Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Comprehensive Equilibrium Analysis of the Complexation of Cu(II) by Tetrathia-14-crown-4 in a Synergistic Extraction System Employing Didodecylnaphthalene Sulfonic Acid

Bruce A. Moyer[a]; Lætitia H. Delmau[a]; G. N. Case[a]; Sixto Bajo[a]; C. F. Baes Jr.[a]
[a] Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

To cite this Article Moyer, Bruce A. , Delmau, Lætitia H. , Case, G. N. , Bajo, Sixto and Baes Jr., C. F.(1995) 'Comprehensive Equilibrium Analysis of the Complexation of Cu(II) by Tetrathia-14-crown-4 in a Synergistic Extraction System Employing Didodecylnaphthalene Sulfonic Acid', Separation Science and Technology, 30: 7, 1047 — 1069

To link to this Article: DOI: 10.1080/01496399508010332

URL: http://dx.doi.org/10.1080/01496399508010332

SEPARATION SCIENCE AND TECHNOLOGY, 30(7–9), pp. 1047–1069, 1995

COMPREHENSIVE EQUILIBRIUM ANALYSIS OF THE COMPLEXATION OF Cu(II) BY TETRATHIA-14-CROWN-4 IN A SYNERGISTIC EXTRACTION SYSTEM EMPLOYING DIDODECYLNAPHTHALENE SULFONIC ACID

Bruce A. Moyer,* Lætitia H. Delmau,†† G. N. Case, Sixto Bajo,† and C. F. Baes, Jr.§
Chemical and Analytical Sciences Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6119

ABSTRACT

Liquid-liquid extraction experiments, UV/vis spectra, and equilibrium modeling by use of the program SXLSQA have been employed to reveal the origin of synergism in the extraction of Cu(II) from sulfuric acid by the tetradentate macrocycle tetrathia-14-crown-4 (TT14C4) combined with the cation exchanger didodecylnaphthalene sulfonic acid (HDDNS) in toluene. The key feature of the system is the 1:1 complexation of Cu(II) by TT14C4. HDDNS functions both as a source of exchangeable protons and as a solvating agent that promotes the formation of small, hydrated aggregates. In the absence of the cation-exchange vehicle provided by HDDNS, the macrocycle does not extract Cu(II) detectably. Combined with HDDNS, however, TT14C4 significantly enhances the extraction of the metal by HDDNS. Comparative UV/vis spectrophotometry indicates the formation of the deep-blue chromophore attributed to the complex ion $Cu(TT14C4)^{2+}$, wherein the planar set of four *endo* sulfur donor atoms of TT14C4 circumscribes the metal cation. Modeling of the extraction and spectral absorbance data by use of the program SXLSQA supports the conclusion that this 1:1 complex accounts for essentially all of the extracted Cu(II) in excess of that extracted by HDDNS alone. The best model includes HDDNS aggregates incorporating $Cu(TT14C4)^{2+}$ or Cu^{2+} ions. In the analysis, activity effects in both aqueous and organic phases have been taken into account by the Pitzer and Hildebrand-Scott treatments, respectively, with explicit inclusion of the formation of

---

[*] Author to whom correspondence should be addressed.
[††] Undergraduate Research Participant.
[†] Visiting Scientist, Paul Scherrer Institute, Wurenlingen, Switzerland.
[§] Consultant, Oak Ridge, TN.

aqueous hydrogen sulfate ion. The model accounts for the effect of variation of the solute components $CuSO_4$, H_2SO_4, HDDNS, and TT14C4.

INTRODUCTION

Macrocyclic extractants represent effective chemical tools for achieving high selectivity in the solvent extraction of metal cations (1-6). A useful approach to exploiting the selectivity of macrocyclic extractants has been introduced by mixing a macrocycle of interest with a cation exchanger in the organic phase (3). This approach has led to selective extractions of alkali-, alkaline-earth, and transition-metal cations (3,7-12). In such systems, the cation exchanger is essentially a lipophilic organic acid (e.g., carboxylic, sulfonic, or phosphonic acid) and confers control of the extractive driving force by pH variation. On the other hand, the macrocycle confers selectivity according to its bonding preferences and thus promotes selectively enhanced cation exchange. To the extent that the net extraction exceeds the sum of the separate effects of the two extractants, the extraction is said to be synergistic, a term attributed to Coleman (13).

Since such selective synergism primarily arises from the coordination properties of the macrocycle, the question of greatest interest to us concerns the nature of the macrocycle-metal interaction. Unfortunately, organic-phase interactions of the cation exchanger with the macrocycle and aggregation of the cation exchanger and its salts hinder attempts to probe this question. Consequently, the modeling programs SXLSQ (14) and its more powerful successor SXLSQA (15) were developed and have in fact proven helpful in elucidating extractions of Cs^+ (16), Sr^{2+} (17), Ra^{2+} (18), Mn^{2+} (12), Cu^{2+} (19), and Zn^{2+} (20) ions. Understanding of these systems has been especially promoted when modeling of equilibrium data has been combined with spectral measurements sensitive specifically to the coordination environment of the metal ion (12,17,19,20).

We examine here a model system comprised of the tetradentate macrocycle tetrathia-14-crown-4 (TT14C4) and the cation exchanger didodecylnaphthalene sulfonic acid (HDDNS) in toluene (9-11). An effective cation exchanger for extraction from acidic media, HDDNS exhibits weak selectivity (7-9). However, the combination of TT14C4 with HDDNS gives good Cu(II) selectivity in extractions from sulfuric acid, undoubtedly owing to favorable coordination of Cu(II) by the macrocycle (9). Previous workers have shown that TT14C4 binds Cu(II) to form the 1:1 complex ion CuB^{2+} (B = TT14C4) in aqueous solution (21). Further, TT14C4 gives the maximum complex stability within the series of tetradentate thia ethers of varying ring size. We earlier showed that the synergistic effect in the extraction of Cu(II) from sulfuric acid by members of this same series of macrocycles in combination of HDDNS correlates with the aqueous stability constants, suggesting that the synergism originates in the formation of the 1:1 complex in the solvent (10).

In this paper, we present evidence that the synergism in the extraction of Cu(II) from sulfuric acid by HDDNS combined with TT14C4 indeed may be attributed to the formation of the CuB^{2+} ion as incorporated into organic-phase aggregates involving HDDNS and its Cu(II) salt. To support this conclusion, distribution data have been collected as a function of the concentrations of the organic-phase components TT14C4 and HDDNS and the aqueous-phase components $CuSO_4$ and H_2SO_4. These data were modeled by use of SXLSQA, using an earlier model for the extraction of Cu(II) from sulfuric acid by HDDNS alone (19) and new Pitzer parameters for the calculation of aqueous activity coefficients (22). The extraction data have been augmented by spectral measurements to test the proposed model and to confirm the presence of the CuB^{2+} complex responsible for the synergism. Finally, we propose a generic model covering this class of synergistic extraction and present a critique of the modeling as applied to such systems.

EXPERIMENTAL SECTION

Materials and methods used in measurements of extraction of Cu(II) by gamma tracer counting have been described previously (9-11). Table 1 defines the data sets used here. Two data sets consisting of 128 points for HDDNS used alone (Experiment #1) and 11 data points corresponding to the variation of sulfuric acid concentration (Experiment #4) have been reported elsewhere (11,19); all other data were determined in this work. Distribution coefficients (D_{Cu}) were defined as $D_{Cu} = [Cu]_{org}/[Cu]_{aq}$.

The precision of Experiment #1 was reported earlier (19). Inspection of duplicates in Experiments #2 - #4 showed that the precision of D_{Cu} values was ±5% at HDDNS concentrations above 1×10^{-3} M but worsened at lower concentrations. For HDDNS concentrations in the inclusive ranges 1.0×10^{-3} M to 2.1×10^{-4} M and 2.0×10^{-4} M - 1.0×10^{-4} M, precision was approximately equal to 7.5% and 20%, respectively. Data collected at HDDNS concentrations below 1×10^{-4} M were judged unusable and were rejected.

The attainment of equilibrium, reversibility of the extractions, and constancy of D_{Cu} at low loading have been demonstrated under conditions essentially the same as those used here (9-11,19). No extraction of sulfuric acid is expected at aqueous sulfuric acid concentrations below 1 M (19). TT14C4 distributes from toluene to water negligibly (9), as is also true for HDDNS and its salt $Cu(DDNS)_2$ (19). We further neglect the small volume changes due to the mutual solubility of water and toluene.

Despite its lipophilicity, TT14C4 distributes slightly from toluene to water containing elevated concentrations of Cu^{2+} ions. This effect arises from the formation of the aqueous complex ion $[Cu(TT14C4)]^{2+}$ (11) with a two-phase equilibrium constant of 0.87 (23). Less than 2% of the aqueous Cu(II) in our experiments will thus be bound by TT14C4, and less than 2% of the TT14C4 will be distributed to the aqueous phase.

Spectra were collected at 25.0 ± 0.5 °C on a Cary 219 UV/vis spectrophotometer using 0.1-cm quartz cells and a toluene reference. Absorbances were taken at the band maxima in the range 390 - 396 nm, and small corrections were applied for the absorbance

TABLE 1. EXPERIMENTAL CONDITIONS[a]

System	Exper. #	$[\mathrm{DDNS}]_T$[b]	Maximum $[\mathrm{Cu}]_{org}/[\mathrm{DDNS}]_T$[c]	$[\mathrm{TT14C4}]_T$	Maximum $[\mathrm{Cu}]_{org}/[\mathrm{TT14C4}]_T$[c]	$[\mathrm{Cu(II)}]_T$[b]	$[\mathrm{H_2SO_4}]_T$	No. Points
Extraction		$[\mathrm{DDNS}]_T = [\mathrm{HDDNS}]_T$[b]				(Initial aqueous Cu(II) molarity) $[\mathrm{Cu(II)}]_T = [\mathrm{CuSO4}]_T$		
HDDNS alone	1	1.00×10^{-4} - 1.00×10^{-1}	7.65×10^{-2}	0		1.24×10^{-8} - 1.30×10^{-2}	0.0300 - 1.00	128
HDDNS + TT14C4	2	1.00×10^{-4} - 5.00×10^{-2}	2.38×10^{-3}	1.00×10^{-6} - 2.00×10^{-2}	6.09×10^{-3}	1.24×10^{-8} - 7.63×10^{-5}	0.300	95
	3	1.00×10^{-4} - 5.00×10^{-2}	1.02×10^{-1}	1.00×10^{-4} - 2.00×10^{-2}	1.32×10^{1}	1.00×10^{-6} - 5.00×10^{-3}	0.300	81
	4	0.0100	7.59×10^{-3}	5.00×10^{-3}	1.52×10^{-2}	7.60×10^{-6} - 7.60×10^{-5}	0.0300 - 1.00	11
Absorbance		$[\mathrm{DDNS}]_T = [\mathrm{HDDNS}]_T + 2 \times [\mathrm{Cu(DDNS)_2}]_T$[b]				(Organic Cu(II) molarity) $[\mathrm{Cu(II)}]_T = [\mathrm{Cu(DDNS)_2}]_T$		
	5	$2.50 \times 10^{-2} + 2 \times [\mathrm{Cu(II)}]_T$	7.19×10^{-2}	1.25×10^{-3}	1.68×10^{0}	2.10×10^{-4} - 2.10×10^{-3}	0	10
Variation $[\mathrm{Cu(II)}]_T$	6	$0.0 + 2 \times [\mathrm{Cu(II)}]_T$	5.00×10^{-1}	5.00×10^{-3}	1.26×10^{0}	1.05×10^{-3} - 6.28×10^{-3}	0	3
	7	$0.0 + 2 \times [\mathrm{Cu(II)}]_T$	5.00×10^{-1}	2.50×10^{-3}	2.51×10^{0}	3.14×10^{-3} - 6.28×10^{-3}	0	4
	8	$0.0 + 2 \times [\mathrm{Cu(II)}]_T$	5.00×10^{-1}	1.25×10^{-3}	5.02×10^{0}	2.09×10^{-4} - 6.28×10^{-3}	0	12
Variation $[\mathrm{TT14C4}]_T$	9	$0.0 + 2 \times [\mathrm{Cu(II)}]_T$	5.00×10^{-1}	2.50×10^{-4} - 7.50×10^{-3}	4.20×10^{0}	1.05×10^{-3}	0	22

[a] In the experiments, toluene was employed as the diluent, the phase ratio was 1, and the temperature was 25.0 ± 0.1 °C. Subscript T refers to total (i.e., initial) molarities. The number of data points in each subset is indicated at right. Numerical tabulations of the data will be furnished upon request.

[b] $[\mathrm{DDNS}]_T$ is defined as the sum of the initial HDDNS molarity $[\mathrm{HDDNS}]_T$ and twice the initial organic-phase copper molarity $[\mathrm{Cu(DDNS)_2}]_T$ of the stoichiometric copper salt of HDDNS. For extraction experiments (#1 - #4), copper was initially in the aqueous phase as the sulfate salt, and therefore $[\mathrm{DDNS}]_T = [\mathrm{HDDNS}]_T$ and $[\mathrm{Cu(II)}]_T = [\mathrm{CuSO_4}]_T$. For spectral-absorbance experiments (#5 - #9), an organic phase containing TT14C4 was mixed with an organic phase containing $\mathrm{Cu(DDNS)_2}$ and optionally HDDNS (Experiment #5 only); no aqueous phase was effectively present, except for a drop of water to ensure water saturation. Thus, in the spectral experiments, $[\mathrm{DDNS}]_T = [\mathrm{HDDNS}]_T + 2 \times [\mathrm{Cu(DDNS)_2}]_T$ and $[\mathrm{Cu(II)}]_T = [\mathrm{Cu(DDNS)_2}]_T$. For purposes of calculation, the program SXLSQA formally considers the Cu(II) to have originated in the aqueous phase.

[c] $[\mathrm{Cu}]_{org}$ is the equilibrium organic-phase Cu(II) molarity.

of HDDNS. The precision was taken as 0.05 times the absorbance plus 0.005 when the absorbance was lower than 2; otherwise, the error was assumed to be 10%.

Absorbance experiments #5 - #9 (Table 1) were carried out by mixing toluene solutions of $Cu(DDNS)_2$ and TT14C4 in the presence of a small drop of water to ensure water saturation; solutions in Experiment #5 contained additionally 2.50 x 10^{-2} M HDDNS. Stock solutions of $Cu(DDNS)_2$ were prepared by the method described earlier (19) involving repeated equilibration of HDDNS solutions with 0.2 M $CuSO_4$. It was noted that after the $Cu(DDNS)_2$ and TT14C4 solutions were mixed, the resulting solutions exhibited haziness that gradually disappeared over the period of several hours on standing, whence the solutions appeared clear without centrifugation or filtration. In view of earlier results (12,17,24), we interpret this observation as phase separation of displaced water.

The general least-squares program SXLSQA (12,15) was employed in modeling the extraction and absorbance behavior. Goodness of fit was judged by the agreement factor σ, essentially the factor by which the model exceeds the experimental error on average (14,15). Volume parameters for aqueous ions were adopted from earlier work (19). Likewise, the basis for assignment of solubility parameters (δ) needed for calculating organic-phase activity coefficients via the Hildebrand-Scott treatment (25) was also adopted from earlier work (19); the value δ = 10.66 $cal^{1/2}$ $cm^{-3/2}$ for TT14C4 was approximated from group contributions (26). The Pitzer treatment (27) was used for the calculation of aqueous-phase activity coefficients, taking into account formation of hydrogen sulfate ion, three-ion interactions, and unsymmetrical mixing effects (22). Since activity corrections have been applied in both phases, the reported equilibrium constants refer to the state of infinite dilution. Finally, hydration numbers corresponding to organic-phase species were assigned according to earlier recommendations (12,19).

RESULTS AND DISCUSSION

Extraction by HDDNS Alone

The extraction of Cu(II) by HDDNS alone in toluene was modeled in a previous study (19). Cation exchange of Cu^{2+} ions into a fourfold HDDNS aggregate and deaggregation suffice to describe the extraction behavior to within experimental error:

$$(HA)_4\,(org) + Cu^{2+}\,(aq) \rightleftharpoons CuH_2A_4\,(org) + 2\,H^+\,(aq) \qquad (1)$$

$$1/4\,(HA)_4\,(org) \rightleftharpoons HA\,(org) \qquad (2)$$

where HA represents HDDNS; waters of hydration (W) will generally not be shown except in the summary tables. Recently, a new set of Pitzer parameters has been recommended for the H_2O-H_2SO_4-$CuSO_4$ system (22). Adopting the new aqueous-phase treatment, we repeated the refinement of the log*K* values corresponding to eqs. 1 and 2 using 120 data points of Experiment #1 corresponding to the extraction of Cu(II) from 0.3 M H_2SO_4 under low-loading conditions. The refined log*K* values in Table 2 differ little from the parameters of the best model described earlier ($\sigma = 1.05$; cf., $\sigma = 1.01$ (19)). In modeling the data in systems containing both HDDNS and TT14C4, the parameters shown in Table 2 were held fixed and shall hereafter be referred to as the HDDNS model.

Referring only to that portion of data in Fig. 1 acquired with HDDNS in the absence of the thia macrocycle (see Experiment #1), good agreement between the data and calculated curve may be seen. A "knee" in the curve marks a transition between the dilute region where primarily monomeric HDDNS is the effective form of the extractant and the more concentrated region where aggregated HDDNS is the effective form of the extractant. Thus, for the dilute region, the effective reaction becomes

$$4\,HA_{(org)} + Cu^{2+}_{(aq)} \rightleftharpoons CuH_2A_{4\,(org)} + 2\,H^+_{(aq)} \qquad (3)$$

We showed earlier (19) that slopes equal to 4 and 1 would be expected in the dilute and concentrated regions, respectively (cf. reference lines in Fig. 1).

The effect of variation of aqueous sulfuric acid concentration is shown in Fig. 2. Since the activity-coefficient ratio $\gamma_\pm{}^2{}_{CuSO_4}/\gamma_\pm{}^3{}_{H_2SO_4}$ remains within ±20% of unity up to 6 M H_2SO_4 (22), the approximate slope of -2 observed up to 1 M H_2SO_4 in Fig. 2 suggests the release of two protons during the extraction of Cu^{2+} ions by HDDNS alone (eq. 1). The problem of treating the aqueous activity-coefficient variation and incomplete dissociation of H_2SO_4 was dealt with automatically in the computer modeling summarized in Table 2, and although the refinement of the model was carried out at constant 0.3 M H_2SO_4, good agreement with the data was in fact obtained up to 6 M H_2SO_4. The good agreement thus supports a two-proton cation exchange process overall and provides evidence that other effects such as co-extraction of sulfate are inconsequential.

Qualitative Analysis of the Synergistic Extraction

As summarized by Table 1, the different data sets examined here represent four major groups of experiments: extraction of Cu(II) by HDDNS alone (Experiment #1); extraction of Cu(II) by mixtures of HDDNS and TT14C4 (Experiments #2 - #4); absorbance of solutions containing $Cu(DDNS)_2$, TT14C4, and excess HDDNS (Experiment #5); and absorbance of solutions containing only $Cu(DDNS)_2$ and TT14C4 (Experiments #6 - #9). The extraction data cover a range of low and intermediate loadings of the HDDNS, whereas the absorbance data correspond to a regime of intermediate and high loading.

As shown in Figs. 1 and 2, TT14C4 strongly enhances the extraction of Cu(II) by HDDNS. Data shown in these figures were taken from Experiments #1, #2, and #4, which were conducted under conditions of low loading. Attempts to detect any extraction of Cu(II) by TT14C4 in toluene showed that negligible extraction occurs in the absence of HDDNS ($D_{Cu} < 1.0 \times 10^{-5}$) (11). Thus, *the enhanced extraction upon combination of TT14C4 and HDDNS may be attributed to a synergistic effect.*

TABLE 2. MODEL FOR EXTRACTION OF Cu(II) BY HDDNS USED ALONE

Species[a]	Type	Exper.[b]	δ^c	log*K*[d]
$(HA)_4W_{22}$	Reactant	—	8.90	—
$CuH_2A_4W_{22}$	Product	1	8.90	1.274 ± 0.002
HAW_2	Product	1	9.70	- 2.499 ± 0.005

[a] H^+ is the hydrogen ion; A^- is the HDDNS anion; and W is water.

[b] The experimental data used in the least-squares procedure (Experiment #1, Table 1) included only the subset of 120 points at 0.3 M H_2SO_4.

[c] Solubility parameters δ ($cal^{1/2}$ $cm^{-3/2}$) were adopted from earlier recommendations (19) and were not refined.

[d] Log*K* values were refined using SXLSQA, giving an agreement factor $\sigma = 1.03$ (120 points, 0.3 M H_2SO_4); the same log*K* values gave an overall agreement factor $\sigma = 1.05$ (128 points, 0.03 - 1 M H_2SO_4). The corresponding equilibria are given in eqs. 1 and 2. The values of log*K* for $CuH_2A_4W_{22}$ and HAW_2 were held constant in subsequent refining of the log*K* values of the product species in the synergistic systems.

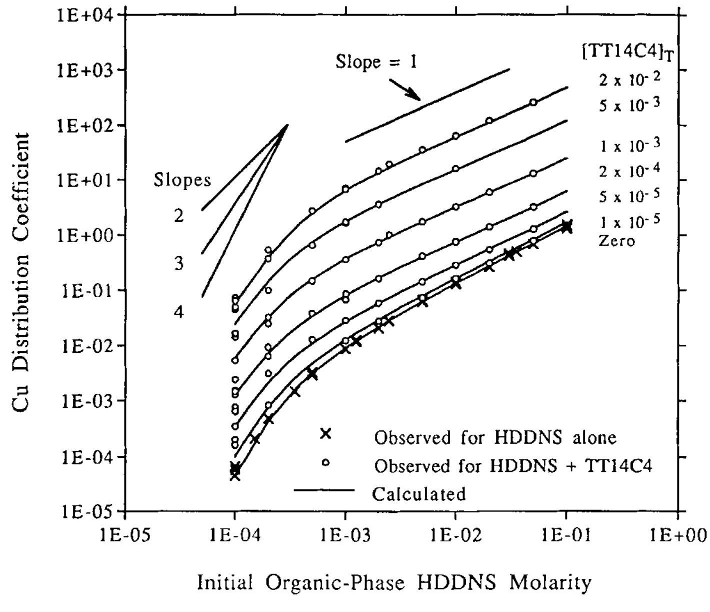

FIGURE 1. Dependence of D_{Cu} on HDDNS molarity at low loading and 0.3 M H_2SO_4. See Experiments #1 and #2 (Table 1). The lowest curve shows the behavior of extraction when no thia macrocycle is present; points are taken from Experiment #1. Initial aqueous copper concentration does not exceed 3×10^{-4} M. Solid curves are calculated based on the extraction model given in Tables 2 and 3. Reference slopes are provided for comparison.

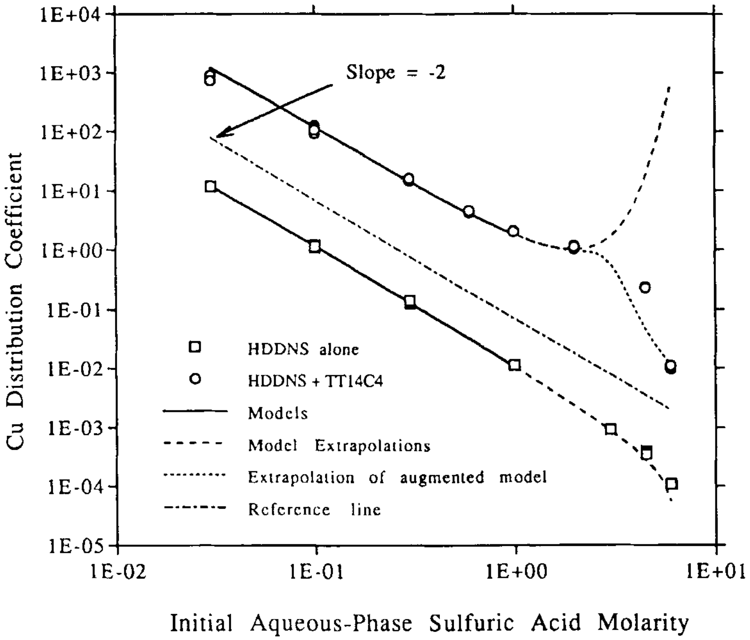

FIGURE 2. Dependence of D_{Cu} on TT14C4 molarity at low loading and 0.3 M H_2SO_4. See Experiment #1 and #2 (Table 1). Points plotted on the ordinate axis represent the distribution coefficients when no thia macrocycle is present. When no HDDNS is present, the distribution coefficients lie below the detection limit (D_{Cu} < 10^{-5}). Solid curves are calculated based on the extraction model given in Tables 2 and 3. A linear reference of slope = 1 is provided for comparison.

Preliminary to computer modeling, inspection of the data with the aid of slope analysis normally reveals qualitative features of the controlling equilibria. It has already been shown (9-11) that D_{Cu} is constant at low Cu(II) loading in the synergistic system, leading to the conclusion that the stoichiometric coefficient of Cu in organic-phase Cu(II) species is unity. From Fig. 1, it may be observed that the "knee" in the curve for HDDNS used alone is preserved in the presence of TT14C4. Two regions of behavior occur regardless of the TT14C4 concentration, and the curves tend to parallel one another in each region. In the region of low HDDNS concentration, the slopes lie in the range 3 - 4, and in the region of high HDDNS concentration, the slopes decrease to near unity (cf. reference lines). Approximately parallel behavior was also seen on replotting the data of Fig. 1 vs. TT14C4 concentration; for $[TT14C4]_T > 2 \times 10^{-4}$, the slopes tend to unity.

Interpretation of these results requires that one consider whether HDDNS interacts strongly or weakly with TT14C4. If this competing interaction is weak, then logically

$$a/a'(\mathrm{HA})_{a'}\,(\mathrm{org}) + b\,\mathrm{B}\,(\mathrm{org}) + \mathrm{Cu}^{2+}\,(\mathrm{aq}) \rightleftharpoons \mathrm{CuB}_b\mathrm{H}_{a\text{-}2}\mathrm{A}_a\,(\mathrm{org}) + 2\,\mathrm{H}^+\,(\mathrm{aq}) \quad (4)$$

where the observed synergism arises from the formation of the mixed species $\mathrm{CuB}_b\mathrm{H}_{a\text{-}2}\mathrm{A}_a$ (B = macrocycle). If a single set of a, a', and b values prevails, it may be shown that the slope in a plot of $\log D_{\mathrm{Cu}}$ vs. $\log[\mathrm{HDDNS}]_\mathrm{T}$ equals the stoichiometric ratio a/a' under conditions of low loading, constant acidity, and a TT14C4 concentration high enough that the extraction of HDDNS alone is negligible. From the slopes observed at high HDDNS and TT14C4 concentrations in Fig. 1 (slope = 0.86 for $[\mathrm{TT14C4}]_\mathrm{T}$ = 0.001 - 0.02 M), one then obtains approximately $a = 3$ or $a = 4$, since $a' = 4$ (eq. 1). This result suggests that the product complex has an average HDDNS aggregation number in the range 3 - 4. With decreasing HDDNS concentration, however, the monomer HA becomes the predominant reactant species, and the slopes in Fig. 1 increase. It follows that the product species remain on average substantially aggregated. Similarly, the unit slopes observed on replotting the data of Fig. 1 vs. TT14C4 concentration imply that $b = 1$ (slope = 0.97 - 1.00 for $[\mathrm{HDDNS}]_\mathrm{T}$ = 0.0001 - 0.05 M).

Since hydrogen bonding involving a thia ether would be expected to be relatively weak, the above logic based on eq. 4 with neglect of interactions between the two extractants appears reasonable. On the other hand, interaction of HDDNS with oxa crown ethers via hydrogen bonding was earlier found to be important (12,14,16,17). In one case (12), the addition of the crown ether dramatically changed the slope of a log-log plot of D_M vs. HDDNS concentration. However, no such change in the slopes are observed in Fig. 1, and strong interaction of HDDNS with TT14C4 thus seems unlikely.

The effect of aqueous sulfuric acid concentration is shown in Fig. 2. Up to 1 M $\mathrm{H_2SO_4}$, an approximate slope of -2 for the combination of HDDNS and TT14C4 again suggests the release of two protons during the extraction of Cu^{2+} ions. In view of the near parallel behavior of the two curves in this region, TT14C4 does not appear to alter the number of proton equivalents exchanged by HDDNS. Enhanced extraction occurs over the entire acidity range up to 6 M $\mathrm{H_2SO_4}$. Complicated behavior may be observed above 1 M $\mathrm{H_2SO_4}$, where a plateau region occurs up to ca. 2 M $\mathrm{H_2SO_4}$, followed by a steep drop-off. The extraction is reversible over the entire acidity range (9-11).

Computer Modeling of the Synergistic Extraction

Extractant-Concentration Dependence. In testing equilibrium models with the program SXLSQA, a stagewise approach was taken starting from limited data sets and simple models. The HDDNS model (Table 2) comprised of the two organic-phase product species $\mathrm{CuH_2A_4}$ and HA together with the organic-phase reactant species $\mathrm{(HA)_4}$ was implicitly incorporated into the evolving synergistic model. In the first stage of testing, the data set included 95 points at low loading (Experiment #2). Proceeding from the slope analysis involving eq. 4, models containing one mixed product species $CuBH_{a-2}A_a$ were tested over a range of values of a. In fact, fair agreement was obtained with $a = 3$, whence $\sigma = 2.68$. The next best model having one mixed species was obtained with $a = 4$, whence $\sigma = 3.70$. All other cases were considerably worse.

Still examining only the 95 points of Experiment #2, we systematically tested the effect of adding one or two more mixed species to the model already containing $CuBHA_3$. Significant improvement was obtained on adding another species, either $CuBH_2A_4$ ($\sigma = 1.75$) or (HA)B ($\sigma = 1.68$). All species $CuB_bH_{a-2}A_a$ containing more than one macrocycle or more than one copper ion were rejected by the regression (*i.e.*, log*K* refined automatically toward large negative values). Likewise, species $(HA)_{a''}B_{b''}$ with a'' or b'' different from 1 were also rejected. The value of σ decreased from 1.75 to 1.35 when the data were further fit by the synergistic model consisting of all three mixed species: $CuBHA_3$, $CuBH_2A_4$, and (HA)B. No further species were adopted, because (a) the fit already approached experimental error, (b) new species individually produced only small decreases in σ, and (c) the largest residuals lay in the least precise portion of the data (i.e., low HDDNS concentration). The equilibria found by the computer analysis are:

$$3/4\ (HA)_4\ (org) + B\ (org) + Cu^{2+}\ (aq) \rightleftharpoons CuBHA_3\ (org) + 2\,H^+\ (aq) \qquad (5)$$

$$(HA)_4\ (org) + B\ (org) + Cu^{2+}\ (aq) \rightleftharpoons CuBH_2A_4\ (org) + 2\,H^+\ (aq) \qquad (6)$$

$$1/4\ (HA)_4\ (org) + B\ (org) \rightleftharpoons (HA)B\ (org) \qquad (7)$$

Loading behavior. Loading behavior often reflects the degree of aggregation (12,19,20,28-30). Points from Experiment #3 shown in Fig. 3 illustrate the decrease in D_{Cu} occurring upon loading to an intermediate level. As shown in Table 1, the maximum HDDNS loading ratio ($[Cu(II)]_{org}/[HDDNS]_T$) achieved in Experiment #3 was 0.102. Thus, up to 20.4% of the cation exchanger was in its anionic form, and up to 40.8% of the assumed fourfold aggregates could each have contained a single Cu(II) ion. No higher HDDNS loadings were examined to avoid formation of species containing more than one Cu(II) ion. On the other hand, the organic-phase Cu(II) concentration was allowed to greatly exceed the TT14C4 concentration, giving appreciable loadings of this extractant.

The synergistic model given by eqs. 5 - 7 was tested on a combined data set of 176 points from Experiments #2 and #3. As shown in Fig. 3, the refined log*K* values gave an acceptable fit to the loading data ($\sigma = 1.54$). Inflections evident in some of the calculated curves (greatly extrapolated to enhance the effect) reflect the depletion of one of the extractants in an excess of the other. Again, tests of models having additional species with varying stoichiometries failed to offer substantial improvement in the fit. Table 3 gives the species in the model together with their final log*K* values; the model so defined will be

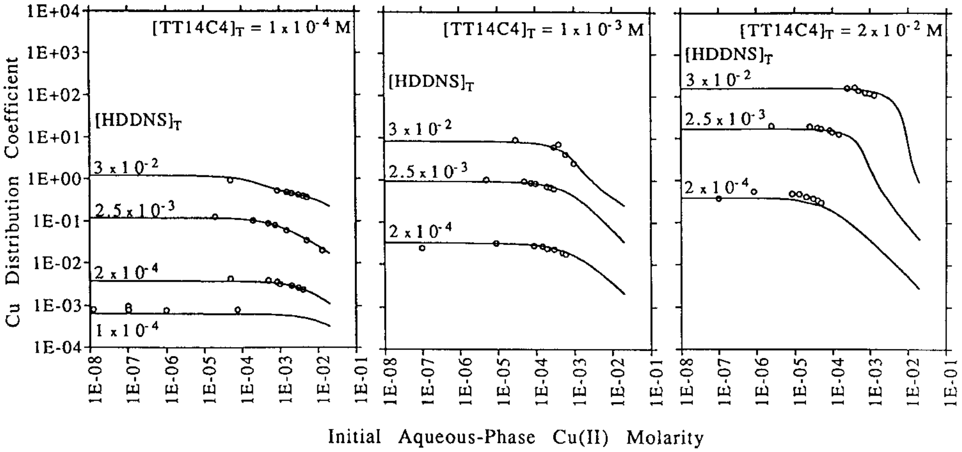

FIGURE 3. Partial loading expressed as the dependence of D_{Cu} on the initial aqueous Cu(II) molarity at different initial concentrations of HDDNS and TT14C4. Sulfuric acid concentration is constant at 0.3 M. See Experiments #2 and #3 (Table 1). Circles represent the experimental points. Solid curves are calculated based on the extraction model given in Tables 2 and 3.

TABLE 3. MODEL FOR SYNERGISTIC EXTRACTION OF Cu(II)

Species[a]	Type	Exper.[b]	δ[c]	log$K$[d]	ε[b,e]
B	Reactant	---	10.66	---	---
$CuBHA_3W_2$	Product	2, 3, 5	8.90	4.804 ± 0.016	7760
$CuBH_2A_4W_4$	Product	2, 3, 5	8.90	4.864 ± 0.062	7760
(HA)BW	Product	2, 3, 5	8.90	- 1.307 ± 0.069	0

[a] H^+ is the hydrogen ion; A^- is the HDDNS anion; B is TT14C4 (tetrathia-14-crown-4); and W is water.

[b] Experiments used in the least-squares procedure are noted in Table 1. Parameters in Table 2 were included in the model but were not refined. Experiment #5 was used only to set the extinction-coefficient value; log$K$ values were refined using only Experiments #2 and #3.

[c] Solubility parameters δ (cal$^{1/2}$ cm$^{-3/2}$) were estimated as described in the Experimental Section and were not refined.

[d] On refinement using SXLSQA, the overall agreement was given by σ = 1.51 (Experiments #2, #3, and #5); for Experiments #2 and #3 only, σ = 1.56; for Experiment #5 only, σ = 0.86. Log$K$ values correspond to eqs. 5- 7.

[e] Molar extinction coefficient in L mol^{-1} cm^{-1}.

referred to as the synergistic model. The solid curves plotted in Figs. 1 - 3 were calculated from this model and generally agree well with the data in all regions up to 1 M H_2SO_4.

In addition to supporting the qualitative analysis presented above, the computer modeling offers some additional insights. First, it indicates a *1:1 Cu:TT14C4 interaction* with no evidence for species having more than one Cu(II) or TT14C4. Second, the coexistence of the species $CuBHA_3$ and $CuBH_2A_4$ in the model explains the intermediate slope of 0.86 obtained at high HDDNS and TT14C4 concentrations in Fig. 1. Third, the inclusion of $CuBHA_3$ in the model reflects a partial deaggregation of $CuBH_2A_4$, which reasonably follows on the expectation that the macrocycle disturbs the hydrogen bonding network within the aggregate; the two species in fact have comparable stabilities. Fourth, *HDDNS interacts at best weakly with TT14C4*, contrasting with the extensive interaction between HDDNS and oxa crown ethers.

Interestingly, the stability of TT14C4 complexes with Cu(II) in the organic phase is not much different from the stabilities observed previously in homogeneous systems. From eqs. 1 and 6, one obtains

$$CuH_2A_4\,(org) + B\,(org) \rightleftharpoons CuBH_2A_4\,(org) \qquad (8)$$

From Tables 2 and 3 the corresponding log*K* value may be found to be 3.59; an analogous treatment of eqs. 1 and 5 gives log*K* = 3.53 for the organic-phase formation of $CuBHA_3$. By comparison, the log*K* value for formation of the CuB^{2+} complex ion in 80% methanol/20% water at 0.1 M $HClO_4$ was reported to be 3.49 at 25 °C (33). In aqueous 0.1 M $HClO_4$ at 25 °C, log*K* has the value 4.34, which decreases to 4.04 at zero $HClO_4$ concentration (21). Equation 8 explains the strong synergism of the extraction system.

Sulfuric Acid Dependence. Although the synergistic model was refined at a single acidity, it agrees reasonably well with the acid-dependence data up to 1 M H_2SO_4. Figure 2 shows the fit and extensions to higher acidities. The good agreement supports a *two-proton cation-exchange process* up to 1 M H_2SO_4, as expressed by eqs. 5 and 6.

Extension of the synergistic model to higher H_2SO_4 concentrations has proved insightful, if only qualitatively. We have suggested (9-11) that the tendency of the acid-dependence curve to level off in the neighborhood of 2 M H_2SO_4 may arise because of co-extraction of sulfate or hydrogen sulfate anions. Indeed, addition of combinations of such species to the model did tend to improve the fit in the plateau region. However, the improvement was only partial and came at the expense of adding several more species to the model to account for only a few data points.

Alternatively, a simple explanation that does not involve new species accounts for the plateau on the basis of species hydration and the known changing water activity. Although the hydration of the organic-phase species has so far not been discussed, each species has in fact been formally assigned a hydration number *w* in Tables 2 and 3 as required by SXLSQA (12,15). Consider, for example, the complete form of eq. 6:

$$(HA)_4(H_2O)_{22}\,(org) + B\,(org) + Cu^{2+}\,(aq) \rightleftharpoons CuBH_2A_4(H_2O)_w\,(org) + 2\,H^+\,(aq) + (22\text{-}w)\,H_2O \qquad (9)$$

Here, the reactant HDDNS aggregate has an average hydration number 22, as established by Karl Fischer titration (19), and the product species has an unknown hydration number designated w. The corresponding expression for the equilibrium constant therefore includes the water activity raised to the power of 22 - w in the numerator. If the water activity remains approximately constant within a set of data, then the assignment of w for $CuBH_2A_4(H_2O)_w$ and other organic-phase species matters little in modeling, formally only affecting the value of log$K$. On fitting the 176 data points of Experiments #2 and #3, where the aqueous ionic strength is approximately constant, changing the species hydration numbers in the synergistic model accordingly produced negligible effect on σ, though log$K$ values changed slightly, as expected (12).

On the other hand, the water activity falls significantly below unity as the H_2SO_4 concentration exceeds 1 M, and in this region the extraction represented in eq. 9 thus depends on the water-activity term a_w^{22-w} if $w \neq 22$. Specifically, if water is released in the reaction (i.e., $w < 22$), eq. 9 is expected to be favored as water activity decreases with increasing H_2SO_4 concentration. Several trials with SXLSQA in fact confirmed this to be the case, and the plateau region in Fig. 2 could be closely modeled up to 2 M H_2SO_4 assuming relatively low hydration numbers given as follows: $CuBHA_3W_2$, $CuBH_2A_4W_4$, and (HA)BW, where W is water. We regard these hydration numbers as only estimates, however, since the data involved are limited and since other combinations of hydration numbers within several units of the values shown in this set of species also gave reasonable approximations of the plateau region. The log$K$ values listed in Tables 2 - 4 depend on the chosen hydration numbers and thus should be considered to have exact meaning only in the context of the models; this same caution applies to the log$K$ values we have published on other systems (12,19,20). Nevertheless, *the results clearly suggest that the synergistic effect is accompanied by the formation of species having greatly reduced hydration compared with the reactant HDDNS aggregates.* In fact, from Karl Fischer titrations and FTIR measurements of the water content of the organic phase in related synergistic systems, it is known that metal-ion binding by crown ethers entails the release of water from the solvent (12,17,19,24), and this is consistent with visual observations here (see Experimental Section). Thus, we prefer this explanation of the plateau region and adopt the hydration numbers shown in Table 3.

At H_2SO_4 concentrations higher than 2 M, the sharp downturn in D_{Cu} points to a strongly competing effect. The synergistic model as formulated clearly predicts the opposite trend on extrapolation (Fig. 2). Since we were able to show with SXLSQA that the formation of aqueous-phase adducts of H_2SO_4 with TT14C4 can account for this downturn, we suggest this type of reaction as a reasonable explanation. Fig. 2 shows one such possibility. In light of the limited data and problems concerning assigning Pitzer parameters to new aqueous species, we followed this question no further. Nevertheless, some support for an aqueous-phase species of TT14C4 arises in light of the fact that the related lipophilic thia ether 6,6-dihexyl-1,4,8,11-tetrathia-14-crown-4 does not exhibit the downturn in the acid dependence but rather exhibits a minimum followed by a region of increasing D_{Cu} as suggested by the extrapolation of the synergistic model in Fig. 2 (31).

Spectral Investigation of the Synergistic Extraction

A spectral approach was employed to probe the key interaction between TT14C4 and Cu(II). Specifically, experiments were conducted to determine the UV/vis spectra of the organic phase in extractions of Cu(II) and to monitor absorbance as a function of organic-phase concentrations of TT14C4, HDDNS, and Cu(II). Absorption bands with maxima located at approximately 395 nm and 585 nm give the deep blue color of organic phases upon extraction of Cu(II). A typical spectrum is shown in Fig. 4, where it may be seen to closely match the spectrum reported for the complex ion $[Cu(TT14C4)]^{2+}$ (32). The bands are thought to arise from ligand-to-metal charge-transfer processes (32,33). Structural studies have shown that TT14C4 coordinates with Cu^{2+} ion to form a planar complex in which the Cu^{2+} ion is incorporated within the cavity of the macrocycle (34); the complex appears to maintain its structural integrity in solution (21,34). Since our modeling rules out any interaction other than 1:1 between Cu(II) and TT14C4 in the extraction system, *the spectral match shown in Fig. 4 conclusively identifies the organic-phase chromophore as the reported complex ion* $[Cu(TT14C4)]^{2+}$. Presumably, this ion resides within an HDDNS aggregate, and water or sulfonate anions occupy the axial sites.

Experiment #5 was conducted to determine if the dependence of the 395-nm absorbance on ligand:metal ratio correlates with the Cu(II) extraction behavior. To fix the organic-phase Cu(II) concentration, the stoichiometric Cu(II) salt of HDDNS (i.e., formally $Cu(DDNS)_2$) was prepared (19) and mixed in various proportions with TT14C4 at constant 2.50×10^{-2} M HDDNS (Table 1). In fitting the 10 absorbance values, the only parameters varied were those of the extinction coefficients; all other parameters in Table 3 were held at the values found in modeling the extraction results. It was assumed that all species having the CuB^{2+} grouping would have an identical extinction coefficient. Agreement to within ±5% ($\sigma = 0.86$) of the observed absorbance values shown in Fig. 5 was obtained using an extinction coefficient of 7760 L mol^{-1} cm^{-1}. Since this value differs by less than 4% from the reported value of 8040 L mol^{-1} cm^{-1} for $[Cu(TT14C4)]^{2+}$ in aqueous solution (21), *the spectral experiment strongly supports the computer model.*

Whereas the systems treated above all involved conditions of low to intermediate loading, a final series of spectrophotometric experiments was conducted to investigate the complexation of Cu(II) by TT14C4 at complete loading. Experiments #6 - #9 in Table 1 were conducted essentially as titrations of $Cu(DDNS)_2$ with TT14C4 (or vice versa).

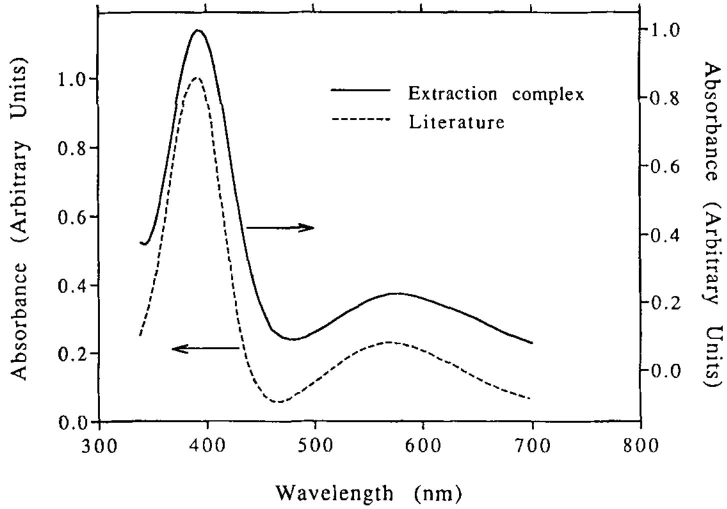

FIGURE 4. Comparison of UV/vis spectra of Cu(II) complexed by TT14C4. Lower curve corresponds to the reported spectrum of the complex ion $[Cu(TT14C4)]^{2+}$ in a solution of 0.1 M $HClO_4$ in 80% methanol (32). Upper curve is the spectrum of the organic phase containing 9.2 x 10^{-4} M TT14C4 and 9.0 x 10^{-3} M HDDNS in toluene after equilibration at an O:A phase ratio of 1:10 with an aqueous solution containing 0.8 M H_2SO_4 and 0.1 M $CuSO_4$ at 25 °C. For clarity, the spectra have been normalized to have a maximum unit absorbance (at ca. 390 nm), and the upper spectrum has been displaced 0.15 absorbance units as indicated on the right axis.

Because the system contains no free HDDNS, it is clear that the model needed to approximate the spectral behavior of Experiments #6 - #9 can have no species in common with the synergistic model (Table 3). Indeed, only species having exchangeable protons could be successfully retained in refining the synergistic model, yielding no way to define the formation constant of the copper salt of HDDNS. Without a link to Table 3, Experiments #6 - #9 were fit as an independent system. Each CuB^{2+} unit was assumed to have the extinction coefficient 7760 L mol^{-1} cm^{-1} found above, since the peak positions and spectral contours were essentially unchanged. It was found that models involving one reactant and two product species gave fits to within the estimated experimental error as summarized in Table 4 for the two best models, designated Models A and B. Plots for the models are given in Figs. 6 and 7. Log*K* values given in Table 4 correspond to organic-phase reactions written in terms of the macrocycle reacting with the Cu(II) salt of HDDNS, best formulated as the organic-phase species Cu_2A_4. For example,

$$Cu_2A_4\,(org) + B\,(org) \rightleftharpoons CuBH_2A_4\,(org) \qquad (10)$$

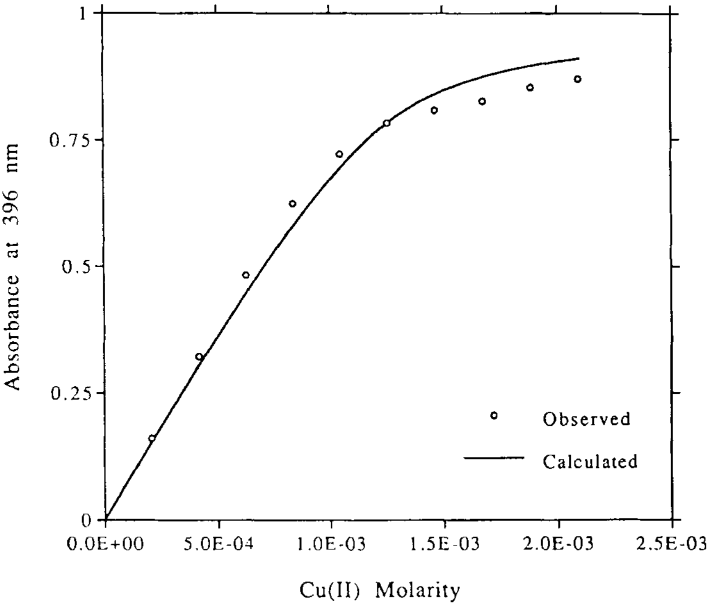

FIGURE 5. Variation of the absorbance at 396 nm for an organic solution containing 1.25 x 10^{-3} M TT14C4 and 0.025 M HDDNS as a function of the concentration of added $Cu(DDNS)_2$. See Experiment #5 (Table 1). Solid curve is calculated based on the extraction model given in Tables 2 and 3.

In a logical manner, the models suppose that TT14C4 adds progressively to Cu_2A_4 to give Cu_2BA_4 and either $CuBA_2$ or $Cu_2B_2A_4$. The results disallow a definitive selection between the two models, though Model A gives less divergence at the extremes. A model having reactants Cu_mA_{2m} (m = 1,2) and products $Cu_{m'}B_bA_{2m'}$ (m' = 2, b = 1,2; m' = 1, b = 1) may possibly offer a complete description, but Occam's razor dictates adding no further species. In any case, the ability of the models to account for the absorbance data supports the assumption ε = 7760 L mol^{-1} cm^{-1} per CuB^{2+} unit, in essence implying that only one type of coordination of TT14C4 with Cu(II) is important, namely formation of the known intracavital complex (21,32-34). It may also be remarked that the log$K$ values 3.68 and 3.88 given by the Models in Table 4 for the formation of Cu_2BA_4 compare with the value 3.53 for eq. 8. Thus, the species Cu_2BA_4 would presumably have one TT14C4-bound and one unbound Cu^{2+} ion within the aggregate.

TABLE 4. MODELS FOR SPECTRAL EXPERIMENTS AT HIGH LOADING

Species[a]	Type	Exper.[b]	δ[c]	log$K$	ε[d]
Model A (σ = 0.92)					
$Cu_2A_4W_{22}$	Reactant	6 - 9	8.90	—	0
$Cu_2BA_4W_{14}$	Product	6 - 9	8.90	3.680 ± 0.063	7760
$CuBA_2W_3$	Product	6 - 9	8.90	1.146 ± 0.022	7760
Model B (σ = 1.00)					
$Cu_2A_4W_{22}$	Reactant	6 - 9	8.90	---	0
$Cu_2BA_4W_{14}$	Product	6 - 9	8.90	3.880 ± 0.066	7760
$Cu_2B_2A_4W_6$	Product	6 - 9	8.90	6.517 ± 0.049	15520

[a] H^+ is the hydrogen ion; A^- is the HDDNS anion; B is TT14C4 (tetrathia-14-crown-4); and W is water. Hydration numbers were chosen to reflect a reasonable decrease in hydration on successive complexation of Cu^{2+} by B. Although the program SXLSQA formally considers $Cu_2A_4W_{22}$ to be a product species formed from the extraction of Cu(II) by HDDNS, it is listed as a reactant species for consistency with the actual experiment.

[b] Experiments used to determine log$K$ values corresponding to the indicated species in regression analysis are noted in Table 1.

[c] Solubility parameters δ ($cal^{1/2}$ $cm^{-3/2}$) were estimated as described in the Experimental Section and were not refined.

[d] Molar extinction coefficient in L mol^{-1} cm^{-1}.

Generic Model and Critique

Based on the present results together with recent work (3,7-12,14,16-20), a generic description of the extraction of metal ions by HDDNS synergized by crown ethers in low-polarity diluents may be proposed. In essence, the synergism may be described in terms of the binding of the metal ion by the macrocycle in the organic phase and the incorporation of the resulting complex into HDDNS aggregates. We restrict our attention to low-loading situations where only species having a single metal ion are formed and refer only to divalent metal ions, though extension to monovalent metal ions may reasonably be expected. HDDNS aggregates to give a species $(HA)_a$, in equilibrium with monomeric HA. At low loading, the aggregate $(HA)_a$, incorporates divalent metal ions by cation exchange to give $MH_{a-2}A_a$, which resists deaggregation on dilution. In low-polarity diluents, crown ethers used alone extract mineral acid salts of metal ions poorly. All synergistic systems that have been studied in detail have involved as the basis for synergism 1:1 interactions between metal and macrocycle, though these systems were deliberately chosen to favor this outcome. The simplest species involving metal ion,

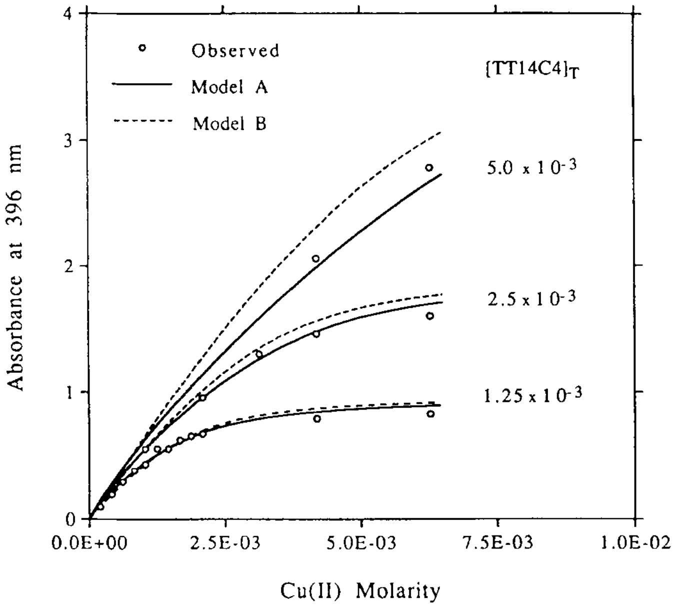

FIGURE 6. Variation of the absorbance at 396 nm for organic solutions each containing one of three different concentrations of TT14C4 as a function of the concentration of added $Cu(DDNS)_2$; no excess HDDNS is present. See Experiments #6 - #8 (Table 1). Solid and dashed curves are calculated based on the extraction models A and B, respectively, given in Table 4.

macrocycle, and HDDNS is MBA_2, which in the presence of excess HDDNS is aggregated to species of the form $MBA_2{\cdot}nHA$. Interactions between B and HA lead to complexes of the form $B_b{\cdot}rHA$. Values of $n + q$ and r vary as a function of HDDNS concentration but tend to maximize at the value of the HDDNS aggregation number a'.

In general, our results clearly suggest that the synergistic effect involves loss of hydration of the metal ion. This conclusion draws upon earlier measurements of organic-phase water content (12,17,19,24) together with the present results in mimicking this effect through SXLSQA modeling. Assignments of species hydration numbers in the models, however, must be regarded as approximations. Hydration numbers of sulfonic acid aggregates tend to be high (36,37), and measurements of organic-phase water contents point to *variable* species hydration numbers, depending primarily on water activity. As water activity decreases, these species gradually lose their waters, simply taking on lower values of w. Since our modeling with SXLSQA employs discrete

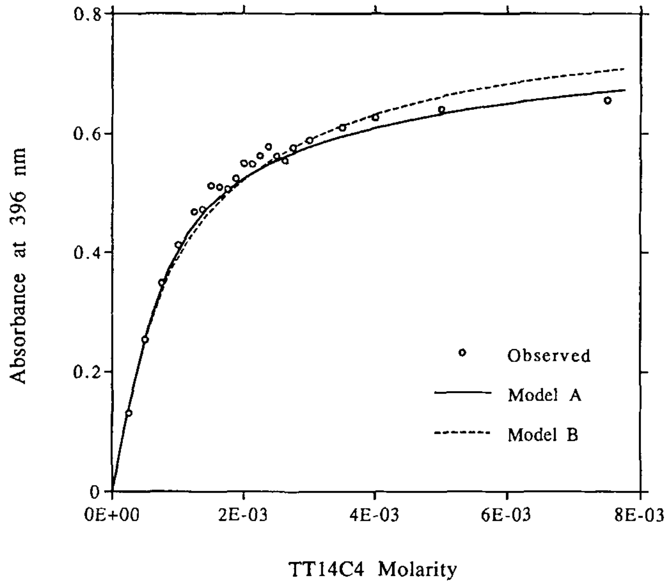

FIGURE 7. Variation of the absorbance at 396 nm for an organic solution containing 1.05 x 10^{-3} M $Cu(DDNS)_2$ as a function of the concentration of added TT14C4; no excess HDDNS is present. See Experiment #9 (Table 1). Solid and dashed curves are calculated based on the extraction models A and B, respectively, given in Table 4.

hydration assignments, continuously varying hydration has been cumbersome to manage computationally. Fortunately, these effects come into play only at high ionic strengths mostly beyond our range of interest.

How one ultimately judges an equilibrium model depends on its usefulness in correlating system observables, predicting new behavior, and understanding underlying chemistry. As we have shown, the simple synergistic model based on eqs. 5 - 7 successfully correlates copper distribution coefficients as a function of the concentration of the four solute components: $CuSO_4$, H_2SO_4, HDDNS, and TT14C4. Its predictive ability was demonstrated by the good agreement with the dependence of the distribution coefficients on loading and sulfuric acid variation. Good consistency was even obtained with spectral experiments that identify the key 1:1 interaction of TT14C4 with the Cu^{2+} ion. Finally, understanding has been increased through mimicking by computer the key interactions underlying behavior. Similarly encouraging results were obtained in the modeling of the synergistic extraction of Mn(II) by HDDNS and a crown ether (12).

Our modeling approach based on speciation may be contrasted with a simple thermodynamic approach reported earlier (35,36). The latter requires only a few adjustable parameters and nicely accounts for the behavior of observables such as concentration quotients and water extraction in several types of ion-exchange reactions. Whereas it may be of interest to determine whether this approach could be usefully applied to the present system, it probably could not be expected to provide much information regarding the nature of organic-phase species. On the other hand, mass-action methods as exemplified by SXLSQA lead directly to postulated species that can be confirmed or disproved by independent experiments. Mass-action methods mostly involving slope analysis have in fact proven to be widely useful and informative in investigations of sulfonic acid extraction systems, as summarized in several reviews (36-38). Our studies show that computer modeling offers high "resolution" in maximizing the information obtained on speciation, as limited mainly by the precision of the data, and the results have indeed been consistent with spectral and physical data where available.

CONCLUSIONS

It was the object of this work to show that the basis of synergism in the extraction of Cu(II) from sulfuric acid by TT14C4 (B) and HDDNS (HA) in toluene arises in the formation of the 1:1 complex ion CuB^{2+} in the organic phase. Results of computer modeling of an extensive set of distribution data augmented by direct UV/vis spectral identification of CuB^{2+} ion conclusively support this hypothesis. Through equilibrium modeling, a set of likely species has been proposed wherein the unit $CuBA_2$ receives further solvation from HA or its salt CuA_2. A weak competition involving the interaction of B and HA probably occurs. Based on the proposed equilibria, the effect of variation of the solute components $CuSO_4$, H_2SO_4, HDDNS, and TT14C4 could be modeled to nearly within experimental error. The hydration of organic-phase species is suggested to be a factor of primary importance in understanding behavior at high H_2SO_4 concentrations. It should be stressed that the modeling only provides a precise *interpretation* of the data and does not necessarily represent the true nature of the system. Although tests of the models developed here appear encouraging, the models should be regarded as hypotheses to be further tested by use of other experimental techniques.

ACKNOWLEDGMENTS

This research was funded by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The participation of Lætitia Delmau in this research was made possible in part by a travel grant from the Rectorat de l'Académie de Paris, and support for Sixto Bajo was in part provided by the Paul Scherrer Institute, Wurenlingen, Switzerland. The authors wish to thank C. F. Coleman for helpful discussions in the preparation of this manuscript.

REFERENCES

1. M. Hiraoka, Crown Compounds: Their Characteristics and Applications, Studies in Organic Chemistry, Vol. 12, Elsevier, New York (1982).
2. Y. Takeda, Topics Current Chem. 121, 1-38 (1984).
3. W. J. McDowell, Sep. Sci. Technol. 23, 1251-1268 (1988).
4. K. Gloe, P. Muhl, and J. Beger, Z. Chem. 28, 1-14 (1988).
5. R. A. Bartsch, Solvent Extr. Ion Exch. 7, 829-854 (1989).
6. B. G. Cox and H. Schneider, Coordination and Transport Properties of Macrocyclic Compounds in Solution, Studies in Physical and Theoretical Chemistry, Vol. 76, Elsevier, New York (1992).
7. W. J. McDowell, B. A. Moyer, G. N. Case, and F. I. Case, Solvent Extr. Ion Exch. 4, 217-236 (1986).
8. W. J. McDowell, B. A. Moyer, S. A. Bryan, R. B. Chadwick, and G. N. Case, Proc. Internat. Solvent Extr. Conf. (ISEC '86), Munchen, Deutsche Gesellschaft fur Chemische Apparatewesen, Chemische Technik und Biotechnologie e. V., Frankfurt am Main, F.R.G., 1986, pp. 477-482.
9. B. A. Moyer, C. L. Westerfield, W. J. McDowell, and G. N. Case, Sep. Sci. Technol. 23, 1325-1344 (1988).
10. B. A. Moyer, R. A. Sachleben, and G. N. Case, Proc. International Solvent Extraction Conference (ISEC '93), York, England, Vol. 1, Society for Chemical Industry, London, 1993, pp. 525-532.
11. B. A. Moyer, G. N. Case, S. D. Alexandratos, and A. A. Kriger, Anal. Chem. 65, 3389-3395 (1993).
12. B. A. Moyer, L. H. Delmau, G. J. Lumetta, and C. F. Baes, Jr., Solvent Extr. Ion Exch. 11, 889-922 (1993).
13. C. F. Baes, Jr., Nucl. Sci. Eng. 16, 405-412 (1963).
14. C. F. Baes, Jr., W. J. McDowell, and S. A. Bryan, Solvent Extr. Ion Exch. 5, 1-28 (1987).
15. C. F. Baes, Jr., B. A. Moyer, G. N. Case, and F. I. Case, Sep. Sci. Technol. 25, 1675-1688 (1990).

16. W. J. McDowell, G. N. Case, J. A. McDonough, and R. A. Bartsch, Anal. Chem. 64, 3013-3017 (1992).

17. S. A. Bryan, W. J. McDowell, B. A. Moyer, C. F. Baes, Jr., and G. N. Case, Solvent Extr. Ion Exch. 5, 717-738 (1987).

18. W. J. McDowell, B. A. Arndsten, and G. N. Case, Solvent Extr. Ion Exch. 7, 377-394 (1989).

19. B. A. Moyer, C. F. Baes, Jr., G. N. Case, G. J. Lumetta, and N. M. Wilson, Sep. Sci. Technol. 28, 81-113 (1993).

20. G. J. Lumetta, B. A. Moyer, P. A. Johnson, and N. M. Wilson, Solvent Extr. Ion Exch. 9, 155-176 (1991).

21. L. S. W. L. Sokol, L. A. Ochrymowycz, and D. B. Rorabacher, Inorg. Chem. 20, 3189-3195 (1981).

22. C. F. Baes, Jr., E. J. Reardon, and B. A. Moyer, J. Phys. Chem. 97, 12343-12348 (1993).

23. B. A. Moyer and G. N. Case, unpublished results.

24. G. J. Lumetta and B. A. Moyer, J. Coord. Chem. 22, 331-336 (1991).

25. J. H. Hildebrand and R. L. Scott, The Solubility of Nonelectrolytes, 3rd ed., Reinhold Publishing Corp., New York (1950).

26. A. F. M. Barton, Handbook of Solubility Parameters and Other Cohesion Parameters, CRC Press, Boca Raton (1983).

27. K. S. Pitzer, in Activity Coefficients in Electrolyte Solutions, 2nd ed., K. S. Pitzer, Ed., CRC Press, Boca Raton, 1991, pp. 75-153.

28. A. van Dalen, Solvent Extraction and Inclusion Compound Formation with Dinonyl Naphthalene Sulphonic Acid, Report RCN 141, Reactor Centrum Nederland, Petten, April, 1970.

29. A. van Dalen, K. W. Gerritsma, J. Wijkstra, J. Colloid Interface Sci. 48, 122-126 (1974).

30. R. Chiarizia, P. R. Danesi, M. A. Raieh, and G. Scibona, J. Inorg. Nucl. Chem. 37, 1495-1501 (1975).

31. B. A. Moyer, R. A. Sachleben, and G. N. Case, unpublished results.

32. E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacher, and L. A. Ochrymowycz, J. Amer. Chem. Soc. 98, 4322-4324 (1976).

33. T. E. Jones, D. B. Rorabacher, and L. A. Ochrymowycz, J. Amer. Chem. Soc. 97, 7485-7486 (1975).

34. M. D. Glick, D. P. Gavel, L. L. Diaddario, and D. B. Rorabacher, Inorg. Chem. 15, 1190-1193 (1976).

35. E. Högfeldt, in Developments in Solvent Extraction, S. A. Legret, Ed., M. R. Masson, Transl. Ed., Ellis Horwood, Chichester, 1988, Chap. 10.

36. E. Högfeldt, R. Chiarizia, P. R. Danesi, and V. S. Soldatov, Chemica Scripta 18, 13-43 (1981).

37. G. Y. Markovits and G. R. Choppin, in Ion Exchange and Solvent Extraction: A Series of Advances, Vol. 3, J. A. Marinsky and Y. Marcus, Eds., Marcel Dekker, New York, 1973, pp. 51-81.

38. E. O. Otu and A. D. Westland, Solvent Extr. Ion Exch. 9, 875-833 (1991).