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EQUILIBRIUM ANALYSIS OF AGGREGATION BEHAVIOR IN THE SOLVENT EXTRACTION OF Cu(II) FROM SULFURIC ACID BY DIDODECYLNAPHTHALENE SULFONIC ACID

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ABSTRACT

By use of the principles of equilibrium analysis, the liquid-liquid cation exchange of Cu(II) from aqueous sulfuric acid at 25 °C by didodecylnaphthalenesulfonic acid (HDDNS) in toluene may be understood in terms of small hydrated aggregated species in the organic phase. Extraction data have been measured as a function of organic-phase HDDNS molarity (1.0×10^{-4} to 1.0×10^{-1}), aqueous copper(II) sulfate molarity (1.2×10^{-8} to 1.3×10^{-2}), and aqueous sulfuric acid molarity (0.03 to 6.0). Graphical analysis of linear regions of the data support a model in which organic-phase aggregates of HDDNS function by cation exchange to incorporate Cu(II) ions with no apparent change in aggregation number at low loading. Supporting FTIR spectra and water-content measurements of HDDNS solutions in toluene show that the HDDNS aggregates are highly hydrated. By use of the computer program SXLSQA, a comprehensive equilibrium model was developed with inclusion of activity effects. Aqueous-phase activity coefficients and degree of aqueous bisulfate formation were estimated by use of the Pitzer treatment. Organic-phase nonideality was estimated by the Hildebrand-Scott treatment and was shown to be a negligible effect under the conditions tested. Excluding aqueous sulfuric acid molarities

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greater than 1, it was possible to model the data to within experimental error by assuming only the equilibrium extraction of Cu^{2+} ion by the aggregate $(HDDNS)_4(H_2O)_{22}$ and the equilibrium dissociation of $(HDDNS)_4(H_2O)_{22}$ to the monomer. The dependence of Cu(II) distribution on aqueous sulfuric acid molarity was shown to be quantitatively consistent with a cation-exchange process. In comparison with the graphical approach, the computer analysis allows comprehensive model testing over large, nonlinear data sets and eliminates the need to make limiting assumptions. Overall, the results provide useful insight toward the development of selective synergistic extraction systems in which HDDNS provides a nonselective cation-exchange vehicle in combination with a selective second extractant.

INTRODUCTION

Progress in understanding equilibria in solvent extraction has been accelerated markedly by the use of computer-modeling techniques (1-21). Modeling has proven to be particularly advantageous in the interpretation of equilibrium data involving complex effects such as competing equilibria, synergism, water extraction, nonideality, and aggregation. Except under contrived conditions, most extraction systems exhibit one or more of these phenomena, increasing the difficulty of simple graphical methods of analysis (18,21). An important recent advance in the evolution of computer modeling of solvent extraction has been the development of the program SXLSQA (14-16), which incorporates the capabilities of its predecessor SXLSQ (13). The program SXLSQA uniquely combines the advantages of broad generality in the formulation of postulated species, of flexibility in accepting a range of data types, and of inclusion of nonideality effects.

In this paper, we present the use of SXLSQA in the analysis of the extraction behavior and aggregation of the representative strong-acid cation exchanger didodecylnaphthalene sulfonic acid (HDDNS). Long-standing questions concerning HDDNS and its smaller congener HDNNS (effectively the only available cation exchangers having the sulfonic acid functionality) have concerned the role of association phenomena in controlling the extraction of metal cations (1,2,13,19-34). Such questions have continued to be important in elucidating synergistic extraction systems in which organophilic acids are combined with macrocyclic metal-ion receptors (13,19-21,35-40) or other extractants (23,25,26,33,34). Whereas spectroscopic studies indicate that the macrocycles function in selected systems by coordination (19,39,40), extraction behavior suggests that the organophilic acids provide a pH-adjustable driving force through cation exchange (35-37). Although computer modeling has in fact facilitated the development of equilibrium models for the observed synergism, it has not been completely successful due to the lack of explicit data concerning the aggregation state of the cation exchangers (13,19,20). Obtaining such "baseline" information is thus the intent of this paper.

The particular system selected for study here involves the extraction of Cu^{2+} ions from aqueous sulfuric acid by HDDNS in toluene. As such, this system represents the direct baseline for an ongoing modeling study of synergism by thia macrocycles (38). Related synergistic systems involving combinations of HDDNS with macrocycles in toluene include extractions of Mn^{2+}, Sr^{2+}, Ra^{2+}, Cs^{+}, Ag^{+}, and other ions (35-40). In all of these systems, HDDNS offers the advantages of low selectivity and acid-range extraction. Specifically needed for developing equilibrium models of these systems is the aggregation number of HDDNS in toluene and knowledge of the deaggregation equilibria. Based on reported investigations of HDNNS, it is known that distribution behavior is a function of aggregation number and thus can be used in reverse as a means to determine aggregation number through mass-action analysis (21,24-29). The reported method utilizes slope analysis of the dependence of metal distribution coefficients D_M ($D_M = [M]_{org}/[M]_{aq}$) on partial loading. We recently showed that comprehensive computer analysis of such data using SXLSQA yields more extensive information while permitting certain assumptions (e.g., ideality of organic-phase species) to be checked for the first time (21). Thus, we have incorporated this approach into the present treatment, expanding the data collection to include a wider range of conditions.

Our modeling here also includes an analysis of the dependence of D_M on aqueous acid concentration. The needed aqueous-phase activity coefficients in the hydrometallurgically important system $CuSO_4$-H_2SO_4-

H_2O were estimated by the application of the Pitzer treatment (41,42) through SXLSQA (15,16). Ultimately, the results may be applied to an understanding of the unusual acid dependence observed in the *synergistic extraction of* Cu^{2+} *ions by combinations of* HDDNS and thia macrocycles (38). More important, the results provide a rigorous check of the assumption that HDDNS is indeed functioning by cation exchange.

EXPERIMENTAL SECTION

Materials

HDDNS was obtained from King Industries and was purified by anion-exchange chromatography (30). Stock solutions of HDDNS were standardized by acid-base titrations in ethanol-water. Toluene was of spectrophotometric-grade (Burdick and Jackson). Water was doubly distilled. ^{64}Cu and ^{67}Cu tracers (NEN Research Products) were received as nitrate salts and were converted to the sulfate form by adding the received solutions to dilute sulfuric acid and evaporating the solutions to dryness. All other chemicals were of reagent quality and were used as received.

FTIR Spectrophotometry and Karl Fischer Titrations

Following an earlier study (21), water-saturated solutions of HDDNS in toluene were prepared by gently stirring the HDDNS solutions in the presence of a drop of pure water at 25.0 ± 0.2 °C for 12 h or longer. Infrared spectra were recorded on a Digilab FTS-60 FTIR spectrophotometer equipped with a modified sample compartment capable of maintaining a constant temperature (25.0 ± 0.5 °C). Spectra of the solutions were recorded in the region 3000-4000 cm^{-1} by the use of either BaF_2 (1.00-mm pathlength) or AgBr (0.5-mm pathlength) solution cells. The spectrum of water-saturated toluene was subtracted from each sample spectrum.

The water content of the same water-saturated solutions of HDDNS used for FTIR spectra (see above) was determined using a Metrohm

Model 652 KF-Coulometer. Aliquots of the HDDNS solutions were withdrawn by syringe through a self-sealing septum and injected directly into the titrator. Water-saturated toluene was employed as a blank.

Cu(II) Distribution Measurements

Gamma scintillation counting techniques were employed using either ^{64}Cu or ^{67}Cu tracers. Aqueous solutions containing $CuSO_4$ (1.2×10^{-8}-1.3×10^{-2} M), H_2SO_4 (0.03-6.0 M), and tracer were equilibrated in capped vials with equal volumes of toluene solutions of HDDNS (1.0×10^{-6}-1.0×10^{-1} M) by gently rocking the vials at 25.0 ± 0.1 °C for a minimum of 12 h; this technique is nondispersive and minimizes entrainment problems in precise distribution measurements, especially at low D_M. Kinetic tests indicated the attainment of equilibrium within 12 h. The separated phases were sampled for counting on a gamma counter equipped with a well-type sodium iodide detector. Distribution coefficients (D_{Cu}) were calculated as $D_{Cu} = [Cu]_{org}/[Cu]_{aq} = (C_{org} - C_b)/(C_{aq} - C_b)$, where C_{org}, C_{aq}, and C_b are the counts registered in a given time interval for the organic phase, the aqueous phase, and background, respectively. At HDDNS concentrations below ca. 1.0×10^{-4} M, the scatter of values of D_{Cu} was judged unacceptable (greater than ±20%), and all data collected in this range were rejected. The relative precision error at $[HDDNS]_{tot} = 1.0 \times 10^{-4}$ was found to be ±20%, decreasing to an average value of ±3.7% when $[HDDNS]_{tot} \geq 5.0 \times 10^{-4}$. All measurements were expressed on the molarity scale, and the small volume changes due to the solubility of water in pure toluene and to the solubility of toluene in the aqueous phases were neglected in all cases.

Loss of HDDNS and its Cu(II) salt $Cu(DDNS)_2$ to the aqueous phase was assumed to be negligible. Although no direct measurements of the loss of HDDNS, HDNNS, or their salts appear to have been reported (39), negligible loss has been inherently assumed in successful literature treatments of the equilibrium behavior of HDNNS (23-33), suggesting that this assumption must be good to within experimental tolerance. That HDDNS and $Cu(DDNS)_2$ distribute negligibly to aqueous solution is here supported by demonstrating that the theoretical loading ratio (i.e., $[\mathrm{Cu}]_{\mathrm{org,max}}/[\mathrm{HDDNS}]_{\mathrm{tot}} = 0.5$) may be attained on repeated contacts of toluene solutions of HDDNS with aqueous $CuSO_4$ solutions. In this demonstration, six solutions of 0.00800 M HDDNS were contacted in parallel with six aqueous solutions of 0.01-0.5 M $CuSO_4$. The technique employed mildly dispersive contacting of the solutions in capped vials at a phase ratio ($\phi_{\mathrm{o/a}} = V_{\mathrm{org}}/V_{\mathrm{aq}}$) of 3 by a circular end-over-end agitation for 10 min at room temperature. At the end of a 5-min settling period, the pH of each phase was measured, and the equilibrated aqueous phases were replaced by fresh aqueous solutions. Over a total of five such contacts, the pH of each equilibrated aqueous phase stabilized. On addition of ^{64}Cu tracer, a final contact was performed by gentle rocking at 25 °C for 12 h ($\phi_{\mathrm{o/a}} = 2$). From the determined distribution coefficients D_{Cu}, the equilibrium organic-phase copper molarities $[\mathrm{Cu}]_{\mathrm{org}}$ of the loaded solutions were found to lie in the range 0.00406-0.00423 with an average value of 0.00414 ± 0.00007; this gives $[\mathrm{Cu}]_{\mathrm{org,max}}/[\mathrm{HDDNS}]_{\mathrm{tot}} = 0.518$ (theor., 0.500).

Computer Modeling

Modeling of the distribution data was carried out by use of the general least-squares program SXLSQA (14-16). Operationally, this program iteratively refines a set of trial equilibrium quotients Q_i or constants K_i corresponding to a proposed set of equilibria until no further improvement in the agreement between the calculated and the observed quantities (in this case, D_{Cu}) is obtained. The ability of a given model to fit a particular set of data according to the least squares criterion is given by the *agreement factor* σ defined as

$$\sigma = \left[\frac{\sum_i w_i \left(Y_i - Y_{c,i} \right)^2}{\left(N_o - N_p \right)} \right]^{1/2} , \qquad (1)$$

where Y_i is the ith observed experimental quantity (i.e., D_{Cu} in this study), $Y_{c,i}$ is the corresponding quantity calculated from the model being tested, w_i is the weighting factor defined as the reciprocal of the square of the estimated uncertainty (σ_i) of Y_i, N_o is the number of observations, and N_p is the number of adjustable parameters (i.e., equilibrium quotients and possibly activity-coefficient parameters). In the present case, the relative errors σ_i/Y_i were found to have the following values: σ_i/Y_i = 0.20 ($[HDDNS]_{tot} = 1.0 \times 10^{-4}$), 0.10 ($1.0 \times 10^{-4} < [HDDNS]_{tot} < 5.0 \times 10^{-4}$), and 0.037 ($[HDDNS]_{tot} \geq 5.0 \times 10^{-4}$). In a systematic testing of equilibrium models, the best model is usually chosen as that exhibiting the minimum value of the agreement factor σ. If the uncertainty in the data is correctly estimated, σ will approach unity for a perfectly fitting model (13).

RESULTS AND DISCUSSION

Slope Analysis of Distribution Measurements

Equilibrium distribution coefficients D_{Cu} are reported herein for toluene solutions of HDDNS (1.0×10^{-4}-1.0×10^{-1} M) contacted at unit phase ratio ($\phi_{o/a} = 1$) with aqueous solutions containing $CuSO_4$ (1.2×10^{-8}-1.3×10^{-2} M), H_2SO_4 (0.03-6.0 M), and tracer at 25.0 ± 0.1 °C. Totaling 134 data points, the data set thus permits the analysis of the effects of the analytical organic-phase HDDNS molarity $[HDDNS]_{tot}$, partial loading of the solvent (actual maximum loading ratio in the data set is $[Cu]_{org}/[HDDNS]_{tot} = 0.08$), and aqueous acidity. Consistent with our earlier modeling studies, our basic approach in the analysis of this system has been to progress from familiar graphical methods to rigorous computer modeling. The graphical methods facilitate making general correlations, establishing linear relationships, identifying anomalies, and drawing qualitative conclusions. As we have shown elsewhere (18,21), simplifying assumptions allow the graphical methods to be applied quickly but introduce limitations on the rigor of the conclusions and on the range and types of data that may be examined. Little effort will be made to introduce corrections for the simplifying assumptions in the graphical analysis presented here, since this is essentially the task of the computer analysis carried out in the following section.

A general treatment employed in interpreting the cation exchange behavior of HDDNS and HDNNS (21,24-29) adapted to the present case posits that the extraction of Cu^{2+} ions takes place by the incorporation of the cation into an organic-phase aggregate without change in the aggregation number *a*:

$$H_aA_a \text{ (org)} + Cu^{2+} \text{ (aq)} \rightleftharpoons CuH_{a-2}A_a \text{ (org)} + 2H^+ \text{ (aq)} \quad . \qquad (2)$$

If the metal-cation loading $[Cu]_{org}$ is sufficiently small compared to $[HDDNS]_{tot}$, if the equilibrium sulfuric acid molarity $[H_2SO_4]_{aq}$ is constant and much greater than the equilibrium aqueous cation molarity $[Cu^{2+}]_{aq}$, if a is sufficiently large and constant, and if the organic phase behaves as an ideal solution, the application of the principles of slope analysis (1,2) based on eq. 2 as the predominant equilibrium leads to two predictions of interest here. First, D_{Cu} is expected to be independent of $[Cu^{2+}]_{aq}$ at constant values of $[HDDNS]_{tot}$, indicating that the metal cation is mononuclear in both phases (assuming mononuclearity in the aqueous phase). Second, the slope of the plot of $\log D_{Cu}$ vs. $\log[HDDNS]_{tot}$ is expected to be unity. These predictions are in fact typically met in the cation exchange of metals by sulfonic acid extractants when the sulfonic acid is essentially completely aggregated.

Under conditions of low loading and constant acidity, the extraction of Cu^{2+} ions by HDDNS at $[HDDNS]_{tot} \geq 0.01$ indeed meets the expectations of aggregated behavior according to eq. 2 but departs from expected behavior at lower HDDNS molarities. When the loading ratio $[Cu]_{org}/[HDDNS]_{tot}$ does not exceed 0.003 (hereafter designated as the regime of low loading), the constancy of D_{Cu} vs. $[Cu^{2+}]_{aq}$ at $[H_2SO_4]_{aq} = 0.3$ was found to be met at all HDDNS molarities within the tolerance of our measurements; thus, polynuclear organic-phase metal complexes and loading effects are discounted below this loading limit. As shown in Fig. 1, the plot of $\log D_{Cu}$ vs. $\log[HDDNS]_{tot}$ at low loading displays a slope of unity (actually 1.02 ± 0.02) when the analytical HDDNS molarity falls

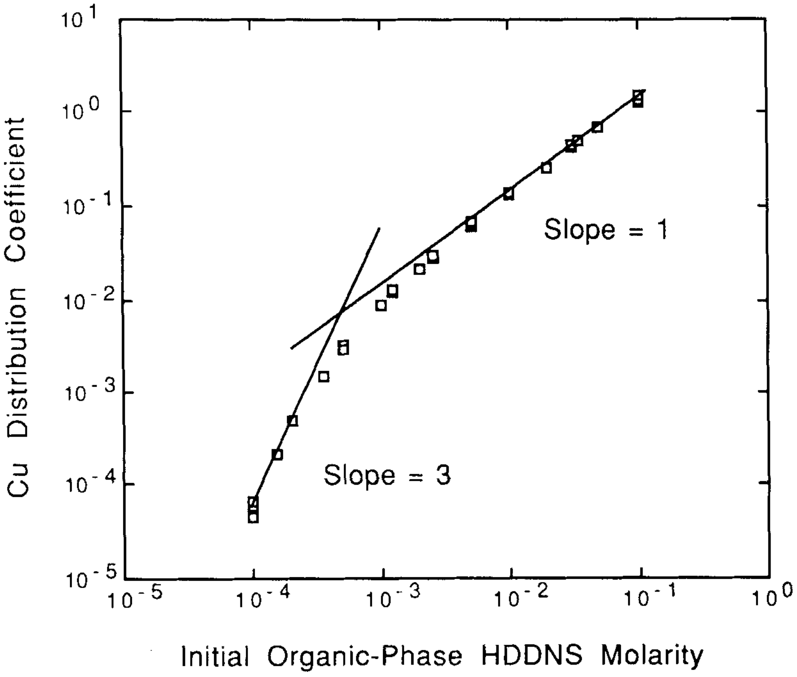
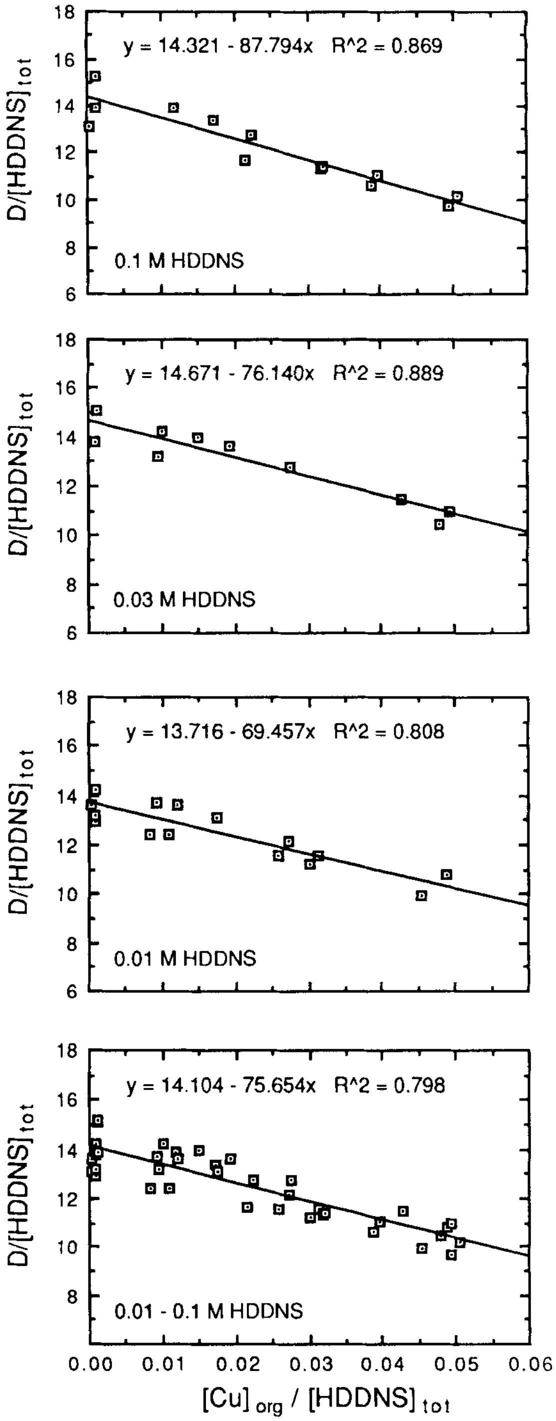


FIGURE 1. Plot of $\log D_{Cu}$ vs. $\log[HDDNS]_{tot}$ for low Cu(II) loading ratios ($[Cu]_{org}/[HDDNS]_{tot}$ < 0.003) at 25 °C. The solid lines give reference slopes of 1 and 3 as indicated. The initial aqueous phases consisted of 0.3 M H_2SO_4, 1.2 x10^{-8}-3.0 x 10^{-4} M $CuSO_4$, and tracer. As was the case in all experiments, toluene was employed as the diluent, and contacts were carried out at a phase ratio of 1.

in the range $0.01 \leq \log[HDDNS]_{tot} \leq 0.1$. However, below this range, the slope steepens to approximately 3 as shown. Owing to loss of precision at HDDNS molarities below ca. 0.0001, it was not possible to determine whether the slope of 3 observed is in fact the limiting slope.

The increase in slope as the HDDNS concentration decreases (Fig. 1) may be readily interpreted as a deaggregation process by writing a more general form of eq. 2:

$$(a_2/a_1)H_{a_1}A_{a_1}(org) + Cu^{2+}(aq) \rightleftharpoons CuH_{a_2-2}A_{a_2}(org) + 2H^+(aq) \quad . \qquad (3)$$


y = 14.321 - 87.794x R^2 = 0.869
0.1 M HDDNS
y = 14.671 - 76.140x R^2 = 0.889
0.03 M HDDNS
y = 13.716 - 69.457x R^2 = 0.808
0.01 M HDDNS
y = 14.104 - 75.654x R^2 = 0.798
0.01 - 0.1 M HDDNS
D/[HDDNS]$_{tot}$
6
8
10
12
14
16
18
0.00
0.01
0.02
0.03
0.04
0.05
0.06
[Cu]$_{org}$ / [HDDNS]$_{tot}$

($H_{a_1}A_{a_1}$ and $CuH_{a_2-2}A_{a_2}$ are respectively designated as species 1 and 2; these designations are used as subscripts to identify the corresponding aggregation numbers a_1 and a_2.). Under the same assumptions applied to eq. 2, slope analysis based on eq. 3 more generally equates slopes of plots of $\log D_{Cu}$ vs. log[HDDNS]$_{tot}$ to the ratio a_2/a_1. Thus, the increase in slope with decreasing HDDNS concentration below ca. 0.005 M implies that the predominant equilibrium shifts to one with a_2/a_1 at least 3. An increase in slope observed in analogous plots of metal ion extraction by HDNNS was also interpreted in terms of deaggregation of the sulfonic acid (28).

Whereas the above analysis requires low metal loading and yields information on *relative* aggregation numbers, the effect of partial loading of the HDDNS aggregates yields information on ***absolute*** aggregation numbers. (Conversely, data collected at low loading provide no information on absolute aggregation number.) Based on eq. 2, the treatment given originally by van Dalen (25,26) and used by others (21,24,27-29) may be described in terms of a linear dependence of the distribution coefficient D_{Cu} on the organic-phase Cu(II) molarity $[Cu]_{org}$ at constant aqueous acidity and HDDNS molarity. For convenience, we express the relationship in a rearranged form:

$$\frac{D_{Cu}}{[\mathrm{HDDNS}]_{tot}} = \frac{-Q}{[\mathrm{H}^+]^2}\left(\frac{[\mathrm{Cu}]_{org}}{[\mathrm{HDDNS}]_{tot}}\right) + \frac{Q}{a[\mathrm{H}^+]^2}, \qquad (4)$$

where Q is the equilibrium concentration quotient corresponding to eq. 2. It follows that the value of a is given by the negative ratio of the slope to the intercept in plots of D_{Cu}/[HDDNS]$_{tot}$ vs. $[Cu]_{org}$/[HDDNS]$_{tot}$. Figure 2 shows such plots for HDDNS molarities 0.01, 0.03, and 0.1 at 0.3 M

FIGURE 2. Plots of D_{Cu}/[HDDNS]$_{tot}$ vs. $[Cu]_{org}$/[HDDNS]$_{tot}$ for 0.01 M (A), 0.03 M (B), 0.1 M (C), and 0.01-0.1 M (D) HDDNS in toluene at 25 °C. The solid lines denote linear least-squares fits (see Table 1). The initial aqueous phases consisted of 0.3 M H_2SO_4, 1.5 x10^{-5}-1.0 x 10^{-2} M $CuSO_4$, and tracer.

TABLE 1. AGGREGATION NUMBERS FROM SLOPE ANALYSIS OF PARTIAL-LOADING DATA[1]

$[HDDNS]_{tot}$	Slope	y-Intercept	*a*	No. Pts	Precision
0.01	-69.6 ± 9.2	13.73 ± 0.21	5.1 ± 0.7	16	±4.6%
0.03	-76.8 ± 9.9	14.68 ± 0.28	5.2 ± 0.7	10	±4.1%
0.1	-87.8 ± 10.1	14.33 ± 0.30	6.1 ± 0.7	13	±4.7%
0.01-0.1	-76.0 ± 6.3	14.10 ± 0.17	5.4 ± 0.4	39	±4.2%

[1] Data and experimental conditions are given in Fig. 2 and its caption. Linear least-squares analysis was based on the equilibrium given in eq. 2 and the expression given in eq. 4.

H_2SO_4. If it may be assumed that the aggregation number *a* is constant over a range of HDDNS molarities, eq. 4 allows the partial-loading data to be correlated over all of the data as shown in the plot D given in Fig. 2. Table 1 summarizes the results. Given the uncertainties of the individual values of *a* reported in the table, the analysis leads to the preliminary conclusion that the aggregation number (*a*) of HDDNS in the range 0.01-0.1 M is 4-7.

The validity of slope analysis described by eqs. 2 and 4 hinges on assumptions of ideal behavior of organic-phase species, neglect of species consisting of two Cu(II) ions in a single aggregate, constant aqueous acidity, and the existence of a single equilibrium (eq. 2). The first and second assumptions may be justified on the basis of an analysis of Zn^{2+} extraction from aqueous nitric acid by HDDNS in CCl_4 (21), where it was found both that near ideal behavior was obeyed and that the extraction of the second metal ion begins when the loading ratio ($[Cu]_{org}/[HDDNS]_{tot}$) approaches $1/a$. Since the maximum value of $[Cu]_{org}/[HDDNS]_{tot}$ employed here was 0.05, approximately 25% of the aggregates would be expected to contain a single Cu(II) ion each if the aggregation number is 5. Constant aqueous acidity (third assumption) is approximately true for 0.01 and 0.03 M HDDNS, where the increase in aqueous acidity due to cation exchange is less than 1%; but in the case of 0.1 M HDDNS, the maximum acidity change over the whole range of loading is ca. 3%, significant in view of both the total decrease in D_{Cu} (ca. 25%) and the inverse 2nd-order hydrogen-ion dependence (eq. 4). In this case, the increased aqueous acidity with increasing loading lowers D_{Cu}, thereby decreasing the apparent slope and increasing the derived value of a. Thus, the value $a = 6$ given in Table 1 for 0.1 M HDDNS may be slightly high, though not seriously in view of the precision involved. Finally, the assumption of a single equilibrium (i.e., eq. 2) ignores the obvious deaggregation occurring at [HDDNS] < 0.005. To consider this effect, deaggregation may be represented by

$$H_aA_a \text{ (org)} \rightleftharpoons a \text{ HA (org)} \quad , \qquad (5)$$

and eq. 4 may be modified to take eq. 5 into account by replacing $[\text{HDDNS}]_{tot}$ with the term $([\text{HDDNS}]_{tot} - [\text{HA}])$, where [HA] is the monomer concentration. On the assumption that [HA] = 0.002 when $[\text{HDDNS}]_{tot} > 0.005$, it was found that the derived values of a at 0.01 and 0.03 M HDDNS decrease to 4.1 and 4.9, respectively, while the value of a at 0.1 M HDDNS is practically unaffected. Overall, the assumptions made in the slope analysis are thus tolerable within the range of $4 \leq a \leq 7$, but the combined errors favor the lower part of this range.

Water-Content and Infrared Results

Measurement of the water content of water-saturated toluene solutions of HDDNS at 25.0 °C by Karl Fischer techniques confirmed that the aggregates are highly hydrated, as is well known for both HDDNS and HDNNS (1,19,21,23,24,27,31,32). In the range 0.01-0.1 M HDDNS, a plot of $\log[H_2O]_{org}$ vs. $\log[\text{HDDNS}]_{tot}$ was found to be linear with slope 1.01 ± 0.03 (intercept = 0.75 ± 0.04). Thus, the water content is essentially proportional to the HDDNS concentration, consistent with a constant aggregation number in this range. From the results, the number of water molecules per HDDNS molecule at unit water activity was found to be 5.4 ± 0.3. FTIR spectra of the solutions exhibited the broad water band with maxima at 3425 cm^1 observed previously (19,21,24,31).

Computer Modeling

Problem Definition. By use of the program SXLSQA, the conclusions made in the graphical analysis can be tested, refined, and extended. Further, the data may be treated comprehensively rather than in small subsets. By including estimates for activity effects in both the aqueous and organic phases, the models become thermodynamically rigorous.

Proceeding from the graphical analysis, all computer models were based on an extraction equilibrium (eq. 6) together with a deaggregation equilibrium (eq. 7):

$$\begin{aligned}&(a_2/a_1)\mathrm{H}_{a_1}\mathrm{A}_{a_1}\mathrm{W}_{w_1}(\mathrm{org}) + m_2\,\mathrm{Cu}^{2+}(\mathrm{aq}) \rightleftharpoons \\ &\mathrm{Cu}_{m_2}\mathrm{H}_{a_2-2m_2}\mathrm{A}_{a_2}\mathrm{W}_{w_2}(\mathrm{org}) + 2m_2\,\mathrm{H}^{+}(\mathrm{aq}) + \{(a_2/a_1)w_1 - w_2\}\mathrm{W}\ (\mathrm{aq}) \qquad (6)\end{aligned}$$

$$\begin{aligned}&(a_3/a_1)\mathrm{H}_{a_1}\mathrm{A}_{a_1}\mathrm{W}_{w_1}(\mathrm{org}) \rightleftharpoons \\ &\qquad\qquad \mathrm{H}_{a_3}\mathrm{A}_{a_3}\mathrm{W}_{w_3}(\mathrm{org}) + \{(a_3/a_1)w_1 - w_3\}\mathrm{W}\ (\mathrm{aq})\ . \qquad (7)\end{aligned}$$

Here, the presence of water (W) in the organic-phase species has been explicitly recognized. Continuing the use of subscripting from eq. 3, the postulated organic-phase species respectively include the HDDNS aggregate, the extraction complex, and a subaggregate ($a_3 < a_1$): $\mathrm{H}_{a_1}\mathrm{A}_{a_1}\mathrm{W}_{w_1}$ (species 1), $\mathrm{Cu}_{m_2}\mathrm{H}_{a_2-2m_2}\mathrm{A}_{a_2}\mathrm{W}_{w_2}$ (species 2), and $\mathrm{H}_{a_3}\mathrm{A}_{a_3}\mathrm{W}_{w_3}$ (species 3). For both convenience and consistency with earlier work (13,19-21), the aggregate $\mathrm{H}_{a_1}\mathrm{A}_{a_1}\mathrm{W}_{w_1}$ is defined here as the reactant species.

An equilibrium model here consists of the set of stoichiometric coefficients corresponding to the postulated species (eqs. 6 and 7) together with the corresponding equilibrium constants (or quotients) and all of the associated activity and volume parameters. Each organic-phase species i may be uniquely identified by the three integers m_i, a_i, w_i corresponding respectively to the number of metal ions, sulfonate anions, and associated water molecules; the number of hydrogen ions is then defined according to charge neutrality. By reference to eq. 6, equilibrium constants K_{m_2,a_2,w_2} associated with the formation of species m_2,a_2,w_2 may then be defined on the molarity scale as

$$K_{m_2,a_2,w_2} = \frac{\left[Cu_{m_2}H_{a_2-2m_2}A_{a_2}W_{w_2}\right] y_{m_2,a_2,w_2} \left[H^+\right]^{2m_2} y_H^{2m_2}\, a_W^{(a_2/a_1)w_1-w_2}}{\left[H_{a_1}A_{a_1}W_{w_1}\right]^{(a_2/a_1)} y_{m_1,a_1,w_1}^{(a_2/a_1)} \left[Cu^{2+}\right]^{m_2} y_{Cu}^{m_2}} , \qquad (8)$$

where the indicated molar activity coefficients are designated by the variable y and the activity of water is indicated by a_W. Recognizing that eq. 7 is the special case of eq. 6 where $m_3 = 0$, K_{0,a_3,w_3} may be obtained with appropriate modification of eq. 8. Equilibrium quotients Q_{m_2,a_2,w_2} replace K_{m_2,a_2,w_2} in models involving the assumption of ideality and may be obtained from eq. 8 by setting some or all activity coefficients y equal to unity; the water activity a_W in either case is calculated from the Gibbs-Duhem relationship.

Karl Fischer results (above) provide a basis for reasonable assignment of the number of water molecules in the aggregates. For the reactant aggregate $H_{a_1}A_{a_1}W_{w_1}$, the Karl Fischer results give $w_1 = 5.4(a_1)$. From published data for HDNNS (24), it is expected that the hydration of the extraction complex $Cu_{m_2}H_{a_2-2m_2}A_{a_2}W_{w_2}$ and subaggregate $H_{a_3}A_{a_3}W_{w_3}$ should not be much different from w_1, and thus for all models we set $w_1 = w_2 = w_3$, except when $a_3 = 2$ or 1 we arbitrarily choose $w_3 = 5$ or 2, respectively. Only when the water activity a_W varies significantly (as it does here when the aqueous sulfuric acid concentration is raised to high values) do the assignments of the species hydration numbers play a substantive role in determining the ability of a given model to fit the data; however, for the majority of data modeled, a_W variation was unimportant.

Modeling with Assumption of Ideality. Owing to the large number of hypothetical equilibria and activity effects that may be tested with the program SXLSQA, a staged approach was employed so that the essential features of the best fitting models could be quickly identified and fixed. In the first stage, ideal behavior in both phases was assumed, and only data at a fixed aqueous acidity of 0.3 M H_2SO_4 were modeled.

Since the aqueous ionic strength and composition remain approximately constant under these conditions, aqueous activity coefficients and water activity must also remain constant. For simplicity, aqueous activity coefficients were set equal to unity, and aqueous bisulfate was taken to be undissociated (actually, the degree of dissociation $\alpha = 0.21$ at 0.3 M H_2SO_4 as calculated from the Pitzer parameters given below), giving an assumed aqueous hydrogen ion molarity of 0.3. All organic-phase activity coefficients were also set equal to unity. Owing to the constant, near-unit water activity in the data set, the assignments of w_1, w_2, and w_3 (see above) have no material influence on the goodness of fit. However, the hydration assignments do *influence the values obtained for the equilibrium quotients* Q, *which* incorporate the water activity (calculated for the ideal case) raised to the appropriate power (which may be large as shown in eq. 8).

Within the range $[\mathrm{HDDNS}]_{\mathrm{tot}} = 0.01\text{-}0.1$ (42 data points), the modeling results essentially support the conclusions of the graphical analysis described above and show that a single equilibrium (i.e., eq. 6) accounts for the data nearly to within experimental error. As summarized in Fig. 3, good fits could only be obtained when $a_1 = a_2$ (with $m_2 = 1$) in agreement with the slope analysis. It may be observed that the response surface $\sigma = f(a_1, a_2)$ exhibits a diagonal trough with a shallow minimum at $a_1 = a_2 = 5$ ($Q_{1,5,27} = 0.801 \pm 0.003$, $\sigma = 1.29$); an almost identical fit was obtained with $a_1 = a_2 = 4$ ($Q_{1,4,22} = 0.696 \pm 0.004$, $\sigma = 1.34$). A similar trough was noted in the case of Zn^{2+} ion extraction by HDDNS in CCl_4 (21).

On expanding the data set to include 120 points covering the full range $[\mathrm{HDDNS}]_{\mathrm{tot}} = 0.0001\text{-}0.1$ at 0.3 M H_2SO_4, it was found that including a deaggregation equilibrium (eq. 7) in the model successfully explains the curvature in the plot shown in Fig. 1. Ideality was assumed as before. In view of the results obtained above with 42 data points, no further testing of eq. 6 with $a_1 \neq a_2$ was attempted. Models tested included those combinations of a_1 (where $a_2 = a_1$ and $m_2 = 1$) and a_3 having the values $a_1 = 3$ to 9 and $a_3 = 1$ to $(a_1 - 1)$. The best fit was found at $a_1 = 4$ and $a_3 = 1$ ($Q_{1,4,22} = 0.714 \pm 0.002$, $Q_{0,1,2} = -2.489 \pm 0.006$, $\sigma = 1.06$), where all regions of the data were fit to nearly the estimated

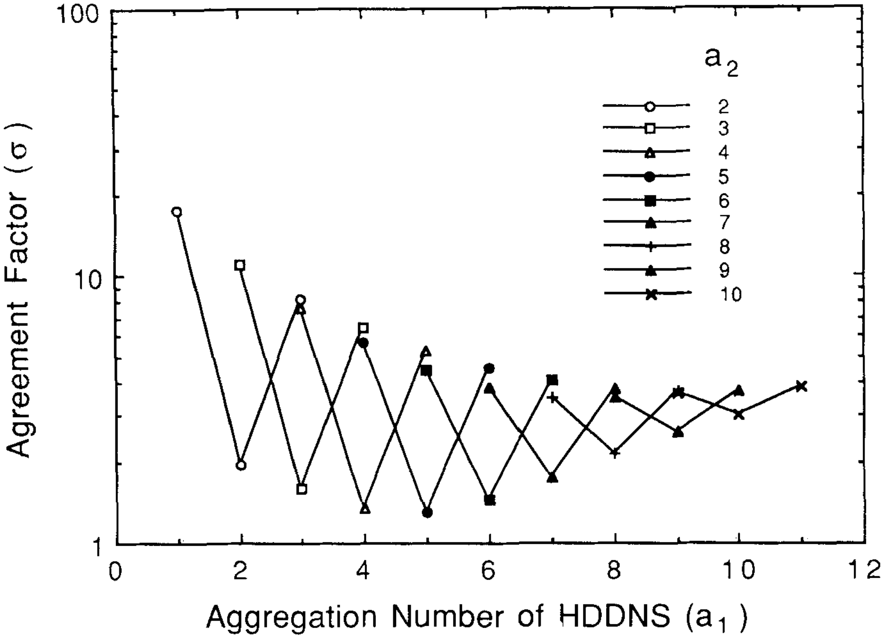


FIGURE 3. Agreement factors for combinations of assumed aggregation numbers a_1 and a_2 in the modeling of 42 data points under the assumption of ideality. The data set covered the ranges $[HDDNS]_{tot}$ = 0.01-0.1 and $[CuSO_4]_{aq,initial} = 1.0 \times 10^{-7}$-$1.0 \times 10^{-2}$ at 0.3 M H_2SO_4; the data are shown in Fig. 1 (points in the range $[HDDNS]_{tot}$ = 0.01-0.1 only) and Fig. 2. Employing eq. 6 as the model equilibrium, the equilibrium quotients were refined to give the lowest agreement factor σ for each combination of a_1 and a_2.

experimental error. An acceptable fit was also found for $a_1 = 5$ and $a_3 = 1$ ($\sigma = 1.29$), but this model exhibited clear systematic error in the region $[HDDNS]_{tot} < 0.01$. Models having the values a_1 = 3-5 with $a_3 = 2$ gave poor agreement with the data.

From the modeling results, the two equilibria given by eqs. 6 and 7 with coefficients $a_1 = a_2 = 4$ and $a_3 = 1$ and with the assumption of ideality have been found to quantitatively account for the complete range of data at 0.3 M H_2SO_4 remarkably well. The set of organic-phase species in the most successful model thus consists of $H_4A_4W_{22}$,

$CuH_2A_4W_{22}$, and the monomer HAW_2; as discussed above, the hydration numbers of the latter two species are rather arbitrary. Corrections made automatically in the program for the small increase in acidity due to cation exchange and for the deaggregation of HDDNS clearly reduce the ambiguity in the conclusions of the graphical analysis.

Consistent with the slope analysis (see above), the computer treatment produced no evidence for species containing multiple metal ions ($m_2 > 1$), since good fits were readily obtained with $m_2 = 1$. This result agrees with the earlier observation (21) that uptake of a second Zn^{2+} cation per aggregate is less favorable than uptake of the first.

We note that the aggregation number $a_1 = 4$ found here for HDDNS in toluene lies considerably below the range 9-20 suggested earlier based on fitting extraction data in a synergistic system in which HDDNS was combined with a crown ether (13). Although there is little reason to suspect the quality of the earlier data, it appears likely that insufficient data were collected to adequately assess the complexity of the system. In particular, the minimum HDDNS molarity used was 6×10^{-4} M, and the systems were limited to low loading. Thus, the deaggregation equilibrium was not obvious, and the fits were insensitive to aggregation number. It may now be possible to perform a reassessment of the synergistic system in light of our current model.

By reference to published results for carbon tetrachloride diluent (21), it may be noted from the present results that the use of toluene diluent reduces the aggregation tendency of HDDNS. For the case of toluene, the best aggregation number a_1 for HDDNS is found here to be 4, whereas CCl_4 gives $a_1 = 6$. In addition, deaggregation occurs at 2×10^3 M in toluene (from the "knee" in the curve of Fig. 1) vs. 4.4×10^{-6} M in CCl_4. Aggregation processes involving amphiphilic molecules in nonpolar media have been explained in terms of a matching of the solubility parameter of the aggregate ($\delta_{aggregate}$) with that of the diluent ($\delta_{diluent}$) (22). As a first approximation, each unit increment in aggregation number is supposed to entail a constant decrement in the value of $\delta_{aggregate}$. For monomeric HDDNS, estimated to have $\delta = 9.7$, a constant decrement of ca. 0.2 in $\delta_{aggregate}$ per unit increment in aggregation number was suggested (21). Thus, to meet the condition

$\delta_{aggregate} = \delta_{diluent}$ in toluene ($\delta_{diluent}$ = 8.9 (43-45)), HDDNS will be expected to have an aggregation number of 4, in agreement with the modeling. For CCl_4 diluent (δ = 8.55 (43-45)), the expected aggregation number is 6. Since the value of 6 was in fact found to be the most likely aggregation number of HDDNS in CCl_4 (21), this treatment of aggregation appears to have qualitative utility for rationalizing aggregation behavior in this system.

Modeling with Assumption of Nonideality. Having largely answered the questions associated with the stoichiometry of the organic-phase species, it remains to explore the effects of nonideality and aqueous acidity and to calculate the thermodynamic equilibrium constants (eq. 8) corresponding to eqs. 6 and 7 with $a_1 = a_2 = 4$ and $a_3 = 1$. Nonideality is treated in SXLSQA (16) using the semiempirical equations of Pitzer (41,42) for aqueous ions and using the regular-solution approach of Hildebrand and Scott (46) for organic-phase species. Although the nonideality treatments greatly increase the complexity of the problem handled by the computer, the task of the user of SXLSQA essentially reduces to supplying reliable values for the various parameters involved. Tables 2-4 summarize the complete models tested together with their corresponding parameters and agreement factors.

Examination of the effect of various assignments of solubility parameters (δ) for organic-phase species revealed that organic-phase nonideality plays essentially no role in shaping the extraction behavior of the system under the conditions used. As discussed above, it is expected that $\delta_{aggregate} = \delta_{diluent}$. This was found to be the case in the extraction of Zn^{2+} ion by HDDNS in CCl_4 (21) and is also the case here. The value of $Q_{1,4,22}$ (i.e., where from eq. 6 $m_2 = 1$, $a_1 = a_2 = 4$, and $w_1 = w_2 = 22$) was refined against 42 distribution coefficients ($[HDDNS]_{tot}$ = 0.01-0.1 and $[H_2SO_4]_{aq}$ = 0.3), fixing the value $\delta_{1,4,22}$ in the range 8.4-9.3 and assuming ideal aqueous behavior. The resulting agreement factors (σ) varied less than ±0.001 units but minimized at $\delta_{1,4,22} = \delta_{toluene}$ = 8.9. Refining both $Q_{1,4,22}$ and $Q_{0,1,2}$ against the expanded 120-point data set ($[HDDNS]_{tot}$ = 0.0001-0.1 and $[H_2SO_4]$ = 0.3) showed a similar insensitivity of fitting to assignment of the monomer solubility parameter $\delta_{0,1,2}$ in the range 8.7-9.8 (using $\delta_{1,4,22}$ = 8.9). Essentially the same result was

TABLE 2. VOLUME PARAMETERS USED IN MODELS I-III[1]

Species	Model	FW	$\phi_{v,i}^o$	$S_{v,i}$	V_{org}
H^+	I-III	1.008	0	0	
Cu^{2+}	I-III	63.546	-27.76	3.73	-28
HSO_4^-	I-III	97.070	37.88	2.18	
SO_4^{2-}	I-III	96.062	13.98	8.64	
$CuSO_4$	I	159.608	-13.78	12.37	

[1] The models are valid for 25 °C. See text for sources of the data. The apparent molar volume $\phi_{v,i}$ of an ion i is given generally by the formula $\phi_{v,i}^o + S_{v,i}\ \{2I/[z_i(1 + z_i)]\}^{1/2}$, where $\phi_{v,i}^o$ is the apparent molar volume at infinite dilution, $S_{v,i}$ is the proportionality constant, and z_i is the ionic charge. This expression follows from the Masson equation (49,50) assuming the additivity of ionic volumes. Listed values of $\phi_{v,i}^o$ and $S_{v,i}$ were estimated by applying the arbitrary convention $\phi_{v,i}^o$ = 0 and $S_{v,i}$ = 0 for the H^+ ion (49,50); values for HSO_4^- ion were obtained by a refinement procedure (see text); neutral $CuSO_4$ was assumed to behave as if it were dissociated. The H^+, HSO_4^-, and SO_4^{2-} parameters are valid up to 6.0 M H_2SO_4 (see text); the estimated Cu^{2+} and $CuSO_4$ parameters have little effect at the low $CuSO_4$ concentrations employed here and may not be optimum at higher $CuSO_4$ concentrations. FW is the formula weight. V_{org} is the partial molar volume of a species in the organic phase.

obtained when the aggregate was assumed to be either a trimer ($m_2 = 1$, $a_1 = a_2 = 3$, and $w_1 = w_2 = 16$) or a pentamer ($m_2 = 1$, $a_1 = a_2 = 5$, and $w_1 = w_2 = 27$). Thus, in all further refinements $\delta_{0,1,2}$ was fixed at the value of 9.7 suggested earlier (21), and $\delta_{1,4,22}$ was fixed at the δ value of toluene (8.9).

In all models in which the activity coefficients of aqueous-phase species were calculated, the association of H^+ and SO_4^{2-} ions to give HSO_4^- as an identifiable aqueous-phase species was explicitly assumed. The HSO_4^- formation constant together with the ion-interaction parameters for the H_2SO_4-H_2O system were taken from the literature (47); the small effects of mixing monovalent and divalent cations and of mixing monovalent and divalent anions (41,42) were neglected. The stoichiometric mean molal activity coefficients for sulfuric acid

TABLE 3. AQUEOUS-SPECIES PARAMETERS USED IN MODELS I-III[1]

Pitzer Parameters:[2]

Interaction	Model	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	α_1	α_2
Cu^{2+}-SO_4^{2-}	I	0.05	2.01	64.0	0.095	1.4	12.0
	II,III	0.2340	2.527	-48.33	0.0044	1.4	12.0
Cu^{2+}-HSO_4^-	I	0.4857	2.002		0.0099	2.0	
	II	0.6345	3.140			2.0	
		± 0.0609	± 0.677				
	III	0.4799	2.282			2.0	
		± 0.0623	± 0.243				
H^+-SO_4^{2-}	I-III	0.0027			0.0416	2.0	
H^+-HSO_4^-	I-III	0.2103	0.4711			2.0	

Aqueous Equilibrium Constants:[3]

Reaction	Model	$\log_{10}K$
$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$	I-III	1.98
$SO_4^{2-} + Cu^{2+} \rightleftharpoons CuSO_4$	I	2.40

[1] The models are valid for 25 °C. See text for sources of the data.

[2] Values having an indicated uncertainty were refined using published activity-coefficient data (Model II) or experimental values of D_{Cu} (Model III) as described in the text. All other values were obtained from published sources and used unchanged.

[3] The constants are expressed here in molarity units.

calculated by SXLSQA from the reported Pitzer parameters and HSO_4^- formation constant agreed with the published calculated values (within ±0.0002 units). The parameters are valid to a maximum molality of 6.0 (4.8 M at 25 °C) (47).

The program SXLSQA makes use of aqueous and organic molar-volume parameters to make internal conversions between concentration scales (molarity and molality), to calculate organic-phase

TABLE 4. ORGANIC-SPECIES PARAMETERS USED IN MODELS I-III[1]

Organic-Species Parameters:[2]

Species	Type	Model	δ	$\log_{10}K$
$H_4A_4W_{22}$	Reactant	I	8.9	
		II	8.9	
		III	8.9	
$CuH_2A_4W_{22}$	Product	I	8.9	1.279 ± 0.002
		II	8.9	1.114 ± 0.003
		III	8.9	1.221 ± 0.011
HAW_2	Product	I	9.7	-2.503 ± 0.006
		II	9.7	-2.497 ± 0.009
		III	9.7	-2.499 ± 0.005

Refinement Conditions:[3]

Model	Parameters Refined	Max. $[H_2SO_4]_{aq}$	Max. $[CuSO_4]_{aq}$	σ
I	$K_{1,4,22}, K_{0,1,2}$	1.0	1.3×10^{-2}	1.17
II	$K_{1,4,22}, K_{0,1,2}$	1.0	1.3×10^{-2}	1.65
III	$K_{1,4,22}, K_{0,1,2}, \beta^{(0)}, \beta^{(1)}$	1.0	1.3×10^{-2}	1.01

[1] The models are valid at 25 °C and have been tested for the following maximum concentration conditions: aqueous phase, 1.0 M H_2SO_4 and 1.3×10^{-2} M $CuSO_4$; organic phase (toluene diluent), 0.1 M HDDNS and $[Cu]_{org}/[HDDNS]_{tot} < 0.08$ (loading). Apparent molar volumes V_{org} of organic-phase components were assigned the values: toluene (FW = 92.144), 106.9; HDDNS (FW = 544), 535.0; and H_2O, (FW = 18.015), 18.0. Values of V_{org} were estimated from density data (44,48) or from group parameters (45). δ is the Hildebrand solubility parameter ($cal^{1/2}$ $cm^{-3/2}$); the value of δ used for toluene was 8.898 (43-46).

[2] The formation equilibria are given by eqs. 6 and 7. Refined equilibrium constants are defined by eq. 8 and were obtained by using all of the parameters listed in Tables 2 and 3 and this table to calculate species molarities, species activity coefficients, and water activity. The hydration of the third species, HAW_2, has been arbitrarily assigned the value of 2.

[3] The agreement factor σ is defined by eq. 1. In SXLSQA, equilibrium constants are refined in their logarithmic form.

activity coefficients, and to estimate volume changes due to mass transfer (16). The values used are shown in Tables 2-4. Molar volumes V_{org} of organic-phase components (toluene and extracted water) were calculated from the densities of the pure phases at 25 °C (44,48). For HDDNS, group parameters were used to estimate V_{org} (45). The molar volume V_{org} of extracted Cu^{2+} was equated with the limiting apparent aqueous molar volume at infinite dilution ($\phi_{v,i}{}^{o}$); although it is required by SXLSQA, this parameter has little importance here in view of the low organic-phase loadings studied.

Single-ion Masson coefficients $\phi_{v,i}{}^{o}$ and $S_{v,i}$ for the calculation of apparent molar volumes of individual aqueous ions were estimated either from published Masson coefficients for electrolytes (49,50) or from density data (51). The estimation procedures used both the convention of zero coefficients for H^+ ion and the assumption of additivity of ionic volumes at constant ionic strength (49,50). Coefficients $\phi_{v,i}{}^{o}$ and $S_{v,i}$ for $SO_4{}^{2-}$ ion were estimated from the Masson coefficient for Na_2SO_4 and from the single-ion values given for Na^+ (49,50). In the case of $HSO_4{}^-$ ion, $\phi_{v,i}{}^{o}$ and $S_{v,i}$ were determined here from published density data for H_2SO_4-H_2O solutions at 25 °C (51). The method employed was essentially that of previous workers (52) except that the published Pitzer parameters and $HSO_4{}^-$ dissociation constant (47) were used here for the calculation of the molarities of the ions H^+, $SO_4{}^2$, and $HSO_4{}^-$ together with the total volume ionic strength for any given formal H_2SO_4 concentration. The refined values of $\phi_{v,i}{}^{o}$ and $S_{v,i}$ for $HSO_4{}^-$ ion were taken as those which produced apparent molal volumes of sulfuric acid in best agreement (least-squares criterion) with apparent molal volumes derived from the reported densities up to 6 M H_2SO_4; calculated densities agreed with the literature values (51) to within ±0.002 g/cm^3 up to 4.6 M and within ±0.005 g/cm^3 in the range 4.6-6.0 M. Coefficients $\phi_{v,i}{}^{o}$ and $S_{v,i}$ for Cu^{2+} ion were estimated from available Masson coefficients (49). Formation of neutral $CuSO_4$ species from the association of Cu^{2+} and $SO_4{}^{2-}$ ions (Model I only) was arbitrarily assumed to involve no volume change. Since the formal aqueous $CuSO_4$ concentrations were always low in this study, the coefficients $\phi_{v,i}^{o}$ and $S_{v,i}$ assigned to Cu^{2+} ion and neutral $CuSO_4$ have little importance here and may not apply to systems having higher levels of copper.

Pitzer parameters for interactions of Cu^{2+} ion in the $CuSO_4$-H_2SO_4-H_2O system were found to be decisive in determining the success of modeling the dependence of Cu(II) distribution coefficients D_{Cu} on sulfuric acid molarity. The only reported parameters directly applicable to the aqueous $CuSO_4$-H_2SO_4-H_2O system were obtained by including the weak formation of neutral aqueous $CuSO_4$ species and by equating the unknown Cu^{2+}-HSO_4^- interaction parameters with Cu^{2+}-ClO_4^- interaction parameters (12). As summarized in Tables 2-4, we tested the reported parameters unchanged in a fit of our extraction data (Model I), refining only the formation constants $K_{1,4,22}$ and $K_{0,1,2}$ associated with organic-phase species. In the fit, 128 data points were used, including the 120 data points at 0.3 M H_2SO_4 and 8 additional points in the range 0.03-1.0 M H_2SO_4; data collected at higher H_2SO_4 molarities were excluded from the fit to avoid complication from possible mineral-acid extraction at high acid concentrations (24) and to avoid exceeding the valid range of the published aqueous parameters (12). As shown in Fig. 4, Model I gives a good representation (σ = 1.17) of the dependence of D_{Cu} on sulfuric acid molarity in the range of the fit (0.03-1.0 M H_2SO_4), though the model underestimates D_{Cu} when extrapolated to higher H_2SO_4 acid molarities.

Alternately, it was found that the variation of D_{Cu} with H_2SO_4 molarity could be modeled without explicitly including the formation of neutral aqueous $CuSO_4$ species. The advantages of neglecting the association equilibrium in treating aqueous ionic activity coefficients in sulfate solutions of divalent metals have been discussed (12,53-55); chief among these advantages is the reduction in the number of parameters. Single-electrolyte interaction parameters for the $CuSO_4$-H_2O system have been published according to this treatment (55) and were used here without modification along with the published (47) single-electrolyte parameters for the H_2SO_4-H_2O system (Table 3). The additionally needed Cu^{2+}-HSO_4^- interaction parameters ($\beta^{(0)}$, $\beta^{(1)}$, and

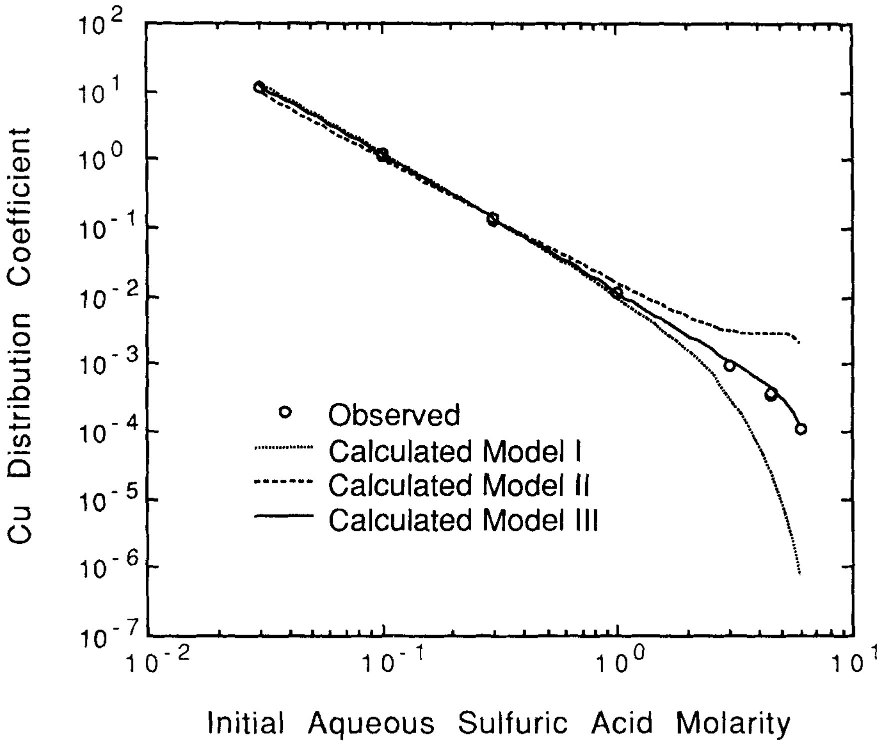


FIGURE 4. Comparison of Models I-III in describing the dependence of D_{Cu} on the initial aqueous H_2SO_4 molarity. The data set fit by the models included the full 128 data points in the ranges $[HDDNS]_{tot}$ = 0.0001-0.1, $[CuSO_4]_{aq,initial}$ = 1.2 x 10^{-8}-1.3 x 10^{-2}, and $[H_2SO_4]_{aq,initial}$ = 0.03-1.0. Models were extrapolated to $[H_2SO_4]_{aq,initial}$ = 6.0. Data are shown here for aqueous H_2SO_4 molarities up to 6.0 M, $[HDDNS]_{tot}$ = 0.01, and negligible loading ($[Cu]_{org}/[HDDNS]_{tot}$ < 0.003). Parameters used in the fit are summarized in Tables 2-4.

C^{ϕ}) and the mixing parameters (θ and Ψ) associated with mixing $CuSO_4$ and H_2SO_4 in the ternary $CuSO_4$-H_2SO_4-H_2O system are currently unavailable. In treatments of the $FeSO_4$-H_2SO_4-H_2O (56) and the $NiSO_4$-H_2SO_4-H_2O (57) systems, it was shown that $\beta^{(0)}$ and $\beta^{(1)}$ parameters for the M^{2+}-HSO_4^- interaction together with a minor mixing parameter were sufficient to model a range of data types. Following this precedent, we refined $\beta^{(0)}$ and $\beta^{(1)}$ parameters for the Cu^{2+}-HSO_4^- interaction using published (58) stoichiometric mean activity coefficients of H_2SO_4 in the $CuSO_4$-H_2SO_4-H_2O system. These data could be fit to within ±5% over the reported concentration ranges (to maximum concentrations of 1.2 M $CuSO_4$ and 1.8 M H_2SO_4); however, agreement was worse (±10%) at low concentrations of $CuSO_4$ and could not be improved by including mixing parameters. The values of $\beta^{(0)}$ and $\beta^{(1)}$ so obtained were then used in Model II in which the extraction data (128 data points) were fit by refinement of $K_{1,4,22}$ and $K_{0,1,2}$ only. As shown in Fig. 4, Model II is inferior to Model I (σ = 1.65), exhibiting clear systematic error in the range of the fit (0.03-1.0 M H_2SO_4) and overestimating D_{Cu} when extrapolated to 6 M H_2SO_4. Since the values of $\beta^{(0)}$ and $\beta^{(1)}$ employed in Model II lead to poorly estimated activity coefficients at low Cu(II) concentrations, the validity of Model II appears dubious. An in-depth analysis of the $CuSO_4$-H_2SO_4-H_2O system is in progress (59).

Excellent results, however, were obtained by simultaneous refinement of $\beta^{(0)}$, $\beta^{(1)}$, $K_{1,4,22}$, and $K_{0,1,2}$ (Model III) in fitting the extraction data over the range of acidities 0.03-1.0 M H_2SO_4. As shown in Fig. 4, the fit in this concentration range is essentially perfect (σ = 1.01). Further, the model provides a reasonable representation of the variation of D_{Cu} with acidity up to 6 M H_2SO_4, even explaining the rapid drop of D_{Cu} between 4 and 6 M H_2SO_4. Although the good extrapolation of Model III to acidities higher than 1 M H_2SO_4 may be fortuitous, the results suggest that possible effects such as extraction of H_2SO_4 may actually be minor.

Model III was selected as the most useful of the three tested models for representation of the extraction of Cu^{2+} ion from 0.03-6.0 M H_2SO_4 by HDDNS in toluene. Figures 5 and 6 show the good agreement obtained by Model III in describing the dependence of D_{Cu} on initial HDDNS and initial $CuSO_4$ molarities, respectively. It should be noted that any of the three models give approximately the same goodness of fit for the majority of the data at 0.3 M H_2SO_4 (120 points). Table 4 gives the logarithms of the equilibrium constants for the two principle extraction equilibria (eqs. 6 and 7). The value of $\log K_{0,1,2}$ varies negligibly among the three models, whereas $\log K_{1,4,22}$ depends slightly on the model. If Model II is discounted owing to its high agreement factor, the best

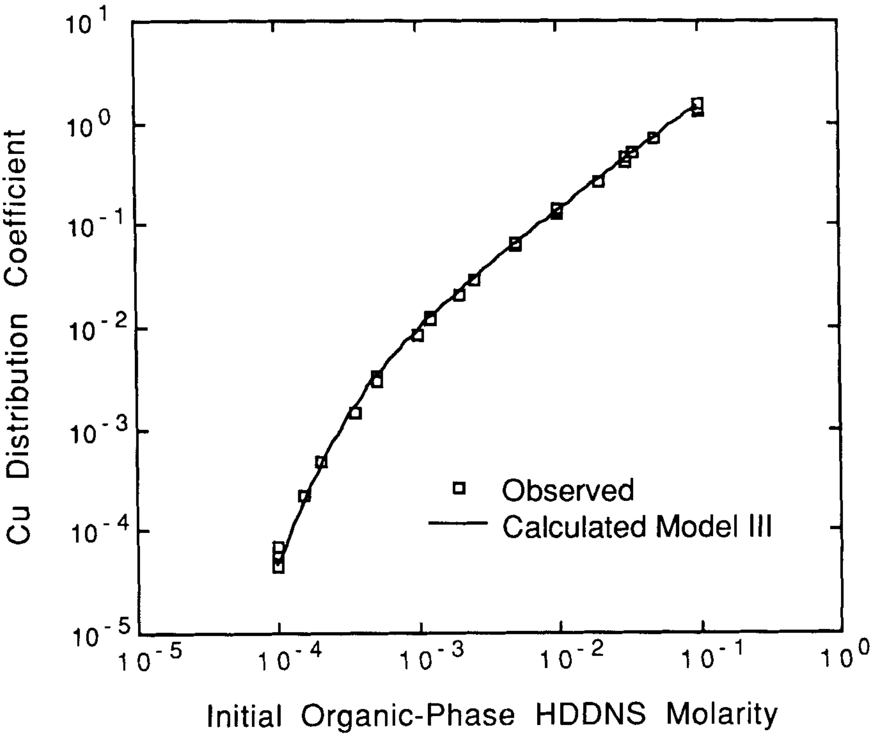


FIGURE 5. Fit of Model III to D_{Cu} as a function of the initial organic-phase HDDNS molarity. The data shown here are the same as those shown in Fig. 1.

fitting models I and III in fact produce reasonably close estimates for $\log K_{1,4,22}$. It may be observed that the refined values of $\beta^{(0)}$ and $\beta^{(1)}$ describing the Cu^{2+}-HSO_4^- interaction in Model III are approximately the same as the values used in Model I based on $Cu(ClO_4)_2$.

The presented analysis clearly suggests the existence of the organic-phase species $H_4A_4W_{22}$, $CuH_2A_4W_{22}$, and the monomer HAW_2 (notwithstanding the ambiguity in the hydration numbers of the latter two species). Confidence in this model stems from the rigorous application of the law of mass action, the elimination of assumptions and shortcuts, the relative simplicity of the proposed organic-phase

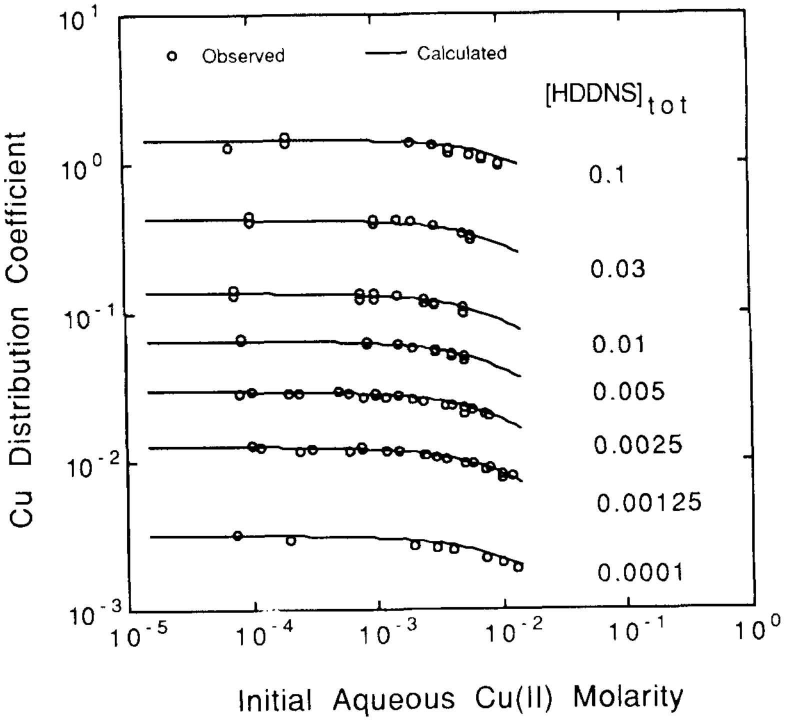


FIGURE 6. Fit of Model III to D_{Cu} as a function of the initial aqueous $CuSO_4$ molarity. The data shown here include the points used in Fig. 2 together with points at lower $[HDDNS]_{tot}$.

speciation, the goodness of fit, and the large data set employed. It is necessary to stress that the model, however compelling, is only a precise *interpretation* of the data and does not necessarily represent the true nature of the system. Thus, conclusions based on modeling results such as these should be treated as hypotheses to be tested by use of other experimental techniques.

CONCLUSIONS

The extraction of Cu^{2+} ion from aqueous solutions of H_2SO_4 (0.03-1.0 M) and $CuSO_4$ (1.2×10^{-8}-1.3×10^{-2} M) by HDDNS (1.0×10^{-4}-1.0×10^{-1} M) in toluene has been successfully modeled based on a cation exchange process. The model postulates the organic-phase species $H_4A_4W_{22}$, $CuH_2A_4W_{22}$, and HAW_2 and takes into account nonideality effects in both phases. According to the model, HDDNS exists predominantly in the form of the tetramer $H_4A_4W_{22}$ in the range 0.01-0.1 M HDDNS, and Cu^{2+} ions are extracted to give $CuH_2A_4W_{22}$ ($\log K_{1,4,22} = 1.22 \pm 0.01$). Dissociation of the aggregate $H_4A_4W_{22}$ gives the monomer HAW_2 with arbitrarily assigned hydration number ($\log K_{0,1,2} = -2.499 \pm 0.005$). Organic-phase nonideality effects could not be detected and thus appear to play a minor role in the equilibrium chemistry. Aqueous-phase nonideality was estimated according to two approaches differing in whether the association equilibrium to give aqueous neutral $CuSO_4$ species was included explicitly. While both approaches provide reasonable fits to the data, neglect of the association offers the advantage of simplicity.

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