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CROWN ETHERS AS SOLVENT EXTRACTION REAGENTS: WHERE DO WE STAND?*

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ABSTRACT

It is perhaps prophetic that among the first applications of crown ethers was their use as solvent extraction reagents. In 1962 the compound 2,3,11,12-dibenzo-1,4,7,10,13,16-hexaoxacycloocta-2,11-diene, now mercifully called dibenzo-18-crown-6, was identified and was found to form alkali-metal-salt adducts that were soluble in organic solvents. These serendipitously discovered extraction properties of crown ethers were later used to compare the complex-formation properties of metal ions with crown ethers, and it was observed that salts of organophilic anions were more readily transferred to aprotic solvents. Picrate salts were extensively used in this role. However, those seeking analytical or process applications of the unusual complexing abilities of macrocycles needed the aqueous anion to be one of the more common mineral acid anions such as chloride, nitrate, or sulfate. This problem was circumvented in the late 1970's when it was discovered that crown ethers mixed with an organophilic cation exchanger such as alkyl phosphoric, alkyl-aryl sulfonic, or carboxylic acid, would produce synergistic extraction systems having excellent and selective affinities for a large number of metal ions. In 1981, macrocyclic compounds with

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attached carboxylic acid groups were synthesized and found to be excellent extractants. In addition to liquid-liquid extraction, much work has been done using macrocycles as separation agents in membranes and resin beads. Fundamental research is now beginning to provide the stoichiometries and structures of some of the organic-phase complexes produced and an understanding of the reactions in these extraction systems. At the same time, some potential uses of these systems are beginning to be identified.

INTRODUCTION

Some of the first uses of crown ethers were as solvent extraction reagents in which picrate was used as the organophillic anion. The purpose of these experiments was to examine the relative complexation of alkali metals with crown ethers by measuring their extraction, or more usually, photometrically meauring picrate extraction, into chloroform solutions of the various crown ethers as an indicator of strength of complexation.(1-6) The crown-ether/chloroform/water/metal-picrate extraction systems are, in fact, synergistic since the distribution coefficients obtained with the crown-ether/picrate combinations are often greater than the sums of those obtainable with the same concentrations of the reagents used separately. Since 1967, when Pederson published studies of alkali metal extraction by crown ethers in chloroform, many similar studies using picrate as the anion and chloroform as the carrier diluent have been reported. (See for example references 7 to 40.) Such studies have served to establish the selectivity and general behavior of the crown ethers, particularly with regard to complexation with the alkali and alkaline earth metals. These studies have also attracted the attention of solvent extraction and ion exchange chemists since selective extraction of alkali and alkaline earth elements are usually not easily accomplished.

In the early history of crown ethers as solvent extraction reagents, most of the available crown ethers and related macrocycles were poorly suited for practical solvent extraction reagents, particularly in process solvent extraction, and only marginally suited for analytical chemistry procedures. For example, the benzo-substituted crowns have very limited solubility in the low polarity diluents such as aliphatic (kerosene-like) and substituted aromatic diluents and thus would not be usable in preferred process solvent extraction

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diluents. Other crown ethers, having no substituents on the crown ring, are highly soluble in aqueous systems and are thus not useful in practical systems. Further, practical process (and often analytical) systems are limited to the use of sulfate, nitrate, and chloride as anions. Extraction from these common mineral acid systems by crown ethers alone are usually not practical.(41) In addition to the use of organophilic aqueous phase anions such as picrate, thiocyanate, perchlorate, iodide, and others, several other strategies have been used to adapt crown ethers for use in practical extraction systems. The first, on which the other three are dependent, has been to attach organophilic substituents to the crown ether ring so that the crown ether stays in the organic phase and is not lost to the aqueous phase. Four other strategies have dealt with the problem of transferring a highly-hydrated mineral-acid anion and cation to an organic phase of low polarity. They are 1) using a high anion concentration in the aqueous phase, 2) using additives or "modifiers" to increase the organic phase polarity and improve the ion solubilizing ability of the organic diluent, 3) adding an organophilic acid to the organic phase to act as a reusable cation exchanger, and 4) attaching a pendent acid group to the crown ether structure so that it becomes both a size-selective coordinator and a cation exchanger.

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It should also be noted that these versatile complexing agents have been applied to separations utilizing liquid membrane, supported membrane, and column chromatography technologies.(42-51) In all of these, the extraction equilibria are expected to be identical to that found for the same compound in liquid-liquid extraction systems; however, the kinetics of the system will be different; i.e., slower in membrane systems because of the time necessary for diffusion of the metal ions through the organic phase and because the interfacial area is usually more limited than in a solvent extraction dispersion. Membrane systems will not be included here because of limited space. Also beyond the scope of this paper is the potential application of this science to biological reactions where molecular recognition by pre-positioned binding sites is an important part of life processes. A fundamental understanding of the structure and bonding in macrocycle/metal complexes may contribute to the unraveling of complex interactions occuring in living organisms such as the recognition of foreign protein by antibodies or the functioning of enzymes and hormones. Such information about crown ethers is being generated.

The purpose of this paper is to examine the progress that has been made to date toward the use of crown ethers and related macrocycles as practical analytical and process solvent extraction reagents. It is not an exhaustive review of the subject, but enough material has been covered, I believe, to provide a good perspective of "Where we stand". Much of the information herein has been gratefully appropriated from the referenced publications. A little of it we have generated in our own laboratories.

DISCUSSION

Requirements for a Successful and Practical Solvent Extraction Reagent

Reagent distribution and solubility: Reagents for hydrometallurgical processes, such as the recovery of copper or uranium from ore leach liquors or the reprocessing of nuclear fuel, must be soluble in kerosene-like diluents (possibly with some aromatic content) and virtually insoluble in (that is, not distributed to) the aqueous phases against which they are to be equilibrated including both value-bearing head solutions and stripping solutions. In addition, any adducts that the reagent may form with anions from the aqueous phase (example, amine salt as extractant) or with metal ions from the aqueous phase (organic acid salt as extractant) including the organic-phase-extracted complex must also be soluble in the organic diluent chosen and not soluble in, or distributed to, the aqueous phase. If any of these processes carry the reagent into the aqueous phase in any significant amounts (greater than a few parts per million), economically important quantities of the reagent will be continuously lost to the discarded aqueous raffinate solution. The cost of replacing this reagent can easily exceed the value of the recovered metal. For this reason, solid ion exchangers are often used in situations where the metal concentration in solution is low or the value of the recovered metal is not great.

Few crown ethers meet the above criteria. The distribution to water of simple unsubstituted oxa crown ethers such as 12-crown-4 (12C4) or 18-crown-6 from a 0.1 M solution in toluene is 80 to 90%. Benzo-14-crown-4 (B14C4), *tert.*-butylcyclohexano-15-crown-5 (*t*BC15C5), *tert.*-butylbenzo-15-crown-5 (*t*BB15C5), dicyclohexano-18-crown-6 (DC18C6), di(*tert.*-butylcyclohexano)-18-crown-6 (D(*t*BC)18C6), di(*tert.*-butylbenzo)-18-crown-6- (D(*t*BB)18C6), dicyclohexano-21-crown-7 (DC21C7), and di(*tert.*-butylbenzo)-21-crown-7 (D(*t*BB)21C7), in use in

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the author's laboratory, range in distribution to water from a 0.1 M solution in toluene from 5% for DC18C6 to ~ 0.1% for the di(*tert.*-butyl)-substituted compounds. It is obvious that organophilic substituents are necessary to achieve an acceptably low aqueous-phase distribution for the crown ethers. This was recognized by many in this field some years ago, and Tusek, Danesi, and Chiarizia published the synthesis of a bis(3,5-di *tert.*-butylbenzo)-18-crown-6 as an example of the type of crown ether required.(52)

Aqueous anion: Another requirement usually included in process solvent extraction (process SX) applications is that the anion in the head aqueous solution be one of the common mineral acid anions, sulfate, chloride, or nitrate. This is usually because of economic considerations (other reagents are too expensive) and sometimes because of corrosion problems in available or affordable materials of construction for the chemical process equipment. Crown ethers alone in low-polarity solvents do not extract alkali, alkaline earth, or first-row transition elements from dilute mineral acid solutions with any reasonable distribution coefficients.(41) Distribution coefficients are almost always lower than 1, being ca. 10^{-4} to 10^{-5} for 0.1 *M* crown ether in toluene in many cases.(53,54) Presumably, this is because of the large amount of energy required to remove the water of hydration from the anion (and perhaps the cation) or to transfer the hydrated ions to the organic phase. Extraction of metals from high concentrations of the inorganic anions, nitrate and chloride, have been reported, with mercury showing the highest distribution coefficient of the metals tested.(53) The additives, dinonylnaphthalene sulfonic acid (HDNNS), tributyl phosphate (TBP), and caprylic acid, increased the extraction of potassium and rubidium somewhat.(55) Gloe et. al.(54) examined a variety of systems and found acceptably high extractions for some metals with chloride and thiocyanate.

Although anions such as picrate, thiocyanate, iodide, bromide, and perchlorate have a degree of organophilicity and may allow the metal ion to be extracted by the crown ether as the existing aqueous salt, the use of such anions in processes is usually not acceptable because of cost or because the inclusion in the aqueous phase of these salts or acids complicates disposal of the raffinate waste.(56) These constraints are less severe in analytical applications.

If a solvent extraction system is to be used in an assay or analytical laboratory, some loss of the reagent to the aqueous phase can be tolerated; but obviously, not much loss of the complex can be tolerated. Also, a wider choice of diluents is acceptable for use in analytical applications. Thus, diluents such as ether, chloroform, or carbon tetrachloride, while generally very undesirable in a process, may be useful in the analytical laboratory. In general, a much wider range of solubility properties can be tolerated in analytical than in process applications.

Selectivity: For many applications, the ideal extractant would be completely selective; that is, it should extract the desired element with a high distribution coefficient and extract nothing else. Few extraction systems meet these standards. Usually one is lucky to find a system that extracts the desired element reasonably well and extracts little of the undesired elements in the particular solution with which they are faced. Multiple extractions and/or countercurrent systems are standard techniques for dealing with less-than-perfect separations. Reagents for analytical separations usually need quantitative extractions for the desired element but can often tolerate extraction of several other ions since prior removal of strongly competitive ions may be possible. Thus, the analytical SX reagent may need to be selective only within certain classes of elements. In some process applications, the ability to extract more than one element is useful if selective stripping can be done.

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Stripping: Irreversible extraction, or extraction that is so strong as to be difficult to reverse by simple means, is usually useful only in analytical chemistry where methods such as spectrophotometry, flame photometry, atomic absorption, or nuclear radiation counting may be used to make the desired determination with the element in the organic phase. (57-60) In all process applications in current use and in many analytical applications, it is necessary to back extract or "strip" the element of interest from the organic extractant into a new aqueous phase. The desired element is usually concentrated both on extraction and on stripping. This is one of the advantages solvent extraction can offer over resinous ion exchange. Crown ether extraction systems can be stripped by one or more of the methods common in other solvent extraction procedures such as changing the aqueous acidity or anion concentration from that in the original aqueous phase or contacting the organic phase with an aqueous phase containing a different anion.

Costs: The discussion of costs of SX reagents could become very complicated since acceptable costs depend on so many factors. Although it can be said in general that analytical applications can tolerate higher reagent costs than can processes, a wide range of allowable reagent costs are possible in process applications. The following factors all allow a higher acceptable reagent cost: (a) high value (or perceived high value) of the recovered material, (b) high concentration of the material to be recovered in the feed stream, and (c) a low rate of reagent loss in the process.

In making a preliminary judgment about the economics and the possible success of an SX reagent, one should remember at least the following: 1) Experimental reagents can (and usually do) cost orders-of-magnitude more than the same reagent manufactured in quantity. Thus, judging process economy on the basis of cost of the experimental reagents is probably not valid. 2) Estimating the cost of synthesizing reagents is difficult. The price of everything tends to decrease as soon as substantial demand is established. 3) If a process for separating the element already exists, it is difficult to implement the use of the new method, even though it is better. Investment in hardware to do the separation the old way and human resistance to change require that the new separation be not just better, but much, much better; so much better that large financial advantages are immediately apparent. As an example; - reagents better than TBP (tributyl phosphate) as regards organic phase solubility and loss to the aqueous phase, i.e., trihexyl phosphate and tri(2-ethylhexyl) phosphate,(61) have been known for several years. They are available, their price is approximately that of TBP, and their performance is sufficiently like TBP that they could be used in the same equipment; and yet these compounds are not used, in fact, have never even been tried in process scale.

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Toward the Use of Crown Ethers as Solvent Extraction Reagents

Analytical Procedures:

There have been many reports in the literature that describe separations of ions, particularly the alkali and alkaline earth ions, using crown ethers. Some of these separations appear suitable for (or were designed for) use in analytical procedures(62-65), although in most cases it is not known whether the procedure is actually being used or not. In several analytical procedures, the ion-of-interest is extracted into the crown-ether-containing organic phase, and the analysis is performed without removing (stripping) the ion from the organic phase. By way of example, Xie, Wang, and Lang describe a procedure for the determination of copper and lead by atomic absorption after extraction with crown ethers.(66) Aleksyuk, Nazarenko, and

Table 1

Separation Factors for Radium from Selected Elements When Extracted from a Solution of the Mixed Nitrates

Ba - 9.3	Li - 8.8×10^3
Sr - 12.3	Zn - 7.0×10^6
Ca - >58	Th - 3.7×10^6
Mg - >564	U - 6.2×10^6
Be - 2×10^6	Cs - 1.9×10^5

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Pyatnitskii extracted metal ions into a mixture of crown ethers and a sulfophthalein dye (the dye probably acting as a cation exchanger) and measured the resulting organic-phase color change. (67) Takagi et. al. (68) reported the use of a crown ether that formed a colored complex with potassium or rubidium on extraction into a chloroform solution of the chromogenic crown ether reagent. Several reviews of the use of crown ethers as analytical separations agents have been published. (69-71) The author and his colleague, G. N. Case, use a toluene solution composed of DC21C7 (dicyclohexano-21-crown-7), 0.05 *M*, an organophilic neocarboxylic acid, 2-methyl-2-heptylnonanoic acid, 0.1 *M*, a fluor, PBBO [2-(4'-biphenylyl-6-phenylbenzoxazole)], 4 g/L, and an energy transfer agent, naphthalene, 180 g/L to quantitatively extract radium for analysis with the PERALS (Photon-Electron Rejecting Alpha Liquid Scintillation) spectrometer. (57) The extraction is made from ~ 0.5 *M* nitrate solution at pH 10 to 12. Under these conditions, the extraction coefficient is >150, and the separation factor from barium is 9 to 10. Separation factors from some other commomly-associated metals are shown in Table I. (72)

Because of the reasonably large separaration from barium, it is possible to make an initial concentration of radium from dilute sources by co-precipitation with barium sulfate. The barium/radium sulfates are then converted to carbonate with potassium carbonate, dissolved in dilute acid, and the radium extracted quantitatively into the scintillator. Since the organic extract already contains a fluor and an energy transfer agent, it can be counted in a PERALS detector without further treatment. This method is both more rapid and more accurate than most presently used procedures and is being considered by several laboratories for environmental monitoring of radium.

Process Solvent Extraction:

Five promising approaches to practical use of crown ethers as extractants were mentioned in the Introduction.

The first, adding substituents to the macrocycle to make it more organophilic, has been widely practiced. (73,74) To a large extent this synthesis of substituted macrocycles has been the result of scientific curiosity in general and not directed strongly toward improved solvent extraction performance except for a few notable examples. (52,75-77) Many compounds suitable for solvent extraction research are now commercially available in experimental quantities. In general, these are the dicyclohexano- and di(tert.-butylbenzo)-substituted compounds. Attempts to prepare more highly organic-weighted compounds are currently being made.

The second approach, loading the aqueous phase with an "inert" salt or acid, has been and is being explored. (53,54) This is a promising approach if a macrocycle is used that is already sufficiently substituted so that its tendency to distribute to the aqueous phase is small. Jepson and co-workers (78-80) have partitioned calcium and other metals between concentrated aqueous salt solutions and organic solutions of crown ethers in isotope-separation processes. Salting the aqueous phase in this way may reduce the aqueous loss to an acceptable level. The difficulties in the salting approach are: 1) It is sometimes difficult to find a sufficiently "inert" cation; and at concentrations sufficient to produce the desired salting effect, the salting cation may compete effectively for the macrocycle. Distribution coefficients and loading will thus be lowered to unacceptable levels. 2) The cost of salt for a highly salted system and the disposal of raffinate may pose serious problems if the salt cannot be recycled in some way.

The third approach, using additives or modifiers to increase the tolerance of the organic phase to polar inorganic ions, has also been sucessful in some cases. Acceptable extractions have been achieved(41) and processes have been outlined using modified diluents. The addition of a cresol or a substituted cresol has been proposed for a process for extracting potassium chloride from Dead Sea brines. (81,82) Similarly, the extraction of potassium chloride from magnesium chloride has been found to be increased by the addition of nonylphenol or 2-ethylhexanol. The use of nitrobenzene as a diluent has been proposed in a process for the extraction of cesium and strontium from nuclear fuel reprocessing waste. (83-85) The problems with these approaches to the practical use of crown ethers have been loss of the diluent or modifier to the aqueous phase. This loss may be tolerable in some situations, but in others either cost or environmental concerns may make this approach unacceptable.

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In the fourth approach, a high-molecular-weight organophilic acid is mixed with an organophilic crown ether in the diluent. In this system, the organic-phase acid can exchange its proton for the metal ion, and the resulting organophilic salt can be coordinated by the crown ether. The problems of the transfer of an inorganic anion to the organic phase are thus avoided. In addition, it is usually possible to use simple diluents with such systems. Toluene, octane, dodecane, and kerosene have all been successfully employed. The organophilic acid and the crown ether often form intermolecular compounds in these mixtures thereby enhancing the organophilicity of both components usually at the expense of decreased synergism. In the author's laboratory, tests with octane as the diluent have shown that the distribution coefficients obtained are similar to those obtained with toluene as the diluent, phase separations are better, and metal separation factors are as good or better. In addition to the work at Oak Ridge National Laboratory,(86,87) these mixed acid/crown-ether systems have been explored at Brigham Young University,(88,89) Tennessee Technological University,(90) and the University of South Carolina, Columbia.(91) From this last location comes a full-fledged process designed to remove cesium and strontium from nuclear waste.

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Mixtures of organophilic acids and crown ethers often display synergistic extraction properties; that is, the extraction coefficient obtained with the mixture is greater than the sum of the extraction coefficients obtained with the separate reagents. Figure 1 illustrates the described synergistic effect in which dicyclohexano-18-crown-6 (DC18C6) and a neocarboxylic acid are used to extract strontium.(92)

In the author's laboratory, a variety of organophilic acids have been tested for this application(92), and bis(2-ethylhexyl)phosphoric acid (HDEHP), didodecylnaphthalene sulfonic acid (HDDNS), and several 17- to 24-carbon neocarboxylic acids have been chosen as suitable for further investigation.

With the above approach, several separations have been identified that appear to have the potential for useful and practical solvent extraction systems. Figure 2a shows the separation of potassium from the other alkali metals using DC18C6 and HDDNS 0.1:0.05 *M* in toluene. Actually, the maximum extraction for potassium with this mixture occurs at a 1:1 ratio and had the distribution coefficients for potassium been measured at that ratio, they would have been higher. Also, in general, higher distribution coefficients are obtained for the alkalis and lower distribution coefficients for the alkaline earths with di(*tert.*-butylbenzo)-18-crown-6 (D(tBB)18C6), but our data are less complete for this crown ether. Strontium, barium and radium, also extracted by these systems, can be subsequently or previously separated from the potassium by using DC18C6 with a carboxylic acid. Most of the alkalis or alkaline earths can easily be separated from the first-row

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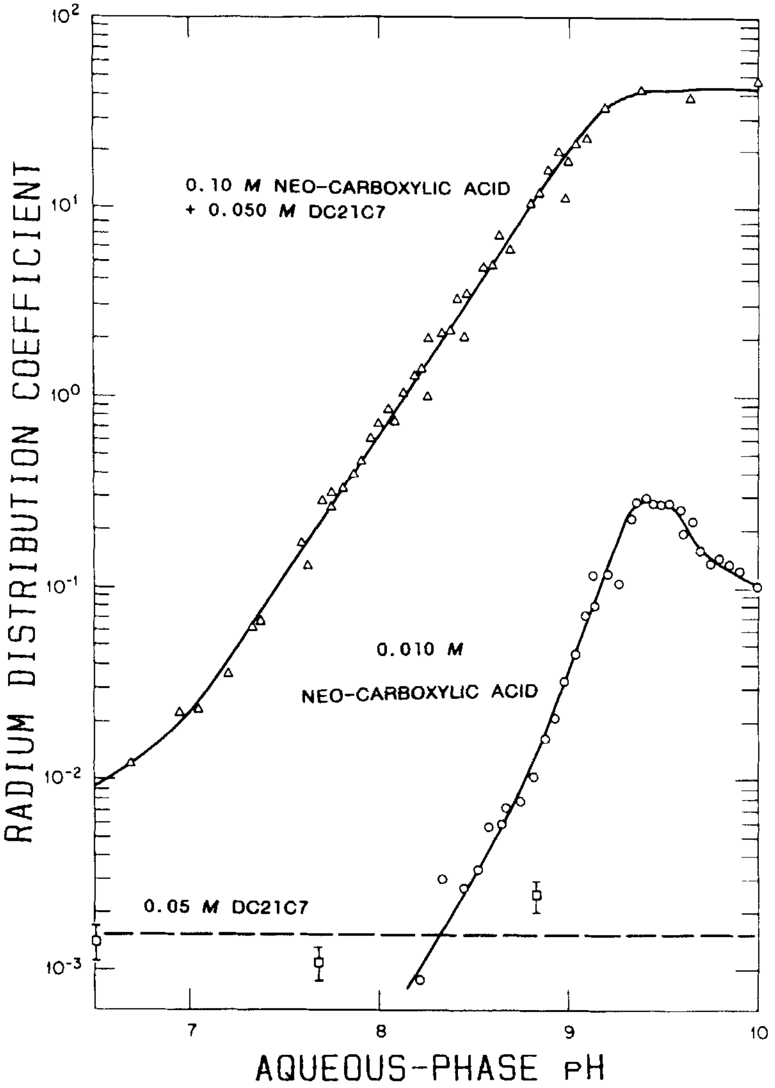

Fig. 1. Radium Extraction from 4 M $NaNO_3$ by DC21C7, a Neo-carboxylic Acid, and The Two Mixed.

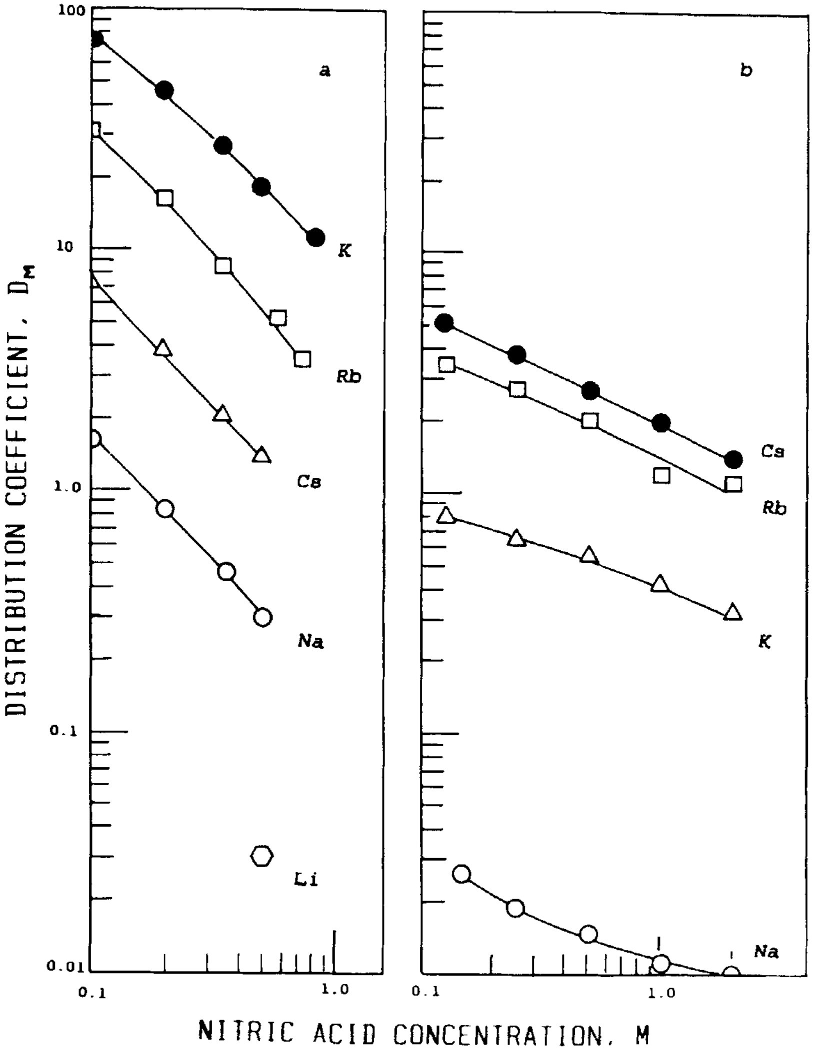

Fig. 2. Alkali Metal Extraction by Didodecylnaphthalene sulfonic acid (HDDNS) As Modified by DC18C6 (a) and D(tBB)21C7 (b).

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transition elements using HDDNS and the appropriately substituted 15C5, 18C6, or 21C7 (compare the separations in Ref. 92 with those in Ref. 93). The use of a carboxylic acid enhances the extraction of alkaline earth elements relative to the alkali metals. In a few trials these separations worked equally well from nitrate, chloride, or sulfate media. Thus the aqueous anion appears to make little difference in the extraction and separation of the relatively non-complexing alkali and alkaline earth elements. Very recently three additional separations have emerged from our systematic studies of the mixed crown ether - organophilic acid systems that appear to have high potential as practical and useful solvent extraction systems. The extraction of radium has been mentioned previously. The other two are 1) a selective extraction for cesium and 2) a selective extractant for copper(II), silver, and possibly gold. (94) The reagent that would be necessary for the selective extraction of cesium was predicted from systematic studies of the macrocycle/organophilic-acid systems. It was observed that benzo-substituted crown ethers were, in general, more selective for alkali metals, whereas cyclohexano-substituted macrocycles were selective for alkaline earths. (93) Choosing the 21-crown-7 ring as the correct size for cesium and *tert.*-butylbenzo as the necessary organophilic substituent (since the benzo substituted 21C7 without a *tert.*-butyl group is not sufficiently soluble in low polarity solvents, ~ 0.01 *M* in toluene, less in dodecane) resulted in the prediction that di(*tert.*-butylbenzo)-21-crown-7 should synergize the extraction of cesium selectively. This crown ether was not available but was synthesized for us at the organic chemistry laboratories of Texas Tech University under the direction of Professor R. A. Bartsch. We were extremely gratified to find that the predicted compound was, indeed, an excellent and selective synergist for cesium. Figure 2b shows distribution coefficients for cesium and several other elements using this crown ether and HDDNS in toluene in a 0.05:0.05 *M* mixture. It is believed that this extraction system has the characteristics necessary to be of practical usefulness either in a separation process or an analytical procedure. It should be noted that the radiation stability of this system has not been determined, and this would be necessary before serious consideration of the extractant system in nuclear fuel reprocessing schemes would be possible.

Although most of the investigations here and elsewhere have been with oxa crowns, the thia-crowns have also received some deserved attention. (35, 94-103) In order to be useful, it is necessary that these compounds meet the same criteria of solubility and distribution that were outlined above for extraction reagents in general. Actually, the thia-crowns appear to be more organophilic than the corresponding oxa-crowns. Bruce A. Moyer of our group found that tetrathia-14-crown-4 in combination with HDDNS is selective for copper and silver from acid sulfate solutions of the kind resulting from a sulfuric acid leach of oxidized-layer copper ore. Iron (III) and (II), the principal impurities in this leach liquor, are not extracted. This

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compound, or substituted variations, appears to have properties that give it considerable potential as a process copper extractant.

In the fifth approach to usable crown ether extraction systems, a proton-ionizable group is attached to the crown ether structure so that the crown ether molecule is both a cation exchanger and a coordinator.(104-113) This arrangement has the potential for being both a stronger and more selective extractant system than one in which the organophilic acid is simply mixed with a crown ether. However, the reagent may be more expensive to make and perhaps more fragile in the presence of strong reagents or radiation. Again, tests for reagent stability have not yet been performed with these compounds.

Exellent selectivity for lithium has been reported for one of the carboxylic acid crown ethers.(114) The position of the acid group relative to the crown compound cavity should be important in the complexation of a given ion, and such a study of crown ethers with pendent phosphonic acid groups has confirmed that this is true, at least in the extraction of alkali metals.(104) The effects of various solvents on the selectivity of the carboxylic acid crown ethers for alkali metals have also been studied.(115)

And last, but not least, a considerable amount of fundamental chemical information exists in the literature on crown ether solvent extraction systems which cannot be covered in this paper (for example see Refs 73 and 116 to 120). It must suffice to say that enough is known about the extracted species and their structures to be a useful guide in the design of new reagents and extraction systems.

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CONCLUSIONS

The use of macrocyclic compounds, or more broadly, pre-positioned multidentate coordinators, as separations agents, is an emerging technology with potential (including, eventually, applications in biological systems) that we are only beginning to recognize. It appears that certain macrocycles have sufficient metal ion selectivities to make simple some otherwise difficult separations by solvent extraction methods. Separations of Group I and II and first-row transition metals from complex matrices can reasonably be applied now in analytical procedures and perhaps in some specialized processes. Reagent cost, and in some cases aqueous distribution of the reagent, prevent the macrocyclic compounds from being appropriate for large scale processes at this time. However, use of these compounds in analytical and specialized small-scale procedures will undoubtedly inspire preparative organic chemists to develop economical methods of synthesizing these compounds with the necessary phase distribution and metal coordinating properties. There appears to the author to be little doubt that macrocyclic compounds will play an important part in separations chemistry in the near future.

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