values arising from covalency of d character. Indeed, a linear relationship was found for these ions. The remaining B^{+3} ions have unfilled d orbitals and might be expected to have smaller radii. The radii derived for Co^{+3}, Ni^{+3}, Cr^{+3}, V^{+3}, Mn^{+3}, Rh^{+3}, and Sc^{+3} are listed in Table IV along with those of Ahrens. Since a significant amount of covalency in the B–O bonds exists, these radii should be called effective rather than ionic radii. As expected, all of the effective radii are smaller than those listed by Ahrens. The radii of Co^{+3} (low spin) and Ni^{+3} agree well with those recently quoted by Blasse.[24] The sixfold radius of Sc^{+3} is in excellent agreement with the value determined by Müller-Buschbaum and Schnering[25] in $CaSc_2O_4$ and by Cruickshank[26] in $Sc_2Si_2O_7$ (0.73).

(24) G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 748 (1965).
(25) H. Müller-Buschbaum and H. Schnering, *Z. Anorg. Allgem. Chem.*, **336**, 295 (1965).

A similar plot for the A^{+3} ions resulted in a rapid increase in slope as r_A decreases, thus preventing the determination of the 12-fold radii. Dalziel[27] and Schneider, *et al.*,[3] found the same effect. This increase may be caused by the deviation from 12-fold coordination. Coppens and Eibschütz[11] showed a very irregular coordination of the Gd^{+3} and Y^{+3} ions in $GdFeO_3$ and $YFeO_3$.

(26) D. W. J. Cruickshank, H. Lynton, and G. A. Barclay, *Acta Cryst.*, **15**, 491 (1962).
(27) J. A. W. Dalziel, *J. Chem. Soc.*, 1993 (1959).

Solubility of Copper(I) Bromide in Sodium Bromide Media

By DENNIS G. PETERS and RANDALL L. CALDWELL

Pure, solid copper(I) bromide, CuBr, has been prepared by means of controlled-potential coulometry, and a study was performed of its solubility in aqueous sodium bromide media ranging in concentration from approximately 0.05 to 1.5 F. Within this range of bromide concentrations, the predominant species of copper(I) are $CuBr_2^-$ and $CuBr_3^{2-}$. At an ionic strength of 2.0 and a temperature of 25°, the concentration equilibrium constants for the reactions $CuBr(s) + Br^- = CuBr_2^-$ and $CuBr_2^- + Br^- = CuBr_3^{2-}$ are $K_1K_2K_{s0} = (3.8 \pm 0.4) \times 10^{-3}$ and $K_3 = 10.2 \pm 0.9$, respectively. Potentiometric measurements have demonstrated that dimeric or higher polymeric forms of copper(I) are not present to any significant extent in the solutions investigated. In a solution consisting of 1 F sodium bromide and 1 F sodium nitrate, the formal potential ($E°'$) for the copper(I)–copper(0) couple is close to −0.111 v *vs.* sce or +0.130 v *vs.* nhe.

During a recent chronopotentiometric investigation of the reduction of copper(I) to copper metal in potassium bromide medium,[1] it was discovered that the only study of the solubility of copper(I) bromide (CuBr) in bromide solutions was published by Bodländer and Storbeck[2] over 60 years ago. However, the solubility data reported by these workers were obtained at inconstant ionic strength under somewhat unfavorable conditions for which, owing to atmospheric oxidation as well as disproportionation of copper(I), a mixture of elemental copper, copper(I), and copper(II) existed. Furthermore, aside from a single measurement of the solubility of CuBr in 0.5 F potassium bromide solution, the bromide ion concentrations employed by Bodländer and Storbeck were comparatively low and confined to a relatively narrow range of values. Only a partial description of the solubility behavior of CuBr in bromide solutions is obtainable from this previous work, and heretofore no quantitative information has

(1) D. G. Peters and L. A. Franklin, *J. Electroanal. Chem.*, **9**, 385 (1965).
(2) G. Bodländer and O. Storbeck, *Z. Anorg. Allgem. Chem.*, **31**, 458 (1902).

been available concerning the identities and stabilities of the soluble copper(I) species which exist at high bromide concentrations.

The goals of the present investigation were the accurate measurement of the solubility of CuBr in relatively concentrated sodium bromide media, the identification of the species of copper(I) present in such solutions, and the evaluation of the equilibrium constants for the pertinent chemical reactions. In the work discussed below, controlled-potential coulometry has been employed as a technique both for the *in situ* preparation of pure solid CuBr and for the determination and study of the solubility of CuBr in sodium bromide solutions equilibrated with this solid.

Experimental Section

Reagents.—Stock solutions containing known initial concentrations of copper(II) bromide and sodium bromide, from which copper(I) was electrochemically generated, were prepared by weight from reagent grade chemicals. Sufficient sodium nitrate was included in each stock solution to provide an ionic strength of 2.0.

Controlled-Potential Coulometric Preparation of Copper(I) Bromide.—The electrochemical preparation of copper(I) bromide solutions in equilibrium with solid CuBr was performed in a conventional three-electrode coulometric cell. A large platinum gauze electrode served as the generator cathode. The platinum wire auxiliary electrode and the saturated calomel reference electrode (sce) were placed in separate compartments (porous Vycor tubes) containing either sodium nitrate or sulfuric acid solution. An electronic, controlled-potential coulometric titrator, ORNL Model Q-2005-X50 (commercially available from the Indiana Instrument and Chemical Corp., Bloomington, Ind.) was used in the generation of copper(I) and in the subsequent solubility measurements. The preparation of CuBr and the equilibration of the solid with the bromide solution were carried out at a temperature of 25.00 ± 0.05°, maintained by circulation of thermostated water through a jacket surrounding the cell.

To begin a solubility experiment, an aliquot of the stock solution was pipetted into the cell. Since copper(I) is rapidly oxidized by oxygen, high-purity nitrogen or argon, presaturated with water vapor, was bubbled through the solution for at least 15 min prior to the start of electrolysis to expel dissolved oxygen. Thereafter, the flow of nitrogen or argon was continued throughout the preparation and equilibration steps. For the reduction of copper(II) to copper(I), the potential of the platinum gauze cathode was controlled at −0.06 v vs. sce. This potential was chosen from knowledge of the electrochemistry of copper(II) and copper(I) in a bromide medium.[1] The relative quantities of copper(II) bromide and sodium bromide in the original stock solution were always adjusted so that the solubility of CuBr would be exceeded. Thus, during the course of the reduction of copper(II) to copper(I), a precipitate of CuBr formed. It was essential to the success of the present experiments that the reduction of copper(II) to copper(I) be quantitatively complete and also that no metallic copper be formed. The quantity of copper(II) coulometrically reduced to copper(I) was always in excellent agreement with the value predicted from the amount of copper(II) originally taken. Following this quantitative reduction, the potential of the platinum cathode was maintained at −0.06 v vs. sce for an additional 3–9 hr so that solubility equilibrium might be attained. Variations of the equilibration time within this range had no effect on the observed solubility of CuBr.

Measurement of Solubility of Copper(I) Bromide.—After equilibration of the bromide solution with solid CuBr, a 25.00-ml aliquot was transferred for analysis to a second coulometric cell equipped with a platinum gauze electrode. To prevent solid CuBr from being drawn up into the pipet, the sample was pipetted through a sintered-glass filter stick. To the 25-ml sample was added approximately 50 ml of 3.0 F sodium bromide solution. This high bromide concentration improves the controlled-potential coulometric determination of copper(I) by causing greater separation of the potentials for the copper(II)–copper(I) and copper(I)–copper(0) half-reactions.[1] In addition, a high bromide concentration prevents the precipitation of solid CuBr upon the surface of the platinum gauze electrode during the measurement step. Such precipitation can occur if one attempts to analyze a sample containing a high concentration of copper in the presence of a relatively small concentration of bromide; the resulting precipitate adheres tightly to the electrode, decreases the effective electrode area, and lengthens the time required for the analysis. The solution was deaerated with nitrogen as before, but it was unnecessary to maintain a constant temperature during the analysis.

Because of the unavoidable oxidation of some copper(I) back to copper(II) during the sampling operation, all copper(I) was first quantitatively oxidized to copper(II) at a controlled potential of +0.50 v vs. sce. Following the oxidation, the copper(II) was reduced to copper(I) at a potential of −0.06 v vs. sce. The measurement of the quantity of copper(II) reduced to copper(I) in this latter step was taken as the solubility of CuBr in the original bromide medium.

Confirmation of Identity of Copper(I) Bromide.—To establish

that the solid phase formed in the electrochemical preparation of copper(I) bromide was actually CuBr, a sample of the solid material was analyzed. The solid was suction filtered from the original bromide solution, washed with an approximately 1:1 mixture of ethanol and ethyl ether, and suction dried. These manipulations were performed as quickly as possible in order to minimize oxidation of the CuBr by atmospheric oxygen. Next, the solid was dissolved in 1 F aqueous ammonia; then, the resulting solution was transferred to a volumetric flask and 1 F ammonia was added to adjust the volume.

The analysis for copper was accomplished by the controlled-potential reduction of copper(II) to copper(I) in a chloride medium at 0 v vs. sce[3] in the cell described above. Ten-milliliter aliquots of the ammonia solution of CuBr were neutralized with concentrated hydrochloric acid; then a 1-ml excess of hydrochloric acid was added. Approximately 20 ml of saturated potassium chloride solution was introduced and the sample solution was diluted to about 70 ml with water. In our experiments, the dissolved oxygen in the aqueous ammonia used to dissolve the CuBr was sufficient to oxidize chemically all copper(I) to copper(II). Therefore, no preliminary adjustment of the oxidation state of copper was required.

A potentiometric titration with silver nitrate was used for the determination of bromide. A 10.00-ml sample of the ammonia solution of CuBr was pipetted into a beaker containing a magnetic stirring bar, a silver indicator electrode, and a saturated calomel reference electrode. Enough 1 F nitric acid was added to the sample to neutralize the ammonia, to increase the solution volume to approximately 75 ml, and to make the acid concentration about 0.8 F prior to the start of the titration.

For duplicate 10-ml samples of the original ammonia solution of CuBr, the average quantities of copper and bromide were found to be 0.0722 and 0.0730 mmole, respectively.

Results and Discussion

Table I summarizes the results of solubility measurements for eight different bromide concentrations. Each value observed for the solubility of CuBr is the average of three or four separate experiments. For purposes of comparison and later discussion, Table I lists theoretical values, predicted from the equilibrium constants determined in this study, for the solubility of CuBr and for the individual concentrations of CuBr$_2$$^-$ and CuBr$_3$$^{2-}$ in equilibrium with the solid. It should be emphasized that the data and conclusions presented in this report pertain to an ionic strength of 2.0 and that no attempt has been made to calculate activity coefficients for the various copper(I) species. Therefore, the equilibrium constants are based upon analytical concentrations rather than activities, are properly called *concentration equilibrium constants*, and are valid only for the specified ionic strength.

In general, the solubility S may be expressed as the sum of the concentrations of all soluble ionic and molecular copper(I) species

$$S = [\text{Cu}^+] + [\text{CuBr(aq)}] + [\text{CuBr}_2{}^-] + [\text{CuBr}_3{}^{2-}] + \ldots$$

Mononuclear complexes beyond CuBr$_3$$^{2-}$ have not been included in this relation, nor have any polynuclear copper(I) species such as Cu$_2$Br$_3$$^-$, because the solubility data are explicable without consideration of these complexes. As described below, the absence of significant concentrations of polynuclear species has been established by means of potentiometry. The same conclusion was reached by Bodländer and Storbeck[2]

(3) D. G. Peters and S. A. Cruser, *J. Electroanal. Chem.*, **9**, 27 (1965).

TABLE I

SOLUBILITY OF COPPER(I) BROMIDE AS A FUNCTION OF BROMIDE
CONCENTRATION (TEMPERATURE 25°, IONIC STRENGTH 2.0)

[Br⁻], M	Obsd soly, S, F	Calcd soly, S, $F \times 10^3$	Calcd [Cu-Br₂⁻], $M \times 10^3$	Calcd [CuBr₃²⁻], $M \times 10^3$
0.051	0.00035 ± 0.00002	0.29	0.19	0.10
0.102	0.00079 ± 0.00001	0.79	0.39	0.40
0.206	0.00223 ± 0.00001	2.39	0.78	1.61
0.495	0.0104 ± 0.0001	11.2	1.9	9.3
0.595	0.0151 ± 0.0001	15.8	2.3	13.5
0.798	0.0282 ± 0.0002	27.2	3.0	24.2
1.01	0.0456 ± 0.0018	42.4	3.8	38.6
1.52	0.118 ± 0.008	93.3	5.8	87.5

from measurements of the electromotive force of concentration cells containing copper(I).

If the concentration of each species in the preceding equation is written in terms of the bromide concentration, the stepwise formation constants (K_n) for the copper(I) bromide complexes, and the conventional solubility product constant (K_{s0}) for CuBr, one obtains

$$S = \frac{K_{s0}}{[\text{Br}^-]} + K_1K_{s0} + K_1K_2K_{s0}[\text{Br}^-] + $$
$$K_1K_2K_3K_{s0}[\text{Br}^-]^2 + \ldots$$

Graphical Presentation of Solubility Data.—Sillén[4] has described several graphical techniques for the presentation and interpretation of equilibrium data. The solubility behavior of CuBr in sodium bromide solutions may be portrayed, as shown in Figure 1, by a plot of the logarithm of the solubility S *vs.* the logarithm of the free bromide concentration. The solid points on this graph correspond to the experimental results listed in Table I, while the open circles represent data of Bodländer and Storbeck.[2] The solid curve in Figure 1 depicts the variation of the solubility of CuBr with bromide concentration and has been drawn to agree only with the experimental points obtained in the present investigation. Two features of a plot such as Figure 1 should be noticed. First, a linear relationship always exists between the logarithm of the concentration of any species in the chemical system and the logarithm of the bromide concentration. Second, the slope of the straight line for each species is *equal* in magnitude but *opposite* in sign to the charge of that particular species.

An inspection of the solid curve in Figure 1 reveals that the slope of the plot of the logarithm of S *vs.* the logarithm of [Br⁻] is close to +1 at low bromide concentrations but increases to approximately +2 at high concentrations of bromide. These observations indicate that a singly charged anionic complex is predominant at low bromide concentrations, whereas the important species at higher concentrations of bromide is a doubly charged anion. The ions CuBr₂⁻ and CuBr₃²⁻ are candidates which fit these requirements best. The polynuclear complexes Cu₂Br₃⁻ and Cu₂Br₄²⁻ cannot be excluded on the basis of charge alone,

(4) L. G. Sillén in "Treatise on Analytical Chemistry," Vol. I, I. M. Kolthoff and P. J. Elving, Ed., Interscience Publishers, Inc., New York, N. Y., 1959, Part I, pp 277–317.
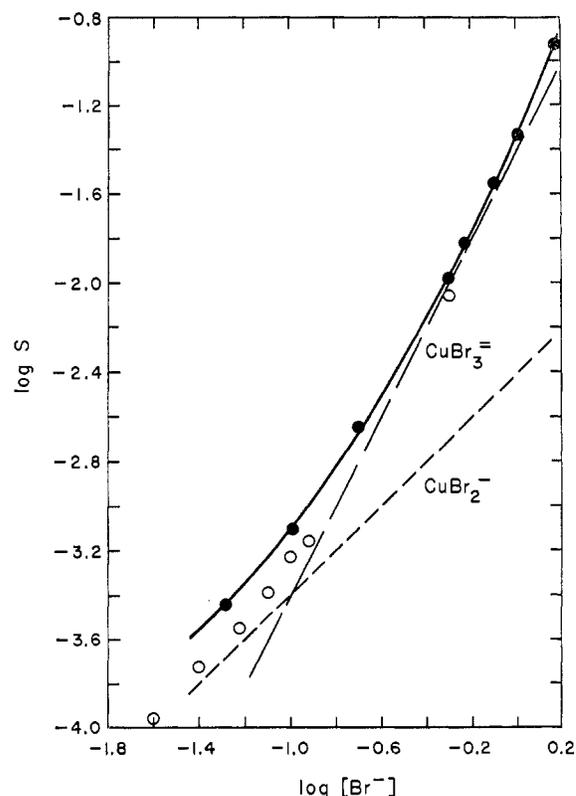
Figure 1.—Logarithm of the solubility of CuBr in sodium bromide media as a function of the logarithm of the free bromide concentration. The solid points and the solid curve represent the results of the present work at 25° and an ionic strength of 2.0 (Table I). The open circles are data reported by Bodländer and Storbeck. The dashed, straight lines show the predicted logarithmic variations of the CuBr₂⁻ and CuBr₃²⁻ concentrations, as calculated from the experimental results.

because these species would also yield straight lines with slopes of +1 and +2, respectively; however, the potentiometric evidence cited below demonstrates that these dimeric anions are not present to any significant extent. Since the simple cuprous ion Cu⁺ and the soluble uncharged molecule CuBr(aq) would generate straight lines with respective slopes of −1 and 0, these species are definitely unimportant within the range of bromide concentrations investigated.[5] Therefore, the solubility of CuBr is expressible by the equation

$$S = [\text{CuBr}_2^-] + [\text{CuBr}_3^{2-}] = K_1K_2K_{s0}[\text{Br}^-] + K_1K_2K_3K_{s0}[\text{Br}^-]^2$$

(5) Both referees suggested that CuBr(aq) be included as a possible species in the mathematical analysis of the experimental data (Table I). If such a reinterpretation is performed, the following results are obtained from least-squares computations.

$$\text{CuBr(s)} = \text{CuBr(aq)}; \quad K_1K_{s0} = 2.4 \times 10^{-4}$$
$$\text{CuBr(aq)} + \text{Br}^- = \text{CuBr}_2^-; \quad K_2 = 4.8$$
$$\text{CuBr}_2^- + \text{Br}^- = \text{CuBr}_3^{2-}; \quad K_3 = 36$$

Values of the solubility of CuBr at each bromide concentration, calculated from this latter set of equilibrium constants, do agree slightly better with the observed solubilities in Table I. However, this new set of values is unrealistic in at least two ways. First, the predicted concentration of CuBr(aq) in equilibrium with solid CuBr is abnormally large compared to analogous compounds such as AgBr; furthermore, the data of Bodländer and Storbeck and some untabulated (semiquantitative) results of our own indicate that the solubility of CuBr reaches at least a minimum of 1×10^{-4} F at bromide concentrations near 0.01 M. Second, CuBr₃²⁻ would not be expected to be more stable than CuBr₂⁻, because CuBr₃²⁻ has a higher charge and because the formation of tetrahedral CuBr₃²⁻ from linear CuBr₂⁻ requires a change in stereochemistry and bonding.

Calculation of Free Bromide Concentration.—One can calculate the equilibrium concentration of free bromide ion by correcting the original bromide concentration for the quantity of bromide consumed by the formation of $CuBr_2^-$ and $CuBr_3^{2-}$ as well as that present in the CuBr precipitate. The appropriate relation is

$$[Br^-] = [Br^-]_0 - ([Cu^{2+}] - S) - 2[CuBr_2^-] - 3[CuBr_3^{2-}]$$

where $[Br^-]$ is the final equilibrium bromide concentration, $[Br^-]_0$ the original bromide concentration derived from the amounts of sodium bromide and copper(II) bromide in the stock solution, $[Cu^{2+}]$ the original concentration of copper(II), $[CuBr_2^-]$ and $[CuBr_3^{2-}]$ the concentrations of the two complexes, and S the observed solubility of CuBr. Notice that the term $([Cu^{2+}] - S)$ is equivalent to the *concentration* of bromide precipitated as CuBr. This equation was applied in an iterative manner to provide the best correlation between the calculated bromide concentration and the values for $[CuBr_2^-]$ and $[CuBr_3^{2-}]$. Since the equilibrium bromide concentration for most experiments was substantially higher than the concentration of either $CuBr_2^-$ or $CuBr_3^{2-}$, it was unnecessary to know *a priori* precise values for $[CuBr_2^-]$ and $[CuBr_3^{2-}]$. Good preliminary estimates of $[CuBr_2^-]$ and $[CuBr_3^{2-}]$ could be made, however, because the logarithmic concentrations of these ions must be described in Figure 1 by two straight lines with slopes of $+1$ and $+2$, respectively. Therefore, accurate values for the free bromide concentration were obtained after no more than two iterative calculations.

Evaluation of Equilibrium Constants.—Since $CuBr_2^-$ and $CuBr_3^{2-}$ are the only species which contribute significantly to the solubility of CuBr, the experimental solubility curve (solid line) shown in Figure 1 was considered to be composed of two straight lines—one corresponding to $CuBr_2^-$ with a slope of $+1$ and the other to $CuBr_3^{2-}$ with a slope of $+2$. The exact positions of these lines were determined from a least-squares analysis of the experimental data. The least-squares computations involved the assumption that the standard deviation for the free bromide concentration, calculated as described above, was zero in each experiment. Two dashed lines showing the logarithmic concentrations of $CuBr_2^-$ and $CuBr_3^{2-}$ as a function of the logarithm of the bromide concentration are included in Figure 1. Table I contains a summary of values for the individual concentrations of $CuBr_2^-$ and $CuBr_3^{2-}$ determined from the positions of the straight lines. The sum of these two concentrations, which represents the calculated or predicted solubility of CuBr, is in reasonable agreement with the observed solubility at each bromide concentration.[5]

The intersection of the lines for $CuBr_2^-$ and $CuBr_3^{2-}$ marks the point at which the concentrations of these two species are equal in the equilibrium expression

$$CuBr_2^- + Br^- \rightleftharpoons CuBr_3^{2-}; \quad K_3 = \frac{[CuBr_3^{2-}]}{[CuBr_2^-][Br^-]}$$
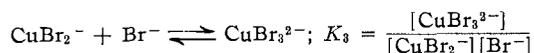
Since $[CuBr_2^-] = [CuBr_3^{2-}]$, $K_3 = 1/[Br^-]$ and $pK_3 = \log [Br^-] = -1.01 \pm 0.03$. Therefore, the

third stepwise formation constant K_3 is 10.2 ± 0.9. Individual values for K_1, K_2, and K_{s0} cannot be determined from the data of the present investigation. The evaluation of these equilibrium constants requires that solubility measurements be extended to bromide concentrations much lower than 0.05 M, so that definite domains in which Cu^+ and $CuBr(aq)$ predominate can be found. Unfortunately, for bromide concentrations below 0.01 M, disproportionation of copper(I) into copper(II) and elemental copper becomes appreciable and the experimental techniques used in this study are no longer applicable.

The equilibrium constant for the reaction

$$CuBr(s) + Br^- \rightleftharpoons CuBr_2^-$$
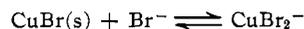
is $K_1K_2K_{s0}$ and may be computed from the equation for the straight-line corresponding to the $CuBr_2^-$ ion in Figure 1. The result of this calculation is $K_1K_2K_{s0} = (3.8 \pm 0.4) \times 10^{-3}$ at 25° and an ionic strength of 2.0. While the original measurements of Bodländer and Storbeck[2] pertain to solution temperatures from 18 to 20° and ionic strengths between 0.025 and 0.08, Latimer[6] reinterpreted the data of these workers and asserted that $K_1K_2K_{s0}$ is 4.6×10^{-3} at 25° and infinite dilution. Since the numerator and denominator of the equilibrium expression for the above reaction both contain a first-order concentration term for a singly charged anion, the equilibrium constant should be relatively insensitive to changes in ionic strength. The agreement between the constant quoted by Latimer and that evaluated in the present study supports this conclusion.

At bromide concentrations greater than 1.0 M, the experimental solubility curve shown in Figure 1 begins to deviate detectably from the calculated line for the $CuBr_3^{2-}$ ion. Such an observation hints that the species $CuBr_4^{3-}$ might exist at high bromide concentrations. However, this aspect of the solubility problem was not pursued further because of practical problems involved in the preparation of concentrated sodium bromide solutions containing large amounts of copper(I). One problem is that migration of ions during the electrochemical generation of high concentrations of copper(I) alters the ionic strength of the solutions, thereby causing activity coefficients to vary. This latter factor, rather than the formation of $CuBr_4^{3-}$, could account entirely for the unexpectedly large difference between the observed and predicted solubility of CuBr at the highest bromide concentration in Table I.

Absence of Dimeric Copper(I) Species.—It was important to establish if any dimeric (or polymeric) forms of copper(I) exist in sodium bromide media, especially at high bromide concentrations where the solubility of CuBr increases rapidly. This possibility was tested through measurements of the potential of a copper indicator electrode immersed in a solution containing a variable concentration of copper(I).

(6) W. M. Latimer, "Oxidation Potentials," 2nd ed, Prentice-Hall, Inc., New York, N. Y., 1952, p 186.

The preparation of a known concentration of copper(I) and the measurement of the potential of the copper indicator electrode were accomplished in the following way. Copper(I) was generated in the three-electrode coulometric cell described earlier by the controlled-potential dissolution of a pure copper anode in 1.0 F sodium bromide–1.0 F sodium nitrate medium at 25°. The other two electrodes were a platinum wire auxiliary electrode and a saturated calomel reference electrode. We prepared 11 different concentrations of copper(I) ranging from approximately 1.1×10^{-4} to 1.5×10^{-2} F by repeatedly starting and stopping the anodization. Each time the electrolysis was stopped, the total formal concentration of copper(I) generated up to that point was calculated from the integrator readout of the coulometer, and the potential of a copper wire indicator electrode *vs.* a second saturated calomel electrode was measured with a precision potentiometer. Steady potential readings, with an uncertainty less than 0.5 mv, were obtained within 2–3 min after each interruption of the anodization.

Figure 2 shows a plot of the potential of the copper indicator electrode *vs.* the logarithm of the formal concentration of copper(I). For copper(I) concentrations greater than approximately 1.0×10^{-3} F, the experimental points fall almost perfectly on a straight line with a reciprocal slope of 57 mv. According to the Nernst equation, the reciprocal slope of this line should have a value of 59 mv if monomeric copper(I) species alone are present. The experimental result provides good evidence that only mononuclear copper(I) complexes exist in significant concentrations in the sodium bromide solutions studied. This conclusion is strengthened by the fact that, as the copper(I) concentration increases above 1×10^{-3} F, the individual experimental points display no tendency to curve away from the straight line toward lower values for the reciprocal slope. In other words, although the formation of dimeric species should be favored by an increase in the total concentration of copper(I), the data indicate that dimerization does not occur to any measurable extent.

The deviation of the experimental points corresponding to the four lowest concentrations of copper(I) from the straight line in Figure 2 requires an explanation. We believe the cause of these discrepancies to be the extraneous *chemical* reaction between the copper anode and traces of oxygen remaining in the solution at the start of the experiment. As a consequence of this reaction, the actual concentration of copper(I) would be larger than that expected from the anodic polarization of the copper electrode, and the potential of the copper wire indicator electrode would appear to be too anodic or too positive. However, this effect diminished rapidly as the total concentration of copper(I) was increased during the course of the experiment.

Formal Potential for the Copper(I)–Copper(0) Couple. —If a copper electrode is inserted into a 1 F sodium bromide–1 F sodium nitrate medium containing copper(I) at a hypothetical concentration of exactly 1 F, the potential of the copper electrode, measured against
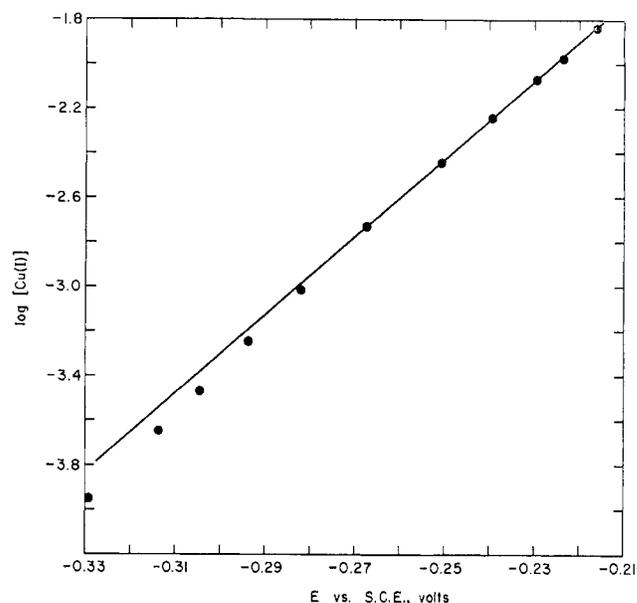
Figure 2.—Variation of the potential of a copper indicator electrode *vs.* the logarithm of the total formal concentration of copper(I) at 25° in a 1.0 F sodium bromide–1.0 F sodium nitrate electrolyte solution. The straight line has a reciprocal slope of 57 mv, indicating that only monomeric forms of copper(I) are present in significant concentrations.

the normal hydrogen electrode (nhe) at 25°, is defined as the *formal* potential, $E^{\circ\prime}$, for the copper(I)–copper(0) couple in that solution. Although the maximum attainable concentration of copper(I) in this medium is slightly less than 0.05 F (Table I), a value for the formal potential can nevertheless be obtained if one extrapolates the straight line in Figure 2 to a copper(I) concentration of 1 F and reads the potential corresponding to that point on the abscissa. This procedure yields a formal potential of -0.111 v *vs.* sce or $+0.130$ v *vs.* nhe. The result includes no correction for liquid-junction potentials and no consideration of the fact that the reciprocal slope of the straight line in Figure 2 does not have the theoretical value of 59 mv.

The formal potential may be compared with the standard potential for the half-reaction

$$CuBr_2^- + e = Cu + 2Br^-$$
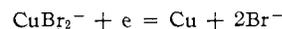
which has a value calculated from free energy data[1] to be -0.071 v *vs.* sce or $+0.170$ v *vs.* nhe. The *standard* potential for the $CuBr_2^-$–Cu half-reaction pertains to a solution containing $CuBr_2^-$ at unit activity. On the other hand, the *formal* potential refers to a system in which the total concentration of all copper(I) species is 1 F; however, the equilibrium constant (K_3) of 10.2 for the formation of $CuBr_3^{2-}$ from $CuBr_2^-$ at an ionic strength of 2.0 indicates that the concentration of $CuBr_2^-$ itself is only about 0.089 M. Therefore, the formal potential should be more cathodic or more negative than the standard potential. The 40-mv difference between the two potentials is consistent with the difference in the $CuBr_2^-$ concentrations and with reasonable estimates of the activity coefficients for $CuBr_2^-$

and Br⁻ in a 1 F sodium bromide–1 F sodium nitrate medium, but a quantitative correlation is impossible.

Vibrational Spectra of BrO⁻, BrO₂⁻, Br₃⁻, and Br₅⁻

BY J. C. EVANS AND G. Y-S. LO

Vibrational spectra (laser-excited Raman and infrared) for the bromite and hypobromite ions in aqueous solution were obtained. Bond-stretching force constants were calculated and these, taken with published data for BrO₃⁻ and the ClOₙ⁻ (n = 1, 2, or 3) series, indicate that the chemical-bonding changes in these two series are similar. If the observed increase in bond strength with increase in n is due to increasing p–d π bonding, it appears that 2p–4d π bonding in BrOₙ⁻ is as effective as 2p–3d π bonding is in ClOₙ⁻. A proposed explanation for the instability of BrO₄⁻ assumes that this is not the case. Spectral features additional to those assigned to the oxyanions were observed under certain conditions; these were assigned to Br₃⁻ and Br₅⁻.

Introduction

With the exception of perbromates, salts of the oxyacids of bromine have been known and used for many years,[1] but vibrational spectroscopic studies of the series have apparently been confined to the bromate ion. The present study was aimed at obtaining vibrational data for the remaining known ions in this series, the bromite and the hypobromite ions; the fundamental modes of these were assigned. In addition, under certain conditions, low-frequency Raman bands which were partly but not entirely assignable to Br₃⁻ were observed. The study was, for this reason, extended to include solutions of Br₂ and Br⁻ in several different solvents; the presence of Br₅⁻ was invoked to explain the additional spectral features.

Experimental Section

Raman spectra of solution and solid samples were obtained using a Perkin-Elmer LR1 photoelectric-recording instrument equipped with a Spectra-Physics 125 helium–neon laser emitting approximately 70 mw at 6328 A; polarization measurements were made using a half-wave, retardation-plate polarizer mounted in the laser beam, and instrumental polarization corrections were determined by making measurements with bands of known depolarization ratios. Infrared measurements were made using Beckman IR9 and IR11 instruments. Purified Br₂ (Dow), reagent grade NaOH, KOH, Ba(OH)₂, and KBr, and fractionally distilled acetonitrile, methanol, and propanol were used. Published procedures[2] were followed in the preparation of OBr⁻ and BrO₂⁻ solutions and of solid NaBrO₂.

Results

Figures 1 to 5 illustrate the spectra while Table I summarizes the frequency assignments. Within experimental uncertainty of approximately ±2 cm⁻¹, no differences in frequency were observed between spectra of solutions containing different cations and the mean values are quoted. The oxyanion solutions were yellow and, with the 6328-A exciting frequency, there was no absorption to produce distortion of the Raman spectrum; solutions of the tribromide and pentabromide were deep red and some distortion was inevitable. For the present qualitative purposes this absorption is not a significant deficiency.

Discussion

a. Hypobromite Ion.—The initial reaction product of Br₂ and OH⁻ at 0° is the hypobromite ion; Figure 1 illustrates a typical Raman spectrum. The strong, polarized band at 620 cm⁻¹ is the fundamental mode of the diatomic BrO⁻. It was accompanied by a polarized band of variable relative intensity at 807 cm⁻¹ (BrO₃⁻) and, on occasion, by a polarized band at 709 cm⁻¹ (BrO₂⁻). These assignments are based on the spectral changes observed as the reaction was carried further through the BrO₂⁻ stage to the final product, BrO₃⁻; earlier studies[3] had established the four fundamental modes of BrO₃⁻.

When excess Br₂ was added, the BrO⁻ band disappeared, the BrO₃⁻ band at 806 cm⁻¹ was enhanced, and three overlapping, polarized bands appeared in the region below 300 cm⁻¹ (Figure 1). These three bands are assigned to the interaction products of Br₂ and Br⁻; the latter is a product of the main reaction

$$Br_2 + 2OH^- \longrightarrow BrO^- + Br^- + H_2O$$

and, with excess Br₂ present

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$

and

$$Br_2 + Br_3^- \rightleftharpoons Br_5^-$$
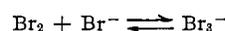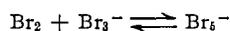
may occur.

(1) A recent review of this topic which contains a comprehensive bibliography follows: Z. E. Jolles, Ed., "Bromine and Its Compounds," Academic Press Inc., New York, N. Y., 1966.

(2) See ref 1, pp 155, 160.

(3) J. H. Hibben, "The Raman Effect and Its Chemical Applications," ACS Monograph No. 80, 1939, p 439.