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BY DI(2-ETHYLHEXYL) PHOSPHORIC ACID*

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ABSTRACT

Although the macrocyclic polyethers, known as crown ethers, complex metal ions and do so preferentially according to the size correspondance between the ion and the crown ether cavity, their usefulness as liquid-liquid extraction reagents has been limited by the necessity of solubilizing the anion in the organic phase. The common mineral acid anions are difficult to transfer to the organic phase and organophilic anions are expensive or impractical. A method is described that avoids this problem by combining organic-soluble cation exchangers with the crown ethers in the organic phase. The resulting mixtures show synergistic extraction for cations, and for the alkali metal ions the synergistic effect is size-selective. The size-dependence of the synergistic extraction in the system di(2-ethylhexyl) phosphoric acid/crown ethers parallels the extraction of picrate salts of the alkali metals and of the complex formation of the alkali picrates with crown ethers. A preliminary evaluation of concentration dependencies in the extraction of potassium by di(2-ethylhexyl) phosphoric acid-dicyclohexo-18-crown-6 mixtures in benzene suggests an organic phase complex containing two alkyl phosphoric acid groups and one crown ether per potassium.

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INTRODUCTION

Although the existence of cyclic polyether compounds has been known for several decades, Pedersen (1-4) was the first to systematically synthesize and investigate the properties of these unusual molecules. The most notable of these properties is their ability to form complexes with alkali metal salts and to form the strongest complexes when there is good correspondence between the size of the alkali metal ion and the cavity in the cyclic polyether. Pedersen synthesized a large number of polyethers with cavity sizes appropriate for all the alkali metals. He called these compounds "crown" ethers because of their structural resemblance to a crown and created a trivial nomenclature in which the number of atoms in the polyether ring was denoted by a number followed by the word "crown," followed by the number of ether oxygens. Thus, 18-crown-6 is an eighteen atom ring consisting of 12 carbon atoms and six oxygen atoms.

Stability constants for many alkali metal-crown ether complexes have been measured by various methods both in water solution and in methanol solution (5). These measurements show the expected tendency for the crown ether-alkali metal pairs with the best size-correspondence to be most stable. They also show the stability in the presence of water to be less, indicating competition between the crown ether complexing and ion hydration. Since most of the crown ethers were organophilic to some degree and since they would complex and solubilize a variety of alkali metal salts into organic phases, they were used to transfer to organic phases catalytic agents that are normally soluble only in an aqueous phase. This procedure is referred to as phase-transfer catalysis.

The possibility of using crown ethers as liquid-liquid extraction (solvent extraction) reagents in analytical and hydrometallurgical applications was quickly recognized.

Frensdorff used solvent extraction of alkali metal picrates by chloroform solutions of crown ethers as a means of evaluating the relative strength of crown ether complexes (6). Size selectivity was observed as expected. Distribution coefficients, D_M (organic phase metal concentration/aqueous phase metal concentration) were very low but were larger when the large organophyllic picrate anion was used than when mineral acid anions such as sulfate, chloride or nitrate were used. The difficulty of solubilizing the mineral acid anions in non-polar organic phases is a primary problem in applying the size selective properties of crown ethers to hydrometallurgical or analytical extraction problems since economics and practicality often dictate the use of the common mineral acids. A process for the separation of potassium chloride from other metal chlorides in a brine solution has been developed using the concept of an anion-solvating diluent (7). A polar solvent, m-cresol, was found suitable for solvating the chloride anion and enhancing the extraction of the potassium-chloride ion pair into the organic phase.

McDowell and Shoun have used a different approach to the problem of anion solvation (8). In their work, they mixed an organic-phase soluble cation exchanger with the crown ether so that the necessity of transferring the inorganic anion to the organic phase is eliminated. In this system the cation in the aqueous phase is exchanged at the interface for the hydrogen of the organic-phase acid. The metals then exist as an organic-phase-soluble salt

with which the crown ether can easily coordinate. Large and dramatic effects by dicyclohexo 18-crown-6 on the order of extraction of alkali metals by di(2-ethylhexyl) phosphoric acid (HDEHP) have been observed and reported (8,9). This study expands upon these early observations and reports a systematic examination of the extraction behavior of the alkali metals with several crown ethers mixed with HDEHP.

EXPERIMENTAL

Crown ethers were obtained from Parish and Aldrich Chemical Companies at stated purities of 99+% and were used without further purification. No attempts were made to separate the structural isomers of the dicyclohexo-substituted crown ethers and the results reported thus represent a compositional average of the two isomers. The HDEHP was purified by copper(II) precipitation and molecular distillation according to published procedures (10,11). The didodecyl naphthalene sulfonic acid (HDDNS) was prepared in this laboratory and the neocarboxylic acid (V-Acid) was obtained from Shell Development Laboratories and purified by molecular distillation.

All alkali metal salts used were reagent grade. The radionuclides were obtained from New England Nuclear Company. Their radiochemical purity was verified by gamma spectrometry. The nuclides used were ^{22}Na , ^{42}K , ^{86}Rb , and ^{134}Cs , and were chosen to ensure that they did not give rise to radioactive daughters that might interfere with the experiment. Lithium was determined by atomic emission spectrometry using a Perkin-Elmer Model 460 atomic absorption spectrophotometer. Reagent grade benzene was used as the diluent in all experiments.

The organic phase for the liquid-liquid extractions was prepared by diluting the appropriate, weighed amount of reagent with benzene. In the systematic studies, where extraction reagents were used separately or combined, the formal concentration of crown ether was 0.250 M and that of HDEHP was 0.125 M. In these tests, the experimental procedure involved the equilibration of approximately 10 ml of the aqueous phase with approximately 10 ml of the organic extractant phase. The pH of the solution was adjusted to near 6 using a 0.125 M solution of the metal hydroxide under study. The radioactive tracer was added, and the phases were mixed for five minutes to ensure that equilibrium was obtained. Mixing was accomplished in a 30 ml vial using a magnetic stirrer and the aqueous phase pH was monitored with an Orion Model 801 digital pH meter. Dilute nitric acid was added incrementally by a microburet to titrate the solutions to lower pH values. After each acid addition and equilibration, stirring was stopped and the phases were allowed to separate. Aliquots of 0.200 ml of each phase were removed for analysis and counted on a single channel Packard Auto-Gamma scintillation spectrometer. Counting times were adjusted to give statistical counting errors of less than 1% with the exception of extremely low counting samples. Titration-equilibrations were performed with crown ether alone, HDEHP alone, and with the two reagents mixed.

Phase separation was poor above a pH of about 5.5 when HDEHP was present because of the conversion of a large fraction of HDEHP to the interface-active alkali metal salts above this pH. Extraction coefficients at pH values below 2.5 for systems containing HDEHP and at all pH values when using crown ethers alone were very low ($D_M \leq 10^{-4}$); thus the counting rates obtained in the organic layer in these equilibrations were near the analytical limit.

RESULTS AND DISCUSSION

Preliminary Tests

Crown ethers were tested in combination with a variety of available extractants. These included tributylphosphate, trioctylphosphine oxide, a secondary and tertiary alkyl amine, a carboxylic acid, a sulfonic acid, and HDEHP. Cations and associated anion systems were chosen that were known to give moderate extraction, and a crown ether was chosen for test that had a cavity to match the ion diameter. No synergistic effect was noted with the neutral phosphorus extractants and only a slight synergistic effect with the amines. All the extractants that were cation exchangers showed sizable synergistic effects.

These are listed in Table 1. Di(2-ethylhexyl)phosphoric acid was chosen for further systematic examination because of the existence of a large body of data on the extraction of alkali metals by this reagent.

Size-Selective Synergism

A typical illustration of the synergistic effect of the crown ether on alkali metal extraction by HDEHP is shown in Fig. 1. The effect varies with pH, and the synergistic factor (distribution coefficient for the mixture, divided by the sum of the distribution coefficients for the individual components used alone) is a maximum at about pH 4. In all equilibrations where the crown ether was used alone, distribution coefficients for the

alkali metals were $\leq 10^{-4}$ and there was no dependence on aqueous phase pH within experimental detection. The lack of pH dependence (Item 5, Table 2) is as would be expected for this reagent since the crown ether should extract by neutral molecule association and not by cation exchange.

The extraction of alkali metals by HDEHP is a cation exchange process and a plot of $\log D_M$ vs pH should have a slope of 1 as has been demonstrated by earlier work (12). The data shown in Items 4 and 6, Table 2 and in the lower group of curves in Fig. 2 are in reasonable agreement with this idea and show further that under the conditions of this work (trace metal ion; no competition for extraction) there is little difference in the extraction coefficients for the various alkali metals.

The upper group of curves in Fig. 2 shows the effect of adding 0.25 M DC18C6 to the HDEHP solution. The extraction of all the alkali metals is synergized, with potassium extraction being synergized most strongly, as would be expected from the correspondence in ion and cavity size. Synergistic factors were calculated using corresponding data for other crown ethers plus data for extraction by the crown ether alone, for each of the crown ethers tested, grouped in sets like that in Fig. 1 and smoothed by least-squares. The resulting set of curves of synergistic factor vs pH for CD21C7 - HDEHP mixtures may be seen in Fig. 3. Rubidium extraction is synergized most strongly. Table 3 lists the synergistic factors obtained at pH 4 and the extraction coefficient at this pH for the synergistic mixture (0.125 M HDEHP + 0.25 M CE) for the alkali metals lithium through cesium. The crown ethers: C15C5, DC18C6, and DC21C7 synergize most strongly an alkali metal expected to fit the crown ether cavity (see synergistic factors in Tables 3 and sizes in Table 4). However, the extraction of lithium and cesium are not

synergized most strongly by 12C4 and DC2468 respectively as would be expected from size considerations; instead, the strongest synergistic effect is on sodium and potassium for 12C4 and on potassium for DC24C8, although these effects are small. It appears further that DC18C6 produces the strongest interaction for every alkali metal except sodium, for which C15C5 is most effective. Several possible reasons may be cited for the above observed interactions. Lithium is a highly hydrated ion, and competition of water for the coordinative bonding may hinder the formation of crown ether complexes. In addition, 12C4 is somewhat water soluble (we do not have a quantitative measurement) and a direct comparison with the less aqueous-soluble C15C5 and DC18C6 may not be appropriate. For the heavier alkalis, a lower charge density may reduce their ability to complex with crown ethers, and the uncertainty of the effective cavity-size in the larger, flexible polyether rings may attenuate the size-selective effect in adduct formation.

Comparison with Picrate Extraction

Although these experiments represent a system that is quite different from the one used by Frensdorff, the relationships between the distribution coefficients found in our work are similar to the relationships of the distribution coefficients reported for the picrate system (see Table 5). Figure 4 shows the ratio of the distribution coefficient of the alkali metals (scaled according to their ionic diameter on the abscissa) to that of the alkali metal expected to interact most strongly with a given crown ether because of size considerations. Data for both the present work and Frensdorff's work are included. While the extraction of picrate salts does show the selectivity of the crown ethers, the distribution coefficients obtained were extremely low when calculated on the basis of the total metal ion concentration. Frensdorff's experiments involved the

extraction of 7×10^{-5} M alkali metal picrate solutions by an equal concentration of crown ether. However, the total metal ion concentration in each case was 0.1 M since the extractions were made using a 0.1 M metal hydroxide solution as the aqueous phase. The use of the cation-exchanger HDEHP in the present study maintained the selectivity of the crown ethers while increasing the distribution coefficients by a factor of over one thousand in many cases.

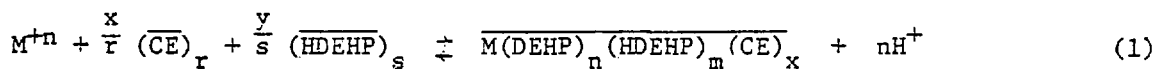
The synergistic extraction data are in agreement with the alkali picrate extraction data of Frensdorff in regard to the size selective behavior of the crown ethers. For dicyclohexo-24-crown-8, both this work and the earlier work of Frensdorff found a stronger interaction with potassium than with cesium. For 12-crown-4, the possible aqueous solubility of the complex combined with the strong interaction of lithium with HDEHP precluded any definitive determination of size effects. It should be noted that while the interaction of the crown ethers with certain "best-fit" alkali metals is size selective, it is not specific in that the extraction of other alkali metals is also synergized, although not as strongly.

A major result of this investigation is the demonstration that the crown ethers can be used to synergize the liquid-liquid extraction (or phase transfer) of ions by organophilic cation exchange extractants in a size selective manner. This result suggests the possibility that this principle can be applied to all cation exchange extraction systems. Thus, a new parameter is made available in the continuing endeavor to develop extraction systems more specific for a given ion. Possibilities for new extractant systems with entirely

new selectivities thus exist by mixing these size selective synergistic agents with familiar cation exchangers. Work is presently underway to explore these possibilities.

Stoichiometry of the Complex

The DC18C6-HDEHP system was chosen for further study to try to establish the stoichiometry of the organic phase species. A general reaction for the extraction of the alkali metals by the extractant system crown ether-HDEHP can be written as follows:



where the overlined species represent organic soluble compounds. Since loading curve experiments exhibited an initial slope of 1.0 (Table 2) indicating that the extracted species was mononuclear (assuming a mononuclear aqueous phase metal ion) the following equilibrium quotient can be written for the reaction:

$$Q = \frac{[\overline{M(DEHP)_n(HDEHP)_m(CE)_x}] [H^+]^n}{[M^{+n}] [\overline{HDEHP}]^{y/s} [CE]^{x/r}} \quad (2)$$

The distribution coefficient is defined as the concentration of the metal in the organic phase divided by the concentration of the metal in the aqueous phase:

$$D = \frac{[\overline{M(DEHP)_n(HDEHP)_m(CE)_x}]}{[M^{+n}]} \quad (3)$$

Therefore substitution of the distribution coefficient into the equilibrium expression and rearrangement of terms yields:

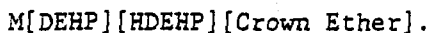
$$\log D = \log Q + npH + y/s \log [HDEHP] + x/r \log [CE]. \quad (4)$$

In order to determine the stoichiometric coefficients for each of the

reactants in equation 1, a series of experiments were run in which only one of the concentration parameters was varied and all of the other conditions were held as nearly constant as feasible. From the slope of log D versus the logarithm of the concentration of the reactant varied, as determined by a least-squares fit, coefficients were obtained for Eq. 4, and these are listed in Table 2, Items 2, 3, and 4.

As expected, the pH dependence of the extraction by crown ether alone was zero. The expected value for the slope of the crown ether dependence with HDEHP present was 1.0 assuming the crown ether to be monomeric in solution ($r = 1$), but there appears to be a substantial deviation toward lower values. The values of x/r less than one could result from competing equilibria consuming crown ether, partial association of the crown ether, or significant solubility of the complex in the aqueous phase.

When used alone, HDEHP is known to be a dimer in benzene at the concentrations used in these experiments [$s = 2$ in Eq. (1)]; therefore the values of y/s which were essentially 1.0 indicates a value of $n+m = 2$ and of $m = 1$ suggesting that there is one neutral HDEHP solvating the metal ion in the organic phase. When HDEHP alone is the extractant it has been shown that the alkali metals can be coordinated by at least three additional neutral HDEHP molecules (12). All of these parameters taken together suggests an extracted species of the stoichiometry:



Further work needs to be done to examine the possibility of crown ether-HDEHP interaction in the organic phase and define distribution of the crown ether to various aqueous phases before a firm conclusion about complex stoichiometry can be made.

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Table 1. Liquid cation exchanger - crown ether synergism

Mixture	Aq. phase	Element	Dist. coef.	Syn. factor
V-acid: DC18C6 ^a	10 ⁻⁴ <u>M</u> , pH 6	K	10 ⁻²	300
HDDNS: DC18C6 ^b	10 ⁻⁴ <u>M</u> , pH 1	K	20	50
HDEHP: DC18C6	10 ⁻⁴ <u>M</u> , pH 4	K	1.4	370
HDEHP: C15C5	10 ⁻⁴ <u>M</u> , pH 6	Na	3.0	30

^aV-acid = a "neo" carboxylic acid, 15-19 carbons on the alkyl groups.

^bHDDNS = didodecyl naphthalene sulfonic acid.

Table 2. Stoichiometric ratios for the crown ether-HDEHP extraction system

Item	Reactant varied	Li	Na	K	Rb	Cs
1.	Metal ion concentration	-	1.15	1.00	0.95	0.92
2.	HDEHP concentration	-	0.96	0.92	1.12	0.92
3.	DC18C6 concentration	-	0.80	0.70	0.84	0.62
4.	pH dependence (HDEHP + DC18C6) (range 2-6)	0.96	0.84	0.58	0.67	0.93
5.	pH dependence (DC18C6 alone) (range 2-6)	0.05	-0.02	-0.01	0.00	0.01
6.	pH dependence (HDEHP alone) (range 2-6)	0.91	0.96	0.84	0.86	0.94

Table 3. Distribution coefficients and synergistic factors for the extraction of the alkali metals by crown ethers (0.25 M) and HDEHP (0.125 M) in benzene from dilute aqueous solutions at pH 4.0

Crown ether	Li		Na		K		Rb		Cs	
	D	SF	D	SF	D	SF	D	SF	D	SF
12C4	0.0124	1	0.005	5	0.011	5	0.0033	2	0.0042	2
C15C5	0.038	3	0.221	160	0.166	65	0.156	85	0.0724	30
DC18C6	0.081	6	0.070	50	1.44	400	1.01	360	0.267	100
DC21C7	--	-	0.055	40	0.180	50	0.261	120	0.151	60
DC24C8	0.059	4	0.051	30	0.256	95	0.126	60	0.209	70

Table 4. Size parameters for alkali metal ions and macrocyclic polyethers

Alkali metal	Ionic diameter (Å)	Crown ether	Cavity diameter (Å)
Lithium	1.36	14-crown-4	1.2 - 1.5
Sodium	1.94	15-crown-5	1.7 - 2.2
Potassium	2.66	18-crown-6	2.6 - 3.2
Rubidium	2.94	21-crown-7	3.4 - 4.3
Cesium	3.34	24-crown-8	4.5 - 5.6

Ionic diameters and cavity diameters through 21-crown-7 are from Ref. 5. 24-crown-8 cavity diameter was measured using CPK molecular models.

Table 5. Distribution coefficients of crown ethers with alkali metal ions

Crown ether	Li	Na	K	Rb	Cs
	Distribution coefficients				
12C4 + HDEHP	1.24E-2	5.05E-3	1.10E-2	3.28E-3	4.20E-3
Di-(t-BuC)14C4* + picrate	7.70E-5	-	-	-	0
C15C5 + HDEHP	3.76E-2	2.21E-1	1.66E-1	1.56E-1	7.24E-2
t-BuC15C5* + picrate	1.12E-5	1.38E-4	6.09E-5	-	2.80E-5
DC18C6 + HDEHP	8.09E-2	6.96E-2	1.44E00	1.10E00	2.67E-1
DC18C6* + picrate	2.31E-5	1.79E-4	5.45E-4	-	3.09E-4
DC21C7 + HDEHP	-	5.53E-2	1.80E-1	2.61E-1	1.51E-1
DC24C8 + HDEHP	5.87E-2	5.06E-2	2.56E-1	1.26E-1	2.09E-1
DC24C8* + picrate	2.03E-5	6.23E-5	1.41E-4	-	1.27E-4

*Calculated from values given in Ref. 6.

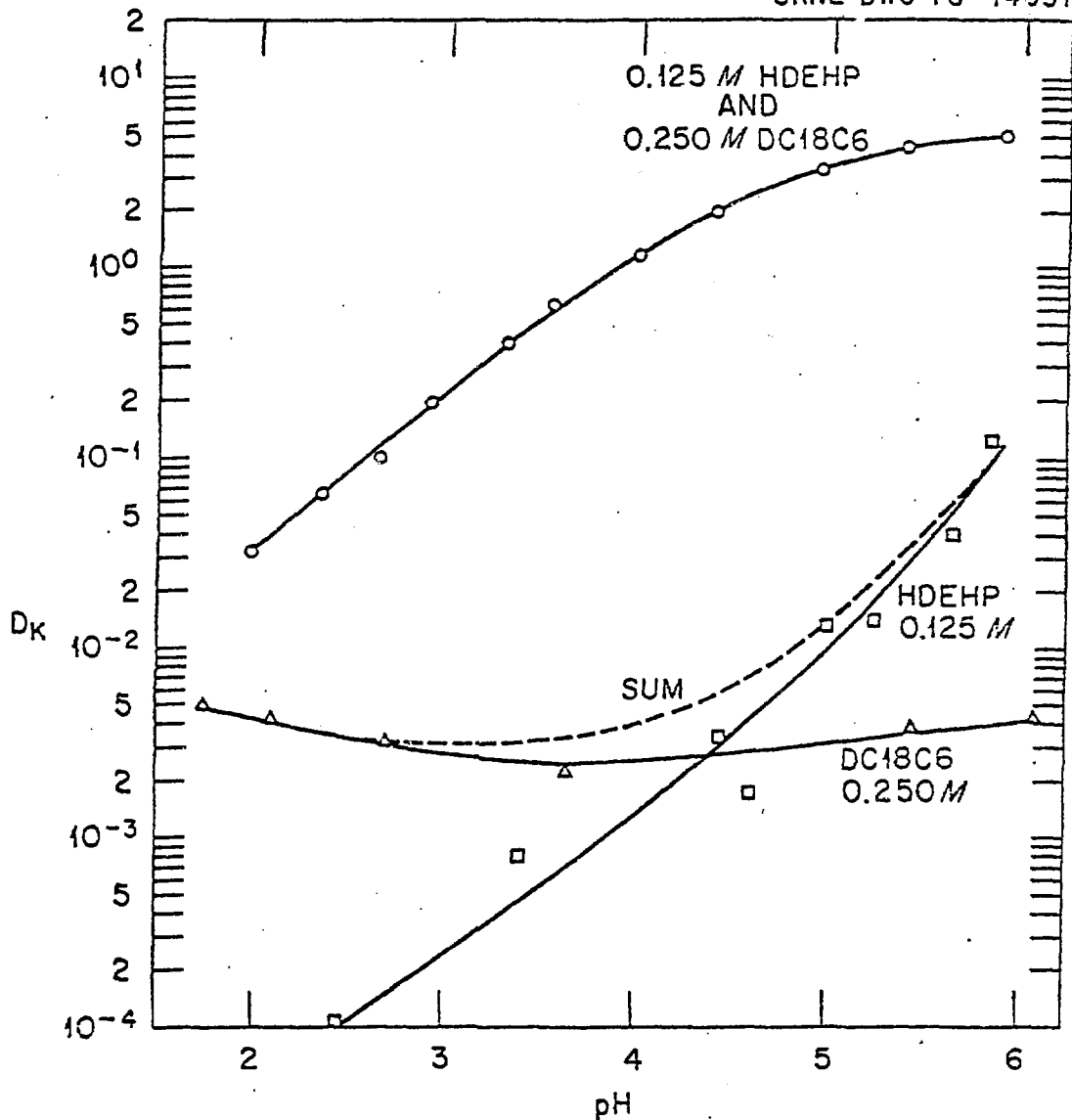


Fig. 1. Extraction of potassium from nitrate medium by 0.250 M DC18C6, by 0.125 M HDEHP, and by a solution of these two reagents together at the same concentrations all as a function of aqueous-phase pH. The synergistic factor is the ratio of the distribution coefficient obtained with the mixture to the sum of those obtained by the reagents when used alone.

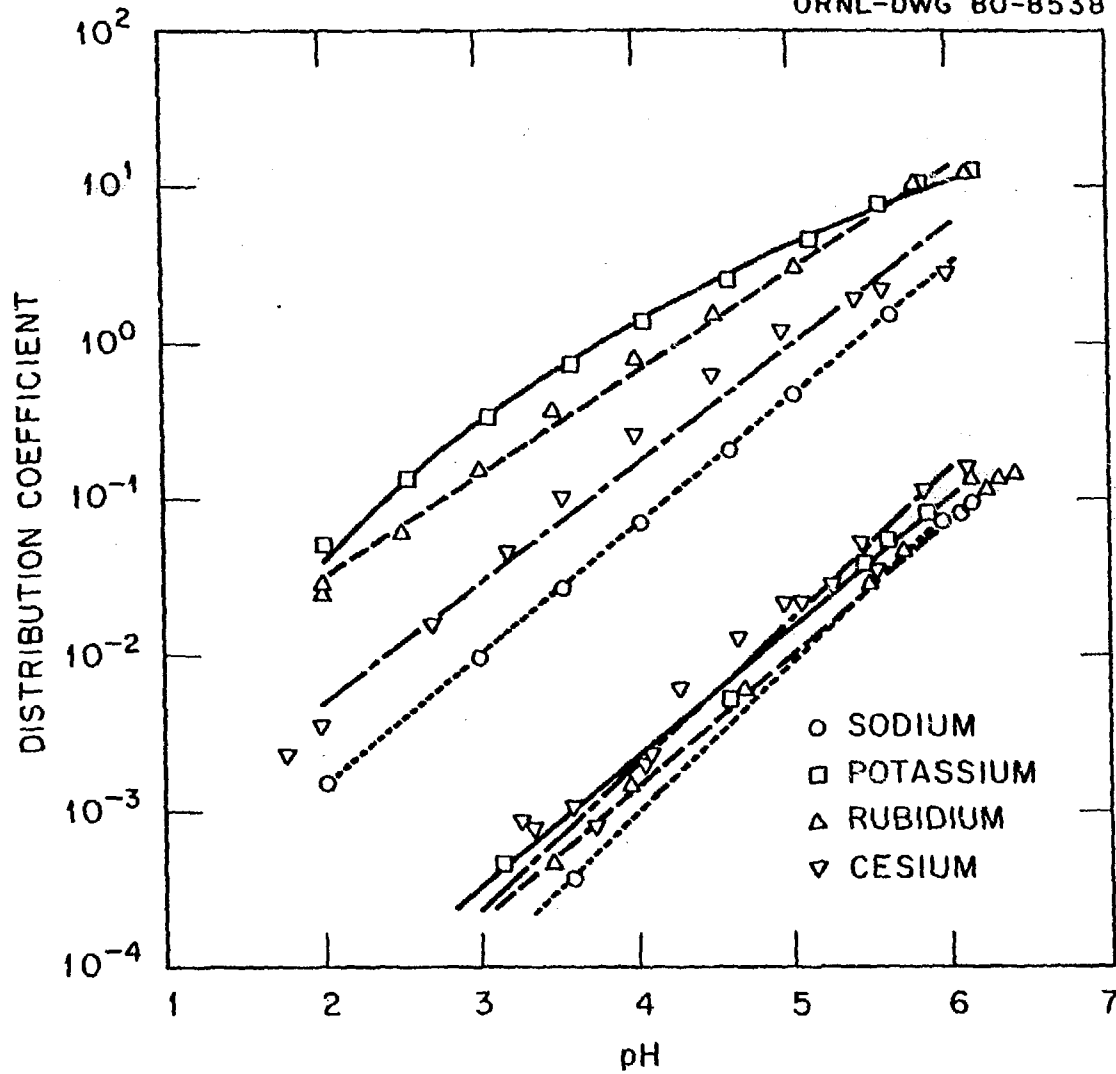


Fig. 2. The effect of 0.250 M DC18C6 on the extraction of the alkali metals from nitrate solutions by 0.125 M IDEHP as a function aqueous-phase pH.

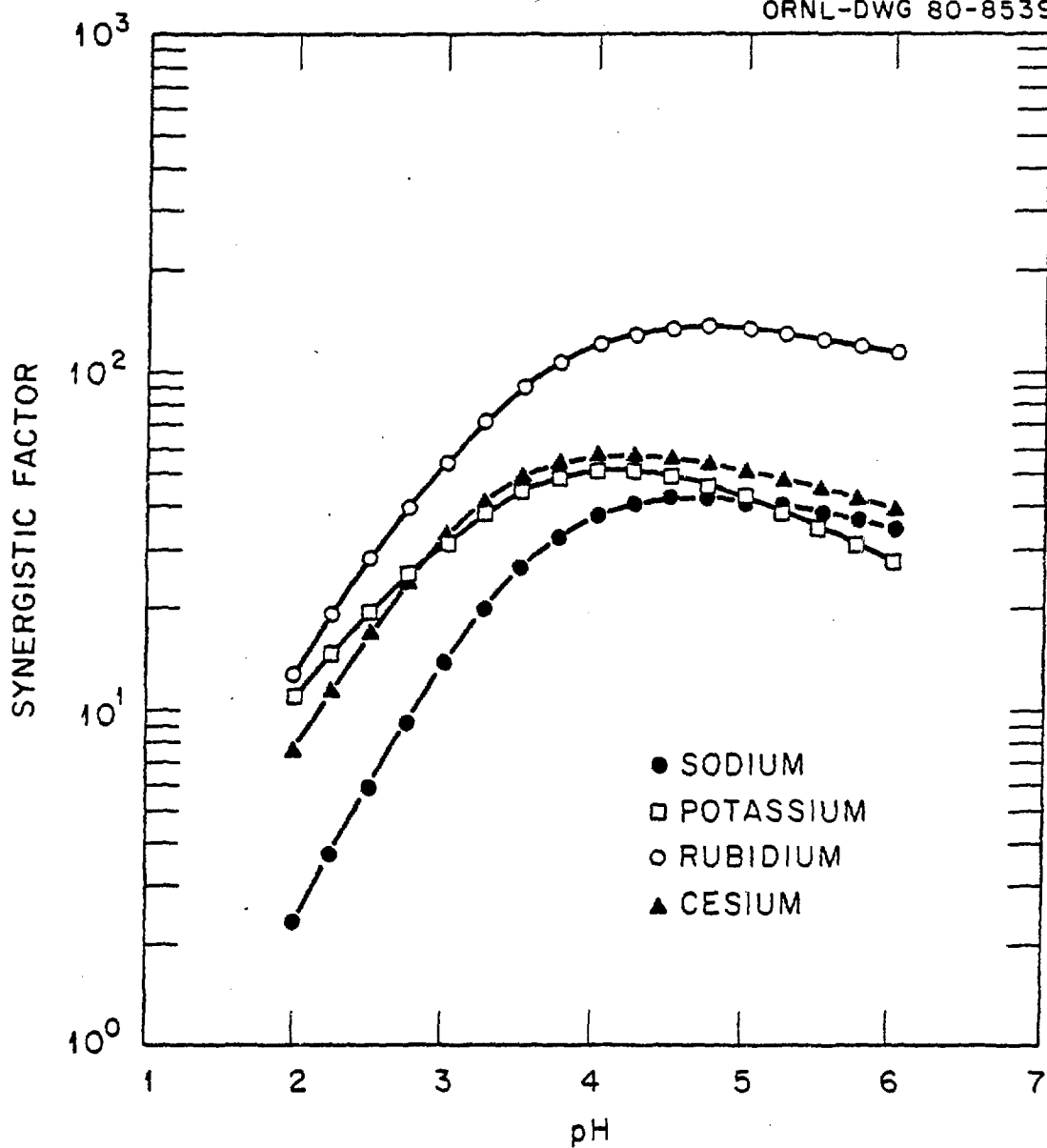


Fig. 3. Synergistic factors produced by the mixture 0.25 M DC21C7 - 0.125 M HDEHP as a function of aqueous-phase pH.

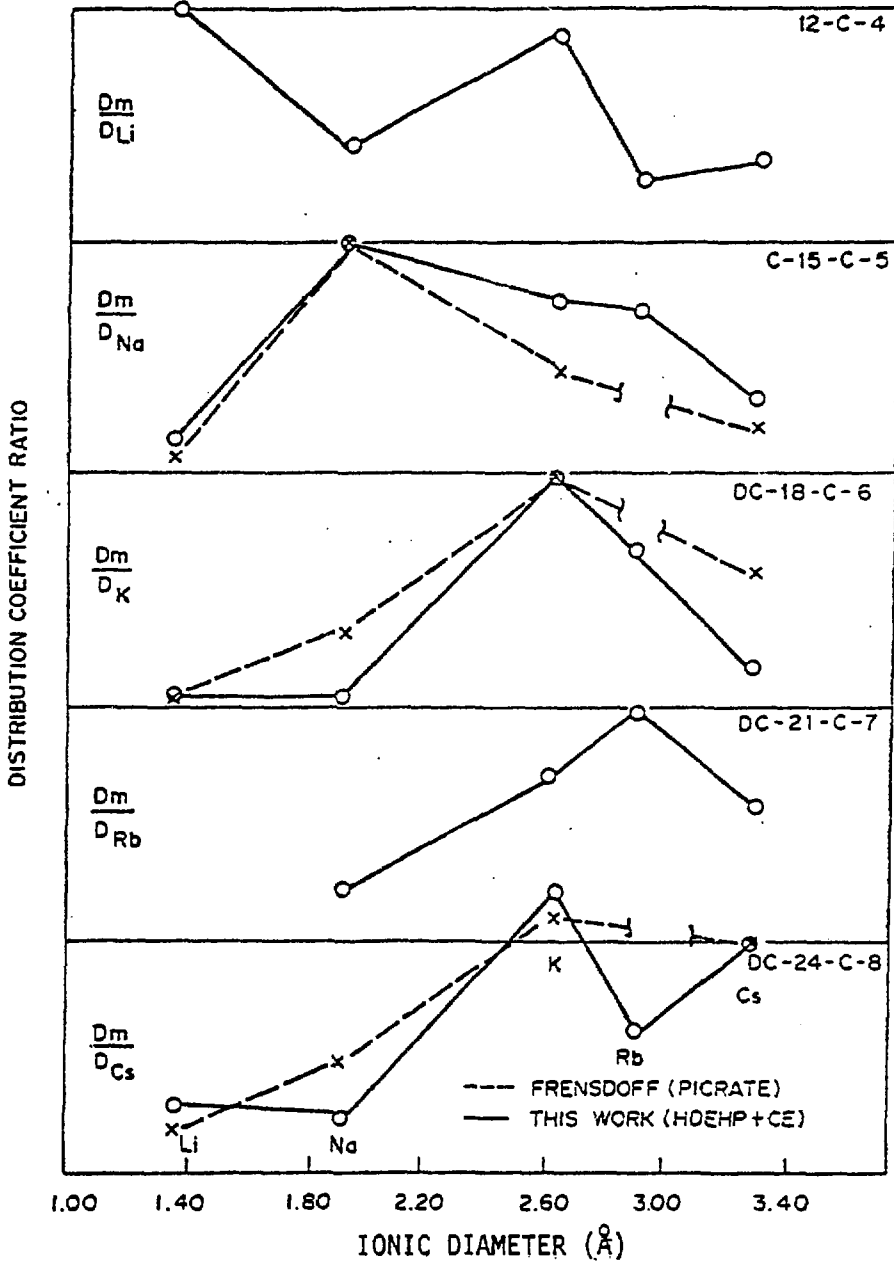


Fig. 4. A comparison of the crown ether-HDEHP extraction of alkali metals with their extraction by crown ethers as the picrates. The ratio of the distribution coefficient for a given metal to that of the metal expected to be best extracted by that crown ether (because of size) is presented vs. ionic diameter.