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STUDIES OF THE SIZE-SELECTIVE EXTRACTION OF ALKALI METAL IONS BY THE SYNERGISTIC EXTRACTION SYSTEM, CROWN ETHER-DI(2-ETHYLHEXYL) PHOSPHORIC ACID-BENZENE

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ABSTRACT

In order to take practical advantage of the size-selective cation-coordinating ability of the cyclic polyethers (crown ethers), experiments seeking a means of avoiding the problem of solubilizing a mineral-acid anion in a nonpolar organic diluent were performed. Mixtures of several known extractants and crown ethers were tried. Results presented indicate that organic soluble cation exchangers mixed in solution with crown ethers produce a synergistic extractant mixture that largely exhibits the size-selective properties expected of the crown ether. Data are presented for the extraction of macro concentrations of alkali metals by di(2-ethylhexyl) phosphoric acid — dicyclohexyl-18-crown-6 mixtures at a single pH, and at nonloading condition(Σ metal conc <0.04 $\underline{M}$) as a function of pH, 2 to 6. In both cases potassium is synergized most strongly presumably because of its best fit to the crown ether cavity. Other data indicate, however, that the size-fit principle is not as consistent for all alkali metal ions and crown ethers as for potassium and dicyclohexyl-18-crown-6. Other effects such as competition for ion hydration and aqueous-phase distribution of the complex may have important effects that have not been elucidated.

INTRODUCTION

Crown ethers are a class of macrocyclic polyether molecules that are known to form relatively strong complexes with alkali metal cations. The strength of association of the crown ether with the metal ion appears to be greater when there is correspondence between the crystal diamter of the metal ion and the size of the cavity in the polyether ring. Thus by varying the size of the polyether ring, it is possible to effect a selective interaction of the various alkali metals with crown ethers.

In general, the crown ethers have limited solubility in aqueous solutions, which makes them good candidates for solvent extraction reagents. Frensdorff has examined size-selective behavior in the extraction of alkali metal picrates by various crown ethers (1,2). These studies demonstrated the selective extraction of sodium by *t*-butylcyclohexyl-15-crown-5 and the enhanced extraction of potassium by dicyclohexyl-18-crown-6 both consistent with the size-fit idea.

Other workers have studied the use of crown ethers as extraction reagents and demonstrated size selectivity in extractions using dibenzo-18-crown-6 and dicyclohexyl-18-crown-6 (3-7). Because of the difficulty in transferring a mineral acid anion to the organic phase to preserve electrical neutrality, almost all studies have used picrate, tetraphenylborate, or dipicrylamine salts to provide a large polarizable anion so that the ion-pair can be extracted. Distribution coefficients (D_M = organic-phase metal concentration divided by aqueous-phase metal concentration) for the picrate salts are of the order of 10^{-4} to 10^{-5}. The poor extractability of these salts, the necessity of converting the aqueous system to one in which the anion is a large polarizable quasi-organic species, and the cost of reagents make such systems unattractive in process application.

Marcus and Asher have recognized the problem of anion transfer and attempted to solve the problem by using highly polar organic solvents to solvate the anion and increase its solubility in the organic phase (8). This creates problems in practice since the polar organic solvent may be appreciably soluble in the aqueous layer. In reporting a study of 27 polar organic solvents, they found that distribution ratios of about 0.5 could be obtained for 0.1 M potassium chloride using m-cresol as the organic-phase diluent.

McDowell and Shoun have investigated an alternative approach to increasing the usefulness of crown ethers as extraction reagents (9). They theorized that by including an organic soluble — aqueous insoluble cation exchanger in the organic solution with the crown ether, the metal ion could be transferred to the organic phase by cation exchange, thus avoiding the problem of anion transfer. Once the cation was extracted into the organic phase, it was thought that the size-selective interaction of the crown ether with the extracted cation should still occur. This study reports the results of some preliminary investigations of the use of cation exchangers and neutral species extractants as coextractants with crown ethers and a more detailed study of the selective extraction of potassium by dicyclohexyl-18-crown-6 (DC18C6) and di(2-ethylhexyl) phosphoric acid (HEDEHP).

EXPERIMENTAL

Crown ethers were obtained as 99+% purity materials from Aldrich or Parrish chemical companies and used without further purification. No attempts were made to separate the geometric isomers of the dicyclohexyl-substituted compounds. All other extraction reagents were obtained from stock and were purified by conventional procedures. Reagent-grade benzene was used as the organic-phase diluent.

All alkali metal radioisotopic tracers were analyzed for radiochemical purity by gamma spectrometry. Counting was done to <1% statistics except for some organic phases which had extremely low counting rates. Lithium was determined by atomic absorption spectrophotometry using a Perkin-Elmer Model 460 spectrometer.

The experiments in which aqueous-phase pH was varied consisted of equilibrating 10 ml of an organic phase containing 0.250 M crown ether and 0.125 M HDEHP and of each of these reagents alone at the same concentration with 10 ml of an aqueous phase. Before examination of extraction behavior began but while the phases were being equilibrated, the aqueous phase was adjusted to pH 6 using 0.125 M alkali metal hydroxide. Following pH adjustment, the tracer was added. After a 5-min equiliration period, an aliquot of each phase was withdrawn for counting in an automated gamma scintillation spectrometer. Separate experiments have shown that a 5-min equilibration time is more than sufficient to assure equilibrium. The solution was then titrated to the next pH value with a dilute solution of nitric acid. The total metal ion concentration in the sample never exceeded 0.04 molar. Extraction data above a pH of 5.5 are less reliable than at lower values since the interface active nature of the HDEHP-metal salt interfered with complete phase separation.

Experiments in which pH was not a variable employed batch equilibration procedures in 30-ml separatory funnels. The pH was adjusted, then measured in the presence of all reagents after equilibration. In Fig. 1 the total initial alkali metal ion concentration was 0.5 M, 0.1 M in each metal.

RESULTS AND DISCUSSION

Initial Tests

In the initial tests, two crown ethers, dicyclohexyl-18-crown-6 and cyclohexyl-15-crown-5, were tested with several familiar solvent extraction reagents for their ability to enhance the extraction of various cations. For the cation exchange extractants, the alkali metal ions were chosen as ions to be tested since more data are available on their extraction. For the anion (amine) and neutral species extractants (phosphorous compounds), other ions that were known to extract with these reagents and should have about the right size relationship

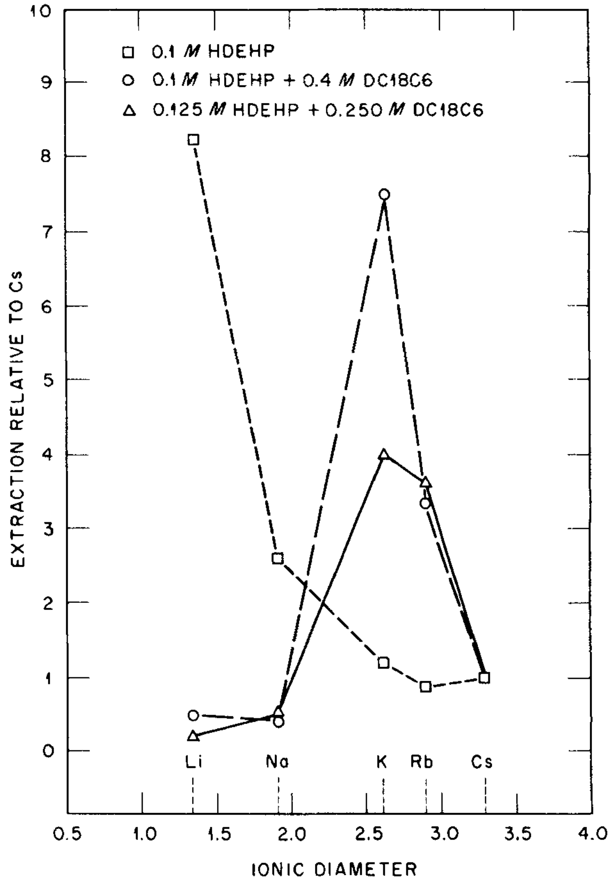

FIGURE 1. Extraction of alkali metals by a mixture of dicyclohexyl-18-crown-6 and di(2-ethylhexyl) phosphoric acid (HDEHP) compared with extraction by HDEHP alone. For data set □ and ○ the aqueous phase is 0.1 M at pH 4.8, and the HDEHP is 50% converted to the salt form. Data set △ are from the titration data at the point where 50% HDEHP is converted.

to the crown ether were chosen. The results of these tests are presented in Table 1. For each reagent– crown ether pair, a synergistic factor (S) was calculated from the following relationship

$$S = \frac{D_{(r+ce)}}{D_r + D_{Ce}} , \qquad (1)$$

TABLE 1

Tests for Synergism with Crown Ethers

Reagent	Crown ether	Aqueous phase	Element extracted	$D_{(r+ce)}$	S
Versatic acid*	DC18C6	10^{-4} M KNO_3 pH=6	K	0.01	300
Didodecylnaphthalene sulfonic acid	DC18C6	10^{-4} M KNO_3 pH=1	K	20	50
Di(2-ethylhexyl) phosphoric acid	DC18C6	10^{-4} M KNO_3 pH=4	K	1.4	400
Di(2-ethylhexyl) phosphoric acid	C15C5	10^{-4} M $NaNO_3$ pH=4	Na	0.22	160
Didodecylamine	C15C5	4.0 M $NaNO_3$ 0.2 M HNO_3	Th	0.6	9
Trioctylphosphine oxide	C15C5	1.0 M HNO_3	Eu	0.3	1
Tributyl phosphate	C15C5	1.0 M HNO_3	U(VI)	0.2	1.1

*A carboxylic acid with a tertiary carbon at the alpha position having a methyl and two C(7) to C(9) alkyl chains as substitutes.

where D_r and D_{ce} are the distribution coefficients of the individual reagents used alone, and $D_{(r+ce)}$ is the distribution coefficient for the reagents used together. The highest values of the synergistic factor were obtained for cation exchange reagents as opposed to neutral solvating reagents or anion exchange reagents as had been expected. Since considerable information exists on the extraction of alkali metals by HDEHP (10,11), and since a good synergistic effect was produced with this reagent, it was chosen for use as a coextractant with the crown ethers. The following discussion is concerned with the use of HDEHP with dicyclohexyl-18-crown-6.

Systematic Experiments with HDEHP as Coextractant

The HDEHP system does exhibit some selectivity for the extraction of alkali metals at the low alkali metal concentrations used in the titration experiments in this work (10,11). However, little separation was observed here using the one-component (HDEHP) system, with the exception of lithium, which exhibits an enhanced interaction with HDEHP. This behavior of lithium is probably due to the fact that its charge-to-radius ratio is much greater than the other alkali metals. Upon the addition of DC18C6, the distribution coefficients of the alkali metals increased by a significant amount, and the separation factors between the alkali metals are also increased.

In an early experiment (9) the effect of DC18C6 on the relative extraction of the alkali metals by HDEHP was observed under conditions where the total metal ion was more than the HDEHP could extract, thus producing conditions of competition between the alkali metal ions for extraction. The relative extractions of the alkali metals (related to Cs) from this experiment are compared in Fig. 1 with those resulting from a system containing HDEHP alone. For this experiment, each alkali metal was 0.1 M, and the 0.1 M HDEHP had been converted 50% to the alkali metal salt by the addition of part of the sodium as sodium hydroxide. The equilibrium aqueous-phase pH was 4.8.

Also included in this figure are the data from the titration experiments at low metal concentrations, with each alkali metal in a separate experiment so that no extraction competition existed. The point at which the HDEHP was 50% converted to the salt was also chosen in each case here to calculate the relative extraction. Note that under both conditions the relative extraction of potassium is greatly enhanced when DC18C6 is present compared to its position when HDEHP is used alone. The relative extraction of the alkali metal ions by HDEHP can be correlated with their charge/crystal radius ratio. However, when DC18C6 is present in the organic phase, this effect appears to be overridden by a size-selection synergistic effect in which the size-fit between DC18C6 and potassium predominates.

Synergistic factors. Because the distribution coefficients for extraction by the crown ether alone were very low, 10^{-5} to 10^{-4}, and thus contained much experimental scatter, all of the experimental distribution coefficients obtained as a function of pH for crown ethers alone, HDEHP alone, and the mixtures were fitted to a regression equation. The synergistic factors, as defined above, were calculated from the fitted curves according to Eq. (1). A plot of the synergistic factors obtained for the extraction of alkali metals by DC18C6 and HDEHP as a function of pH is shown in Fig. 2. Potassium and rubidium exhibited the largest synergistic effects, as would be expected from a match of their ionic diameters with the cavity size of DC18C6.

Comparison of size-selective synergism with earlier work. In order to compare the size-selective synergistic-solvent extraction effect found in this study (using a crown ether mixed in organic-phase solution with a liquid cation exchanger) with the size-selective extraction of alkali metal picrates observed by Frensdorff (1), separation factors R_{M^+} were calculated from the distribution coefficients D_{M^+} for both systems according to the following equation

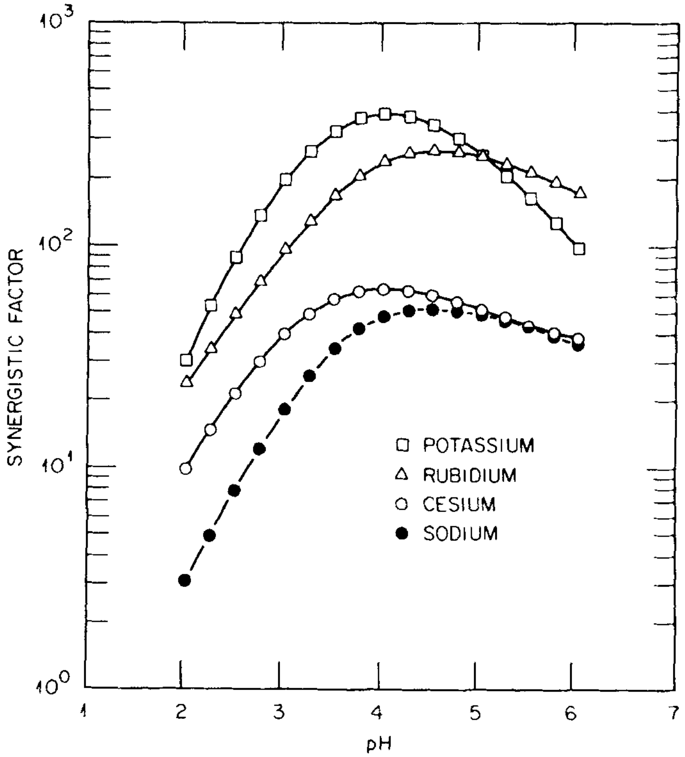

FIGURE 2. The synergistic factor, S, for the extraction of alkali metals by a mixture of 0.125 M dicyclohexyl-18-crown-6 and 0.125 M HDEHP over the added effect of these reagents used separately.

$$R_{M^+} = \frac{D_{M^+}}{D_{K^+}}. \qquad (2)$$

The separation factors obtained are compared in Table 2.

The data show that not only does the HDEHP—crown ether coextractant system give separation factors for the alkali metals very similar to those observed in extraction of picrates by crown ether solutions, but an increase in the distribution coefficient of greater than 1000 is obtained as compared to using the crown ether alone.

TABLE 2

Comparison of the Synergized Extraction System with the Picrate Extraction System

Alkali metal	Distribution coefficient		Separation factor, R_{M^+}*	
	HDEHP+DC18C6 (nitrate)	DC18C6 (picrate)	HDEHP+DC18C6 (nitrate)	DC18C6 (picrate)
Lithium	8.09E-2	2.31E-5	0.06	0.04
Sodium	6.96E-1	1.79E-4	0.05	0.03
Potassium	1.44E00	5.45E-4	1.00	1.00
Rubidium	1.01E00	-	0.70	-
Cesium	2.67E-1	3.09E-4	0.18	0.57

$$*R_{M^+} = \frac{D_{M^+}}{D_{K^+}}.$$

Current work is under way to systematically evaluate the relationship between crown ether ring size and the synergized extraction of the alkali metals using HDEHP and other organic-soluble cation exchangers.

Preliminary investigation of complex stoichiometry. The pH dependence of the log extraction coefficient was found to be 0 for extraction with HDEHP. Loading curves for the HDEHP-DC18C6 mixture implied monomeric potassium in the organic phases. There is a significant deviation from unity in the slope of the log distribution coefficient vs log reagent concentration for both HDEHP and DC18C6 for the system containing potassium; the slope does approach 1 for sodium. It is felt that the deviation from the expected value of 1 results from either competing equilibria or from the aqueous solubility of the complex ion. More experimental work will be required to determine the extent to which solubility affects the reagent dependence slopes determined in this work. A slope of 1.0 for the extraction coefficient dependence on HDEHP concentration would suggest that there is one DEHP anion and one neutral HDEHP solvating the metal ion if one assumes that

HDEHP (which is known to be a dimer in benzene at the concentrations used in this work) remains a dimer in the presence of DC18C6. Using these limited data and the above assumptions, a possible formula for the extracted species would be M(DEHP)(HEDHP)(DC18C6).

Further work is in progress to study the more detailed behavior of this and similar cation exchange--crown ether systems and to define more exactly the extracted species.

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