The molar absorptivities thus obtained, as well as the constants given by the solubility data, were tested by computing the absorption curve of 2.72 M KBr in which the concentration of TlBr was 18.25×10^{-5}. This is shown by the broken curve D of Fig. 2. Agreement with the observed (solid) curve is satisfactory, which confirms our contention that use of K_{4c} is justified at KBr concentrations less than 3.50 M.

While it must be agreed that the assignment of formulas and stability constants for complexes are in this and similar cases simply an attempt to fit an experimental curve with an equation in the form of a power-series, we conclude that the assumption of the existence of TlBr, $TlBr_2^-$, and $TlBr_4^{---}$ is adequate to account for the results of solubility and optical absorption experiments.

Acknowledgment.—We wish to acknowledge the assistance of Professor H. Freund and Mr. C. R. Schneider in making the polarographic measurements.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KANSAS, LAWRENCE, KANSAS

Electrochemical and Infrared Evaluation of the Formation Constants of Aquo-Copper(II) Complexes in Nitromethane

BY ROBERT C. LARSON AND REYNOLD T. IWAMOTO

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The individual formation constants for aquo-copper(II) complexes in nitromethane have been evaluated by electrochemical and spectrophotometric methods. These values have been compared with those calculated for aquo-copper(II) complexes in ethanol from previously published data. Average log k values in nitromethane are 2.90, 1.92, 1.22, 0.94, 0.52, and $\sim$0.50. Log k values in ethanol are -0.23, -0.51, -0.86, -0.93, -1.14, and -1.17.

During the last decade there has been a growing interest in the use of non-aqueous solvents to obtain information fundamental to better understanding the nature of ion–solvent interactions. Surprisingly, the effect of residual water on the behavior of ions in non-aqueous media, however, has received very little careful systematic consideration—not as much as it deserves. The fact that even solvents of 99.98% purity, *i.e.*, 0.02% in water, are still *ca.* 0.01 M in water, a value of the same order of magnitude as the limited solubility of inorganic substances in non-aqueous solvents, makes it imperative that this problem is examined carefully before many more studies in this area are undertaken.

Jørgensen[1] and Minc and Libuś[2] have examined the formation of aquo-copper(II) ions, among other transition group metals, in ethanol and have derived some quantitative information on the selectivity of solvation by water molecules. An average formation constant, $(k_1 k_2 k_3 \ldots k_6)^{1/6}$, of $10^{-0.73}$ has been reported by Jørgensen. Individual aquo-copper(II) formation constants in ethanol have been evaluated from the data of Minc and Libu by a $\bar{n}$ *vs.* $-\log\,[H_2O]$ plot. An "average" formation constant of $10^{-0.81}$ has been computed from the individual k's.

In a preliminary study[3] of solvent effects on the polarographic behavior of copper(II) ion, two well separated waves of equal height were observed in nitromethane with these $E_{1/2}$ values

$E_{1/2\,\mathrm{Cu(II),Cu(I)}}$ $> +0.8$ v. *vs.* s.c.e.
$E_{1/2\,\mathrm{Cu(I),Cu(Hg)}}$ $+0.21$ v. *vs.* s.c.e.

The large positive shift of the Cu(II),Cu(I) half-wave potential in nitromethane from that for the same couple in water ($E^0_{\mathrm{Cu(II),Cu(I)}} = -0.09$ v. *vs.* s.c.e.) is due to the lower solvation energy of Cu(II) ion in nitromethane. The Cu(II),Cu(I) half-wave potential, as might be expected, shifts markedly to more negative values on the addition of water. This marked shift is caused by an increase in the solvation energy of copper(II) ion as a result of selective solvation by water molecules.

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[1] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 175 (1954).

[2] S. Minc and W. Libuś, *Roczniki Chem.*, **29**, 1073 (1955).

[3] I. V. Nelson, R. C. Larson, and R. T. Iwamoto, *J. Inorg. & Nuclear Chem.*, to be published.

Clearly, the effect of residual water on the polarographic behavior of Cu(II) ion in nitromethane is quite different from that expected on the basis of information (formation constants) available for ethanol medium. An attempt has been made, therefore, to obtain quantitative information, in the form of stability constants, on the interaction of water with copper(II) ion in nitromethane, with the hope that such information will be of assistance in scrutinizing the results of studies of inorganic ions, particularly cations, in non-aqueous media.

Experimental

Reagents and Solutions.—Nitromethane solutions of copper(II) perchlorate were prepared in two ways: (1) by dissolving weighed amounts of reagent grade copper(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) or copper(II) perchlorate *x*-hydrate and (2) by treating a weighed piece of clean electrolytic copper foil with a suspension of excess nitrosyl perchlorate as described by Hathaway and Underhill.[4] Copper(II) perchlorate *x*-hydrate is the perchlorate obtained on heating the hexahydrate *in vacuo* at 60° for 48 hr. The dried perchlorate was stored over phosphorus pentoxide. In the nitrosyl perchlorate method, the excess nitrosyl perchlorate was filtered off after complete oxidation of the copper metal, and the solution was degassed with pre-purified nitrogen until odor-free of oxides of nitrogen. The copper(II) concentration of solutions prepared by the nitrosyl perchlorate method was calculated directly from the weight of copper metal taken. The copper(II) concentration of solutions prepared by the first method was obtained indirectly through Karl Fischer analysis of the water content of the copper(II) perchlorate solutions and knowledge of the added and residual water content of the solvent. All solutions were tested for and found to be free of chloride.

Fisher certified reagent grade nitromethane was purified by passing 1-l. batches through a 2.5 cm. (i.d.) × 35 cm. column of Woelm chromatographic neutral alumina, activity grade 1. The purification assembly was kept protected from atmospheric moisture with calcium chloride drying tubes. Three passes, with a fresh bed of alumina being used for each pass, reduced the water content to *ca.* 3×10^{-3} *M*.

Voltammetric and spectrophotometric solutions were prepared by volumetric dilution of stock solutions into flasks containing weighed amounts of water. The weighed amounts of water also served as an "internal" standard for the Karl Fischer titrant. The titer of the Karl Fischer reagent was calculated from the difference in weight of added water and the difference in ml. of Karl Fischer reagent required for two solutions. Solutions used in the voltammetric study were 2.11×10^{-3} *M* in copper(II) ion, and those used in the infrared study were between 0.02 and 0.1 *M* in copper(II) ion. In addition voltammetric solutions were 0.1 *M* in tetraethylammonium perchlorate.[5]

Apparatus.—Current-voltage curves were obtained with a Leeds and Northrup Electrochemograph, Type E. The electromotive force recorded by the instrument was checked with a potentiometer. The current-voltage curves were corrected for the *iR* drop across the cell. The temperature of the cell was maintained constant at 25 ± 0.2°.

The rotating platinum electrode was a *ca.* 0.4 mm. diameter platinum wire sealed in a soft glass tubing with only 1/16 in. protruding. The tip was polished with crocus cloth and jeweler's rouge. A Sargent Synchronous Rotator was used to rotate the electrode at *ca.* 600 r.p.m. With the small electrode area, currents of *ca.* 5 μamp. were obtained for *ca.* 2 m*M* solutions of copper(II) perchlorate. The electrode was pretreated before each run by scanning cathodically to the deposition potential of copper, followed by anodic stripping at +1.5 v. *vs.* s.c.e. until the current returned to zero. Failure to pre-treat the electrode in the manner described resulted in highly irreversible waves for the Cu(II) to Cu(I) reduction.

The cell and cell arrangement, including the use of the aqueous saturated calomel reference electrode, have been discussed previously.[5] All potentials listed in this paper have been measured against the aqueous saturated calomel electrode.

Infrared spectra were obtained with a Perkin-Elmer Model 21 spectrophotometer (NaCl optics). Calcium fluoride cells (0.1 mm.) were used.

Results

Voltammetric Investigation.—The experimental data for the voltammetric study of the interaction of small amounts of water in nitromethane with copper(II) ion were summarized as shown in Figure 1 (half-wave potential for the reduction of

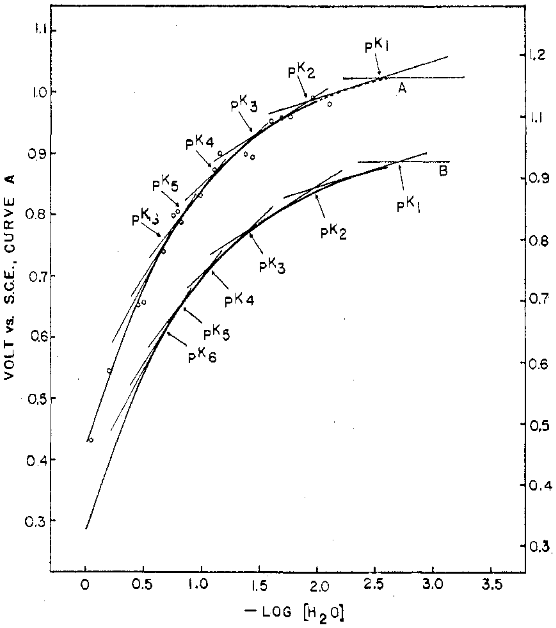

Fig. 1.—Half-wave potential, $E_{1/2}$, for the Cu(II),Cu(I) wave in nitromethane as a function of $-\log[H_2O]_{total}$ (curve A) and $-\log[H_2O]_{free}$ (curve B). "Dried" copper(II) perchlorate was used to prepare the Cu(II) solutions.

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[4] B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3705 (1960).

[5] R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, **82**, 3239 (1960).

copper(II) ion to copper(I) ion *vs.* the negative log of the total water concentration). The upper curve in Figure 1 (solutions prepared from hydrated or "dried" copper(II) perchlorate) shows the experimentally observed dependency of the half-wave potential for the Cu(II),Cu(I) wave on total water concentration. A similar curve was obtained for solutions of Cu(II) prepared from copper metal and nitrosyl perchlorate.

The change in half-wave potential for the Cu(II),Cu(I) wave with water concentration is due entirely to the complexation of copper(II) ion by water. There appears to be practically no change in the solvation energy of copper(I) ion as evidenced by the fact that the Cu(I),Cu(Hg) half-wave potential remains essentially constant over the range of water concentration studied. Change in liquid junction potential is also insignificant over the range of water concentration investigated.[6]

The Cu(II),Cu(I) waves start in a normal manner but are drawn over at the top. Because of this feature of the waves, the slopes of the plots of E *vs.* log $(i_d - i/i)$ are somewhat greater than the reversible value of 0.060. Careful examination of the E *vs.* log $(i_d - i/i)$ plots, however, revealed that the initial portions of the waves do have the proper reversible slope. The true reversible half-wave potentials, plotted in Figure 1, were obtained by extrapolating this initial section of the E *vs.* log $(i_d - i/i)$ plots to the log $(i_d - i/i) = 0$ line. Representative data of $E_{1/2}$ values and slopes evaluated from $E_{3/4}$ and $E_{1/4}$ of the copper(II),(I) waves and of $E_{1/2}$ values and slopes evaluated from the initial portion of the waves are presented in Table I.

The dependency of the half-wave potential for the Cu(II),Cu(I) wave on the concentration of water is given by the expression[7]

$$E_{1/2} = E^{0\prime} - 0.059 \log \left[1 + \frac{[H_2O]}{K_1} + \ldots.. \frac{[H_2O]^N}{K_1 \ldots K_N}\right] \tag{1}$$

where

$$K_1 = \frac{[Cu^{++}][H_2O]}{[Cu(H_2O)^{++}]} = \frac{1}{k_1} \tag{2}$$

and

$$K_N = \frac{[Cu(H_2O)_{N-1}{}^{++}][H_2O]}{[Cu(H_2O)_N{}^{++}]} = \frac{1}{k_N} \tag{3}$$

TABLE I

$E_{1/2}$ VALUES AND SLOPES FOR THE Cu(II),Cu(I) WAVE

pH_2O	$E_{1/2}$ *vs.* S.C.E. (Observed)	Slope ($E_{1/4} - E_{3/4}$)	$E_{1/2}$ *vs.* S.C.E. (Corrected)	Slope (Foot of Wave)
2.12	0.940	0.108	0.975	0.064
1.77	.946	.094	.960	.060
0.79	.782	.074	.805	.060
.46	.618	.087	.652	.061
.21	.518	.080	.545	.063

K_1 is the reciprocal of the formation constant k_1 and is also the dissociation constant for the species $Cu(H_2O)^{++}$. $K_1 \ldots . K_N$, rather than $k_1 \ldots .. k_N$, are used in this paper for convenience in presenting the experimental data (hereafter, therefore, k_i refers to the i*th* formation constant, and K_i refers to the reciprocal of the i*th* formation constant). $E^{0\prime}$ in the expression above includes: the standard potential for the Cu(II),Cu(I) couple, activity coefficients for Cu(II) and Cu(I) ions, and the proportionality constants relating polarographic current to the concentrations of Cu(II) and Cu(I) ions. In deriving the expression above, the assumption has been made that in nitromethane Cu(I) ion does not interact with water to form aquated ions, or if it does, the formation constant(s) is very small—much smaller than those for Cu(II) ion.[8] This assumption is based on the constancy of the half-wave potential for the Cu(I),Cu(Hg) wave over a wide range of water concentration. $E_{1/2 Cu(I),Cu(Hg)}$ is +0.220 v. *vs.* s.c.e. in *ca.* 10^{-3} *M* water solution and +0.205 v. *vs.* s.c.e. in *ca.* 1 *M* water solution.

Equation 1 indicates that a plot of $E_{1/2}$ *vs.* $-\log [H_2O]$ is a composite curve consisting of a number of straight line sections with slopes of 0.059 n, where n represents the number of water molecules attached to a copper(II) ion. If the formation constants are far enough apart and a fairly large number of potential measurements are available, unlike the curves in Figure 1, the plots of $E_{1/2}$ *vs.* $-\log [H_2O]$ would consist of a number of well defined straight line sections which intersect at $pH_2O = pK_i$. Such plots furnish an excellent simple method for the evaluation of formation or dissociation constants. Because of the closeness of the formation constants for aquated copper(II) ion, however, there are no obvious straight line sections in the upper curve in Figure 1. However, by drawing straight lines with slopes

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[6] Unpublished results. This conclusion is based on the fact that the half-wave potentials for the oxidation of 4,7-dimethyl ferroin at a rotating platinum electrode in nitromethane 4×10^{-3} *M* in water and 1.23 *M* in water are identical to within 1 mv. Both waves are reversible.

[7] H. A. Laitinen, "Chemical Analysis," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 286.

[8] If we assume that only a monoaquated Cu(I) species is formed over the range of water concentration studied, the 0.015 v. shift in $E_{1/2 Cu(I),Cu(Hg)}$ suggests a formation constant for $Cu(H_2O)^+$ of *ca.* 1.

of 0.059 n tangent to the curve, as shown in Figure 1, one can obtain approximate values of $pK_2 \ldots pK_N$. Because it is impossible to prepare absolutely dry nitromethane, pK_1 cannot be evaluated by the method just described. Approximate values for K_1 were obtained by inserting the graphically evaluated values of $K_2 \ldots K_N$ in the expression

$$E_{1/2(1)} - E_{1/2(2)} = \log \frac{K_1K_2 \ldots K_N + K_2 \ldots K_N [H_2O]_2 + K_3 \ldots K_N[H_2O]_2^2 \ldots}{K_1K_2 \ldots K_N + K_2 \ldots K_N[H_2O]_1 + K_3 \ldots K_N[H_2O]_1^2 \ldots} \quad (4)$$

Equation 4 is derived from (1). Average values of 2.66 (Fig. 1) and 2.83 (for copper(II) solutions prepared from copper metal and nitrosyl perchlorate) were obtained for pK_1. These pK_1 values indicate the points of intersection of the tangents $E_{1/2} = E^{0\prime} + 0.059 \log K_1/[H_2O]$ and $E_{1/2} = E^{0\prime}$ and provide, thereby, the means for evaluating $E^{0\prime}$. For the two sets of data, +1.026 v. *vs.* s.c.e. (Fig. 1) and +1.072 v. *vs.* s.c.e. (Cu–$NOClO_4$ solutions) were obtained for $E^{0\prime}$.

The upper curve in Figure 1 indicates the pH_2O dependence of the half-wave potential of the Cu(II),Cu(I) wave only insofar as the total water concentration is not too far different from the free water concentration. Because of the low copper(II) ion concentration, at high total water concentrations the difference between the total water and the free water concentrations is negligible. However, at low total water concentrations the difference becomes significant, and the curve no longer depicts the true pH_2O dependence of the half-wave potential of the Cu(II),Cu(I) wave. The upper curve in Figure 1, therefore, was corrected in the region of low total water concentration in the following manner. The concentration of free water for a particular point on the curve was obtained by first evaluating the concentration of free copper(II) ion for the particular point. This calculation involved the use of the Nernst expression

$$E_{1/2} = E^{0*} + 0.059 \log \frac{[Cu^{++}]_0}{[Cu^{+}]_0} \quad (5)$$

E^{0*} in this expression differs from $E^{0\prime}$ in equation 1 in that it does not contain the proportionality constants relating polarographic current to the concentrations of Cu(II) and Cu(I) ions. Substituting 1/2 $[Cu(II)]_{total}$ for $[Cu^{+}]_0$, one can compute $[Cu^{++}]_0$ using $E^{0\prime}$ for E^{0*}. The calculated $[Cu^{++}]_0$ at the half-wave potential was doubled for the concentration of free copper(II) ion in the bulk of the solution. For solutions in which the monohydrated species predominate, the free water concentration is equal to the total water concentration less the difference between the total copper(II) ion concentration and the free copper(II) ion concentration, *i.e.*, the bound water.

$$[H_2O]_{free} = [H_2O]_{total} - [Cu(H_2O)^{++}] \quad (6)$$

For solutions in which both the dihydrate and monohydrate are present, the concentration of free water is calculated by simultaneously solving the equations

$$[Cu(H_2O)^{++}] + [Cu(H_2O)_2^{++}] = [Cu^{++}]_{total} - [Cu^{++}]_{free} \quad (7)$$

$$\frac{[Cu(H_2O)^{++}][H_2O]}{[Cu(H_2O)_2^{++}]} = K_2 \quad (8)$$

$$[H_2O]_{free} = [H_2O]_{total} - ([Cu(H_2O)^{++}] + 2[Cu(H_2O)_2^{++}]) \quad (9)$$

The correct values for $-\log [H_2O]$ were larger by *ca.* 0.20 unit at $E_{1/2}$ of 1.020 and 0.07 unit at $E_{1/2}$ of 0.950. The calculated values of pH_2O_{free} were used to obtain the lower curve in Figure 1. From such corrected curves new sets of pK values, now based on more accurate values for the free water concentration, were obtained. Values of pK_1 were evaluated, as previously discussed, and new values of $E^{0\prime}$ were determined. The corrected curves (lower curve in Figure 1) appear to be good representations of the formation curves of aquo–copper(II) ions, as calculation of free water concentrations with the new sets of constants and the new half-wave potentials gave free water values which differed by only negligible amounts from the previously calculated free water values.

The graphically evaluated constants are at best good approximations of the dissociation constants. Better values were calculated through the method of successive approximations by substituting the graphically evaluated constants, except for the constant being evaluated, into equations 1 and 4. Equation 4 was used to evaluate the constants from the data in Figure 1, and equation 1 was used to evaluate the constants from the data for (Cu–$NOClO_4$) solutions. Evaluation of the constants with equation 4 requires the use of pairs of $E_{1/2}$ and pH_2O values preferably from sections of the curve where the constant being evaluated was most influential. Knowledge of the value of $E^{0\prime}$ is not necessary. On the other hand, $E^{0\prime}$ is needed to evaluate the constants with equation 1. In both methods the graphically

TABLE II

AVERAGE VALUES OF pK OR LOG k (ELECTROCHEMICAL)

	$E^{0\prime}$ *vs.* S.C.E.	pK_1	pK_2	pK_3	pK_4	pK_5	pK_6	pK_7	pK_8	pK_9
Figure 1										
Graphically evaluated values—upper curve Fig. 1	1.026 v.	2.60	1.92	1.47	1.14	0.85	0.72	0.65	0.55	0.35
Graphically evaluated values—lower curve Fig. 1	1.024 v.	2.75	1.97	1.42	1.10	.80	.70	.65	.55	.35
1st set—method of successive approximations	[a]	2.75	1.83	1.18	1.10	.53	.50	~ .50	~ .50	~ .50
2nd set—method of successive approximations	1.036 v.	2.88	1.94	1.22	1.04	.53[c]	.50	~ .50	~ .50	~ .50
Cu(II) (Cu–$NOClO_4$) Solutions										
Graphically evaluated values—$[H_2O]_{\text{total}}$	1.075 v.	2.89	2.02	1.41	0.93	.70	.54	.50	.40	.30
Graphically evaluated values—$[H_2O]_{\text{free}}$	1.072 v.	3.01	1.94	1.33	.90	.70	.54	.50	.40	.30
1st set—method of successive approximations	1.060 v.	2.80	1.97	1.07	.96	.50	~ .50	~ .50	~ .50	~ .50
2nd set—method of successive approximations	[b]	2.82	1.98	1.06	.99	.50[c]	~ .50	~ .50	~ .50	~ .50

[a] $E^{0\prime}$ was not evaluated. [b] $E^{0\prime}$ within experimental error of 1.060. [c] Values are those from 1st set of log k's evaluated by method of successive approximations.

evaluated constants were successively replaced by the newly calculated values. Because only minor differences in the constants were found between the second and first sets of calculated values, the approximation technique was terminated after two sets of calculations.

The calculation of pK_6 was complicated by the uncertainty of the graphically evaluated values for pK_7, pK_8, and pK_9.

Average calculated values of pK or log k are presented in Table II.

Strict interpretation of the limiting slope of 0.53 for the two curves at high water concentrations requires postulation of a limiting "hydration" number (N) of 9. Other than to point out that in this case water molecules in the secondary solvation sphere (assigning 6 water molecules to the primary solvation sphere) could be involved in governing the redox property of copper(II) ion, discussion of the significance of this "hydration" number is deferred until further investigation of this observation is completed.

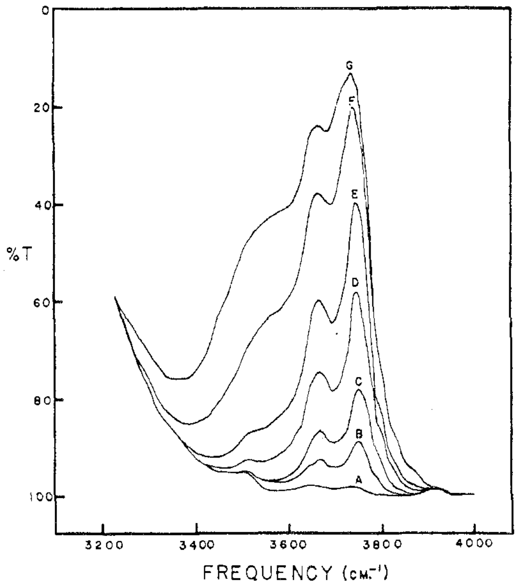

Fig. 2-a.—Infrared spectra of nitromethane containing varying amounts of water: (A) 0.005 M, (B) 0.048 M, (C) 0.105 M, (D) 0.241 M, (E) 0.437 M, (F) 0.875 M, (G) 0.950 M.

Spectrophotometric Investigation.—The infrared spectrum of nitromethane containing a small amount of water has two sharp absorption bands which can be ascribed to water at *ca.* 3660 and 3740 cm.$^{-1}$ (Figure 2-a). The proportionality of the intensity of the double band to the water content suggests that these bands were incorrectly reported[9] to be part of the nitromethane spectrum. The spectra of solutions of nitromethane in which

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[9] P. A. D. de Maine, *J. Mol. Spect.*, **4**, 407 (1960).

the copper(II) to water ratio was such that practically all the water would be expected to be associated with copper(II) indicate that coördinated water does not absorb at 3740 cm.$^{-1}$ and only slightly at 3660 cm.$^{-1}$. Free water in equilibrium with aquo–copper(II) ions in nitromethane, therefore, can be determined by infrared spectrophotometry (Figure 2-b). The free water concentration has been used to evaluate the formation constants of the aquo–copper(II) complexes.

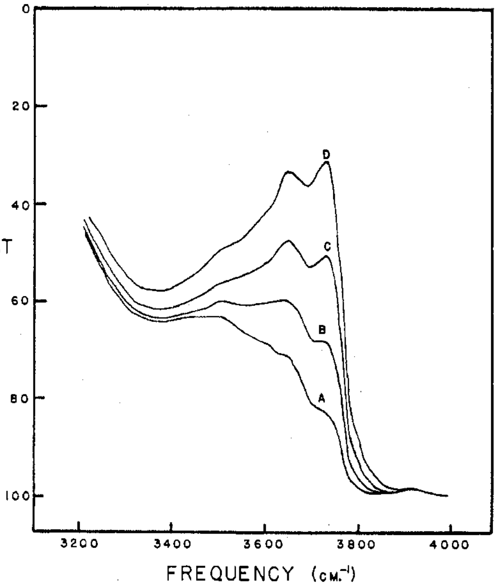

Fig. 2-b.—Infrared spectra of nitromethane containing 5.01×10^{-2} M $Cu(ClO_4)_2$ and varying amounts of water: (A) 0.224 M, (B) 0.336 M, (C) 0.510 M, (D) 0.846 M.

Bjerrum[10] has shown that the concentration constants of a complex system may be determined from a knowledge of $\bar{n}$, the average number of ligands attached to the metal ion, as a function of the concentration of free ligand.

For the complexation reactions and equilibria with which we are concerned

$$Cu^{++} + H_2O = Cu(H_2O)^{++}$$

$$k_1 = \frac{[Cu(H_2O)^{++}]}{[Cu^{++}][H_2O]} \quad (10)$$

$$Cu(H_2O)^{++} + H_2O = Cu(H_2O)_2{}^{++}$$

$$k_2 = \frac{[Cu(H_2O)_2{}^{++}]}{[Cu(H_2O)^{++}][H_2O]} \quad (11)$$

$$Cu(H_2O)_{N-1}{}^{++} + H_2O = Cu(H_2O)_N{}^{++}$$

$$k_N = \frac{[Cu(H_2O)_N{}^{++}]}{[Cu(H_2O)_{N-1}{}^{++}][H_2O]} \quad (12)$$

$\bar{n}$ may be expressed in terms of the species existing in solution as follows

$$\bar{n} = \frac{\sum\limits_{n=1}^{n=N} nCu(H_2O)_n{}^{++}}{[Cu^{++}] + \sum\limits_{n=1}^{n=N} [Cu(H_2O)_n{}^{++}]} = \frac{[Cu(H_2O)^{++}] + 2[Cu(H_2O)_2{}^{++}]}{[Cu^{++}] + [Cu(H_2O)^{++}] +} \frac{\ldots .N[Cu(H_2O)_N{}^{++}]}{[Cu(H_2O)_2{}^{++}] + \ldots [Cu[H_2O)_N{}^{++}]} \quad (13)$$

For brevity the participation of nitromethane in the reactions and equilibria involved has been neglected. Inserting the formation constants of the system and eliminating $[Cu^{++}]$ from both the numerator and denominator, one obtains the following unambiguous connection between $\bar{n}$, the formation constants, and the free water concentration

$$\bar{n} + (\bar{n} - 1)[H_2O]k_1 + (\bar{n} - 2)[H_2O]^2k_1k_2 + \ldots\ldots + (\bar{n} - N)[H_2O]^N k_1k_2\ldots k_N = 0 \quad (14)$$

k_1, $k_2 \ldots k_N$ are reserved, as previously mentioned, for the formation constants of the system, and $K_1, K_2 \ldots K_N$ are the reciprocal of the formation constants, *i.e.*, $K_1 = 1/k_1$.

The concentration of free or unbound water in nitromethane solutions of water–copper(II) perchlorate was determined from the intensity of the 3740 cm.$^{-1}$ band and a previously obtained plot of absorbance *vs.* water concentration. The absorbance–water concentration plot is quite linear up to 0.3 M water but falls off slowly at higher water concentrations, probably as the result of association of water molecules.

From the concentration of free water, $\bar{n}$ was calculated according to

$$\bar{n} = \frac{[H_2O]_{total} - [H_2O]_{free}}{[Cu^{++}]_{total}} \quad (15)$$

The $\bar{n}$ values were used to obtain the formation curve, $\bar{n}$ *vs.* pH_2O_{free}, of the successive aquo-copper complexes (Figure 3). Because of the closeness of successive formation constants and inherent errors in the method (1% in Karl Fischer titrations, 1–2% in determining and reproducing infrared absorptions), a smooth curve, instead of a curve with defined breaks, was obtained. Results of studies carried out with copper(II) solutions prepared by the nitrosyl perchlorate method (open circles in Figure 3) are within experimental error of those obtained with solutions of hydrated copper(II) perchlorate. Definition of the curve at low values of $\bar{n}$ is governed by the residual water content of the solvent nitromethane, and at high

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[10] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1957.

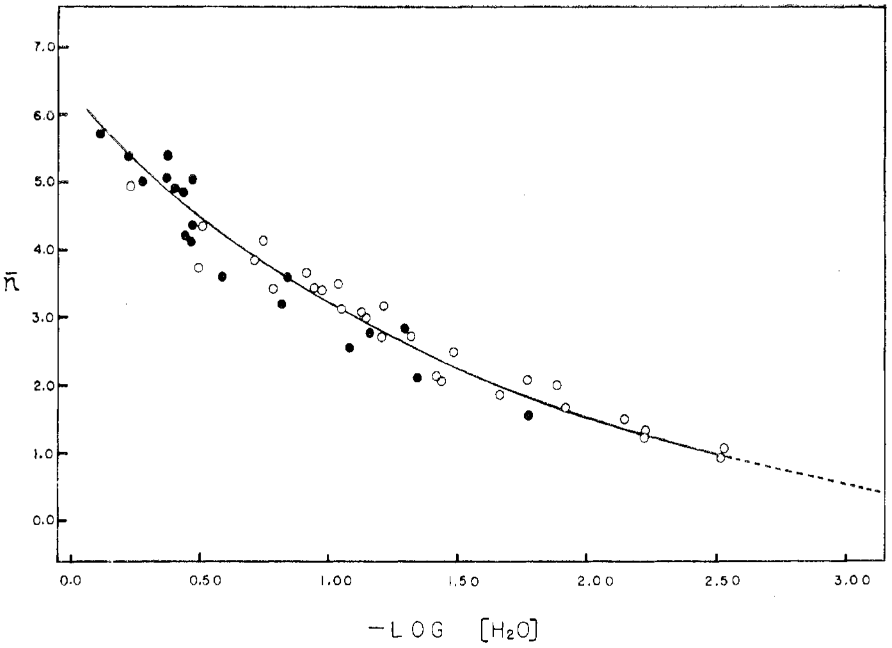

Fig. 3.—Average ligand number, $\bar{n}$, for the system Cu^{++}–H_2O as a function of $-\log[H_2O]$.

values of $\bar{n}$ by the solubility of water and hydrated copper(II) perchlorate.

Temporary constants for aquo–copper(II) complexes were determined from Figure 3 by assuming that when $\bar{n} = n - 0.5$ the solution contains about equal amounts of $Cu(H_2O)_{n-1}^{++}$ and $Cu(H_2O)_n^{++}$ species. The formation constants, it turns out, are the reciprocals of the free water concentrations at half-integral values of $\bar{n}$, *i.e.*

$$k_n = \frac{[Cu(H_2O)_n^{++}]}{[Cu(H_2O)_{n-1}^{++}][H_2O]} = \left(\frac{1}{[H_2O]}\right)_{\bar{n} = n - 0.5} \quad (16)$$

Temporary constants thus determined are presented in Table III.

Table III

Temporary Formation Constants for Aquo–Copper(II) Complexes in Nitromethane (Spectral)

$\bar{n}$ values		
0.5	$pK_1 = 3.06$	$k_1 = 1.15 \times 10^3$
1.5	$pK_2 = 2.02$	$k_2 = 1.05 \times 10^2$
2.5	$pK_3 = 1.37$	$k_3 = 2.34 \times 10$
3.5	$pK_4 = 0.90$	$k_4 = 7.94$
4.5	$pK_5 = 0.51$	$k_5 = 3.23$
5.5	$pK_6 = 0.26$	$k_6 = 1.82$

The graphically evaluated temporary constants were substituted into equation 14 and better values of the formation constants were obtained by the method of successive approximations. These values are presented in Table IV. No values are listed for k_6 as all values calculated were larger than those for k_5.

Table IV

Formation Constants for Aquo–Copper(II) Complexes (Spectral)

k (sought)	$\bar{n}$	pH_2O	pK	Av. pK
k_1	1	2.51	2.94	
	0.5	3.06	2.95	2.94
k_2	1.24	2.26	1.89	
	1.50	2.02	1.91	1.89
	1.76	1.82	1.88	
k_3	2.24	1.52	1.33	
	2.50	1.37	1.31	1.31
	2.76	1.24	1.30	
k_4	3.26	1.00	0.84	
	3.50	0.90	.85	0.85
	3.76	.80	.86	
k_5	4.24	.60	.48	
	4.50	.51	.52	0.52
	4.76	.42	.57	

Calculation of Individual Formation Constants for Aquo–Copper(II) Complexes in Ethanol.—Minc and Libuś' data on the fraction of coördinating positions around copper(II) ion occupied by ethanol *vs.* the mole fraction of ethanol were formulated into a $\bar{n}$ *vs.* pH_2O curve by conversion of their values for mole fraction of ethanol in the coördinating sphere of copper(II) ion to average number of water molecules bound to each copper(II) ion ($\bar{n}$) and of mole fraction of ethanol into molar concentration of water. By the use of equation 14 and the technique of successive approximations, the graphically evaluated temporary formation constants from the $\bar{n}$ *vs.* pH_2O

curve were refined; the values are listed in Table V.

TABLE V

LOG k VALUES FOR AQUO–COPPER(II) IONS IN ETHANOL

	Graphically evaluated values from $\bar{n}$ *vs.* $p\text{H}_2\text{O}$ curve	Refined constants by method of successive approximations			
		Set 1	Set 2	Set 3	Average[a]
k_1	+0.60	−0.29	−0.16	−0.30	−0.23
k_2	−0.43	−0.68	−0.40	−0.56	−0.51
k_3	−0.74	−0.89	−0.83	−0.89	−0.86
k_4	−0.96	−0.89	−0.97	−0.89	−0.93
k_5	−1.20	−0.96	−1.22	−1.44	−1.14
k_6	−1.56	−1.14	−1.23	−1.07	−1.17
				"av."	−0.81

[a] Average of value from Set 2 and of the average value of Sets 1 and 3.

Discussion

Although the electrochemical solutions were 0.1 M in $(\text{C}_2\text{H}_5)_4\text{NClO}_4$, the average individual formation constants obtained by the electrochemical method are in excellent agreement with the average individual formation constants obtained by the spectrophotometric method. (Table VI). The extent of association of Cu^{++} and ClO_4^- in nitromethane, therefore, appears to be very small in comparison with the association of Cu^{++} and water.

TABLE VI

COMPARISON OF FORMATION CONSTANTS OBTAINED BY ELECTROCHEMICAL (E) AND SPECTROPHOTOMETRIC (S) METHODS

	log k_1	log k_2	log k_3	log k_4	log k_5	log k_6
E	2.85	1.96	1.14	1.02	0.52	0.50
S	2.94	1.89	1.31	0.85	0.52	...

The formation constants in nitromethane are larger than in ethanol, (1) because the low compatibility of water and nitromethane as opposed to the high compatibility of water and ethanol enables Cu(II) to compete more successfully for water molecules in nitromethane than in ethanol and (2) because of the lower solvation energy of copper(II) ion in nitromethane than in ethanol as indicated by the more positive half-wave potential for the reduction of Cu(II) ion in nitromethane ($E_{1/2\text{-Cu(II,I),nitromethane}} = 1.05$ v. *vs.* s.c.e.; $E_{1/2\text{Cu(II,I),-ethanol}} = 0.33$ v. *vs.* s.c.e.).[11] The low compatibility of water and nitromethane encourages greater selective solvation of copper(II) ion by water molecules. Although the solvation energy of water in ethanol is large, there nevertheless is some selective solvation of copper(II) ion by water molecules, as shown by Minc and Libuś. There is, however, little possibility that the behavior of copper(II) ions in ethanol can be distorted by residual water, as better than 99% of the copper(II) ions in a 0.01 M water solution remain unhydrated, and *ca.* 95% in a 0.1 M water solution. Such is not the case with the "chemistry" of copper(II) ion in nitromethane. In nitromethane 0.01 M in water, only *ca.* 6% of the copper(II) ions are unhydrated. Care, therefore, must be exercised in interpreting any results for copper(II) ion in nitromethane as those for free copper(II) ion. With *ca.* 50% of the copper(II) species present as $\text{Cu(H}_2\text{O)}^{++}$ and 40% as $\text{Cu(H}_2\text{O)}_2^{++}$, the behavior of copper(II) perchlorate in nitromethane 0.01 M in water is somewhere between that for monohydrated copper(II) ion and dihydrated copper(II) ion.

Interestingly, the formation constants for aquo–copper(II) ions in nitromethane are very similar to those for copper–pyridine complexes in water:[12] log k_1, 2.52; log k_2, 1.86; log k_3, 1.31; and log k_4, 0.85.

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[11] (a) Unpublished results; (b) Cu(I) appears to be solvated to the same extent in both nitromethane and ethanol. ($E_{1/2\ \text{Cu(I),Cu(Hg)nitromethane}} = +0.220$ v. *vs.* s.c.e.; $E_{1/2\text{Cu(I),Cu-(Hg)ethanol}} = +0.245$ v. *vs.* s.c.e.)

[12] R. J. Bruehlman and F. H. Verhoek, *J. Am. Chem. Soc.*, **70**, 1401 (1948); J. Bjerrum and E. J. Nielsen, *Acta Chem. Scand.*, **2**, 297 (1948).