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Investigations of Ion-Size-Selective Synergism in Solvent Extraction

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ABSTRACT

Organophilic crown ethers and other similar macrocyclic compounds produce a synergistic enhancement of the extraction of several metal ions by organic-phase-soluble carboxylic, phosphoric, and sulfonic acids. Ions examined include the alkali metals, the alkaline earths, and some first-row transition elements. In many cases, the synergistic effects are clearly related to the correspondence of the ion size to the macrocycle cavity diameter. In other cases this is less true, and occasionally, complete lack of synergism or even antagonism is observed. These phenomena have been investigated by systematic studies of the systems involved, by equilibrium studies of selected extraction systems, and by vapor-pressure osmometric studies of the intermolecular bonding between the organic-phase macrocycles and acids. Lack of synergism (when it is expected from size correspondence) does not appear to be due to bonding interactions between the macrocycle and the extractant acid. Other considerations suggest that synergism may depend on the degree to which the macrocycle can surround the ion. Possibilities for metal ion separations are noted, and the directions for further, needed investigations are indicated.

INTRODUCTION

Several investigators have noted the unique complex-forming ability of the macrocyclic ethers called "crown" ethers (1-7), and in earlier publications we have shown their ability to synergize the

extraction of alkali and alkaline earth ions into toluene solutions of alkyl phosphoric acids (8,9). The most interesting feature of this synergistic effect was that it appears to be size-selective; that is, in many cases, the synergism was greatest where the crown ether cavity corresponded to the diameter of the ion being extracted (8,9). This effect appeared to be most pronounced for potassium and the 18-crown-6 cavity and was nearly as impressive for sodium and the 15-crown-5 compounds; however, it was slightly less dramatic for rubidium and cesium with 21-crown-7. The 12-crown-4 and 24-crown-8 compounds demonstrated very small synergistic effects. In these early experiments (7), it was recognized that the smaller-cavity compounds 12-crown-4 (12C4) and cyclohexo-15-crown-5 (C15C5) were not sufficiently organophilic to be predominantly organic-phase distributed; consequently, it was not possible to attribute their lack of synergistic effect wholly to ineffective complexing of the alkali metal ion. It was obvious that more investigations, both systematic and fundamental, of the size-selective synergistic effect were needed with compounds having good organic-phase distribution over the entire cavity size range. This paper describes some systematic phase-distribution studies of the macrocycles themselves and some selected studies of synergism that allow further conclusion about the nature of size-selective synergism.

EXPERIMENTAL

Reagents

Bis(2-ethylhexyl)phosphoric acid (HDEHP), obtained from Mobil Chemical Corporation, was found to contain <0.5% monoalkyl phosphoric acid and to have a neutral equivalent of 323.5 (theoretical, 322.6). It was used without purification. The carboxylic acid, Versatic Acid 1519 (V-acid), was an experimental product of Shell Development Company. It was purified by molecular distillation in a spinning-cone molecular still. A center cut was taken that has a neutral equivalent of 277. This carboxylic acid is reported to

branch at the alpha carbon with one methyl group and two other chains varying from heptyl to nonyl. The didodecylnaphthalene sulfonic acid (HDDNS), obtained from King Industries, is a naphthalene sulfonic acid with two, branched 12-carbon chain groups attached to the naphthalene nucleus. The material was received as a 39% solution in mixed heptane and methanol. Our attempts to crystallize, distill, or purify by ion exchange methods were not successful. For use, the original solvents were removed by vacuum evaporation in a rotary evaporator, and the residue was dissolved in the diluent of choice for the experiments. The acid content of the solution was titrated with standard base, and the required concentration was prepared by dilution.

Toluene was used as the reagent carrier diluent in all experiments as a compromise between the proprietary, kerosene-like diluents commonly used in process solvent extraction and the more polar organic solvents. Reagent-grade toluene was used without further purification.

The crown ethers and other macrocyclic compounds were obtained from Parish Chemical Company and Aldrich Chemical Company or were prepared at The Georgia Institute of Technology under a subcontract with C. L. Liotta. All compounds were considered better than 95% pure by the supplier — some better than 99% pure, and no additional purification was done. The dicyclohexo compounds were mixtures of the stereoisomers and were used without separation.

All other chemicals used were reagent grade.

Experimental Procedure

Equilibrations were usually performed in vials or small separatory funnels of the appropriate size. In cases where two-phase titrations were performed, however, an equilibration vessel equipped to hold pH electrodes, a capillary-tipped burette, and a stirrer were used. The temperature was $23 \pm 1^\circ\text{C}$. Tests were performed to ensure that equilibrium was attained with the particular equilibration method being used.

Analyses for sodium, potassium, rubidium, and cesium in the equilibrated phases were performed by radiotracer methods employing gamma-emitting nuclides. Appropriate radionuclides were added to the head aqueous solutions, and 0.1- to 1.0-mL samples of the equilibrated phases were counted using a "well" type sodium iodide crystal and a multichannel analyzer. Radium was assayed by direct liquid scintillation alpha counting using a PERALS spectrometer that allowed the ^{226}Ra alpha energy to be isolated and beta-gamma radiation to be rejected (10). Lithium was determined by atomic absorption using a Perkin-Elmer 5000 Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Chloroform was used as the diluent in most of the early solvent-extraction tests with macrocyclic compounds (1-7) because many of them were soluble in this solvent but not in other common solvents. Chloroform is not, however, a practical diluent for process solvent-extraction systems. Because of its polar nature and hydrogen bonding characteristics, the bonding ability of many coordinative solvent-extraction reagents is sharply reduced in chloroform over what is found in other, less polar diluents. Thus, because of the desire to study the solvent-extraction bonding behavior of the macrocyclic compounds in a more "inert" environment and in one that more nearly approximates process diluent conditions, we have sought macrocycles that are soluble in toluene. Table 1 lists the common names and abbreviations and shows the solubilities of a number of macrocycles that we have tested, together with their distribution to water from a 0.1 M solution in toluene. Both cyclohexo substitution on the macrocycle ring and branched alkyl substitution on the cyclohexo ring appear to improve organic-phase solubility and to reduce distribution to aqueous phases. The compounds chosen for our original tests (denoted by asterisks in Table 1) are reasonably soluble in toluene and cover the ion-size range of interest. Figure 1 shows the structures of these compounds and their cavity sizes.

TABLE 1.
Organic-Phase Solubilities and Aqueous-Phase
Distributions of Some Macroyclic Compounds

Compound	Abbreviation	Solubility in Toluene (M)	Dist. to Water (%)	Cavity Size (\AA)
12-Crown-4	12C4	Infinite	90	1.2 - 1.5
*Benzo-14-Crown-4	B14C4	>0.1	<2	1.2 - 1.5
*Octamethylperhydrocycloctetrafur-furylene	OMPCTFF	0.123	<0.1	1.2 - 1.5
Cyclohexo-14-Crown-4	C14C4	Infinite	50	1.2 - 1.5
Cyclohexo-15-Crown-5	C15C5	Infinite	30	1.7 - 2.2
*tert-Butylcyclohexo-15-Crown-5	TBC15C5	Infinite	<1	1.7 - 2.2
Dibenzo-18-Crown-6	DB18C6	<0.01	—	2.6 - 3.2
Diformyldibenzo-18-Crown-6	DFDB18C6	<0.01	—	2.6 - 3.2
Dibutylcyclohexo-18-Crown-6	DBDB18C6	<0.01	—	2.6 - 3.2
*Di- <i>tert</i> -butyldibenzo-18-Crown-6	DTBDB18C6	>0.2	<0.1	2.6 - 3.2
*Dicyclohexo-18-Crown-6	DC18C6	>0.5	7	2.6 - 3.2
*Di- <i>tert</i> -butyldicyclohexo-18-Crown-6	DTBDB18C6	>0.2	<0.1	2.6 - 3.2
*Dicyclohexo-21-Crown-7	DC21C7	Infinite	0.2	3.4 - 4.3
*Dicyclohexo-24-Crown-8	DC24C8	Infinite	0.2	4.5 - 5.6
Tetramethyltetraazacyclotetradecane	TMTACTD	>0.1	—	—
<i>meso</i> -Tetraphenylporphine	MTTPP	0.008	0.1	—

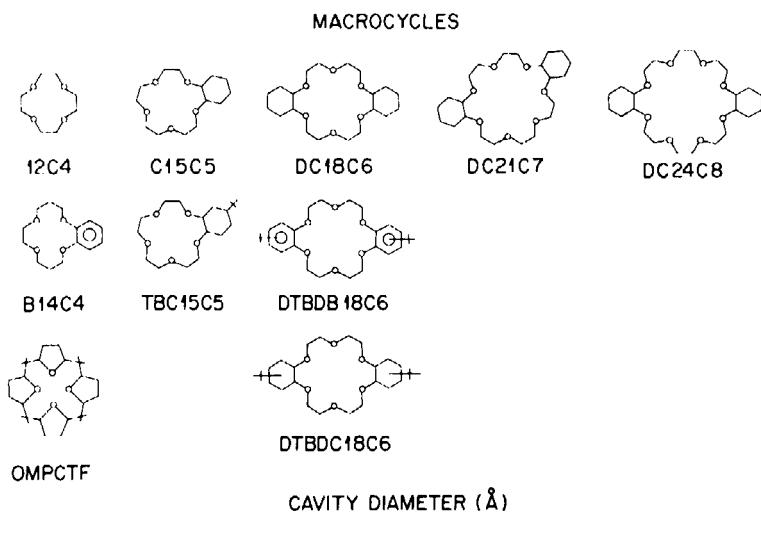


FIGURE 1. Macrocycles presently in use in the test program. 12C4 and 15C5 are highly aqueous-phase distributed and so are not currently used in liquid-liquid extraction experiments.

Alkali Metal Extraction

Earlier work (8) showed potassium extraction by HDEHP to be strongly synergized by DC18C6, sodium extraction to be somewhat less synergized by C15C5, and rubidium and cesium only moderately synergized by DC21C7. Lithium showed no synergism by 12C4 — the compound expected to fit that ion — and little synergism by other crown ethers. DC24C8 synergized all of the ions poorly.

It is evident from Table 1 that 12C4 is largely distributed to water; thus, other macrocycles of the same cavity size were sought which would be more organophilic. The compounds OMPCTF and B14C4 were found suitable and were tested for lithium synergism in both sulfonic and phosphoric acid extraction. Synergistic effects were small in the best situations (i.e., where each of the alkali metals was present in 0.5 M concentration). At lower aqueous ionic strength, the macrocycles appeared to antagonize the extrac-

tion of lithium and all the alkali metals. This result suggested that hydrogen bonding to form an intermolecular compound between the acid and the macrocycle might be responsible for the antagonistic effect. However, measurements of the particle concentration of the compounds separately and mixed, using a vapor-pressure osmometer, did not indicate any intermolecular compound formation. Perhaps the most plausible explanation remaining for the lack of synergism is that the coordinative bonding strength of the crown ether oxygens is not sufficient to replace the water coordinated to the strongly hydrated lithium ion. This, however, does not explain the antagonism observed in some cases. Similar behavior of alkaline earths is also reported in this paper.

Figure 2 shows the synergistic effect of the three most effective crown ethers on the extraction of the alkali metals from a solution 0.5 M in each as the nitrates by 0.1 M HDDNS in toluene. As shown with HDEHP, the effect is most dramatic with C15C5 and DC18C6.

The extraction of sodium and potassium by crown ether-HDDNS mixtures is shown in another way in Figs. 3 and 4, respectively. Here, the extraction by HDDNS alone, by the crown ether alone, and by crown ether-HDDNS mixtures is shown as a function of equilibrium aqueous nitric acid concentration. The synergistic factor,

$F_{\text{syn}} = D(\text{mix})/(D(\text{acid}) + D(\text{coordinator}))$, for sodium is 73 at 0.1 M HNO_3 and decreases to 55 at 3 M HNO_3 , primarily due to an increase in the distribution of neutral sodium nitrate to the crown ether alone at high aqueous nitrate concentration. In Fig. 4, potassium extraction is shown by HDDNS alone and as synergized by DC21C7, C15C5, and DC18C6. The DC18C6 produces the strongest synergistic effect (about 100), while both the larger and smaller crown ethers are less effective. Synergized extraction coefficients for potassium by HDDNS are high enough in this system to be useful in analytical or process separations. Analysis of a potassium extraction isotherm for extraction from Searles Lake brine indicated 97% potassium recovery in three stages.

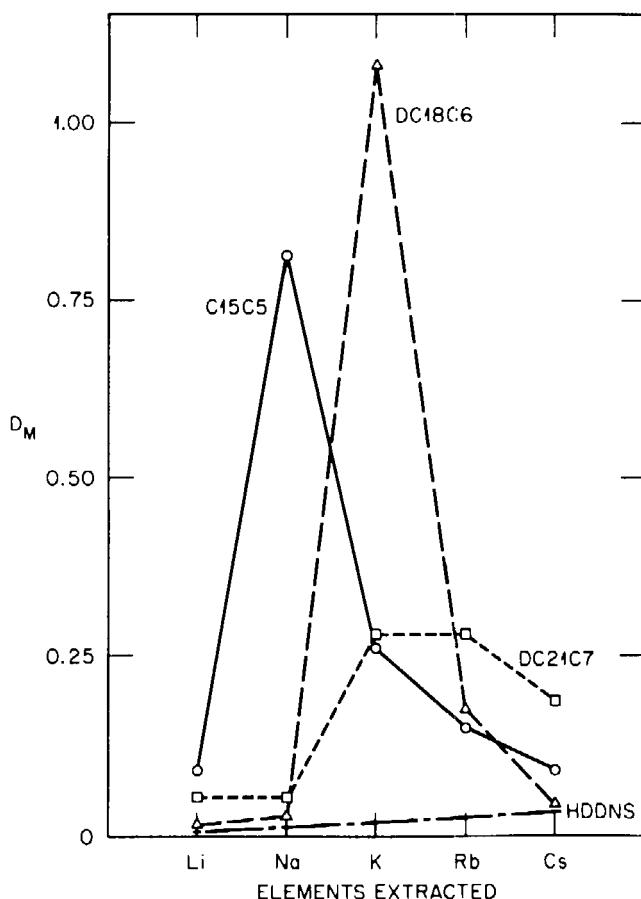


FIGURE 2. Competitive extraction of alkali metals from an aqueous phase 0.5 M in each metal nitrate by 0.1 M HDDNS in toluene and that concentration of HDDNS plus 0.05 M C15C5, DC18C6, or DC21C7.

Reagent concentration dependence experiments in the HDEHP crown ether systems indicated an organic-phase complex with the alkali metals consisting of one crown ether, one HDEHP, and one alkali metal. Figure 5 shows similar data for the HDDNS-DC18C6 systems — the HDDNS system showing the strongest synergism. Most of the points fall sufficiently close to a slope of 1 to support

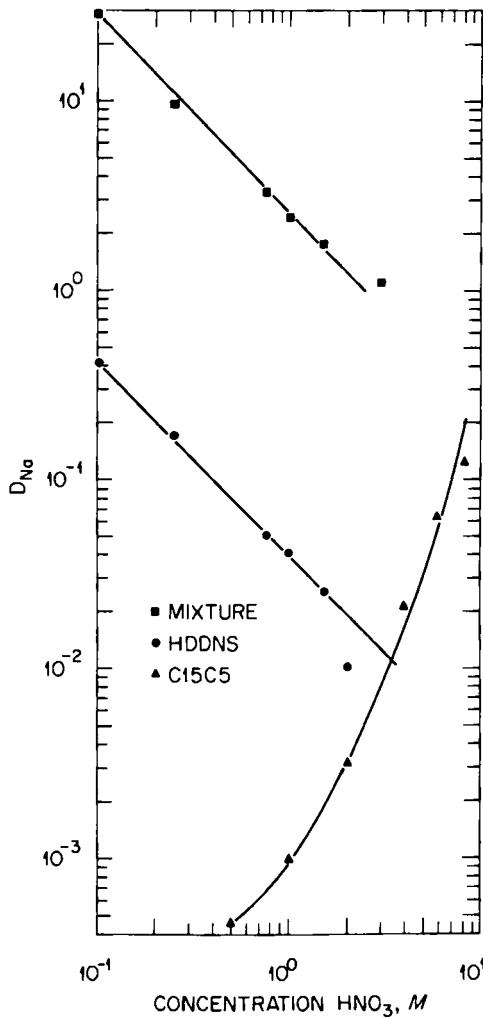


FIGURE 3. Extraction of 10^{-4} M sodium from nitric acid by 0.1 M HDDNS in toluene, 0.1 M C15C5 in toluene and a mixture of the two reagents at that concentration each.

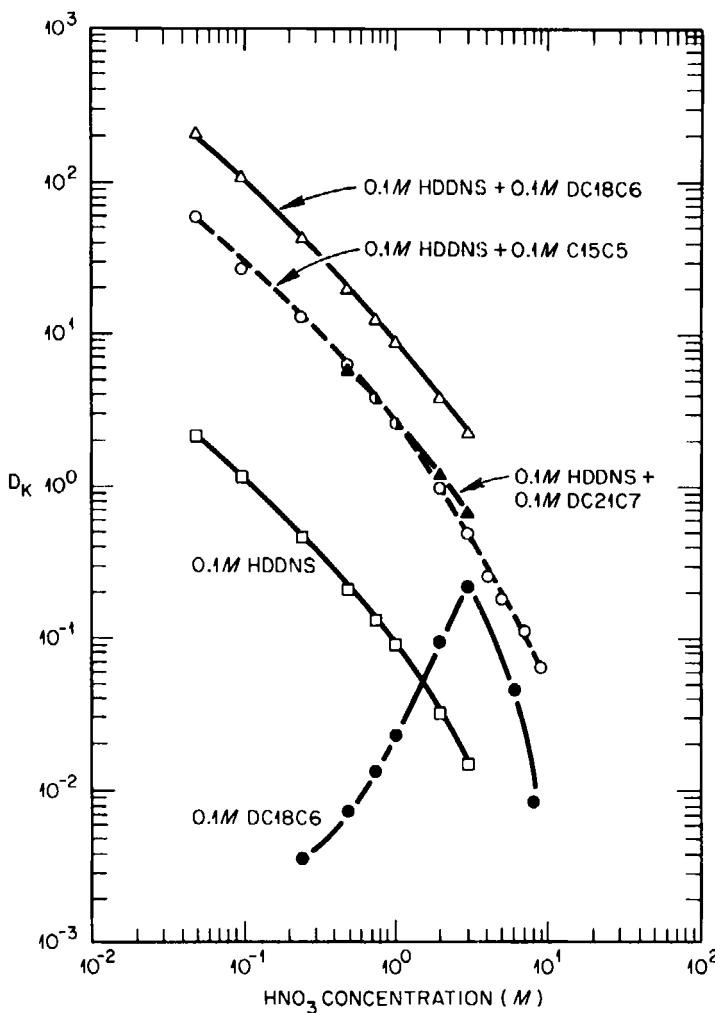


FIGURE 4. Extraction of 10^{-4} M potassium from nitric acid by 0.1 M DC18C6 in toluene, 0.1 M HDDNS in toluene and mixtures of HDDNS and DC18C6, C15C5, or DC21C7 with HDDNS, each reagent at 0.1 M concentration.

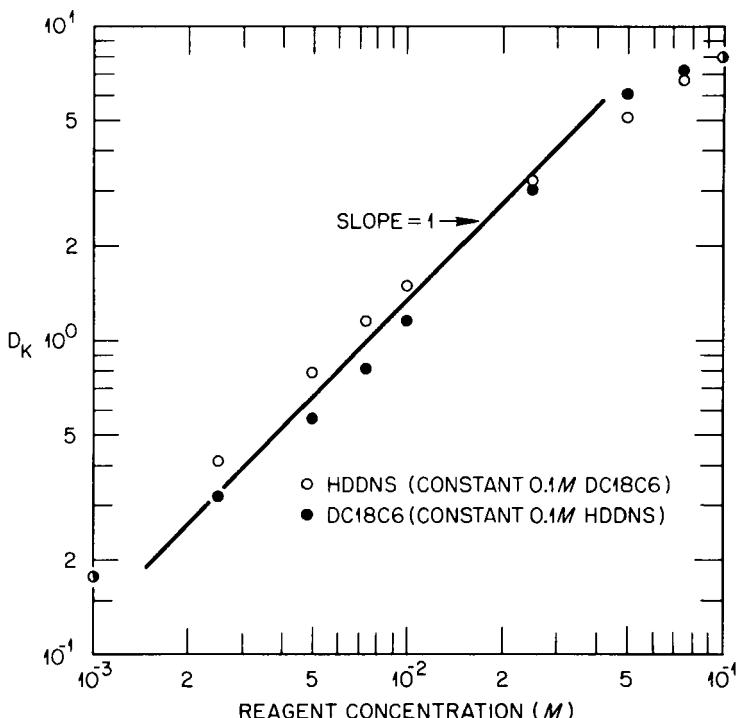


FIGURE 5. Reagent concentration dependence of potassium extraction by HDDNS and DC18C6 each in the presence of the other at 0.1 M constant concentration.

the idea that a 1:1:1 complex also exists in this system. Experiments in which the total HDDNS + DC18C6 concentration was kept constant while the ratio varied gave a peak near 0.5 mol fraction in agreement with the reagent dependence data.

Alkaline Earth Extraction

Carboxylic acids are known to have a degree of selectivity for alkaline earths. For example, the Separations Science Data Base (11) presently has 30 entries in which a carboxylic acid is used to extract an alkaline earth. Thus, carboxylic acids were chosen as the class of compounds to use in these initial tests,

and a survey was made of the behavior of several carboxylic acids available in our laboratory. Table 2 shows the results of this survey. Both neotridecanoic acid and hexafluorobutyric acid would have been reasonable candidates as the cation exchanger, but V-acid was chosen for this work because of availability and because of our previous experience with the compound.

Figures 6, 7, and 8 show distribution coefficients as a function of aqueous-phase pH for the extraction of calcium, barium, and strontium by 0.1 M V-acid in toluene and 0.5 M V-acid + 0.05 M concentrations of various crown ethers. Strontium and barium extractions are synergized by all of the crown ethers tested, some very strongly. Calcium, however, (Fig. 6) is synergized only slightly by TBC15C5 and DC24C8 and is antagonized by the other crown ethers. It is particularly noteworthy that the synergistic effect produced on strontium extraction by DTBDB18C6 is so much smaller than that produced by DC18C6 and DTBDC18C6. This large difference suggests two possible reasons:

1. The strontium ion prefers the oxygen bonding sites arranged in some geometry that can be attained by the more flexible cyclohexo-substituted crown ether but not so easily attained by the more rigid benzo-substituted compound.
2. The electron withdrawing benzene rings are reducing the electron donating ability of the adjacent ether oxygens strongly (12,13).

The lack of synergism and the appearance of antagonism with calcium in this system are problems not presently understood, nor is the fact that, in the alkali metals, lithium shows little or no synergism in these systems, and indeed also shows antagonism in some cases. We have no data on magnesium and beryllium in the same system.

A more detailed examination of the synergistic effect of two crown ethers, DC18C6 and DC21C7, on the extraction of strontium,

TABLE 2.
Aqueous-Phase Distribution of High-Molecular-Weight Carboxylic Acids

Compound Name/Diluent	Percent Distribution from 0.1 M Sol. to Water 1st Equil.	Percent Distribution from 0.1 M Sol. to Water 2d Equil.	Half-Neutralization pH Over Water 4 M NaNO ₃	Percent Distribution from 0.1 M Sol. 0.75 in Na form to 4 M NaNO ₃ 1st Equil.	Percent Distribution from 0.1 M Sol. 0.75 in Na form to 4 M NaNO ₃ 4th Equil.
Versatic Acid 1519/Toluene	0.12	0.10	11.3	9.6	1.92
Versatic Acid 1519/Dodecane	0.19	0.40	11.0	9.4	—
Neotridecanoic/Toluene	0.04	0.26	9.7	9.5	2.12
Neotridecanoic/Dodecane	0.11	0.47	9.3	9.2	—
Lauric/Toluene	0.39	0.24	—	—	—
Lauric/Dodecane	0.14	0.22	—	—	—
Hexafluorobutyric/Toluene	99.7	99.7	1.3	0.8	99.9+
Hexafluorobutyric/Dodecane	—*	—	—	—	—
Empol 1014/Toluene	0.15	0.07	—	—	—
Empol 1014/Dodecane	1.44	0.26	—	—	—
Synaptic "A"/Toluene	0.25	0.16	—	—	—
Synaptic "A"/Dodecane	0.24	0.21	—	—	—

*Indicates third phase or emulsion formation.

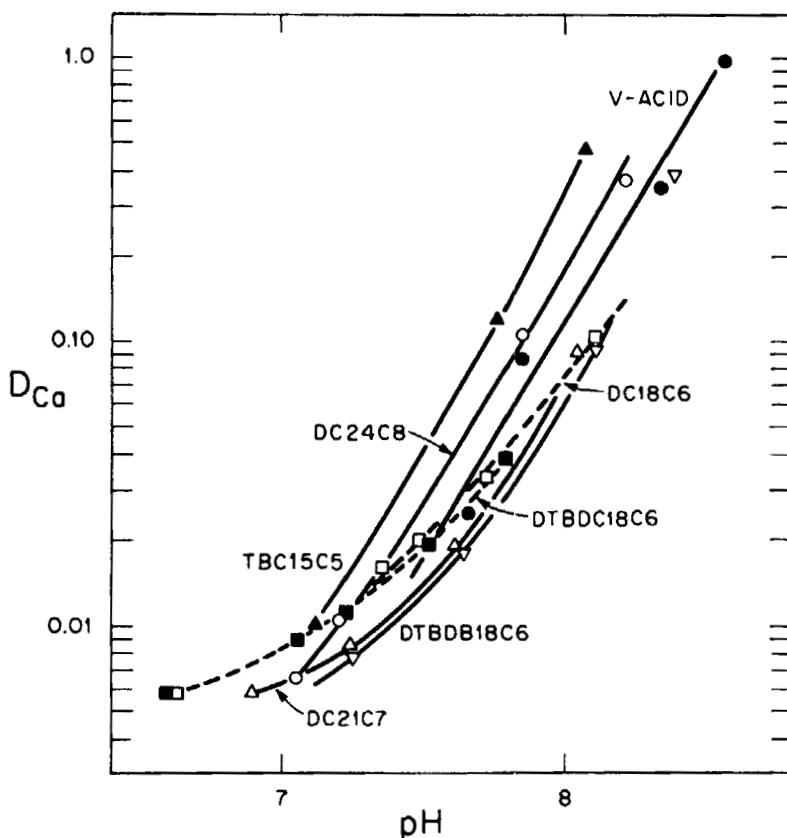


FIGURE 6. Extraction of calcium by 0.1 M Versatic Acid 1519 and in admixture with various crown ethers.

barium, and radium may be seen in Figs. 9, 10, and 11. The extraction curves with V-acid alone are in the same order as those found for phosphoric acids in earlier studies and of the same magnitude and general shape as the curve for the extraction of strontium by V-acid found earlier (14,15). The values in ref. 15 cannot, however, be directly compared with present results because octane was the diluent used in the earlier work, and toluene was used in the present work. From the work in ref. 15, the extraction maxima

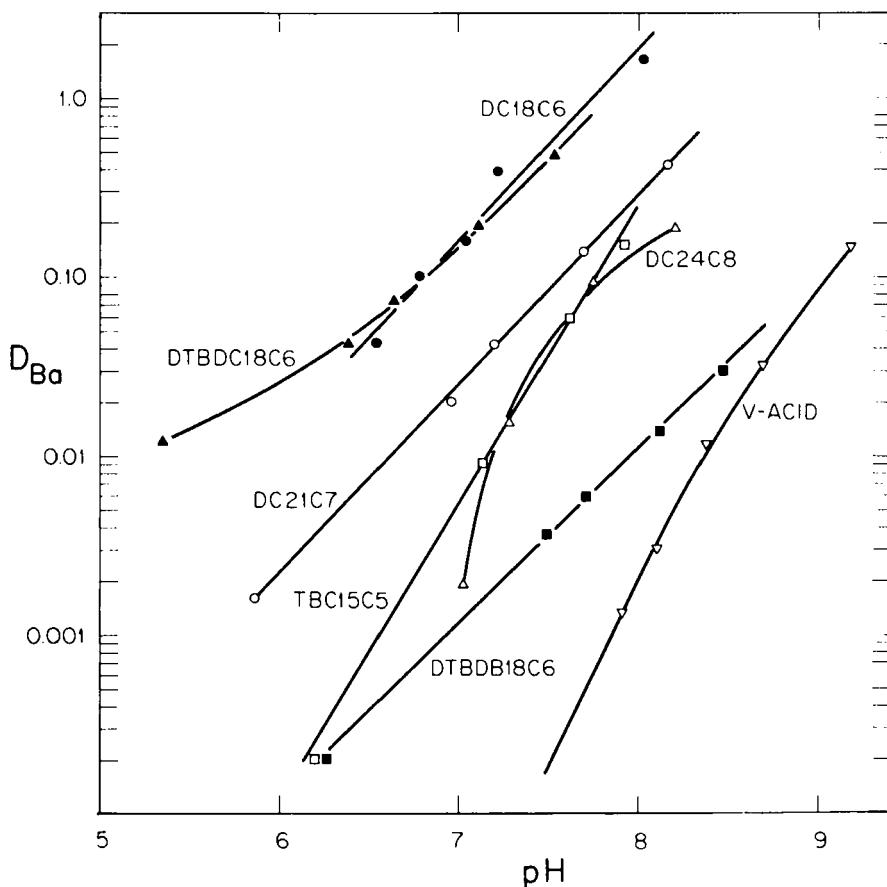


FIGURE 7. Extraction of barium by Versatic Acid 1519 0.1 M in toluene and as synergized by various crown ethers.

were shown to occur where the sodium salt/acid form ratio in the bulk organic phase matched that of the alkaline earth salt plus coordinating acid. The shape of the acid-alone curves in Figs. 9-11 are the same, indicating the same kind of salt-plus-additional-neutral-acid complexes in the organic phase, probably primarily $\text{SrA}_2 \cdot 3\text{HA}$, where HA represents the carboxylic acid.

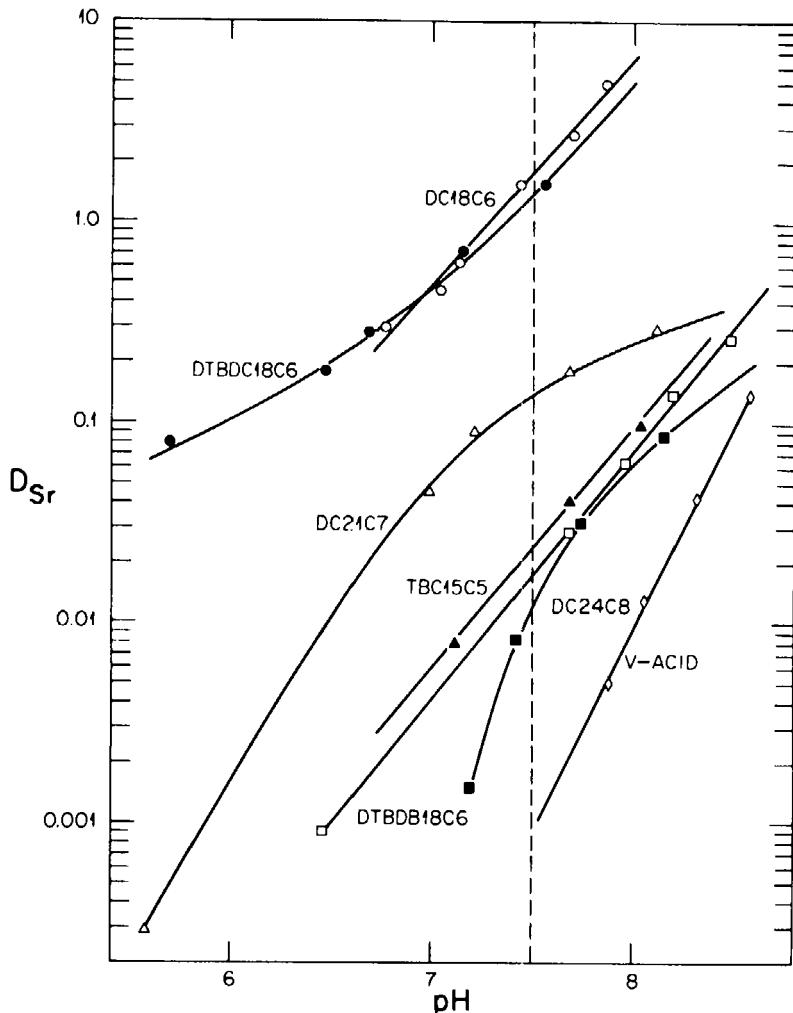


FIGURE 8. Extraction of strontium by Versatic Acid 1519 0.1 M in toluene and as synergized by various crown ethers.

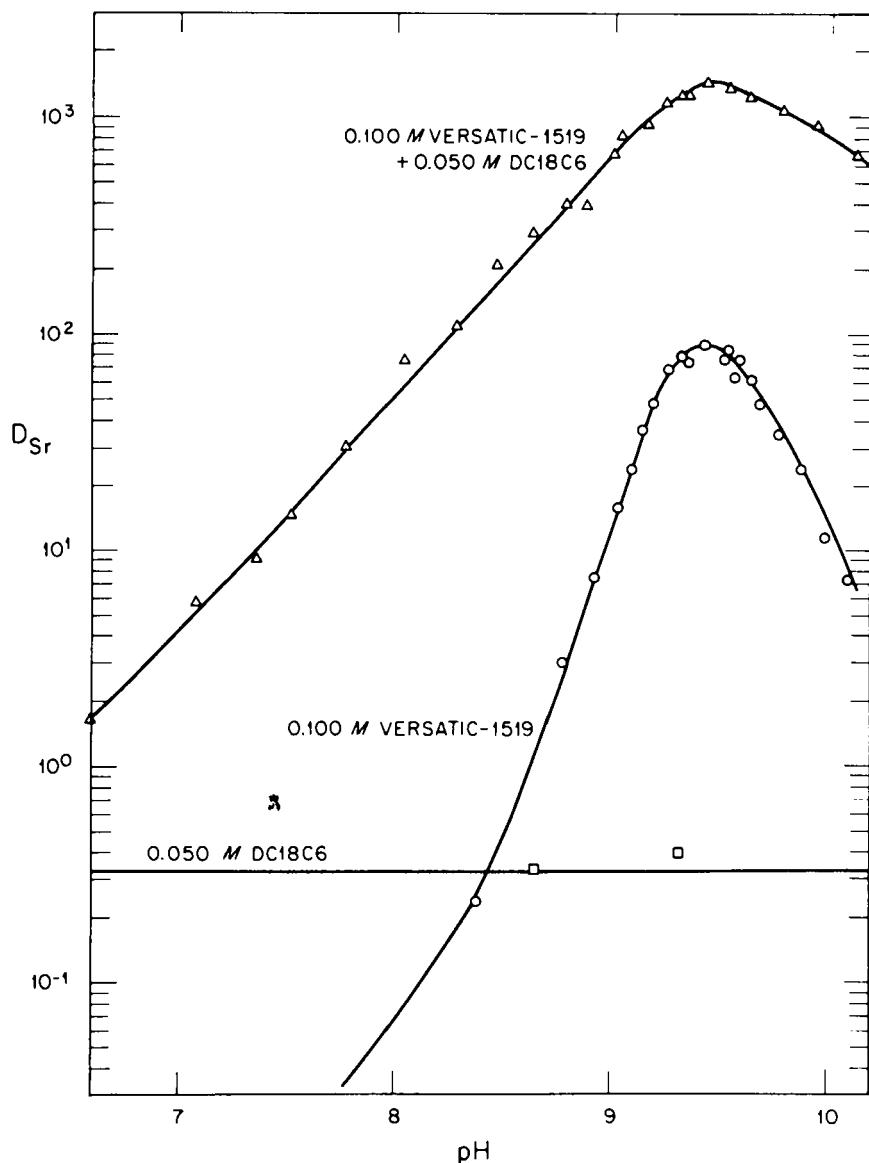


FIGURE 9. Extraction of strontium from 4.0 M NaNO_3 by 0.05 M DC18C6, 0.1 M Versatic Acid and by a mixture of the two reagents at these concentrations.

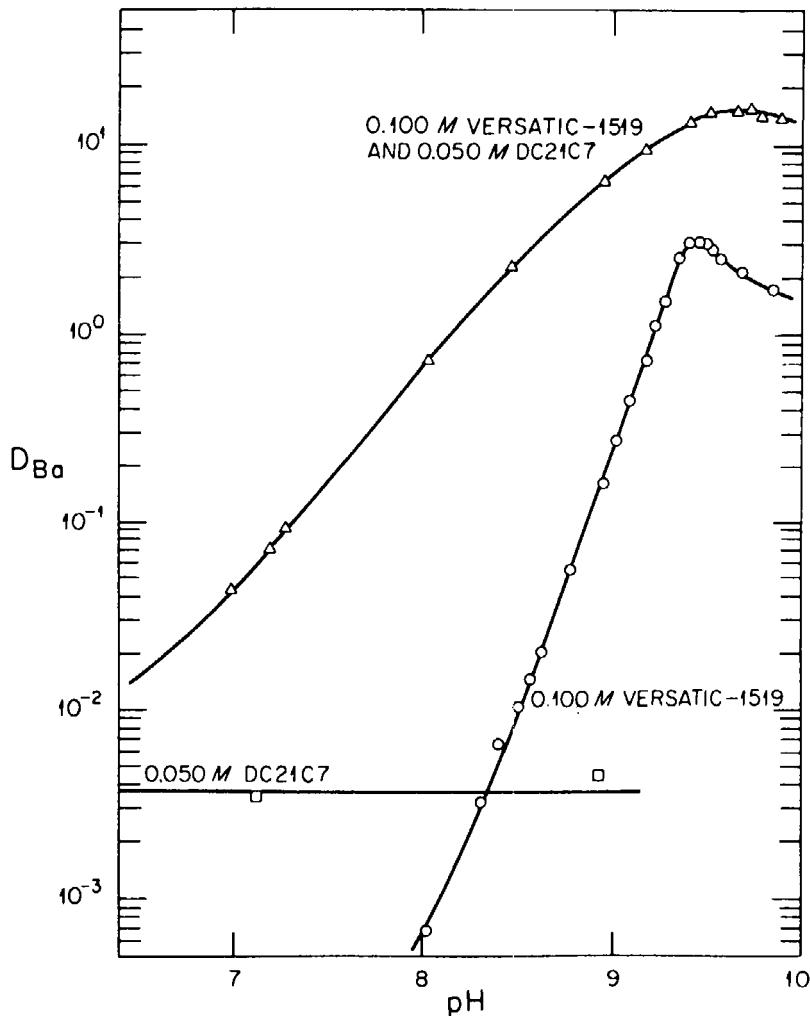


FIGURE 10. Extraction of barium from 4.0 M NaNO_3 by 0.05 M DC18C6, 0.1 M Versatic Acid, and by a mixture of the two reagents at these concentrations.

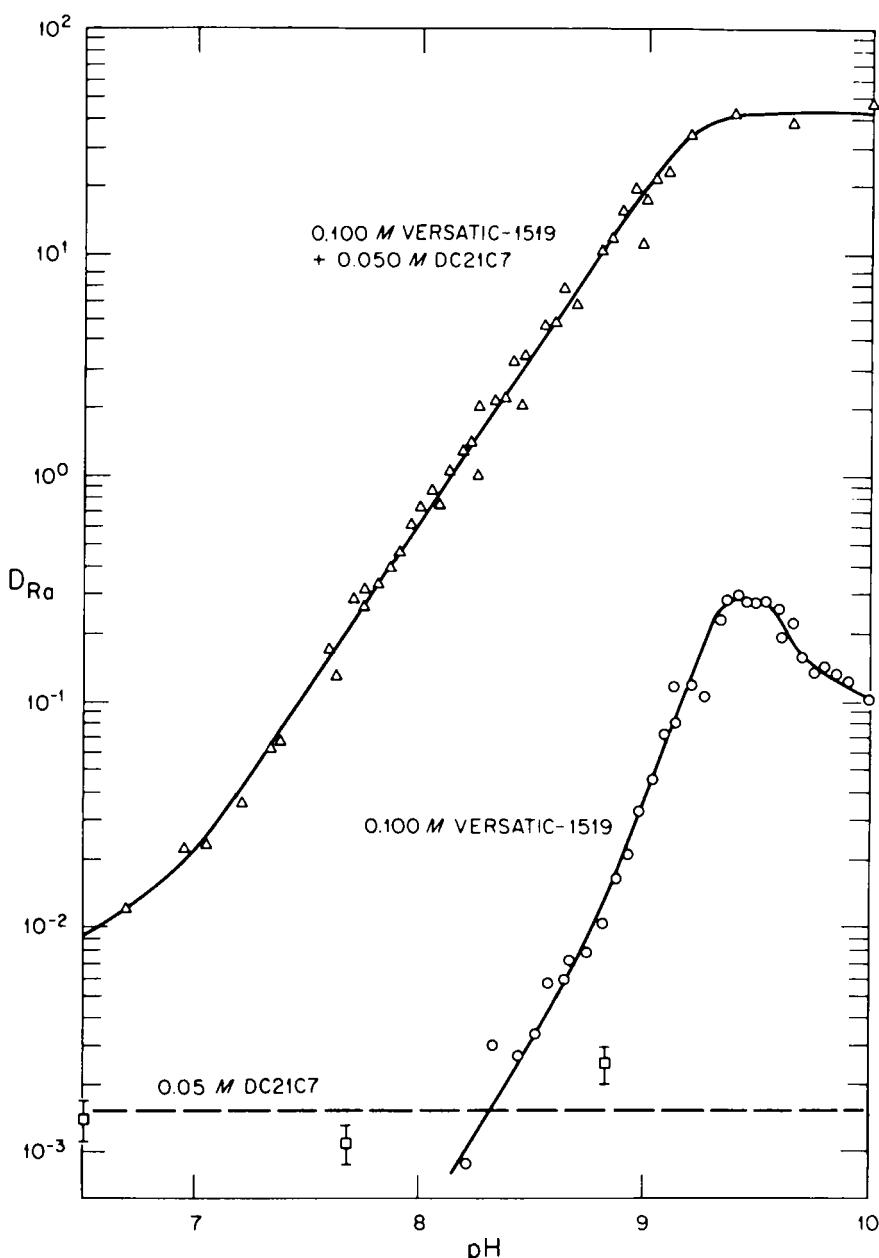


FIGURE 11. Extraction of radium from 4.0 M NaNO₃ by 0.05 M DC18C6, 0.1 M Versatic Acid, and by a mixture of the two reagents at these concentrations.

The shapes of the curves for the synergistic system extraction by V-acid plus crown ethers suggest that the coordination function of the neutral acid is being taken over by the macrocycle. The sharp peaks seen in the V-acid-alone curves do not appear. It is suggested that the coordination positions in the mixed crown ether-V-acid complex are filled by the crown ether and thus the unique complex composition-matching Na/HA ratio confers no special advantage on the extraction properties of the system.

The synergistic factor for strontium extraction as a function of pH is shown in Fig. 12. The shape of this curve is similar to those found in earlier synergistic studies with HDEHP and crown ethers (8,9). The maximum synergistic effect appears to occur near the intersection of the curves for extraction by the acid and the crown ethers alone in the cases observed.

Drawing from earlier work with the alkali metals and HDEHP and from some preliminary experiments with the alkaline earth/

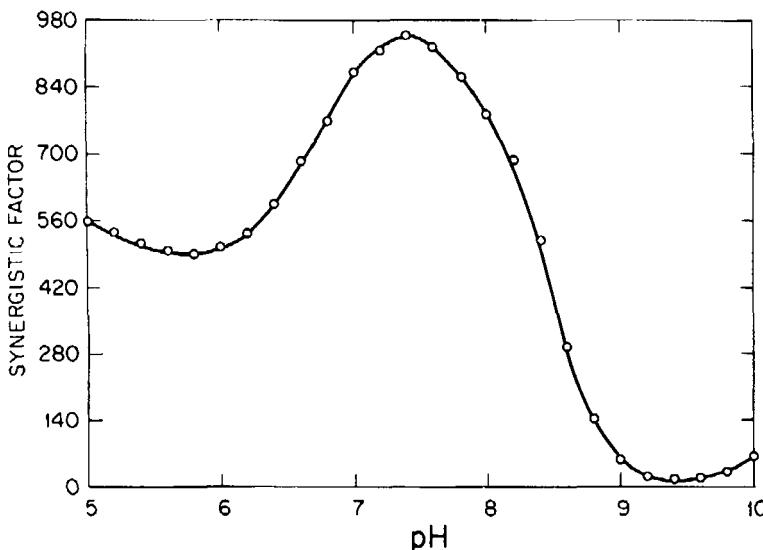


FIGURE 12. Synergistic factors for strontium extraction by DC18C6 and Versatic Acid as a function of pH, taken from Fig. 9.

crown ether/Versatic Acid system, we have taken as a first working assumption that one crown ether, along with sufficient acid to neutralize the ionic valence of the metal, would constitute the complex in solution in the organic phase. At present no direct reagent-dependence measurements have been made on this system, but continuous-variation experiments on radium, barium and strontium extraction as a function of Versatic Acid/crown ether mole ratio give results suggesting that the ratio alkaline earth/V-acid/crown ether is indeed 1:2:1. Figure 13 shows the continuous-variation curves for strontium extraction at two different pH values.

Multidentate vs Monodentate Coordination

The extra stability conferred on a complex by the chelate effect is well known and is discussed in numerous references (16). In many cases, a large portion of this increased stability is attributed to a smaller, more positive decrease in Δ entropy values in complex formation in the multidentate systems (17),

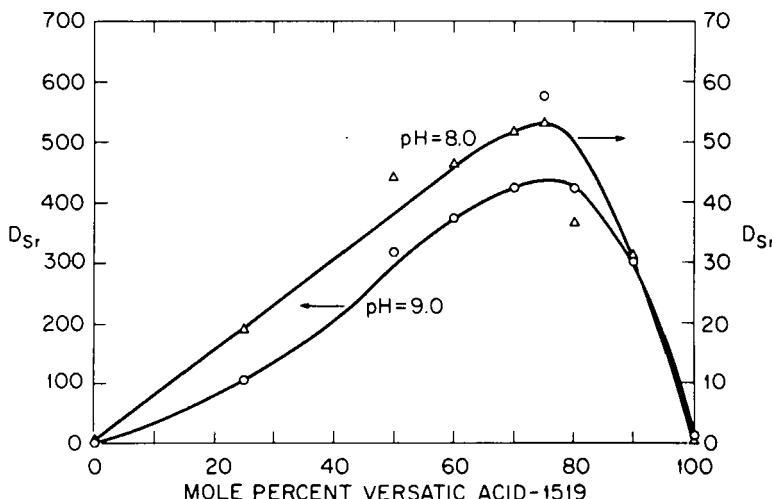


FIGURE 13. Strontium extraction vs a function of continuous variation of Versatic Acid/DC18C6 mole ratio.

although enthalpy contributions appear to be important in some cases. The increased stability of complexes of cyclic polyethers over their linear counterparts was noted in the early work of Frensdorff (5), and the term macrocyclic effect has been given to this increased stability by Cabbiness and Margerum (18). We have compared the crown ether synergistic effect observed here with that produced with some monodentate oxygen donor ligands. Figure 14 shows the effects produced by 0.3 M trioctylphosphine oxide and by hexyl ether compared with that produced by 0.05 M DC18C6 on strontium extraction by Versatic Acid. At pH 7.5, the extraction coefficient with 0.05 M DC18C6 is 85 times that produced by an equal concentration of trioctylphosphine oxide oxygen bonding sites, although the latter are much stronger coordinators. The synergistic factor with TOPO is about 2, as opposed to that with DC18C6, which is approximately 170. The extraction of $\text{Sr}(\text{NO}_3)_2$ by TOPO alone is significant. When the coordinating oxygens are the ether oxygens in organophilic hexyl ether (that should be of comparable coordinating strength to those of the crown ether), the ratio of distribution coefficients, crown ether/hexyl ether, is $1.7/0.0023 = 739$.

It is interesting to note that although the slope is 2 for the log strontium distribution versus pH curve with V-acid alone and with V-acid plus hexyl ether, the addition of DC18C6 or TOPO produces a lower slope. Because the organic-phase species have not been characterized, no explanations of these different slopes can be made.

SUMMARY

The crown ethers and related oxygen-donor-containing macrocycles can act as neutral-species extractants for metals (metal salts) if the macrocycle is sufficiently organophilic. The addition of cyclohexo and alkyl-substituted cyclohexo groups greatly increases the organic-phase distribution of crown ethers. Some crown ethers and related macrocycles form synergistic extraction systems when mixed with organic-phase-soluble acids (cation

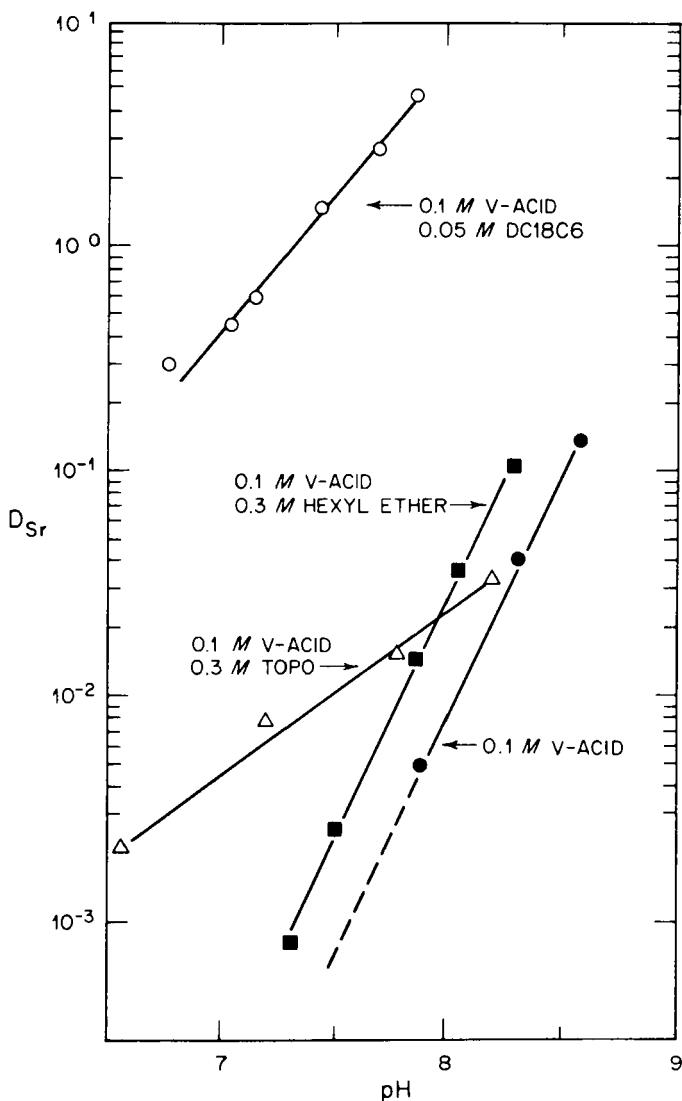


FIGURE 14. The comparison of the synergistic extraction effect produced by monodentate coordinators hexyl ether and TOPO with the effect produced by the macrocyclic coordinator DC18C6.

exchangers), and these systems exhibit a selectivity for the metal ions that most nearly corresponds to the macrocycle cavity size. This "size selective" synergistic effect is most prominent in the 15C5 (1.7-2.2 Å) to 21C7 (3.4-4.3 Å) size range. Larger and smaller macrocycles are much less effective with both alkali and alkaline earth elements.

The comparisons of macrocycles with monodentate oxygen coordinators of equal or greater individual coordinating power indicate macrocycle bonding to be much stronger, confirm the chelate and macrocycle effects observed by earlier workers, and suggest a strong contribution to the system stability due to a reduction in entropy.

More systematic investigations and much investigation into complex stoichiometries need to be made to understand these synergistic extraction effects.

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