

### Studies of Double-Layer Effects at Single-Crystal Gold Electrodes. 3. Reduction Kinetics of Fluoropentaamminecobalt(III) Cation in Aqueous Solutions

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The effect of the double layer on the reduction kinetics of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  cation was studied at four different single-crystal gold substrates. The electron-transfer rate constants increase in the order  $\text{Au}(210) < \text{Au}(110) < \text{Au}(100) < \text{Au}(111)$  at constant electrode potential. The value of the experimental transfer coefficient ( $\alpha_{\text{ex}}$ ) also depends on the crystallographic orientation of the gold substrate and in general decreases with increasing concentration of the supporting electrolyte. The observed changes are smaller than those observed previously for the reduction of the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation. Analysis of the double-layer effect for this system shows that the effective charge on the reactant is +1.6. The fact that the effective charge is lower than the formal charge of +2 is attributed to the presence of a dipole moment in the complex due to the anionic fluoride ligand. As a result, the complex is oriented at a positively charged interface with the fluoride anion in a region of higher positive potential, and the electrostatic double-layer effect is less than it would be for a reactant that is a point charge on the outer Helmholtz plane.

#### Introduction

In previous papers<sup>1,2</sup> in this series, studies of double-layer effects on the electroreduction of  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  were reported at single-crystal gold electrodes in dilute aqueous solutions of perchloric acid. By using gold electrodes with a variety of crystallographic orientations, kinetic data were obtained over a wide potential range. These experiments showed that high quality kinetic data may be obtained at single-crystal electrodes. Moreover, they confirmed the conclusion of Frumkin<sup>3</sup> that the nature of the metal electrode affects a simple outer sphere electron-transfer reaction only through its point of zero charge (pzc). In the case of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ , the double-layer corrected kinetic data are characterized by a very large apparent transfer coefficient, both at mercury<sup>4</sup> and at gold.<sup>1</sup> In earlier work,<sup>5</sup> this observation was attributed to the reaction site for this system being closer to the electrode than the outer Helmholtz plane (oHp), which defines the distance of closest approach of the predominant counterions to the electrode|solution interface. However, a much more realistic explanation of the double-layer effect is based on the distribution of charge within the reactant.<sup>1,6</sup> Because a significant fraction of the positive charge in the reactant is located on the ammine ligand, which comes closer to the interface than the central Co atom, the double-layer effect is larger than that for a reactant in which the charge is all located on the central metal atom.

Because the formal charge on the reactants studied earlier is high, ion pairing plays an important role in the electrode kinetics. Kinetic data for both  $[\text{Co}(\text{NH}_3)_6]^{3+}$  and  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  are obtained in a potential region where the polarizable gold electrode is positively charged. As a result the reactants are strongly repelled from the double-layer region. Because the reacting ions are paired to some extent with the anion of the electrolyte, namely, perchlorate, the species reaching the electrode have both 3+ and 2+ charges, the latter corresponding

to the ion pair. Analysis of the double-layer effect for the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  system confirmed that the predominant reactant is  $[\text{Co}(\text{NH}_3)_6\text{ClO}_4]^{2+}$ , the contribution of the unpaired cation to the observed current being negligible.

In the present paper, the studies at single-crystal gold electrodes are extended to the system  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ . Earlier work<sup>7,8</sup> showed that double-layer effects for this reaction are large but quite different from those for  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . This is mainly due to the fact that the formal charge on the reactant is now 2+, and that ion pairing effects are different. Details of our results and their analysis are presented in this paper.

#### Experimental Section

A conventional three-electrode jacketed cell was used throughout the experiment. The working electrode was a gold single-crystal cut to  $1/2^\circ$  accuracy (Metal Crystals and Oxides Ltd., Cambridge, U.K.). Detailed preparation of the electrode before the measurement is described elsewhere.<sup>1,2</sup> The hanging meniscus technique was used to make contact between the crystal face of the electrode and the solution. A saturated calomel electrode connected to the cell through a Luggin capillary was used as a reference electrode. A gold counter electrode completed the setup. The experiments were conducted at a constant temperature of 25 °C under an argon atmosphere. The cleanliness and quality of the electrode surface was verified by cyclic voltammetry. The glassware was cleaned in boiling 50% nitric acid and washed carefully in Nanopure water of maximum resistivity 18 MΩ cm (Barnstead). All solutions were prepared from Nanopure water.

Perchloric acid of reagent ACS grade, 70% in water was purchased from Acros Organics and used as received. The synthesis of the  $[\text{Co}(\text{NH}_3)_5\text{F}](\text{ClO}_4)_2$  electrolyte was in large part based on a procedure given in *Inorganic Synthesis*.<sup>9</sup> Fluoropentaamminecobalt(III) nitrate was synthesized from  $\text{Co}(\text{NO}_3)_2$  in two steps. First the (carbonato)pentaamminecobalt(III) nitrate was prepared. Then the carbonato group was replaced by a fluoro substituent according to the following

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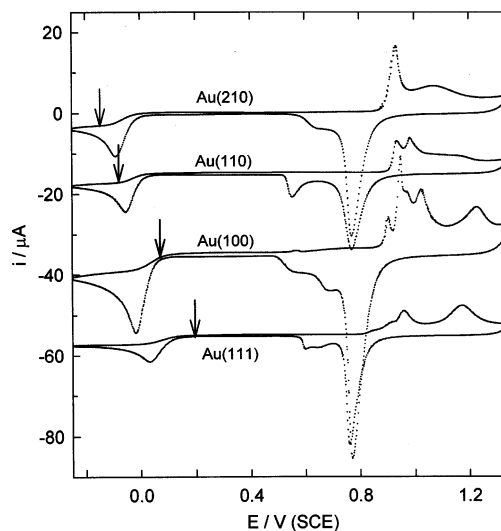
procedure: 10 g of (carbonato)pentaamminecobalt(III) nitrate was suspended in 25 mL of water; then 4.5 g of ammonium hydrogen fluoride and 15 g of ammonium fluoride were added; the reaction mixture was kept at approximately 90 °C in a water bath for 1 h with occasional stirring; the mixture was then cooled to room temperature and 75 mL of water was added to keep the product in solution; the solution was filtered, and 20 g of solid ammonium nitrate was added to the filtrate. Pink crystals separated immediately after the mixture was cooled in an ice-salt bath. The product was collected on a filter, washed with 10 mL of ice-cold water and dried at 90 °C yielding 75.5% of product. The perchlorate salt was prepared by dissolving 4 g of  $[\text{Co}(\text{NH}_3)_5\text{F}](\text{NO}_3)_2$  in 120 mL of water containing some sodium fluoride. Then 60 mL of saturated sodium perchlorate solution was added, and the solution was cooled in an ice bath to separate the crystals. All chemicals used were of the best quality available from the manufacturer. The carbonato as well as fluoro complex were tested for their electrochemical purity on a Au(210) electrode. The test showed only one irreversible peak for each compound. The peak potential of carbonato complex was shifted by about 0.15 V from that of the fluoro complex. The purity of the  $[\text{Co}(\text{NH}_3)_5\text{F}](\text{ClO}_4)_2$  salt was confirmed by UV-vis spectroscopy in aqueous solutions ( $\lambda_{\text{max}}^1 = 352$  nm and  $\lambda_{\text{max}}^2 = 510$  nm in 0.01 M  $\text{HClO}_4$ ) and by  $^1\text{H}$  NMR measurements in dimethyl sulfoxide.  $[\text{Co}(\text{NH}_3)_5\text{F}](\text{ClO}_4)_2$  gives two peaks at  $\delta_1 = 3.62$  ppm and  $\delta_2 = 2.25$  ppm with an integrated ratio 4:1. For comparison, the  $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$  salt gives just one peak at  $\delta = 3.25$  ppm corresponding to six equivalent  $\text{NH}_3$  groups.

Cyclic voltammograms were obtained using a Princeton Applied Research/PAR 173 potentiostat with a PAR 175 universal programmer employing positive feedback  $iR$  compensation. Data were collected in digital form with a PowerLab/4s four-channel analyzer (AD Instruments). Details concerning the determination of the double parameters are described elsewhere.<sup>1,2</sup> Kinetic parameters were obtained from the cyclic voltammograms using semi-integration analysis, as described previously.<sup>10</sup>

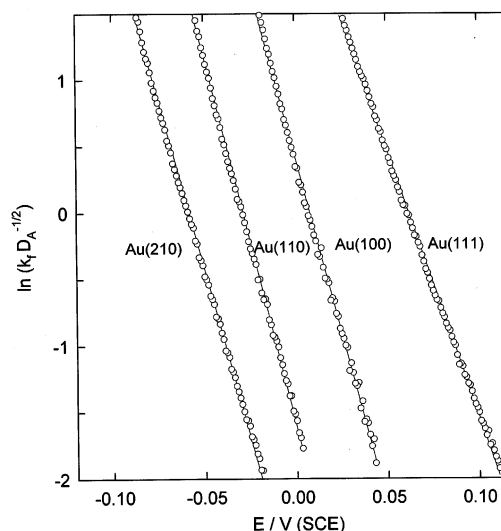
## Results

Cyclic voltammetric data obtained at four single-crystal Au electrodes for the reduction of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  in 0.0092 M  $\text{HClO}_4$  are shown in Figure 1. First of all it is clear that the electrode process is irreversible, just as it was in the case of  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . Because the Co(II) product is very labile, no current due to the oxidation of  $[\text{Co}(\text{NH}_3)_5\text{F}]^+$  is observed on the positive going sweep. Second, the reaction occurs in a more negative potential range with respect to the pzc than that for  $[\text{Co}(\text{NH}_3)_6]^{3+}$ . When the data for the two reactions are compared, it is clear that the transfer coefficient for the fluoro system is quite different from that for the hexaamminecomplex. This conclusion is based on the shapes of the reduction current profiles observed at each single crystal. In making this comparison it should be kept in mind that the present data in Figure 1 were obtained at a scan rate of 50  $\text{mV s}^{-1}$  whereas the earlier results involved a scan rate of 20  $\text{mV s}^{-1}$ .

Values of the forward rate constant as a function of electrode potential were extracted from the cyclic voltammetric data as described earlier.<sup>1,2</sup> Because the value of the diffusion coefficient for the reactant is not known in  $\text{HClO}_4$ , the data are presented as  $\ln(k_f D_A^{-1/2})$  where  $k_f$  is the forward rate constant and  $D_A$  is the diffusion coefficient. From the results obtained with 0.0092 M  $\text{HClO}_4$ , which are presented in Figure 2, it is clear that the rate constant for a given potential increases in the order Au(210) < Au(110) < Au(100) < Au(111). Similar data were

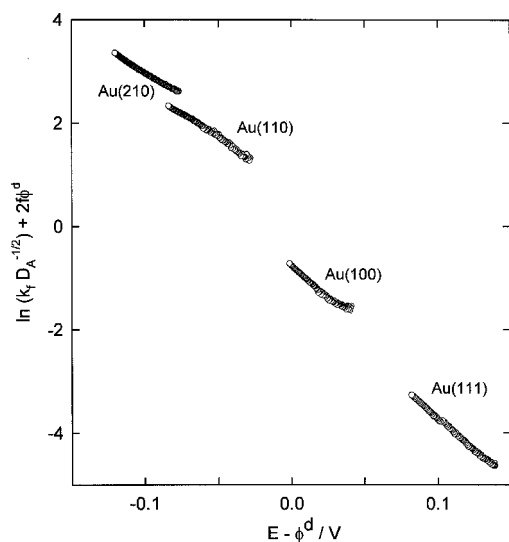


**Figure 1.** Cyclic voltammograms for the reduction of  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.0092 M  $\text{HClO}_4$  at four single-crystal gold electrodes ( $T = 25$  °C): Au(210); Au(110) (shifted down by 15  $\mu\text{A}$ ); Au(100) (shifted down by 35  $\mu\text{A}$ ); Au(111) (shifted down by 55  $\mu\text{A}$ ). The electrode potential was scanned continuously in the range from  $-0.25$  to  $+1.35$  V against the SCE at a rate 50  $\text{mV s}^{-1}$ . The arrows indicate the potential of zero charge at each electrode.



**Figure 2.** Logarithmic plot of the reduction rate constant for  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.0092 M  $\text{HClO}_4$  at four single-crystal gold electrodes as a function of applied potential obtained by semiintegration of voltammograms in Figure 1.

obtained at three other  $\text{HClO}_4$  concentrations, namely, 0.0138, 0.0372, and 0.092 M. The most clear expression of the double-layer effect is the marked decrease in  $\ln(k_f D_A^{-1/2})$  with an increase in electrolyte concentration. For example, at a potential of +0.05 V, this quantity decreases from a value of +0.473 at 0.092 M  $\text{HClO}_4$  for the Au(111) electrode. This corresponds to an attractive double-layer effect whose magnitude decreases with an increase in ionic strength. The other experimental quantity of relevance is the transfer coefficient. The experimental transfer coefficient  $\alpha_{\text{ex}}$  obtained from the slopes of the plots in Figure 2 was lowest for Au(111) and higher at the other electrodes. A summary of the values of  $\alpha_{\text{ex}}$  is given in Table 1. In addition the value of  $\alpha_{\text{ex}}$  decreases somewhat with an increase in electrolyte concentration, as expected when a double-layer effect is present. The values of  $\alpha_{\text{ex}}$  for this system are significantly smaller than those obtained earlier for  $[\text{Co}(\text{NH}_3)_6]^{3+}$  because of the smaller double-layer effect.



**Figure 3.** Corrected Tafel plots for the reduction of  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.092 M  $\text{HClO}_4$  at Au(210), Au(110), Au(100), and Au(111) electrodes. The charge on the reactant was assumed to be 2+.

**TABLE 1: Summary of the Experimental Transfer Coefficients for the Reduction of  $5 \times 10^{-4}$  M  $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$  Ion in Perchloric Acid at Single-Crystal Gold Electrodes**

electrode	$\alpha_{\text{ex}}$ (0.0092 M)	$\alpha_{\text{ex}}$ (0.0138 M)	$\alpha_{\text{ex}}$ (0.041 M)	$\alpha_{\text{ex}}$ (0.092 M)
Au(111)	$1.04 \pm 0.01$	$0.99 \pm 0.01$	$1.03 \pm 0.01$	$0.99 \pm 0.01$
Au(100)	$1.38 \pm 0.02$	$1.30 \pm 0.02$	$1.27 \pm 0.02$	$1.21 \pm 0.01$
Au(110)	$1.44 \pm 0.02$	$1.40 \pm 0.02$	$1.24 \pm 0.01$	$1.09 \pm 0.01$
Au(210)	$1.33 \pm 0.02$	$1.27 \pm 0.02$	$1.23 \pm 0.02$	$1.18 \pm 0.01$

The double-layer effect for the kinetics of the electrode reaction was analyzed using the model originally due to Frumkin.<sup>11</sup> For the simple electrode reaction



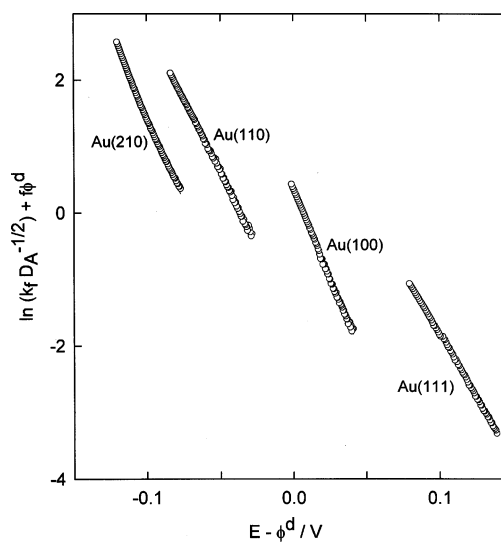
the rate constant for the forward reduction reaction is given by

$$\ln k_f = \ln k_{f0} - z_A f \phi^d + \alpha_a f (\phi^d - \phi^m) \quad (2)$$

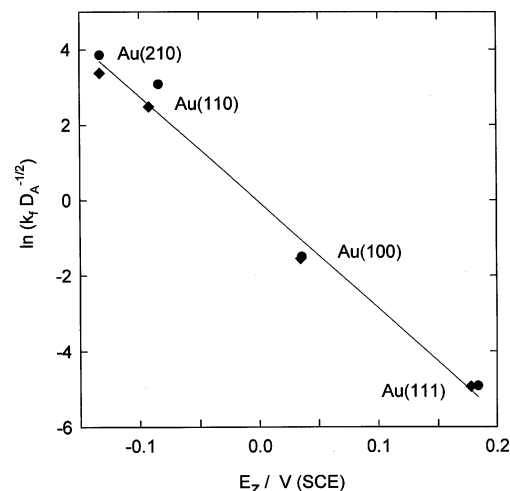
where  $z_A$  is the charge on the reactant,  $\phi^m$  is the electrode potential on the rational scale,  $\phi^d$  is the potential drop across the diffuse layer,  $\alpha_a$  is the apparent transfer coefficient,  $k_{f0}$  is the value of  $k_f$  when both  $\phi^m$  and  $\phi^d$  are zero, and  $f = F/RT$ . Corrected Tafel plots (cTps) were constructed by assuming that  $z_A$  is equal to +2 and retaining the experimental potential scale  $E$ . The results for different Au single crystals at an electrolyte concentration of 0.092 M  $\text{HClO}_4$  are shown in Figure 3. According to electron-transfer theory for an outer sphere reaction, data obtained at different electrodes should fall on one straight line whose equation is

$$\ln k_f + z_A f \phi^d = \ln k_{fE} + \alpha_a f (\phi^d - E) \quad (3)$$

where  $\ln k_{fE}$  is the value of  $\ln k$  when both  $\phi^d$  and  $E$  are zero. It is clear from the results in Figure 3 that cTps assuming  $z_A = 2$  do not fall on one straight line. The average slope of these plots yields an apparent transfer coefficient of 0.53. The reason for the failure of the data to follow this form of the Frumkin model may be that the reactant reaches the electrode and reacts as an ion pair with a net charge of +1. To test this hypothesis, cTps were also made with  $z_A = 1$  (see Figure 4). In this case, the failure to follow the Frumkin hypothesis is much stronger. In addition, the value of  $\alpha_a$  is higher, the average value being



**Figure 4.** Corrected Tafel plots as in Figure 3 but with the charge on the reactant set equal to 1+.



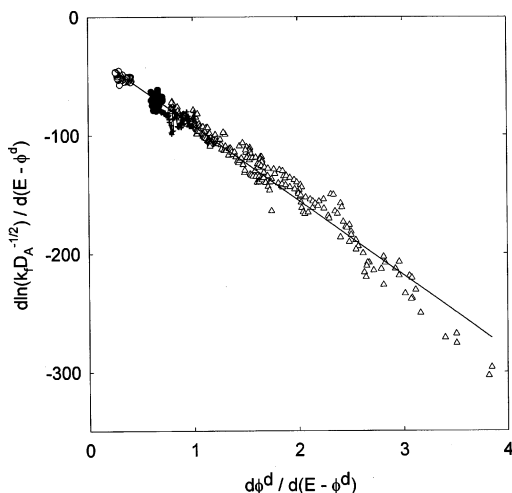
**Figure 5.** Plot of the logarithm of the reduction rate constant for  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.0092 M  $\text{HClO}_4$  (○) and 0.092 M  $\text{HClO}_4$  (●) electrolyte obtained (measured or extrapolated) at the potential of zero charge against the value of the potential of zero charge of the four single-crystal gold electrodes used. The experimental conditions are identical with those in Figure 1.

1.20. Clearly, the results cannot be rationalized using the simple Frumkin model with integral values for the charge on the reactant.

Another way of examining the data is to plot the observed rate constant at the pzc against the pzc on the reference electrode scale used in the experiments. Data obtained in the present experiments for the highest and lowest concentrations of perchloric acid are shown in Figure 5. The results fall on a linear plot and are independent of ionic strength within experimental error. If there is no ionic specific adsorption at the pzc, as may be assumed for the present system, then double-layer effects disappear and eq 3 becomes

$$\ln k_{fz} = \ln k_{fE} - \alpha_a f E_z \quad (4)$$

where  $\ln k_{fz}$  is the rate constant at the pzc and  $E_z$  is the pzc. It follows that the apparent transfer coefficient may be estimated from the slope of the linear plot in Figure 5. The value obtained is  $\alpha_a = 0.72$ . This clearly falls between the estimates obtained from cTps made by assuming  $z_A = 2$  ( $\alpha_a = 0.53$ ) and from cTps with  $z_A = 1$  ( $\alpha_a = 1.20$ ). This suggests that the simple



**Figure 6.** Plot of  $d(\ln k_f - \ln D_o^{1/2})/d(E - \phi^d)$  against the double-layer parameters  $d\phi^d/d(\phi^m - \phi^d)$  for the reduction of  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.0092 M  $\text{HClO}_4$  supporting electrolyte at Au(210) ( $\Delta$ ), Au(110) ( $\bullet$ ), Au(100) (+), and Au(111) ( $\circ$ ) electrodes obtained after the data were passed through a seven-point Savitzky–Golay filter before the differentiation procedure. The solid line represents the best linear least-squares fit.

Frumkin model would apply if the charge on the reactant were intermediate between 1 and 2.

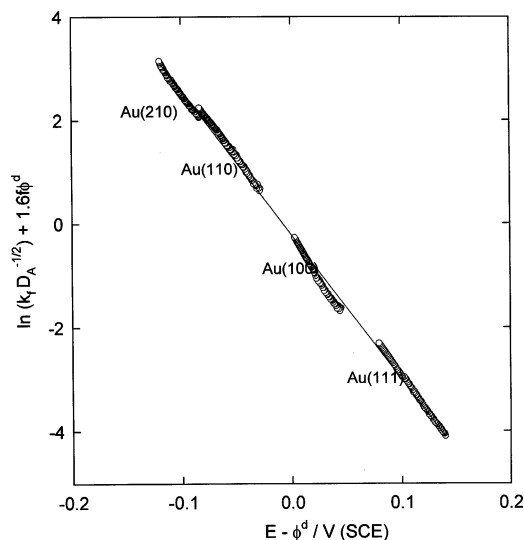
The above results may be rationalized in terms of the distribution of charge within the reactant, as discussed in recent papers.<sup>6,12</sup> Because one of the ligands in the reactant is an anion, this species has a dipole moment. When it reacts at a positively charged electrode, the reactant is oriented in the electrode's field with the anionic ligand closest to the electrode.<sup>13</sup> In this orientation the anionic ligand experiences the highest field at the interface. On the other hand, the central Co(III) ion, whose charge is greatly reduced from the formal value of +3 on the basis of quantum chemical calculations,<sup>6</sup> experiences a smaller field and potential. The formal charge on Co(II) is partially distributed over the  $\text{NH}_3$  ligands. As a result an estimate of the effective charge on the reactant at the outer Helmholtz plane (oHp) shows that it is less than 2+.

To test this hypothesis, kinetic data at a single electrolyte concentration were analyzed further. Data for the rate constant against electrode potential may be analyzed at one concentration using a finite difference technique to obtain the charge density on the reactant.<sup>14</sup> When this method is applied to kinetic data involving one reactant, the result is

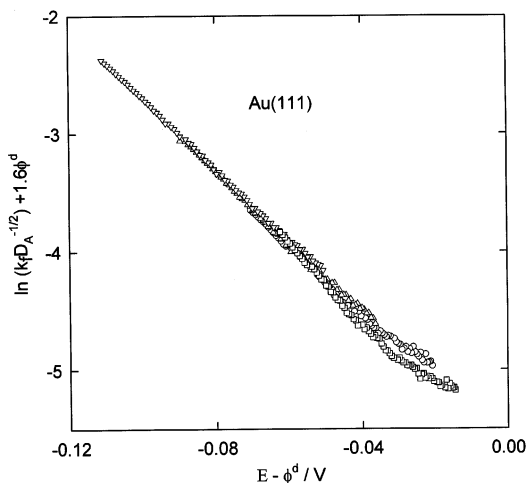
$$\frac{d \ln k_f}{d(E - \phi^d)} = \alpha_a f - z_A f \frac{d\phi^d}{d(E - \phi^d)} \quad (5)$$

Accordingly, a plot of  $d \ln k_f/d(E - \phi^d)$  against  $d\phi^d/d(E - \phi^d)$  should be linear with a slope of  $-z_A f$ .

Results obtained from kinetic data measured at the lowest ionic strength are shown in Figure 6. Because the experimental results were obtained digitally for small increments in  $E$ , a smoothing procedure was used before applying a finite difference method to estimate the derivative. In this way the large errors associated with numerical differentiation are reduced in magnitude. The data obtained at four different gold single crystals fall on one straight line with a value of 1.6 obtained from the slope for smaller values of  $d\phi^d/d(E - \phi^d)$ . For values of  $d\phi^d/d(E - \phi^d)$  greater than 3.0, there is an increase in the slope. This suggests that the effective charge  $z_{\text{eff}}$  on the reactant



**Figure 7.** Corrected Tafel plot for the reduction of the  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion in 0.092 M  $\text{HClO}_4$  supporting electrolyte at Au(210), Au(110), Au(100), and Au(111) electrodes assuming an effective charge of 1.6.



**Figure 8.** Corrected Tafel plot for the reduction of  $5 \times 10^{-4}$  M  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  ion at Au(111) electrode obtained at four different concentrations of perchloric acid: 0.092 M ( $\nabla$ ), 0.041 M ( $\Delta$ ), 0.0138 M ( $\circ$ ), and 0.0092 M ( $\square$ ). The effective charge on the reacting species is assumed to be +1.6.

increases in the vicinity of the pzc. Such a result can be explained by reorientation of the reactant in the region of the pzc.

The kinetic results were further tested by constructing cTps using  $z_{\text{eff}}$  as the charge on a single reacting particle. As can be seen from the plot in Figure 7, when  $z_{\text{eff}}$  is set equal to 1.6 for an electrolyte concentration of 0.092 M  $\text{HClO}_4$ , the kinetic data lie on one cTp for the four single-crystal Au electrodes used in the present study. The value of  $\alpha_a$  estimated from the slope is 0.70. This result agrees well with that obtained from an analysis of the data at the pzc (Figure 5).

The applicability of  $z_{\text{eff}}$  in explaining double-layer effects as a function of electrolyte concentration is illustrated in Figure 8 for the Au(111) electrode. It is clear that the data fall on a single plot when the double-layer correction appropriate for the given electrolyte concentration is applied. The cTps are linear except for the potential region closest to the pzc where the slope decreases slightly. Similar results were obtained at the other Au surfaces.



## Discussion

The present system provides an example of a double-layer effect with a nonintegral effective charge. This result is almost certainly due to the dipole moment in the reactant, which results from the fact that one of the ligands is an anion. Our results illustrate the importance of studying a given reaction at electrodes with differing pzcs. Interpretation of the double-layer effect would be much more difficult if data were available only at one electrode.

When the charge in the reactant cannot be approximated by a point charge, a more appropriate way of writing eq 2 is<sup>1,6</sup>

$$\ln k_f = \ln k_{f_0} - \langle w \rangle / RT - \alpha f \phi^m \quad (6)$$

where

$$\langle w \rangle = (1 - \alpha)w_A + \alpha w_B \quad (7)$$

Here,  $w_A$  is the work done to bring the reactant A to the reaction site,  $w_B$  is that for the product, and  $\langle w \rangle$  is an average work for reactant and product whose value depends on the symmetry of the Gibbs energy barrier for the reaction. The cTp for the reaction is

$$\ln k_f + w_A / RT = \ln k_{f_0} - \alpha (F\phi^m - w_A + w_B) / RT \quad (8)$$

On the basis of the above analysis, the value of  $w_A$  is given to a good approximation by

$$w_A = 1.6F\phi^d \quad (9)$$

For a reaction in which A and B can be represented as point charges, the difference in the work terms is given by

$$w_A - w_B = F\phi^r \quad (10)$$

where  $\phi^r$  is the potential experienced by the point charge at the reaction site. Equation 8 can then be used to determine the apparent transfer coefficient  $\alpha_a$ .<sup>15</sup> However, without detailed information about the distribution of charge in both reactant and product, a relationship between  $w_A$ ,  $w_B$ ,  $\phi^r$ , and  $\phi^d$  cannot be written. Thus, the apparent transfer coefficient is defined empirically as

$$\alpha_a = - \frac{d(\ln k_f + w_A / RT)}{fd(\phi^m - \phi^d)} = \frac{\alpha d(F\phi^m - w_A + w_B)}{Fd(\phi^m - \phi^d)} \quad (11)$$

On the basis of geometrical considerations,<sup>1,6</sup> the cobalt atom is certainly in the diffuse layer. The fact that the value of  $\alpha_a$  is significantly greater than 0.5 can only be assessed with detailed information about the charge distribution in the reacting system.

Another possible explanation for the present results is that a parallel reaction is involved with participation of both the unpaired cation and an ion pair with a charge of +1. Under these circumstances the forward rate constant is given by<sup>16</sup>

$$k_f = k_M \rho_M \exp(-z_A f \phi^d) + k_{MAE} (1 - \rho_M) \exp[-(z_A - 1) f \phi^d] \quad (12)$$

where  $k_M$  and  $k_{MAE}$  are the rate constants for the unpaired and ion-paired species, respectively, and  $\rho_M$ , the fraction of the reacting cation present as the unpaired species in the bulk of the solution. The results shown in Figure 5 may now be reconsidered on the basis of a parallel reaction mechanism. At

the pzc, in the absence of double-layer effects, eq 12 becomes

$$k_{fz} = k_{ME} \rho_M e^{-\alpha_M f E_z} + k_{MAE} (1 - \rho_M) e^{-\alpha_{MA} f E_z} \quad (13)$$

$k_{ME}$  and  $k_{MAE}$  are the standard rate constants for reaction of the unpaired ion and ion pair, respectively (under conditions for which both  $E$  and  $\phi^d$  are zero);  $\alpha_M$  and  $\alpha_{MA}$  are the corresponding transfer coefficients. The slope of the plot in Figure 5 is now

$$\frac{d \ln k_{fz}}{dE_z} = \frac{-\alpha_M f k_{ME} \rho_M e^{-\alpha_M f E_z} - \alpha_{MA} f k_{MAE} (1 - \rho_M) e^{-\alpha_{MA} f E_z}}{k_{ME} \rho_M e^{-\alpha_M f E_z} + k_{MAE} (1 - \rho_M) e^{-\alpha_{MA} f E_z}} \quad (14)$$

Thus, the value of  $\alpha_a$  determined from this plot is a weighted average of the individual transfer coefficients  $\alpha_M$  and  $\alpha_{MA}$ . Because  $E_z$  changes significantly with the nature of the gold surface, one would expect a nonlinear result. In addition, the slope of the plot should depend on ionic strength, whereas the experimental results are independent of ionic strength. Thus, it is clear that a parallel reaction mechanism with component reactions occurring at similar rates is not involved.

In an earlier study of this reaction at a mercury electrode,<sup>8</sup> the double-layer effect was analyzed by assuming that the charge on the reactant was +2. Because the kinetic data were obtained at potentials positive of the pzc, the orientation effect that leads to an effective reactant charge less than +2 should also play a role at mercury. If it is assumed that  $z_{\text{eff}}$  is equal to 1.6 for this system, the value of  $\alpha_a$  obtained from the cTps would be higher and closer to the result obtained here. The reduction of  $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$  was also studied in the presence of specifically adsorbed nitrate anions to examine discreteness-of-charge effects. These results should be reexamined using the lower reactant charge to reassess the effects of the adsorbed anions on the electroreduction kinetics.

Finally, Weaver<sup>17</sup> suggested that the present system could be used as a probe reaction to determine the effective potential at the oHp. It is clear from the present results that the double-layer effect for this reaction is too complex to use it as a double-layer probe. In fact, a detailed examination of this system should include a study of double-layer effects over as wide a potential range as possible. It is quite likely that the effective charge increases as the pzc is approached from positive charges and has a completely different value at negative charge densities on the electrode.

Kinetic studies of cationic complexes with a mix of neutral and anionic ligands would help to elucidate further orientation effects in electrode kinetics.

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