10^{-1}$- $4X10^{-3}$ M, while in case of

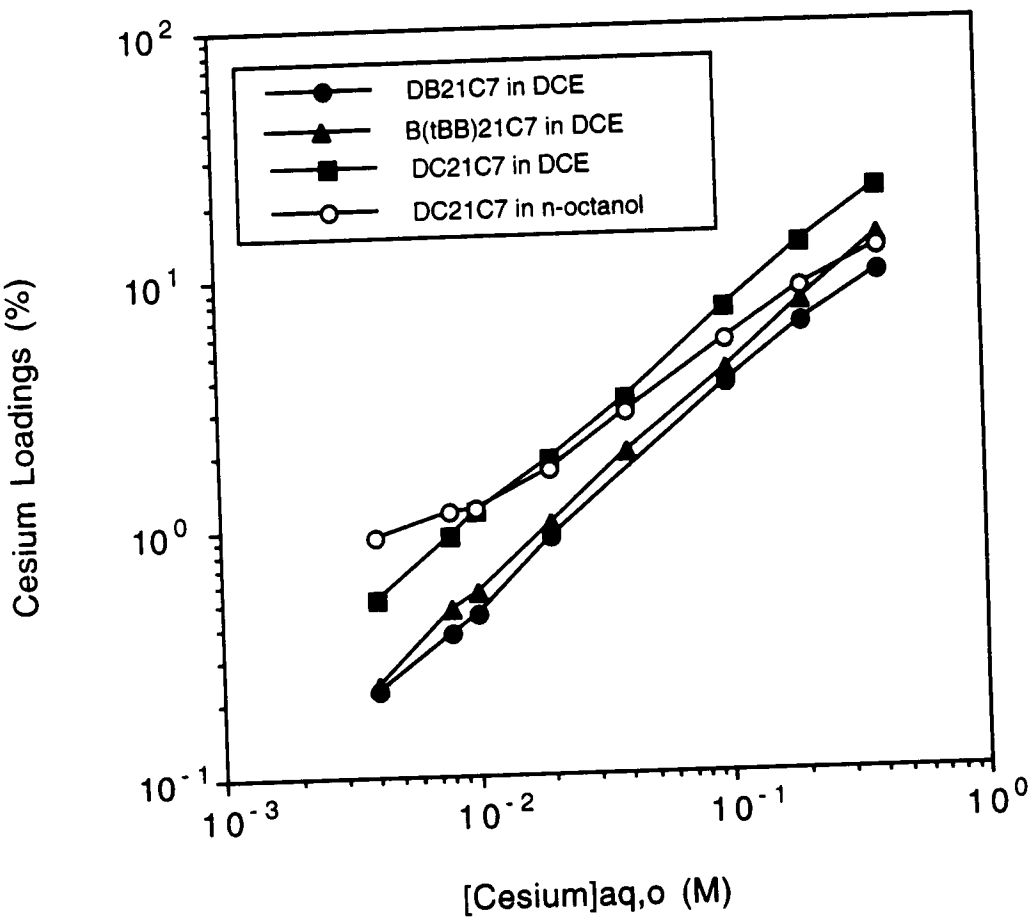


Figure 9. Plot of cesium loadings for solvent extraction by each of crown ether solutions.

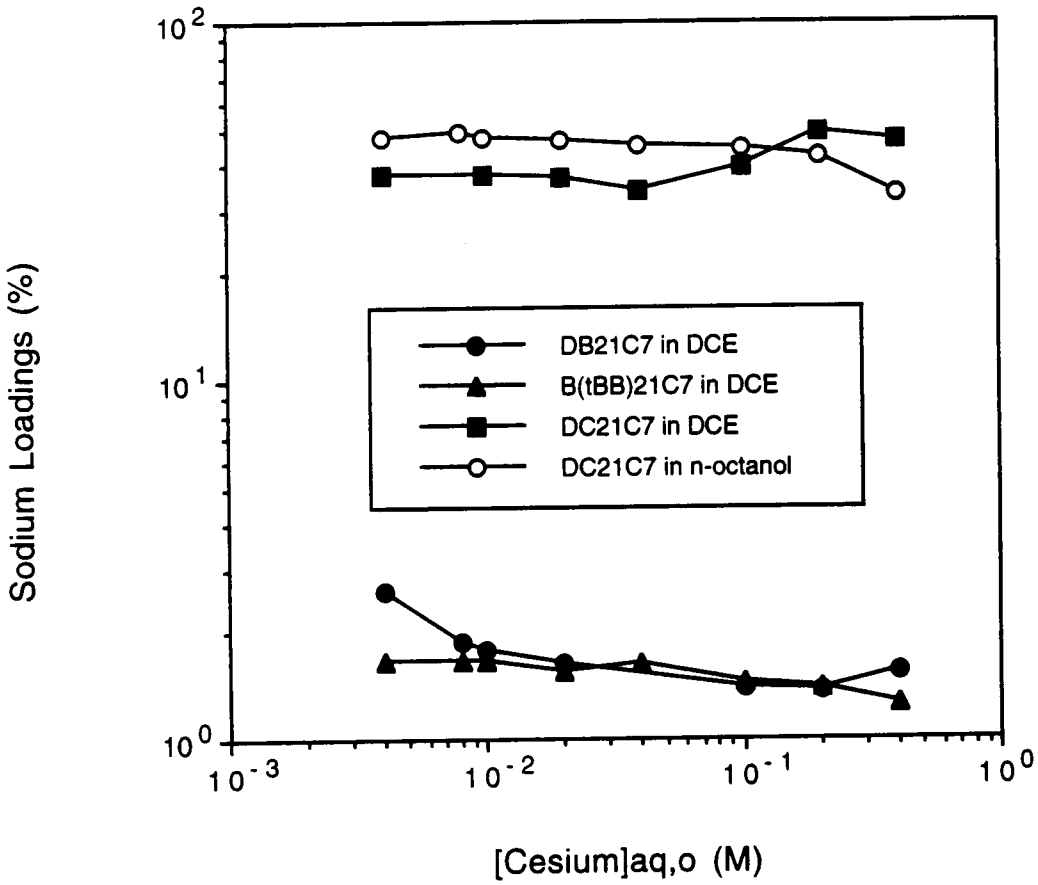


Figure 10. Plot of sodium loadings for solvent extraction by each of crown ether solutions.

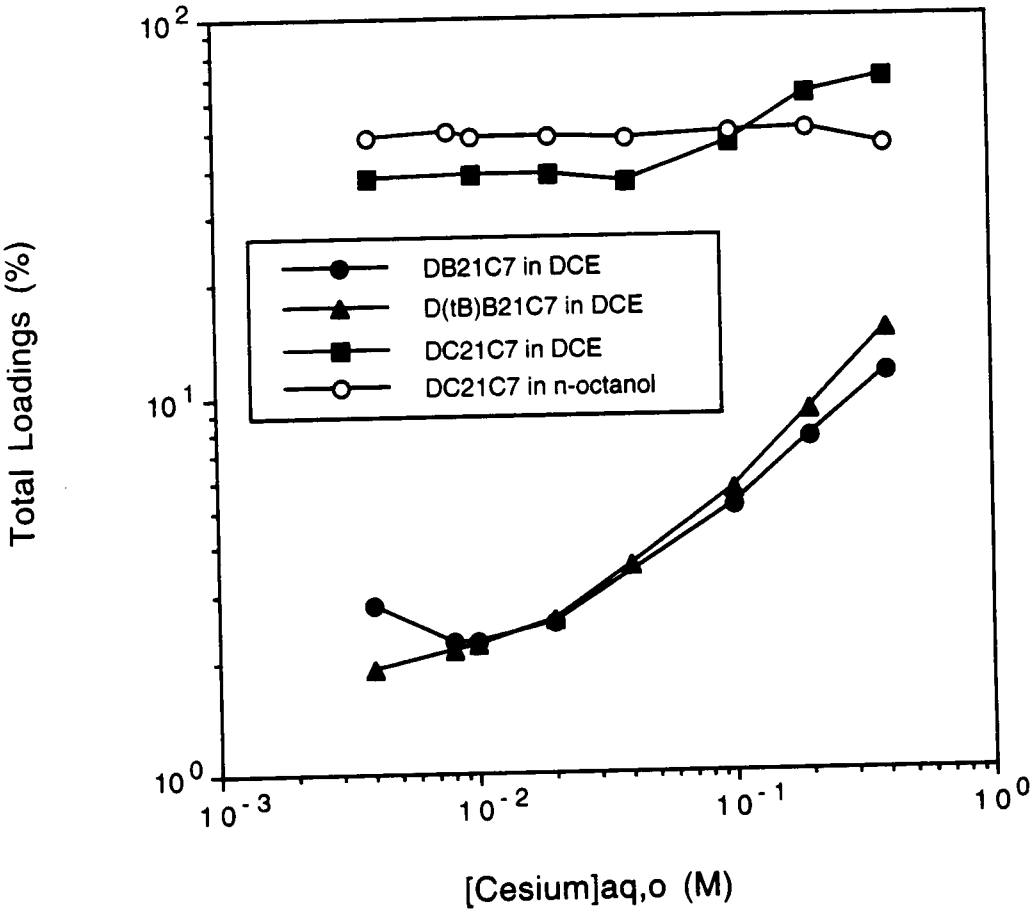


Figure 11. Plot of total metal loadings for solvent extraction by each of crown ether solutions.

DB21C7 and B(tBB)21C7 the selctivity either remained constant or slightly incresed (1.5 folds increase incase of B(tBB)21C7. It indicates that DC21C7 should be a good cesium extractant at low initial aqueous phase cesium concentrations. Even at higher concentrations DC21C7 seems to be a promising extractant for the systems where amount and not the selectivity is of importance. Experiments at lower concentrations could not be conducted due to the detection limit of the analyzing instrument. Further experiments are needed for low concentration case. Since real wastes usually have trace concentrations of cesium, the trend indicates that these crown ethers will exhibit greater cesium selectivity at such low concentrations.

Extraction data with DC21C7 also highlight one important factor, called the diluent effect. DC21C7 behaved quite differently in the two diluents investigated. The phenomena such as ionization and aggregation which determine the solvent extraction process are dependent on various diluent properties, including dielectric constant, dipole moment, and viscosity [Deng et al., 1994]. The diluents in this case seemed to have a very prominent effect on the cesium and sodium loading but not much effect was observed on selectivity. Similar effect was observed earlier by Deng et al.[1994].

In light of the above extraction data, it is hard to say which crown ether is the optimum extractant for cesium. All the crown ethers exhibited some cesium selectivity, which is consistent with what is expected from their ring size. However, these crown ethers

have relatively low distribution coefficients and selectivity as far as practical applications are concerned. Distribution coefficients greater than 10 and selectivities greater than 10^4 are considered to be good for practical applications. Although DC21C7 shows total metal (cesium and sodium) extraction loading (Figure 11) of about 68% in DCE, it has very low cesium selectivity(Figure 8). Out of 68% only 21% was cesium loading, this was the highest cesium loading observed among all the crown ethers investigated. B(tBB)21C7 which exhibits highest cesium selectivity (107) in the concentration range tested, showed only 19% cesium Loading.

Cesium and sodium extraction data were modeled using computer program SXLSQI (Base, ref. 6), to understand the equilibrium aspects of solvent extraction by crown ethers. SXLSQI, the modified version of SXLSQA (Base et al, 1990), has the ability to model equlibria involving free ions in the organic phase. A set of product species are assumed in the organic phase and fed in the program as the model along with the data set. The program then calculates the activity coefficients of the species and adjusts the formation constants of product species to give a best fit to data set. SXLSQI employs the least squares fitting to give the best fit data set. It also calculates the agreement factor σ, a measure of goodness of fitting. σ decreases towards unity for better fitting models (Deng et al., 1995). Usually the model exhibiting minimum σ is chosen as the best model. Only the solvent extraction by crown ethers in DCE are modeled in this study. The cesium and sodium are found to form 1:1 complexes with crown ethers. The extraction of

$CsNO_3$ and $NaNO_3$ by crown ether (B) is represented by equations 1-4. The values of formation constants for crown ether-cesium complexes were used as calculated by Deng et al.(1995). Crown

$$Cs^+ + NO_3^- + B \overset{K_{ex}}{\rightleftharpoons} CsBNO_3 \qquad (1)$$

$$Cs^+ + NO_3^- + B \overset{K_{ex\pm}}{\rightleftharpoons} CsB^+ + NO_3^- \qquad (2)$$

$$Na^+ + NO_3^- + B \overset{K_{ex}}{\rightleftharpoons} NaBNO_3 \qquad (3)$$

$$Na^+ + NO_3^- + B \overset{K_{ex\pm}}{\rightleftharpoons} NaB^+ + NO_3^- \qquad (4)$$

ether-sodium complexes formation constants were found using the program to fit the data to the above model represented by equations 1-4. The logarithm values of the equilibrium constants (formation constants) and the correlation factors are summarized in Table 3. Plots of the data and calculated models according to the values in Table 3 are given in figure 12 - 17.

In all the cases a good fit for cesium was obtained. Sodium extraction data was also very well fitted. With the help of these models cesium distribution coefficients, loadings and selectivities

Table 3. Formation constants and agreement factors for cesium nitrate and sodium nitrate extraction by crown ethers, as calculated by SXLSQI

Crown Ether	Cs+LogKex	Cs+LogKex±	Na+LogKex	Na+LogKex±	Agreement Factor (σ)
DB21C7	0.12	-4.51	*	-5.67	5.08
B(tBB)21C7	0.13	-4.64	-2.12	-7.50	1.87
DC21C7	0.49	-3.20	-4.21	-5.94	2.66

* This species was not found to be present

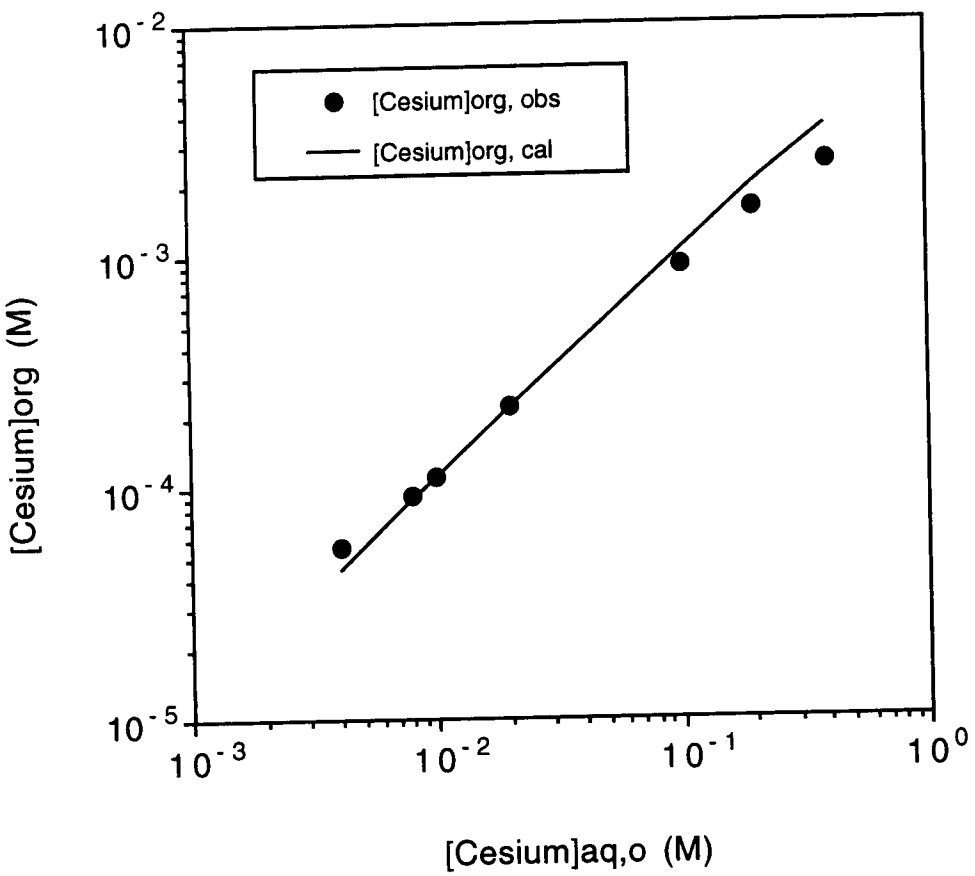


Figure 12. Comparison of calculated (solid line) and observed (symbols) cesium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M dibenzo-21-crown-7 using 1,2-dichloroethane as the diluent.

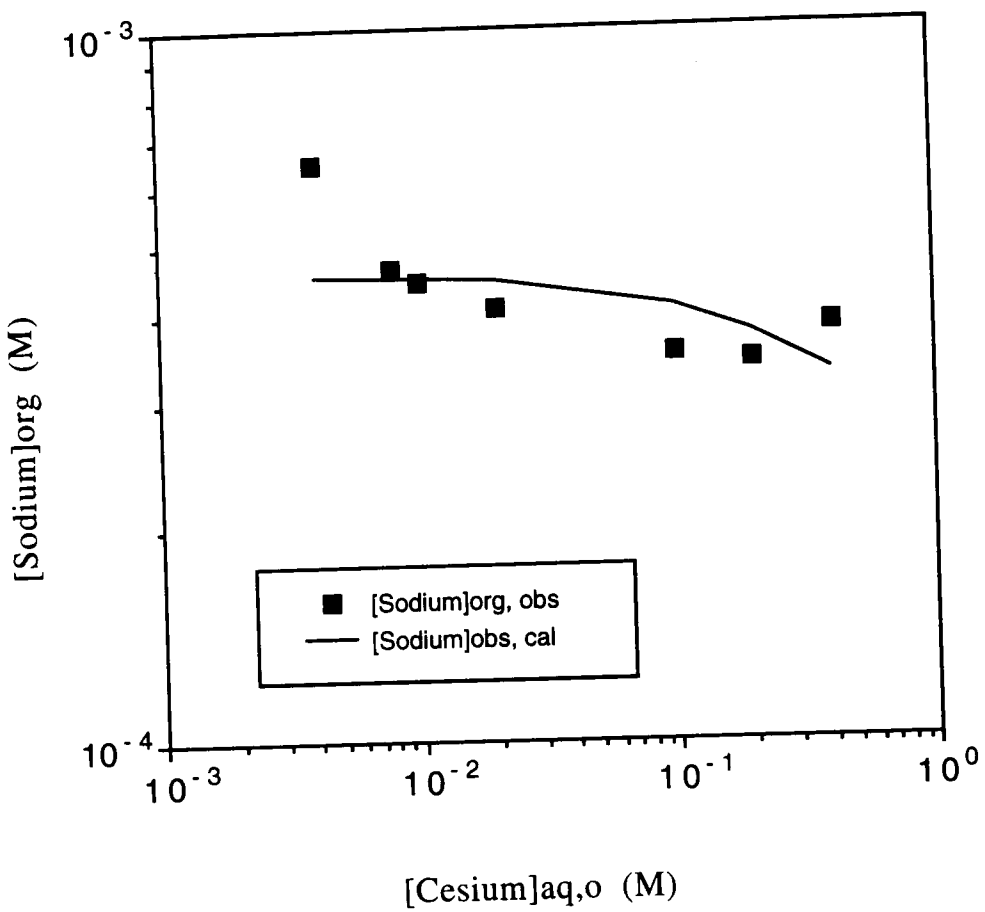


Figure 13. Comparison of calculated (solid line) and observed (symbols) sodium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M dibenzo-21-crown-7 using 1,2-dichloroethane as the diluent.

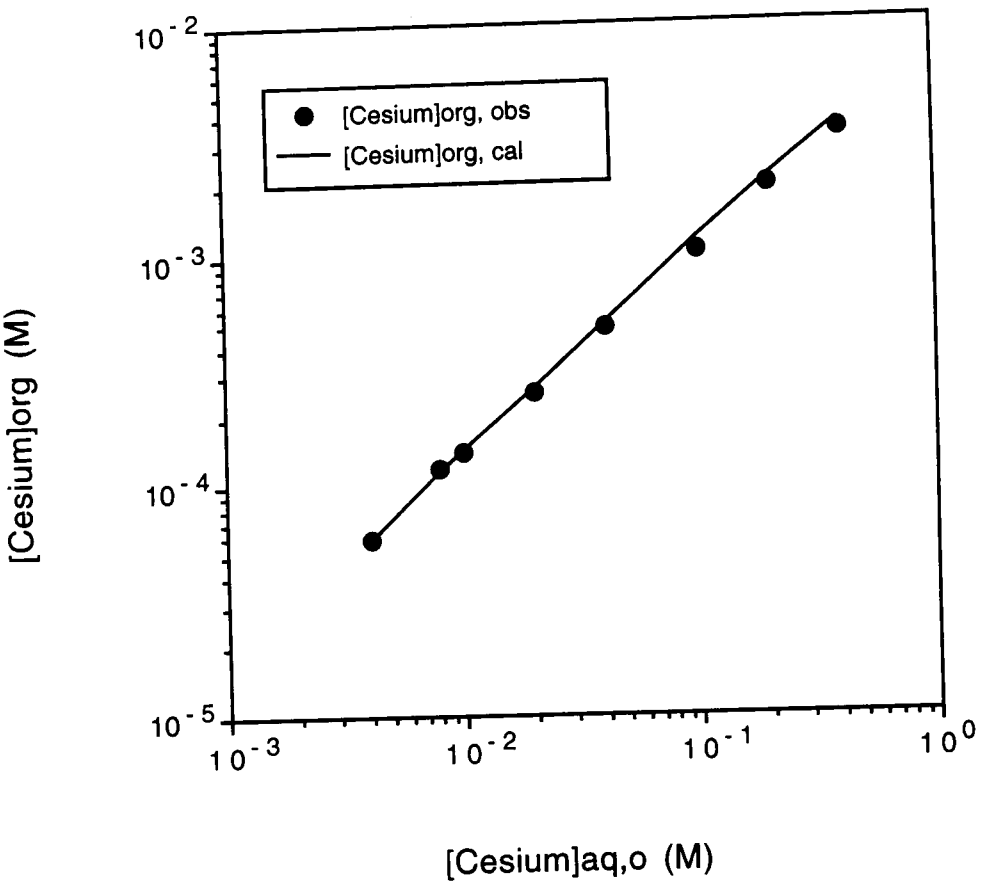


Figure 14. Comparison of calculated (solid line) and observed (symbols) cesium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M bis(t-butylbenzo)-21-crown-7 using 1,2-dichloroethane as the diluent.

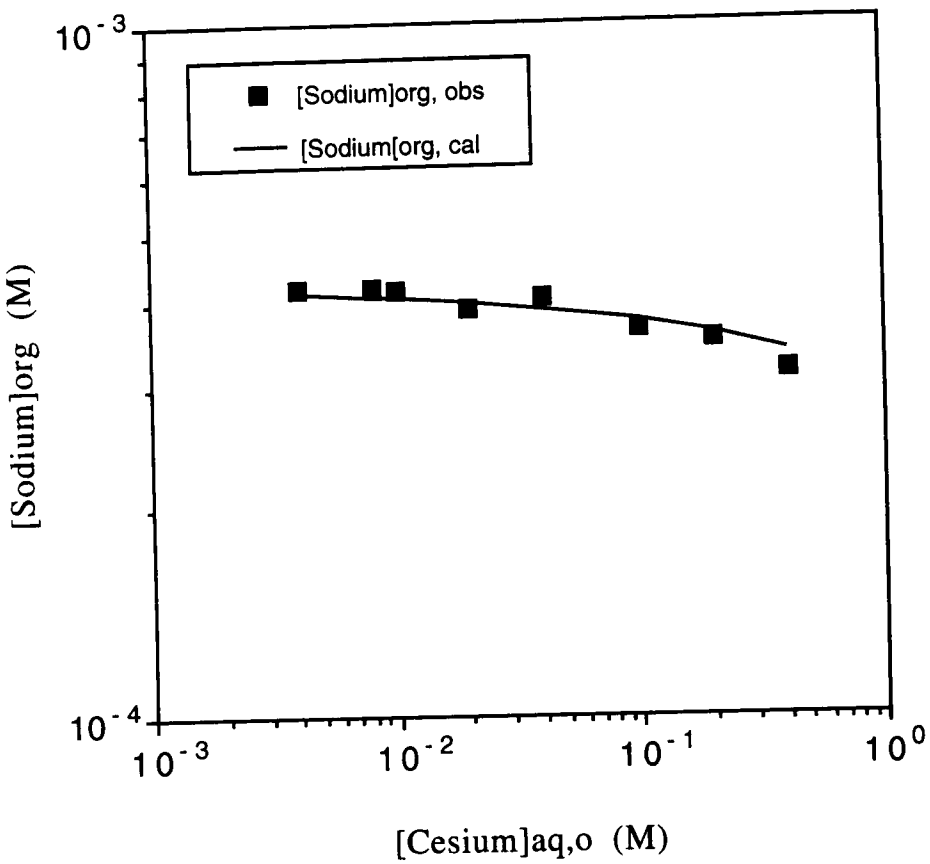


Figure 15. Comparison of calculated (solid line) and observed (symbols) sodium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M bis(t-butylbenzo)-21-crown-7 using 1,2-dichloroethane as the diluent.

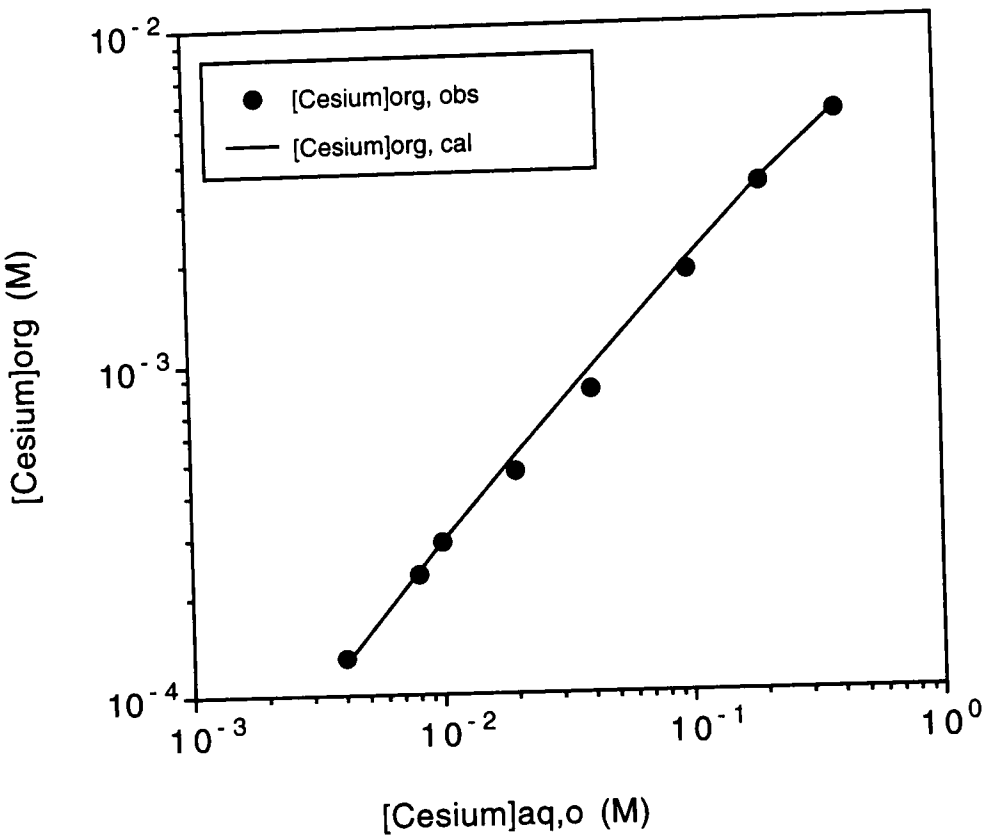


Figure 16. Comparison of calculated (solid line) and observed (symbols) cesium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M dicyclohexano-21-crown-7 using 1,2-dichloroethane as the diluent.

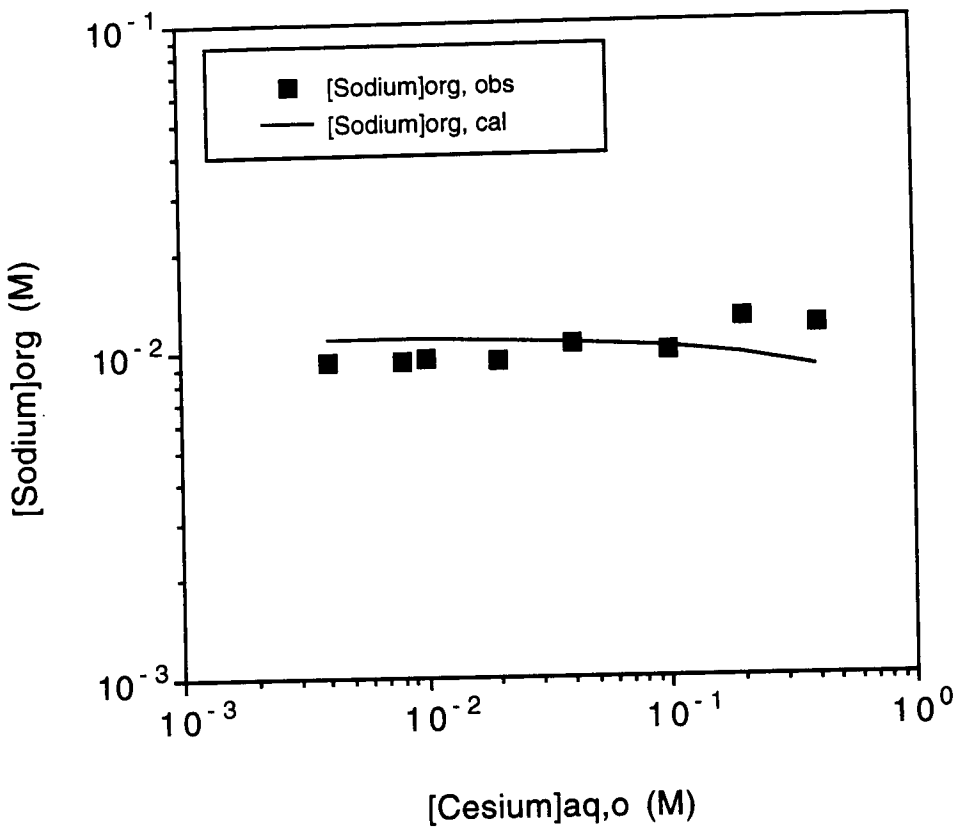


Figure 17. Comparison of calculated (solid line) and observed (symbols) sodium ion concentration in the organic phase versus the initial aqueous phase concentration of cesium, for extraction by 0.025 M dicyclohexano-21-crown-7 using 1,2-dichloroethane as the diluent.

can be estimated at intial aqueous cesium concentrations other than those tested here.

Synergistic Systems

As mentioned earlier, several workers have used a combination of crown ethers and organophillic cation exchangers to enhance the extraction and selectivity of a metal ion. The crown ethers used in these tests were generally those which have previously shown some selectivity of that metal. Since the crown ethers tested here exhibited some cesium extraction efficiency and selectivity, they have some potential of being practical extractants. In further experiments such combinations of crown ethers with some cation exchange extractants were investigated.

A variety of available organophilic extractants were used in this study: DP, 2,6DT4MP, 1,3DP1,3PD, HMNA and BAMBP. 2,6DT4MP [Gulis et al., 1989] and BAMBP [Horner et al., 1963] had been found to exhibit cesium selectivity. Some work previously done in alkali metal extraction by synergistic combination of crown ethers and some organophilic cation exchangers in toluene showed positive results. Therefore, for further experiments, toluene was chosen as a diluent [McDowell et al., 1992]. Toluene alone was not found to have any detectable extraction of cesium and sodium. DCE was also tested as a diluent for synergistic extractions. Synergistic factors are calculated and discussed wherever it was possible. Synergism is said to be obtained when synergistic factors are greater than 1.

For solution in toluene synergistic factors were not calculated because of metal extraction by toluene alone being less than detection limit. As discussed previously, the extraction by organic acids is pH dependent, and significant extraction is found to take place at high pH; thus these synergistic combinations were tested at pH 10, 12 and 14 respectively. The extraction by crown ethers alone is assumed to be independent of pH [McDowell, W.J., unpublished results]. Cesium and sodium were extracted from an aqueous solution containing 0.01 M $CsNO_3$ and 3 M $NaNO_3$ for extraction by DP and DT4MP while 0.40 M $CsNO_3$ and 3 M $NaNO_3$ was used in all other cases. The loadings in these systems are calculated on the basis of organic acid concentrations.

Results of cesium and sodium extraction by synergistic combinations of DP and crown ethers in DCE and toluene are presented in Tables 4 and 5 respectively. DP alone shows little cesium extraction in DCE and essentially none in toluene. pH, as expected, was found to have significant effects on cesium and sodium loading and selectivity. Both cesium and sodium loadings went up with an increase in the pH in both the diluents. Selectivity showed an interesting trend in toluene, first, decreased as the pH increased from 10 to 12, and then increased from pH 12 to 14. Since this combination in DCE was not tested at pH 10, no comments can be made about the trend. The highest cesium loading and selectivity was observed with D(tBB)21C7 in DCE at pH 14. Cesium extraction at pH 14 was synergized by crown ether-DP combination in DCE for all the three crown ethers (Synergistic factors discussed

Table 4. Cesium and sodium extraction data for solvent extraction by dodecylphenol using 1,2-dichloethane as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.01M

pH = 12

EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+loading%	D(Na+)	D(Cs+)	Total Loading%	Selectivity	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + DP	0.05	5.10(±0.47)E-03	5.62(±0.13)E-05	20.40(±1.88)	0.22(±0.01)	1.70E-03	5.65E-03	20.62	3.32	-	-
B(tBB)21C7 + DP	0.05	1.73(±0.25)E-03	2.87(±0.02)E-04	6.93(±1.00)	1.15(±0.01)	5.77E-04	2.95E-02	8.08	51.11	-	-
DC21C7 + DP	0.05	1.08(±0.02)E-02	2.58(±0.09)E-04	43.56(±0.76)	1.03(±0.04)	3.64E-03	2.65E-02	44.59	7.27	-	-
DP	0.025M	1.33(±0.14)E-03	-	5.34(±0.56)	-	4.45E-04	-	-	-		

pH= 14

EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	Selectivity	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + DP	0.05	5.77(±0.21)E-03	1.47(±0.09)E-04	23.11(±0.84)	0.59(±0.04)	1.93E-03	1.49E-02	23.69	7.73	6.11	1.54
B(tBB)21C7 + DP	0.05	2.74(±0.22)E-03	1.39(±0.01)E-03	10.96(±0.91)	5.57(±0.06)	9.14E-04	1.62E-01	16.53	177.15	63.20	0.72
DC21C7 + DP	0.05	1.09(±0.07)E-02	3.46(±0.03)E-04	43.68(±2.98)	1.39(±0.01)	3.65E-03	3.59E-02	45.07	9.82	10.67	0.34
DP	0.025	2.71(±0.19)E-03	1.53(±0.15)E-05	10.85(±0.77)	0.06(±0.01)	9.05E-04	1.53E-03	10.91	1.69		

Note : The loadings in all the synergistic combinations are based on 0.025 M extractant concentration
Fsyn(M) represents the synergistic factor for metal M

Table 5. Cesium and sodium extraction data for solvent extraction by dodecylphenol using toluene as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.01M

pH = 10									
EXTRACTANT	[EX]tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + DP	0.05 M	4.20(±0.18)E-04	8.57(±0.46)E-06	1.68(±0.07)	0.034(±0.002)	1.40E-04	8.58E-04	1.71	6.12
B(tBB)21C7 + DP	0.05 M	3.16(±0.01)E-04	1.06(±0.19)E-05	1.263(±0.003)	0.04(±0.01)	1.05E-04	1.06E-03	1.31	10.08
DC21C7 + DP	0.05 M	6.29(±0.01)E-04	3.67(±0.15)E-06	2.52(±0.01)	0.015(±0.001)	2.10E-04	3.67E-04	2.53	1.75
DP	0.025 M	1.98(±0.43)E-04	-	0.79(±0.17)	-	6.59E-05	-		
pH = 12									
EXTRACTANT	[EX]tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + DP	0.05 M	5.46(±0.21)E-03	2.01(±0.04)E-05	21.83(±0.86)	0.081(±0.002)	1.82E-03	2.02E-03	21.91	1.11
B(tBB)21C7 + DP	0.05 M	4.96(±0.30)E-03	2.34(±0.29)E-05	19.84(±1.22)	0.09(±0.01)	1.66E-03	2.35E-03	19.93	1.42
DC21C7 + DP	0.05 M	6.01(±0.14)E-03	3.64(±0.26)E-06	24.04(±0.56)	0.015(±0.001)	2.01E-03	3.65E-04	24.05	0.18
DP	0.025 M	5.41(±0.14)E-03	-	21.65(±0.56)	-	1.81E-03	-	-	-
pH = 14									
EXTRACTANT	[EX]tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+ Loading	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + DP	0.05 M	6.06(±0.23)E-03	9.03(±0.17)E-04	24.25(±0.92)	3.61(±0.07)	2.02E-03	9.92E-02	27.86	49.01
B(tBB)21C7 + DP	0.05 M	5.95(±0.16)E-03	1.04(±0.02)E-03	23.78(±0.65)	4.14(±0.08)	1.99E-03	1.16E-01	27.92	58.18
DC21C7 + DP	0.05 M	9.21(±0.10)E-03	2.23(±0.14)E-04	36.84(±0.40)	0.89(±0.06)	3.08E-03	2.28E-02	37.73	7.41
DP	0.025 M	5.29(±0.32)E-03	-	21.15(±1.28)	-	1.77E-03	-	-	-

for all the combination are only for the solutions in DCE). Sodium extraction was slightly synergized by DB21C7-DP combination, for the other two crown ethers (B(tBB)21C7 and DC21C7) negative synergism or antagonism was observed. Maximum synergistic factor of 63.2 was obtained with B(tBB)21C7-DP combination, sodium extraction was antagonized with this system resulting in a increase in selectivity as compared to the crown ethers alone. One important point to be noted here is that the amount of sodium extracted by the combination was greater than that extracted by extractants individually. The combination, however, extracted less sodium than the sum of the amount of sodium extracted by both extractants, thus resulting in antagonism.

2,6DT4MP was a poor extractant of cesium and also of sodium. It exhibited good selectivity of cesium over sodium but low extraction in DCE (Table 6). Since there was no detectable cesium extraction by 2,6DT4MP alone in DCE, synergistic factors could no be calculated. In toluene this system was not found to extract detectable amount of cesium at the pH tested (Table 7).

Table 8 and 9 give the results of cesium and sodium extraction by 1,3DP1,3PD. 1,3DP1,3PD alone in DCE (Table 8) at pH 14 showed some cesium selectivity but in toluene (Table 9) it was sodium selective. In DCE, both cesium and sodium loading increased with increase in pH, for all the extraction systems. An overall increase in selectivity was observed over the pH range 10 to 14. For all the systems in toluene, both cesium and sodium loadings decreased as the pH increased from 10 to 12 and then increased. Selectivity also

Table 6. Cesium and sodium extraction data for solvent extraction by 2,6-di-tert-butyl-4-methylphenol using 1,2-dichloroethane as the diluent

[NaNO3]aq,o = 3.0M
[CsNO3]aq,o = 0.01M

pH = 12									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + 2,6DT4MP	0.05 M	1.73(±0.02)E-03	2.49(±0.10)E-05	6.94(±0.09)	0.100(±0.004)	5.7867E-04	2.5001E-03	7.04	4.32
B(tB)B21C7 + 2,6DT4MP	0.05 M	5.07(±0.37)E-04	1.28(±0.03)E-04	2.03(±0.15)	0.51(±0.01)	1.6912E-04	1.2988E-02	2.54	76.80
DC21C7 + 2,6DT4MP	0.05 M	7.54(±0.11)E-03	1.74(±0.05)E-04	30.16(±0.43)	0.69(±0.02)	2.5200E-03	1.7771E-02	30.86	7.05
2,6DT4MP	0.025 M	1.36(±0.12)E-04	-	0.54(±0.05)	-	4.5368E-05	-	-	-
pH = 14									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + 2,6DT4MP	0.05 M	1.45(±0.07)E-03	3.35(±0.13)E-05	5.83(±0.26)	0.134(±0.005)	4.8600E-04	3.3646E-03	5.96	6.92
B(tB)B21C7 + 2,6DT4MP	0.05 M	3.70(±0.06)E-04	1.31(±0.01)E-04	1.48(±0.02)	0.525(±0.004)	1.2348E-04	1.3306E-02	2.01	107.75
DC21C7 + 2,6DT4MP	0.05 M	7.10(±0.09)E-03	2.12(±0.03)E-04	28.42(±0.36)	0.88(±0.01)	2.3738E-03	2.1646E-02	29.27	9.12
2,6DT4MP	0.025 M	8.96(±0.82)E-05	-	0.35(±0.03)	-	2.9888E-05	-	-	-

Table 7. Cesium and sodium extraction data for solvent extraction by 2,6-di-tert-butyl-4-methylphenol using toluene as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.01 M
pH = 12

EXTRACTANT	[EX]tot.	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + 2,6DT4MP	0.05 M	1.14(±0.04)E-04	-	4.56(±0.17)E-01	-	3.8067E-05	-	-	-
B(tBB)21C7 + 2,6DT4MP	0.05 M	1.51(±0.03)E-04	-	6.04(±0.13)E-01	-	5.0384E-05	-	-	-
DC21C7 + 2,6DT4MP	0.05 M	2.44(±0.13)E-04	-	9.76(±0.53)E-01	-	8.1380E-05	-	-	-
2,6DT4MP	0.025 M	1.76(±0.23)E-04	-	7.05(±0.95)E-01	-	5.8799E-05	-	-	-

Table 8. Cesium and sodium extraction data for solvent extraction by 1,3-diphenyl-1,3-propanedione using 1,2-dichloroethane as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.4 M

pH = 10											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn(Cs+)	Fsyn(Na+)
DB21C7 + 1,3DP1,3PD	0.05 M	1.84(±0.05)E-03	1.04(±0.02)E-03	7.38(±0.21)	4.17(±0.07)	6.1566E-04	2.61E-03	11.55	4.24	-	-
DC21C7 + 1,3DP1,3PD	0.05 M	6.21(±0.05)E-03	4.76(±0.06)E-03	24.85(±0.22)	19.03(±0.25)	2.0749E-03	1.20E-02	43.88	5.80	-	-
pH = 12											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn(Cs+)	Fsyn(Na+)
DB21C7 +1,3DP1,3PD	0.05 M	2.29(±0.04)E-03	1.05(±0.008)E-03	9.20(±0.15)	4.19(±0.03)	7.67E-04	2.62E-03	13.38	3.42	0.42	4.62
B(tBB)21C7 + 1,3DP1,3PD	0.05 M	1.03(±0.07)E-03	3.07(±0.04)E-03	4.13(±0.29)	12.30(±0.15)	3.44E-04	7.75E-03	16.43	22.51	0.93	2.41
DC21C7 + 1,3DP1,3PD	0.05 M	8.21(±0.28)E-03	4.79(±0.02)E-03	32.84(±1.16)	19.16(±0.08)	2.74E-03	1.21E-02	52.00	4.42	0.90	0.69
1,3DP1,3PD	0.025 M	1.14(±0.09)E-04	5.19(±0.60)E-06	0.46(±0.04)	0.02(±0.00)	3.81E-05	1.30E-05	0.48	0.34		
pH= 14											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	Selectivity	Fsyn(Cs+)	Fsyn(Na+)
DB21C7 + 1,3DP1,3PD	0.05 M	1.71(±0.04)E-02	3.26(±0.07)E-03	68.50(±1.73)	13.04(±0.30)	5.7409E-03	8.21E-03	81.53	1.43	1.05	3.59
B(tBB)21C7 + 1,3DP1,3PD	0.05 M	1.27(±0.05)E-02	8.94(±0.04)E-03	50.76(±1.98)	35.76(±0.14)	4.2482E-03	2.29E-02	86.52	5.38	2.30	2.70
DC21C7 + 1,3DP1,3PD	0.05 M	2.07(±0.11)E-02	6.08(±0.25)E-03	82.94(±4.44)	24.33(±1.01)	6.9595E-03	1.54E-02	107.27	2.22	1.02	1.29
1,3DP1,3PD	0.025 M	4.40(±0.008)E-03	6.60(±0.14)E-04	17.62(±0.03)	2.62(±0.06)	1.4706E-03	1.64E-03	20.24	1.12		

Table 9. Cesium and sodium extraction data for solvent extraction by 1,3-diphenyl-1,3-propanedione using toluene as the diluent

[CsNO3] = 0.4 M
[NaNO3] = 3.0 M

pH= 10									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + 1,3DP1,3PD	0.05	2.64(±0.07)E-03	3.21(±0.19)E-04	10.58(±0.29)	1.29(±0.13)	8.8210E-04	8.0463E-04	11.86	0.91
B(tBB)21C7 + 1,3DP13PD	0.05	2.60(±0.16)E-03	2.74(±0.12)E-04	10.38(±0.65)	1.09(±0.08)	8.6611E-04	6.8481E-04	11.48	0.79
DC21C7 + 1,3DP13PD	0.05	2.72(±0.06)E-03	2.45(±0.09)E-04	10.88(±0.23)	0.98(±0.06)	9.0768E-04	6.1252E-04	11.86	0.67
1,3DP13PD	0.025	2.55(±0.22)E-03	2.16(±0.06)E-04	10.19(±0.88)	0.86(±0.04)	8.4972E-04	5.4040E-04	11.05	0.64
pH = 12									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na)	D(Cs)	Total Loading%	S
DB21C7 + 1,3DP1,3PD	0.05	1.29(±0.07)E-03	2.05(±0.04)E-04	5.15(±0.28)	0.82(±0.02)	3.2284E-03	6.8236E-05	5.97	0.021
B(tBB)21C7 + 1,3DP13PD	0.05	1.21(±0.16)E-03	9.86(±0.35)E-05	4.83(±0.65)	0.39(±0.01)	3.0300E-03	3.2879E-05	5.23	0.011
DC21C7 + 1,3DP13PD	0.05	2.05(±0.20)E-03	6.45(±0.50)E-05	8.22(±0.81)	0.26(±0.02)	5.1640E-03	2.1509E-05	8.48	0.004
1,3DP13PD	0.025	1.14(±0.05)E-03	-	4.57(±0.22)	-	2.8633E-03	-	-	-
pH = 14									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + 1,3DP1,3PD	0.05	1.79(±0.02)E-02	3.55(±0.06)E-03	71.56(±0.76)	14.18(±0.26)	5.9994E-03	8.9428E-03	85.75	1.49
B(tBB)21C7 + 1,3DP13PD	0.05	1.13(±0.02)E-02	3.73(±0.05)E-03	45.33(±0.72)	14.93(±0.23)	3.7922E-03	9.4180E-03	60.26	2.48
DC21C7 + 1,3DP13PD	0.05	1.93(±0.04)E-02	6.57(±0.02)E-04	77.12(±1.81)	2.63(±0.01)	6.4682E-03	1.6461E-03	79.75	0.25
1,3DP13PD	0.025	1.24(±0.05)E-02	1.65(±0.15)E-04	49.72(±1.99)	0.66(±0.06)	4.1605E-03	4.1335E-04	50.38	0.10

showed the same trend. Systems in DCE exhibited greater selctivities than those in toluene. DB21C7-1,3DP1,3PD and B(tBB)21C7-1,3DP1,3PD combinations exhibited antagonism in cesium extraction and synergism in sodium extraction at pH 12. DC21C7-1,3DP1,3PD combination antagonized both cesium and sodium extraction at this pH. At pH 14 all the crown ether-1,3DP1,3PD combinations synergized both cesium and sodium extraction. Synergistic factors observed in sodium extraction were higher than those in cesium extraction which resulted in a decrease in cesium selectivity as compared to crown ethers alone.

Tables 10 and 11 give the extraction data by HMNA-crown ether synergistic combinations. Due to the solubility limits 0.015 M HMNA in toluene was used . HMNA by itself in DCE (Table 10) exhibited some cesium selectivity at pH 10 and 14, while in toluene (Table 11) it was found to be sodium selective. In general, both cesium and sodium loading increased with pH in both the diluents tested. Sodium loading increased at a much higher rate than cesium loading in almost all the cases in DCE except HMNA alone. As a result, a decrease in cesium selectivity was observed in all the synergistic combinations in DCE. At pH 14, HMNA systems were almost fully loaded with metal in both the diluents. Selectivity with HMNA alone first decreased from pH 10 to 12 and then increased from pH 12 to pH 14. With toluene as the diluent, cesium and sodium loading almost doubled with increase in pH from 12 to 14 with DB21C7-HMNA and B(tBB)21C7-HMNA combinations. A slight decrease in cesium selectivity was observed in these systems. An

Table 10. Cesium and sodium extraction data for solvent extraction by 2-heptyl-2-methyl-nonanoic acid using 1,2-dichloroethane as the diluent

[CsNO3]aq,o = 0.4 M
[NaNO3]aq,o = 3.0 M

pH = 10											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + HMHN	0.05 M	3.68(±0.42)E-03	1.86(±0.07)E-03	14.73(±1.68)	7.44(±0.27)	1.23E-03	4.67E-03	22.17	3.80	0.75	6.43
B(tBB)21C7 + HMHN	0.05 M	4.69(±0.05)E-04	4.79(±0.08)E-03	1.88(±0.02)	19.18(±0.32)	1.56E-04	1.21E-02	21.06	77.54	1.45	0.93
DC21C7 + HMHN	0.05 M	1.10(±0.04)E-02	7.47(±0.12)E-04	44.19(±1.86)	29.91(±0.47)	3.70E-03	1.91E-02	88.38	5.15	1.40	0.93
HMMN	0.025 M	1.89(±0.05)E-04	2.68(1.58)E-05	0.76(±0.04)	0.11(±0.06)	6.32E-05	6.70E-05	0.84	1.06		
pH = 12											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + HMNA	0.05 M	6.73(±0.40)E-03	2.19(±0.10)E-03	26.94(±1.60)	8.77(±0.42)	2.25E-03	5.51E-03	35.71	2.45	0.78	1.67
B(tBB)21C7 + HMNA	0.05 M	3.18(±0.07)E-03	6.17(±0.09)E-03	12.72(±0.28)	24.71(±0.36)	1.06E-03	1.57E-02	18.71	14.79	1.72	0.80
DC21C7 + HMNA	0.05 M	9.47(±0.33)E-03	5.30(±0.07)E-03	37.87(±1.33)	21.20(±0.30)	3.17E-03	1.34E-02	29.54	4.24	0.94	0.62
HMNA	0.025 M	3.64(±0.31)E-03	3.27(±0.40)E-04	14.58(±1.24)	1.31(±0.16)	1.22E-03	8.19E-04	15.24	0.67		
pH = 14											
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + HMNA	0.05 M	2.28(±0.08)E-02	3.62(±0.09)E-03	91.44(±3.08)	14.48(±0.38)	7.68E-03	9.13E-03	105.92	1.19	0.75	1.28
B(tBB)21C7 + HMNA	0.05 M	1.92(±0.05)E-02	7.46(±0.04)E-03	38.48(±2.04)	29.84(±0.18)	6.46E-03	1.90E-02	106.81	2.94	1.33	1.08
DC21C7 + HMNA	0.05 M	2.20(±0.15)E-02	7.53(±0.31)E-03	88.08(±5.92)	30.14(±1.92)	7.39E-03	1.92E-02	118.22	2.60	0.98	0.76
HMNA	0.025 M	1.74(±0.17)E-02	2.40(±0.24)E-03	69.81(±6.86)	9.63(±0.96)	5.85E-03	6.05E-03	79.44	1.03		

Table 11. Cesium and sodium extraction data for solvent extraction by 2-heptyl-2-methyl-nonanoic acid using toluene as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.4 M

pH=12

EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + HMNA	0.04M	7.04(±0.17)E-03	1.97(±0.10)E-03	46.95(±1.12)	13.12(±0.66)	2.35E-03	4.94E-03	60.07	2.10
B(tBB)21C7 + HMNA	0.04M	6.95(±0.37)E-03	1.92(±0.05)E-03	46.33(±2.45)	12.79(±0.33)	2.32E-03	4.82E-03	59.12	2.08
DC21C7 + HMNA	0.04M	7.61(±0.30)E-03	6.23(±0.07)E-04	50.76(±2.02)	4.16(±0.05)	2.54E-03	1.56E-03	54.92	0.61
HMNA	0.015	8.45(±0.30)E-03	5.06(±0.09)E-04	56.31(±2.02)	3.38(±0.06)	2.82E-03	1.27E-03	59.68	0.45

pH =14

EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + HMNA	0.04M	1.36(±0.009)E-02	3.42(±0.02)E-03	90.54(±0.59)	22.82(±0.13)	4.55E-03	8.63E-03	113.36	1.90
B(tBB)21C7 + HMNA	0.04M	1.37(±0.02)E-02	3.39(±0.04)E-03	91.64(±1.69)	22.59(±0.25)	4.60E-03	8.54E-03	114.23	1.86
DC21C7 + HMNA	0.04M	1.45(±0.05)E-02	2.16(±0.01)E-03	96.86(±3.29)	14.41(±0.10)	4.87E-03	5.43E-03	111.27	1.12
HMNA	0.015	1.70(±0.03)E-02	1.42(±0.06)E-03	113.60(±1.73)	9.46(±0.43)	5.71E-03	3.56E-03	123.06	0.62

The loadings in this system are calculated on the basis of 0.015 M extractant

increase in cesium selectivity was observed with DC21C7-HMNA system in toluene. It can be concluded, that though loading of cesium by crown ether-HMNA system increases with pH, these systems tend to become more sodium selective as pH increases. DB21C7-HMNA combinations in DCE at all the pH levels tested, exhibited antagonism in cesium extraction but synergized sodium extraction. B(tBB)21C7-HMNA combination synergized cesium extraction for all the three pHs. Antagonism was observed in sodium extraction at pH 10 and pH 12, while synergism was observed at pH 14. DC21C7-HMNA exhibited synergism in the cesium extraction at pH 10 but exhibited antagonism at pH 12 and 14. At pH 14 amount of cesium extracted by DC21C7-HMNA combination was more than that extracted by extractants individually. Sodium extraction was antagonized at all the pHs.

Extraction data by BAMBP-CE systems in DCE and toluene are given in Tables 12 and 13 respectively. BAMBP by itself showed some cesium selectivity in DCE at pH 14 but in toluene (at pH 14) it was sodium selective. With DB21C7-BAMBP system in DCE, sodium and cesium loading decreased as pH increased from 10 to 12 and then increased from pH 12 to 14. B(tBB)21C7-BAMBP in DCE exhibited a somewhat different trend, sodium loading first increased as pH was raised from 10 to 12 and then decreased. Cesium loading with this system exhibited the same trend as was observed with DB21C7-BAMBP system. DC21C7 also exhibited almost the same trend as DB21C7-BAMBP, except for cesium loading, which further decreased as the pH increased from 12 to 14. For B(tBB)21C7-BAMBP and

Table 12. Cesium and sodium extraction data for solvent extraction by 4-sec-butyl-2-(∝-methylbenzyl)-phenol using 1,2-dichloroethane as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.4 M

pH = 10											
EXTRACTANT	[EX]tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + BAMBP	0.05 M	3.68(±0.11)E-03	2.12(±0.06)E-03	14.73(±0.44)	8.49(±0.25)	1.23E-03	5.34E-03	23.22	4.34	0.85	5.56
B(tBB)21C7 + BAMBP	0.05 M	6.84(±0.68)E-03	6.06(±0.06)E-03	2.73(±0.27)	24.26(±0.27)	2.28E-04	1.54E-02	26.99	67.52	1.84	1.15
DC21C7 + BAMBP	0.05 M	1.09(±0.04)E-02	8.15(±0.25)E-03	43.48(±1.89)	32.62(±0.99)	3.64E-03	2.08E-02	76.10	5.72	1.53	0.90
BAMBP	0.025 M	2.79(±0.21)E-04	2.39(±0.24)E-05	1.12(±0.08)	0.095(±0.009)	9.32E-05	5.98E-05	1.21	0.64		
pH = 12											
EXTRACTANT	[EX] tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + BAMBP	-	-	-	-	-	-	-	-	-	-	-
B(tBB)21C7 + BAMBP	0.05 M	1.13(±0.08)E-03	5.93(±0.32)E-03	4.53(±0.33)	23.72(±1.28)	3.77E-04	1.50E-02	28.25	39.88	1.79	1.87
DC21C7 + BAMBP	0.05 M	1.08(±0.03)E-02	7.87(±0.30)E-03	43.18(±1.19)	31.46(±1.21)	3.61E-03	2.01E-02	74.65	5.55	1.48	0.90
BAMBP	0.025 M	2.911(±0.53)E-04	3.81(±0.97)E-05	1.16(±0.22)	0.15(±0.04)	9.71E-05	9.52E-05	1.32	0.98		
pH = 14											
EXTRACTANT	[EX] tot	[Na+] org (M)	[Cs+] org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S	Fsyn (Cs+)	Fsyn (Na+)
DB21C7 + BAMBP	0.05 M	4.43(±0.07)E-03	3.48(±0.04)E-03	17.72(±0.28)	13.92(±0.20)	1.48E-03	8.78E-03	31.65	5.94	0.75	1.02
B(tBB)21C7 + BAMBP	0.05 M	9.33(±0.98)E-04	8.61(±0.17)E-03	3.73(±0.39)	34.47(±0.70)	3.11E-04	2.20E-02	38.20	70.77	1.60	0.22
DC21C7 + BAMBP	0.05 M	9.34(±0.15)E-03	9.76(±0.09)E-03	37.37(±0.61)	39.05(±0.37)	3.12E-03	2.50E-02	76.42	8.01	1.32	0.59
BAMBP	0.025 M	3.96(±0.28)E-03	2.17(±0.02)E-03	15.84(±1.14)	8.68(±0.09)	1.32E-03	5.46E-03	24.52	4.13		

Table 13. Cesium and sodium extraction data for solvent extraction by 4-sec-butyl-2-(∝-methylbenzyl)-phenol acid using toluene as the diluent

[NaNO3]aq,o = 3.0 M
[CsNO3]aq,o = 0.4 M

pH = 10									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + BAMBP	0.05 M	7.82(±0.94)E-04	3.18(±0.12)E-04	3.13(±0.38)	1.27(±0.05)	1.9596E-03	1.0603E-04	4.40	0.054
B(tBB)21C7 + BAMBP	0.05 M	7.11(±0.58)E-04	3.10(±0.12)E-04	2.84(±0.23)	1.24(±0.05)	1.7798E-03	1.0343E-04	4.08	0.058
DC21C7 + BAMBP	0.05 M	1.01(±0.12)E-03	1.45(±0.05)E-04	4.05(±0.47)	0.58(±0.02)	2.5352E-03	4.8286E-05	4.63	0.019
BAMBP	0.025 M	-	-	-	-	-	-	-	-
pH = 12									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + BAMBP	0.05 M	1.89(±0.10)E-03	3.82(±0.03)E-04	7.59(±0.41)	1.53(±0.01)	6.3267E-04	9.5689E-04	9.12	1.51
B(tBB)21C7 + BAMBP	0.05 M	1.80(±0.09)E-03	3.68(±0.05)E-04	7.2(±0.38)	1.48(±0.03)	6.0036E-04	9.2328E-04	8.68	1.54
DC21C7 + BAMBP	0.05 M	2.60(±0.07)E-03	1.73(±0.05)E-04	10.41(±0.27)	0.69(±0.02)	8.6799E-04	4.3357E-04	11.10	0.50
BAMBP	0.025 M	-	-	-	-	-	-	-	-
pH = 14									
EXTRACTANT	[EX]tot	[Na+]org (M)	[Cs+]org (M)	Na+ Loading%	Cs+ Loading%	D(Na+)	D(Cs+)	Total Loading%	S
DB21C7 + BAMBP	0.05 M	7.98(±0.54)E-04	1.48(±0.02)E-03	3.19(±0.22)	5.94(±0.08)	2.6617E-04	3.7263E-03	9.1331	14.00
B(tBB)21C7 + BAMBP	0.05 M	7.57(±0.39)E-04	1.48(±0.01)E-03	3.03(±0.16)	5.94(±0.05)	2.5261E-04	3.7240E-03	8.9668	14.74
DC21C7 + BAMBP	0.05 M	1.39(±0.08)E-03	6.40(±0.01)E-04	5.58(±0.32)	2.56(±0.04)	4.6497E-04	1.6041E-03	8.1395	3.45
BAMBP	0.025 M	4.86(±0.04)E-04	4.78(±0.16)E-05	1.95(±0.02)	0.19(±0.01)	1.6229E-04	1.1952E-04	2.1383	0.74

DC2C17-BAMBP systems, selectivity decreased at pH 12 and then again increased at pH 14 with maximum at pH 14. For DB21C7, maximum selectivity occurred at pH 12. In toluene, sodium selectivity first increased at pH 12 and then decreased at pH 14 with all the crown ether-BAMBP systems. Cesium loading continuously increased with pH for all the systems in toluene. Selectivity also exhibited a direct relationship with pH. BAMBP-crown ether systems, surprisingly, were found to be poorly loaded. Although selectivity as high as 70.77 was observed with BAMBP-B(tBB)21C7 in DCE system, the loadings were low. DB21C7-BAMBP combination antagonized cesium extraction and synergized sodium extraction at pH 10 and pH 14. Amount of cesium extracted by this combination once again, were higher than those when extractants used individually. DC21C7-BAMBP synergized cesium extractions and antagonized sodium extraction at all the three pHs. Synergistic factors could not be determined due to bad experimental data. B(tBB)21C7-BAMBP combination exhibited synergism in both cesium and sodium extraction at pH 10 and pH 12. At pH 14 this combination synergized cesium extraction and antagonized sodium extraction.

A closer examination of all the synergistic data showed that the maximum cesium selectivity in DCE was observed with the B(tBB)21C7- 2,6DT4MP combination. A selectivity of 107.75 was observed with this combination. The extractants in this system exhibited maximum selectivity but are poorly loaded. All the crown ether combinations with HMNA in DCE showed the best loadings, but these systems exhibited poor selectivities. BAMBP-B(tBB)21C7

combination in DCE was found to have the best balance of loading and selectivity as compared to all other systems in DCE. At pH 14, this combination exhibited a cesium loading of 34.43% and selectivity of 70.77. It exhibited a good balance of loading and selectivity. With DP-B(tBB)21C7 combination in toluene, a maximum selectivity of 58.18 was observed at pH 14. Cesium loading for this system was once again low. This system also exhibited best synergism for cesium extraction (Fsyn(Cs+) = 63.20). For all the other combinations either very low cesium synergism (synergistic factors greater than 10 are considered to be good) or antagonism was observed. HMNA-crown ether combinations in toluene, exhibited the best total metal loading but poor selectivity as compared to all other combinations. Maximum cesium loading was also observed with this system. One important point to be remembered is that for crown ether combination with DP and 2,6DT4MP the initial aqueous cesium concentration was 0.1 M, while it was 0.4 M for all other systems. This difference in the initial aqueous cesium concentration could be a cause for observed high synergism. If that's the case very high synergism could be observed at even lower initial aqueous concentrations of cesium; the concentration of cesium in the real waste is 10^{-3} M - 10^{-5} M.

Conclusions

- The amount of cesium extracted increased with increase in initial aqueous cesium concentration for all the crown ethers tested.

- Cesium loadings in the range of 0.22 -21.2% were obtained by the crown ethers. DC21C7 exhibited maximum metal(cesium and sodium)loadings.

- Cesium distribution coefficients in the range of $6.20X10^{-3}$ - $6.12X10^{-2}$ were obtained. Highest distribution coefficients were obtained by DC21C7.

- Cs+: Na+ separation factors more than 10^2 were obtained. Benzo crowns showed highest selectivity.

- Extraction behavior was successfully modeled in terms of 1:1 complexes with dissociation of organic-phase ion pairs. Equilibrium constants are shown in table 7.

- Most organic acid-crown ether systems tested poorly synergized cesium extraction, even antagonism was observed in some cases.

- BAMBP - B(tBB)21C7 combination in DCE exhibited the best balance of cesium loading (34.43%) and cesium selectivity (70.77).

- Synergistic Extraction increased with increase in pH from 10 to 14.

- DCE was better diluent than toluene for synergistic extractions.

- Extraction was too weak in the chosen diluents for practical applications.

VI. RECOMMENDATIONS FOR FUTURE WORK

To better understand and improve the cesium extraction by crown ethers its necessary to perform some other tests. The following recommendation are made for future work.

1. Test the crown ethers as well as the synergistic systems at lower initial aqueous cesium concentrations (10^{-5}-10^{-3} M).
2. Test the effect of crown ether concentration on cesium extraction. Increase in crown ether concentration can increase the distribution coefficient of metals.
3. Determine the effect of variation in sodium ion concentration.
4. Test some other organic acids, which are known to form complexes with cesium ion, in combination with crown ethers.
5. Determine the diluent effect and find suitable diluent. Choice of diluent can also be a factor effecting the distribution coefficient.
6. Examine the effects of other metal ions present in the waste.
7. Find some other processes, e.g. membranes, which can utilize crown ethers to separate cesium from radioactive waste.
8. Conduct cost analysis for cesium removal.

REFERENCES

REFERENCES

1. Antaya, B. L., "Cesium Extraction from HNO_3 Solution using Crown Compounds in a Matrix solution of Didodecylnaphthalene Sulphonic Acid/Tributyl Phosphate/Kerosene", M. S. Thesis, University of South Carolina, 1981

2. Attiyat, A. S. et. al., "FIA Potentiometric and Solvent Extraction Studies of Alkali Metal and Alkaline Earth Cation Complexation by Bis(tert-butybenzo)-21-Crown-7", Analytical Letters, 26(7), 1413-1424, 1993

3. Bartsch, R. A., "Effect of Structural Variation within Proton-Ionizable Crown Ethers upon the Selectivity and Efficiency of Solvent Extraction of Alkali Metal and Alkaline Earth Cations" Solvent Extraction and Ion Exchange, 7(5), 829-854, 1989

4. Baes, C. F., Jr., "The Synergistic Effects in Organophosphate Extraction Systems", Nuclear science and Engineering, 16, 406-412, 1963

5. Base, C. F., Jr., et al., "SXLSQA A Computer Program for Including both Compex Formation and Activity effects in the Interpretation of Solvent Extraction Data", Solvent Extraction and Ion Exchange, 25(13-15), 1675-1688,1990

6. Base, C. F., Jr., "SXLSQI" unpublished work, 1995

7. Blasius, E., and Nilles, K. H., "The Removal of Cesium from Medium Active Waste Solutions-I" Radiochemica Acta 35, 173-182, 1984

8. Blasius, E., and Nilles, K.H., "The Removal of Cesium from Medium Active Waste Solutions-II" Radiochemica Acta 36, 207-214, 1984

9. Charewicz, W.A., Heo, G.S., and Bartsch, R.A., "Comparison of Highly Lipophilic Crown Ether Carboxylic Acids for Transport of Alkali Metal Cation from Aqueous Solutions into Chloroform", Analytical Chemistry, 54, 2094-2097 1982

10. Charewicz, W.A., and Bartsch, R.A., "Competitive Transport of Alkali Metal Ions from Aqueous Solutions into Toluene by Highly Lipophilic Crown Ether Carboxylic Acids", Analytical Chemistry, 54, 2300-2303, 1982

11. Deng, Y., Sachleben, R. A., Moyer, B. A., Bailey, D. R., and Davis, M. C., "Selective Solvent extraction of Cesium by Crown Ethers as 18-Crown-6, 21-Crown-7 and 24-Crown-8 Derivatives" To be published, 1994

12. Deng, Y., Sachleben, R. A., Palmer, D. A., and Moyer, B. A., "Equilibrium Aspects of the Extraction of Cesium Nitrate by Dicyclohexano-21-Crown-7, Dibenzo-21-Crown-7, and Bis-[tert-Alkylbenzo]-21-Crown-7 in 1,2-Dichloroethane" To be published, 1995

13. Dansi, P. R., Meider-Gorican, H., Chiarizia, R., and Scibona, G., "Extraction Selectivity of Organic Solutions of a Cyclic Polyether with respect to the Alakli Cations", Journal of Nuclear Chemistry, 37, 1479-1483, 1975

14. Frensdorff, H.K., "Stability Constants of Cyclic Polyether Complexes with Univalent Cations" Journal of American Chemical Society, 93, 600-606, 1971

15. Gerow, I. H., "The use of Macrocyclic Polyethers to Remove Cs^+ from acidic Nuclear Waste by Solvent Extraction" PhD dissertation, University of South Carolina, 1979

16. Gerow, I. H., Smith, J. E., and Davis, M. W. "Extraction of Cs^+ and Sr^+ from HNO_3 solution using Macrocyclic Polyethers", Separation Science and Technology, 16 (5), 519-548, 1981

17. Gulis, G., "Separation of Cesium from Intermediate Level Liquid Radioactive Waste by Solvent Extraction with Antioxidants", Journal of Radioanalytical and Nuclear Chemistry,129(2), 265-272, 1989

18. Horner, D. E., Crouse, D. J., Brown, K. B., and Weaver, B., "Fission Product Recovery from Waste Solutions by Solvent Extraction", Nuclear Scienec and Engineering, 17, 234-245, 1963.

19. Hudson, M. J., "An Introduction to some Aspects of Solvent extraction Chemistry", Hydrometallurgy, 9, 149-168, 1982.

20. International Atomic Enerfy Agency, Vienna 1993 "Feasibility of Sep and Utilization of Cs and Sr from High Level Liquid Waste - Technical Report Series No. 356.

21. Kinard, W. F., McDowell W. J. and Shoun R. R., "Studies of the Size-Selective Extraction of Alkali Metal Ions by the Synergistic Extraction System, Crown Ether-Di(2-Ethylhexyl)Phosphric Acid-Benzene", Separation Scienec and Technology,15(4) 1013-1024,1980

22. Marcus, Y., and Asher, L.E., "Extraction of Alkali Halides from Their Aqueous Solutions by Crown Ethers", 82(11), 1246-1254, 1978

23. McDowell, W. J., and Shoun, R. R. "An Evaluation of Crown Compounds in Solvent Extraction of Metals" International Solvent Extraction Conference'77

24. McDowell, W.J., Case, G.N., and Aldrup, D.W., "Investigation of Ion-Size-Selective Synergism in Solvent Extraction", 18(14&15), 1483-1507, 1983

25. McDowell, W. J., Moyer, B. A., Case, G. N., and Case, F. I., "Selectivity in Solvent Extraction of Metal Ions by Organic Cation Exchangers Synergized by Macrocycles: Factors Relating to Macrocycle Size and Structure", Solvent Extraction and Ion Exchange, 4(2) 217-236, 1986

26. McDowell, W.J., "Crown Ethers as Solvent Extraction Reagents: Where Do We Stand?", Separation Science and Technology, 23(12&13), 1251-1268, 1988

27. McDowell, W.J., Arndsten, B.A., and Case, G.N., "The Synergistic Solvent extraction of Radium from Alkaline Nitrate Media by Dicyclohexano-21-crown-7 combined with 2-heptyl-2-methyl nanoic acid Equilibrium Reactions and Metal Ion Competetion", Solvent Extraction and Ion Exchange, 7(3),377-393, 1989

28. McDowell, W.J., and McDowell, B.L., "Solvent Extraction Methods for the Analytical Separation of Environmental Radionuclides", ACS Symposium Series, 509, 206-217, 1992

29. McDowell, W. J., Case, G. N., McDonough, J. A., and Bartsch, R. A., "Selective Extraction of Cesium from Acidic Nitrate Solutions with Didodecylnaphthalenesulfonic Acid synergized with Bis(tert-butylbenzo)-21-crown-7", Analytical Chemistry, 64, 3013-3017, 1992

30. McDowell, W. J., Kinard, W. F., and Shoun, R. R., "Size selective Synergism by Crown Ethers in the Extraction of Alkali Metals by Di(2-Ethylhexyl) Phosphoric Acid" Unpublished results

31. Morrison, G. H., and Freiser, H., Solvent Extraction in Analytical Chemistry, John Wiley and Sons, Inc. 1966

32. Nakamura, H., Takagi, and Ueno, K., "Complexation and Extraction of Alkali Metal Ions by 4'-Picrylaminobenzo-18-Crown-6 Derivatives", Analytical Chemistry, 52,1668-1671,1980

33. Pedersen, C.J., "Cyclic Polyethers and their Complexes with Metal Salts" Journal of American Chemical Society, 89, 2495-2496, 1967

34. Pedersen, C.J., "Crystalline Salt Complexes of Macrocyclic Polyethers" Journal of American Chemical Society, 92, 386-391, 1970

35. Rais, J., and Selucky, P., "New Extraction Agents for Cesium-III Complex formed between some Sodium Salts and 2,3,11,12-Dibenzo-1,4,7,10,13,16-Hexaoxocyclo-Octadeca-2,11-Diene/Dibenzo-18-Crown-6", Radiochemical Radioanalytical Letters, 6(4), 257-264,1971

36. Riley, R. G., Zachara, J. M., and Wobber, F. J., "Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research", U.S. Dept. of Energy, Washington, D.C., 1992.

37. Sakamato, H., Goto, H., Doi, K., and Otomo, M., "Compositional Variation of Ionizable Crown Ether-Alkali Metal Ion Complexes in the solvent Extraction Using Several extraction Solvents", Chemical Letters, 1535-1538, 1992

38. Shuler, R. G., Bowers, C. B., Smith, J. E., Brunt, V. V., and Davis, M. W., "The Extraction of Cesium and Strontium from Acidic High Activity Nuclear Waste Using a Purex Process Compatible organic Extractant. Solvent Extraction and Ion Exchange - 3(5), 567-604, 1985

39. Schulz, W.W., and Bray, L.A., "Solvent Extraction Of Byproduct ^{137}Cs and ^{90}Sr from HNO_3 Solutions - A Technology Review and Assessment", Separation Science and Technology 22(2&3), 191-214, 1987

40. Treybal, R.E., Mass Transfer Operations, McGraw Hill Corporation, 1980

41. Vibhute, R. G., and Khopkar, S. M., "Solvent Extraction Separation of Cesium with Dibenzo-24-Crown-8 from Picrate Solution" Journal of Radioanalytical and Nuclear Chemistry, 152 No. 2 487-496, 1991

42. Walkowiak, W., Kang, S. I., Stewart, L. E., Ndip, G., and Bartsch, R. A., "Effect of Ring Size Variation within Lipophilic Crown ether Caroboxylic Acid on the Selectivity and Efficiency of Competitive Alkali-Metal Cation Solvent Extraction into Chloroform" Analytical Chemistry, 62, 2022-2026, 1990

APPENDICES

Appendix I[a]

Amount of Activity in 10-Year-Old Waste and Relative Toxicity Due to Radionuclides

Isotope	Half Life (years)	Total activity[b] (curies)	Relative toxicity[c]
^{90}Sr	28.8	$2.0X10^8$	$2X10^9$
^{137}Cs	30.0	$2.0X10^8$	$3X10^7$
^{147}Pm	2.6	$6.7X10^7$	$1X10^6$
^{106}Ru	1.0	$3.5X10^5$	$1X10^5$
^{238}Pu	89	$1.7X10^5$	$1X10^5$
^{244}Cm	18.1	$1.2X10^3$	$6X10^4$
^{151}Sm	90	$4.6X10^6$	$4X10^4$
^{239}Pu	$2.4X10^4$	$1.7X10^4$	$1X10^4$
^{129}I	$1.6X10^7$	31	$1.7X10^3$
^{99}Tc	$2.1X10^5$	$3.0X10^4$	300
79Se	$7X10^4$	280	120
135Cs	$2.0X10^8$	$3.1X10^3$	100
126Sn	10^5	$1X10^3$	100
93Zr	$9.5X10^5$	$6.7X10^3$	30
94Nb	$2X10^4$	3.2	3
107Pd	$7X10^8$	26	3
158Tb	150	0.5	$4X10^{-5}$

[a]This table was taken from DP-MS-73-58 by R. F. Bradley, W. H. Hale, and R. M. Wallace of the Savannah Laboratory, E. I. du Pont de Nemours, Aiken, South Carolina 29801

[b]Assumed as a basis for this report and do not represent the actual quantities(classified) to be processed.

[c]Ratio of concentration in waste to maximum permissible concentration in public zone water.

Appendix II

Properties and Uses of Cs-137

Properties [IAEA Report, 1993]

1. Half life: 30 years
2. Decay: 94.6% gamma radiation of 0.66 MeV
3. Specific activity: 10-18 Ci/g as CsCl
4. Thermal heat output: 0.07W/g
5. Ionic diameter: 3.3 Å

Uses [Shulz et al., 1987]

1. Food preservation by irradiation
2. Sterilization of medical supplies
3. Irradiation of hides
4. Irradiation of municipal waste

Appendix III. Cesium and sodium extraction data for solvent extraction by crown ethers of 21C7 family are given in following tables.

[DB21C7]org,o = 0.025M
[NaNO3]aq,o = 3.00M

[Cs+] aq,o (M)	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+Loading%	D(Cs+)	D(Na+)	Total Loading%	S
4.00E-01	3.83(±0.12)E-04	2.46(±0.07)E-03	1.53(±0.05)E+00	9.86(±0.30)E+00	6.20E-03	1.28E-04	11.39	48.53
2.00E-01	3.41(±0.11)E-04	1.57(±0.01)E-03	1.36(±0.05)E+00	6.27(±0.04)E+00	7.91E-03	1.14E-04	7.63	69.50
1.00E-01	3.51(±0.08)E-04	9.10(±0.24)E-04	1.40(±0.03)E+00	3.64(±0.09)E+00	9.19E-03	1.17E-04	5.04	78.45
2.00E-02	4.07(±0.27)E-04	2.22(±0.22)E-04	1.62(±0.11)E+00	8.87(±0.89)E-01	1.12E-02	1.36E-04	2.51	82.74
1.00E-02	4.42(±0.38)E-04	1.12(±0.06)E-04	1.77(±0.15)E+00	4.47(±0.24)E-01	1.13E-02	1.47E-04	2.22	76.86
8.00E-03	4.62(±0.18)E-04	9.31(±0.05)E-05	1.85(±0.07)E+00	3.72(±0.02)E-01	1.18E-02	1.54E-04	2.22	76.35
4.00E-03	6.51(±0.03)E-04	5.51(±0.1)E-05	2.60(±0.01)E+00	2.20(±0.05)E-01	1.40E-02	2.17E-04	2.82	64.31

III.A. Cesium and sodium extraction data for solvent extraction by dibenzo-21-crown-7 using 1,2-dichloroethane as the diluent

[B(tBB)21C7]org,o = 0.025M
[NaNO3]aq,o = 3.00M

[Cs+] aq,o (M)	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+Loading%	D(Cs+)	D(Na+)	Total Loading%	S
4.00E-01	3.13(±0.03)E-04	3.28(±0.08)E+00	1.25(±0.01)E+00	1.35(±0.03)E+01	8.29E-03	1.05E-04	14.75	79.32
2.00E-01	3.49(±0.14)E-04	1.91(±0.14)E-03	1.39(±0.05)E+00	7.66(±0.55)E+00	9.67E-03	1.17E-04	9.05	82.93
1.01E-01	3.63(±0.09)E-04	1.03(±0.01)E-03	1.45(±0.04)E+00	4.11(±0.04)E+00	1.03E-02	1.21E-04	5.56	85.17
4.00E-02	4.02(±0.41)E-04	4.82(±0.09)E-04	1.61(±0.16)E+00	1.93(±0.03)E+00	1.22E-02	1.34E-04	3.54	91.12
2.00E-02	3.89(±0.12)E-04	2.52(±0.06)E-04	1.55(±0.05)E+00	1.01(±0.02)E+00	1.28E-02	1.30E-04	2.56	98.48
1.01E-02	4.12(±0.04)E-04	1.38(±0.020E-04	1.64(±0.02)E+00	5.51(±0.09)E-01	1.39E-02	1.37E-04	2.19	100.94
8.00E-03	4.16(±0.24)E-04	1.17(±0.02)E-04	1.66(±0.10)E+00	4.67(±0.10)E-01	1.48E-02	1.39E-04	2.13	106.87
4.00E-03	4.15(±0.02)E-04	5.86(±0.13)E-04	1.66(±0.07)E+00	2.35(±0.05)E-01	1.49E-02	1.39E-04	1.90	107.41

III.B. Cesium and sodium extraction data for solvent extraction by bis(tert-butylbenzo)-21-crown-7 using 1,2-dichloroethane as the diluent

[DC21C7]org,o = 0.025M
[NaNO3]aq,o = 3.00M

[Cs+] aq,o (M)	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+Loading%	D(Cs+)	D(Na+)	Total Loading%	S
4.00E-01	1.17E-02	5.31(±0.38)E-03	4.6900E+01	2.12(±0.15)E+01	1.3465E-02	3.9307E-03	68.10	3.43
2.00E-01	1.23(±0.33)E-02	3.28(±0.22)E-03	4.92(±1.33)E+01	1.31(±0.09)E+01	1.6706E-02	4.1213E-03	62.30	4.05
1.00E-01	9.81(±0.13)E-03	1.83(±0.02)E-03	3.92(±0.05)E+01	7.30(±0.39)E+00	1.8478E-02	3.2799E-03	46.50	5.63
4.00E-02	8.43(±0.40)E-03	8.05(±0.20)E-04	3.36(±0.16)E+01	3.21(±0.08)E+00	2.0556E-02	2.8178E-03	36.81	7.29
2.00E-02	9.22(±0.11)E-03	4.67(±0.23)E-04	3.68(±0.04)E+01	1.86(±0.09)E+00	2.3924E-02	3.0842E-03	38.66	7.76
1.00E-02	9.17(±0.06)E-03	2.85(±0.02)E-04	3.74(±0.14)E+01	1.140(±0.007)E+00	2.9162E-02	3.1345E-03	38.54	9.30
8.00E-03	9.27(±0.14)E-03	2.27(±0.03)E-04	1.40(±0.05)E+01	9.09(±0.13)E-01	2.9290E-02	3.1017E-03	14.91	9.44
4.00E-03	9.32(±0.26)E-03	1.30(±0.03)E-04	3.72(±0.10)E+01	5.20(±0.11)E-01	3.3700E-02	3.1158E-03	37.72	10.82

III.C. Cesium and sodium extraction data for solvent extraction by dicyclohexano-21-crown-7 using 1,2-dichloroethane as the diluent

[DB21C7]org,o = 0.025M
[NaNO3]aq,o = 3.00M

[Cs+] aq,o (M)	[Na+]org (M)	[Cs+]org (M)	Na+Loading%	Cs+Loading%	D(Cs+)	D(Na+)	Total Loading%	S
4.00E-01	8.27(±0.32)E-03	3.07(±0.42)E-03	3.30(±0.13)E+01	1.22(±0.17)E+01	7.74E-03	2.77E-03	45.20	2.80
2.00E-01	1.05(±0.03)E-02	2.16(±0.05)E-03	4.19(±0.12)E+01	8.62(±0.02)E+00	1.09E-02	3.52E-03	50.52	3.10
1.01E-01	1.105(±0.007)E-02	1.362(±0.009)E-03	4.41(±0.03)E+01	5.44(±0.04)E+00	1.37E-02	3.70E-03	49.54	3.71
4.00E-02	1.13(±0.05)E-02	7.12(±0.80)E-04	4.50(±0.20)E+01	2.84(±0.32)E+00	1.81E-02	3.77E-03	47.84	4.81
2.00E-02	1.17(±0.03)E-02	4.24(±0.11)E-04	4.68(±0.12)E+01	1.69(±0.04)E+00	2.17E-02	3.92E-03	48.49	5.53
1.01E-02	1.19(±0.02)E-02	2.98(±0.12)E-04	4.77(±0.07)E+01	1.19(±0.05)E+00	3.05E-02	4.00E-03	48.89	7.63
8.00E-03	1.23(±0.01)E-02	2.91(±0.16)E-04	4.93(±0.05)E+01	1.16(±0.06)E+00	3.78E-02	4.13E-03	50.46	9.15
4.00E-03	1.19(±0.02)E-02	2.30(±0.04)E-04	4.77(±0.07)E+01	9.22(±0.16)E-01	6.12E-02	3.99E-03	48.62	15.32

III.D. Cesium and sodium extraction data for solvent extraction by dibenzo-21-crown-7 using n-octanol as the diluent

VITA

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