Chloro Complexes of Copper(I) and Copper(II) in Dimethyl Sulfoxide

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The chloro complexes of copper(I) and copper(II) in dimethyl sulfoxide have been studied. The copper(I) complexes have been examined by several potentiometric methods, and the copper(II) complexes by spectrophotometry and by different potentiometric techniques. The stepwise formation constants for $CuCl$ and $CuCl_2^-$ are $10^{6.0 \pm 0.2}$ and $10^{6.2 \pm 0.2}$, and those obtained for $CuCl^+$; $CuCl_2$; $CuCl_3^-$; and $CuCl_4^{2-}$ are $10^{4.4 \pm 0.1}$; $10^{3.0 \pm 0.1}$; $10^{4.0 \pm 0.5}$ and $10^{1.6 \pm 0.3}$; and $10^{2.0 \pm 0.1}$.

Introduction

The chloro complexes of copper(II) and copper(I) have been studied in acetonitrile.[1,2] Copper(II) froms four soluble complexes, $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$, with stepwise formation constants of $10^{9.7}$, $10^{7.9}$, $10^{7.1}$, and $10^{3.7}$, respectively.[1] Copper(I) forms two soluble chloro complexes $CuCl$ and $CuCl_2^-$, with stepwise formation constats of $10^{4.9}$ and $10^{5.9}$. Silver(I) has been studied in acetonitrile[3,4] and in dimethyl sulfoxide.[3,5,6] In both solvents, insoluble AgCl and soluble $AgCl_2^-$ are formed, with solubility product and overall formation constant, $\beta_{AgCl_2^-}$, of of $10^{-12.4}$ and $10^{12.6}$, respectively, in acetonitrile; and $10^{-10.4}$ and $10^{11.9}$ in dimethyl sulfoxide. It was shown that the solubility of silver halides parallels the relative solvating ability of the solvents for silver(I),[3] from which it can be concluded that dimethyl sulfoxide solvates silver(I) more strongly than does acetonitrile. The information available on silver(I) in the two solvents, on copper(II) and copper(I) in acetonitrile, and the similarity of silver(I) and copper(I), make the study of copper(II) and copper(I)-chloro complexes in dimethyl sulfoxide of special interest.

During preparation of this paper, a report on the chloro complexes of copper(II) and copper(I) in dimethyl sulfoxide appeared in print,[7] indicating that copper(II) forms three soluble complexes, $CuCl^+$, $CuCl_2$, and $CuCl_3^-$, with stepwise formation constants

of $10^{4.5}$, $10^{3.0}$, and $10^{1.6}$ and that copper(I) forms two soluble complexes, $CuCl$ and $CuCl_2^-$, with stepwise formation constants of 10^6 and $10^{5.95}$.

The study described in this paper we hope will contribute along with the electrochemical work (potentiometry with a copper indicator electrode for copper(I)-chloro complexes, and with platinum and graphite indicator electrodes for monitoring copper(II)-copper(I)-chloride systems) of Le Demezet and co-workers[7] to the establishment of a firm, definitive picture of these copper-chloride complex-formation systems in dimethyl sulfoxide. In our study, the examination of copper(II)-chloro complexes was made by spectrophotometry and by potentiometry with chloride and copper ion- selective electrodes, and with a platinum electrode for monitoring a copper(II)-copper(I)-chloride system. For the copper(I)-chloro complex study, potentiometry with copper amalgam and copper indicator electrodes and voltammetry at the dropping mercury and dropping amalgam electrodes were carried out.

Experimental Section

Bulk dimethyl sulfoxide obtained from Crown-Zellerbach was vacuum distilled (40° at *ca.* 1.5 mm) twice over calcium hydride, the first and last 10% of the distillate being discarded in each distillation. The freshly distilled dimethyl sulfoxide was stored in the dark under nitrogen. Tetraethylammonium perchlorate (TEAP) obtained from Eastman Organic Chemicals was recrystallized twice from water and dried at 80° for 12 hrs. Eastman Organic Chemicals tetraethylammonium chloride (TEACl) was recrystallized three times from acetonitrile, washed with ether, and dried at 110° in a vacuum oven for 12 hrs.

Cu(ClO₄)₂.4DMSO: The dimethyl sulfoxide complex of copper(II) perchlorate was prepared by methods described in the literature.[8,9] The copper content of the pale blue powder was estimated by EDTA titration with murexide,[10] and the perchlorate by a

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(3) D.C. Luchrs, R.T. Iwamoto, and J. Kleinberg, *Inorg. Chem., 5,* 201 (1966).
(4) R. Alexander, E.L.F. Ko, and A.J. Parker, *J. Am. Chem. Soc., 89,* 3703 (1967).
(5) M. Le Demezet, C. Madec, and M. L'Her, *Bull. Soc. Chim. Fran.,* 1970, p. 365.
(6) D.C. Luehrs, R.W. Nicholas, and D.A. Hamm, *J. Electroanal. Chem., 29,* 417 (1971).
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(8) J. Selbin, W.E. Bull, and L.H. Holmes, Jr., *J. Inorg. Nucl. Chem., 16,* 219 (1961).
(9) F.A. Cotton and R. Francis, *J. Am. Chem. Soc., 82,* 2986 (1960).
(10) F.J. Welcher, «The Analytical Uses of Ethylenediamminetetra-acetic Acid», Von Nostrand, N.Y., 1958, p. 242.
(11) F.J. Welcher, «Organic Analytical Reagents», Von Nostrand, N.Y., 1948, p. 544.

gravimetric nitron procedure.[11] *Anal.:* Calcd for $Cu(ClO_4)_2 \cdot 4DMSO$: Cu, 11.05; ClO_4, 34.62. Found: Cu, 11.02; ClO_4, 34.85.

CuCl₂·2DMSO: The dimethyl sulfoxide complex of copper(II) chloride was prepared by the same procedures used for the perchlorate. The copper content of the emerald green powder was estimated by EDTA titration with murexide indicator; the chloride by potentiometric titration with silver nitrate.

Anal.: Calcd for $CuCl_2 \cdot 2DMSO$: Cu, 21.87; Cl, 24.40. Found: Cu, 21.82; Cl, 24.13.

Solutions of copper(I) perchlorate were prepared by reduction of copper(II) perchlorate in dimethyl sulfoxide by copper metal. Typically, 0.4 g of $Cu(ClO_4)_2 \cdot 4DMSO$ was dissolved in 25 ml of deaerated dimethyl sulfoxide, and the resulting solution was warmed to 60° over copper wire. Nitrogen was passed slowly through the solution for a period of two hours during which time the blue solution became colorless, indicating reduction of the copper(II) to copper(I). Completeness of reduction was checked polarographically.

Voltammetric Measurements. Current-potential curves were obtained with a controlled potential polarograph designed by Underkofler and Shain[12] and modified by Marcus and Hawley.[13] The dropping mercury electrode was of conventional design with a drop time of 3.5 sec and a flow rate of 1.56 mg Hg/sec when measured with an open circuit and a 60–cm head of mercury. A dropping amalgam electrode was prepared and used according to Manahan and Birch.[14] The rotating platinum electrode was also of conventional design. A platinum foil served as the auxiliary electrode and a saturated aqueous calomel electrode prepared in the laboratory as the reference in all measurement. All solutions were 0.1 F in tetraethylammonium perchlorate and were deaerated with purified nitrogen for five to ten minutes prior to each measurement.

Potentiometric Measurements. Potential measurements were made with a Leeds and Northrup Model 8691 millivolt potentiometer. Titrations of copper-(II) with chloride (TEACl) were followed using an Orion Model 94-17A chloride ion specific electrode or an Orion Model 94-29A cupric ion specific electrode trode. Titrations of copper(I) with chloride (TEACl) were followed by a copper wire or copper-amalgam pool[15] indicating electrode. The copper wire electrode was preconditioned by heating the copper wire in a stream of hydrogen at 350° for 30 minutes, cooling in a hydrogen stream, and storage in a dry nitrogen atmosphere before each use. The titrations of copper(II) and copper(I) mixtures were followed with a platinum foil electrode. No pretreatment of the platinum was used. The reference electrode for all potentiometric measurements was a silver/silver chloride electrode in dimethyl sulfoxide ("DMSO" re-

ference). The electrode was prepared by electrolyzing silver chloride onto a silver foil by using the foil as an anode in 2 F hydrochloric acid solution. The silver chloride coated foil was placed in a reference compartment containing solid potassium chloride and potassium perchlorate. The compartment was filled with dimethyl sulfoxide which was 0.10 F in tetraethylammonium perchlorate. The potential of the electrode would then follow the half-reaction:

$$Ag + KCl + ClO_4^- = AgCl + KClO_4 + e^-.$$
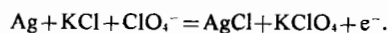
The references compartment was separated from the solution by a bridge compartment filled with dimethyl sulfoxide which was 0.10 F in tetraethylammonium perchlorate. The bridge compartment was flushed before each titration. The use of dimethyl sulfoxide in the reference and bridge minimized junction potentials; the use of only moderately soluble chloride salt in the reference keeps the silver chloride from dissolving to form the dichloro complex and prevents chloride leakage into the solutions. The potential of the reference electrode measured against an aqueous calomel electrode was −165.5 mv. After a two month period, the potential drifted to −186 mv.

Spectral Measurements. Beckman DU, Cary Model 14 and Perkin-Elmer Model 421 spectrophotometers were used in spectral measurements. All solutions were maintained at constant ionic strength with tetraethylammonium perchlorate.

Results

Spectrophotometric Study The spectrum of copper(II) in dimethyl sulfoxide has been reported.[16] Copper(II) solutions in dimethyl sulfoxide show an unsymmetric, low intensity *d-d* absorption band in the near infrared at 852 nm ($\varepsilon_M = 35.2$ liter mole⁻¹ cm⁻¹). As chloride is added, the band increases in intensity and moves continuously to higher wavelengths. At a chloride to copper(II) ratio of 1:1, the band shifts to 908 nm ($\varepsilon_M = 77$ liter mole⁻¹ cm⁻¹); at a 2:1 ratio, the band is at 955 nm ($\varepsilon_M = 94.2$ liter mole⁻¹ cm⁻¹); and at a 3:1 ratio, the band position is 1000 nm ($\varepsilon_M = 99.0$ liter mole⁻¹ cm⁻¹). At higher chloride to copper(II) ratios, the absorption band increases in intensity only slightly and shifts slowly to higher wave lengths. In the ultraviolet region, copper(II) solutions show an intense absorption band at 289 nm ($\varepsilon_M = 4.11 \times 10^3$ liter mole⁻¹ cm⁻¹); with increasing chloride to copper(II) ratios, the band shifts slightly to higher wave lengths with slight increases in intensity. At a chloride to copper ratio of 5:1, the band has moved to 294 nm ($\varepsilon_M = 4.62 \times 10^3$ liter mole⁻¹ cm⁻¹). The band does not shift appreciably with further increase in chloride to copper(II) ratio, but increases in intensity and becomes distorted on the high wavelength side. At ratios above 200:1, a new band appears at 440 nm, which increases in intensity along with the band at 294 nm with increasing chloride.

(12) W.L. Underkofler and I. Shain, *Anal. Chem.,* 35, 1778 (1963).
(13) M.F. Marcus and M.D. Hawley, *J. Electroanl. Chem.,* 18, 175 (1968).
(14) S.E. Manahan and G. Birch, *Anal. Chem.,* 39, 1182 (1967).
(15) S. Ahrland and J. Rawsthome, *Acta Chem. Scand.,* 24, 157 (1970).
(16) H.L. Schläfer and H.P. Opitz, *Z. Elektrochem.,* 65, 372 (1961).

Examination of plots of molar absorptivities *vs* mole ratio at wavelengths of 1100 nm, 1300 nm, and 1500 nm (Figure 1), shows well-defined breaks at 1:1 mole ratio and less well-defined breaks at 2:1 and 3:1 mole ratios, indicating that three complexes are formed at stoichiometric chloride to copper(II) ratios, CuCl$^+$, CuCl$_2$, and CuCl$_3^-$. The sharpness of the break at 1:1 indicates that the first complex is quite stable; the less well-defined breaks at 2:1 and 3:1 may be taken to mean that both complexes exist in appreciable concentrations at these ratios and that their stepwise formaion constants are of the same order of magnitude. The band at 440 nm in copper(II) solutions containing high concentrations of chloride has been assigned to a charge transfer absorption of the tetrachloro-cuprate species, CuCl$_4^{2-}$.[17] No new bands were observed at ratios of up to 1000:1.
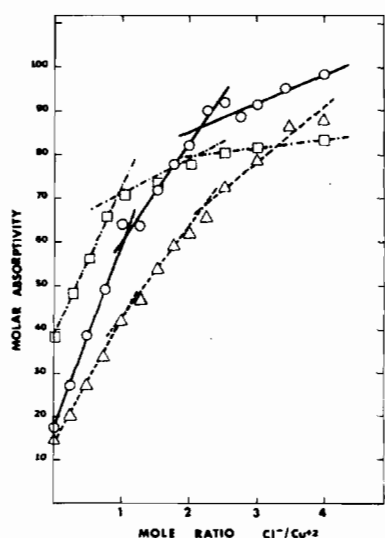

Figure 1. Molar absorptivity-mole ratio plots for mixtures of copper(II) and chloride in dimethyl sulfoxide maintained 0.1 *F* TEAP. —O—1100 nm, ---△---1300 nm, .—.□.—.— 1500 nm.

Both copper(II) perchlorate and copper(II) chloride obeyed Beer's law in the ultraviolet and infrared regions and it is assumed that the monochloro complex also obeys Beer's law. The stepwise formation constant for the monochlorocopper(II) complex can be obtained by the graphical method of Hildebrand and Benesi.[18] Plots of $[Cu^{2+}]$ $C_{Cl^-}/\Delta A$ *vs* $[Cu^{2+}]$ give straight lines of slope $1/\Delta\varepsilon$ and intercept of $1/\Delta\varepsilon$ K_{CuCl^+}, where C_{Cl^-} is the total chloride concentration, ΔA is the difference in the absorbance of the solution containing both complexed and uncomplexed copper(II) and the absorbance of the solution containing only the uncomplexed copper(II), $\Delta\varepsilon$ is the difference between the molar absorptivities of CuCl$^+$ and Cu^{2+}, and K_{CuCl^+} is the first stepwise formation constant. The constant obtained from the analysis of

the absorbance of solutions 5×10^{-4} *F* in copper(II) and 1×10^{-4} to 4×10^{-4} *F* in chloride at three wavelengths in the infrared region (1000 nm, 1100 nm, and 1300 nm, using a 10 cm cell) is $10^{4.4\pm0.1}$. The constant obtained from the analysis of absorbances of solutions 5×10^{-4} *F* in copper(II) and 1×10^{-4} to 4×10^{-4} *F* in chloride at three wavelengths in the ultraviolet region (330 nm, 340 nm, and 350 nm, using a 1 cm cell) is $10^{4.4\pm0.1}$ The second stepwise formation constant, K_{CuCl_2}, can be estimated if the assumption is made that at chloride to copper(II) ratios slightly over 1:1, only the monochloro and the dichlorocopper(II) complexes exist in appreciable concentrations. A plot of $[CuCl^+]$ $(C_{Cl^-} - [CuCl^+])/\Delta A$ *vs* $[CuCl^+]$ gives a straight line of slope $2/\Delta\varepsilon$ and an intercept of $1/\Delta\varepsilon$ K_{CuCl_2}, where all terms are as defined before and $\Delta\varepsilon$ is the difference between the molar absorptivities of CuCl$^+$ and CuCl$_2$. The formation constant K_{CuCl_2}, obtained from the analysis of solutions 4×10^{-3} *F* in copper(II) and 4×10^{-3} to 6.5×10^{-3} *F* chloride at three wavelengths in the infrared region (1000 nm, 1100 nm, and 1300 nm, using a 2 cm cell) is $10^{3.4\pm0.4}$. The error and the difficulty in obtaining straight lines for the plots are a probable indication that the trichloro complex exists in some concentration in this region. For this reason, the third stepwise formation consant, $K_{CuCl_3^-}$, could no be determined. The fourth stepwise formation constant $K_{CuCl_2^-}$, can be obtained from the data at 440 nm. Neither the concenteration of the tetrachlorocopper(II) complex nor the molar absorptivity is known. However, if experimental conditions are such that the formal chloride concentration is aproximately equal to the free chloride and the only species absorbing at 440 nm is the tetrachlorocopper(II) complex, the following can be shown:

$$1/K_{CuCl_4}{}^{2-} = \frac{[CuCl_3^-][Cl^-]}{[CuCl_4^{2-}]} = \frac{(C_{Cu^{2+}}+C_{Cl^-})\varepsilon_M b}{A} - C_{Cl^-}$$

where ε_M is the molar absorptivity of the tetrachloro complex, A is the absorbance of the complex at 440 nm, and b is the cell path lenght. Measurements on two or more solutions with the same formal copper(II) concentration but differing formal concentrations of chloride allow the resulting equations to be solved simultaneously for $K_{CuCl_4^{2-}}$ and ε_M. The value for the constant obtained in this manner is $10^{2.0\pm0.1}$ and the molar absorptivity is 8.8×10^2 liter mole^{-1} cm^{-1}.

No evidence for polynuclear complexes could be detected in the infrared or the far infrared.

Electrochemistry. Before the electrochemistry of copper(II)-chloro complexes can be investigated, the electrochemistry of copper(I) and copper(I)-chloro complexes must be studied.

Polarography of Copper(I)-Chloro Complexes. The reduction of copper(II) at the dropping mercury electrode (d.m.e.) in dimethyl sulfoxide proceeds by two single-electron reductions, the copper(II) to copper(I) reduction overlapping the copper(I) to copper-amalgam reduction. At high copper(II) concentrations (greater than $10^{-3}F$), maxima occur and the waves cannot be studied. At lower concentrations, the waves are well

(17) C. Furlani and G. Morpurgo, *Theoret. Chim. Acta* (Berl.), *1*, 102 (1963).
(18) H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc.*, *71*, 2703 (1949).

behaved and $E_{1/2}$ values may be obtained from the current-potential curves. Plots of $E_{d.m.e.}$ vs log $i/(i_d - i)$ for that part of the curve from $\frac{1}{2}i_d$ to i_d for the copper(I) to copper-amalgam reduction yield straight lines of average slope -0.059 ± 0.002 v (indicating a one-electron reduction) and an average $E_{1/2}$ for the copper(I)/copper-amalgam couple of -0.095v vs SCE. In the equation, i_d is the limiting current of the reduction step and i is the reduction current at a given potential. The oxidation of copper from a dropping copper amalgam electrode (d.a.e.) proceeds by two one-electron oxidations. Plots of $E_{d.a.e.}$ vs log $(i_d - i)/i$ for the region up to $\frac{1}{2}i_d$ for the oxidation of copper to copper(I) give straight lines with an average slope of -0.062 ± 0.002 v and an average $E_{1/2}$ for the copper(I)/copper-amalgam of -0.088 ± 0.005 v vs S.C.E. In the presence of excess chloride, the cathodic wave for the copper(I)/copper-amalgam step shifts to a more negative potential and assumes a more irreversible shape as indicated by slopes greater than -0.059 v for plots of $E_{d.m.e.}$ vs log $i/(i_d - i)$; typical slopes are -0.077 v in 0.15 F chloride and -0.081 v in 0.25 F chloride. Slopes reflecting a more reversible electrochemical process are not obtained from the $E_{d.m.e}$ vs log $i/(i_d - i)$ plot of data from the foot of the wave as was done for copper(I) in acetonitrile.[1] The use of the dropping amalgam electrode did not improve the reversibility.

For reversible systems, the formulas and the overall formation constants for the complexes may be evaluated from the expression below for the dependency of the $E_{1/2}$ on the ligand concentration: The K's are

$$(E_{1/2})_c - (E_{1/2})_s = -0.059 \log\{1 + K_1[Cl^-] + ... + K_1...K_p[Cl^-]^p\}[19]$$

stepwise formation constants, p is the maximum number of ligands complexed to the metal, and $(E_{1/2})_c$ and $(E_{1/2})_s$ represent the half-wave potentials of the complexed metal and the uncomplexed metal, respectively. Similar plots for the quasi-reversible copper(I) chloride system in dimethyl sulfoxide may lead to the establishment of the formulas and to rough approximations of the formation constants of the complexes. Plots of $(E_{1/2})_c - (E_{1/2})_s$ vs pCl for solutions which are 10^{-4} F in copper(I) and 10^{-3} to 2.5×10^{-1} F in chloride give slopes typically from 0.107 to 0.123 v, indicating the presence of the dichlorocopper(I) complex in this range of chloride concentration. The overall formation constant $\beta_{CuCl_2^-}$ evaluated from these plots is $10^{12.4 \pm 0.2}$. Similar plots using the oxidation of the copper-amalgam dropping electrode into solutions ranging from 7.5×10^{-2} to 1.25×10^{-1} F chloride gave slopes ranging from 0.075 to 0.125 v and overall formation constants from $10^{10.2}$ to $10^{12.2}$.

Potentiometric Study of Copper(I)-Chloro Complexes. The stepwise and overall formation constants for the copper(I)-chloro complexes were evaluated from data obtained by the potentiometric titration of copper(I) with chloride. Typically, copper(I) solutions in the concentration range of 10^{-3} to 10^{-2} F

(19) H.A. Laitinen, «Chemical Analysis», Mc Graw Hill Book Co., Inc., New York, N.Y., 1960, p. 236.

were titrated with about 2×10^{-1} F tetraethylammonium chloride solutions and followed by a copper wire electrode or a copper-amalgam pool electrode. The Nernstian parameters of the indicating electrodes were determined by recording the potentials of a series of copper(I) solutions of known concentrations. The slope of $E_{Cu(Hg)}$ vs log $[Cu^+]$ plots for the amalgam pool electrode was 0.058 ± 0.001 v and the formal standard potential, $E^{o'}$, was 0.135 ± 0.001 v vs the "DMSO" reference. For the copper wire electrode, the slope was 0.060 ± 0.001 v and the formal standard potential was 0.235 ± 0.003 v vs the "DMSO" reference electrode. The titration curves show one break at a chloride to copper(I) ratio of 2:1, indicating that the first and second stepwise formation constants are of the same order of magnitude. From the potential data beyond the endpoint break, the value for the overall formation constant, $\beta_{CuCl_2^-}$, was calculated to be $10^{12.19 \pm 0.02}$ for the copper-amalgam pool data and $10^{12.1 \pm 0.1}$ for the copper wire data, in excellent agreement with the value obtained by voltammetry. No indication of the formation of higher order complexes was observed in solutions containing up to 100:1 chloride to copper(I) ratios. The first and second stepwise formation constants may be calculated from the potential data of the titration before the endpoint. If the free chloride concentration is assumed to be negligible in this region, the following relationships hold: The uncomplexed copper(I) is

$$C_{Cu(I)} = [Cu^+][CuCl] + [CuCl_2^-]$$

$$C_{Cl^-} = [CuCl] + 2[CuCl_2^-]$$

calculated from the Nernst expression, and the concentrations of the other complex species are calculated from the above expressions. The uncomplexed chloride can be calculated from the overall formation constant and the concentrations of free copper(I) and dichlorocopper(I), which gives all of the information needed to establish the stepwise formation constants. Using the value of $10^{12.19}$ for the overall formation constant, the average value for the first stepwise formation constant, K_{CuCl}, of $10^{5.68 \pm 0.04}$ was obtained from the copper-amalgam data. The value for the second stepwise formation constant, $K_{CuCl_2^-}$, is $10^{6.51}$. Potential data for the copper wire electrode before the endpoint did not give reproducible results.

Potentiometric Study of Copper(II)-Chloro Complexes. Titrations of copper(II) with chloride were followed by a cupric ion selective electrode or a chloride ion selective electrode. The titration followed by the cupric ion electrode showed one break at a chloride to copper(II) ratio of 3:1 (Figure 2). The 0.400 v break at a 3:1 ratio suggests that three complexes exist over the stoichiometric chloride to copper(II) ratios covered by the titration, and that the three stepwise formation constants must be of nearly the same order of magnitude and larger than the fourth constant. Efforts to establish the overall formation constant $\beta_{CuCl_3^-}$ from potentials beyond the endpoint were unsuccessful, probably due to the response of the electrode at very low uncomplexed copper(II)

concentrations. The stepwise formation constants, K_{CuCl}^+, K_{CuCl_2}, and K_{CuCl_3}, were determined by potential measurement using the chloride ion specific electrode. The Nernstian parameters of the chloride electrode were determined by measurement of the potentials of a series of solutions of known chloride concentration in dimethyl sulfoxide. The slope of a E_{Cl^-} vs log $[Cl^-]$ plot was -0.061 ± 0.001 v and the formal standard potential was -0.162 ± 0.001 v vs the "DMSO" reference electrode.
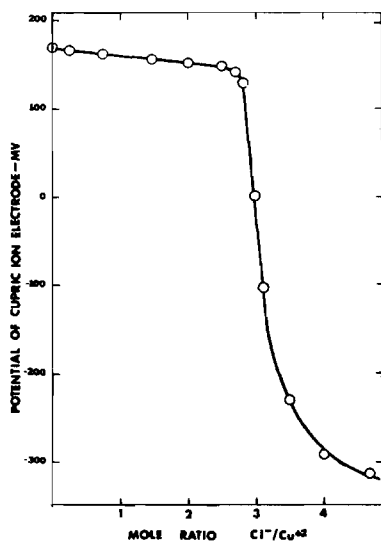

Figure 2. Titration curve of 7×10^{-3} F copper(II) in dimethyl sulfoxide with 0.153 F TEACl. The potential is followed with an Orion Model 94-29A cupric ion selective electrode.

The chloride potential data may be analyzed by a graphical degree of formation, or ligand number, method.[20] Spectroscopic data would suggest that at chloride to copper(II) ratios less than 1:1, only one complex, $CuCl^+$, exists in appreciable concentration, The following relationship should hold: where $\bar{n}$,

$$\log \bar{n}/(1-\bar{n}) = \log K_{CuCl^+} + \log[Cl^-]$$

the ligand number, is: (total complexed chloride)/ (total copper(II)). The uncomplexed chloride concentration is calculated from the potential and Nernst equation for the chloride ion selective electrode, $\bar{n}$ is calculated from the formal chloride concentration, the formal copper(II) concentration, and the free chloride concentration. The first stepwise formation constant, evaluated from the intercept of log $\bar{n}/(1 - \bar{n})$ vs log $[Cl^-]$ plots in which the $\bar{n}$'s were less than 0.6, is $10^{4.3 \pm 0.1}$, in good agreement with the constant obtained from spectrophotometric data. The second and third formation constants can be obtained from plots of

$$(\bar{n}-(1-\bar{n})\beta_{CuCl^+}[Cl^-])/(2-\bar{n})[Cl^-]^2 \ vs$$
$$(3-\bar{n})[Cl^-]/(2-\bar{n});$$

(20) F.J.C. Rossotti and H.S. Rossotti, *Acta Chem. Scand.*, 9, 1166 (1955).

the slope of the resulting straight line is β_{CuCl_3} and the intercept is β_{CuCl_2}. The second stepwise formation constant calculated from these plots and from the first stepwise formation constants is $10^{3.0 \pm 0.1}$ and the third stepwise formation constant is $10^{4.0 \pm 0.5}$. The second stepwise formation constant is within the experimental limits of the value obtained from the spectrophotometric method.

Potentiometric Study of Mixtures of Copper(II) and Copper(I). Mixtures of copper(II) and copper(I) were titrated with chloride and the potential followed with a platinum indicating electrode. The Nernstian parameters of the platinum electrode were determined from plots of E_{Pt} vs log $[Cu^I]/[Cu^{II}]$. The plots were linear with slopes of -0.060 ± 0.005 v and with formal standard potentials of 0.059 ± 0.013 v vs the "DMSO" reference electrode. The titration curve shows a single, large break to more positive potentials at a ratio of chloride to copper(I) of 2:1 (Figure 3), indicating complexation of copper(I); as more chloride is added and the copper(II) becomes complexed the potential levels off and begins to drop, indicating that the trichlorocopper(II) complex must exist in appreciable amount at the high stoichiometric ratios of chloride to copper(II).
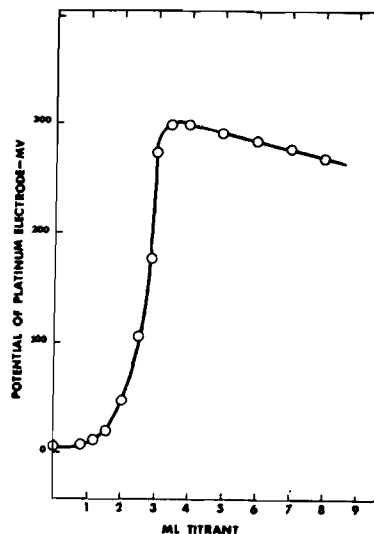

Figure 3. Titration of 16.00 ml of a solution 2.3×10^{-2} F in copper(I) and 3.2×10^{-3} F in copper(II) in dimethyl sulfoxide with 0.268 F TEACl. The potential is followed with a platinum electrode.

The stepwise formation constants for the copper-(I)-chloro complexes may be calculated in the same manner as those calculated from the copper-amalgam potentiometric data if an overall formation canstant, β_{CuCl_2}, is assumed. It the same overall formation constant used in the copper-amalgam calculation is used, the stepwise formation constants are found to be $10^{6.2 \pm 0.05}$ and $10^{6.0 \pm 0.05}$.

The stepwise formation constants for the copper-(II)-chloro complexes cannot be calculated from the data since previous work has indicated that the

first three constants are large and of nearly the same order of magnitude. However the overall formation constant for the trichloro complex may be evaluated from potentials beyond the 3:1 chloride to copper(II) ratio by plotting the E_{Pt} vs log [Cl$^-$]. In the limit of high formal chloride concentration, the added chloride concentration is the same as the free chloride concentration, and the plot of potential vs log [Cl$^-$] should be a straight line of slope $-(n - 2)$ 0.059 v and an intercept of:

$$E^{0'} + (n-2) \ 0.059 \ \log \ \beta_{CuCl_3^-} - (n-2) \ 0.059 \ \log \ \beta_{CuCl_n^{2-n}}.$$

The experimental slope is -0.060 v, indicating that n is 3 and the complex formed is $CuCl_3^-$. The overall formation constant obtained from the plots is $10^{9.3\pm0.3}$.

Discussion

The average value for the overall formation constant of $CuCl_2^-$ obtained from polarography ($10^{12.4\pm0.2}$), copper wire potentiometry ($10^{12.1\pm0.1}$), and copper-amalgam potentiometry ($10^{12.19\pm0.2}$) is $10^{12.2\pm0.1}$, in agreement with the value of $10^{11.95\pm0.1}$ obtained by Le Demezet and coworkers.[7] The values for the first stepwise formation constant, K_{CuCl}, obtained from copper-amalgam potentiometry and from platinum wire potentiometry are $10^{5.68\pm0.04}$ and $10^{6.2\pm0.05}$, respectively. The average of the two is $10^{6.2\pm0.2}$, in excellent agreement with the value of $10^{6.0\pm0.5}$ from Le Demezet and coworkers.[7]

The reduction of copper(I) at the d.m.e. in dimethyl sulfoxide (0.1 F TEAP) proceeds at -0.095 v vs S.C.E., more positive than the -0.32 v vs S.C.E. potential in acetonitrile (0.1 F TEAP).[1] The reduction potential of ferrocene in acetonitrile (0.1F TEAP), measured against a saturated aqueous calomel electrode, is about 0.1 v more positive than the reduction of ferrocene in dimethyl sulfoxide (0.1 F TEAP), also measured against a saturated aqueous calomel electrode.[21] This difference represents the difference in junction potentials for the saturated aqueous calomel electrode in the two solutions. Therefore, part of the difference between the reduction potentials of copper(I) in the two solvents must be due to this change in junction potential, but the rest must be due to solvation effects. This suggests that copper(I) is more solvated in acetonitrile than in dimethyl sulfoxide since it is more difficult to reduce in the former solvent. The stronger solvation of copper(I) in acetonitrile is reflected in the first stepwise formation constants for the complex in the two solvents. The constant in acetonitrile ($K_{CuCl} = 10^{4.3}$) is smaller than the corresponding constant in dimethyl sulfoxide ($K_{CuCl} = 10^{6.0}$). Acetonitrile complexes the copper(I) more strongly, shifting the complex formation equilibrium to the dissolution side. The second stepwise formation constants are the same ($K_{CuCl_2} = 10^{6.2}$ in dimethylsulfoxide and $10^{5.9}$ in acetonitrile), indicating that the solvent probably plays little part in the second

equilibrium. This would be expected if the main solvent interaction were with the cation.

The average value for the first formation constant of the monochlorocopper(II) complex in dimethyl sulfoxide obtained from ultraviolet and infrared data, and potentiometry with the chloride ion selective electrode is $10^{4.4\pm0.1}$. The value obtained by Le Demezet and coworkers[7] is $10^{4.5}$; no estimation of uncertainty was given. The second stepwise formation constant was calculated to be $10^{3.4\pm0.4}$ from spectrophotometric data. By potentiometric means, the second stepwise formation constant was determined to be $10^{3.0\pm0.1}$. The value of the second stepwise formation constant obtained from the data of Le Demezet and coworkers[7] was $10^{3.0}$. From β_{CuCl_3} values obtained from potentiometric methods, $10^{11.3}$ from the chloride selective electrode data and $10^{9.3}$ from platinum data, values of $10^{4.0}$ and $10^{1.6}$ were obtained for the stepwise formation constant $K_{CuCl_3^-}$. The cupric ion selective electrode data and the spectrophotometric data suggest that a value of $10^{1.6}$ would be too small for the third stepwise formation constant. The data suggest that the three formation constants must be of nearly the same order of magnitude and the value would be expected to be slightly higher than 10^3. The value obtained from the potentiometric chloride data, $10^{4.0}$, may be high, since errors accumulate in the higher order constants calculated by this technique. The value obtained by Le Demezet and coworkers[7] by potentiometric titration using a platinum electrode is $10^{1.6}$, in agreement with the value obtained by platinum potentiometry in this work. The value of the fourth stepwise formation constant obtained by spectrophotometry is $10^{2.0\pm0.1}$. This lends further evidence to the suggestion that $10^{1.6}$ is a low value for the third stepwise formation constant, since the first three constants should be larger than the fourth, as suggested by the data obtained with the cupric ion selective electrode.

The formation constants for the copper(II)-chloro complexes in acetonitrile are $10^{9.7}$, $10^{7.9}$, $10^{7.1}$, and $10^{3.7}$, each larger than the corresponding stepwise formation constants in dimethyl sulfoxide.[1] If, as in the case of copper(I), the solvation of the cation greatly affects the complex formation equilibrium, it can be concluded that copper(II) is solvated more strongly by dimethyl sulfoxide than by acetonitrile. Since copper(II) would have six solvent molecules in the primary coordination sphere,[16] and the addition of one chloride would displace one solvent molecule, all stepwise complex formation equilibria would show this solvent effect.

It is interesting to note that the solvation of copper(I) and silver(I) in dimethyl sulfoxide and in acetonitrile differ in that copper(I) is solvated more strongly by acetonitrile while silver(I) is more strongly solvated by dimethyl sulfoxide.

In summary, the stepwise formation constants of copper(I) and copper(II) in dimethyl sulfoxide were determined by spectrophotometric and electrochemical techniques. The values obtained for copper(I) are: $K_{CuCl} = 10^{6.0\pm0.2}$, $K_{CuCl_2} = 10^{6.2\pm0.2}$; for copper(II): $K_{CuCl^+} = 10^{4.4\pm0.1}$, $K_{CuCl_2} = 10^{3.0\pm0.1}$ $K_{CuCl_3} =$

(21) W.C. Boring, Ph.D. Thesis, Kansas University, Lawrence, Kansas, 1972.

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$10^{4.0\pm0.5}$ and $10^{1.6\pm0.3}$, $K_{CuCl_4^{2-}} = 10^{2.0\pm0.1}$. It is to be noted that these values are formal formation constants in which ion-pairing of the type Cu^{2+}, ClO_4^-, or $(C_2H_5)_4N^+$, $CuCl_2^-$, has been neglected.