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Stability, Electronic Spectra, and Structure of the Copper(II) Chloride Complexes in *N*,*N*-Dimethylformamide

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The stability constants and the electronic spectra of three copper(II)–chloro complexes formed in dimethylformamide (DMF) solutions of constant 1 M ionic strength have been calculated. The spectrophotometric measurements were performed at wavelengths ranging from 260 to 500 nm and in the near-infrared from 700 to 1600 nm. The matrix rank treatment of more than 1000 spectrophotometric data demonstrates a minimum of four absorbing species: one free copper and three chloro complexes. An original computer program, based upon a combined linear least-squares and a Marquardt method, has been written and used to calculate the stability constants and the extinction coefficients of the complexes at different wavelengths. The overall apparent stability constants β_1, β_3, and β_4 of $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$, respectively, were found to be many orders of magnitude higher than in water: $\log \beta_1 = 3.76$ [illegible] 0.13; $\log \beta_3 = 9.78 \pm 0.18$; $\log \beta_4 = 10.78 \pm 0.17$. The absence of $CuCl_2$ can be accounted for by auto complex formation, leading to $CuCl^+$ and $CuCl_3^-$. Compared to those of aqueous solutions, the charge-transfer bands of the chloro complexes are shifted from 20 to 40 nm toward higher wavelengths. In the near-infrared range, the positions of the maxima of the d–d transition bands demonstrate a D_{4h} configuration for $CuCl(DMF)_3^+$ ($\lambda_{max} = 870$ nm) and the D_{2d} configuration of a flattened tetrahedron for $CuCl_3(DMF)^-$ and $CuCl_4^{2-}$, absorbing respectively at 1100 and 1200 nm.

Introduction

Aqueous copper(II) chloride solutions were recently studied by Khan and Schwing,[1] who concluded that four successive mononuclear species were present simultaneously absorbing between 240 and 380 nm and above 600 nm. The first three complexes $CuCl^+$, $CuCl_2$, and $CuCl_3^-$ have only one absorption band in the UV region respectively at 250 nm for $CuCl^+$ and $CuCl_2$ and at 270 nm for $CuCl_3^-$. $CuCl_4^{2-}$ was found to have three peaks at 240, at 265–270, and at 370–380 nm.

This work concerns the formation of copper(II) chloride complexes in a nonaqueous solvent, dimethylformamide (DMF) which has a still high dielectric constant ($\epsilon = 36$) and a Gutmann donor number (DN = 26.6) comparable to that of water (DN = 18). It is part of our general investigation of the influence of the nature of the solvent upon the nature, stability, and structure of the chlorocuprates. Spectrophotometric investigation of the UV, visible, and near-infrared regions makes possible the calculation of the electronic spectra of each individual species and, thus, provides information about the solvation of the copper(II)–chloro complexes in DMF.

The basic knowledge of copper complexes in nonaqueous media and the understanding of the particular influence of these nonaqueous solvents upon the characteristics of the individual species are actually of major importance in organic synthesis and catalytic reactions.

The monomeric copper(II) chloride species have been intensively studied in the solid state; the structures are generally correlated to the nature of the cations with corresponding distorted octahedral or flattened tetrahedral copper(II) ion configurations (D_{4h} or D_{2d} symmetry). Most of the results have been given for the tetrachlorocuprate anions with attribution of the charge-transfer and the d–d transition bands.[2–5]

Comparison of the solid-state studies with comparable solution results sometimes leads to interesting identical qualitative conclusions.[6–8] Furlani and Morpurgo postulated the D_{2d} symmetry for the tetrachlorocuprates, as they found comparable charge-transfer and d–d transition band spectra in the solid state and in some solvents such as nitromethane, acetonitrile, and dimethylformamide.[7]

Gutmann and co-workers have shown, spectrophotometrically, the existence of four chloro complexes in dimethylformamide,[9] in acetonitrile and in trimethyl phosphate.[10] They postulated a very small stepwise formation constant for $CuCl_2$ and suggested relative magnitudes for the other species' constants.

Potentiometric data have been obtained in dimethyl sulfoxide for copper(I)– and copper(II)–chloro complexes with identification of $CuCl^+$, $CuCl_2$, and $CuCl_3^-$;[11] this three-complex model has also been proposed by Scharff,[12] from potentiometric and spectrophotometric data, by using the molar ratio method for solutions of copper(II) chloride in propylene carbonate.

Manahan and Iwamoto concluded that values of stepwise formation constants of $CuCl^+$ and $CuCl_2$ in acetonitrile are quite high.[13]

Sawada and co-workers suggested band assignments for $CuCl_3^-$ and $CuCl_4^{2-}$ in acetic acid, though calculations were performed at only one wavelength.[14]

These conclusions have been compared to results obtained in the solid state and in some solvents by Katzin, who has studied the promotion from the octahedral to the tetrahedral configuration of the first transition elements' chlorides and the corresponding absorption changes.[15]

This review shows the limited and particular nature of the description of the copper(II) chloride species: incomplete and sometimes contradictory detection of the chlorocuprates, variable assignment of the absorption bands not corresponding always to the same product, and little information on the stability of the species present in the different media. Rigorous conclusions are obtained for the copper(II) chloride species in the solid state, but the comparisons with the liquid-state

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measurements produce, again, various and different interpretations for the same constituents.

In this work, the solvent effect on the copper(II)–chloro complexes will be based on a quantitative point of view, considering the nature, stability, and electronic spectra of each individual species. Our study's conclusions are obtained from an analysis of the largest range of spectrophotometric data possible for this system. All UV, visible, and near-infrared measurements have contributed to the knowledge of quantitative characteristics of each chlorocuprate defined in the DMF–copper(II) chloride solutions. This kind of investigation has the difficulties inherent in spectrophotometric data analysis used to calculate equilibrium constants and electronic spectra of individual species. These have been discussed elsewhere.[16,17] In spite of these problems, in this study of the effects of the solvation of the copper(II) species on the electronic spectra of the chlorocuprates, we show how quantitative conclusions can be well established from a very large set of optical density data.

Experimental Section

Reagents. The dimethylformamide (DMF) (Fluka) was used after distillation under reduced pressure at less than 80 °C, the temperature limit above which DMF starts to decompose; the residual water (280 ppm) in the solvent has no effect on the stability of the copper chloride solution spectra. The important absorption of DMF under 260 nm was the limit of the wavelength range used. The DMF purity was controlled by conductivity measurements as recommended by Juillard.[18]

Lithium chloride and perchlorate (Merck) were dried and used without further purification. The choice of the lithium salts was related to the higher solubility at 25 °C of LiCl as opposed to sodium or tetraethylammonium chloride.

The solid $[Cu(DMF)_x](ClO_4)_2$ was prepared by gentle heating under reduced pressure of DMF containing a definite amount of $Cu(ClO_4)_2 \cdot 6H_2O$ (Alfa). The separated solid was dissolved in successively smaller volumes of pure DMF, and the solution was distilled again. After five or six distillations, the residual solution was cooled and green-blue crystals appeared. The solid was dried and microanalysis showed that x had the value of 4 or 6 depending on the temperature of the cooling bath, as already noted by Schneider.[19] For our study, the concentration of the copper(II) salt in the copper chloride solution was 5×10^{-4} M. The stock solution of $[Cu(DMF)_4](ClO_4)_2$ was standardized by EDTA at pH 9.5 with murexide, giving a result independent of the water content.[20] During the experiments, the concentration of the chloride ion ranged from 5×10^{-4} to 0.6 M and the 1 M ionic strength was maintained constant with lithium perchlorate. These experimental conditions gave a satisfactory scale of optical density measurements with a 1-cm cell in the UV–visible wavelength range and allowed us to neglect the formation of polynuclear species. For the near-infrared measurements, the copper(II) concentration $[Cu^{2+}]$ was augmented to 10^{-2} M and the $[Cl^-]$ ranged from 10^{-2} to 1 M. The spectrophotometric reference solution was the same over the entire concentration range and contained 0.5 molar equiv of lithium perchlorate and chloride.

As the DMF–copper(II) chloride solutions were stable only for a short time, each solution was prepared by dilution of the stock solution, the free copper(II) ion being added just prior the spectrophotometric measurements. The color of the copper(II) chloride mixtures changed from greenish yellow to dark yellow as chloride ion concentration increased.

The optical densities were obtained with a Cary 17D (Varian) instrument equipped with a Cary digital interfacing and a "PERIFERIC ZIP 30" rapid printer and puncher which records the data at each selected wavelength. The numerical treatment of the data was performed from a home terminal by an UNIVAC 1110 computer. The absorption of the solutions was both registered and punched at selected wavelengths in the UV–visible range from 260 to 550 nm and from 700 to 1600 nm in the near-infrared (in general each 10 nm).

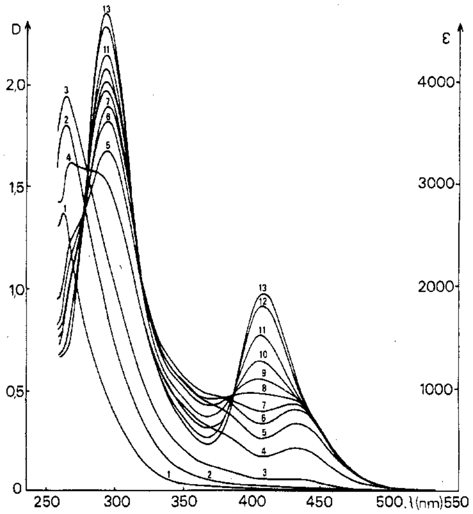

Figure 1. UV–visible absorption curves of DMF–copper(II) chloride solutions ($[Cu^{2+}]_{solvated} = 5 \times 10^{-4}$ M). Spectrum/$[Cl^-]$: 1/0, 2/5 $\times 10^{-4}$ M, 3/10^{-3} M, 4/2 $\times 10^{-3}$ M, 5/4 $\times 10^{-3}$ M, 6/10^{-2} M, 7/2 $\times 10^{-2}$ M, 8/4 $\times 10^{-2}$ M, 9/6 $\times 10^{-2}$ M, 10/10^{-1} M, 11/2 $\times 10^{-1}$ M, 12/4 $\times 10^{-1}$ M, 13/6 $\times 10^{-1}$ M.

Results and Discussion

(a) Spectra of the Copper(II) Chloride–DMF Solutions. The absorption variations, depending on the analytical chloride ion concentration C, are presented in Figure 1. We notice an absorption band maximum at 262 nm for the pure solvate $[Cu(DMF)_4]^{2+}$: the symmetrical part of the visible expanded tail under 260 nm is hidden by the solvent absorption (spectrum 1). For the stoichiometric mixture, $[Cu^{2+}] = [Cl^-] = 5 \times 10^{-4}$ M, the spectrum maximum shifts toward 268 nm and its intensity increases to reach a maximum value when $C = 10^{-3}$ M (spectra 2, 3). This maximum corresponds to the formation of another species, $CuCl^+$, probably predominant at this chloride ion concentration over more coordinated species. A very broad peak appears at 435 nm, and the variation of spectra 2 and 3 between 350 and 410 nm suggests a shoulder formation probably around 385 nm, characteristic of a new complex. When the chloride concentration is increased, the maximum at 268 nm decreases, and when $C = 2 \times 10^{-3}$ M (spectrum 4), a new absorption band maximum around 295 nm distinctly appears. This feature becomes most apparent when C reaches the value of 4×10^{-2} M. The peak's intensities increase regularly, and the maxima are stabilized at 296, 385, and 435 nm (spectra 4–7). When C is higher than 0.040 M, the two maxima at 385 and 435 nm coalesce and a single band maximum forms at 411 nm. Then, again upon an increase in the chloride ion concentration, an identical feature of the spectra is observed with the two maxima at 296 and 411 nm, as seen on spectrum 13 when C reaches 0.6 M. These two absorption maxima are characteristic of the most highly coordinated species, $CuCl_4^{2-}$, as will be discussed later. The extinction coefficients measured for the highest chloride ion concentration ($\simeq 3$ M) are 5060 $M^{-1}\,cm^{-1}$ at 296 nm and 2220 $M^{-1}\,cm^{-1}$ at 411 nm. Four isosbestic points can be observed on the experimental spectra: 280, 317, 387, and 445 nm (Figure 1, spectra 8–13); they all characterize two absorbing species present in the mixture, but a third, hidden, complex which depends on the chloride ion concentration seems to be always present.

The near-infrared spectra are recorded up to 1600 nm: beyond this value, no further significant absorption nor maxima variations are noted with increasing chloride ion concentration.

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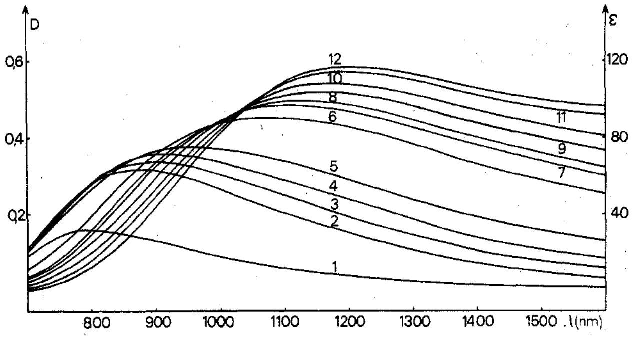

Figure 2. Near-infrared absorption curves of DMF–copper(II) chloride solutions ($[Cu^{2+}]_{solvated} = 10^{-2}$ M). Spectrum/[Cl^-]: 1/0, 2/10^{-2} M, 3/1.3 × 10^{-2} M, 4/1.6 × 10^{-2} M, 5/2 × 10^{-2} M, 6/3 × 10^{-2} M, 7/4 × 10^{-2} M, 8/5 × 10^{-2} M, 9/10^{-1} M, 10/2 × 10^{-1} M, 11/5 × 10^{-1} M, 12/1 M.

In the 700–1600 nm wavelength range, the spectra show a regular shift of the absorption maximum from 790 to 1200 nm. The solvated copper(II) ion has an absorption maximum at 790 nm, characteristic of the copper(II) ion in a square-planar structure. For higher chloride ion concentration, this maximum shifts to 1200 nm. For $C = 0.5$ M or greater it remains stable, even when the chloride ion reaches the solubility limit in DMF, roughly 3 M. This band is then characteristic of the most chloride-substituted complex.

(b) Numerical Analysis of the Optical Densities, $D_{i_{exptl}}$. The optical density variations were plotted, for each wavelength between 260 and 550 nm and also between 700 and 1600 nm, as a function of the chloride ion concentration. These experimental plots were used to get N optical density values for each selected wavelength, $D_{i_{exptl}}$, for the computation. Finally, we considered a set of 25 wavelengths in the UV–visible range with $N = 43$ for each wavelength; in the near-infrared range 15 wavelengths, with $N = 17$, were taken into account. The computation analysis was undertaken for the whole set of 1330 experimental values.

(c) Number of Chloro Complexes. Hugus and El-Awady[21] have recently described a matrix rank method for determining the minimum number of absorbing species present in a mixture. This analysis is obtained from a set of $N \times L$ data, where L is the number of wavelengths, and requires only N larger than L, i.e., more optical density values than wavelengths. The matrix rank treament applied to the two sets of our 1075 UV–visible and our 255 infrared data led clearly to a minimum of four individual absorbing species. Consequently, the quantitative interpretation of the whole set of data implied a minimum of three copper(II)–chloro complexes, the fourth absorbing species being the free solvated copper(II) ion.

(d) Theoretical Expressions and Calculated Models. For the mathematical treatment, we used two parameters, β_j and ϵ_j, respectively, the overall formation constants and the specific extinction coefficients of the successive mononuclear complexes. The analytical expressions concerning the conservation of mass, the theoretical optical density, $D_{i_{th}}$, and the free-ligand concentration, c, have been previously reported for spectrophotometric studies of comparable systems.[1,16] Nevertheless, we recall that for each wavelength l, the S_l function of the parameters β_j and ϵ_j, in terms of the free-ligand concentration c, is expressed by

$$S_l = S_l(\beta_j,\epsilon_j,c_i) = \sum_{i=1}^{N}\left(\frac{D_{i_{exptl}} - D_{i_{th}}}{D_{i_{exptl}}}\right)^2 \qquad (1)$$

The corresponding standard deviation σ_l describes the relative agreement between experimental and calculated optical density values of each wavelength. There is a final criterion which must be taken into account for the whole set of data. The quadratic mean, σ, must be expressed in terms of σ_l and L:

$$\sigma = \left(\frac{\sum_{l=1}^{L}\sigma_l^2}{L}\right)^{1/2} \qquad (2)$$

The order of magnitude of σ is the statistical criterion for the model which best represents physical reality. The computer analysis for the determination of the best β_j and ϵ_j values, over all the spectrum in the UV–visible and near-infrared ranges, was based upon an original computer program recently developed by us and reported elsewhere.[17] This program combines a classical least-squares method analytically expressed by Byē et al.[22] and a Marquardt method[23] which enhances the process of reaching the minimum of S_l. The computation was performed for three different models which seemed the most reasonable for the spectrophotometric evidence after the matrix rank analysis. These models are represented as follows. [1,2,3]: three successive species, $CuCl^+$, $CuCl_2$, and $CuCl_3^-$, qualitatively proposed by Scharff in propylene carbonate solutions[7] and quantitatively by Courtot in Me_2SO solutions.[11] [1,3,4]: these species are $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$, which are in agreement with Gutmann's postulated model, with a negligible presence of $CuCl_2$.[9] [1,2,3,4]: four successive species, $CuCl^+$, $CuCl_2$, $CuCl_3^-$, and $CuCl_4^{2-}$, proposed in aqueous solutions by Khan and Schwing.[1]

(e) Stability Constants of the DMF–Copper(II) Chloride Complexes. All the results of the computation are reported in Table I. σ_1 and σ_2 correspond to the computational analysis of UV–visible and near-infrared data, respectively. The value reported in the last line of Table I is the average of σ_1 and σ_2 and refers to the 1330 data used over the whole spectrum.

Table I. Numerical Conclusions of the Theoretical Models for the DMF–Copper(II) Chloride Solutions

	[1,2,3]	[1,3,4]	[1,2,3,4]
$\log \beta_1$	3.15 ± 0.09	3.76 ± 0.13	4.41 ± 0.10
$\log \beta_2$	6.01 ± 0.15		8.98 ± 0.09
$\log \beta_3$	7.04 ± 0.16	9.78 ± 0.18	12.04 ± 0.16
$\log \beta_4$		10.78 ± 0.17	12.94 ± 0.14
σ_1(UV-visible)	0.064	0.038	0.015
σ_2(IR)	0.075	0.035	0.037
σ	0.068	0.036	0.026

The more complicated the model, the lower the σ_1 value in the UV–visible as expected. But this result is not in agreement with the σ_2 values which do not decrease regularly: the presence of four successive species does not lead necessarily to a better quantitative conclusion. Consequently, the rough infrared results favor the [1,3,4] model. Considering the [1,3,4] and the [1,2,3,4] models for the whole UV–visible–IR area, there is obviously no significant difference between the two σ values, compared to the drastic higher σ obtained for the [1,2,3] model. Despite the more favorable numerical result for the [1,2,3,4] model, the [1,3,4] model can also be considered as satisfactory with σ equal to 0.036. Finally, when two or several models lead to comparable σ values, the simplest model, involving in this case the $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$ species, is taken as the best quantitative conclusion. But this result will be confirmed by other, following, considerations.

All the β_j have been calculated with an incertitude corresponding to a 95% confidence interval; the log β_j values, in

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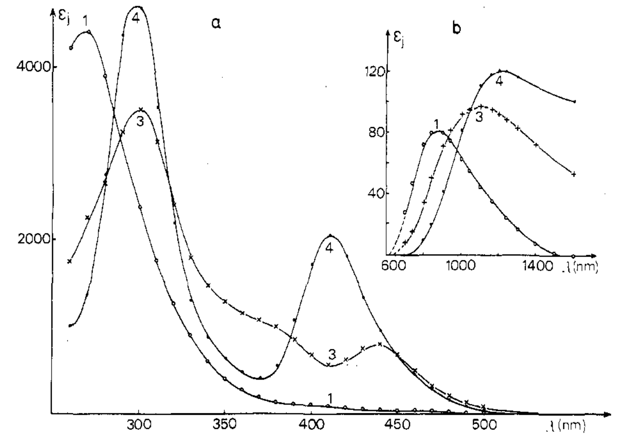


Figure 3. Electronic spectra of DMF–copper(II) chloride complexes $CuCl^+$ (1), $CuCl_3^-$ (3), and $CuCl_4^{2-}$ (4): (a) UV–visible region; (b) near-infrared region.

the case of the [1,3,4] model, are log $\beta_1 = 3.76 \pm 0.13$, log $\beta_3 = 9.78 \pm 0.18$, and log $\beta_4 = 10.78 \pm 0.17$.

In addition, the computation results show clearly that quantitative conclusions from spectrophotometric data must be obtained according to the following rules: First, the absorption data representing the whole spectrum must be computed; a one- or two-wavelength treatment leads necessarily to an approximate result and can even give erroneous conclusions. Second, a proposed qualitative model has to be challenged by several other models to ensure the uniqueness of the quantitative model. Third, it is necessary to compare the features of the calculated spectra with those of the experimental one in order to eliminate the so-called "computer species".

(f) Electronic Spectra of the DMF–Copper(II) Chloride Complexes. The electronic spectra of the individual chloro complexes obtained from the DMF–copper(II) chloride solutions for the [1,3,4] model are plotted in Figure 3a (UV–visible). The following characteristics should be noted.

$CuCl^+$: the spectrum shows its band maximum at 268 nm with an extinction coefficient of 4440 M^{-1} cm^{-1}. The UV part of this calculated spectrum under 260 nm is hidden by the solvent absorption. The visible part of the $CuCl^+$ spectrum shows an expanded branch with a very low absorption between 400 and 500 nm. A very small shoulder is located around 400 nm: this band is reported but not identified by Katzin.[15]

$CuCl_3^-$: the calculated spectrum presents an absorption maximum at 300 nm (3520 M^{-1} cm^{-1}) and a second maximum of lower intensity at 440 nm (820 M^{-1} cm^{-1}). This spectrum is also characterized by a large shoulder around 380 nm (1000 M^{-1} cm^{-1}). Thus, the UV–visible spectrum of $CuCl_3^-$ obtained from DMF solutions could be split up into at least three Gaussian functions.

$CuCl_4^{2-}$: the tetracoordinated complex has a UV–visible spectrum with two intensive maxima at 296 nm (4700 M^{-1} cm^{-1}) and 411 (2080). These peaks are reported and identified for the tetrachlorocuprate complex in other solvents and in the solid state.[7,13]

(i) Whatever the model used the calculated absorption maxima for the two most highly coordinated chloro complexes are surprisingly very close, despite highly different stability constants. Comparing the three-complex model to the four-complex one, the calculated spectrum of $CuCl^+$ in [1,2,3] or [1,3,4] is, in the [1,2,3,4] model, geometrically divided between two superimposed Gaussian functions both centered at 268 nm; these [1,2,3,4] calculated plots correspond to the spectrum assigned to $CuCl^+$ (5900 M^{-1} cm^{-1}) and to $CuCl_2$ (3660 M^{-1} cm^{-1}). Consequently, the input of the two new parameters, β_2 and ϵ_2, in the [1,2,3,4] calculation leads to an artificial conclusion only in order to reach a good fit. For this reason, $CuCl_2$ can be considered as a "computer species" and the [1,2,3,4] model can be rejected.

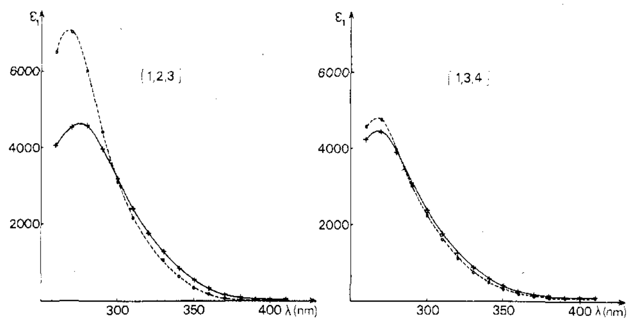


Figure 4. Pseudoexperimental (- - -) (see text) and calculated (—) $CuCl^+$ electronic spectra for the two different models [1,2,3] and [1,3,4].

Table II. Pseudoexperimental and Calculated $CuCl^+$ Spectra

model	$CuCl^+$ spectrum	λ_{max}, nm	ϵ_1, M^{-1} cm^{-1}	spectrum area, cm^2
[1,2,3]	pseudoexptl	268	7080	74.4
	calcd	276	4600	64.5
[1,3,4]	pseudoexptl	268	4760	54.2
	calcd	268	4440	53.6

Table III. Comparative Isosbestic Point Wavelengths (nm)

	calcd isosbestic points	
obsd isosbestic points[a]	[1,3,4][b]	[1,2,3]
280	280	266
317	316	314
387	387	390
445	447	444

[a] Figure 1. [b] Figure 3.

(ii) Our discussion of the three-complex models is based on the $CuCl^+$ calculated spectrum (Figure 4). The experimental spectrum 2 in Figure 1 is obtained from a DMF–copper(II) chloride solution containing stoichiometric copper(II) and chloride concentrations (5×10^{-4} M). At this low chloride ion concentration highly coordinated species remain negligible. The extinction coefficients of the calculated [1,2,3] and [1,3,4] $CuCl^+$ electronic spectra should be compared to this 5×10^{-4} M solution spectrum, after correction for the absorption due to free copper and to the very low concentrations of the other chlorocuprate complexes. Consequently, the experimental spectrum of the 5×10^{-4} M copper(II) chloride solution, corrected in this way, is a good approximation of a pseudoexperimental spectrum of $CuCl^+$. The numerical results of the comparison are reported in Table II and indicate clearly that the [1,3,4] model is the best representation of physical reality.

(iii) Another interesting conclusion results from the comparison of the calculated and the experimental isosbestic points appearing in Figure 1. In Table III, we report the wavelengths which characterize these particular absorption points, observed in Figure 1, and those calculated for the [1,3,4] model. The last column of Table III indicates the calculated isosbestic points in the case of the [1,2,3] model.

For the three last calculated isosbestic points the corresponding [1,3,4] wavelengths are closer to the experimental results, though only 2 or 3 nm separates all the concerned wavelengths. But, the differences at 280 nm indicate unambiguously the excellent correlation between observed and [1,3,4] calculated isosbestic points.

All these considerations favor the [1,3,4] model: in other words, the fit is the best if the presence of $CuCl^+$, $CuCl_3^-$ and

$CuCl_4^{2-}$ is taken into account. The absence of $CuCl_2$ was indeed postulated by Hubacek and Gutmann[9] due to its self-dissociation into $CuCl^+$ and $CuCl^{3-}$ as fast as it was formed.

Our results demonstrate clearly that the dichlorocuprate molecule is not stable enough to give spectrophotometric evidence in the UV–visible region.

(g) d–d Transition Bands of the DMF–Copper(II) Chloride Complexes. The Table I penultimate line indicates the numerical results obtained from the near-infrared measurements. The σ_2(IR) value does not surprisingly decrease in terms of more complicated models. This quantitative result is consistent with the previous UV and visible region conclusions. The individual spectra of $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$, plotted in Figure 3b, are calculated as far as we know for the first time from near-infrared optical density measurements. The monochlorocuprate has a maximum at 870 nm (80 M^{-1} cm^{-1}), the trichlorocuprate at 1100 nm (97 M^{-1} cm^{-1}) and the tetrachlorocuprate at 1200 nm (120 M^{-1} cm^{-1}). Furlani and Morpurgo have also indicated an absorption maximum of 110 M^{-1} cm^{-1} at 1180 nm for the pseudotetrahedral $CuCl_4^{2-}$.[7]

The DMF-solvated copper(II) ion has its near-infrared maximum at 790 nm (32 M^{-1} cm^{-1}), consistent with a square-planar coordination geometry. The extinction coefficient of 120 M^{-1} cm^{-1} for $CuCl_4^{2-}$ is consistent with the d–d band in a noncentrosymmetric copper(II) system as predicted by ligand field spectra calculations.[6] On the other hand, Katzin dissolved $CuCl_2$ in DMF and observed a broad peak at 945 nm with an intense peak at 440 nm and weak one at 395 nm; the addition of excess LiCl shifted the 945-nm maximum to around 1200 nm, and a new peak was visible at 410 nm.[15] Our calculations completely corroborate these observations.

As a conclusion of our near-infrared investigation, we assign the peaks at 870 and 1100 nm to the monochlorocuprate and to the trichlorocuprate, respectively. Finally, this quantitative analysis shows good evidence for the $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$ species system; as for the copper(II) d–d transition band maxima, they are in excellent agreement with ligand field theory.[6]

(h) Dimethylformamide and Copper(II) Solvation Effects. Our DMF results compared to those obtained in water and in other nonaqueous solvents show significant differences in both nature and stability of the formed chloro complexes. Concerning their electronic spectra in the UV–visible range, the comparison is limited to the water and DMF results, since no other investigation of these characteristics was performed up to now.

Nature and Stability of the Complexes. The striking differences between our results in DMF and in water are (i) the large increase of the overall stability constants and (ii) the absence of $CuCl_2$ among the species formed.

(i) The overall formation constant of $CuCl^+$ is increased by about a factor 10^3 and that of $CuCl_3^-$ by a factor of 10^{10}. Consequently, the formation curves of the copper(II)–chloro complexes in DMF, represented in Figure 5, show a wide range of existence for $CuCl_3^-$, as was found in Me_2SO.[11] $CuCl_3^-$ is already formed at rather low chloride ion concentration: its degree of formation is 10% at the formation maximum of $CuCl^+$ and already 50% when the chloride/copper(II) ion concentration ratio is only 2.

If the overall formation β_4 of $CuCl_4^{2-}$ is high, its stepwise formation constant K_4, on the contrary, is rather low (about 10 mol^{-1}). Consequently, in the explored chloride ion concentration range, the $CuCl_4^{2-}$ formation does not reach 100%; the intensities of its absorption maxima at 296 and 411 nm increase regularly with increasing chloride ion concentration, up to the solubility limit level of lithium chloride in DMF.

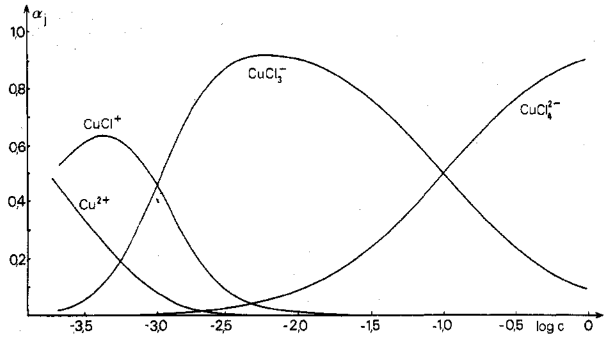
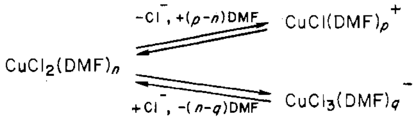


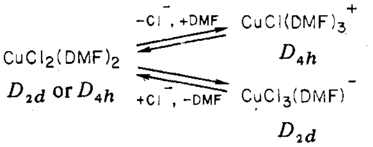
Figure 5. Formation curves of the individual copper(II) chloride complexes in 1 M Li(ClO_4^-,Cl^-)–DMF solutions.

As pointed out by Ahrland in his recent review,[24] such an increase in stability has also been observed for other halides when changing from water to Me_2SO and could, at least partly, be accounted for by the fact that the complexation entropies are more favorable in nonaqueous solvents, such as Me_2SO or DMF, than in the highly structured solvent H_2O.

(ii) Moreover, the large β_1 and β_3 values could also be accounted for by auto complex formation from $CuCl_2$, which, in our system, is shown by the absence of $CuCl_2$. According to Gutmann's views,[25] auto complex formation has to be expected in our system, as the solvent DMF and the anionic ligand Cl^- have similar donor numbers, and it should proceed according to the general scheme:



As we have already pointed out, $CuCl_3(DMF)_q^-$ and $CuCl_4^{2-}$ have in DMF no d–d transition band below 1100 nm, thus, probably having the D_{2d} flattened tetrahedral structure, with $q = 1$. On the other hand, $CuCl(DMF)_p^+$ with its d–d transition band at 870 nm probably has the same tetragonally distorted octahedral structure as the copper(II)–DMF solvate, with a D_{4h} configuration of the equatorial nearest neighbors. The solvation number p should then be equal to 3. Nothing can be said about the structure of $CuCl_2(DMF)_n$. But, in either D_{4h} or D_{2d} symmetry, n should be equal to 2 and the auto complex formation could then be written:



The structural change from D_{4h} to D_{2d}, which occurs in one of the steps between $CuCl^+$ and $CuCl_3^-$, can also contribute to the great stability of $CuCl_3^-$.[24]

Charge-Transfer Bands of the Complexes. Compared to their spectra in aqueous solutions,[1] the CT spectra of $CuCl^+$, $CuCl_3^-$, and $CuCl_4^{2-}$ in DMF exhibit a shift of the major absorption bands, ranging from 20 to 40 nm, toward higher wavelengths. Secondary maxima are formed in the visible region for $CuCl_3^-$ and, to a lesser extent, for $CuCl^+$ also.

The specific extinction coefficients of the individual species at the band maxima are found to be slightly higher in DMF than in water.

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(24) J. J. Lagowski, "The Chemistry of Nonaqueous Solvents", Vol. VA, Academic Press, New York, 1978.

(25) V. Gutmann, "Coordination Chemistry in Nonaqueous Solutions", Springer-Verlag, New York, 1968.

Thus, the influence of solvation upon the charge-transfer spectra affects the positions, but roughly not the intensities, of the band maxima. Nothing can be said about the modification of the d–d transition bands, when changing from H_2O to DMF solvent, as the spectrophotometric study of the aqueous solutions was not made over 800 nm.

Summary

The spectrophotometric analysis of the copper(II) chloride in dimethylformamide solutions and the numerical treatment of optical densities from the ultraviolet, visible, and near-infrared regions show accurately the presence of four absorbing species: the free copper(II) ion and the three mono-, tri-, and tetrachloro complexes. The absence of $CuCl_2$ can be attributed to auto complex formation, due to the similar coordinating properties of the solvent and the ligand.

The overall stability constants are found to be much higher than in aqueous solutions: $\log \beta_1 = 3.76 \pm 0.13$; $\log \beta_3 = 9.78 \pm 0.18$; $\log \beta_4 = 10.78 \pm 0.17$.

The charge-transfer bands of the individual calculated spectra have maxima at 268 nm for $CuCl^+$, at 300, 385, and 440 nm for $CuCl_3^-$, and at 296 and 411 nm for $CuCl_4^{2-}$. Their broad d–d transition bands are centered at 870 nm for $CuCl^+$, at 1100 nm for $CuCl_3^-$, and at 1200 nm for $CuCl_4^{2-}$. This quantitative information about the d–d bands is, to our knowledge, given for the first time for chlorocuprates in solution. It enables the structural conclusion that, in DMF, $CuCl^+$ probably is the square-planar ion $CuCl(DMF)_3^+$ and that $CuCl_3^-$ and $CuCl_4^{2-}$ are flattened tetrahedrons with one molecule of DMF coordinated to copper in the $CuCl_3(DMF)^-$ ion of D_{2d} symmetry.

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Registry No. $CuCl(DMF)_3^+$, 73824-84-7; $CuCl_3(DMF)^-$, 73824-85-8; $CuCl_4^{2-}$, 44000-59-1.

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Electron-Transfer Reactions of Copper Complexes. 1. A Kinetic Investigation of the Oxidation of Bis(1,10-phenanthroline)copper(I) by Hydrogen Peroxide in Aqueous and Sodium Dodecyl Sulfate Solution

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The kinetics and stoichiometry of the hydrogen peroxide oxidation of Cu(I) to Cu(II) have been investigated for the bis(1,10-phenanthroline) complex in both aqueous and micellar sodium dodecyl sulfate solution. At pH 5.8 (phosphate buffer, $\mu_{tot} = 0.15$ M) the Cu(I):H_2O_2 stoichiometry is 2:1. Under pseudo-first-order conditions the reaction rate is first order in oxidant and reductant, is zero order in hydrogen ion ($5.8 \leq \text{pH} \leq 7.8$), and reaches a limiting value at high phenanthroline concentrations. The following rate parameters are obtained in the presence of excess ligand: $k_2 = (3.91 \pm 0.06) \times 10^3$ M^{-1} s^{-1}, $\Delta H^{\ddagger} = 5.8 \pm 0.4$ kcal/mol, and $\Delta S^{\ddagger} = -24 \pm 1$ eu. Carrying out the reaction in 0.05 M sodium dodecyl sulfate changes the Cu(I):H_2O_2 stoichiometry to 1:1, removes the phenanthroline dependence, and slows the reaction 20-fold. A mechanism involving electron transfer by OH radicals is proposed. The implications of the relatively modest micelle effects are discussed. Comparisons are made between metal–micelle complexes and redox metalloproteins with kinetically accessible active sites.

Introduction

Although there have been many investigations of organic reactions in detergent media,[1] there have been very few reports on micelle effects on electron-transfer reactions involving metal systems. These few include studies of inner- and outer-sphere redox reactions on polyelectrolyte[2,3] and micellar surfaces[4,5] as well as micellar photoredox reactions.[6] In this paper we report a kinetic study of the influence of sodium dodecyl sulfate (SDS) micelles on the rate of Cu(I) oxidation in aqueous solution.[7] Rate studies in surfactant media can provide mechanistic details about electrostatic and hydrophobic influences on not only inorganic redox reactions but also biological electron transfers which take place on membrane surfaces or at protein–substrate interfaces.

A better understanding of electron transfer in copper and iron metalloproteins has come from a study of their reactions with inorganic redox reagents.[8] Useful insights have resulted from comparing the protein–inorganic electron-transfer processes to those that occur between two inorganic complexes.

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(7) The following nomenclature will be used throughout this paper: phen = 1,10-phenanthroline; dmp = 2,9-dimethyl-1,10-phenanthroline; bpy = 2,2′-bipyridyl; SDS = sodium dodecyl sulfate, cmc = critical micelle concentration.

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