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Selectivity and Equilibria in Extraction with Macrocycles in Synergistic Combination with Organophilic Acids

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ABSTRACT

Reported here is the behavior of several organophilic macrocyclic polyethers (crown ethers) as coordinative extraction synergists in combination with 1) a long-chain neo carboxylic acid, 2) an alkyl phosphoric acid, and 3) an alkyl-aryl sulfonic acid. Selected combinations of these organophilic cation exchangers and macrocyclic coordinators were examined as extractants for alkali, alkaline earth, and first-row transition elements from nitrate systems. Both synergistic and antagonistic effects were produced. Macrocycles having a cavity size to fit the metal ion usually produced the largest synergistic effect; however, the nature of the substituents on the macrocyclic ring also has a strong effect on selectivity. In general, alkali metal ions prefer to bond to benzo-substituted crown ethers while alkaline earth ions prefer to bond to cyclohexano-substituted ones. Iron, cobalt, and nickel extractions are antagonized by the macrocycles while copper is synergized only slightly and manganese and zinc moderately strongly. Evidence indicates that the organic-phase complex consists of a single macrocycle ring per metal together with acid anions sufficient to neutralize the metal valence. Sometimes neutral acid molecules are also included. Complicating features of the chemistry of these systems include the tendency of the crown ethers to form strong intermolecular compounds with the organophilic acids and the tendency of these acids and their salts to form aggregates.

INTRODUCTION

The ability of crown ethers to form coordination complexes with alkali and alkaline earth ions in polar solvent systems (water, water-alcohol, alcohol, chloroform, and ethylene dichloride) is well known and documented.(1) Some of the earliest work with crown ethers was a demonstration of their complexation with alkali metal ions by extraction of picrate salt of the metal into a chloroform solution of crown ethers.(2-6) The phenomenon of size selectivity in complexation was thus demonstrated. The use of organophilic acids to serve as organic phase cation exchangers in combination with organophilic crown ethers has been shown to allow extraction of alkali, alkaline earth, and other ions into organic solvents of low polarity such as toluene.(7-10) The organophilic acids that have been used in systematic studies are shown in Fig. 1.

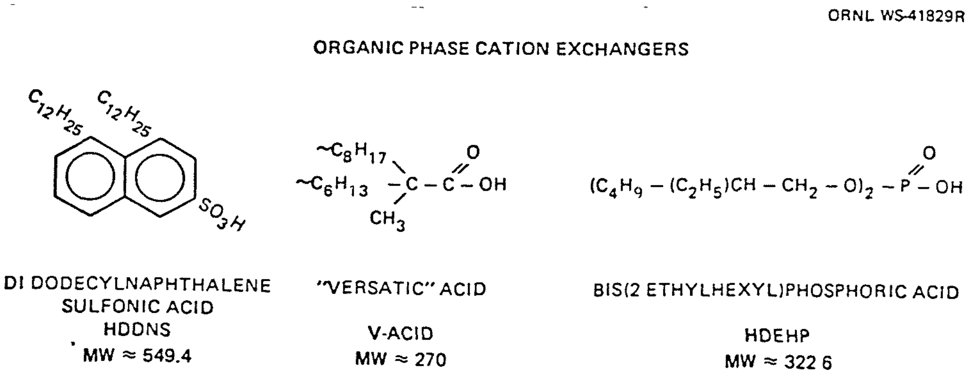

FIGURE 1. The Organic-Phase-Soluble Acids Reported in This Paper. All three compounds are liquids at room temperature.

The use of organic solvents (diluents) of low polarity allows the experimental system to more closely approximate the type of system that might be practical in a process where inexpensive diluents of low toxicity and high flash point are demanded. However, it also requires that macrocycles be chosen that are soluble in diluents of low polarity and that distribute to aqueous phases only slightly. The metal/salt adducts of these macrocycles should also be organophilic. A number of macrocycles have been found to fit these requirements. The ones used in this work are shown in Fig. 2.

The use of an organophilic acid (cation exchanger) in combination with an organophilic macrocycle in a diluent is believed to allow 1) the formation (perhaps at the organic/aqueous interface) of an organophilic salt of the metal ion, 2) the coordination of the metal ion by the macrocyclic compound accompanied by shedding of all or most of metal ion's water of hydration, and 3) transfer of the resulting organophilic complex to the organic phase.

Reported here are the results of, and conclusions from, several investigations using the reagents shown in Figs. 1 and 2.

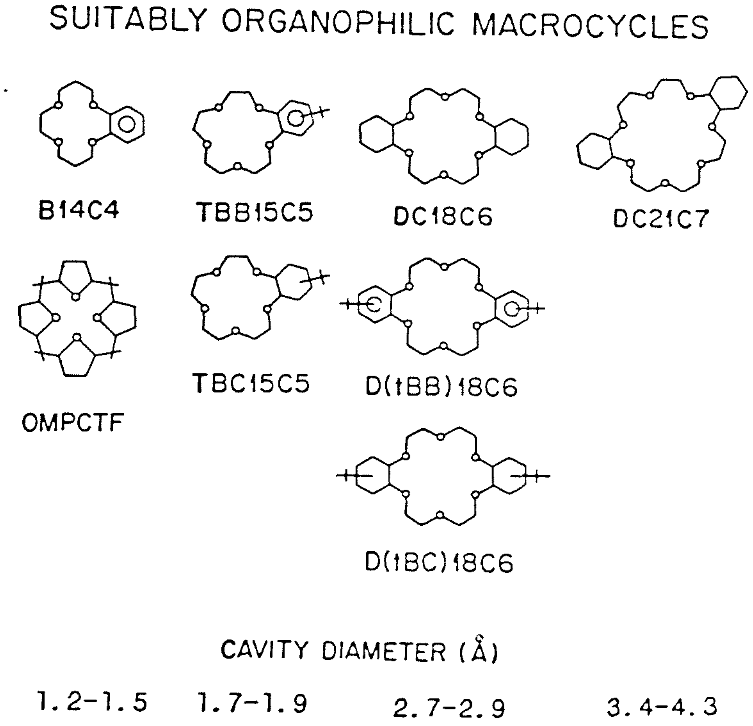

FIGURE 2. The Organic-Phase-Soluble Macrocycles Used as Synergists. B14C4 = benzo-14-crown-4, TBB15C5 and TBC15C5 = t-butylbenzo-15-crown-5 and t-butylcyclohexano-15-crown-5, DC18C6 = docyclohexano-18-crown-6 (tBB and tBC are t-butylbenzo and t-butylcyclohexano), DC21C7 = dicyclohexano-21-crown-7, ONPCTF = octamethylperhydrocyclotetrafurfurylene.

EXPERIMENTAL

Bis(2-ethylhexyl) phosphoric acid (HDEHP) was purified by Cu(II) precipitation and molecular distillation.(11,12) The neo carboxylic acid called "versatic acid 1519" (V-acid) was obtained from Shell Development Laboratories and purified by molecular distillation. The didodecylnaphthalene sulfonic acid (HDDNS) was obtained from King Industries of Norwalk Connecticut and purified by published ion-exchange procedures.(13) Crown ethers were obtained from Aldrich and Parish chemical companies. The macrocycles were stated to be 99% pure by infrared measurements by the supplier and were used as recieved.

The two-phase equilibrations were made in small separatory funnels or vials at room temperature, 23 to 25°C. Analyses of the equilibrated phases were usually by radiotracers, sometimes by atomic absorption spectrometry.

RESULTS AND DISCUSSION

HDEHP has considerable selectivity of its own for the alkalis and alkaline earths (See Fig. 3). For example, lithium is extracted more than the other alkali metals and beryllium more than the other alkaline earth metals. The addition of crown ethers to the system does, however, change the selectivity. Figure 3 illustrates synergism by two different concentrations of DC18C6. Extractions with the carboxylic acid, V-acid, show a strong preference for the alkaline earth elements over the alkali metals and strong synergistic effects by crown ethers are seen in the extraction of the alkaline earths. At pH 8.5 strontium extraction is synergized by a factor of approximately 1000 by DC18C6 and barium and radium by a factor of approximately 100 by DC21C7. Although insufficient detailed studies have been made, it appears that excellent selective separations of the alkaline earths from each other and from the alkali metals are possible using carboxylic acids with crown ethers.

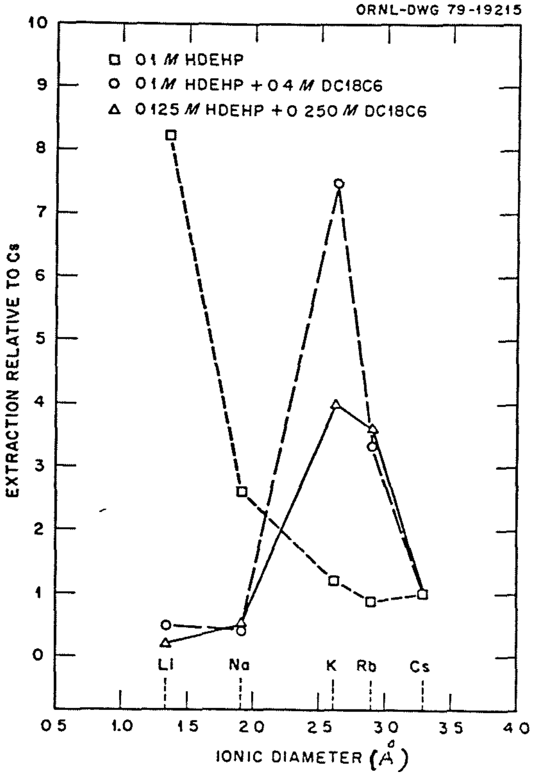

FIGURE 3. Synergistic Effects Produced by Two Different Concentrations of DC18C6 on Alkali Metal Extraction from a Solution 0.1 M in Each Alkali Metal Nitrate by 0.1 M HDEHP in Toluene.

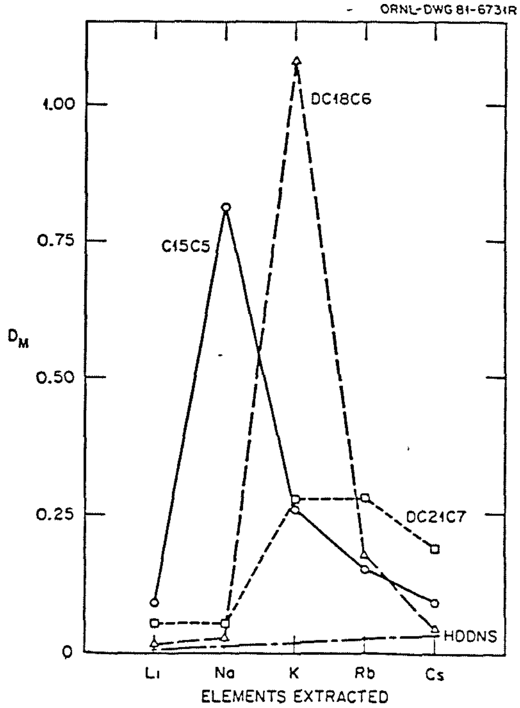

FIGURE 4. The Effects of Three Crown Ethers (0.05 M) on the Extraction Selectivity of 0.1 M HDDNS in Toluene for Alkali Metals from an Aqueous Solution 0.1 M in Each Alkali Metal Nitrate. (Fig. from Ref. 8)

Organophilic sulfonic acids used alone should be less selective than carboxylic or phosphoric acids because the sulfonic acid oxygens complex metals poorly. The data in Fig. 4 are consistent with this idea. Under these conditions we might expect most of the extraction selectivity shown by crown ether - sulfonic acid mixtures to be due largely to the crown ether. Strong size-selective synergism is seen in Fig. 4 where all the alkali elements were mixed in the same aqueous solutions (competitive extraction) and in Fig. 5 (from Ref. 10) where the metals were extracted separately at tracer level. But note also in Fig. 5 that there are significant differences between benzo- and cyclohexano-substituted crown ethers of the same size and that for potassium, rubidium, and cesium the benzo-substituted crowns produce the largest synergistic effect and thus, presumably, the strongest bond with the alkali metal.

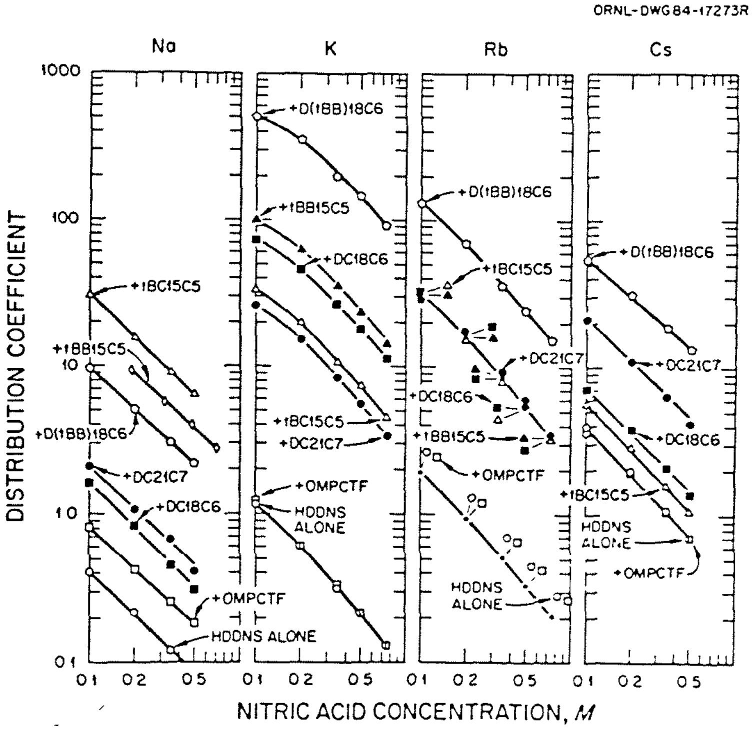

FIGURE 5. Extraction of Tracer-Level Sodium, Potassium, Rubidium, and Cesium from Nitric Acid by Toluene Solutions 0.1 M in HDDNS and 0.05 M in Macrocycle.

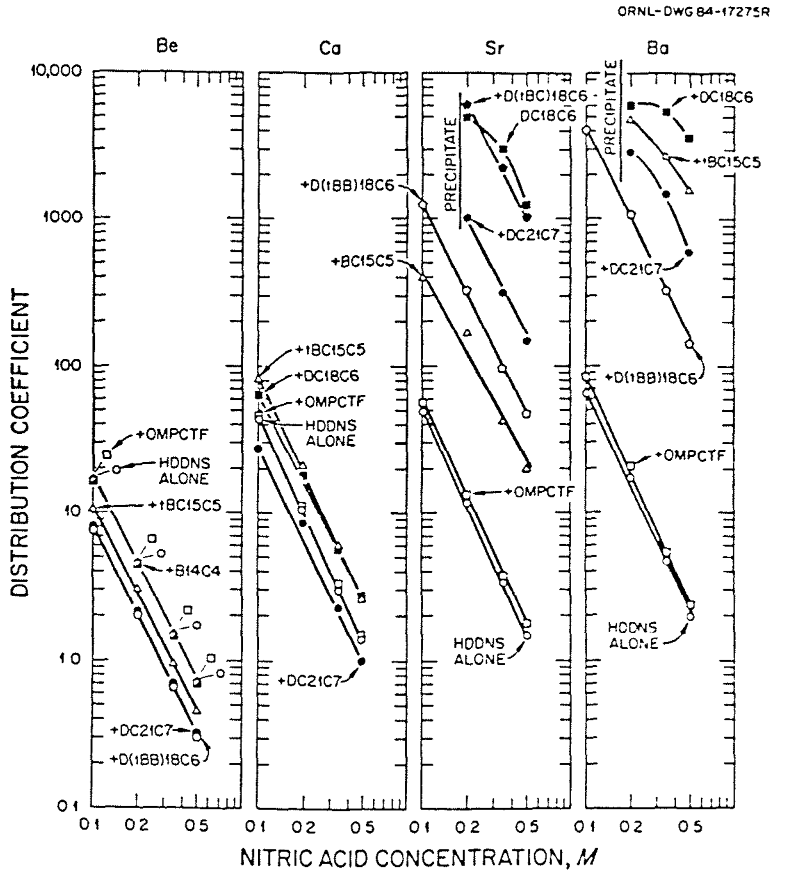

FIGURE 6 The Extraction of Tracer-Level Beryllium, Calcium, Strontium, and Barium from Nitric Acid by Toluene Solutions 0.1 M in HDDNS and 0 05 M in Macrocycles.

Figure 6 (from Ref. 10) shows the extraction of tracer-level alkaline earths with HDDNS and HDDNS plus crown ethers. Beryllium is not synergized, calcium only slightly, and strontium and barium very significantly. Note that here the benzo-substituted crowns are less effective synergists than the cyclonexano-substituted crowns. The benzo- and cyclohexano-substituted crown ethers reverse their selectivity between alkali and alkaline earth elements. For example, the extraction coefficient for potassium is 350 using the benzo-substituted crown but only 46 using the cyclohexano -substituted crown while for strontium the coefficients are 300 for the benzo- and 6000 for the cyclohexano-substituted compound. Rubidium and cesium both show stronger extraction with the benzo compound while, again, barium shows a strong preference for the cyclohexano-substutited compound. Inductive effects would be expected to reduce the electronégativity (basicity) of four of the six ether oxygens thus reducing their bonding strength and synergistic effect but would not explain an increase as in the case of potassium, rubidium and cesium. Further, *ion/cavity size correspondence seems to have little to do with this phenomenon.*

The cyclohexano-derivatives of crown ethers are known(14) to be more flexible than are the benzo-derivatives and this suggests the following speculation: 1) The more rigid benzo-substituted crown may maintain a cavity in solution thus allowing the alkali metal to profit in overall reaction energy from the fact that it is not necessary to rearrange the coordinating oxygens of the benzo-substituted compound into a cavity (entropy effect). 2) The doubly-charged alkaline earth ions may attempt to pull the bonding oxygens into some configuration not easily attained by the benzo-substituted crown ether (steric effect).

The 15C5 ring is the correct size to accept first-row transition metal ions; however, for the series of divalent elements manganese through zinc, only the end elements are synergized significantly. Copper is synergized very slightly and Fe(II), Co(II), and Ni(II) are antagonized (Fig. 7).

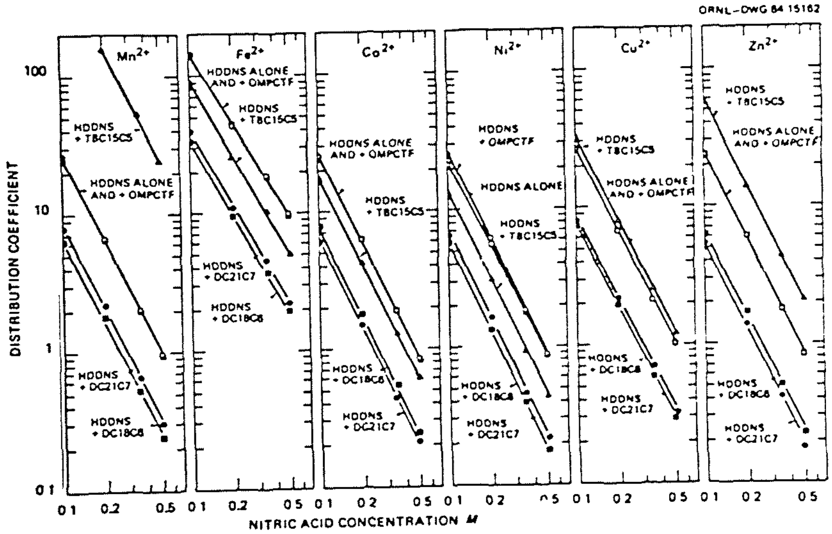

FIGURE 7. The Extraction of Tracer-Level Mamganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II), and Zinc(II) from Nitric Acid by toluene solutions 0.1 M HDDNS + 0.05 M tBC15C5 (Data from Ref. 10.)

In order to explain the *observed antagonistic* effect, one must propose reactions between the macrocycle and the organic acid that compete with metal complexation. Such reactions have been confirmed using vapor pressure osmometric (VPO) and infrared methods. For HDDNS and tBC15C5 two intermolecular adducts are required to satisfy least-squares fitting of the VPO data, tBC15C5$_2$(HDDNS)$_5$ and tBC15C5(HDDNS)$_3$. Since VPO measurements show HDDNS alone in toluene to be aggregated, a range of combining ratios in the adducts between HDDNS and tBC15C5 is suggested. *The differences in the effect of added tBC15C5 on extraction across* the divalent transition elements Mn through Zn (See Fig. 8) suggest that the structural-preference energy or ligand-field stabilization energy (LFSE) that would allow Fe(II), Co(II), and Ni(II) *to bond strongly with strong electron donors such as nitrogen is not available in the bond* to the weak electron donor oxygens in the crown ether. Further, the fact that five bonding sites are offered by the crown ether and two by the sulfonic acid argues for pentagonal bipyramid geometry and this is not consistent with the *usual pusedo-octahedral complex preference of* Fe(II), Co(II), Ni(II), and Cu(II). In other words, the structural and bonding preferences of these elements are not satisfied by tBC15C5 plus 2DDNS^{-1}. The organic phase (extraction) complexes formed in these studies have not been completely characterized. Studies to do this are underway. However, we do know that the crown ethers form adducts or complexes with the sulfonic acid but in diferent (average) combining ratios with different crown ethers. Also, for *those systems examined,* the evidence thus far (slope analysis and least-squares fitting of equilibrium data and isolation and analysis of solid compounds) indicates one crown ether per metal atom in the organic-phase complex. Various amounts of the sulfonic acid appear to be bonded depending on the concentration of *metal in the organic* phase. Infrared, proton nuclear magnetic resonance, and vapor pressure osmometry studies indicate that for the complex of strontium with DC18C6 and DDNS^{-1} the stoichiometry is $Sr(DDNS)_2 \cdot DC18C6 \cdot 2H_2O$ and that the strontium is within the DC18C6 ring. Studies of the extraction of very low concentrations of manganese (< 0.001 *M*) indicate the formation of the complex $Mn(DDNS)_2 \cdot 4HDDNS$. The macrocycle tBB15C5 does not form a complex with manganese.

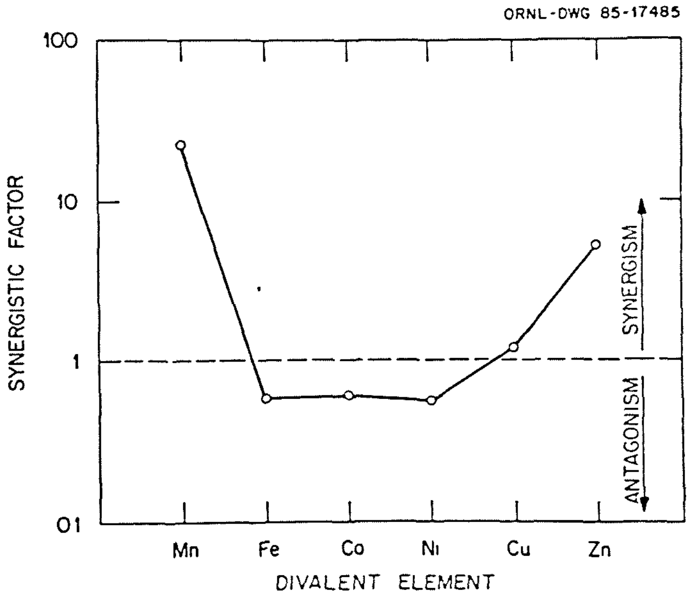

FIGURE 8. Synergistic Factors ($D_{mixture}/D_{HDDNS}$) for the First-Row Transition Elements Mn Through Zn due to the Addition of 0.05 M tBC15C5 to 0.1 M HDDNS in Toluene. The aqueous phase was 0.2 M nitric acid. (Fig from Ref. 10)

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