

Extraction of Nickel(II), Copper(II), and Zinc(II) in Carbon Tetrachloride with Monothiodibenzoylmethane and Derivatives

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The overall stability constants of nickel(II), copper(II), and zinc(II) chelates with SDBM (monothiodibenzoylmethane) and SDBM derivatives such as F-SDBM (*p*-fluorobenzoyl)-(thiobenzoyl)methane) and C₂H₅-SDBM (*p*-ethylthiobenzoyl)benzoylmethane) in aqueous solution have been determined by means of the extraction and the back-extraction methods. In all cases, the extraction equilibrium of zinc was achieved within 30 min, while that of copper required about 2 h. The extraction equilibrium of nickel was irreversible within 2 h. The distinct influence of substituents on the chelate stability was not observed. The rate constants of the back-extraction of Cu(SDBM)₂ chelate in carbon tetrachloride with an uncomplexed SDBM were -4.77 M min⁻¹. The rate constant of the back-extraction increased about 10 times by addition of chloride ion. The back-extraction of Cu(SDBM)₂ may proceed through the following steps, that is, hydrogen ion assisted in the dissociation of Cu(SDBM)₂ followed by reaction of chloride ion.

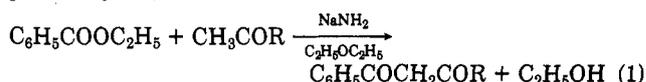
It is well-known that solvent extraction and potentiometric titration have been used for studying complex formations of metal chelates in an aqueous solution. The values of the stability constant of monothio β -diketone chelates for transition metal ions are generally greater than those of the parent β -diketone chelates under the same conditions (1-7). It has been suggested that this arises from π bonding between d orbitals of transition-metal ions and vacant d orbitals on the sulfur atom (2). However, the values of the stability constant of metal chelates with monothio β -diketone like SDBM (monothiodibenzoylmethane) obtained by the solvent extraction method are reported as the order of Zn(II) > Ni(II) (8), while those obtained by the potentiometric method (1-4) obey the Irving-Williams order (9) like Cu(II) > Ni(II) > Zn(II) (1-4). In the present paper, the abnormal phenomenon described above has been investigated by analyzing the behavior of nickel(II), copper(II), and zinc(II) with SDBM in the extraction and the back-extraction. New monothio β -diketones, F-SDBM (*p*-fluorobenzoyl)(thiobenzoyl)methane) and C₂H₅-SDBM (*p*-ethylthiobenzoyl)benzoylmethane), have also been synthesized and used in order to clarify the role of the terminal groups of SDBM on their chelate stability. In our earlier work, it has been demonstrated (10-12) that solvent extraction techniques provide a simple and convenient way to examine fast reaction kinetics involving metal chelate and other metal complex formations (13). Many extraction kinetics of metal chelates have been reported (10-12, 14-16), but no back-extraction techniques have been applied to the clarification of their back-extraction equilibrium. Therefore the application of the solvent extraction technique to the study of the back-extraction kinetics of metal chelate formations in the Cu(II)-SDBM-CCl₄ system has also been examined.

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EXPERIMENTAL SECTION

Apparatus. A Cary-14 recording spectrophotometer, Gilford 2400 spectrophotometer, Perkin-Elmer 521 infrared cord spectrophotometer, Varian NMR spectrophotometer, mass spectrometer (University Analytical Center), Beckman 1019 pH meter, Eberbach boxtype shaker, Wilkens-Anderson Co. Lo-Tem Bath, Precision clinical centricon, and NaI(Tl) well type scintillation counter (Kobe Kogyo) were used.

Synthesis of β -Diketones. New β -diketones of F-DBM and C₂H₅-DBM were synthesized by the acylation of methyl ketones with aromatic esters by means of sodium amide as reported previously (17)



where, R = C₆H₄F (F-DBM), C₆H₄C₂H₅ (C₂H₅-DBM).

Three hundred milliliters of absolute ether were placed in a 500-mL three-necked round-bottomed flask equipped with ground glass joints, a magnetic stirrer, a removable glass plug, and an air condenser. A solution of 0.3 mol of ketone in 50-mL of absolute ether was added during 5-10 min to the stirred suspension of 0.6 mol of sodium amide. After 5 min the sodium derivative of the ketone was assumed to be formed. The calculated amount of ester (0.6 mol) in 50-mL of absolute ether was then added, and the mixture was stirred on a steam bath for 2 h on refluxing. The mixture containing a gelatinous precipitation formed was filtered. The sodium salt of the β -diketone thus separated was poured into 300 mL of water, neutralized with diluted hydrochloric acid, and extracted with ether. The ether solution was distilled off, and the residue was dissolved in acetone. A hot filtered solution of copper acetate saturated in 300-mL of water was added to the acetone solution, and the mixture was allowed to stand until it had cooled to room temperature. After being filtered and washed with hot water, the green copper salt of the β -diketone was dried by suction in air. The bulk of the recrystallized salt was shaken with 200 mL of 10% sulfuric acid and 200 mL of ether until the ether phase was light yellow. The salt was dried over anhydrous sodium sulfate. The solvent was evaporated off in air. F-DBM was recrystallized from ether. F-DBM is a yellow needle crystal, mp 66-67 °C. C₂H₅-DBM gives yellowish brown oil, thermal decomposition at 97-100 °C under 0.5 torr.

Synthesis of Monothio β -Diketones. New monothio β -diketones of F-SDBM and C₂H₅-SDBM were synthesized by the reaction of hydrogen sulfide with β -diketones in absolute ethanol in the presence of hydrogen chloride as reported previously (18)



where, R' = C₆H₄F (F-SDBM), R'' = C₆H₄C₂H₅ (C₂H₅-SDBM).

A solution of β -diketone (0.5-2.0 g) in absolute alcohol (200 mL) was cooled to 0-5 °C with ice. Dry hydrogen chloride was passed into the solution for 30 min, followed by dry hydrogen sulfide for 1-2 h. During the passage of the hydrogen sulfide, the solution became deep red. The solution was allowed to stand overnight and then was poured into ice water (300 mL). After 30 min, the mixture was extracted with ether. The ether after extraction was dried over anhydrous sodium sulfate and evaporated off in air. The F-SDBM (monothio F-DBM) was purified by using the back-extraction method. The ether solution of F-SDBM was shaken with 0.1 M NaOH solution. After 1.0 M HCl was added to the aqueous solution, F-SDBM was again

extracted with pure ether and dried over anhydrous sodium sulfate. The excess solvent was evaporated off in air, yielding the pure compound of a needle red crystal. F-SDBM is a red needle crystal, mp 76–78 °C. C₂H₅-SDBM is red oil, thermal decomposition at 40 °C under 0.5 torr.

Other Reagents. Metal perchlorates in deionized water (1.0 M) were used as the stock solution. Deionized water was used throughout this investigation. All other reagents were reagent grade materials. The radioisotope, ⁶⁵Zn, was purchased from the New England Nuclear Corp.

Distribution Coefficient of Ligands. The distribution coefficients of undissociated SDBM, F-SDBM, and C₂H₅-SDBM between carbon tetrachloride and water were obtained as follows: 5 mL of 10⁻² M carbon tetrachloride solution of ligand was shaken vigorously with 10 mL of an aqueous solution of pH 1.5–8 containing 0.1 M NaClO₄. The vessel is composed of 50-mL vials fitted with polyethylene lines and plastic caps. After being shaken for 0.5–1 h at 25 °C, 5 mL of the aqueous solution was shaken again with 5 mL of pure carbon tetrachloride. The centrifugation procedure after each of extraction steps was carried out in order to separate the phases clearly. The concentration of neutral ligand in carbon tetrachloride was determined spectrophotometrically. Molar absorption coefficients of the ligands in carbon tetrachloride were 15 831 at 4125 Å for SDBM, 16 316 at 4125 Å for F-SDBM, and 12 675 at 4150 Å for C₂H₅-SDBM.

Acid Dissociation Constant of Ligands. In order to obtain the acid dissociation constant of ligands, the pH at which half of the ligands were extracted, pH_{1/2}, between 10⁻³ M SDBM, F-SDBM, and C₂H₅-SDBM in carbon tetrachloride and various buffer solutions containing 0.1 M NaClO₄ at 25 °C was determined. The aqueous solution was made up to 10⁻² M sodium acetate in the acidic region or 10⁻² M sodium borate in the basic region, and its pH was adjusted to a desired value with 1 M NaOH or 1 M HCl. After 10 mL of the two phases had been shaken for 0.5–1 h at 25 °C, the concentration of ligands in carbon tetrachloride was determined spectrophotometrically. The pH was checked again by a Beckman glass electrode with Beckman Buffer solution of pH 4, 7, and 10.

Distribution Coefficient of Chelates. The extractions were performed between 30 mL of an aqueous solution containing 0.1 M individual metal ions and 2 mL of 10⁻² M SDBM, F-SDBM, and C₂H₅-SDBM in carbon tetrachloride for 1 h at 25 °C. In order to get the distribution coefficient of chelates, the pH at which metals can be extracted quantitatively was adopted. The extraction pH was pH 8 for Ni, pH 3 for Cu, and pH 6–10 for Zn, respectively. After centrifugation, 1 mL of organic phase was taken into another extraction container and diluted 10 times with pure carbon tetrachloride. It was then shaken with 5 mL of 1 M NaOH for 1 h in order to remove free ligand. Moreover, 25 mL of aqueous solution after extraction was placed in an extraction vial and shaken with 5-mL of pure carbon tetrachloride. The organic phase was shaken with 5 mL of 1 M NaOH. The concentration of neutral chelates in carbon tetrachloride was then determined spectrophotometrically. In the case of the zinc chelate system, 1 mL of pyridine was added to the organic phase before washing with 1 M NaOH to prevent the decomposition of zinc chelate remaining in carbon tetrachloride as zinc pyridine adduct. Molar absorption coefficients of the chelates in carbon tetrachloride used in this investigation were 8875 at 4350 Å for Ni(SDBM)₂, 20 725 at 4125 Å for Cu(SDBM)₂, 36 425 at 4100 Å for Zn(SDBM)₂Py_n (n = 1–2), 9643 at 4350 Å for Ni(F-SDBM)₂, 20 119 at 4125 Å for Cu(F-SDBM)₂, 35 923 at 4100 Å for Zn(F-SDBM)₂Py_n (n = 1–2), 8991 at 4350 Å for Ni(C₂H₅-SDBM)₂, 16 979 at 4125 Å for Cu(C₂H₅-SDBM)₂ and 29 090 at 4100 Å for Zn(C₂H₅-SDBM)₂Py_n (n = 1–2), respectively. If the excess ligand is removed, some decomposition of chelates may occur and therefore a deceptively low value of the distribution coefficient will be obtained. This has also been ascertained by spectrophotometry as follows: When the solution of chelates in carbon tetrachloride was shaken with 1.0 M NaOH solution, decomposition of copper(II) and nickel(II) chelates with SDBM, F-SDBM, and C₂H₅-SDBM was not entirely observed because the absorption spectra of chelates in carbon tetrachloride before and after shaking the organic solution with 1.0 M NaOH solution gave almost the same curves. When zinc(II) chelates in carbon tetrachloride with or without pyridine were shaken with 1.0 M NaOH solution, the decomposition of their complexes was

observed. Percentage of the decomposition of their complexes was 91% for Zn(SDBM)₂, 96% for Zn(F-SDBM)₂ and Zn(C₂H₅-SDBM)₂, and 30–50% for their pyridine adducts. However, there was no problem for the determination of the distribution coefficient of zinc chelates as their pyridine adducts by spectrophotometry. In conclusion, it was possible to determine the distribution coefficient of copper(II), nickel(II), and zinc(II) chelates with SDBM, F-SDBM, and C₂H₅-SDBM even if carbon tetrachloride solution containing chelates with or without unreacted ligand was shaken with 1.0 M NaOH solution. We also tried to determine the distribution coefficient of chelates with excess ligand by atomic absorption method and tracer method with ⁶⁵Zn. The procedures were as follows: The extractions were carried out between 10 mL of an aqueous solution containing 10⁻⁴ M individual metal ions and 10 mL of 10⁻³ M SDBM in carbon tetrachloride for 1 h at 25 °C. The extraction pH was 8 for Ni, 3 for Cu, and 6–10 for Zn, respectively. After centrifugation, 3 mL of the organic phase was transferred into another extraction container and shaken with 3 mL of 4 M hydrochloric acid solution for 1 h to strip metals from the organic phase. Moreover, 5 mL of an aqueous solution was taken into another extraction container after extraction and shaken with 5 mL of pure carbon tetrachloride. Three milliliters of the organic phase was shaken with 3 mL of 4 M hydrochloric acid after back-extraction for 1 h to strip metals from the organic phase. Then, the concentration of metals in 4 M hydrochloric acid solution was determined by means of a Perkin-Elmer 303 atomic absorption spectrophotometer. In the case of zinc chelate systems, ⁶⁵Zn tracer was also used for the determination of the distribution coefficient of zinc chelates after equilibrium. We also tried to determine the distribution coefficients of metal chelates when 5 × 10⁻³ M metal ions was extracted with 10⁻³ M ligand in carbon tetrachloride under the same conditions described above.

Extraction and Back-Extraction of Nickel(II), Copper(II), and Zinc(II)-SDBM, F-SDBM, and C₂H₅-SDBM-Carbon Tetrachloride System. The extractions were carried out between 10 mL of an aqueous solution containing 10⁻⁴ M individual metal ions and the same volume of an organic solution containing 10⁻³ M SDBM, F-SDBM, and C₂H₅-SDBM in carbon tetrachloride under the conditions of various pH. The 0.1 M NaClO₄ solution was used as the ionic medium. The two phases had been shaken for 30 min in the extraction and the back-extraction of 10⁻⁴ M Ni(II), Cu(II), and Zn(II)-10⁻³ M SDBM, F-SDBM, and C₂H₅-SDBM-carbon tetrachloride in order to check the extraction equilibrium at 25 °C. When the rates of their extraction and back-extraction were investigated, both phases were shaken for from 5 min to 2.5 h at 25 °C. The distribution of the metal was determined spectrophotometrically by the same method used in the determination of the distribution coefficient of chelates. The pH of an aqueous phase was checked again after the extraction. The back-extraction of the metals from the organic phase was performed with an aqueous buffer solution having a pH appropriate to the desired condition. The distribution of the metals was determined as in the case of extraction. The extraction behavior of zinc was also studied by using ⁶⁵Zn tracer.

Back-Extraction Kinetics of Copper(II) SDBM Chelate in Carbon Tetrachloride. The Cu(SDBM)₂ in carbon tetrachloride was prepared by extracting 10⁻⁴ M Cu²⁺ ion at pH 3 with 10⁻³ M SDBM in carbon tetrachloride. This organic solution was contacted vigorously with various aqueous solutions at 25 °C as previously described (10). The ionic strength of the aqueous phase was kept at 0.1 M NaClO₄.

THEORETICAL SECTION

When a metal ion, M²⁺, reacts with SDBM, F-SDBM, and C₂H₅-SDBM (abbreviated as HR) in carbon tetrachloride and is extracted as the neutral chelate, the overall extraction processes can be written as in Figure 1. The equilibrium relations can be expressed by the following equations:

$$K_{DR} = \frac{[\text{HR}]_o}{[\text{HR}]} \quad (3)$$

$$K_a = \frac{[\text{H}^+][\text{R}^-]}{[\text{HR}]} \quad (4)$$

$$K_{Dc} = \frac{[MR_2]_o}{[MR_2]} \quad (5)$$

$$\beta_2 = \frac{[MR_2]}{[M^{2+}][R^-]^2} \quad (6)$$

$$\alpha_M = \frac{[M^{2+}]}{C_M} \quad (7)$$

$$D_M = \frac{[MR_2]_o}{C_M} = \frac{[MR_2]}{[M^{2+}]} \alpha_M = \frac{\beta_2 K_a^2 K_{Dc} [HR]_o^2}{K_{Dr}^2 [H^+]} \alpha_M \quad (8)$$

where β_2 means the stability constant of the chelate, K_{Dr} the distribution coefficient of the reagent, K_a the enol dissociation constant of the reagent, K_{Dc} the distribution coefficient of the chelate, α_M conditional constant of the metal, C_M total concentration of the metal, and D_M the distribution ratio of the metal, $[\]$ and $[\]_o$ designate the concentration of the chemical species in the aqueous and the organic phases, respectively.

When $D_M = 1$, $\alpha_M = 1$, and $\text{pH} = \text{pH}_{1/2}$ in the half extraction, the overall stability constant of chelate in an aqueous phase can be calculated by using next the equation.

$$\log \beta_2 = -2 \log K_a + 2 \log K_{Dr} - \log K_{Dc} - 2\text{pH}_{1/2} - 2 \log [HR]_o \quad (9)$$

RESULTS AND DISCUSSION

Synthesis and Properties of β -Diketones and Their Monothio Derivatives. The yields of new β -diketones and their monothio derivative after purification were 41% for F-DBM, 66% for C_2H_5 -DBM, 69% for F-SDBM, and 37% for C_2H_5 -SDBM, respectively. The properties of the β -diketones were as follows: The characteristic bands of F-DBM are 2625, 3400 ($\pi-\pi^*$, λ_{\max} , Å) for UV and visible spectra, 1592 ($\nu(\text{C}=\text{O})$, cm^{-1}) for IR spectra, 6.68 (chelate ring-H, δ , ppm), and 16.85 (enol-H, δ , ppm) for NMR signals, and those of C_2H_5 -DBM are 2600, 3450 ($\pi-\pi^*$, λ_{\max} , Å), 1671 ($\nu(\text{C}=\text{O})$, cm^{-1}), 6.77 (chelate ring-H, δ , ppm), and 16.82 (enol-H, δ , ppm), respectively. The molar absorption coefficients at λ_{\max} of each of the UV and visible peaks of β -diketones in carbon tetrachloride were 8000 at 2625 Å and 22 400 at 3400 Å for F-DBM and 4800 at 2600 Å and 17 000 at 3450 Å for C_2H_5 -DBM, respectively. The properties of monothio β -diketones were as follows: The characteristic bands of UV and visible spectra (λ_{\max} , Å) of the products were 2650, 3275, 4125 ($\pi-\pi^*$) for F-SDBM and 2675, 3375, 4150 ($\pi-\pi^*$) for C_2H_5 -SDBM, respectively. Infrared spectra (cm^{-1}) of the products were 815 (F-SDBM), 816 (C_2H_5 -SDBM) for $\nu(\text{C}=\text{S}) + \delta(\text{CH})$, 1261 (F-SDBM), 1231 (C_2H_5 -SDBM) for $\nu(\text{C}=\text{S})$, and 1592 (F-SDBM), 1606 (C_2H_5 -SDBM) for $\nu(\text{C}=\text{O})$. Nuclear magnetic resonance spectra of ligands in carbon tetrachloride were 7.27 (F-SDBM), 7.20 (C_2H_5 -SDBM) for chelate ring-H (δ , ppm) and 15.50 (F-SDBM), 15.95 (C_2H_5 -SDBM) for enol/thioenol-H (δ , ppm).

The molar absorption coefficients at λ_{\max} of each of the UV and visible peaks of monothio β -diketones in carbon tetrachloride were 12 389 at 2650 Å, 13 584 at 3300 Å, and 16 316 at 4125 Å for F-SDBM, 12 968 at 2675 Å, 12 245 at 3375 Å, and 12 675 at 4150 Å for C_2H_5 -SDBM, and 13 932 at 2650 Å, 12 665 at 3275 Å, and 15 831 at 4125 Å, respectively. Mass spectra of F-SDBM and C_2H_5 -SDBM were determined to confirm the position of sulfur in the chelating reagents. The spectra of the ions at m/e 121 ($C_2H_5\text{CS}^+$) and m/e 123 ($\text{FC}_6\text{H}_4\text{CO}^+$) of F-SDBM indicate that the sulfur atom is attached to the carbon near C_6H_5 . The spectra of the ions at m/e 105 ($C_6H_5\text{CO}^+$) and m/e 149 ($C_2H_5C_6H_4\text{CS}^+$) of C_2H_5 -SDBM show that the sulfur atom is attached to the carbon near $C_2H_5C_6H_4$. The reaction mechanism in the syn-

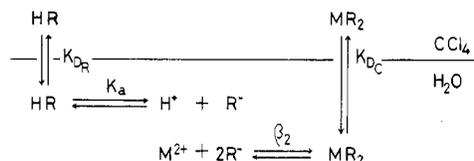


Figure 1. Scheme for the overall extraction processes.

thesis of monothio β -diketones probably proceeds through the keto form of the diketones, because the concentration of hydrogen chloride in the reaction mixture is an important factor. The position of sulfur of the reaction, $\text{C}=\text{O}$ to $\text{C}-\text{SH}$ generally occurs at the groups of higher electron release ability. Our findings are in accordance with the information of Berg and Reed (19), who cite that the order of preference for the site of attack appears to be: $\text{CH}_3 > \text{C}_6\text{H}_5 > \text{OC}_2\text{H}_5 > \text{C}_4\text{H}_9\text{S} > \text{CF}_3$, since mass spectra calculations reveal that the sulfur attached to the carbon adjacent to the groups of higher electron ability such as $p\text{-C}_2\text{H}_5\text{-C}_6\text{H}_4 > \text{C}_6\text{H}_5 > p\text{-FC}_6\text{H}_4$.

Stability of Monothio β -Diketones and Their Metal Chelates. The SDBM and STTA (monothiothenoyltrifluoroacetone) are useful for the solvent extraction reagents among various monothio derivatives of β -diketones (20). The purified STTA was sealed in a brown-colored bottle in a nitrogen atmosphere and stored in a refrigerator kept at 5 °C. The STTA when stored in this manner was quite stable during the storage, but once it was placed in the air, it slowly turned dark by oxidation (18); however the crystals of SDBM and F-SDBM are stable in desiccator containing concentrated sulfuric acid at 25 °C, but the ligands in carbon tetrachloride at 25 °C were unstable and used within 2 days. The C_2H_5 -SDBM is viscous liquid at 25 °C and more unstable than the crystals of SDBM and F-SDBM, and the solution of C_2H_5 -SDBM in carbon tetrachloride has to be used within 1 day. Therefore these reagent solutions were prepared just before use. These ligands are oxidized and decomposed to give sulfur and corresponding β -diketones or disulfides. The stability of the solutions was checked at regular intervals by spectrophotometry using the data of the absorbance of λ_{\max} of ligands. The stability of ligands in carbon tetrachloride increases in the order, C_2H_5 -SDBM < F-SDBM < SDBM. In general, the reagent solutions of the sulfur-containing chelating reagents, especially alkyl and halogen substituted reagents, for example, of 8-mercaptoquinolines (21) and diphenylthiocarbazon (22) are unstable and form oxidized products. The stability of the reagents must be checked before use. The reagents in an aqueous phase were more unstable than in carbon tetrachloride and decomposed within 1 day. The reagents of SDBM and F-SDBM in carbon tetrachloride can easily be back-extracted with 1.0 M NaOH solution, but the back-extraction of C_2H_5 -SDBM solution has to be repeated with 1.0 M NaOH. Nickel and copper chelates with SDBM, F-SDBM, and C_2H_5 -SDBM in carbon tetrachloride are stable and remain in the organic phase when the solutions were shaken with 1.0 M NaOH solution, but 91–96% of the zinc chelates decomposed under the same condition. The decomposition of the pyridine adducts of zinc chelates with SDBM, F-SDBM, and C_2H_5 -SDBM was about 30–50% and the adducts show the absorption spectra, like λ_{\max} (Å) 4050 and 2825 in the case of $\text{Zn}(\text{SDBM})_2\text{Py}_n$ ($n = 1-2$). It is interesting that $\text{Zn}(\text{S-}\beta\text{-diketone})_2$ forms an adduct with 1 or 2 mol of pyridine derivatives (23) and TOPO (tri-*n*-octylphosphine oxide) (14) because zinc chelates with thioxine, dithizone, and toluene dithiol are said not to form adducts with monodentate ligands of oxygen and nitrogen containing organic bases.

Distribution Coefficient of Ligands. The K_{Dr} of the ligands was determined as previously described from the data of (absorbance of organic phase)/(absorbance of organic phase after back-extraction from aqueous phase) after equilibrium.

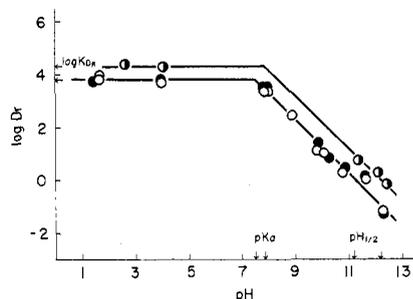


Figure 2. Distribution ratio of ligands between carbon tetrachloride and water as a function of pH: (O) SDBM, (●) F-SDBM, (◐) C₂H₅-SDBM.

The values obtained were 3.78 for SDBM, 3.70 for F-SDBM, and 4.34 for C₂H₅-SDBM, respectively. These values were constant in the region of pH 1.5–5 (Figure 2). The K_{DR} of SDBM is almost the same as that of F-SDBM, but C₂H₅-SDBM has more a hydrophobic group and gives a higher K_{DR} values. The distribution coefficient, $\log K_{DR}$, of SDBM between carbon tetrachloride and water changes with the conditions of an aqueous phase. The value reported were 5.8 for 0.1 M KCl solution of pH 2 (24) and 6.32 ± 0.07 for 0.1 M NaClO₄ solution containing buffer solutions of HCl–KCl (pH 1.0–2.2) or HCl–potassium acid phthalate (pH 2.2–3.6) (25), respectively. These values are larger than the present result, 3.78 for SDBM. This result may be caused by the difference of the ionic medium and the buffer solution or the difference of experimental technique such as centrifugation or standing time of the phases after extraction equilibrium. These factors will give some different result, because SDBM is somewhat unstable and is liable to undergo hydrolysis and oxidation in water or in solution-containing solvents such as dioxane (2). We also observed that the reagents in an aqueous phase were more unstable than in carbon tetrachloride and so they were studied as soon as possible.

Acid Dissociation Constant of Ligands. The K_a of the ligands can be calculated by the following equation (26):

$$D_R = \frac{[\text{HR}]_o}{[\text{HR}] + [\text{R}^-]} = \frac{[\text{H}^+]K_{DR}}{[\text{H}^+] + K_a} \quad (10)$$

where D_R is the distribution ratio of ligands between carbon tetrachloride and water and can be measured by the data of $A_{\text{final}}/(A_{\text{org}} - A_{\text{final}})$ vs. pH plots after equilibrium. The figures of these plots gave the slope of -1 (Figure 2). When $K_a \gg \text{H}^+$, $D_R = 1$, $\text{pH} = \text{pH}_{1/2}$

$$D_R = \frac{[\text{H}^+]K_{DR}}{K_a} \quad (11)$$

$$\text{p}K_a = -\log K_a = \text{pH}_{1/2} - \log K_{DR}$$

The values obtained were 7.32 for SDBM, 7.50 for F-SDBM, and 7.80 for C₂H₅-SDBM, respectively. The $\text{p}K_a$ of SDBM has already been reported as 6.48 in 20 vol % ethyl alcohol (24), 5.82 ± 0.12 in 0.1 M NaClO₄, 8.17 ± 0.03 in 50% aqueous dioxane (25), $7.0 + 10.9n_2$ in n_2 mole fraction of dioxane (27). The difference of these results may be caused by the hydrolysis and oxidation of SDBM in water or in solutions containing ethyl alcohol and dioxane under different conditions (2). We also observed that the ligands in water or in solution containing ethyl alcohol were oxidized and decomposed to give sulfur and corresponding β -diketones or disulfides. They were studied as soon as possible. The C₂H₅ group of benzene ring has an electron-releasing nature and increases the $\text{p}K_a$ values. The F group of the benzene ring has an electron-withdrawing nature, but the $\text{p}K_a$ value of F-SDBM is approximately that of SDBM. The position of the SH group may play an im-

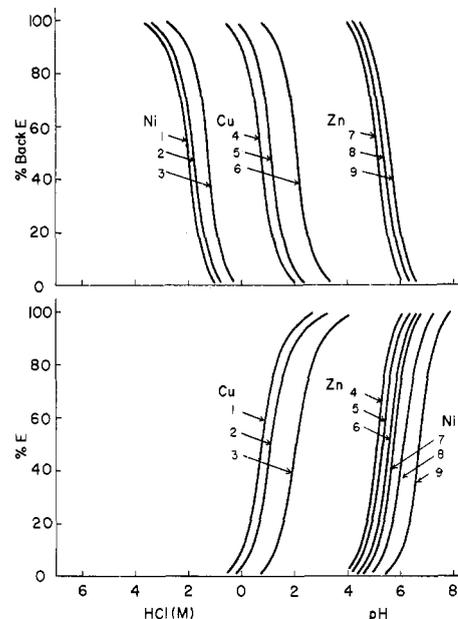


Figure 3. Extraction and back-extraction of the 10^{-4} M Ni(II), Cu(II), and Zn(II)– 10^{-3} M SDBM, F-SDBM, and C₂H₅-SDBM–carbon tetrachloride system: (extraction) SDBM, 2, 5, 7; F-SDBM, 1, 4, 8; C₂H₅-SDBM, 3, 6, 9; (back-extraction) SDBM, 3, 5, 8; F-SDBM, 2, 4, 7; C₂H₅-SDBM, 1, 6, 9.

portant role, that is, the SH group of F-SDBM is near the C₆H₅ group, while that of C₂H₅-SDBM is near the C₂H₅C₆H₄ group. In general, the chemical shift of the thiol proton of *N*-(*p*-substituted phenyl)- β -mercaptocinnamamides has a linear correlation with their $\text{p}K_a$ values (28). This fact is also found in monothio β -diketones (3).

Distribution Coefficient of Chelates. The values of the distribution coefficient of neutral chelates, K_{DC} , were determined as previously described. The values of the distribution coefficient of chelates with both excess and deficient ligand gave almost the same values. These results were summarized as Table I. The values of K_{DC} of Cu(SDBM)₂ and Zn(SDBM)₂ obtained with the atomic absorption and ⁶⁵Zn tracer methods were somewhat smaller than those obtained by spectrophotometry. These results obtained by spectrophotometry and atomic absorption methods may be almost due to errors resulting from the determination of a very small amount of neutral chelates distributed into an aqueous phase. Judging from sensitivity and accuracy of the analytical methods, the reasonable value of the distribution coefficient of chelates, $\log K_{DC}$, in carbon tetrachloride may be obtained by means of atomic absorption and tracer methods. It is interesting that the values of nickel chelate are smaller than those of copper and zinc chelates. Similar results were found in nickel(II) and zinc(II) chelates with *N*-(*p*-substituted phenyl)- β -mercaptocinnamamides (25, 28). The structure of complexes such as tetrahedral zinc chelates (11) and square-planar nickel chelate (27) may play an important role in the distribution of neutral complexes. It should be noted that the K_D for the chelates, K_{DC} , is less than that for the reagents, K_{DR} , having coordination atoms of (O, S) like thio β -diketone (8, 25) and of (N, S) like dithizone (29) in nonpolar solvents such as carbon tetrachloride and chloroform, because, in general, the K_{DC} is larger than K_{DR} having coordination atoms of (O, O) like β -diketone (30) and of (O, N) like oxine (31) in nonpolar solvents.

Extraction and Back-Extraction of Nickel(II), Copper(II), and Zinc(II)–SDBM, F-SDBM, and C₂H₅-SDBM–Carbon Tetrachloride System. The pH dependence of the extractability of 10^{-4} M metals with 10^{-3} M monothio β -diketones in carbon tetrachloride was examined as previously described (Figure 3). The effects of the contact

Table I. Logarithm of the Stability Constants, $\log \beta_2$, for Ni(II), Cu(II), and Zn(II) Complexes with Monothio- β -diketones of SDBM, F-SDBM, and C_2H_5 -SDBM

metals	ligands	$-2 \log K_a$	$2 \log K_{DR}$	$-\log K_{DC}$	$-2 \text{pH}_{1/2}$	$-2 \log [\text{HR}]_0$	$\log \beta_2$	
Ni	SDBM	14.64	7.46	-2.60 ^a	-11.40 ^e	6.05	14.15 ^g	
		14.64	7.46	-2.60 ^a	2.60 ^f	6.05	28.15 ^g	
		14.64	7.46	-2.83 ^b	-11.40 ^e	6.05	13.92 ^g	
		14.64	7.46	-2.83 ^b	2.60 ^f	6.05	27.92 ^g	
		14.64	7.46	-2.14 ^c	-11.40 ^e	6.05	14.61 ^g	
		14.64	7.46	-2.14 ^c	2.60 ^f	6.05	28.61 ^g	
							14.94 (9)	
							19.5 (2)	
							20.72 (4)	
							21.65 (27)	
							22.2 (3)	
		F-SDBM	15.00	7.40	-2.79	-12.30 ^e	6.05	13.36 ^g
			15.00	7.40	-2.79	3.60 ^f	6.05	29.26 ^g
		C_2H_5 -SDBM	15.60	8.68	-3.11	-13.40 ^e	6.20	13.97 ^g
			15.60	8.68	-3.11	4.00 ^f	6.14	31.31 ^g
Cu	SDBM	14.64	7.46	-3.73 ^a	-2.10	6.05	22.32	
		14.64	7.46	-2.40 ^b	-2.10	6.05	23.65	
		14.64	7.46	-2.21 ^c	-2.10	6.05	23.84	
							> 23 (2)	
							21.12 (4)	
							22.15 (27)	
							22.6 (3)	
							23.33	
		F-SDBM	15.00	7.40	-3.62	-1.50	6.05	22.68
		C_2H_5 -SDBM	15.60	8.68	-3.54	-4.20	6.14	13.66
	Zn	SDBM	14.64	7.46	-3.85 ^a	-10.64	6.05	15.31
			14.64	7.46	-2.20 ^b	-10.64	6.05	15.16
			14.64	7.46	-2.35 ^c	-10.64	6.05	15.51
								15.99 (9)
								16.8 (2)
							17.92 (4)	
							20.29 (3)	
							14.57 ^g	
		F-SDBM	15.00	7.40	-3.58	-10.30	6.05	15.58 ^g
		C_2H_5 -SDBM	15.60	8.68	-3.64	-11.20	6.14	

^a UV and visible method, with deficient ligand. ^b Atomic absorption method, with excess ligand. ^c Atomic absorption method, with deficient ligand. ^d Tracer method, with excess ligand. ^e Extraction. ^f Back-extraction. ^g Apparent stability constants.

time, that is, the shaking time, on the extraction and the back-extraction rate were also investigated (Figure 4). The extraction of Zn was carried out within 30 min while that of copper requires about 2 h to reach its extraction equilibrium. The extraction of nickel required over 2 h to reach its extraction equilibrium. The pH range of the back-extraction of nickel shifts to a lower pH than that of the extraction. It is said that the establishment of extraction equilibrium of nickel with DBM requires several days (32), while the extraction of nickel with STTA required 1 h to reach its extraction equilibrium (14). In a 10^{-4} M Ni- 10^{-3} M SDBM- CCl_4 extraction system, nickel cannot be extracted at all in the range of pH 3.82-4.6 when shaken for 22 h and 25 min. The $Ni(SDBM)_2$ extracted at pH 8.0 could not be back-extracted at all at pH 4.45 when shaken for 19 h and 10 min. However nickel can easily be back-extracted at pH 4.20 within 15 min when 10^{-2} M 1,10-phenanthroline was added to the extraction system. In that case, 1,10-phenanthroline does not act as an adduct-forming agent for metal chelate observed in nickel dithizonate (33) but as a masking agent for nickel ion. The ligand exchange reaction between $Ni(SDBM)_2$ and oxine in carbon tetrachloride proceeds quickly as in the exchange reaction between nickel dithizonate and oxine (34), and then nickel can easily be back-extracted at pH 4.1 within a few min. The slow rate of establishment of extraction equilibrium of nickel complex may be explained by a change upon the addition of a second molecule of ligand, from a paramagnetic octahedral monochelates species $[Ni(H_2O)(chel)]^+$ to a diamagnetic square-planar bis chelated species $[Ni(chel)_2](chel = \text{monothio } \beta\text{-diketone})$ (27). The $\text{pH}_{1/2}$ values of copper were 1.05 for SDBM, 0.75 for F-SDBM, and 2.10 for C_2H_5 -SDBM

and those of zinc were 5.32 for SDBM, 5.15 for F-SDBM, and 5.60 for C_2H_5 -SDBM. In the case of nickel, the $\text{pH}_{1/2}$ values after shaking for 2 h were 5.70 (extraction) and -1.30 (back extraction) for SDBM, 6.15 (extraction) and -1.80 (back extraction) for F-SDBM, and 6.95 (extraction) and -2.00 (back extraction) for C_2H_5 -SDBM (Figure 3). It is interesting that the extraction and the back extraction of copper and zinc with monothio β -diketones take place at lower pH region in the order of F-SDBM > SDBM > C_2H_5 -SDBM, while those of nickel proceed in the order of SDBM > F-SDBM > C_2H_5 -SDBM for the extraction and C_2H_5 -SDBM > F-SDBM > SDBM for the back extraction. In general, nickel chelates show the electronic spectra of d-d transition, while copper chelates form stable complex with strong ligand field. The $d\pi$ - $d\pi$ back donation, ligand field, and the configuration of (O, S) ligands on metal, that is, cis or trans form, in the chelates, which are probably the driving force may have some effect on the extraction equilibrium correlating with the chelate stability.

Stability Constant of Nickel(II), Copper(II), and Zinc(II) Chelates with SDBM, F-SDBM, and C_2H_5 -SDBM in an Aqueous Solution. The stability constants of metal chelates with monothio β -diketones in an aqueous solution, $\log \beta_2$, were determined as previously described and are listed in Table I together with the values of $\log K_a$, $\log K_{DR}$, $\log K_{DC}$, $\text{pH}_{1/2}$, and $\log [\text{HR}]_0$. The value of $\log \beta_2$ of copper chelate obtained by solvent extraction is in good agreement with the results determined by potentiometric titration (3, 27). In the extraction of nickel chelate, unusual extraction behavior was observed and it was difficult to get true $\log \beta_2$ of $Ni(SDBM)_2$ without its real equilibrium value.

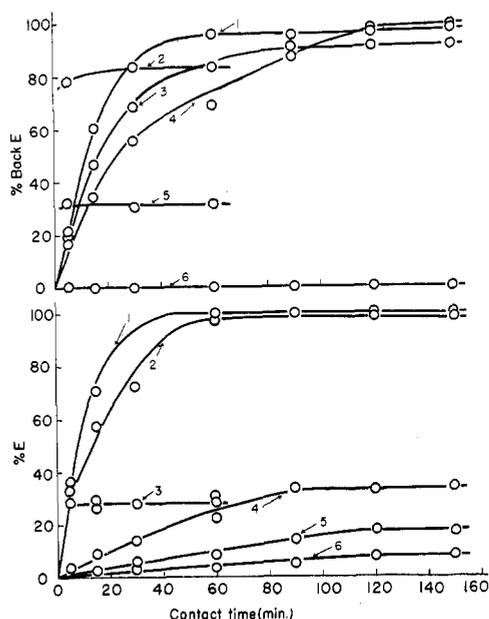


Figure 4. Rates of extraction and back-extraction of the 10^{-4} M Ni(II), Cu(II), Zn(II)- 10^{-3} M SDBM, F-SDBM, and C_2H_5 -SDBM-carbon tetrachloride system at different pH values: (extraction) 1, Ni, C_2H_5 -SDBM, pH 8.0; 2, Cu, C_2H_5 -SDBM, pH 4.0; 3, Zn, SDBM, pH 5.1; Zn-F-SDBM, pH 4.9; Zn- C_2H_5 -SDBM, pH 5.3; 4, Ni, SDBM, pH 5.67; 5, Cu, F-SDBM, pH 0.25; Ni, F-SDBM, pH 5.74; 6, Cu, SDBM, pH 0.20; (back-extraction) 1, Cu, C_2H_5 -SDBM, pH 1.0; 2, Zn, SDBM, pH 4.8; 3, Cu, SDBM, pH 0.7; 4, Cu, F-SDBM, pH -0.3; 5, Zn, F-SDBM, pH 5.3; Zn, C_2H_5 -SDBM, pH 5.8; 6, Ni, SDBM, pH 4.89; Ni, F-SDBM, pH 5.04; Ni, C_2H_5 -SDBM, pH 5.27.

However, it should seem that nickel is more stable than zinc on the basis of the experimental results in Ni- and Zn-STTA-cyclohexane extraction systems (14). Although it is reported that the stability constants of nickel chelates were smaller than those of zinc chelates in sulfur-oxygen coordinating ligands such as SDBM (8, 24), and *N*-(*p*-substituted phenyl)- β -mercaptocinnamamides (28), the results seem to have some problem, because the authors do not ascertain the back-extraction behavior of these chelates. It is strange that the $\log \beta_2$ of zinc chelates gives lower values than the results obtained by potentiometric titration. In this experiment, the extractions of zinc with monothio β -diketones are carried out with carbon tetrachloride instead of chloroform (8). The extractions of zinc and nickel with DBM and oxine take place in the same pH region, while using thiooxine and dithizone, zinc can be extracted at a lower pH region than nickel (35). However, it is interesting that the pH range of the extraction for zinc with monothio β -diketone such as STTA (monothiohenyltrifluoroacetone) in cyclohexane is higher than that of nickel and the zinc chelate forms stable adducts with TOPO (14), because zinc chelates with thiooxine and dithizone do not form adducts. It is also reported that $Zn(S-\beta\text{-diketone})_2$ forms adducts with various nitrogen-containing organic bases (23). When the determination of the $\log \beta_2$ of zinc chelates by potentiometric titration was carried out in 75 vol % dioxane, the $Zn(S-\beta\text{-diketone})_2$ may form adducts with dioxane to give higher $\log \beta_2$ values. It is also observed that zinc chelates in carbon tetrachloride form some insoluble chelate. From these facts, the $\log \beta_2$ values of the chelates obtained by the solvent extraction method may be different from those obtained by the potentiometric titration. The extraction equilibrium of Zn was rapid, but that of Ni is slow. In the case of zinc ion, the water removal from the octahedral zinc hexahydrate appears to play a key role in the rate-determining step (15). The presence of terminal aromatic ring substituents of monothio β -diketones would be expected to weaken the metal-water bonds and facilitate the loss of water as observed

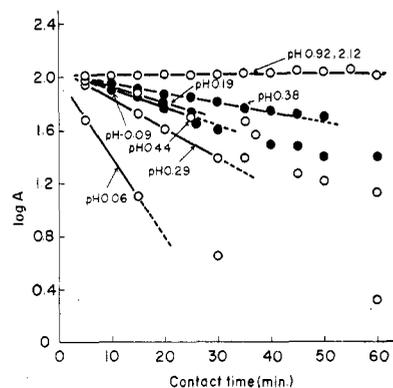


Figure 5. Effect of pH on back-extraction of Cu(II)-SDBM chelates in carbon tetrachloride at different pH values: (●) pH adjusted by perchloric acid; (○) pH adjusted by hydrochloric acid.

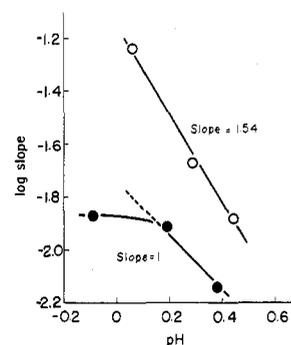
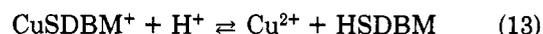


Figure 6. Effect of pH on back-extraction of Cu(II)-SDBM chelates in carbon tetrachloride as a function of log slope of Figure 5: (●) pH adjusted by perchloric acid; (○) pH adjusted by hydrochloric acid.

in zinc chelates with dithizone substituents (11). In the case of nickel ion, the change from a paramagnetic octahedral monochelated species $[Ni(H_2O)_6(chel)]^+$ to a diamagnetic square-planar bis chelated species $[Ni(chel)_2]$ (chel = monothio β -diketone) may play an important role on the extraction rate (27). The distinct influence of substituents on chelate stability was not observed.

Back-Extraction Kinetics of Copper(II) SDBM Chelate in Carbon Tetrachloride. Although many extraction kinetics of chelates have been reported (15, 16, 36), little attention has been given to its back-extraction equilibrium. The attainment of equilibrium of copper SDBM chelates requires 2 h. The back-extraction equilibrium of $Cu(DBM)_2$ was investigated as the representative model of monothio β -diketone chelates. The reaction of $Cu(SDBM)_2$ can simply be represented as follows:



The extractions were carried out under vigorous shaking or mixing, for the extent of the extraction is independent of the contacting rate of both phases. The plots of $\log [Cu(SDBM)_2]_{t=0}/[Cu(SDBM)_2]_t$ vs. time (min), that is, $\log A$ vs. t (time) under various pH adjusted by perchloric acid, gave the straight line, which showed the first-order reaction in $Cu(SDBM)_2$ (Figure 5). The log slope ($\log A$ vs. t (min)) vs. pH (pH 0.2-0.4) plots gave the straight line of slope 1. However, the plot deviates from the straight line and becomes a plateau at a lower pH region (pH < 0.2) (Figure 6). The plots of $\log [Cu(SDBM)_2]_{t=0}/[Cu(SDBM)_2]_t$ vs. time (min), that is $\log A$ vs. t (time) at pH 0.20 under varying concentration of SDBM in carbon tetrachloride, showed the straight line. The log slope vs. $\log [HSDBM]_0$ plots at pH 0.20 also gave the straight line of slope -1. These results show that the

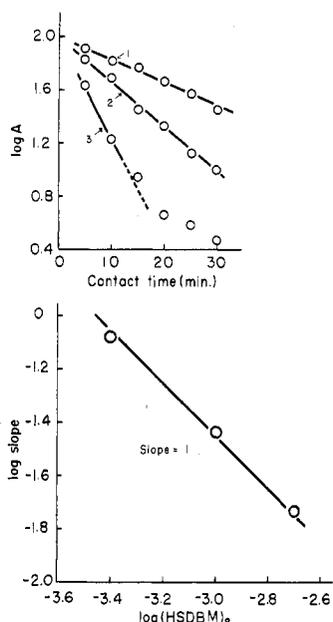


Figure 7. Effect of SDBM concentration in organic phase on back-extraction of Cu(II)-SDBM chelates in carbon tetrachloride at pH 0.20: (log (HSDBM)₀) 1, -2.70; 2, -3.00; 3, -3.40.

reaction order with respect to the SDBM concentration is -1 (Figure 7). As the back-extraction seems to be the reverse reaction of forward extraction (16) the rate of back-extraction of chelate in the presence of free ligand can generally be written

$$-\frac{d[\text{Cu}(\text{SDBM})_2]}{dt} = k'[\text{H}^+][\text{Cu}(\text{SDBM})_2]_0[\text{HSDBM}]_0^{-1} \quad (14)$$

$$\log \text{slope} = \log k'[\text{H}^+][\text{HSDBM}]_0 \quad (15)$$

$$\log k' = \log \text{slope} + \log [\text{HSDBM}]_0 + \text{pH} \quad (16)$$

From the experimental results, the rate constants were calculated by using eq 16, $\log k' = -4.77 \text{ M min}^{-1}$. The plots of $\log [\text{Cu}(\text{SDBM})_2]_{t=0}/[\text{Cu}(\text{SDBM})_2]_t$ vs. time (min), that is, log A vs. t (time) under various pH adjusted by hydrochloric acid, also gave the straight line, which showed the first-order reaction in Cu(SDBM)₂ (Figure 5). The log slope (log A vs. t (min)) vs. pH (pH 0-0.5) plots gave the straight line of slope 1.5 when pH of an aqueous solution was adjusted by using hydrochloric acid instead of perchloric acid (Figure 6). The plots of $\log [\text{Cu}(\text{SDBM})_2]_{t=0}/[\text{Cu}(\text{SDBM})_2]_t$ vs. time (min), that is, log A vs. t (time) at pH 0.11 adjusted by perchloric acid under various concentration of chloride ion, showed the straight line (Figure 8) and the log slope vs. log [Cl⁻] (-1.4 to 0) plots at pH 0.11 also gave the straight line of slope 1. These results show that the reaction order with respect to the chloride concentration is 1. Then, the rate of back-extraction in the presence of chloride ion can be written

$$-\frac{d[\text{Cu}(\text{SDBM})_2]}{dt} = k''[\text{H}^+][\text{Cl}^-][\text{Cu}(\text{SDBM})_2]_0[\text{HSDBM}]_0^{-1} \quad (17)$$

$$\log \text{slope} = \log k'' = \log k''[\text{H}^+][\text{Cl}^-][\text{HSDBM}]_0^{-1} \quad (18)$$

$$\log k'' = \log \text{slope} + \text{pH} - \log [\text{Cl}^-] + \log [\text{HSDBM}]_0 \quad (19)$$

From the experimental results, the rate constants were calculated by using eq 19. $\log k'' = -3.45 \text{ M min}^{-1}$. The rate constant of back-extraction increased about 10 times by an addition of chloride ion. The chloride complex formation, CuCl⁺, in the aqueous phase may increase the back-extraction

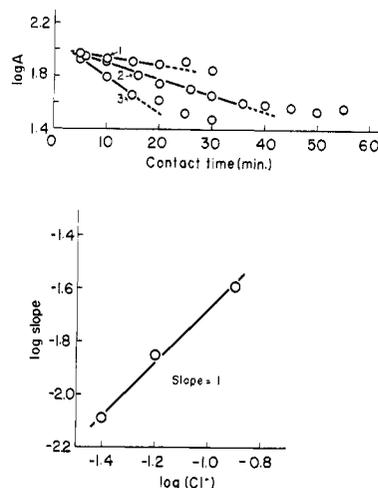


Figure 8. Effect of chloride ion on back-extraction of Cu(II)-SDBM chelates in carbon tetrachloride at pH 0.11: (log (Cl⁻) 1, -1.4; 2, -1.20; 3, -0.90.

rate of Cu(SDBM)₂ chelate. The acceleration of the extraction rate is also observed in the Fe(III)-TTA-benzene system in the presence of chloride ion (37). Although copper 2-methyloxine chelate could be back-extracted with EDTA (ethylenediaminetetraacetic acid) and its derivatives (38), the Cu(SDBM)₂ in carbon tetrachloride could not be back-extracted at pH 5.62-8.95 in the presence of 10⁻³-10⁻¹ M EDTA. The back-extraction may proceed through the reaction steps, that is, a hydrogen ion assisted in the dissociation of Cu(SDBM)₂ followed by reaction of chloride ion.

ACKNOWLEDGMENT

The authors acknowledge E. Uhlemann of Leipzig, Anorganisches und Physikalisches Institute der Karl-Marx Universität, who provided the SDBM reagent.

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RECEIVED for review July 16, 1980. Accepted March 9, 1981.

Foam Prevention in Purge and Trap Analysis

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Volatile organics are often separated from water samples by bubbling an inert gas through the water and collecting the organics on a sorbent trap, a technique known as purge and trap. Unfortunately, during the analysis of many water samples, foam can climb through the apparatus and contaminate the trap. This research project has investigated both chemical and mechanical antifoaming techniques. A total of 27 potential chemical antifoaming agents were evaluated for their ability to control foam. Two silicone-based commercial antifoam emulsions, Dow Corning Antifoam C and General Electric AF-72, were rated superior overall. The final protocol specifies use of 2 drops of purified silicone antifoam emulsion (General Electric AF-72) in a 5.0-mL sample which is purged in a 60-mL purge flask. The procedure was validated with seven volatile compounds (29-159 ng) spiked into four wastewaters. Mean recovery (vs. purge of distilled water) was 97%.

Foams are agglomerations of gas bubbles separated from each other by thin liquid films (1). Surface-active solutes impart a surface elasticity to the liquid which allows formation of foam (1-5). The object of an antifoaming agent is to alter the surface characteristics of the liquid to disfavor foaming by decreasing surface viscosity and increasing rate of drainage. The chemical and physical properties desirable in an antifoaming agent include: (a) insolubility; (b) dispersion over the liquid surface; (c) inertness; and (d) nonvolatility. On the basis of reviews of chemical antifoams (1-8), commercial silicone antifoams appear to be the most generally suitable since they are active at low concentrations and act on most types of foams.

Mechanical antifoaming techniques have the advantage that no chemical contaminants are introduced. Suggested methods include centrifugation (4), tangential air blasts (4), heat (4, 9), and narrow constrictions (10).

Elimination of foaming by headspace purge techniques (11) or foam traps (12, 13) has also been suggested. These can be useful antifoaming techniques, but they depart significantly from the usual purge and trap in that gas is no longer bubbled through the sample and system dynamics are significantly altered.

Silicone antifoaming agents have been found effective in purge and trap analysis (9, 13), although in one report gradual decreases in sensitivity and carrier gas flow were observed (13). By use of a mass spectrometer as the gas chromatographic (GC) detector, significant persistent contaminants were observed with the use of a silicone antifoam (9).

The object of this research was to develop a protocol for the handling of samples which foam during purge and trap analysis. Foam can climb through the apparatus, enter the trap and invalidate the analytical data by irreversibly contaminating the trap. The protocol developed had to be simple, reproducible, accurate, and congruent with the Bellar and Lichtenberg (14-17) technique currently used for priority pollutant analyses. Addition of chemical antifoaming agents and modification of glassware were considered potentially useful techniques. The goal was to develop a procedure (a) requiring minimal attention by the analyst, (b) utilizing a minimally modified apparatus, (c) providing efficient recovery of priority pollutants, and (d) adding no new artifacts to the analysis.

EXPERIMENTAL SECTION

Model Compounds. Test compounds were chloroform, 1,1,1-trichloroethane, carbon tetrachloride, bromodichloromethane, trichloroethylene, 1,1,2-trichloroethane, bromoform, 1,1,2,2-tetrachloroethane, toluene, and chlorobenzene.

A stock solution in methanol was used to fortify water and wastewater samples. Aqueous stock solutions were prepared fresh daily by addition of 1 μ L of the methanol standard to 100 mL water or foaming solution.

Standard Foaming Solution. The standard foaming solution contained 3 g/L NH_4Cl , 1 g/L K_2HPO_4 , 0.25 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 0.25 g/L KCl in distilled water which had been purged under nitrogen for 16 h at a pH of 7.1 to simulate the mineral content in an environmental sample. The antifoaming abilities of several antifoams were tested on the surfactant sodium dodecyl sulfate (50 mg/L) and confirmed by using dodecylbenzenesulfonate (50 mg/L) or egg albumin (100 mg/L).

Foaming Test. The method found most reliable was the passage of a known volume of gas through the test solution followed by measurement of the volume of foam. Nitrogen (~100 mL) was bubbled through 25 mL of the test solution containing the test antifoam in a 44 \times 2.5 cm i.d. fritted glass chromatography column. The foam height was measured immediately after stopping the N_2 flow. The value reported was the ratio of the volume of foam to volume of gas introduced ($V_{\text{foam}}/V_{\text{N}_2}$). Several other test methods, including equilibrium foam height and foam half-life, were investigated and found inadequate.

Analysis. The purge and trap system was patterned after the system developed by Bellar and Lichtenberg (11, 13-17). Samples were analyzed on a Fisher-Victoreen 4400 gas chromatograph with a flame ionization detector (FID) and a Tracor Model 700 Hall electrolytic conductivity detector operated in the halide mode. The split ratio between the two detectors was approximately 1:1. The chromatography column was a 2 mm i.d. \times 180 cm glass column packed with 0.2% Carbowax 1500 on 60/80 mesh Carbowax C. The column temperature was held at 60 $^\circ\text{C}$ for 4 min and then programmed at 6 $^\circ\text{C}/\text{min}$ to a final temperature of 180 $^\circ\text{C}$. Samples were purged onto the Tenax sorbent trap for 12 min