

TABLE I
SUMMARY OF AB PATTERNS AND CHEMICAL SHIFTS FOR
METAL-EDTA COMPLEXES

Metal ion	δ_{CH_2} , ppm vs. TMS*	$\delta_{\text{CH}_2} -$ $\delta_{\text{C}_2\text{H}_4}$, ppm	J , cps	$\delta_A -$ δ_B , ppm
Cd(II)	3.11	0.47	17.1	0.17
Y(III)	...	0.59	16.8	0.19
Zr(IV) (pH 3.5)	3.84	0.62	17.1	0.26
Zr(IV) (pH 5.0)	3.78	0.68
Hf(IV) (pH <4.3)	3.83	0.65	17.1	0.20
Hf(IV) (pH 6.8)	3.78	0.70	17.1	0.13
Pd(II) (bidentate)	4.01	0.50	16.7	0.27
Pd(II) (tetradentate)	3.23	-0.40	16.7	0.51
Co(III) (out-of-plane)	4.25	0.4	18.7	0.17
Co(III) (in-plane)	4.05	0.2	15.8	0.36
Mo(VI)	3.57	-0.16	16.7	0.31
Mo(V)	3.43	0.79	17.6	0.30
Y ⁴⁻	3.09	0.51		
HY ³⁻	3.44	0.39		
H ₂ Y ²⁻	3.74	0.25		
Mg(II)	3.12	0.53		
Ba(II)	3.03	0.65		
Zn(II)	3.29	0.51		
Hg(II)	3.27	0.52		
Pb(II)	3.68	0.58		
Al(III)	3.67	0.56		

now. Included in this table are the nmr chemical shift data for the various forms of the uncomplexed ligand as well as for those metal ions which do not exhibit an AB splitting pattern for the methylenic resonances. The first column of the table summarizes the chemical shift relative to TMS* for the center of the quartet due to the methylenic resonance.

The second column indicates the position upfield from the methylenic resonance of the ethylenic resonance; a minus sign indicates that the ethylenic resonance is downfield relative to that for the methylenic resonance. Reference to the second column indicates that for the majority of the chelate systems the ethyl-

enic resonance is from 0.5 to 0.8 ppm upfield from the methylenic resonance. The most extreme exception to this is the tetradentate complex of palladium(II) where the ethylenic resonance is 0.4 ppm downfield from the methylenic resonance. Because this has been attributed to the in-plane carboxylate groups this characteristic may be indicative when observed for other EDTA complexes, as for example the second quartet of cobalt(III), which is only 0.2 ppm upfield from the methylenic resonance. The downfield position of the ethylenic resonance in the case of the molybdenum(VI) complex may be indicative of such in-plane bonding but probably is due to the unique characteristics of this complex in which two metal ions are coordinated to one EDTA ligand.

Another interesting aspect of the data in Table I is the consistency of the values for the coupling constant. All of the complexes with the exception of the cobalt(III) system have coupling constants within a few tenths of an average value of 16.9 cps. For the cobalt(III) complex the in-plane quartet appears to have a low coupling constant with a value of 15.8 cps while the out-of-plane group has an enhanced value of 18.7 cps. Another aspect of interest is that the chemical shift differences for the methylenic AB patterns appear to average between 0.2 and 0.3 ppm; however, the in-plane quartets for the palladium(II) complex and the cobalt(III) complex have distinctly larger chemical shift differences.

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Double Layer and Catalytic Effects in the Polarography of Aquopentaamminecobalt(III)

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In contrast with Vlček,² the polarographic prewave that appears when halide ion is added to $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ solutions is explained in terms of a chemical reaction between the mercury electrode and the complex and also in terms of the changes in the electrical double-layer structure produced by specific adsorption of the halide on the electrode. The values of the changes in diffuse layer potential required to account for the observed current-potential behavior are calculated.

Vlček² has reported several instances in which single, well-formed polarographic waves observed for ions

such as $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{CH}_3\text{COO}^{2+}$ become split waves when small quantities of halide ions are added to the supporting electrolyte. The new waves that result upon addition of halide can occur at about the same potential as that at which the corresponding

(1) Alfred P. Sloan Research Fellow.

(2) (a) A. A. Vlček and J. Kuta, *Nature*, **185**, 95 (1960); (b) A. A. Vlček, *Progr. Inorg. Chem.*, **5**, 295 (1963).

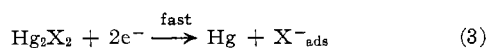
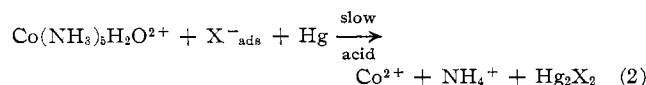
halide-containing cobalt(III) cation is reduced, and this coincidence led Vlček to interpret his data on the basis of an electrode surface-catalyzed ligand substitution reaction of the type



followed by the electrode reaction. The rates of reactions such as (1) in homogeneous solution are known³ to be too low by several orders of magnitude to account for the magnitude of the polarographic currents observed by Vlček, so that a very dramatic and unusual surface catalysis had to be invoked.

There are two alternative explanations for Vlček's results which deserve consideration because they do not involve a reaction as unlikely as reaction 1.

Chemical Catalysis by Halide.—The first explanation derives from the fact that all of the cobalt(III) complexes that have been examined by Vlček are thermodynamically capable of spontaneously oxidizing the mercury electrode. The experimental evidence is that the rate of reaction between the complexes and the mercury is negligible *in the absence of halide*, but in the presence of halide this rate could be much greater. It is particularly significant in this regard that in every instance in which Vlček observed that the addition of halide split the polarographic wave for a cobalt(III) complex into two waves, the new wave rose from the anodic background and passed through the zero-current axis with no inflection. This behavior can be accounted for with the following mechanism in which X^- is a halide ion adsorbed on the mercury electrode surface



The actual electrode reaction is the fast reduction of Hg_2X_2 which releases halide for reuse in reaction 2. In effect, the combination of halide and mercury acts as a catalyst for the otherwise slow reduction of the cobalt(III) complex. The magnitude of the current obtained from this catalytic process will depend on the rate of reaction 2. It should be emphasized, however, that, in contrast to the mechanism of Vlček, reactions 2 and 3 do not require that any bond formation occur between cobalt(III) and halide.

A mechanism somewhat similar to reactions 2 and 3 was suggested by Laitinen, Frank, and Kivalo^{4a} some time ago to account for the effects of added halide on the polarographic behavior of $\text{Co}(\text{NH}_3)_6^{3+}$

Reference should also be made to an important but relatively unknown recent paper of Tanaka and co-workers,^{4b} who studied the influence of anions on the polarography of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and concluded that reactions such as (2) and (3) are responsible for the observed behavior.

Double-Layer Effects.—A second explanation of

Vlček's results depends upon the changes in the structure of the electrical double layer produced by added halide. The halide anion is certainly⁵ adsorbed on the mercury electrode surface which carries a positive electronic charge at the potentials where the polarographic wave occurs (-0.1 v vs. sce). The halide adsorption decreases the magnitude of the positive potential that tends to repel cations from the electrode surface, and the measured rate of the irreversible electrode reaction would therefore be expected to increase.⁶ The "new waves" observed by Vlček might then correspond not to the reduction of a new cobalt(III) complex that had been catalytically generated, but to the reduction of the original aquo complex at a more positive potential.

The two explanations outlined above were tested by studying the polarographic behavior of the $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ cation as a function of the ionic strength and composition of the supporting electrolyte. The resulting data appear to confirm that, depending upon the electrode potential, either reaction 2 or double-layer structure controls the rate of the electrode reaction.

Experimental Section

A three-electrode polarograph constructed from solid-state operational amplifiers (G. A. Philbrick Researches, Inc., Types P65AU and P75AU) was employed. The polarograms were recorded point by point by setting the potential of the dme at a selected value and recording the current at that potential with a high-precision undamped pen-and-ink recorder. The current for five to ten drops from the electrode was recorded at each potential, the potential changed by 10 mv, and the process repeated. The polarograms presented in the figures were obtained by connecting the resulting closely spaced current-potential data points.

The dme was mechanically rapped to provide a drop time of 4.0 sec at all potentials. The capillary produced a mercury flow rate of 0.60 mg/sec with a mercury column height of 61.5 cm.

The cell and circuitry were entirely conventional. Solutions were deaerated with nitrogen which had been passed through a vanadous washing tower and over hot copper turnings.

Sodium perchlorate was prepared by neutralizing reagent grade sodium carbonate with perchloric acid. All acidic supporting electrolyte solutions contained 0.01 M HClO_4 in order to prevent precipitation of cobalt(II) hydroxide at the electrode surface. Thus, the lowest ionic strength that could be studied in acid solution was 0.01 M.

Experiments were also performed with basic supporting electrolytes composed of NaOH and NH_4OH . In these solutions calculations based on the cobalt(II)-ammonia complex formation constants⁷ predict that cobalt(II) hydroxide should precipitate at the electrode surface. However, careful examination of the current-time curves for individual drops revealed no irregularities, and separate experiments with homogeneous solutions containing cobalt(II), NH_3 , and NaOH convinced us that the formation of cobalt(II) hydroxide did not occur within 4 sec (the drop time) with the small cobalt(III) concentrations employed. This fortuitous circumstance allowed useful data to be obtained at pH values greater than would have been possible if equilibrium had been instantaneously achieved.

The $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and $\text{Co}(\text{NH}_3)_6^{2+}$ were prepared and recrystallized according to standard procedures. The

(3) B. Adell, *Z. Anorg. Chem.*, **246**, 303 (1941).

(4) (a) H. A. Laitinen, A. J. Frank, and P. Kivalo, *J. Am. Chem. Soc.*, **75**, 2865 (1953); (b) N. Tanaka, Y. Sato, and R. Tamamushi, *Rev. Polarog. (Kyoto)*, **12**, 127 (1964).

(5) P. Delahay, "Double Layer and Electrode Kinetics," Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 4.

(6) P. Delahay, ref 5, Chapter 9.

(7) "Stability Constants," The Chemical Society, London, 1964.

concentration of the cobalt(III) species was $5 \times 10^{-4} M$ in every case.

Results and Discussion

Figure 1 shows the effects of increasing amounts of bromide ion on the polarograms of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+} \rightleftharpoons \text{RH}_2\text{O}^{3+}$ in an acidic supporting electrolyte having an ionic strength, μ , of 1.0. The prewave observed behaves just as described by Vlček for his experiments in $0.9 F \text{ NaClO}_4$ - $0.1 F \text{ HClO}_4$. A polarogram for $5 \times 10^{-4} M \text{ Co}(\text{NH}_3)_5\text{Br}^{2+}$ in this supporting electrolyte is included in Figure 1 for comparison. The behavior of RH_2O^{3+} in Figure 1 is critically dependent on the ionic strength of the supporting electrolyte solution. Figure 2 shows the dramatically different behavior that is obtained at $\mu = 0.01$. Figure 3 shows the dependence of the prewave on ionic strength at a fixed concentration of bromide.

The strong ionic strength dependence of the prewave in Figures 2 and 3 is hard to reconcile with a current-limiting mechanism involving rapid ligand substitution as proposed by Vlček. It seems more likely that the peaked character of the prewave which develops at lower ionic strengths arises in the following way: The current rises from the anodic background and becomes cathodic when the potential reaches the value where reduction of the chemically formed Hg_2Br_2 can proceed. The magnitude of the cathodic current at the maximum is limited by the rate of reaction 2, which is in turn affected by the amount of bromide adsorbed on the electrode. As the potential becomes more negative the amount of adsorbed bromide decreases, which decreases the rate of reaction 2, and the current falls. The current increases again at still more cathodic potentials because the uncatalyzed direct reduction of RH_2O^{2+} can then proceed. The ionic strength influences the current-potential behavior by its effect on the rate of reaction 2 (an anion-cation reaction) and because the amount of adsorbed bromide available for participation in reaction 2 decreases as μ increases owing to the competition between perchlorate and bromide for adsorption sites on the electrode.

Good circumstantial evidence supporting this account of the behavior of the current-potential curves between $+150$ and 0 mv is afforded by the current-time curves for individual drops and by the dependence of the current on the height of the mercury reservoir: Throughout this potential range the current-time curves are abnormal (they display inflections midway in the drop-life) and the current is nearly independent of the reservoir height. The presence of a kinetically limited chemical reaction preceding the electrode reaction is thus clearly indicated.

To test that reaction 2 does proceed under polarographic conditions the concentration of RH_2O^{3+} in a $0.01 M \text{ HClO}_4$ solution initially $5 \times 10^{-4} M$ in RH_2O^{3+} and $2 \times 10^{-4} M$ in Br^- was monitored polarographically after the addition of excess metallic mercury to the cell. The concentration of RH_2O^{3+} started decreasing immediately and within 20 min about 20% of

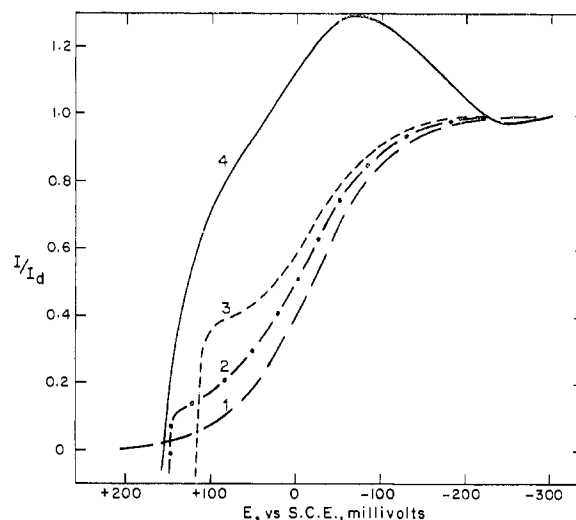


Figure 1.—Effect of bromide on polarography of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ with $\mu = 1.0$; supporting electrolyte $0.99 M \text{ NaClO}_4$ - $0.01 M \text{ HClO}_4$; $[\text{Br}^-]$: 1, 0; 2, $1.75 \times 10^{-4} M$; 3, $3.75 \times 10^{-4} M$; 4, 0 with $5 \times 10^{-4} M \text{ Co}(\text{NH}_3)_5\text{Br}^{2+}$.

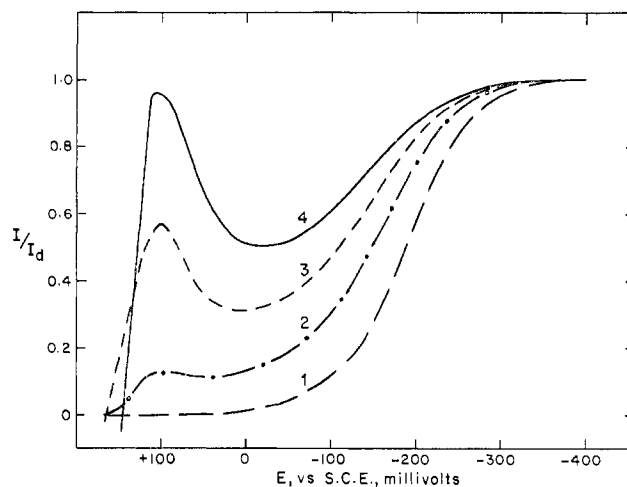


Figure 2.—Effect of bromide on polarography of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ with $\mu = 0.01$; supporting electrolyte $0.01 M \text{ HClO}_4$; $[\text{Br}^-]$: 1, 0; 2, $0.75 \times 10^{-4} M$; 3, $1.25 \times 10^{-4} M$; 4, $1.75 \times 10^{-4} M$.

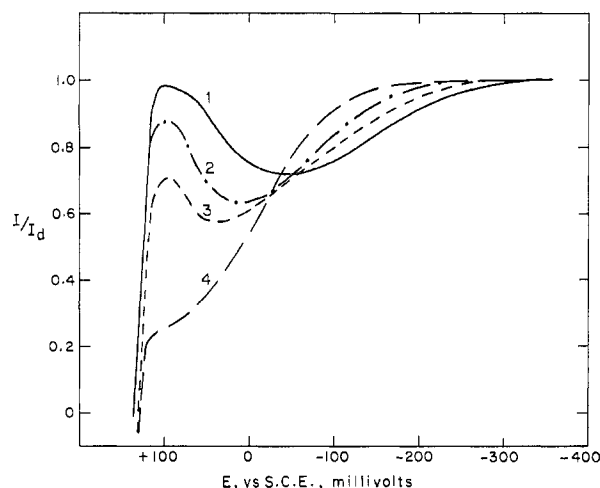


Figure 3.—Effect of ionic strength on polarographic prewave for $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$; $[\text{Br}^-] = 2.5 \times 10^{-4} M$; supporting electrolyte $0.01 M \text{ HClO}_4$ plus NaClO_4 to give ionic strength of: 1, 0.01; 2, 0.05; 3, 0.10; 4, 1.0.

the RH_2O^{3+} had disappeared and the mercury pool was covered with a precipitate of Hg_2Br_2 .

The Effect of Double-Layer Structure.—The effect of added bromide on the polarographic waves in Figure 2 cannot be explained on the basis of reactions 2 and 3 at potentials between *ca.* -50 and -200 mv. Here the current increases, rather than decreases, as the potential becomes more cathodic because the rate-limiting step has become the direct electroreduction of RH_2O^{3+} . However, at any one potential, the current is increased by the addition of bromide just as was true when reaction 2 was the rate-limiting step. This behavior seems clearly to be the result of the changes in double-layer structure produced by the bromide: The bromide ion is specifically adsorbed on the mercury electrode at the potentials involved (-50 to -200 mv).^{5,8} This adsorption lowers the positive charge on the electrode, which increases the rate of the irreversible reduction of the tripositive cation.⁶ Such double-layer effects on the electrode reaction rates are observed, as expected, in other supporting electrolytes as well. Figure 4 shows polarograms obtained for RH_2O^{3+} in $0.1 M$ NaOH – $0.1 M$ NH_4OH ($\mu = 0.1$). (The cobalt(III) complex exists as ROH^{2+} at pH values higher than *ca.* 6.⁹) The addition of bromide ion continues to accelerate the electrode reaction at potentials between -100 and -400 mv. It would be very difficult to explain this behavior in terms of a ligand-exchange mechanism because the RBr^{2+} complex is completely unstable in this alkaline solution. When RBr^{2+} itself was used to obtain polarograms in $0.1 M$ NaOH – $0.1 M$ NH_4OH the purple color characteristic of the RBr^{2+} cation changed the instant that the complex was added to the alkaline solution into the reddish orange color characteristic of ROH^{2+} , and the polarograms obtained were identical with those in Figure 4.

Even $\text{Co}(\text{NH}_3)_6^{3+}$, which is much less substitution-labile than RH_2O^{3+} or RBr^{2+} , shows a polarographic prewave in the presence of bromide in $0.1 M$ NaOH – $0.1 M$ NH_4OH (Figure 5). It seems certain that the prewaves produced by bromide ion in these basic solutions cannot result from ligand substitution, and the same can be inferred about the prewaves obtained with RH_2O at pH 2.

Calculation of Changes in Double-Layer Potentials.—The explanation proposed here to account for the bromide-produced acceleration of the electrode reactions (at potentials where reaction 2 can be neglected) depends upon the assertion that significant changes in ϕ_2 , the potential drop across the diffuse double layer, are produced by the adsorption of bromide on the mercury surface. To test this interpretation the changes in ϕ_2 necessary to account for the observed current-potential behavior were calculated. The values of $\Delta\phi_2$ in Table I were calculated by the following procedure: In bromide-free perchlorate supporting electrolyte having an ionic strength of 0.27 and a pH of

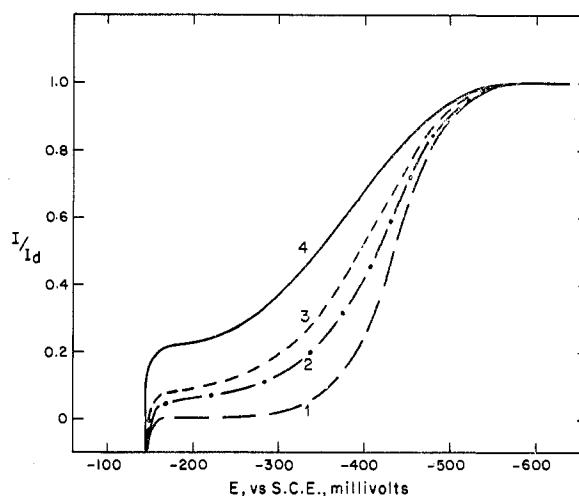


Figure 4.—Effect of bromide on polarography of $\text{Co}(\text{NH}_3)_6\text{H}_2\text{O}^{3+}$ in alkaline solution; supporting electrolyte $0.1 M$ NaOH – $0.1 M$ NH_4OH ; $[\text{Br}^-]$: 1, 0; 2, $3 \times 10^{-3} M$; 3, $5 \times 10^{-3} M$; 4, $1 \times 10^{-2} M$.

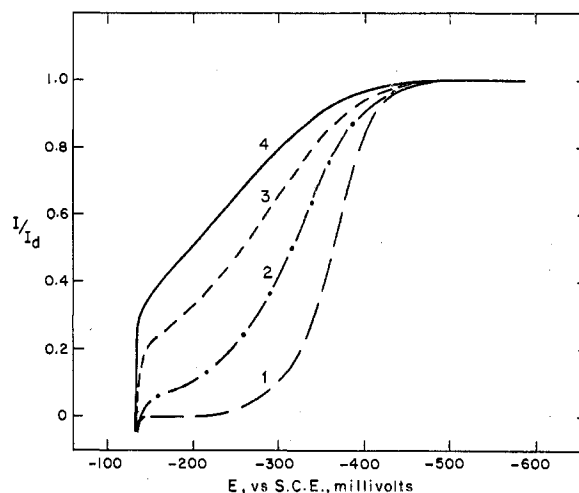


Figure 5.—Effect of bromide on polarography of $\text{Co}(\text{NH}_3)_6^{3+}$ in alkaline solution; supporting electrolyte $0.1 M$ NaOH – $0.1 M$ NH_4OH ; $[\text{Br}^-]$: 1, 0; 2, $1 \times 10^{-3} M$; 3, $2 \times 10^{-3} M$; 4, $3 \times 10^{-3} M$.

2.0, the irreversible RH_2O^{3+} wave was analyzed ($\log \lambda$ vs. E plots)¹⁰ between $+40$ and -40 mv to provide a value of $\alpha n_a = 0.54$. This supporting electrolyte and potential interval were chosen because they correspond to very small absolute values of ϕ_2 ¹¹ which were neglected in the determination of αn_a . The resulting value of αn_a was assumed to be independent of ionic strength or the concentration of bromide. Sets of polarograms such as those in Figure 2 were then analyzed, and the changes in the diffuse layer potential, $\Delta\phi_2$ between the bromide-containing and the bromide-free solutions at each value of μ were evaluated according to the Frumkin equation,¹² which reduces for this case to

$$\Delta\phi_2 = \frac{RT}{F(\alpha n_a - Z)} \ln \frac{\lambda}{\lambda_0} \quad (4)$$

(10) P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, p 78.

(11) H. Wroblewa, Z. Kovac, and J. O'M. Bockris, *Trans. Faraday Soc.*, **61**, 1523 (1965), Table 14.

(12) A. N. Frumkin, *Z. Physik. Chem.*, **164A**, 121 (1933); cf. ref 6.

(8) W. Lorenz, *Z. Physik. Chem.*, **224**, 145 (1963).

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 387.

where λ_0 and λ are the Koutecky parameters¹⁰ which measure the reaction rate in bromide-free and in bromide-containing solutions, respectively, at each potential; $\alpha n_a = 0.54$ and $Z = +3$ for RH_2O^{3+} in acidic supporting electrolyte. At potentials where the current was too small to be measured accurately in bromide-free solutions the necessary λ_0 values were obtained by extrapolation of the $\log \lambda$ vs. E plots to the potential of interest. The values of $\Delta\phi_2$ which resulted are listed in Table I. They are of reasonable magnitude and display the expected qualitative dependence on ionic strength and bromide concentration.

TABLE I
CALCULATED DIFFERENCES IN ϕ_2 POTENTIAL, $\Delta\phi_2$, BETWEEN BROMIDE-CONTAINING AND BROMIDE-FREE SUPPORTING ELECTROLYTE SOLUTIONS
Reduction of $5 \times 10^{-4} M \text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$; $\text{HClO}_4 = 0.01 M$; μ adjusted with NaClO_4

[Br ⁻], $M \times 10^{-4}$	Potential, mv vs. sce				
	0	-40	-80	-120	-160
	$\Delta\phi_2$, mv				
	$\mu = 0.01$				
0
1.25	34.9	27.6	21.4	17.6	15.1
1.75	43.0	34.1	27.4	22.2	18.5
2.50	53.5	42.6	34.2	28.4	24.4
3.75	64.5	52.2	43.0	36.4	30.8
	$\mu = 0.1$				
1.25	14.7	9.5	8.3	5.8	
1.75	17.8	12.0	10.3	7.3	
2.50	21.6	14.6	11.5	8.1	
3.75	37.1	19.8	16.1	10.1	
	$\mu = 1.0$				
1.25	3.8	3.2			
1.75	4.0	3.6			
2.50	4.8	4.6			
3.75	7.0	5.5			

Perchlorate Adsorption.—In perchlorate media the effects produced by the addition of halide occur in the presence of an already substantial double-layer effect arising from the adsorption of the perchlorate supporting electrolyte. Figure 6 shows how great an effect the adsorption of perchlorate produces. Curve 1, obtained in a NH_4OH – NH_4F supporting electrolyte, should be essentially free of effects arising from anion adsorption. The addition of increasing amounts of NaClO_4 led to curves 2 and 3. The large evident increases in the rate of the electrode reaction at all potentials result because the ϕ_2 potential changes sign (from positive to negative) as the negative charge due to the adsorbed perchlorate is greater than the positive electronic charge on the electrode.¹¹ For this reason the values of $\Delta\phi_2$ in Table I are only valid for the particular perchlorate supporting electrolyte in which they were measured. They would not apply, for example, to

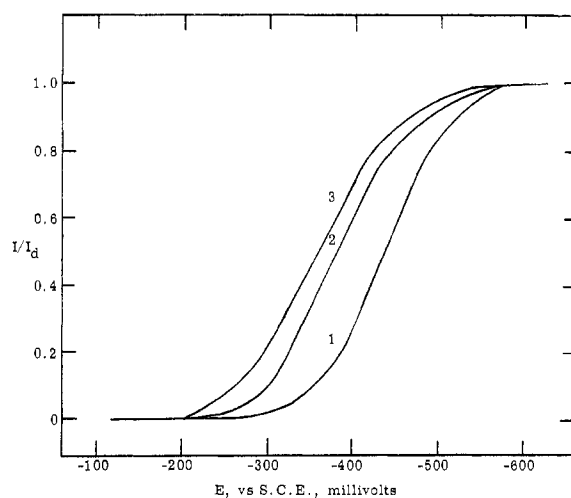


Figure 6.—Effect of perchlorate on polarography of $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$; supporting electrolyte $0.1 M \text{NH}_4\text{F}$ – $0.1 M \text{NH}_4\text{OH}$; concentration of NaClO_4 : 1, 0; 2, 0.05 M ; 3, 0.1 M .

nonperchlorate supporting electrolytes even at the same ionic strengths.

Effects of Other Adsorbed Anions.—Chloride, iodide, and thiocyanate ions also accelerate the rate of reduction of RH_2O^{3+} . To produce effects comparable to those caused by bromide more chloride but less iodide or thiocyanate is required. Thus, the accelerating effects are not unique with bromide and call for a general explanation. The strong ionic strength dependence of the bromide catalysis, its persistence at pH values where RBr^{2+} is totally unstable, and the reasonable magnitudes of the changes in ϕ_2 potential that account for the magnitude of the acceleration all combine to lead us to the conclusion that the changes in double-layer structure produced by added halide can account adequately for the observed polarographic behavior.

The observation that polarograms for the reduction of 0.5 mM solutions of cobalt(III)–amine complexes can be obtained in alkaline electrolytes without interference from precipitation of cobalt(II) hydroxide has encouraged us to begin experiments in supporting electrolytes composed of NaOH and NaF from which little or no specific adsorption of the anions present is expected.^{4a} Absolute values for ϕ_2 rather than differences in ϕ_2 potentials should be obtainable from such electrolytes, although complications may arise because of ion-pair formation between the cobalt(III) complex cations and fluoride and hydroxide anions.

Acknowledgment.—This work was undertaken as a result of extensive discussion between Professor Lucien Gierst and F. C. A. while the latter spent a sabbatical leave at the Free University of Brussels. The work was supported in part by the National Science Foundation.