[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE CATHOLIC UNIVERSITY OF AMERICA]

Cupric Complex Ions. I. Absorption Spectra and Equilibria in the Cupric–Nitrite System

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The addition of nitrite ions to a solution of a cupric salt produces a deep green solution, due to the formation of cupric–nitrite complexes. Previous studies of these complexes appear to have been confined to attempts to prepare cupric nitrite and its "double salts."[3]

The present paper is a study of these cupric–nitrite complexes by systematic measurements of the optical extinction of solutions containing cupric ions and nitrite ions at a number of different concentrations and at two ionic strengths. The objectives were the establishment of their formulas and dissociation constants and the use of these to determine the characteristic absorption spectra of the individual complexes.

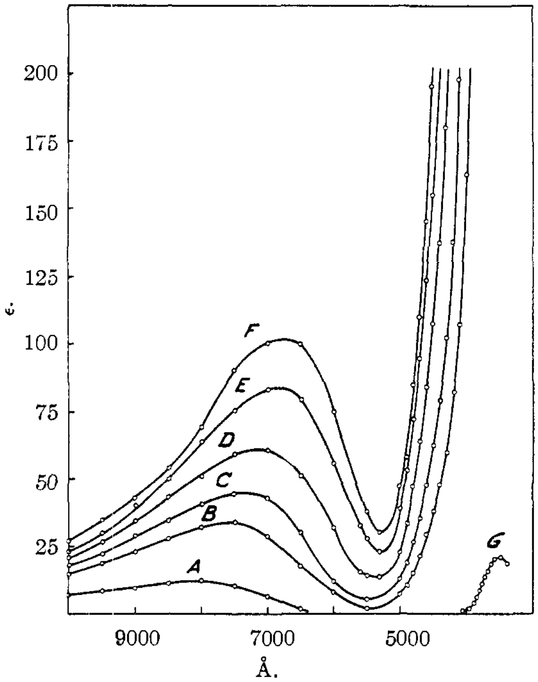

Fig. 1—Specific extinction of solutions, containing cupric ion and various concentrations of nitrite ion. For comparison, the extinctions of cupric ion and of nitrite ion are included. A, Cu^{++}; B, Cu^{++} in 0.2*f*NO_2^-; C, Cu^{++} in 0.5*f*NO_2^-; D, Cu^{++} in 1*f*NO_2^-; E, Cu^{++} in 4*f*NO_2^-; F, Cu^{++} in satd. $NaNO_2$; G, NO_2^-.

The measurements were made at 25° on solutions containing various concentrations of cupric nitrate, sodium nitrite up to 0.7 formal, and made up to an ionic strength of 1 with sodium nitrate; and on a similar set with sodium nitrite up to 4 formal at an ionic strength of 5. The transmission of each solution was measured in comparison with the transmission of a solution containing the same concentration of sodium nitrite, made up to the same ionic strength with sodium nitrate. Both nitrate and sodium ions appear to be optically and chemically inert in such solutions in the spectral region studied.

The measurements in the visible and near infrared were made with a Coleman spectrophotometer, while those in the violet and near ultraviolet were made with a small prism monochromator augmented with filters, using a photocell and direct current amplifier. A number of filter combinations were found which, while they transmitted only 1 to 5% of the light from the monochromator, transmitted sufficiently narrow spectral regions that a large part of the scattered light was eliminated.

The results obtained with some of the solutions are shown in Fig. 1, together with the absorption spectrum of cupric ion and nitrite ion. The water molecules which are undoubtedly coördinated with the ions are omitted from the formulas throughout.

Treatment of the Data.—The extinction data could be interpreted only as due to the successive formation of complexes containing one cupric ion and one, two, and three nitrite ions.

The equilibria considered are

$$CuNO_2^+ \rightleftarrows Cu^{++} + NO_2^-$$

$$K_1 = \frac{[Cu^{++}][NO_2^-]}{[CuNO_2^+]} \tag{1}$$

$$Cu(NO_2)_2 \rightleftarrows CuNO_2^+ + NO_2^-$$

$$K_2 = \frac{[CuNO_2^+][NO_2^-]}{[Cu(NO_2)_2]} \tag{2}$$

$$Cu(NO_2)_3^- \rightleftarrows Cu(NO_2)_2 + NO_2^-$$

$$K_3 = \frac{[Cu(NO_2)_2][NO_2^-]}{[Cu(NO_2)_3^-]} \tag{3}$$

The optical extinction coefficient is

$$C\bar{\epsilon} = [Cu^{++}]\epsilon_{Cu^{++}} + [CuNO_2^+]\epsilon_1 + [Cu(NO_2)_2]\epsilon_2 + [Cu(NO_2)_3^-]\epsilon_3$$

or, using (1), (2) and (3)

$$\Delta\bar{\epsilon} = \frac{K_2K_3[NO_2^-]\Delta\epsilon_1 + K_3[NO_2^-]^2\Delta\epsilon_2 + [NO_2^-]^3\Delta\epsilon_3}{K_1K_2K_3 + K_2K_3[NO_2^-] + K_3[NO_2^-]^2 + [NO_2^-]^3} \tag{4}$$

where C is the total cupric ion concentration, $\bar{\epsilon} = (1/lC) \log_{10} I_0/I$; ϵ_1, ϵ_2 and ϵ_3 are the extinction coefficients of the first, second and third complexes; and $\Delta\bar{\epsilon} = \bar{\epsilon} - \epsilon_{Cu^{++}}$, $\Delta\epsilon_1 = \epsilon_1 - \epsilon_{Cu^{++}}$, $\Delta\epsilon_2 = \epsilon_2 - \epsilon_{Cu^{++}}$ and $\Delta\epsilon_3 = \epsilon_3 - \epsilon_{Cu^{++}}$; l is the length of the cell in centimeters.

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[3] For example, Kurtenacher, *Z. anorg. Chem.*, **82**, 204 (1913).

K_1 and ϵ_1 were found from solutions containing a large excess of cupric ion with the smallest practicable concentrations of nitrite ion. Under these circumstances, the third complex is essentially absent and the second is present only to a minor extent. On the assumption that only the first complex is present and that $[Cu^{++}] = C$, equation (4) reduces to

$$\frac{N}{C\Delta\bar{\epsilon}} = \frac{K_1}{\Delta\epsilon_1}\frac{1}{C} + \frac{1}{\Delta\epsilon_1} \qquad (5)$$

where N is the total nitrite ion concentration. If the above assumptions are valid, a plot of $N/C\Delta\bar{\epsilon}$ as a function of $1/C$ will be linear, with an intercept of $1/\Delta\epsilon_1$ at $1/C = 0$, and a slope of $K_1/\Delta\epsilon_1$. The results with solutions 0.02 formal in nitrite are shown in Fig. 2. The wave lengths chosen as the most reliable were those for which both the cupric and nitrite absorptions are quite small.

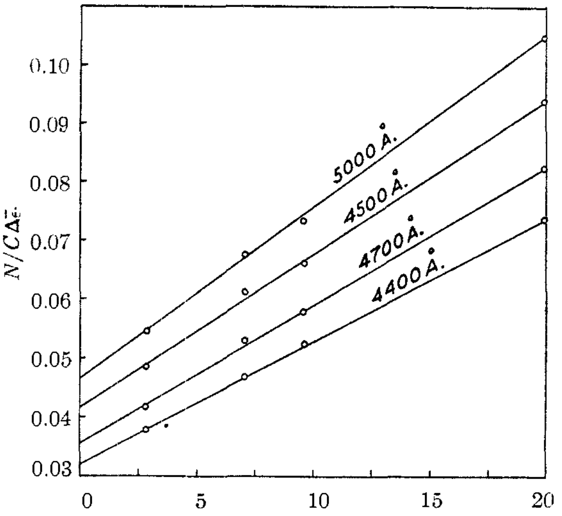

Fig. 2.—Graphs of equation (5) for solutions with 0.02 formal nitrite ion at various wave lengths. For 5000 Å. the ordinates should be multiplied by 5 and for 4700 Å. by 2.

The values of K_1 obtained in this way were consistent and gave a value of 0.063 ± 0.010 at an ionic strength of 1.

In finding the other K's and the ϵ's the extinction of the third complex was assumed to be that of cupric ion in saturated sodium nitrite solution, although this may be somewhat low. The values of K_2, K_3 and ϵ_2 were obtained by fitting the data to equation (4). The extinction coefficients of the complex ions were assumed to remain unchanged in the solutions of both ionic strengths. The measured extinction coefficient of cupric ion, which is slightly greater at an ionic strength of 5 than at 1, was used to calculate the $\Delta\epsilon$'s.

The values of the equilibrium constants obtained in this way and an estimate of their reliability are given in Table I.

TABLE I

	IONIC STRENGTH 1	IONIC STRENGTH 5
K_1	0.063 ± 0.01	0.055 ± 0.01
K_2	0.60 ± 0.1	0.50 ± 0.1
K_3	6 ± 3	2.5 ± 1

No attempt was made to estimate activities. The K's are in terms of formal concentrations.

The extinction coefficients for the complexes were calculated by using the equilibrium constants given above. Figure 3 shows the ordinary logarithms of the several extinction coefficients plotted as a function of the wave length. The errors in determining the constants are reflected in the accuracy of the extinction coefficients.

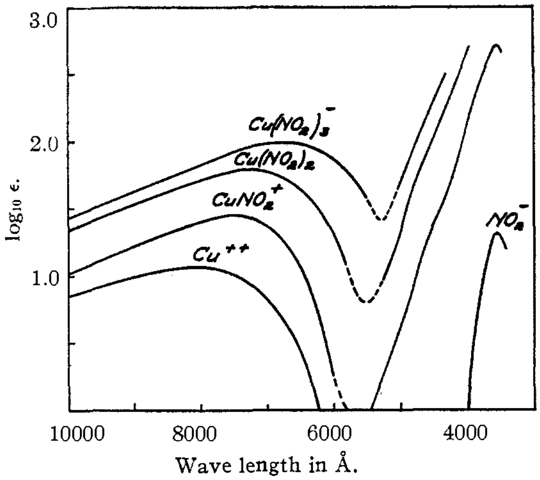

Fig. 3.—Logarithms of the calculated extinction coefficients of the three cupric–nitrite complexes.

The extinctions of the first and third complexes are known the best, probably to within 10 to 20%, while the extinction of the second complex may be in error by as much as 30 to 40%. However, this accuracy is entirely adequate for any theoretical interpretation of the spectra of these complexes.

The distribution of cupric ion among the various complexes at an ionic strength of 1 as a function of the actual nitrite ion concentration is shown in Fig. 4.

Discussion

Several significant conclusions can be drawn from the results of these experiments:

1. The values of K_1, K_2 and K_3 show that each successive nitrite ion is attached to the cupric ion with uniformly increasing difficulty. There is no indication that $CuNO_2^+$ and $Cu(NO_2)_3^-$ are peculiarly stable or unstable compared to $Cu(NO_2)_2$.[4] It is probable that higher complexes would be formed at nitrite ion concentrations substantially greater than 8 formal or in complex salts in the solid state.

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(4) Compare Job, *Compt. rend.*, **198**, 827 (1934), who found, for example, evidence for the existence of $CuBr^+$ and $CuBr_3^-$ but not for $CuBr_2$.

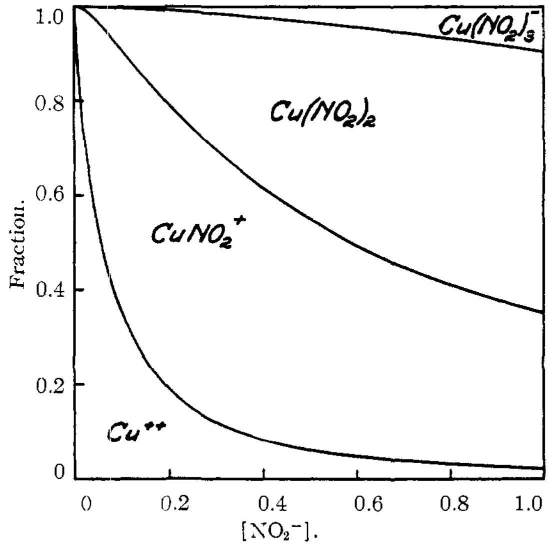

Fig. 4.—Distribution of cupric ion among the free (hydrated) and complex ion forms as a function of the actual (free) nitrite ion concentration.

2. The extinction curves for the three complex ions show a uniform trend, shown in Fig. 3. In particular, the absorption of cupric ion in the red is enhanced strongly as nitrite ions successively replace the water molecules which normally surround it in solution.

3. The intensity of the absorption in both the red and the violet, as measured by the integral of $\epsilon d\nu$ over the band or very roughly by the maximum value of the extinction coefficient, is relatively low, even in the higher complexes. For comparison, while the extinction coefficient of cupric ion is 13 at 8000 Å., it is 3,000 and rising at 2,000 Å.[5] These two absorption bands of cupric ion have an entirely different order of magnitude of intensity. For this reason the red absorption of cupric ion is probably caused by transitions to one or more of the numerous lower electronic levels of Cu^{++} and which are forbidden for dipole radiation to a first approximation. These transitions are broadened and increased in intensity by the Stark effect from solvation or complex formation.[6] Similar considerations apply to the absorption region in the violet. An electron transfer,[7] such as is responsible for the ultraviolet absorption of halide ions and for the violet absorption of cupric halide complex ions, seems to be out of the question.

4. The absorption of the complex ions in the red appears to be an intensification of the very weak red absorption of cupric ion, and that in the violet an intensification of the near ultra-violet absorption of nitrite ion, cupric ion, or of both.

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Summary

Measurements of the absorption spectrum in the visible and adjacent spectral regions of solutions containing cupric and nitrite ions are consistent with the successive formation with increasing difficulty of the complex ions CuNO$_2^+$, Cu(NO$_2$)$_2$ and Cu(NO$_2$)$_3^-$. The instability constants of these complex ions are approximately 0.063 ± 0.01, 0.60 ± 0.1 and 6 ± 3 at an ionic strength of 1; and 0.055 ± 0.01, 0.50 ± 0.1 and 2.5 ± 1 at an ionic strength of 5.

The solutions are green because of absorption in the red and blue spectral regions. These two absorption regions are apparently an intensification and shift toward the visible of the normal cupric ion and nitrite ion absorptions. The small intensity of the absorption in both regions indicates that they are probably forbidden transitions and are not electron transfer spectra.

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(5) Fromherz and Menschik, *Z. physik. Chem.*, **B3**, 1 (1929).

(6) Bethe, *Ann. Physik*, **3**, 133 (1929).

(7) Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942).