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SELECTIVE EXTRACTION OF Cu^{2+} AND Ag^{+} IONS FROM SULFURIC ACID BY SYNERGISTIC COMBINATIONS OF TETRADENTATE THIA MACROCYCLES WITH DIDODECYLNAPHTHALENE SULFONIC ACID

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ABSTRACT

The aqueous-insoluble thia macrocycles tetrathia-14-crown-4 (TT14C4) and tetrathia-16-crown-4 (TT16C4) strongly and selectively synergize the extraction of Cu^{2+} and Ag^{+} ions from aqueous sulfuric acid solutions by the organophilic cation exchanger didodecylnaphthalene sulfonic acid (HDDNS) in toluene diluent. Over a range of sulfuric acid concentrations, the selectivity is given by the order $Ag^{+} > Cu^{2+} > Mn^{2+}$, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, where synergism occurs only for Ag^{+} and Cu^{2+}. Selectivity factors greater than 300 have been achieved for Cu^{2+} over ubiquitous Fe^{3+}. The synergistic extraction of Cu^{2+} and Ag^{+} was explored as a function of sulfuric acid concentration, relative concentration of macrocycle vs. HDDNS, and loading.

INTRODUCTION

In recent work (1,2), we have investigated the selectivity of macrocyclic ethers as synergists for the cation-exchange extraction of the divalent first-row transition metals Mn^{2+} to Zn^{2+} from

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nitric acid.[a] With the use of t-butylcyclohexano-15-crown-5 (tBC15C5) as the synergist for either Versatic acid (a high-molecular-weight neo-carboxylic acid) or didodecylnaphthalene sulfonic acid (HDDNS), significant synergism occurred only for Mn^{2+} and Zn^{2+}, metal cations with spherically symmetric electronic ground states. In this respect, Mn^{2+} and Zn^{2+} behave like alkaline-earth cations, which we have shown may be strongly extracted by synergistic combinations of cation exchangers and oxa crown ethers of appropriate size and structure (1-8).

Oxa crown ethers may be considered comparatively weak-field ligands, probably not much different from, if not slightly weaker than, aquo ligands in their ability to split the d orbitals (2,9). Moreover, the geometries of most of the commonly available crown ethers, including tBC15C5, seem ill-suited for the preferred orthoaxial (pseudo octahedral) geometry of many transition-metal complexes. Both of these factors would tend to decrease the ligand-field stabilization energy (LFSE) of crown-ether coordination complexes of the nonspherically symmetric cations Fe^{2+} to Cu^{2+} and therefore select against these metal cations relative to cations immune to changes in LFSE, namely, Mn^{2+} and Zn^{2+}.

In the present work, we have begun to examine the synergistic behavior of macrocyclic extractants that have a more suitable ligand-field strength and geometry for extraction of transition-metal cations having non-zero LFSE. In this regard, tetradentate macrocyclic thia ethers have proven to be attractive to us based on the following reasoning. First, published ligand-field spectrochemical correlations (10) show that ligands based on amine or thia-ether donor groups have greater ligand-field strength than ligands bonding through oxygen atoms. Second, the tetradentate feature can potentially accommodate the needed 6-coordinate, pseudo-octahedral geometry, such that the remaining two coordination sites could be occupied by anions to give a neutral complex. Third, the weak basicity exhibited by thia-ethers with respect to protonation and hydrogen bonding (11-13) would be expected to discourage complications stemming from loss of the macrocycle to the aqueous phase, acid and water extraction, and strong associative interactions between the macrocyclic synergist and the cation exchanger. Such complications, some of which have been encountered with the macrocyclic oxa-ethers (1-8), seriously limit one's ability to characterize extraction equilibria, even employing computer-modeling techniques (14).

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[a] Since most aqueous metal cations discussed in this paper exist primarily in the form of the simple aquo complexes, we will for convenience uniformly treat all metal species as if this were the case by using Arabic superscripts to indicate both charge and oxidation state.

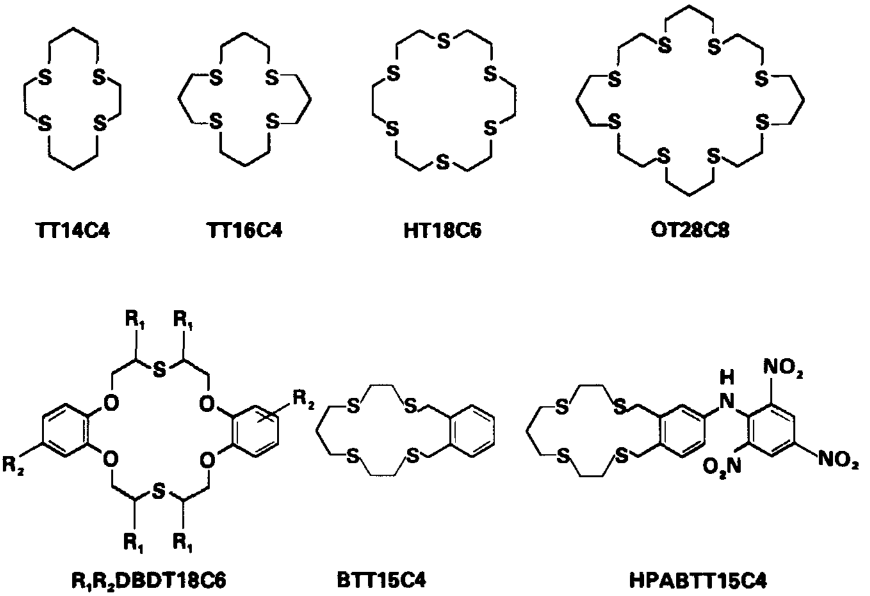

Fig. 1. Macrocyclic Thia Ethers Used in Solvent Extraction Research. For short abbreviations, the "crown" system has been employed. Thus, TT14C4 is tetrathia-14-crown-4, TT16C4 is tetrathia-16-crown-4, HT18C6 is hexathia-18-crown-6, OT28C8 is octathia-28-crown-8, R_1R_2DBDT18C6 is the set of dibenzodithia-18-crown-6 compounds with various alkyl substituents, BTT15C4 is benzotetrathia-15-crown-4, and HPABTT15C4 is the ionizable macrocycle picrylaminobenzotetrathia-15-crown-4.

By reference to the hard-soft-acid-base (HSAB) classification system (11), the "soft" character of the thia-ether donor group would be expected to lead to strong adducts with "soft" metal ions like Ag^+, Au^+, Cu^+, Pd^{2+}, and Hg^{2+}. Not surprisingly, monofunctional thia ethers have found significant application as strong, selective extractants in the concentration and analysis of such metals (15). In this connection, it may be noted that Ag^+, Au^+, Cu^+, Hg^{2+}, and Pd^{2+} ions ordinarily possess low coordination numbers (11) and accordingly get extracted by monodentate thia ethers as species containing only one or two sulfur-donor ligands (15).

By progressing to macrocyclic thia ethers such as those depicted in Fig. 1, it is generally hoped to optimize selectivity by appealing to the geometrical coordination requirements of a given metal. Table I summarizes the reported solvent extraction results using the macrocycles shown in Fig. 1. A widely recognized feature of the coordination chemistry of some thia macrocycles is the ability to assume an exodentate (i.e., "inside-out") conformation as shown in the structures of $(NbCl_5)_2(TT14C4)$ (27) and pure crystalline TT14C4 (28). Thus, at least for the unsubstituted thia crowns, the baseline selectivity in extraction may be expected to qualitatively resemble that of the monofunctional thia ethers. As shown in Table I, the macrocycles indeed select some or all of the metal ions Ag^+, $Au^{3+/+}$, Cu^+, Pd^{2+}, and Hg^{2+} over Group I and II metal ions plus the divalent first-row transition metal ions Mn^{2+} to Zn^{2+}. It has been pointed out that the decisive factor in producing this selectivity for soft metals is the presence of the thia-ether donor group (24). Some variation in the selected soft metals in Table I provides an indication that the selectivity within the soft-metal class may be controlled through macrocycle structure.

Although all of the divalent cations Fe^{2+} to Zn^{2+} have been classified as "borderline" Lewis acids in the HSAB classification system (11), only Cu^{2+} has been found to be extractable by any of the macrocyclic thia ethers (Table I). Furthermore, of the thia macrocycles tried, only tetrathia-14-crown-4 (TT14C4) has been shown to extract Cu^{2+}, though the extraction is weak by comparison with the soft metals. Probably because the softer Cu^+ cation is the more extractable form of copper using thia macrocycles, Cu^{2+} has not received much attention. However, in situations where it is desirable to separate copper from solutions containing high concentrations of reducible cations like Fe^{3+}, extraction of copper as Cu^{2+} would clearly be advantageous.

In homogeneous aqueous solution, complexation constants in the range 160 to 21,800 M^{-1} in 0.1 M $HClO_4$ at 25 °C (29) indicate favorable coordination of Cu^{2+} ion by certain thia macrocycles. In a series of tetradentate macrocyclic thia ethers of various sizes, TT14C4 gave the maximum complexation constant with Cu^{2+}. For the isolated compound $Cu(TT14C4)(ClO_4)_2$, an X-ray structure determination showed the centrally coordinated Cu^{2+} cation to lie in the plane of four equidistant sulfur donor atoms with the perchlorate anions occupying the axial coordination sites in monodentate fashion (30). On the basis of the aqueous complexation constants and X-ray structural results, TT14C4 is, in fact, thought to represent an optimum ligand geometry for the coordination of Cu^{2+} (29). Thus, it is reasonable to propose to exploit these favorable properties of TT14C4 for separating Cu^{2+} ions from aqueous solutions.

Like the majority of extraction systems employing crown ethers (31), the cases cited in Table I rely mostly on the co-extraction of anions from the aqueous phase. In such cases, the extractability of metal cations is highly medium dependent, and

Table I. Solvent Extraction of Metals Using Thia Macrocycles

Macrocycle[a] (B)	Strongly Extracted Metals[b]	Partially Extracted Metals[b]	Rejected Metals[b]	Co-Extracted Anions[c] (A^-)	Postulated Complexes[e]	References
TT14C4	$Ag^+, Hg^{2+}, CH_3Hg^+, Cu^+$	Cu^{2+}, Pd^{2+}	$Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Tl^+$	Pic^-	$AgBA, AgB_2A, HgBA_2, CuBA, PdBA_2, PdB_2A_2$	16-19
TT14C4	Cu^+	Cu^{2+}		BCG,TB		16
TT14C4	Ag^+, Hg^{2+}, Cu^+		Cu^{2+}	Cl^-, ClO_4^-	$AgBA, AgB_2A, HgBA_2$	17,20-22
TT14C4	Cu^+, Cu^{2+}			BPh_4^-		17
HT18C6	Ag^+, Hg^{2+}			Pic^-	$AgBA, Ag_2BA_2$	19
HT18C6	Ag^+, Hg^{2+}			Cl^-, ClO_4^-	$AgBA, HgBA_2$	23
OT28C8	Ag^+, Hg^{2+}			Cl^-, ClO_4^-	$AgBA, AgB_2A, HgBA_2$	20-22
R_1R_2DBDT18C6	Ag^+, Pd^{2+}, Au^{3+}	Cu^+, Hg^{2+}	$Cu^{2+}, Ni^{2+}, K^+, Sr^{2+}, Zn^{2+}$	Pic^-		24
R_1R_2DBDT18C6	Ag^+			PF_6^-, ClO_4^-		
R_1R_2DBDT18C6		Ag^+		NO_3^-		
R_1R_2DBDT18C6	Ag^+			$(DEHP^-)$[d]		
BTT15C4	Ag^+, Cu^+, Au^+		$Cu^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}$	ClO_4^-		25
HPABTT15C4	Ag^+, Cu^+		$Na^+, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pd^{2+}, Hg^{2+}$	$(PABTT15C4^-)$[d]	AgL,CuL	26

[a] Structural formulas and names for the macrocycles are given in Fig. 1.

[b] The extractability of a given metal was categorized qualitatively from reported distribution coefficients; roughly, the three categories correspond respectively to $D_M > 10$, $0.1 < D_M < 10$, and $D_M < 0.1$.

[c] BCG ≡ bromocresol green, TB ≡ thymol blue, Pic^- ≡ picrate, BPh_4^- ≡ tetraphenylborate, and $DEHP^-$ ≡ di-2-ethylhexylphosphate (organophilic anion).

[d] These organophilic anions together with their conjugate acid forms remain entirely in the organic phase. No anion transfer need occur.

[e] In work carried out with high-dielectric-constant diluents such as nitrobenzene (18,19-23), the anions may dissociate, giving charged organic-phase species.

often large, poorly hydrated anions like picrate must be used to effect the extraction. By contrast, use of macrocycles as synergists for organophilic cation exchangers allows for strong, selective extraction without the necessity to transfer aqueous anions (1-8). One of the systems listed in Table I, in fact, employs di-2-ethylhexylphosphoric acid (HDEHP) as the cation exchanger for Ag^+ extraction synergized by alkyl-substituted dibenzodithia-18-crown-6 (R_1R_2DBDT18C6). In the case of picrylaminobenzotetrathia-15-crown-4 (HPABTT15C4), the macrocycle incorporates the cation-exchange feature in an ionizable side group for the extraction of Ag^+ and Cu^+. Based on the results shown in Table I, however, neither R_1R_2DBDT18C6-HDEHP nor HPABTT15C4 seem to be good candidates for the selective extraction of Cu^{2+}, especially in view of the hydrolysis problems that would likely be encountered for other cations like Fe^{3+} that may be present at the pH values required for extraction.

As a test of the reasoning given above, it was first our object to survey the extraction behavior and selectivity of TT14C4 and TT16C4 as synergists for HDDNS in the extraction of the divalent first-row transition metals Mn^{2+} to Zn^{2+}. The choice of HDDNS as an economical cation exchanger provides a comparison with previous data (1,2) using the oxa-crown ethers as synergists for HDDNS; in addition, HDDNS allows cation exchange to take place under highly acidic conditions where metal ion hydrolysis and pH control present little difficulty and where important possible applications exist. We view the relatively low selectivity of HDDNS and other sulfonic acids as advantages in our studies of synergism because of the greater degree of control of the final selectivity that can be gained by manipulation of macrocycle structure. Upon finding good selectivity for Cu^{2+}, we extended the study to include the metals Ag^+ (possible co-product expected from Table I to be strongly extracted) and Fe^{3+} (major impurity in many applications) and to include a wider range of conditions under which these systems could be exploited for useful separations.

EXPERIMENTAL SECTION

Chemicals

The structure and purification of HDDNS (didodecylnaphthalene sulfonic acid) were described previously (2). TT14C4 and TT16C4 (Fig. 1) were purchased from Aldrich Chemical Company (nominal 95% and 97% purities, respectively). Both compounds were recrystallized from mixtures of ethyl acetate and petroleum ether to remove slight impurities. Good purity was indicated by thin-layer chromatographic tests (one spot detected using silica plates, ethyl acetate elution, Br_2 detection) and by the agreement of the melting points with literature values (32).

Water was doubly distilled in a borosilicate-glass apparatus (first over $KMnO_4$). The toluene diluent (Burdick and Jackson Laboratories) was of "spectro-grade" quality. All other chemicals were of "reagent-grade" quality.

Equilibration and Measurement Techniques

The tracers and scintillation-counting techniques have been described previously (2); the Ag tracer used here was ^{110}Ag. The tracers had been converted before use to the nitrate or sulfate salts as appropriate.

In all equilibrations, toluene was employed as the organic diluent. Except as noted for certain cases, the volume ratio of the two phases was generally 1, and the metals were initially present in the aqueous phase. Trace concentrations of metal salts were employed except in loading studies. All distribution measurements were conducted for each metal separately; i.e., each system contained only a single metal salt at a time.

Four contacting methods were employed. These included (a) rocking the two phases gently (no dispersion) in a separatory funnel in a thermostatted water bath at 25.0 ± 0.1 °C, (b) gently stirring the phases (no dispersion) in capped containers in a thermostatted air box at 25.0 ± 0.3 °C, (c) dispersing the two phases in capped vials using an end-over-end tumbling motion at ambient temperature (23 ± 2 °C), and (d) bubbling N_2 gas in a vented vial containing the two phases at ambient temperature for 15 min (Fe^{2+} extraction tests only). In the third method (used predominantly throughout this work), we employed a uniform contacting time of 30 min, shown by time-dependence studies to be adequate to achieve equilibrium in the extraction of any of the metals examined from sulfuric acid. Under these conditions, the measured metal distribution coefficients (D_M) were, in fact, stable for days within experimental error (±15%) and were not noticeably sensitive to room light as shown by parallel dark tests.

No visible precipitation problems were encountered in any of the synergistic systems using sulfuric acid as the aqueous phase. However, some cloudiness appeared in the organic phase when $[H_2SO_4]_{aq} < 0.1$ M, presumably because of insufficient ionic strength for good coalescence; in such instances, the cloudiness was removed by centrifugation. Checks were made for loss of the tracer to adsorption or precipitation phenomena, but it was, with two exceptions, possible to account (±15%) for all of the initial activity in the system as being distributed between the two homogeneous liquid phases. The exceptions included the use of either macrocycle alone and the use of nitric acid as the aqueous phase; in both cases, significant loss of activity was encountered.

RESULTS AND DISCUSSION

Distribution of Macrocycles

A preliminary test of the distribution of the macrocycles TT14C4 and TT16C4 between toluene and water was conducted by equilibrating solutions of each macrocycle with large volumes of water, evaporating aliquots of the equilibrated solvent, and weighing the residue. The toluene solutions initially contained 0.05 M macrocycle and were rocked gently for approximately 18 h at 25 °C with water at aqueous-to-organic volume ratios varying from 1 to 100. No loss of the macrocycles to water could be detected within the uncertainty of the method, indicating that the distribution coefficient ($D_B = [B]_{org}/[B]_{aq}$) for either macrocycle (B) must be greater than 1×10^3. By reference to previous measurements (6,7), our present results indicate that the thia macrocycles exhibit considerably greater hydrophobicity than related macrocyclic oxa ethers, even compared to crowns having added alkyl substituent groups. One factor contributing to this advantageous property may be the weaker ability (13) of the sulfur atoms to engage in hydrogen bonding. Weak solvation of free thia macrocycles in aqueous media has been documented previously (29).

Extraction of Metals from Nitric Acid

To facilitate direct comparison of results with earlier data reported (1,2) for the oxa-ether macrocycles, it was our original plan to extract tracer quantities of metals from 0.1-0.5-M aqueous nitric acid using toluene solutions containing 0.05 M macrocycle plus 0.1 M HDDNS. Although neither TT14C4 nor TT16C6 synergized the extraction of Sr^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, or Zn^{2+} ions under these conditions, significant synergism was encountered in the extraction of Ag^+. However, severe problems with the reproducibility of the measured Ag^+ distribution coefficients (D_{Ag}) led to an examination of D_{Ag} as a function of time. In the extraction of Ag^+ from 0.3 M nitric acid using 0.05 M macrocycle plus 0.1 M HDDNS (slow stirring at 25 °C), D_{Ag} was well in excess of 1000 after 19 h of contacting using either TT14C4 or TT16C4 as the synergist. Over the course of 5 d, these values plummeted approximately 2 orders of magnitude, approaching the value 14 measured using 0.1 M HDDNS without added macrocycle. The apparent loss of synergism was accompanied by the appearance of white interfacial precipitates. The precipitates were observed over the entire range of aqueous nitric acid concentrations tested (0.1 to 0.5 M). Although the precipitates were not analyzed, they probably may be attributed to the nitric acid-induced decomposition of the macrocycles because (a) the precipitates occur even when no metal is present, and (b) no precipitate forms when using 0.1 M HDDNS alone or when using dilute sulfuric acid instead of nitric acid. Some tendency toward oxidation was noted previously (15) as a potential problem in the use of monofunctional thia-ether extractants. Indeed, the nitric acid oxidation of thia ethers represents a known synthetic method for preparing the corresponding alkyl sulfoxides (33). Recent extraction results (24) for R_1R_2DBDT18C6 (Table I) were obtained using nitric acid media, but the stability of the macrocycle was not discussed.

Extraction Selectivity from Sulfuric Acid

Distribution data for the extraction of the divalent metals Mn^{2+} to Zn^{2+} plus Fe^{3+} from aqueous sulfuric acid solutions are given in Table II. Unlike the nitric acid systems, the sulfuric acid systems give repeatable and stable distribution coefficients after a 15-30-min equilibration time (end-over-end contacting). Measurements not listed in the table showed that neither macrocycle used alone (0.05 M) is capable of extracting any of the metals significantly above the detectability limits of the scintillation-counting techniques used here (i.e., $D_M < 5 \times 10^{-4}$). On the other hand, Table II shows that toluene solutions containing only 0.1 M HDDNS exhibit a limited and essentially nonselective ability to extract the divalent first-row metal cations from dilute sulfuric acid. A similar observation was made for extraction of these metals by HDDNS from nitric acid (1,2). The falloff in D_M with increasing acidity follows from normal mass-action principles and is consistent with cation-exchange equilibria (34).

Figure 2 dramatizes the fact that, of the divalent metal ions Mn^{2+} to Zn^{2+}, only the extraction of Cu^{2+} is synergized by the macrocycles. Since $D_{M \neq Cu}$ appears to be independent of the addition of either macrocycle to HDDNS, it seems likely that even better selectivity for Cu^{2+} could be obtained by raising [macrocycle] relative to [HDDNS]. In terms of the dimensionless "synergistic coefficient" S (defined in the usual way as the metal distribution coefficient in the synergistic system divided by the sum of metal distribution coefficients corresponding to the two separate extractants acting independently), the synergistic enhancement of the Cu^{2+} extraction from 0.3 M H_2SO_4 is 740 and 100 for TT14C4 and TT16C6, respectively. As shown below, S can be increased for tracer-level extraction of Cu^{2+} by employing the more optimum 1:1 ratio of [macrocycle] to [HDDNS]. Unlike previously studied systems involving combinations of oxa crown ethers and cation exchangers such as HDDNS (1,2,35,36), the present combinations of thia macrocycles with HDDNS show no antagonistic effects for any of the metals examined. This may be attributable to the weak ability of the sulfide donor group to accept hydrogen bonds (13) and thereby associate with HDDNS.

Table II. Selectivity of Synergistic Combinations of Thia Macrocycles and HDDNS for First-row Transition Elements[a]

	Aqueous $[H_2SO_4]$	Distribution coefficients						
		Mn^{2+}	Fe^{2+}	Fe^{3+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
0.1M HDDNS	0.03	26			59	99	99	75
0.05M TT14C4 + 0.1M HDDNS	0.03	27			55	92	1400	72
0.05M TT16C4 + 0.1M HDDNS	0.03	28			52	110	363	69
0.1M HDDNS	0.3	1.1	1.5	2.8	1.2	1.3	1.3	1.2
0.05M TT14C4 + 0.1M HDDNS	0.3	1.1	1.5	3.1	1.2	1.3	960	1.2
0.05M TT16C4 + 0.1M HDDNS	0.3	1.1			1.2	1.3	13	1.2
0.1M HDDNS	3.0	0.0068	0.013	0.006	0.014	0.0087	0.012	0.0100
0.05M TT14C4 + 0.1M HDDNS	3.0	0.0071	0.013	0.005	0.014	0.0086	21	0.0096
0.05M TT16C4 + 0.1M HDDNS	3.0	0.0062			0.015	0.0083	1.3	0.0091

[a] Conditions: 23 ± 2°C; equal phase volumes; 30-min contacts in capped vials by end-over-end rotation. Each aqueous phase initially contained only H_2SO_4 (at the molarity given in the table) plus the sulfate salt of the metal to be determined. Fe^{2+} and Fe^{3+} were initially present at 1.0×10^{-4} M; all other metals were present at tracer concentrations only. For the extraction of Fe^{2+}, hydroxylamine sulfate was employed as a holding reductant, and the equilibration was carried out under N_2.

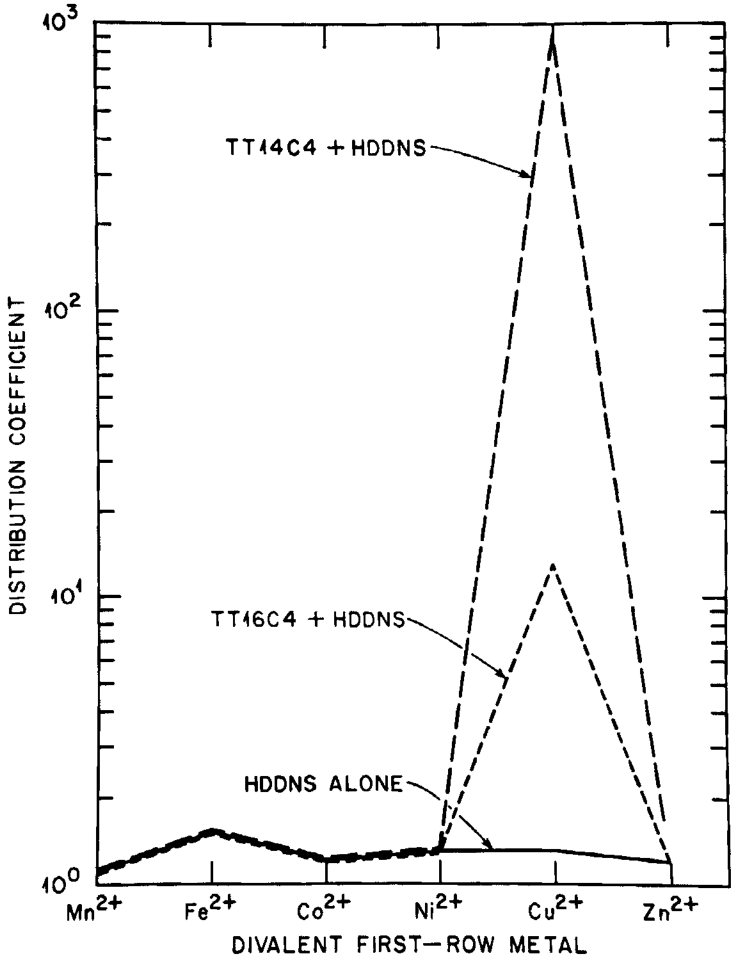

Fig. 2. Selectivity of Synergistic Combinations of Macrocyclic Thia Ethers and HDDNS. Three distribution coefficients are plotted for each divalent metal using the following solvents (toluene diluent): (—) - 0.1 M HDDNS, (---) - 0.05 M TT16C4 + 0.1 M HDDNS, and (— —) – 0.05 M TT14C4 + 0.1 M HDDNS. Conditions: 0.3 M H_2SO_4 containing tracer-level metals as initial aqueous phase and end-over-end contacting at 23 ± 2 °C.

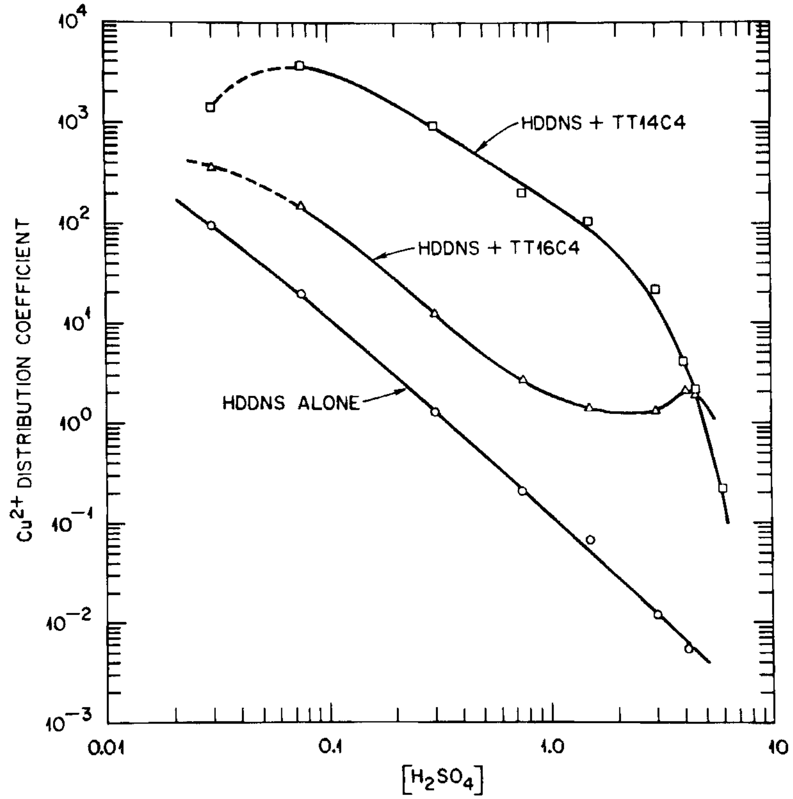

Fig. 3. Effect of Sulfuric-Acid Concentration on Cu^{2+} Extraction. (o) - 0.1 M HDDNS; (Δ) - 0.05 M TT16C4 + 0.1 M HDDNS; (□) - 0.05 M TT14C4 + 0.1 M HDDNS. Conditions: metals at tracer concentrations and end-over-end contacting at 23 ± 2 °C.

Cu^{2+} and Ag^+ Extraction Behavior

To survey some of the conditions under which synergism prevails and to eventually understand the controlling equilibria, we have begun to explore the synergistic extraction of Cu^{2+} and Ag^+ as a function of loading, initial aqueous H_2SO_4, and the ratio [macrocycle]/ ([macrocycle] + [HDDNS]). Strong synergism over a wide range of initial sulfuric acid concentrations in the extraction of trace-level Cu^{2+} and Ag^+ is evident in Figs. 3 and 4. In

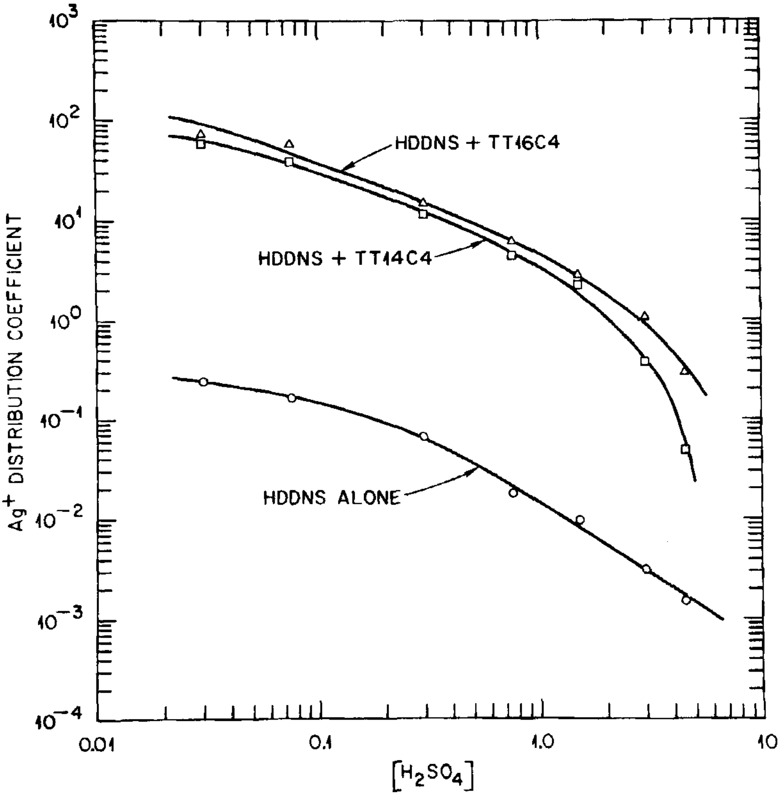

Fig. 4. Effect of Sulfuric-Acid Concentration on Ag^+ Extraction. (o) - 1.0×10^{-4} M HDDNS; (Δ) - 1.0×10^{-4} M TT16C4 + 1.0×10^{-4} M HDDNS; (□) - 1.0×10^{-4} M TT14C4 + 1.0×10^{-4} M HDDNS. Conditions: metals at tracer concentrations and end-over-end contacting at 23 ± 2 °C.

these experiments (plus those in Fig. 2 and Table II), the 2:1 and 1:1 ratios of HDDNS vs. macrocycles were chosen to reflect the respective idealized (i.e., possibly fictitious) stoichiometries Cu(macrocycle)$(DDNS)_2$ and Ag(macrocycle)(DDNS) at maximum loading. As expected from literature data (Table I), Ag^+ gets extracted more strongly than Cu^{2+}, and we therefore employed lower reagent concentrations for Ag^+. Figure 3 shows that, over most of the useful range of initial sulfuric acid concentrations, the smaller macrocycle TT14C4 exhibits the stronger synergism in the extraction of Cu^{2+}, in parallel with the higher Cu^{2+} complexation

Table III. Reversibility of Cu^{2+} Extraction from Sulfuric Acid[a]

Solvent	Aqueous Phase	D_{Cu}
0.05M TT14C4 + 0.1M HDDNS	1.5M H_2SO_4	—
	1.5M H_2SO_4 + ^{110}Cu tracer	100
	1.5M H_2SO_4	91
	6.0M H_2SO_4	0.22
0.05M TT16C4 + 0.1M HDDNS	0.3M H_2SO_4	—
	0.3M H_2SO_4 + ^{110}Cu tracer	11
	0.3M H_2SO_4	14
	1.5M H_2SO_4	1.9

[a] Conditions: toluene diluent, 1:1 phase ratio, end-over-end contacting, 30-min contact time, and 23 ± 2°C. For each of the two solvents shown, four successive contacts were made with the indicated aqueous phases. Only the second aqueous phase initially contained $^{110}CuSO_4$ tracer. Thus, in the third and fourth contacts, equilibrium was approached in the reverse direction.

constant of TT14C4 vs. TT16C4 in homogeneous aqueous solution (29). In the case of Ag^+, however, a significant macrocycle-size effect is not observed (Fig. 4); TT16C4 exhibits the higher synergism, though only slightly. As in the case of Cu^{2+} extraction (Table II), tests using either TT14C4 or TT16C4 alone (1.0×10^{-4} M) generally gave values of D_{Ag} below reliable measurement (ca. 1×10^{-3}). Complicated dependences of D_M on initial sulfuric acid concentration are observed in both Figs. 3 and 4, but in general, it is evident that the extractions of at least tracer levels of the metals from dilute H_2SO_4 may be reversed by contacting the resulting metal-containing solvents with fresh aqueous solutions containing high sulfuric acid concentrations. This point is proven by the experiments described in Table III, showing that D_{Cu} is independent of the direction of transfer.

Experiments are in progress (37) to provide a molecular interpretation of the extraction behavior observed in Figs. 3-5, and we reserve a more detailed accounting for the future. However, based on our previous findings with synergism by oxa crown ethers (1-3,14,35,36), we are tentatively proceeding with the assumption of coordination of the metal by macrocycle coupled with cation exchange by HDDNS with possible complication from co-

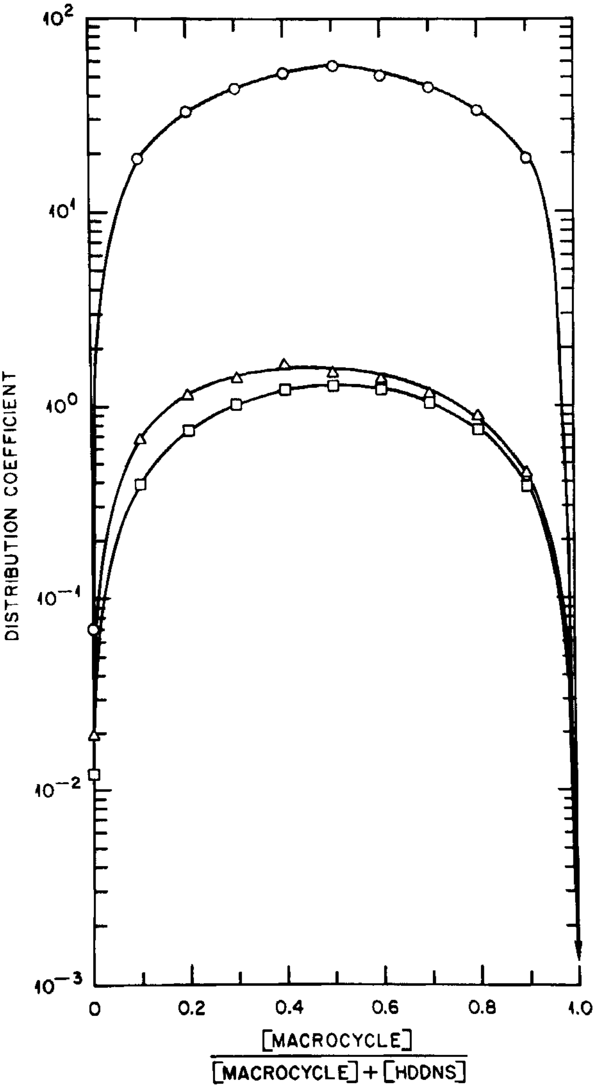

Fig. 5. Continuous-Variation Experiments. (o) - Cu^{2+} extraction from 1.5 M H_2SO_4 with [TT14C4] + [HDDNS] = 0.1 M; (□) - Cu^{2+} extraction from 0.3 M H_2SO_4 with [TT14C4] + [HDDNS] = 0.01 M; (△) - Ag^+ extraction from 1.5 M H_2SO_4 with [TT16C4] + [HDDNS] = 2.0 x 10^{-4} M. Conditions: metals at tracer concentrations and end-over-end contacting at 23 = ± 2 °C.

extraction of sulfate; an unidentified effect apparently defeats the synergism at sulfuric acid concentrations greater than ca. 4 M as shown in Figs. 3 and 4. In Fig. 3, the behavior indicated by the dashed lines is difficult to reconcile with cation-exchange. Since the effect, though reproducible, nearly disappears with the use of gentle phase contacting and lower reagent concentrations (giving lower, more reliable values of D_M), it appears likely that the dashed portions of the curves in Fig. 3 may be attributed to incomplete coalescence (entrainment) caused by the low ionic strength.

Extraction isotherms (loading curves) for Cu^{2+} using the solvent 0.1 M HDDNS + 0.05 M TT14C4 and Ag^+ using 0.001 M HDDNS and 0.001 M TT16C4 from 1.5 M H_2SO_4 were found to exhibit slopes of 1 at low loading, indicating (14) that, for the condition of low loading, (a) D_M is constant, and (b) the metals are each being extracted as monomeric organic-phase species. Similar results were reported for Sr^{2+} (35) and Mn^{2+} (14,36) extraction from nitric acid by HDDNS synergized by substituted oxa crown ethers. Up to at least 56% and 81% of the cation-exchange capacity of the HDDNS for respectively Cu^{2+} and Ag^+, the loading experiments showed no evidence of third-phase formation. Continuous-variation experiments shown in Fig. 5 indicate that the most efficient reagent combinations occur when the macrocycle concentrations are respectively 50% and 40% of the total reagent concentration in the extraction of tracer-level Cu^{2+} and Ag^+.

CONCLUSIONS

The major conclusion of the present work is that the thia macrocycles TT14C4 and TT16C4 (Fig. 1) strongly and selectively synergize the extraction of Cu^{2+} and Ag^+ ions from sulfuric acid by the cation exchanger HDDNS in toluene diluent. Over a range of sulfuric acid concentrations, the selectivity is given by the order $Ag^+ > Cu^{2+} > Mn^{2+}$, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Zn^{2+}, where the metals are at tracer concentrations and studied separately (Table II and Fig. 2). Synergism occurs only for Ag^+ and Cu^{2+} under the conditions studied; the macrocycles neither antagonize nor synergize the HDDNS extraction of the other metals examined. Used alone, the thia macrocycles extract practically no Cu^{2+} or Ag^+ from aqueous H_2SO_4 and thus appear to be useless for this application without an added cation exchanger. On the other hand, HDDNS used alone exhibits a pH-driven ability to extract all of the metals examined but is relatively nonselective.

The extraction of Cu^{2+} and Ag^+ using TT14C4 and TT16C6 as synergists for HDDNS was explored as a function of sulfuric acid concentration (Table II and Figs. 3 and 4), relative concentration of macrocycle vs. HDDNS (continuous-variation, Fig. 5), and loading. In the extraction of Cu^{2+}, TT14C4 synergizes HDDNS more effectively than TT16C4, in parallel with the greater ability of the smaller macrocycle TT14C4 to complex Cu^{2+} in homogeneous aqueous media (29). On the other hand, the two macrocycles exhibit similar abilities to synergize the extraction of Ag^+, with TT16C4 being slightly favored. Although little can be currently said regarding the exact nature of the organic-phase species, both Cu^{2+} and Ag^+ are apparently extracted by the synergistic systems as mononuclear species at low metal concentrations. The extraction of tracer concentrations of Cu^{2+} occurs reversibly under the limited conditions examined, and the extracted Cu^{2+} may be stripped by increasing the aqueous acidity. By comparison to oxa crown ethers, the thia macro cycles TT14C4 and TT16C4 exhibit considerable hydrophobicity and distribute negligibly to water from toluene. Macrocycle instability occurs in the presence of aqueous nitric acid as dilute as 0.1 M (the lowest HNO_3 acidity tested).

Possible applications of these or related synergistic systems examined here include the recovery and analysis of copper and silver from non-oxidizing aqueous media. Potential analytical applications follow not only from the good selectivity in separating Cu^{2+} and Ag^+ from other metals but from the intense blue color (29) of the extracted Cu^{2+} species, making possible spectrophotometric methods. Of greater potential economic impact is the possibility of applications of thia macrocycles to the hydrometallurgical recovery of copper, comprising a growing fraction (ca. 20%) of the total copper ore processed worldwide (38,39). Although large-scale application of the systems reported in this paper presents many problems (not the least of which is the present high cost of the macrocycles), the high selectivity observed in this work seems especially motivating for further developments such as modification of thia-macrocycle structure, use of other cation exchangers, or reconfiguration to supported liquid membranes or resins. In view of the promising nature of the initial results presented here, research in progress (37) is currently directed toward exploring these and other possibilities as well as toward gaining a better understanding of the stoichiometry, equilibrium relationships, and structure of the species involved.

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