Chlorodisilane decomposes by eq 10 and 11. From the determination of the SiH_4:$ClSiH_3$ ratio we have a measure of the $ClSiH$:SiH_2 ratio produced from $ClSi_2H_5$. If the half-lives of ClSiH and SiH_2 are the same, this ratio (1.25) would approximate the $ClSiH$:SiH_2 gas-phase ratio in our system. Since ClSiH probably has a longer half-life than SiH_2, this ratio would be a lower limit. In the pyrolysis of $ClSi_2H_5$ in the presence of $C_2H_5SiH_3$, SiH_2 and ClSiH reacted with $C_2H_5SiH_3$ forming $C_2H_5Si_2H_5$ and $C_2H_5SiH_2SiH_2Cl$ in a ratio of 1.54, respectively. This result suggests that the lower limit of k_{14}/k_{15} is about 2.

$$SiH_2 + C_2H_5SiH_3 \xrightarrow{k_{14}} C_2H_5Si_2H_5 \qquad (14)$$

$$ClSiH + C_2H_5SiH_3 \xrightarrow{k_{15}} C_2H_5SiH_2SiH_2Cl \qquad (15)$$

If the half-life of ClSiH is much longer than that of SiH_2, this ratio would be considerably greater than 2.

Fluorodisilane decomposed *via* eq 6 and 7 to form SiH_2 and FSiH in a ratio of 5 ± 1. Since the half-life of FSiH is undoubtedly greater than that of SiH_2 the $FSiH$:SiH_2 ratio in our system was 0.2 or greater. Since the ratio of $C_2H_5Si_2H_5$ to $C_2H_5SiH_2Si(F)H_2$ from the FSi_2H_5 decomposition in the presence of $C_2H_5SiH_3$ was about 21, it is obvious that SiH_2 insertion into $C_2H_5SiH_3$ was considerably greater than that of FSiH.

The relative half-life of SiF_2 is about 10^5 greater than that of $SiCl_2$.[23,24] From this, we assume that the half-life of HSiF is greater than that of HSiCl. Our data would then suggest that HSiCl inserts into silicon–hydrogen bonds faster than HSiF.

Our data with half-life assumptions ($FSiH > ClSiH > SiH_2$) suggest relative rates of silylene insertions into the silicon–hydrogen bonds of $C_2H_5SiH_3$ are in the order $SiH_2 > ClSiH > FSiH \gg SiCl_2, SiF_2$.

3. Decomposition Modes of Disilanes. Methyldisilane[4] and $1,1\text{-}(CH_3)_2Si_2H_4$[25] decompose by both available 1,2 hydrogen shift routes in nearly statistical ratios. It is obvious that this observation cannot be made for the halodisilanes, especially for $1,1\text{-}F_2Si_2H_4$ where only one route was observed.

Acknowledgment. The authors are indebted to the National Science Foundation and the Army Research Office (Durham) for financial support.

Registry No. Si_2F_6, 13830-68-7; $1,1\text{-}F_2Si_2H_4$, 15857-41-7; FSi_2H_5, 14537-73-6; $1,1\text{-}Cl_2Si_2H_4$, 20424-84-4; $ClSi_2H_5$, 14565-98-1; *sym*-$Cl_2Si_2H_2(CH_3)_2$, 42087-66-1; $F_2Si_3H_6$, 42086-09-9; $1\text{-}FSi_3H_7$, 34551-82-1; $1\text{-}ClSi_3H_7$, 31411-99-1; $Cl_2Si_3H_3(CH_3)_3$, 42086-10-2; $C_2H_5Si_2H_2D_3$, 42087-69-4; $C_2H_5Si_2H_4F$, 42087-70-7; $C_2H_5Si_2HD_3F$, 42087-71-8; $C_2H_5Si_2HD_3Cl$, 42087-72-9; $C_2H_5Si_2H_4Cl$, 42087-73-0.

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Nature and Stability of the $CuCl^+$ Complex in Aqueous Solution

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Received March 15, 1973

Equimolal mixtures of the divalent transition metal perchlorates with magnesium perchlorate are proposed as effectively constant ionic media for the study of weak complexes of the type MX (M = a divalent metal cation, X = anion). Values of the stability constant, β_1, and the molar absorption coefficient, ϵ, of the $CuCl^+$ complex have been determined in equimolal mixtures of copper(II) perchlorate with magnesium(II) perchlorate of the total molalities of 0.40, 1.34, and 2.39 mol kg^{-1}. ϵ is found to be approximately constant (1115 ∓ 80) in dilute and moderately concentrate solutions, while at the highest concentrations of the ionic medium a slight increase in its value takes place, as indicated by additional experiments involving solutions of varying concentration of copper(II) perchlorate and a small concentration of NaCl. From the independently determined product $\epsilon\beta_1{}^\circ$, the value of 1.63 ∓ 0.15 mol^{-1} dm^3 is found for $\beta_1{}^\circ$, the thermodynamic equilibrium constant of the $Cu^{2+} + Cl^- \rightleftharpoons CuCl^+$ reaction at 25°. The variation in the quotient of the activity coefficients of the latter reaction with the concentration of either copper(II) perchlorate or magnesium(II) perchlorate has also been calculated from the spectrophotometric data and is found to be practically the same for the two ionic media. The nature of the $CuCl^+$ complex is discussed on the basis of its uv and visible spectral characteristics and the conclusion is drawn that it consists mainly of the $[CuCl(OH_2)_5]^+$ coordination complex, in which the chloride anion replaces one of the two more distant water molecules of the hexaaquo complex, with a small contribution of the $\{[Cu(OH_2)_6]^{2+}Cl^-\}^+$ outer-sphere ion pair.

Introduction

Constant ionic media are commonly used in determinations of the stability constants of metal complexes in order to maintain constant activity coefficients of reacting species.[1] However, this method becomes unsatisfactory when the ligands are ionic and the stabilities of complexes under investigation are low. It is necessary, in such cases, to vary the concentration of the complexing anion over a broad range, considerably changing, at the same time, the activity coefficients of the reacting species. Adjusting the concentration of the ionic medium so as to obtain a constant formal ionic strength does not, of course, fix the activity coefficients. The difficulties were discussed by Matheson in connection with the determination of the stability constant of the $CuSO_4$ complex in aqueous solution.[2] A new possibility of controlling the activity coefficients in determinations of stability constants of weak anionic complexes arises from our recent observations concerning the activity coefficients in aqueous solutions of a group of divalent metal perchlorates. It has been shown that equimolal solutions, pure or mixed, of $Mn(ClO_4)_2$,

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(1) J. C. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, Toronto, London, 1961, pp 19–27.

(2) R. A. Matheson, *J. Phys. Chem.*, 69, 1537 (1965).

$Co(ClO_4)_2$, $Ni(ClO_4)_2$, and $Zn(ClO_4)_2$ display the same water activities, within experimental error, and also the same activity coefficients of the dissolved salts.[3,4] $Mg(ClO_4)_2$ and $Cu(ClO_4)_2$ display the same behavior up to approximately 1.0 mol kg^{-1}, while at higher concentrations their osmotic and activity coefficients are detectably but only slightly lower than the corresponding values common for the above four metal perchlorates. In addition, the activity coefficient of any species present in minute quantities in equimolal mixtures of the divalent metal perchlorates also remains approximately constant, as exemplified by the $[Co(NO_2)_2(NH_3)_4]^+$-$[Co(NO_2)_4(NH_3)_2]^-$ complex electrolyte, whose activity coefficients were studied by the solubility method.[5]

The above-mentioned thermodynamic properties of aqueous solutions of the group of divalent transition metal perchlorates are accountable in terms of the close similarity of the forms of existence of the dissolved salts. It seems that the divalent metal perchlorates in aqueous solutions exist practically exclusively as the coordination forms consisting of hexaaquo cations, probably with the second layers of hydrogen-bonded water molecules, and coordinatively nonbonded anions.[3] In the present paper we intend to show that equimolal mixtures of the divalent metal perchlorates may play the role of effectively constant ionic media in studies on very weak inorganic complexes in solution. The complex $CuCl^+$ has been chosen as the object of the present investigation. Largely divergent characteristics of this complex have been reported in the literature,[6-11] while its precise nature has never been discussed.

Experimental Section

Materials. Reagent grade hydrated magnesium(II) and copper(II) perchlorates and hydrated copper(II) chloride, as well as sodium chloride, were purified by repeated crystallizations from redistilled water.

Procedures. Spectrophotometric measurements were carried out by means of either a Unicam SP 500 or Zeiss VSU2-P spectrophotometer, the latter being used for the most dilute solutions necessitating 5-cm cells, both equipped with a thermostated cell compartment. The temperature of the solutions under investigation was constant to within 0.1°. The concentrations of the $Cu(ClO_4)_2$ and $CuCl_2$ stock solutions were determined electrogravimetrically as well as by standard EDTA titration. The $Mg(ClO_4)_2$ stock solution was analyzed for magnesium by standard EDTA titration in a pH 10 buffer using murexide indicator, as well as gravimetrically in the form of $Mg_2P_2O_7$. Several analytical determinations were performed in each case. The concentration of NaCl in the stock solution was determined by evaporation and drying weighed amounts of solution. The solutions for spectrophotometric work were prepared by weighing from the stock solutions and doubly distilled water.

Outline of the Method

In the present paper we determine the stability constant of the $CuCl^+$ complex while using equimolal mixtures of $Mg(ClO_4)_2$ and $Cu(ClO_4)_2$ to which minute amounts of NaCl are added. Since there are some general features of the method, which may be of interest in studies on other similar systems, we outline it below in a general way.

Assume that a series of equimolal mixtures of two metal salts, MA_z and $M'A_z$, having a common and noncomplexing anion, A, possesses the properties of a constant ionic medium. Provided that the total concentration of the mixtures is high, small additions of the third salt, $M''X$, containing the weakly coordinating anion X, will have but a negligible effect on the activity coefficients. The coordination equilibria set up under the assumed conditions are expected to be of the types

$$M + X \rightleftharpoons MX \tag{1}$$

$$M' + X \rightleftharpoons M'X \tag{2}$$

while omitting, for the sake of brevity, the participation of the solvent molecules. Although less probable, other types of coordination equilibria cannot be excluded *a priori*. It is assumed, however, that either the consistency of the final results or some additional experiments will provide the necessary check on the assumed reaction scheme.

The molal scale equilibrium quotients of reactions 1 and 2 will be defined as

$$^{m}\beta_1 = m_{MX}/m_M m_X; \quad ^{m}\beta_1' = m_{M'X}/m_{M'} m_X \tag{3}$$

where m_{MX}, $m_{M'X}$, m_M, $m_{M'}$, and m_X are the equilibrium molal concentrations of corresponding species. In accordance with our earlier observations reported in the Introduction these equilibrium quotients are expected to remain constant in the given series of equimolal mixtures of the MA_z and $M'A_z$ salts forming the effectively constant ionic medium. It is common practice, however, to use molar concentrations in the definitions of the stability constants. Transition to the molar scale is simplified by the fact that the volume of solutions containing a constant total number of moles of two salts forming effectively constant ionic media may be assumed to be constant. Denoting the constant volume of isomolal solutions containing 1 kg of solvent as v_0, we have $[MX] = m_{MX}/v_0$, $[M] = m_M/v_0$, $[X] = m_X/v_0$, etc., where [MX], [M], [X], . . . are the equilibrium molar concentrations of corresponding species. Hence, it follows that

$$v_0(^{m}\beta_1) = \beta_1 = [MX]/[M][X] \tag{4}$$

$$v_0(^{m}\beta_1') = \beta_1' = [M'X]/[M'][X] \tag{5}$$

where β_1 and β_1' are the molar scale equilibrium quotients of reactions 1 and 2 or, in other words, the stability constants of the MX and M'X complexes relating to the given ionic medium.

Provided that the total concentration, c_X, of the complex forming anion X is small compared with the concentration of any of the two salts MA_z and $M'A_z$, we may assume that $[M] = c$ and $[M'] = c'$, where c and c' are total concentrations of corresponding salts. On the other hand, the material balance for the complex-forming anion will be given by

$$c_X = [X] + [MX] + [M'X] \tag{6}$$

Suppose that there is a spectral range in which the MX complex exhibits an absorption band, the M cation shows but a small absorption, and all the other species do not absorb light at all. Then

$$E' \equiv E - \epsilon_0 c = \epsilon[MX] \tag{7}$$

where E is the optical density of the solution, ϵ_0 is the molar absorption coefficient of the solvated M cation, and ϵ is the molar absorption coefficient of the MX complex. It may be noted that E' is the directly measurable optical density of the solution containing the MX complex when the reference cell contains the equimolar mixture of MA_z and $M'A_z$. Combination of eq 4–7 leads to the relation

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(3) Z. Libus and T. Sadowska, *J. Phys. Chem.*, 73, 3229 (1969).

(4) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955, pp 482, 485.

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(9) R. Nasanen, *Acta Chem. Scand.*, 4, 140 (1950).

(10) H. McConnell and N. Davidson, *J. Amer. Chem. Soc.*, 72, 3164 (1950).

(11) J. Bjerrum, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, 22, No. 18 (1946).

$$\frac{c_X}{E'} = \frac{1}{\epsilon}\left(1 + \frac{\beta_1'}{\beta_1}\right) + \frac{1 + \beta_1' c_t}{\beta_1 \epsilon}\frac{1}{c} \tag{8}$$

where $c_t = c + c'$ is the total concentration of the ionic medium. It follows that for a series of equimolar solutions c_X/E' should be a linear function of $1/c$, whose intercept and slope should permit the calculation of two of the three parameters ϵ, β_1, and β_1', provided that the third is known.

Magnesium perchlorate may be particularly well suited as one of the two divalent metal perchlorates forming the effectively constant ionic media in studies of the type described. There is evidence that the hydrated magnesium cation shows a uniquely low affinity for chloride anion and probably also other weakly coordinating anions.[12-14] Thus, magnesium chloride in aqueous solution exhibits higher activity coefficients than any other of the divalent metal chlorides.[15] The same is true for the other magnesium(II) salts of strong acids.[4] The results of Angell and Gruen indicate that even in the melted hydrate $MgCl_2 \cdot 6H_2O$ all the water remains bound to the magnesium cation.[16] It seems probable, therefore, that β_1' in eq 8 will be either zero or very small, if $M' = Mg^{2+}$, at least when $X = Cl^-$ in aqueous solution, thus considerably simplifying the study of the chloro complexes of other divalent metals. A further argument in favor of the assumption $\beta_1' = 0$ for $MgCl^+$ will be given in the next section.

Results

Figure 1 shows the uv spectra of isomolal mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ of the total molality of 2.39 mol kg^{-1} containing NaCl at a constant and low concentration, measured against equally concentrated mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ without NaCl added. Accordingly, they represent absorption spectra of the chloro complexes of the cupric ion, without a contribution due to the noncomplexed cupric cations. The intensity of the band with maximum at 251 nm increases with increasing $Cu(ClO_4)_2$ content in the mixture, while the position and shape of the band remain unchanged. It may also be noted that a given percentage reduction in the optical density on receding from the maximum always takes place at the same wavelength, as illustrated in Figure 1. These facts indicate the formation of a single complex, most probably $CuCl^+$, and, hence, the occurrence of the equilibrium formulated as

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+ \tag{9}$$

omitting hydration of the species involved.

In view of the above results, the application of eq 8 to the equimolal mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ containing NaCl at a small concentration seems to be warranted. Corresponding plots are shown in Figure 2. Values of E' were measured at 272 nm, where the absorption due to the noncomplexed cupric ion is relatively small. Equimolal mixtures of three different total molalities, *viz.*, 0.40, 1.34, and 2.39 mol kg^{-1}, were used. To prevent hydrolysis, the solutions were acidified by means of $HClO_4$, whose constant concentration was 0.002 *M* in the first series, 0.003 *M* in the second, and 0.005 *M* in the third. As is seen, the plots of c_{Cl}/E' *vs.* $1/c$ in each case are linear (c_{Cl} is the concentration of NaCl; c is the concentration of $Cu(ClO_4)_2$). This fact indicates that the assumptions underlying eq 8 are correct. We additionally assume that the stability of the $MgCl^+$ complex, if at all existing, is considerably smaller than that of the $CuCl^+$ complex, so that the assumption $\beta_1' = 0$ is permissible. Under this assumption the least-squares method applied to the evaluation of the c_{Cl}/E' *vs.* $1/c$ plots leads to the following results (with the probable errors indicated)

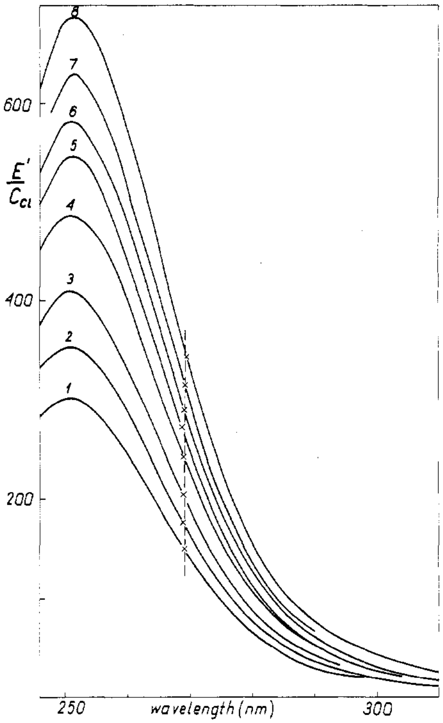

Figure 1. Absorption spectra of isomolar mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ of the total concentration of 2.02 *M* containing NaCl at the constant concentration of 0.010 *M* measured against equally concentrated mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ without NaCl added, at 25°. The dashed line joins points of equal values of $E'/E'_{251\,nm} = 1/2$, E' being defined by eq 7. The concentration of $Cu(ClO_4)_2$ in the mixtures varied from 0.1395 *M* (curve 1) to 0.4059 *M* (curve 8). All solutions were ~0.005 *M* in $HClO_4$ to prevent hydrolysis.

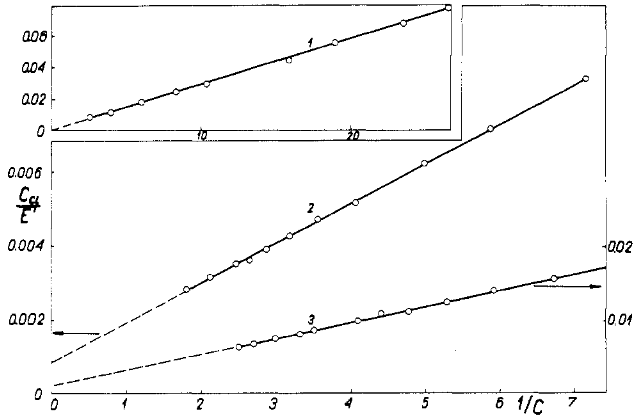

Figure 2. The determination of the stability constant and the molar absorption coefficient for the $CuCl^+$ complex in accordance with eq 8. The data were obtained at 25° for isomolar mixtures of $Cu(ClO_4)_2$ with $Mg(ClO_4)_2$ of the total molarities of 0.39 *M* (curve 1), 1.22 *M* (curve 3, right scale), and 2.02 *M* (curve 2, left scale) containing NaCl at approximately constant and low concentrations (of the order of 0.01 *M*) and $HClO_4$ at the concentration of 0.002–0.005 *M*.

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m_t, mol kg^{-1} (c_t, mol dm^{-3})	0.40 (0.39)	1.34 (1.22)	2.39 (2.02)
ϵ, l. mol^{-1} cm^{-1} (272 nm, 25°)	1146 (±125)	1035 (±70)	1165 (±22)
β_1, mol^{-1} dm^3 (25°)	0.31 (±0.04)	0.44 (±0.03)	0.80 (±0.02)

m_t denoting total molality and c_t total concentration, of the ionic medium.

The above results indicate an approximate constancy of the molar absorption coefficient of the CuCl$^+$ complex in ionic media of the above listed total concentrations. However, since the question of the possible variation of the molar absorption coefficient of the CuCl$^+$ complex with the concentration of the ionic medium is of paramount importance for the present study, an attempt was made to determine its value at the highest possible concentration of Cu(ClO$_4$)$_2$ forming the ionic medium. For this purpose values of E', as defined by eq 7, were determined for a series of concentrated solutions of Cu(ClO$_4$)$_2$ containing NaCl at a low concentration. It may be expected that $[\mathrm{CuCl}] \rightarrow c_{\mathrm{Cl}}$ as $c \rightarrow \infty$ and, consequently, $(E'/c_{\mathrm{Cl}}) \rightarrow \epsilon$ as $c \rightarrow \infty$. Hence, the limiting value of E'/c_{Cl}, possibly attained at sufficiently high concentration of Cu(ClO$_4$)$_2$, should determine the value of ϵ. The determined dependence of E'/c_{Cl} on c, the concentration of Cu(ClO$_4$)$_2$, is shown in Figure 3. As is seen, following the range of a steep increase, the slope of the curve becomes decreasingly smaller at the highest accessible concentrations of Cu(ClO$_4$)$_2$, indicating an approach to the limiting value of E'/c_{Cl}. Considerable scatter of the experimental points observed in the latter region arises from difficulties of direct measurement of E' for the nearly saturated solutions. It seems, however, that the limiting value of the molar absorption coefficient of the CuCl$^+$ complex at the highest concentrations of Cu(ClO$_4$)$_2$ forming the ionic medium is higher than the mean value found from the study of the more dilute isomolar Cu(ClO$_4$)$_2$-Mg(ClO$_4$)$_2$ mixtures, and may amount to 1300 (±80). It follows that, after all, the molar absorption coefficient of the CuCl$^+$ complex shows a small but detectable variation with the concentration of the ionic medium. We have recently found a similar but more pronounced effect for the CuBr$^+$ complex.

Thus, apart from the above small medium effect, the molar absorption coefficients of the CuCl$^+$ complex at 272 nm in dilute and moderately concentrated solutions may well be approximated by the constant value of 1115 (±80) at 25°. This fact permits the determination of the thermodynamic equilibrium constant, $\beta_1°$, of reaction 1 from experiments relating to very dilute solutions of CuCl$_2$ by a procedure similar to that developed by Nasanen.[9] The underlying equation is obtained from the expression

$$\beta_1° = \frac{[\mathrm{CuCl}]}{[\mathrm{Cu}][\mathrm{Cl}]} Y \tag{10}$$

where Y denotes the quotient of the activity coefficients and has the form of

$$\log \frac{E'}{[\mathrm{Cu}][\mathrm{Cl}]} = \log \epsilon\beta_1° - \log Y \tag{11}$$

E' being defined by eq 7. It follows that $\log (E'/[\mathrm{Cu}][\mathrm{Cl}]) = \log \epsilon\beta_1°$ at infinite dilution, where $Y = 1$. Taking into account the concentration range of the solutions involved, a realistic basis for the extrapolation seems to be provided by the Debye-Huckel equation involving the ion-size parameter, $\mathring{a}$, for the activity coefficients. Assuming a common value of $\mathring{a}$ for the two electrolytes CuCl$^+$,Cl$^-$ and Cu^{2+},Cl$^-$ we shall have $\log Y = 4A\sqrt{I}/(1 + B\mathring{a}\sqrt{I})$, whence it follows that a plot of $\log (E'/[\mathrm{Cu}][\mathrm{Cl}])$ *vs.* $\sqrt{I}/(1 + B\mathring{a}\sqrt{I})$ should be linear within the range of low concentrations and have the slope of $4A$, provided that a proper value for $\mathring{a}$ has been chosen (I = ionic strength, $A = 0.5092$, and $B = 0.3286$ for aqueous solutions at 25°). It has been found by trial and error that both conditions are well met for $\mathring{a} = 4.1$ Å, although it must be admitted that the curvature of the plot is not very sensitive to the value of $\mathring{a}$. Nonetheless, the assumed value of $\mathring{a}$ seems to be reasonable if the extensive hydration of the complex ions CuCl$^+$ and Cu^{2+} is taken into account. The necessary values of [Cu] and [Cl] were calculated as $[\mathrm{Cu}] = c - E'/\epsilon$ and $[\mathrm{Cl}] = 2c - E'/\epsilon$, where c denotes total concentration of CuCl$_2$ in the solutions studied. The resulting plot of $\log (E'/[\mathrm{Cu}][\mathrm{Cl}])$ *vs.* $\sqrt{I}/(1 + B\mathring{a}\sqrt{I})$ for dilute solutions of CuCl$_2$ is shown in Figure 4. The product $\epsilon\beta_1°$ found from the intercept of the straight line has the value of 1813 ± 37, whence it follows that $\beta_1° = 1.63 \pm 0.15$ mol^{-1} dm^3 at 25°, if the above quoted value of ϵ (1115 ± 80 at 272 nm) is taken into account.

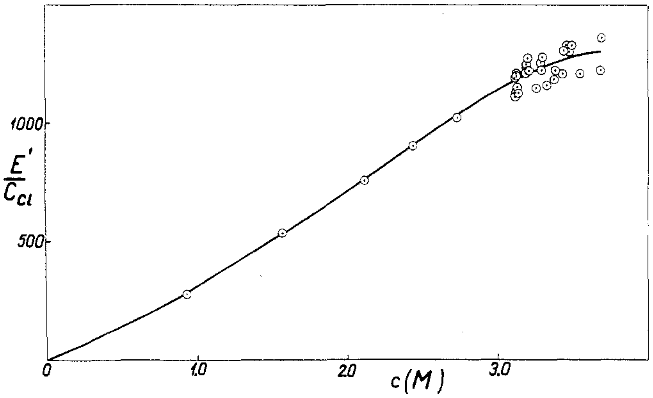

Figure 3. The determination of the molar absorption coefficient at 272 nm of the CuCl$^+$ complex in concentrated solutions of Cu(ClO$_4$)$_2$; see text.

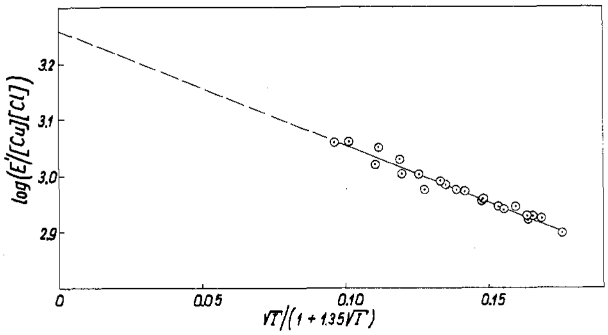

Figure 4. The determination of the $\epsilon\beta_1°$ product for the CuCl$^+$ complex at 272 nm and 25° in accordance with eq 11.

Once the product $\epsilon\beta_1°$ has been determined, eq 11 may yield values of Y from the experimentally determined values of $E'/[\mathrm{Cu}][\mathrm{Cl}]$ for all the solutions, for which the assumption $c_{\mathrm{Cu}} = [\mathrm{Cu}] + [\mathrm{CuCl}]$ is still valid, c_{Cu} denoting the total concentration of copper(II). In the present work it has been used in the calculation of Y for (a) dilute solutions of CuCl$_2$, (b) dilute solutions of CuCl$_2$ in the presence of Mg(ClO$_4$)$_2$ of considerable and varying concentration, and (c) dilute solutions of NaCl in the presence of Cu(ClO$_4$)$_2$ of considerable and varying concentration. The necessary values of [Cl] in all cases were calculated as $[\mathrm{Cl}] = c_{\mathrm{Cl}} - [\mathrm{CuCl}]$, c_{Cl} denoting the total concentration of the chloride anion and [CuCl] being calculated from the measured value of E' at 272 nm, under the assumption that $\epsilon = 1115$. The results obtained are shown in Figure 5 in the form of the Y *vs.* $\sqrt{I}$ plot. While the section of the curve corresponding to the pure and very dilute solutions of $CuCl_2$ most probably is uniquely determined by the ionic strength of the solution, that corresponding to the moderately concentrated solutions of either $Mg(ClO_4)_2$ or $Cu(ClO_4)_2$ is expected to be characteristic for an ionic medium containing mainly hydrated electrolytes of the type $[M(OH_2)_6]^{2+}$,$2ClO_4^-$. Most important in this connection is the fact that the values of Y found in equally concentrated solutions of either $Mg(ClO_4)_2$ or $Cu(ClO_4)_2$ are the same within the experimental error. The coincidence once more shows that aqueous solutions of $Cu(ClO_4)_2$ and $Mg(ClO_4)_2$ are equivalent in determining the activity coefficient of any species present at a small concentration. It should also be noted that the coincidence of the calculated values of Y for the two ionic media would be improbable, if appreciable amounts of the $MgCl^+$ complex in the $Mg(ClO_4)_2$ solutions containing NaCl were formed, thus invalidating the material balance $c_{Cl} = [Cl] + [CuCl]$.

In order to determine the long-wavelength spectrum of the $CuCl^+$ complex, the spectrum of the 0.266 M solution of $Cu(ClO_4)_2$ containing NaCl at a concentration of 0.104 M and a small quantity of $HClO_4$ was measured. Absorption due to the $CuCl^+$ complex was then calculated, while taking into account the known spectrum of the hydrated Cu^{2+} ion and making use of the value of β_1 found from Figure 5 for the formal ionic strength of the solution under investigation. The resulting spectrum of the $CuCl^+$ complex, as well as that of the hydrated curpic ion, is shown in Figure 6.

Spectral changes accompanying formation of the "lower" chloro complexes of the cupric ion in uv spectra are shown in Figure 7. The curves represent the spectra of a series of solutions containing $Cu(ClO_4)_2$ at a low concentration and LiCl at several different concentrations. Pains were taken to determine the spectra down to the lowest wavelengths accessible. For comparison purposes corresponding spectral effects accompanying the formation of the ethylenediamine complexes of copper(II) are shown in Figure 8.

Discussion

Several papers dealing with the formation of chloro complexes of the cupric ion have been published. Most of the older literature has been reviewed by Bjerrum,[11] while ref 6b contains references to the newer publications on the subject. Characteristic spectral effects in the uv spectrum accompanying the formation of chloro complexes of copper(II) attracted the greatest interest and have made spectrophotometry the most frequently used method of investigation in studies on corresponding equilibria. Despite the great abundance of the literature reports, the precise nature of the consecutive chloro complexes of copper(II), as well as their spectral and thermodynamic characteristics, has not been definitely established. This is also true of the $CuCl^+$ complex, for which largely divergent spectral and thermodynamic characteristics have been reported in the literature, as illustrated by the data listed in Table I. While comparing the values of the molar absorption coefficient reported by different authors we may take into account that $\epsilon_{272} = 0.40\epsilon_{250}$, as it follows from the known shape of the absorption spectrum due to the $CuCl^+$ complex on the assumption that λ_{max} is 250 nm.

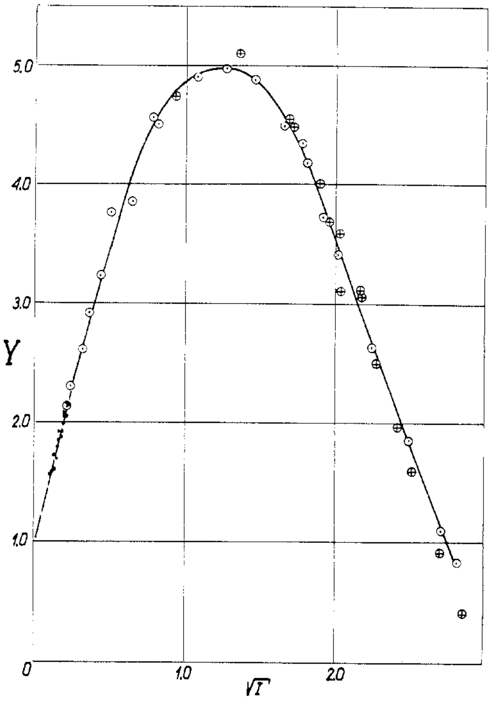

Figure 5. Plot of the quotient of the activity coefficients of the products and reactants of reaction 9 *vs.* square root of the ionic strength: •, solutions of $CuCl_2$; ⊙, solutions of $CuCl_2$ (~0.01 M) in the presence of $Mg(ClO_4)_2$ of varying concentration; ⊕, solutions of NaCl (~0.002–0.003 M) in the presence of $Cu(ClO_4)_2$ of varying concentration; 25°.

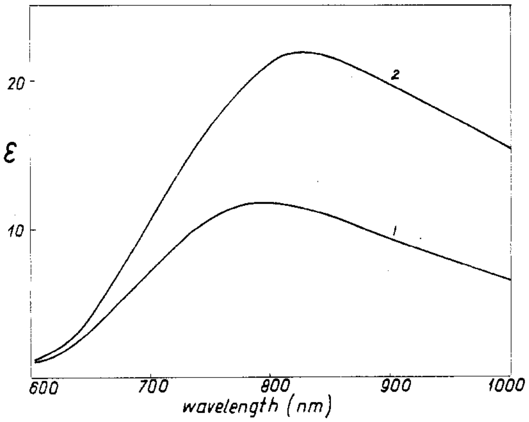

Figure 6. Long-wavelength absorption spectra of the hydrated cupric ion (curve 1) and the $CuCl^+$ complex (curve 2) in aqueous solution at 25°.

Table I. Stability Constants, β_1, and the Molar Absorption Coefficients, ϵ, of the $CuCl^+$ Complex Reported in the Literature

Ref	Method	Ionic strength	Temp, °C	β_1	ϵ
6a	Sp[a]			1	1300 (250nm)
7	ion exchange	0.691 ($HClO_4$)	20	9.60 ± 0.5	
8	Sp	1.0 ($HClO_4$)	22	0.27	3800 (250nm)
9	Sp	0	25	1.11	1478 (272nm)
10	Sp	1.00 ($HClO_4$)	25.2	1.30 ± 0.03	1000 (250nm) 316 (272nm)
11	Sp	0	22.5	$\gtrsim 1$	

[a] Spectrophotometric.

It seems that earlier studies on the $CuCl^+$ complex as well as on other similar systems suffered from the interference of higher complexes and/or from the ignored variation in the activity coefficients of the reacting species. The difficulties arising from these two effects in the evaluation of the experimental data were discussed by Kruh.[8] It is believed that the two sources of error have been eliminated in the procedure applied in this paper, as discussed in the preceding sections. As a result the presently obtained spectral and thermodynamic characteristics of the $CuCl^+$ complex in aqueous solu-

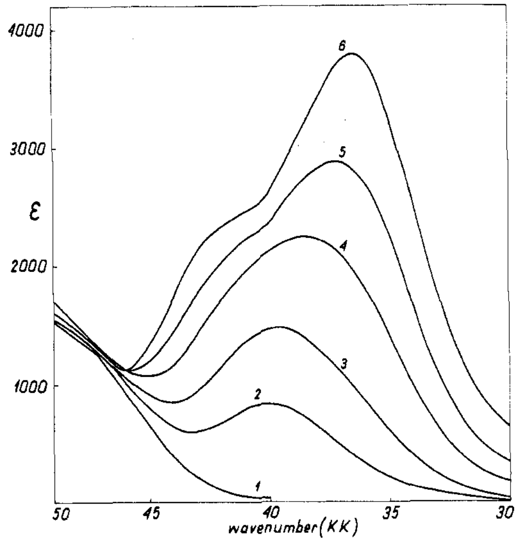

Figure 7. The uv spectral effects accompanying the formation of the lower chloro complexes of copper(II) in aqueous solution. The concentrations of LiCl in the solutions containing $Cu(ClO_4)_2$ at low concentrations were respectively 0.00 (curve 1), 1.18 (curve 2), 2.37 (curve 3), 3.52 (curve 4), 4.72 (curve 5), and 5.90 *M* (curve 6); 25°.

tion seem to be more reliable than those reported by the other authors.

It seems that the small increase in the molar absorption coefficient of the $CuCl^+$ "empirical" complex with increasing concentration of the ionic medium, which becomes detectable at the highest accessible concentrations, may be due to the fact that the complex is an equilibrium mixture of the outer-sphere ion pair and the inner-sphere complex involved in the equilibrium

$$\{[Cu(OH_2)_6]^{2+}Cl^-\}^+ \rightleftharpoons [CuCl(OH_2)_5]^+ + H_2O$$

whose position is expected to depend on the activity of water. However, the fact that the position and intensity of the long-wavelength band (Figure 6) found for the $CuCl^+$ complex both are qualitatively consistent with those expected for the $[CuCl(OH_2)_5]^+$ inner-sphere complex indicates that the latter is the predominant form of existence of the $CuCl^+$ empirical complex.

In order to obtain information on the position of the chloride anion in the $[CuCl(H_2O)_5]^+$ complex, spectral effects within the uv charge-transfer spectrum accompanying formation of the $CuCl^+$ complex may be compared with those accompanying the formation of ethylenediamine complexes of the cupric ion. Corresponding sets of absorption curves are shown in Figures 7 and 8. In the latter figure indicated are the values of $\bar{n}$, the average ligand number of the $Cu(en)_n{}^{2+}$ complexes, calculated on the assumption of complete combination of the amine. As is seen, consecutive formation of the $Cu(en)^+$ and $Cu(en)_2{}^{2+}$ chelate complexes is accompanied by the appearance and increase in intensity of a new charge-transfer band with a maximum at 228 nm, while

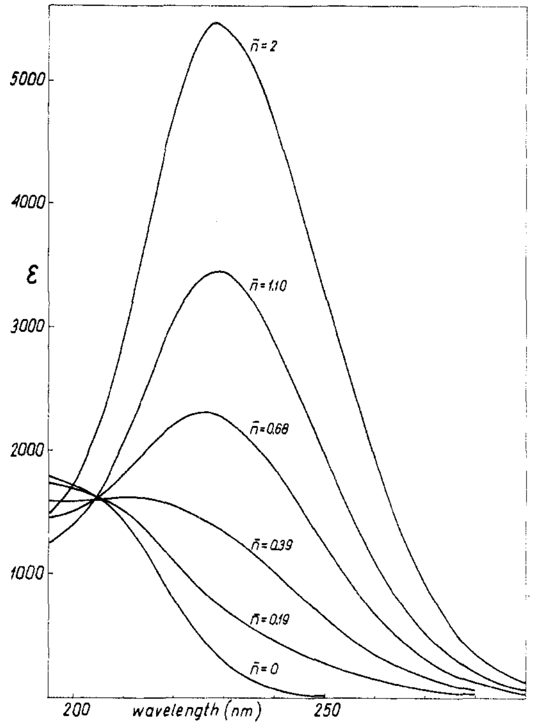

Figure 8. The uv spectral effects accompanying the formation of the ethylenediamine complexes of copper(II) in aqueous solution at 25°. Indicated are values of the average ligand numbers of the complexes.

the higher energy band due to the hexaaquo complex with a maximum at approximately 190 nm at the same time gradually disappears. Since the first two ethylenediamine molecules no doubt displace the four more strongly bound equatorial water molecules in the $[Cu(OH_2)_6]^{2+}$ tetragonally distorted complex, the latter band must be due to the existence of just these water molecules in the complex. On the other hand, formation of the "lower" chloro complexes of copper(II) is not accompanied, as Figure 7 shows, by the disappearance of the 190-nm band while the new band due to the chloro complexes is developed. The conclusion may therefore be drawn that, in this case, the four more strongly bound equatorial water molecules of the $[Cu(OH_2)_6]^{2+}$ aquo complex remain intact. Thus, we conclude that in the $[CuCl(OH_2)_5]^+$ inner-sphere complex the chloride anion replaces one of the two more distant water molecules of the parent hexaaquo complex. Since a similar effect cannot occur in the case of the other divalent metals belonging to the Mn–Zn series, the relatively high stability of the monochloro complex characteristic of the cupric ion becomes understandable.

Acknowledgment. The author thanks Professor W. Libus for helpful discussions and Mrs. G. Czerwinska for technical assistance in performing some of the experiments.

Registry No. $[CuCl(H_2O)_5]^+$, 18155-20-9.