

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN.]

Effect of Iodide and Bromide on the One-Electron Polarographic Reduction of Hexaammine Cobalt(III) Chloride¹

BY I. M. KOLTHOFF AND S. E. KHALAFALLA

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Iodide ion shifts the half-wave potential of the first irreversible reduction wave of hexaammine cobalt(III) ion (denoted as I) to more positive potentials, a marked effect being observed when the iodide concentration is as small as 10^{-6} M (Fig. 1). In solutions 0.1 M in sodium perchlorate and 2 mM in perchloric acid, or 0.1 M in ammonium perchlorate, or 2 M in the latter salt, all in the presence of 0.5 mM of iodide, the wave has the characteristics of that of a reversible reduction. The half-wave potential then corresponds to the formal potential of the system $\text{Co}(\text{NH}_3)_6^{3+} + e \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$. In 0.1 M sodium perchlorate this potential is -0.040 volt at 25°, while in 0.1 and 2 M ammonium perchlorate at 30° it is found to be -0.030 and -0.140 volt *vs.* s.c.e., respectively. In 0.1 M sodium perchlorate and at iodide concentrations between 0.1 and 1 mM a dip in the diffusion current and a minimum current at -0.25 volt are observed. The first wave is split into two well defined waves when the iodide concentration is 0.01 M. These phenomena are accounted for by the effect on the ψ_d potential of a film of chemically adsorbed mercurous iodide and physically adsorbed iodide ions on the surface of the electrode. Adsorbed iodide counteracts and, when present in a concentration of 10^{-2} M, eliminates the decelerating effect of tetrabutylammonium perchlorate on the reduction of I.

Laitinen, *et al.*,²⁻⁴ have made extensive studies of the reduction at the dropping mercury electrode of hexaammine cobalt(III), denoted as I in this paper. The first one-electron reduction step yields a normal diffusion current plateau which, however, at low concentrations of supporting electrolyte exhibits a dip with a minimum current at about -0.8 to -0.9 volt (*vs.* s.c.e.). They attributed these irregularities to the firm adherence of a film, probably of positively charged cobalt(II) hydroxide, to the negatively charged surface of the mercury. In a previous publication⁵ evidence has been presented that the precipitate formed upon interaction with water of the first reduction product $\text{Co}(\text{NH}_3)_6^{2+}$ of I has the composition $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ which on standing decomposes to cobalt(II) hydroxide. The dip disappears at high concentrations of alkali salts of inorganic acids.⁴ This has been attributed⁶ to a compression of the diffuse double layer around the growing mercury drop. At potentials on the dip and at low salt concentrations, the ψ_d ⁷ potential, at the spot where I is reduced, is negative with regard to the potential in the bulk of the solution. The first reduction product of I, presumably $\text{Co}(\text{NH}_3)_6^{2+}$, effuses from the surface of the electrode to the solution and reacts with water to form insoluble positively charged particles of $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ which are attracted to the spot where the ψ_d potential is more negative than in the bulk of the solution. Evidence also has been presented⁶ that flocculation of the charged particles prevents their adherence to the surface of the electrode. For example in dilute sulfate solutions no dip was observed in the current-potential curve. Laitinen, *et al.*,⁴ reported that in the presence of large concentrations of bromide, iodide and thiocyanate, the first reduction wave of I splits into two waves at the positive side of the isoelectric point of mercury (see, *e.g.*, curve g in Fig. 1). We have confirmed their observations but have extended them to the effects of iodide and bromide when present in small concentrations. It has been found in this laboratory⁸ that iodide—even in traces—can suppress polarographic maxima and alter characteristics of waves in a given region of potentials. Con-

siderably less than a monomolecular film of adsorbed mercurous iodide completely suppresses maxima of the first and second kind. The adsorbed film of mercurous iodide behaves like an anionic surfactant. The effects of iodide and bromide on the current-potential curves of I are accounted for in this paper by a decrease of the ψ_d potential by adsorbed films of mercurous iodide and bromide. Only the one-electron waves of I are considered in this paper.

Experimental

For chemicals and experimental procedure reference is made to previous papers.^{5,6} Potassium iodide was an A.R. product of Mallinckrodt Chemical Works. For the purpose of wave analysis, currents were measured using a manual type of polarograph.⁹ Current-potential curves were determined at $25 \pm 0.1^\circ$, and for purposes of wave analysis in 2 M ammonium salts at $30 \pm 0.1^\circ$.

Results

Effect of Iodide Ion.—Potassium iodide, even in extremely small concentrations, shifts the one-electron reduction wave of I to considerably more positive potentials. This is not the result of a chemical interaction between I and iodide with the formation of iodine. In neutral or acid, oxygen-free media no iodine is formed in a mixture 1 mM in both I and iodide. Some typical polarograms, which are not corrected for the residual current, are presented in Fig. 1. With 10^{-6} and 10^{-5} M potassium iodide the half-wave potential is shifted from -0.248 to -0.101 and -0.098 volt, respectively, *vs.* s.c.e. This effect is qualitatively similar to that obtained with a trace of the anionic surfactant sodium dodecyl sulfate⁶ and the opposite of those of cationic and neutral surfactants. When the iodide concentration exceeds 10^{-4} M, the shape of the first reduction wave is affected by the anodic dissolution current of mercury. At concentrations of iodide smaller than 10^{-4} M only one wave is observed, but at higher iodide concentrations two waves appear, a normal value of the first diffusion current being found at about -0.6 volt. The dip with corresponding minimum observed in 0.1 M sodium perchlorate in absence of iodide at about -0.9 volt is not affected by the presence of iodide. At iodide concentrations of the order of 1 mM a dip is also observed at the positive side of the isoelectric point of mercury at -0.2 to -0.3 volt (curves e and f, Fig. 1). From a comparison of Fig. 1 and 2 it appears that both minima (at -0.25 and -0.9 volt) in the presence of 1 mM iodide are about of the same order of magnitude when the concentration of I is equal to or greater than 1 mM. At concentrations of I of 5×10^{-4} M or less no ab-

(1) Financial support by the U. S. Public Health Service and the Louis and Maud Hill Family Foundation, St. Paul, Minnesota, is gratefully acknowledged.

(2) H. A. Laitinen, J. C. Bailar, H. F. Holtzclaw and J. V. Quagliano, *J. Am. Chem. Soc.*, **70**, 2999 (1948).

(3) H. A. Laitinen and P. Kivalo, *ibid.*, **75**, 2198 (1953).

(4) H. A. Laitinen, J. A. Frank and P. Kivalo, *ibid.*, **75**, 2865 (1953).

(5) I. M. Kolthoff and S. E. Khalafalla, *Inorg. Chem.*, **2**, 133 (1963).

(6) I. M. Kolthoff and S. E. Khalafalla, *Rev. of Polarography* (Japan), in press (1963).

(7) A. N. Frumkin, *Z. Elektrochem.*, **59**, 807 (1955).

(8) I. M. Kolthoff and Y. Okinaka, *J. Am. Chem. Soc.*, **83**, 47 (1961).

(9) J. J. Lingane and I. M. Kolthoff, *ibid.*, **61**, 826 (1939).

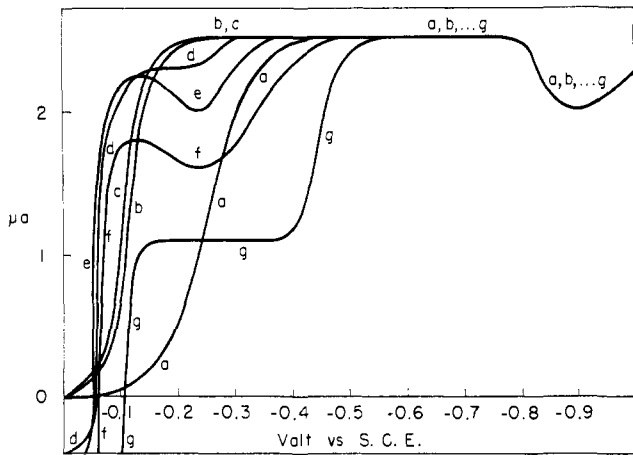


Fig. 1.—Current-voltage curves of 1 mM I in 0.1 M sodium perchlorate: millimolar concentration of potassium iodide: a, 0; b, 0.001; c, 0.01; d, 0.10; e, 0.50; f, 1.0; g, 10.

normalities are observed, either in the absence^{4,6} or presence of iodide. The minima at higher concentrations of I decrease in depth upon gradual addition of perchloric acid (curve e, Fig. 2) and normal current-potential curves are found at or above the acid concentration required to neutralize at the surface of the electrode the ammonia in the reduction product of I.⁵

The effects of iodide on the half-wave potential and on the slope of the E vs. $\log(i_d - i)/i$ plot in 0.1 M sodium perchlorate and in presence of perchloric acid are summarized in Table I. For the purpose of wave analysis, blank experiments with iodide in the absence of I were run and the currents on the reduction waves of I corrected for the contribution of the anodic iodide currents.

TABLE I

CHARACTERISTICS OF THE FIRST REDUCTION WAVE OF I. SOLUTION 1 mM IN I AND 0.1 M IN SODIUM PERCHLORATE AT 25°

| Concn. potassium iodide, mM | Concn. perchloric acid, mM | $-E_{1/2}$ volt vs. s.c.e. | $\Delta E/\Delta \log(i_d - i)/i$ |
|-----------------------------|----------------------------|----------------------------|-----------------------------------|
| 0 | 0 | 0.245 | 0.096 |
| 0 | 10 | .248 | .084 |
| 0.001 | 10 | .101 | .070 |
| .01 | 10 | .098 | .067 |
| .05 | 2 | .086 | .071 |
| .50 | 2 | .040 | .062 |

A corrected current-potential curve in 0.5 mM iodide together with the log plot are presented in Fig. 3. Except for the few points at the most positive potentials where the correction for the iodide wave is appreciable, and the log plot deviates markedly from a straight line, the points at larger currents lie on a straight line with a slope of 0.062. Polarograms without dips, like those in the presence of perchloric acid, also are observed in a supporting electrolyte 0.01 M in ammonium perchlorate and 0.04 M (or more concentrated) in sodium perchlorate. Like perchloric acid, the ammonium salt has a solvating effect on the precipitate formed near the electrode.

In the absence of iodide, the minimum at -0.9 volt decreases with increasing concentration of sodium perchlorate (or other supporting electrolyte). At concentrations of sodium perchlorate of 0.15 M or greater, the minimum in a solution 1 mM in I is eliminated and normal polarogram is observed. The effect of sodium perchlorate concentration on the elimination of the minimum at about -0.25 volt in the presence of 1 mM iodide is identical with that on the minimum at -0.9 volt in the presence or absence of iodide.

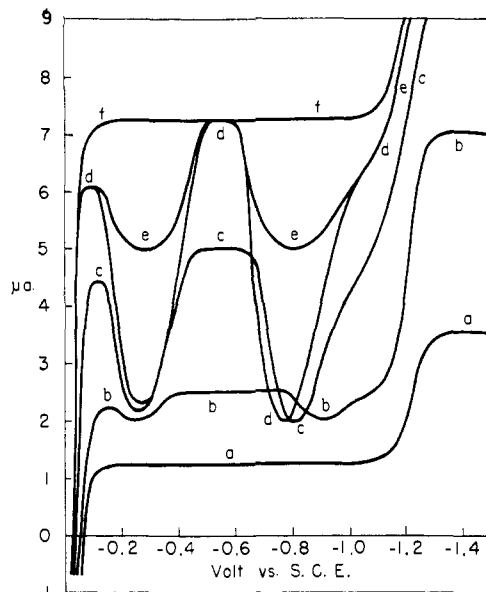


Fig. 2.—Current-voltage curves of I in solutions 0.1 M sodium perchlorate and 1 mM in potassium iodide: millimolar concentration of I: a, 0.5; b, 1.0; c, 2.0; d, 3.0; e and f, same as d but 3 and 6 mM in perchloric acid, respectively.

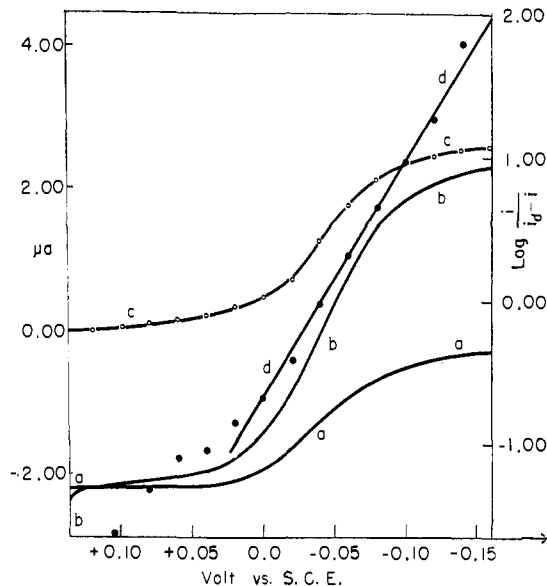


Fig. 3.—Analysis of the first reduction wave of mM I in the presence of 0.5 mM potassium iodide: a, current-potential curve of 0.5 mM iodide in solution 0.1 M in sodium perchlorate and 2 mM in perchloric acid; b, current-potential curve of mM I in same medium; c, same as b but corrected for anodic iodide currents; d, $\log i/(i_d - i)$ vs. E plot of c.

It is of interest to mention that in a solution 1 mM in I, 0.05 M in sodium perchlorate and 1 mM in iodide both minima are eliminated completely in the presence of 0.01 M or more sodium sulfate. The same is found in 0.02 M sodium sulfate in the absence of perchlorate.

For purposes of comparison of the standard potential of system I and its reduction product with data in the literature (see Discussion), a large number of current-potential curves has been run at 30° in 2 M ammonium nitrate and perchlorate in the presence of varying concentrations of iodide. Addition of perchloric acid in excess of the amount necessary to neutralize the ammonia at the surface of the electrode in the reduction product of I has no effect on the characteristics of the waves. Results of the wave analysis in the presence and absence of iodide and of ammonia (after correction for the anodic iodide and ammonia currents) are sum-

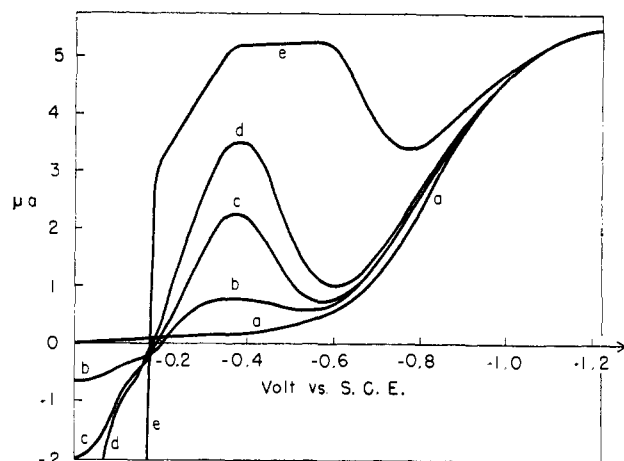


Fig. 4.—Current-voltage curves of solutions 2 mM in I, 0.1 M in sodium perchlorate and 1.5×10^{-4} M in tetrabutylammonium perchlorate: millimolarity of potassium iodide: a, 0; b, 0.15; c, 0.50; d, 1.0; e, 10.

marized in Table II. It is necessary to limit the ammonia concentration to 0.3 M because at higher concentrations the anodic ammonia current in the presence of iodide affects the reduction currents of I so much that the currents, after correction for the anodic currents of the blank, become of questionable significance.

TABLE II

EFFECT OF IODIDE ON CHARACTERISTICS OF FIRST WAVE AT 30° IN 2 M AND 0.1 M AMMONIUM SALTS

| Concn. of I (mM) | Supporting electrolyte | Concn. of iodide (mM) | Concn. of ammonia (M) | $-E_{1/2}$ volt vs. s.c.e. | $\Delta E/\Delta \log (i_d - i)/i$ |
|------------------|---------------------------------|-----------------------|-----------------------|----------------------------|------------------------------------|
| 1 | 2 M NH_4NO_3 | 0 | 0 | 0.304 | 0.078 |
| 1 | 2 M NH_4NO_3 | 0.5 | 0 | .204 | .099 |
| 1 | 2 M NH_4NO_3 | 0.5 | 0.3 | .214 | .091 |
| 0.3 | 2 M NH_4ClO_4 | 0 | 0 | .288 | .085 |
| .3 | 2 M NH_4ClO_4 | 0.3 | 0 | .172 | .071 |
| .3 | 2 M NH_4ClO_4 | .3 | 0.3 | .182 | .073 |
| .3 | 2 M NH_4ClO_4 | .5 | 0 | .144 | .067 |
| .3 | 2 M NH_4ClO_4 | .5 | 0.3 | .155 | .069 |
| .3 | 2 M NH_4ClO_4 | .7 | 0 | .140 | .067 |
| 1 | 0.1 M NH_4ClO_4 | 0 | 0 | .238 | .105 |
| 1 | 0.1 M NH_4ClO_4 | 0.5 | 0 | .030 | .061 |

Current-Time Curves.—In the absence of iodide the current-time curves at the minimum at about -0.9 volt are quite abnormal.⁶ During the first fraction of a second the current increases normally with time to attain thereafter an almost constant value during the lifetime of the drop. The current-time curves then are characterized by continuous oscillations. The same pattern is observed at -0.9 volt in solutions 1 mM in I, 0.1 M in sodium perchlorate and 1 mM in iodide. At -0.1 and -0.5 volt (compare curve f in Fig. 1) the current-time curves have a normal appearance, but at -0.25 volt the precipitate interferes and the current-time curve becomes highly abnormal. The current increases normally during the first 1.5 seconds to reach a maximum value, whereupon it drops to a minimum to decrease very slightly during the further life-period of the drop. The current time curve has an appearance similar to that observed by Delahay and Trachtenberg¹⁰ for 1 mM copper(II) in 0.5 M sodium citrate in presence of 0.3 mM quino-line adsorbate.

Combined Effect of Iodide and Tetrabutylammonium Perchlorate (TBAP).—TBAP in a concentration of 1.8×10^{-5} M eliminates the minimum at -0.8

(10) P. Delahay and I. Trachtenberg, *J. Am. Chem. Soc.*, **79**, 2355 (1957).

volt in a solution 2 mM in I and 0.1 M in sodium perchlorate.⁶ With increasing concentration of TBAP the first irreversible reduction wave of I is shifted to increasingly more negative potentials (curve a in Fig. 4). In the presence of more than 10^{-4} M iodide the first wave reappears, its height increasing with increasing iodide concentration. When the concentration of iodide is 10^{-2} M, a constant value for the limiting current is found between 0.4 and 0.6 volt (curve e, Fig. 4). When corrected for the $t^{1/2}$ effect, this value is 5% smaller than the normal diffusion current in the absence of TBAP. The shape of the first part of the wave in 10^{-2} M iodide corresponds to that of the anodic iodide wave. The experiments in Fig. 4 were repeated in the presence of 0.01 M perchloric acid when the first reduction product of I does not yield a precipitate. The current-voltage curves are practically identical with those in Fig. 4, from which it may be concluded that under the experimental conditions of Fig. 4 the precipitate of $\text{Co}(\text{NH}_3)_4(\text{OH})_2$ does not affect the shape of the polarograms.

Effect of Bromide.—Qualitatively the effects of bromide are similar to, but not nearly as pronounced, as those of iodide. With 1 mM bromide in 0.1 M sodium perchlorate, the half-wave potential is shifted from -0.25 to -0.18 volt as compared to -0.10 with 10^{-6} M iodide. With 10^{-2} M bromide the half-wave potential is -0.06 volt while the current potential curve is practically identical with that observed in the presence of 10^{-4} M iodide (curve f in Fig. 1).

It may be added that chloride also shifts the half-wave potential to more positive values; however, the effect is small and no splitting of the first wave (as in curves d, e, f and g in Fig. 1) is observed, even at relatively high chloride concentrations. In 0.1 M sodium chloride the half-wave potential is -0.18 volt as compared to -0.25 volt in 0.1 M sodium perchlorate.

Discussion

In agreement with Laitinen, *et al.*,³ the first wave of I in solutions of sodium perchlorate and other supporting electrolytes has been found to have the characteristics of a polarographically irreversible reduction. Iodide shifts the half-wave potential to more positive values. In the presence of 0.5 mM iodide the wave acquires the characteristics of that of a reversible reduction as indicated by the value of $\Delta E/\Delta \log (i_d - i)/i$ of 0.061 in 0.1 M ammonium perchlorate supporting electrolyte at 30° and of 0.062 in 0.1 M sodium perchlorate and 2 mM perchloric acid at 25°.

The characteristics of the wave and the slope of the log plot in ammonium salts remain unchanged when perchloric acid in a concentration 2 to 10 mM is added. Thus it may be concluded that in 0.1 M perchlorate plus 0.5 mM iodide the half-wave potential corresponds to the formal potential of the system $\text{Co}(\text{NH}_3)_6^{3+} + e \rightleftharpoons \text{Co}(\text{NH}_3)_6^{2+}$, the $\text{Co}(\text{NH}_3)_6^{2+}$ reacting instantaneously with acid. At 25° the value of the formal potential is -0.040 volt vs. s.c.e. (or 0.201 vs. n.h.e.) and -0.030 volt vs. s.c.e. at 30°.

No data of the formal potential of this system are found in the literature at low ionic strength. Bjerrum¹¹ determined the formal standard potential of the system at 30° in 2 M ammonium nitrate in the presence of a large excess of ammonia to stabilize the cobalt(II) hexaammine. In order to compare his value with that of the half-wave potential in the presence of iodide, current-potential curves of I in a medium 2 M in ammonium nitrate have been run at 30° and analyzed with the results given in Table II. Ammonia in a con-

(11) J. Bjerrum, "Metal Ammine Formation in Aqueous Solutions," P. Haase and Son, Copenhagen, Denmark, 1941, p. 250.

centration of 0.3 *M* shifts the half-wave potential about 10 millivolt to a more negative value. In these concentrated salt solutions iodide again shifts the half-wave potential to more positive values. However, in 2 *M* ammonium nitrate, the slope of the log plot never attains the value characteristic of a reversible one-electron reaction. It is of interest to note that in 2 *M* ammonium nitrate the half-wave potentials in the presence of 0.5 mM iodide are -0.204 and -0.214 volt in the absence and the presence of 0.3 *M* ammonia, respectively. These values compare favorably with that of -0.211 volt reported in 2 *M* ammonium nitrate for the reversible potential of the system by Bjerrum.¹¹ In 2 *M* ammonium perchlorate, the slope of the log plot approaches the theoretical value in the presence of 0.5 to 0.7 mM iodide (Table II). A half-wave potential of -0.140 may be considered to correspond to the formal potential of the system at 30° in 2 *M* ammonium perchlorate. The increase of the potential to -0.030 volt at 30° in 0.1 *M* ammonium perchlorate is attributed to an ionic strength effect, the activity coefficient of the trivalent hexaammine increasing more with decreasing ionic strength than that of the divalent cobalt hexaammine complex. Bjerrum, *et al.*,¹² report that the stepwise stability constant K_n , ($n = 0, 1, \dots, 6$) of the cobalt(II) hexaammine varies with the molar concentration, c , of ammonium nitrate and the centigrade temperature, t , according to $\log K_n = \log K_n^0 + 0.062c - 0.005(t - 30)$. The corresponding equation for the cobalt(III) complex is given by $\log K_6 = 4.06 + 0.18c$. This equation refers to the last dissociation step of this complex and does not give the variation with temperature. The change of the overall stability constant, β^{III} , from 35.21 in 2 *M* ammonium nitrate to 34.36 in 1 *M* ammonium nitrate is 0.85 as compared to six times $0.18\Delta c = 1.08$. Assuming that the above equations hold for a variation of the ionic strength from 2 to 0.1, the difference in half-wave potential $\Delta E_{1/2}$ between that in 2 *M* and 0.1 *M* perchlorate is calculated to be: $\Delta E_{1/2} = 0.061\Delta \log(\beta_{III}/\beta_{II}) = 0.061 \times 6(0.062 - 0.18)(0.1 - 2.0) = 0.082$ volt. Experimentally a difference of $-0.030 + 0.140 = 0.110$ volt was found.

From Fig. 1 it is clear that traces of iodide accelerate the reduction of I. This is attributed to the effect of a film of adsorbed mercurous iodide on the ψ_d potential. A similar effect has been observed in the reduction of copper(II) ions⁸ at the dropping mercury electrode. One wave of normal appearance is observed (curves b and c in Fig. 1) when the iodide concentration is equal to or less than 10^{-5} *M*. At these small iodide concentrations the ψ_d potential is still positive and the precipitate formed from the first reduction product of I

is not attracted to the surface of the electrode. When the iodide concentration becomes greater than 10^{-5} *M* the adsorbed film of mercurous iodide still exerts its accelerating effect on the reduction of I. However, when the potential becomes increasingly more negative the ψ_d potential may become negative and the precipitate can then be attracted to the surface. This accounts for the dip in curves e and f in Fig. 1 and the appearance of two well-defined waves (curve g in Fig. 1) when the iodide concentration is equal to or greater than 10^{-2} *M*. At potentials where free iodide ions are being desorbed (curves d, e, f, and g in Fig. 1) the current starts to increase again to attain the normal value of the diffusion current at potentials where the iodide is practically completely desorbed.

Substances which solubilize $\text{Co}(\text{NH}_3)_4(\text{OH})_2$, like excess of acids or ammonium salts, eliminate abnormalities in current potential curves in the presence and absence of iodide. Sulfate in a concentration of 10 mM eliminates the minima at -0.25 and -0.9 volt found in the presence of iodide. It flocculates the positively charged particles of $\text{Co}(\text{NH}_3)_4(\text{OH})_2$.

The complex shape of the current-potential curves observed in the presence of a combination of iodide and tetrabutylammonium perchlorate (Fig. 4) is accounted for by the simultaneous adsorption of iodide and TBA ions. At potentials in the beginning of the reduction wave of I the adsorbed iodide ions are in excess over adsorbed TBA ions, the latter forming "anionic bridges" with adsorbed iodide ions,¹³ which are the parallel of cationic bridges postulated by Frumkin.¹⁴ The excess of adsorbed iodide ions counteracts the decelerating effect on the reduction of I by TBA. With increasing negative potentials the adsorption of iodide ions decreases and that of TBA ions increases until the adsorbed charge reaches zero.¹³ At still more negative potentials adsorbed cations become in excess over adsorbed iodide ions and the adsorbed TBA ions start to exert their decelerating effect on the reduction of I. The current then starts to decrease (see maxima in curves b, c and d in Fig. 4). When the iodide concentration is 0.01 *M* (curve e in Fig. 4) the adsorbed iodide remains in excess until a limiting current is attained. The value of the negative ψ_d potential, which is responsible for the splitting of the wave in 0.01 *M* iodide in the absence of TBAP (curve g in Fig. 1), apparently becomes considerably less negative by the formation of anionic bridges in the presence of TBAP, and the precipitate formed from the reduction product of I is not being attracted to the surface of the electrode. Again, the current starts to decrease (curve e, Fig. 4) when the adsorbed TBA ions become in excess over adsorbed iodide ions.

(12) J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes. Part II. Inorganic Ligands." The Chemical Society, London, Great Britain, 1958, p. 47.

(13) M. A. V. Devanathan and M. J. Fernando, *Trans. Faraday Soc.*, **58**, 368 (1962).

(14) A. N. Frumkin, *ibid.*, **55**, 156 (1959).