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THE CHARACTERIZATION AND APPLICATION OF SOME ELECTROCHEMICAL RELAXATION TECHNIQUES IN CORRELATING INTERPHASIAL STRUCTURE WITH ELECTROCHEMICAL REACTIVITY

> by Paul Daniel Tyma

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ABSTRACT

THE CHARACTERIZATION AND APPLICATION OF SOME ELECTROCHEMICAL RELAXATION TECHNIQUES IN CORRELATING INTERPHASIAL STRUCTURE WITH ELECTROCHEMICAL REACTIVITY

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This study describes experiments which expose correlations between electrochemical reactivity and the structure of the region of solution immediately adjacent to the electrode surface (the "interphase").

The variation of the electrochemical transfer coefficient (corrected for double-layer effects) with electrode potential was studied over several orders of magnitude in rate for the oxidation and reduction of $M^{3+/2+}$ aquo complexes (M = Cr, Eu, V) and for Co(NH₃)₅F²⁺ reduction. Little or no change in the transfer coefficient was seen for the reduction reactions, whereas a striking potential dependence was observed for the oxidations. This variation is more than that predicted by dielectric-continuum models of ion solvation and is shown to be compatible with a previously reported model involving specific (Hydrogen-bonding) interactions between solvent molecules and ligands in the primary coordination sphere.

The effect on electrochemical redox kinetics of deuterating both the solvent and ligands of transition-metal complexes was considered. It was shown that ratios of double-layer corrected standard rate constants obtained in the two solvents provide information about differences in the intrinsic free-energy barriers to electron transfer which are brought about by solvent deuteration. Larger rate ratios were found than are predicted on the basis of molecular-orbital calculations of the inner-shell contribution to the reorganization energy and predictions made by a dielectriccontinuum model of the outer-shell portion. Again, the results were seen to be compatible with a model which postulates specific rather than general solvent structuring by the reactant ion.

A pulse-polarographic display format and analysis method applied to a collection of current-time transients which result from potential-step perturbations of an irreversible electrode reaction were demonstrated to provide more reliable rate information than a chronoamperometric analysis of individual transients. In addition, pulse polarography was shown to indicate directly the presence in the data of unexpected features which were found to be due to nonideal instrumentation and to adsorption effects.

High-speed dc polarography was evaluated in terms of its suitability for providing electrochemical change-transfer rate information which might be inaccessible by conventional largeor small-amplitude perturbation techniques. Dropping mercuryelectrode flow rates between 1 and 2 mg/sec were shown to be appropriate; larger flow rates were seen to be unacceptable due to stirring or depletion effects. The method under some circumstances separated kinetically controlled polarographic waves which overlap at conventional times and reduced in some cases the effects of polarographic maxima enough to provide access to rate data.

Conventional instrumentation was employed where feasible for the experiments described in this study. For those cases where commercially available equipment did not possess sufficient speed or timing flexibility, a microcomputer-based system for the acquisition and management of electrochemical data was developed and utilized. Its features include the capability to make measurements with 12-bit resolution at rates up to 100 kHz and the ability to provide with 12-bit resolution a voltage output with a submicrosecond settling time and less than 2 mV peak-to-peak noise. Optical and high-speed electrochemical drop-fall detectors were constructed for the purpose of synchronizing timing circuitry with the birth of the new drop. The former were shown to be unacceptable as a consequence of a nonreproducible delay between 20 and 100 msec. The electrochemical detector showed several advantages: it is compatible with potentiostats; it does not constantly impose an ac perturbation on the cell; it requires infrequent adjustment; and it is about 200 times faster than those of comparable design.

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"Forsitan et haec olim juvabit."

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CHAPTER I. INTRODUCTION

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OVERVIEW

The goal of the work described in this thesis is to determine relationships between rates of electrochemical reactions and the structure of the reactants and of the solution region adjacent to the electrode, the so-called "interphase", using conventional approaches when feasible, devising and applying new instruments and methods when previously available strategies are inappropriate. This chapter presents a summary of the information which is sought, the motivation for seeking it, and the tactics for garnering it. A brief description of the energetics of heterogeneous electrontransfer reactions is given, along with a discussion of the use of the electrochemical transfer coefficient and isotopically substituted reagents to provide information about the structure of the solvent in the interfacial region. The use of rate responses to infer structural properties and the characterization of new techniques for developing additional probe reactions are discussed. Intercomparison of techniques is presented as an approach for assessing the reliability of measured rate data.

In spite of recent successes in the chemical modification of electrodes,¹ the ability to tailor an electrochemical surface to suit specific needs continues to elude the electrochemist. The effects of reactant structure on the rates and mechanisms of homogeneous electron transfer between members of inorganic redox couples have received thorough scrutiny,² but the same degree of attention is just beginning to be focused on the electrochemical (heterogeneous) reaction analogs. A complete understanding of the factors which control electrochemical reactivity would pave

the way both toward the inexpensive realization of clean and efficient energy conversion which electrochemistry has promised for many years^{3,4} but not yet provided, and toward the effective arrest of the ubiquitous and costly corrosion⁵ for which electrochemical charge-transfer phenomena provide a most useful model.⁶ The work described herein is one contribution to a major ongoing effort to correlate rates and mechanisms of electrochemical redox reactions with the structure of the reactant and of the environment of the electrode-solution interface.

The study of homogeneous redox processes has identified reaction types of two extremes:² those which proceed with imperceptible perturbation of the primary coordination spheres of ligands about the two reaction centers ("outer-sphere"), and those in which a ligand forms a bridge between the two reactants ("inner-sphere"). Analogous heterogeneous examples and techiques for discriminating between the mechanisms have been described.⁷ A distinguishing feature of outer-sphere electron-transfer processes is that they are believed to be non-adiabatic or only weakly so; that is, the reactant and product free-energy surfaces are only weakly coupled if at all in the vicinity of the activated complex. Because the rates of redox reactions can be significantly larger at electrodes made of some materials than of others and because the composition of the ligands about a transition-metal ion can have a drastic effect on the rates, it is of interest to determine how this "electrocatalysis" arises. One study at Hg electrodes has demonstrated that for some kinds of substituted Cr(III) ammine complexes the rate enhancement afforded by an inner-sphere pathway

is due principally to the increased availability of electroactive species provided by adsorption rather than due to any decrease in the elementary activation barrier.⁸ In another context, experimental evidence has been presented that some metals do indeed lessen the activation energy.⁹

ENERGETICS OF HETEROGENEOUS ELECTRON-TRANSFER PROCESSES

To provide a conceptual basis for the understanding of electrode processes, one may consider a model in which five states are identified, the free-energy profile of which is shown in Figure 1. The states and their respective free energies are as follows: reactant in the bulk of solution (with free energy G_1); reactant at its plane of closest approach to the electrode (G_{11}) ; the activated complex in which, due to the Franck-Condon restriction for a radiationless process, the free energy and interatomic distances of the reaction species prior to the electron transfer equal those of the product species immediately following the transfer (G_+) ; the reaction product adjacent to the electrode (G_{111}) ; and the product in the bulk solution (G_{11}) . Several free-energy differences can be described: the work in bringing the reactant to the surface $(w^r = \Delta G_{11-1} = G_{11} - G_{1})$; the work in removing the product $(w^{P} = \Delta G_{|V-|||} = G_{|V} - G_{|||})$; the free energy of the reaction ($\triangle G^{\circ} = \triangle G_{|V-1} = G_{|V} - G_{|}$; the experimentally measured activation energy $(\Delta G_{app}^{\dagger} = \Delta G_{+-1} = G_{+} - G_{1})$; and that portion of the activation energy which is characteristic of, or "intrinsic" to, a given reactant and electrode combination

 $(\Delta G_{i}^{\dagger} = \Delta G_{+-||} = G_{+} - G_{||}).$



reaction coordinate

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Among contemporary theories to describe redox-reaction kinetics, one due to Marcus has enjoyed considerable success. According to this formulation, the electron-transfer rate constant is described to a good approximation by

In $k_{app} = \ln Z_e - \frac{1}{RT} \left[\frac{\lambda}{4} + \alpha_i (w^p - w^r) + w^r + \alpha_i F(E-E_f) \right]$ (1) where w^r and w^p are defined as above; Z_e is the electrochemical collision frequency; $\lambda/4$ is the "reorganization energy", namely ΔG_{+-11} for the case where there is no "surface driving force" $(G_{11} = G_{111})$; α_i is an integral intrinsic transfer coefficient $(\underline{vide infra})$; E is the electrode potential; and E_f is the formal potential of the couple under scrutiny. The first term within the braces in Equation 1 is called the "intrinsic" portion of the activation energy, the second the "surface therodynamic" the LECTROCHEMICAL TRANSFER COEFFICIENT

That the electrode potential has an effect of the reaction rate provides one of the most commonly employed probes in the study of electrochemical kinetics. Through the well-known correspondence between the electrode potential and the free-energy change occurring in an electrochemical cell, and through the linear free-energy relationship embodied in Equation 1, a change in the electrode potential changes the rate <u>via</u> the bulk driving force. Because the work terms w^r and w^p can be implicitly potential-dependent, additional effects due to potential change is ascribed to the electrochemical rate difference it produces, so that one can define the quantity

$$^{\alpha} \text{ app } = \left(\frac{\partial \Delta G_{\text{app}}}{\partial \Delta G^{\circ}}\right)_{\mu} = \frac{-1}{nF} \left(\frac{\partial \Delta G_{\text{app}}}{\partial E}\right)_{\mu} = \frac{-RT}{nF} \left(\frac{\partial \ln k_{\text{app}}}{\partial E}\right)_{\mu} (2)$$

to describe the symmetry of the free-energy barrier, including "environmental" effects. The corresponding relationship can be written exclusive of double-layer effects

$$\alpha_{1} = \left(\frac{\partial \Delta G_{1}}{\partial \Delta G^{0}}\right) = \frac{\alpha_{app} - \frac{1}{F} \left(\frac{\partial w^{r}}{\partial E}\right)_{\mu}}{1 - \frac{1}{F} \left(\frac{\partial w^{r}}{\partial E}\right)_{\mu} + \frac{1}{F} \left(\frac{\partial w^{P}}{\partial E}\right)_{\mu}}$$
(3)

The integral version of this quantity shown in Equation 1 uses the chord suggested by Equation 3 instead of the slope (partial derivative). A geometric argument can be used to show that for free-energy surfaces which are roughly parabolic, α_1 is about 0.5 for small or moderate values of the bulk thermodynamic term. An important consideration in the assessment of electrochemical reactivity patterns is therefore to apportion the measured activation energies into the intrinsic and thermodynamic segments, the latter not only for the driving force ΔG^{O} but also for the "doublelayer" efects of w^r and w^p.

DEMONSTRATIONS OF SOLVENT STRUCTURING

A significant component of the reorganization energy $\lambda/4$ for an outer-sphere reaction consists in the rearrangement of the ligands and solvent molecules surrounding the reactant ion so that, in keeping with the Franck-Condon limitation, the transition state reflects a condition of metal-ligand bond distances and solvent polarization which is between the reactant and product conditions. Recent study of the effects of ligand composition about transition-metal redox couples on the half-cell reaction entropies^{11,12} has provided compelling evidence for the existence of specific, secondary structuring of solvent molecules which is engendered by solution species. For those cases where the double-layer effects are negligible or known, the potential dependence of the intrinsic electrochemical transfer coefficient could provide an additional test of such a model. A theoretical prediction¹³ based upon the treatment of the solvent as a continuous dielectric medium has received some examination¹⁴. Although the results of this study produced less variation with potential than the dielectric-continuum model presages, evidence is presented in Chapter IV below that under certain circumstances the transfercoefficient dependence upon potential is even stronger than the model anticipates. Indeed, the results can be seen to corroborate the structured-solvent argument.¹⁵

Furthermore, because of the participation of hydrogen bonding in secondary solvent structuring,¹¹ coupled with the sensitivity of the hydrogen-bond strength to the mass of the hydrogen isotope,¹⁶ the measurement of electrochemical reaction rates in D_2^0 solvent in comparison with those in water presents the opportunity to examine those aspects of the model which relate to the specific nature of the secondary structuring. The results of experiments described in Chapter V involving the use of isotopically substituted ligands and solvents substantiate still further the applicability of the structured-solvent model.

USE OF RATE RESPONSES TO PROBE INTERPHASIAL STRUCTURE

A recent discussion has shed light on the measurability and indeed on the significance of electrochemical activation parameters, by explicating the confusion surrounding the temperature dependence

of electrochemical potential scales.¹⁷ Because an experimentally measured ("apparent") activation energy represents an intertwining of work terms and activation information (cf. Equation 1), it is imperative that the adsorption energetics be determined. Two limiting cases can be described: that in which there is significant interaction, often covalent, between an adsorbing species and the electrode ("specific adsorption"); and that in which the interaction is of a fairly weak, nonspecific coulombic nature between a charged reactant species and the electrified electrode-solution interface. When the adsorption is very strong, as is often encountered in the former case, a rapid potentialperturbation technique such as chronocoulometry can be employed to determine the amount of electroactive material immediately adjacent to the electrode.¹⁸ Should the latter situation prevail, however, one must resort to more indirect means. The adsorption coefficient K^r is then given by

$$K^{\Gamma} = 2r(\exp(-zF\phi_{2}/RT))$$
(4)

where r is the radius of the reactant ion of charge z and ϕ_2 is the Galvani potential difference between the bulk of solution and the plane of closest approach of the ion to the electrode.⁹ This potential difference arises from the anisotropy generated in solution by the presence of a charged electrode in a medium of mobile charge carriers (electrolyte ions) whose coulombic attraction or repulsion for the electrode charge is compensated in part by thermal motion of the solution. The factors which determine ϕ_2 are the charge density q^m on the metal and the

specifically adsorbed charge density q', both of which can be assayed for liquid electrodes such as Hg by means of electrocapillary thermodynamics.¹⁹ One theory which is due to Guoy and Chapman²⁰ to describe the dependence of ϕ_2 on $-(q^m + q')$ has enjoyed success despite a recent challenge.^{14,15,21,22} The measured rate responses of mechanistically simple electrode reactions to systematic and known changes of double-layer composition can then be utilized as "kinetic probes" of unknown ϕ_2 values, an application of considerable advantage for solid-electrode studies⁹ where the metastable nature of the solid surface precludes the use of electrocapillary thermodynamics.

EXPERIMENTAL TACTICS IN THE USE OF PERBROMATE PROBES

Cationic complexes of Co(111) have been well categorized as outer-sphere probes for various potential ranges on Hg electrodes^{22,23} and have seen employment at solid electrodes.⁹ The electroreduction of perbromate anion has been suggested as an anionic probe.²⁴ For it to probe successfully the unknown specific adsorption of solution species, the reduction rate of perbromate must be scrutinized in media for which specific adsorption data are available. Typically, these solutions would contain concentrated fluoride salts so that the specific adsorption could be quantified by the Hurwitz-Parsons method.²⁵ Two experimental complications militate against its use:²⁶ The reduction rates are close to the maximum measurable by ordinary dc polarography; and the potential "window" on Hg electrodes has complications at its extremes, namely Hg oxidation in the region of kinetic interest and bromate or solvent reduction very near the onset of the requisite limiting-

current segment. While pulse polarography can be used to measure faster rates, 27 a condition necessary for its employment is the existence of a potential range in which the electrode is ideally polarizable (no charge transfer occurs across the electrode-solution interface). That this region is not present at Hg electrodes 24,26 vitiates the application of pulse polarography.

Time-resolved dc polarography offers the prospect of access to faster rates for such a situation.²⁸ Because the experimental perturbation is the electrode-area growth, no ideally polarizable region is required, which renders the technique amenable to perbromate measurements. The predicted shift²⁹ of the kinetically controlled analyte wave and interference waves described above, which occurs with decreasing current-sampling time following drop birth, suggest that rates may be measurable at potentials closer to those where the Hg-oxidation wave is normally significant and that the limiting current may be less ambiguously determined in concentrated electrolytes. Another advantage of the technique is the reported elimination of complications due to polarographic maxima in electroanalytical work involving Hg drops of forcibly shortened lifetimes.³⁰ Whether the same advantages accrue to measurements of electrochemical reaction rates under the same circumstances has yet to be reported. A systematic evaluation of time-resolved polarography is presented in Chapter VII with an eye toward its suitability for electrochemical rate measurements.

For such purposes, it is desirable to compare rapidly sampled polarographic currents at dropping Hg electrodes where the drop

detachment occurs by natural fall and by forced dislodgement. The latter are experimentally more expedient at the expense of producing additional convection within the solution, a complication absent in the latter case. A signal to synchronize timing circuitry with the birth of the drop is easily derived from the circuit which drives a solenoid to knock drops from the capillary, but some external means of detecting drop fall accurately must be fashioned for natural-drop experiments. Two types of drop-fall detectors were constructed; the characterization of the optical class of detectors and the fabrication of a high-speed electrochemical detector form the subject of Chapter III.

ASSESSMENT OF MEASUREMENT RELIABILITY

Underlying the electrochemist's interpretation of kinetic parameters is an implicit confidence that the rates have been measured reliably. It is worth considering whether this conclusion is warranted: one would find it helpful to know if the surface conditions are reproduced from one experiment to the next; how fast a rate can be measured accurately with the available equipment; and to what extent the choice of experimental technique, data analysis, or instrument design distorts the rate information presented.

Quite apart from the anticipated considerations of reagent purity in the solutions tested, the difference between liquid and solid electrodes is crucial to the first question. There are several well-documented reasons for this. Because the adsorption energetics of solution species at electrodes seldom if ever are less favorable on solid electrodes than on Hg, trace contaminants

whose effects on electrode kinetics are magnified by their concentration in the double layer by adsorption processes are of less consequence at Hg electrodes. Liquid-liquid interfaces are smooth on a molecular scale, and unlike solids the arrangement of surface atoms is not metastable. The surface and geometric areas of liquids therefore always concur, whereas the "surface roughness" of solid electrodes as expressed in the ratio of these areas can differ from unity and can be reproduced only if some pains are taken. The surface of a liquid electrode can be easily renewed, and therefore liquid electrodes do not carry with them a history of previous experiments as solids do.³¹

That Hg-electrode surface conditions can be copied faithfully has received frequent demonstration, making scrutiny of the other two considerations possible through the study of Hg behavior. Measurements of Cr(III) reduction rates in perchlorate electrolytes from two different studies in two different laboratories agree well.^{32,33} Within a given location, one study¹⁴ has shown that systematic differences of 10% in rate parameters assessed by two different analyses of dc polarographic data are readily discernible from those calcutated from chronocoulometric results. In another case, two applications of Co(III) ammine probes^{15,23} produced rate constants in good agreement. In studies at solid electrodes, on the other hand, rate disparities from one experiment to the next of 50% or more are not uncommon.³¹

As to the second and third reliability considerations, an intercomparison of techinques often provides valuable information.

The ranges of rate constants accessible from pulse- and dc-polarographic data overlap considerably. 27, 29 and experiments described in Chapter V and elsewhere³⁴ using these two methods can produce essentially identical rate parameters. Weaver and Anson have described the convergence of reaction rates measured via chronocoulometry and dc polarography and have used this technique-comparison to show the inappropriateness of a spherical-diffusion correction to their polarographic results.¹⁴ Chronocoulometry has been described on purely theoretical grounds as providing a higher information content for kinetic studies than chronoamperometry,³⁵ but an empirical examination of this point has not been reported. Once a give experimental technique has been chosen, the method for the treatment of data can be important. Various time-domain approximations to the complicated rigorous solution of the diffusion equation characterizing chronoamperometry are available³⁶, each with its own range of applicability. The use of Laplace-domain analysis³⁷ has been proposed as a way to utilize all of the currenttime data rather than selected portions, but a demonstration of the relative merits of these methods has not been forthcoming. Enke et. al. have discussed thorougly the determinate error which results from the use of approximate solutions or nomographic methods in the coulostatic technique, as well as experimentally accessible criteria which can indicate the suitability of a particular approximation. Chapter VI describes an assessment of high-speed rate measurements made at Hg electrodes with equipment constructed in this department and provides an experimental demonstration of the superiority of a pulse-polarographic type of display and

data analysis for irreversible chronoamperometric transients. Also presented is a strategy for determining the extent to which the boundary conditions assumed in the solution of the diffusion equations are satisfied by the instrument employed.

There are many instances in which the performance of commercially available instruments is adequate for the rate measurements required by a given study. Most of the experiments described in Chapter IV and V below fall into this category. However, the technique evaluations reported in Chapters VI and VII necessitated considerably more timing flexibility and speed than are possible with conventional instrumentation. For instance, it is desirable in potentialstep techniques to sample the cell current or its time integral within time ranges characteristic of double-layer charging phenomena. Typical double-layer integral capacitances at Hg electrodes are around one microfarad: for uncompensated solution resistances less than 100 ohms, cell time constants would be as large as 100 microseconds. Sampling intervals of 10 microseconds would be sufficient for this task, but such a time is more than three orders of magnitude smaller than the current-sampling time of the pulse-polarographic mode of the redoubtable PAR Model 174 Polarographic Analyzer (EG&G Princeton Applied Research, Princeton, NJ), one of the most commonly used electrochemical instruments. For those cases in which conventional electrochemical instruments did not possess the speed or flexibility required for the studies described herein, a microcomputer-controlled electrochemical data acquisition and management system, the documentation of which comprises Chapter II, was utilized.

CHAPTER II. A MICROCOMPUTER-CONTROLLED ELECTROCHEMICAL DATA-

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ACQUISITION SYSTEM

INTRODUCTION AND GENERAL DESCRIPTION

A general description of the microcomputer system and its laboratory-type peripherals forms the subject of this chapter. Some attention is paid to the steps in its development which were necessary to obtain satisfactory speed and signal-to-noise ratio performance in the potential-generation subsystem. The maximization of the data-acquisition rate is discussed, and specialpurpose accessories which were required for some experiments are described. Finally, an example is presented of a technique which cannot be performed by ordinary instruments but which is readily implemented by a computerized experimental-control system.

A decade ago, a review of electrochemical relaxation-techinque methodology claimed that "...apparently the ultimate in (electrochemical) instrumentation these days is to have your own digital computer in the lab."³⁸ Scarcely two years later, the same author opined that "...today's polarographer is apt to feel obsolescent without a minicomputer.³⁹ The virtual explosion of computer technology since then has put a wide range of processing power into the hands of electrochemists. Recent applications range from a highly sophisticated "soup-to-nuts" Fourier-transform based system capable of viewing in the frequency domain simple diffusion processes as well as complicated reaction mechanisms, 40 to monitoring measurements of ion-selective electrode potentials.⁴¹ Similarly spectacular learning-curve progress in memory fabrication has made possible the manufacture of microprocessors which are capable of mimicking the instruction-set performance of other computers, thereby emulating inexpensively their more costly, albeit more powerful, cousins.

The computer system which was built in our laboratory is based upon the Digital Equipment Corporation LSI-11 central processing unit (CPU), which emulates the instruction set of the PDP-11 family.⁴² Access within the university to the real-time, dualtask operating system RT-11⁴² made high-performance softwaredevelopment tools such as symbolic editing, high-level languageprocessing, and file-minipulating programs immediately available for use in the creation of applications software for the acquisition and reduction of electrochemical data. Because of the considerable time-saving this made possible, efforts could be concentrated on construction of the computer from the circuit-board level, a process which makes computation available at substantially less expense than in ready-made "turn-key" computers.

Figure 2 shows a schematic representation of the computer system. Those subsystems shown in solid-line rectangles are components which are included with the CPU in virtually any computer system of recent vintage: namely, high-speed memory, a console terminal, mass-storage memory, and a hard-copy printer. Interfaces to all but the last of these peripheral devices were used without modification as they came from the manufacturers. This is indicated in Figure 2 as solid-line connections between subsystems. The printer-interface circuitry was constructed from a MDB Model MLSI-1710 general-purpose parallel-interface module (MDB Systems Inc., Orange, CA) and the random logic necessary to pass data between the bus-tending circuits and the Centronics-type inputoutput (1/0) structure of the Printronix Model 300 graphics line printer.



Figure 2. Block diagram of measurement system.

POTENTIAL GENERATION AND MEASUREMENT

What distinguishes a laboratory computer from an ordinary computer is the presence of those accessories which can transform analog voltages to digital binary representations and vice versa (analog-to digital (A/D) and digital-to analog (D/A) converters) and that which can provide accurately spaced timing pulses for sequencing measurements (real-time clock), enclosed in Figure 2 by broken-line rectangles. Twelve-bit A/D and D/A converters are contained on a Data Translation Model DT 1761-SE-C-DMA Analog Input/Output Board (Data Translation Inc., Natick, MA), and the clock is a MDB model MLSI-KW11P circuit. The laboratory peripherals required modifications to perform to the standards required by our experiments.

While the "quasi-differential" nature of the A/D input system (single-ended analog multiplexer and differential input amplifier) provides sufficient noise immunity even in the relatively noisy mainframe environment, the same performance was not seen for the D/A converter. The output of the latter was discovered to contain rather large-amplitude, high-frequency noise, mainly about 200 mV peak-to-peak at a frequency near 400 kHz. Because a design criterion for the potential-generation circuitry was the ability to deliver potential steps with submicrosecond rise time to the potentiostat used for electrode-potential control (see Chapter VI), low-pass filtering of the D/A converter output to remove the noise was not an acceptable alternative inasmuch as a filter time-constant of sufficient magnitude to reduce the noise would also increase the rise time to several hundred microseconds.
Rather than being common-mode (that is, induced equally in both the D/A converter output and its analog return), a condition which could in principle be remedied by employing a differential amplifier at the potentiostat,⁴³ the noise originated in the dc-dc converter whose function is to produce +15 and -15 V analogcircuitry power isolated from the 5 V logic power supply from which it is derived. Such behavior is characteristic of these switching power supplies when they have insufficient output filtering.⁴⁴ A miniature LC-type low-pass filter⁴⁵ with a nominal attenuation over 1000 at 100 kHz was installed on the analog power supply; its effect was to reduce the noise in the D/A converter output to a third of its original magnitude, an amount still too large for precise potential control. Clearly additional noise must be induced in the power-supply leads between the filter and D/A converter, a situation difficult to remedy by retrofitting.

A second D/A converter was available in a staircase-waveform generator built in this department.⁴⁶ This converter met the rise-time specification for our experiments: its settling time is 1 microsecond to within 1 LSB (1 part in 4096) for a 20-volt step. Furthermore, because the long-distance information transmission is accomplished in the digital domain,⁴⁷ noise in the output was found to be less than 2 mV peak-to-peak. An interface, shown in Figure 3, was built to allow the computer to program the D/A converter through the DRV-11 parallel digital port.⁴² In addition, a digital trigger signal generated in response to the LOAD B AND CONVERT command⁴⁶ was derived from gates within the waveform Z I ٩ I പന чш 000+000+00 ----മ 1 1 1 1 1 1 1 1 D V C N U M I L す * * * * * * * * * ഗ \mathbf{O} \mathbf{O} G Ø 74121 σ ----< ω ÷ -S ŝ Ŧ 3M CONNECTOR NATION ഗ + <RR, NN< < 4 0 / / / > 30/JJ> $\mathbf{\nabla}$ **5 m N+NON+0** നവ \mathbf{i} **www.eeee** шш \sim ш $\overline{}$ ----I ഗ **0**-00+000 -0 U T 1 000000000 ıШ NDR 2 < 2 < ר ם

Figure 3. Interface to D/A converter.

generator so that synchronization of electrochemical experiments with potential steps could be effected.

THE TIMING OF COMPUTER-CONTROLLED MEASUREMENTS

Once a sample-and-convert measurement cycle has been completed, the information in the A/D output register must be transferred to the computer's memory for further processing. Two different types of transfers are possible: one in which the CPU interrogates the A/D converter and writes the result into memory ("program control"), and one in which logic associated with the converter uses the computer bus when it is idle to transfer the conversion to a pre-programmed memory location without the intervention of the CPU ("direct memory access", or DMA). In circumstances where the time taken by the computer to ascertain that the conversion is available and to store the result poses no threat to the timing fidelity of subsequent measurements, the former, less complicated approach may be taken. Observations show that the LSI-11 is capable of making measurements under program control at 40-microsecond intervals without introducing timing errors. The length of this period clearly precludes another system-design criterion, namely the ability to make measurements separated by only 10 microseconds. However, the analog I/O board was purchased with an A/D converter which has a conversion time of 8 microseconds or less and DMA logic with typical transfer times of 1 microsecond, thereby ensuring 100 kHz data-acquistion rates in this mode.

The real-time clock counts pulses of a program-selectable, four-frequency oscillator; 100 kHz, 10 kHz, 60 Hz, and external rates are nominally available. However, construction and design

flaws in the clock introduced two unexpected features: first, the behavior of the underflow or overflow signals of the 74193 decade-counter integrated circuits which comprise the programmable modulo-N counter circuit⁴⁸ is such that an extra eight-tenths of the clock period must elapse before the first overflow or underflow signal is generated;⁴⁹ and second, the mask-programmable MOS frequency divider which is supposed to produce a 60-Hz output frequency from the 3.5795 MHz crystal oscillator actually provides pulses at 20-Hz intervals. Neither of these anomalies causes anything more than a minor inconvenience in practice inasmuch as the data-acquistion programs can easily take them into account.

Ostensibly the combination of a clock and A/D converter which are both capable of running at 100 kHz can acquire measurements spaced by 10-microsecond intervals. The fly in the ointment is that as these modules are configured by their manufacturers the CPU must arbitrate every clock-expiration and measurementinitiation transaction, tasks which it is clearly incapable of performing singly every ten microseconds, much less in tandem. Although the A/D converter has externally accessible trigger inputs which can initiate measurements without CPU intervention, the clock is somewhat less than ideal⁵⁰ in that it can neither make use of this feature nor in itself be triggered by an external event, such as the application of a potential step in chronoamperometry or chronocoulometry experiments. Modifications shown in Figure 4a enable the latter objection to be overcome, which enhances the overall timing accurancy. Making the clock's overflow/underflow signal CTFLW available to other circuits, coupled with the pulse-





stretching monostable (shown schematically in Figure 4b) on an external circuit board which can be connected to the clock-trigger input RTCTRG of the A/D converter, removes the former obstacle. Once these enhancements were included, 100-kHz data-acquisition rates were made possible.

ADDITIONAL MEASUREMENT ACCESSORIES

There are circumstances in which data rates even faster than this are required. Instruments are available with so-called "flash-encoder" A/D converters which can digitize voltages twenty or more times faster, usually with some sacrifice in converter resolution. The Biomation Model 820 transient recorder (Gould-Biomation Inc., Santa Clara, CA), an 8-bit, twenty-million samplesper-second waveform recorder, was used for some ultrahigh-speed measurements described in Chapters VI and VII. To take advantage of the digital form of its recorded data, an interface between the transient recorder and the DRV-11 parallel port was constructed (Figure 5). Commands to the transient recorder are distinguished from those to the D/A converter in two ways: data for the latter device must have bit 15 (MSB) set, whereas the "handshake" strobe line CMD (run by bit 0 of the command-status register of the DRV-11) must be turned on as a transient-recorder command is issued and turned off before the next command is sent. In this way, complete remote control of the transient recorder could be brought about. Time-critical, high-speed signals could be digitized 2048 times in as little as 100 microseconds and read into the computer in about 50 milliseconds, all without changing the voltage output by the D/A converter.

IN PIN		03010000000000000000000000000000000000
BIOMATIC NAME (NU	88888888888888888888888888888888888888	CMD FLG D01 003 CMD C00 C1 CH CH CH CH CH CH CH CH CH CH CH CH CH
BERG/3M CONNECTOR DESIGNATION	(3/C) (3/C) (3/K) (3/K) (3/K) (3/K) (3/K) (12/N) (14/R) (1	<pre>(K \ 9) (S \ 15) (S \ 15) (T T \ 38) (T T \ 38) (C T \ 32) (B B \ 24) (B B \ 24) (C T \ 32) (C T \ 29) (C T \ 20) (C T \ 20) (C</pre>
DRV-11 LINE	0UT00 0UT00 0UT001 0UT002 0UT003 0UT008 0UT008 0UT100 0UT110 0UT110	NNNNNN00 NNNNNN00 NNNNN00 N000490 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0

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Figure 5. Interface to Biomation transient recorder.

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One additional channel for timing or status information between experiment circuitry and the computer was set up with the remaining unused DRV-11 command-status register output bit CSR1 and input bit REQ A, shown in Figure 6. This interface was used to synchronize measurement sequences with an external event in a situation where the computer's cycle time or interrupt latency has an immeasurable effect on the accuracy of the experimental information. The most common application of this channel was to receive a trigger signal from a drop-fall detector or the modified driver for the drop-knocking solenoid.⁵¹ Measurements were not made until at least 50 milliseconds after the trigger (see Chapters VI and VII), which results in an inaccuracy that is only a fraction of a percent for the first point and substantially less thereafter. AN ILLUSTRATIVE EXAMPLE

A chief advantage of computer-controlled instrumentation is that once timing and measurement hardware has been suitably assembled, the control is in software. That is, a change in experimental technique can be brought about by the simple expedient of editing a program. Hardware-sequenced instruments, on the other hand, require changes in the control circuitry in order to become capable of measurements for which they were not originally designed. The ease with which a computer-controlled polarographic instrument can be adapted to perform the technique known as firstdrop polarography illustrates this point well.

Figure 7a shows a flow chart for a dc polarographic-measurement program, a technique available on many commercial instruments, albeit not with the same timing flexibility and data-management



Figure 6. Drop-fall trigger input.

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{Common to both a and b}



Figure 7. Flow charts for polarography. a) Conventional b) First-drop.

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capability provided by the computer. In the characterization of depletion effects in time-resolved polarography (see Chapter VII), it is necessary to determine to what extent the concentration polarization brought about by electrolysis at the previous drop has been alleviated by the stirring of the solution produced when the drop fell from the capillary. To do this, one must compare conventional measurements with those made under circumstances in which the concentration is distributed uniformly near the electrode. If one maintains the electrode potential throughout several drop lifetimes at a value where no electrode reaction occurs and, upon detection of the next drop fall, steps the potential to the measurement value, the concentration conditions will be satisfied. A flow chart to perform these "first-drop" measurements can be made from the conventional chart (Figure 7a) by interposing a step to return to the ideally polarized potential ESTART after the measurement has been completed and waiting several drop lifetimes before the next measurement. Figure 7b shows these small modifications; in this way, a technique which cannot be performed by conventional instruments has been made possible by minor changes in the dataacquisition software.

CHAPTER III. SYNCHRONIZATION OF NATURAL DROP-FALL EXPERIMENTS

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INTRODUCTION

There are many types of experiments performed with dropping mercury electrodes (DME) in which measurements must be made at times that are well defined relative to the birth of the drop. The simplest method for measurement synchronization is to dislodge the drop forcibly and simultaneously trigger a timing circuit. However, mechanical drop dislodgment may cause significant disturbance of polarographic diffusion profiles in the growing drop, particularly at subsecond current-sampling times.⁵² An alternative approach is to detect the birth of a new drop following natural gravitational drop fall. Such drop-fall detectors also enable natural drop times to be determined, providing a simple route to the interfacial tension.⁵³

We have been investigating dc polarographic current-time curves at short times (0.01-1 sec) following drop birth to evaluate rapid dc polarography^{52,54} as a method for monitoring the kinetics of electrode reactions.²⁸ For this purpose, as well as other applications where accurate knowledge of the drop time or electrode area is required, it desirable to detect the time of consecutive natural drop fall with millisecond accuracy and in a manner which is compatible with potentiostatic circuitry and automated data acquisition by a laboratory microcomputer.

Although a sizable number of detection techniques have been reported (for example, see citations in refs. 55 and 56), few fulfill the above criteria. Nearly all use either a superimposed ac voltage or light as probes, although an FM transmitter and receiver have been employed to exploit the behavior of a DME

as an antenna.⁵⁷ While the optical detectors⁵⁶ offer the advantage of requiring no electrical connection with the cell, they are subject to serious errors of up to 100 msec,²⁸ as will be shown below. A number of the ac devices described either are not compatible with conventional potentiostat-based instrumentation (e.g., ref. 58), have response times on the order of tens of milliseconds,⁵⁹ or continuously impose an undesirable ac perturbation on the cell and require remote activation and disabling because of limited noise immunity.⁵⁵ A recently reported techique⁶⁰ for making droptime measurements averaged over successive drops is simple in concept but requires adjustment as the cell current is changed, and in the vicinity of the potential of zero charge (pzc) it relies on stray impurity currents. Since these limitations render the previously described detectors inadequate for our purposes, we have developed a faster, more sensitive and versatile device which is described below.

AN EVALUTION OF OPTICAL DETECTION TECHNIQUES

We initially chose the optical method of Hahn and Enke⁵⁶ based upon its lack of interaction with the potentiostat circuitry and simplicity of implementation; Figure 8 presents a schematic diagram. The sudden change in light scattered up the capillary when the drop falls is converted to an electrical signal which is differentiated and amplified to provide a detector pulse which is compatible with transistor-transistor logic. Preliminary time-resolved dc polarographic measurements (see Chapter VII) produced rate constants which decreased monotonically as the sampling time increased and which were inconsistent with previously



Figure 8. Schematic diagram of optical drop-fall detector.

reported values.³² Efforts were undertaken to determine if systematic errors were introduced by any portion of the measurement system.

Upon closer scrutiny it was found that the signal produced by the drop-fall detector occurred no less than 80 msec following the fall of the drop. What appeared to be the source of the delay was that the original designers did not reckon with the inversion produced in the comparator stage of the level shifter (amplifier A4 in Figure 2 of ref. 56). The desired negativegoing logic transition occurred only as the result of noise in the differentiator output on the trailing edge of its output spike. Once this level-inversion discrepancy was rectified, however, a nonreproducible 20 msec delay remained. Since one of our design goals was the capability to sample currents after 50 msec, this performance remained unacceptable.

To meet this goal, it is necessary that the detector error be less than 1 msec. For it to be capable of this, however, it must have preferential frequency response in the 1-10 kHz region. Examination of the original passive components of the differentiator⁵⁶ showed that they limit frequency response to between 0.16 and 3 kHz (unity-gain limits), with maximum gain at 22.5 Hz and gain in excess of 10 at the archetypal noise frequencies 60 and 120 Hz. Even with more appropriate passive components, however, insufficient signal amplitude was present in the necessary frequency range; efforts to remove sources of stray light by optical shielding and to increase the gain of the amplification stage proved equally unsuccessful. Because the light is attenuated appreciably by the fiber optic system, even with the recommended

polishing of the capillary groove and fiber optic ends, we tried attaching a more sensitive photodarlington transistor (2N5777) directly to the capillary groove with the die facing the Hg drop. The buffer amplifier in the detector was replaced by a currentto-voltage converter (10 μ A/V); the a-c component of a typical differentiated output is shown in Figure 9. While the signalto-noise ratio would undoubtedly be increased if the currentto-voltage conversion were preformed directly at the phototransistor, the necessary mounting considerations vitiate such an undertaking. Furthermore, inspection of Figure 9 will reveal that the rise time of the differentiator spike produced by the fall of the drop is approximately 20 msec. This result is not surprising in view of the fact that the drop continues to reflect light after detachment until it falls below the light path, and a 20 msec delay corresponds to the time required for a 2 mm displacement of a freely falling object.

The inevitable conclusion is that the optical detection system is inappropriate for this or any other application where inaccuracies of 20 msec cannot be tolerated. It is still useful in systems such as its original utilization⁵⁶ where a precise albeit inaccurate time delay following the birth of the drop is all that is required.

A HIGH-SPEED ELECTROCHEMICAL DETECTOR

Successful performance was obtained from an alternating-current electrochemical detector. Operation of the detector can be understood with reference to the block diagram (Figure 10) and schematic (Figure 11). Late in the drop life, the monostable which produces the delay for measurement of the dc current (D) returns to its



Figure 9. Differentiated current from photodarlington transistor.



Figure 10. Block diagram of ac drop-fall detector.



stable state and closes the analog switch. An ac perturbation of 10 mV peak-to-peak at 100 kHz is imposed on the cell, and the resulting ac component of the cell current is detected by a tuned amplifier (A). When the electrode area is large enough so that the magnitude of the ac current exceeds the threshold selected by the potentiometer, the logic-level output of the level detector (B) will change states at the frequency of the ac source and activate the missing-pulse detector after a delay to allow for switching transients. The precipitous decrease in electrode area concomitant with drop fall causes the tuned amplifier output to remain below the threshold throughout several ac cycles, long enough for detection of the missing transitions in the level-detector output. Within 100 to 200 μ sec of the fall of the drop, the ac source is disconnected from the potentiostat so that dc measurements can be made. The missing-pulse detector input is inhibited by the gate (C) to prevent noise transients from retriggering the detector, and a signal is sent to the currentsampling circuitry.

The time interval between the fall of the drop and its detection is due to three causes. First, at potentials away from the pzc, the potentiostat must supply charging current to the nascent drop. The resultant current spike (typically 50 μ sec) contains frequency components which can be detected by the tuned amplifier and which may keep the amplifier output above the level-detector threshold for a brief time after the drop has fallen. Second, the tuned amplifier must respond to the sudden change at its input with a deliberately constrained frequency response. Several

periods of oscillation at the center frequency are required to accomplish this. Third, a full period (15 to 20 µsec) of the missing-pulse detection monostable must elapse between the last output transition of the level detector and the production of the trigger signal for the current-sampling circuitry. Finally, noise in the current-to-voltage converter whose power spectrum overlaps the frequency range of the tuned amplifier can delay detection of drop-fall a few additional ac cycles.

The drop-fall detector operates reliably even in noisy environments provided the potentiostat employed has sufficient response at the frequency of the ac perturbation. Although we have chosen a frequency of 100 kHz, the detector is suitable for slower potentiostats providing that a lower frequency is selected, albeit with some lengthening in drop-detection time. This modification needs to be performed only once and is accomplished by varying the passive components in the twin-T networks around amplifiers A1 and $A4^{61}$ and the timing capacitor on MS1. A single selection of the suitable gain (two are available) for the tuned amplifier and of a threshold level appropriate to the current-to-voltage converter setting, to the electrode capacitance, and to the cell resistance generally suffices over a wide potential range (2V or more) for a given set of cell conditions. Since no further adjustments are required, this circuit is very useful as a trigger device for automated instruments, especially those under the control of a laboratory computer. The circuit's independent nature allows the computer to perform lower priority tasks between measurements, instead of requiring that the processor continually

monitor portions of the detection circuitry in order to discern drop fall.⁵⁵

The features of the detector include the temporary disconnection of the self-contained oscillator from the potentiostat by means of an analog switch as soon as drop fall has been detected, which eliminates the need for filtering. A single adjustment generally suffices for a wide range of potentials, and the operation of the detector is unaffected by the presence of the pzc within that range. The response time, between 100 and 200 μ sec is dictated by electrochemical cell characteristics, the frequency of the ac perturbation, and the time window of the missing-pulse detector. Unfavorable cell conditions are those in which large faradaic and nonfaradaic components are present so that the output of the tuned amplifier remains substantial even after the drop has fallen. Such circumstances are encountered, for example, with a solution of 1 mM Cr^{3+} in 1 M NaClO_L(pH 3) at an electrode potential of -1100 mV. vs. SCE where the diffusion-controlled reduction of Cr^{3+} occurs, and the excess electrode charge density is large and negative (ca. -13 μ C cm⁻²).³² The response time was assessed by observing the current-to-voltage converter output on a Biomation Model 820 transient recorder in the pretrigger mode. Detection was considered to have occurred when sinusoidal variations at 100 kHz could no longer be distinguished in the cell current. Thirty determinations yielded an average detection time of 185 μ sec with a standard deviation of 36 usec. Measurements at the growing mercury drop are essentially unaffected by the ac perturbation since it is automatically disconnected within this time scale.

Either individual or successive natural drop times can be conveniently determined to this accuracy, so that current-time curves may be monitored even at subsecond sampling times with high accuracy. In addition to its use as a synchronization device for rapid dc polarography (see ref. 28 for details) and determinations of the excess electrode-charge density from charge-time curves⁶², we have also found it to be highly suitable for obtaining precise surface-tension data from drop-time measurements⁶⁰.

CHAPTER IV. FURTHER OBSERVATIONS ON THE DEPENDENCE OF THE ELECTROCHEMICAL TRANSFER COEFFICIENT UPON THE ELECTRODE POTENTIAL

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INTRODUCTION

A considerable amount of effort has been devoted to providing experimental tests of the prediction of contemporary theories of electron transfer 10,63 that the electrochemical transfer coefficient α for outer-sphere electrode reactions should depend upon the elctrode potential. 14,64-73 It turns out that stringent tests are relatively difficult to design since the predicted dependences are usually small, and the measured (apparent) transfer coefficient α will generally differ from the required "intrinsic" transfer coefficient⁷⁴ α_1 as a result of the influence of the interphasial environment ("double-layer" effects). Thus α is often observed to vary markedly with electrode potential as a result of ionic double-layer effects, and the uncertainties in the required corrections are frequently larger than the residual predicted variations in α_1 . This difficulty is most acute for multicharged reactants and for reactions monitored at solid electrode surfaces where there are considerable uncertainties in the double-layer composition. However, persuasive evidence for a variation of α in approximate accordance with the theoretical predictions¹ has been observed for the electroreduction of tert - nitrobutane and other organic nitro compounds in acetonitrile and dimethylformamide at mercury and platinum electrodes. 70,73 On the other hand, the electroreductions of $Cr(0H_2)_5 0S0_3^+$, $Cr(0H_2)_5 F^{2+}$, and $Cr(OH_2)_{K}^{3+}$ at the mercury-aqueous interface exhibit transfer coefficients both before and after double-layer corrections that are essentially constant over a wide range of electrode potentials, under conditions

where noticeable variations in $\,\,\alpha$ are predicted by the theoretical models. 14

In view of these disparate sets of results, it seems desirable to examine a wider range of inorganic systems at anodic as well as cathodic overpotentials in order to check the generality of the latter behavior. Despite their large charges, redox couples of the type $M_{aq}^{3+/2+}$ (where M is a transition metal and "aq" represents aquo ligands) provide useful model systems for this purpose. Thus a number of such couples, particularly $Cr_{aq}^{3+/2+}$, $Eu_{aq}^{3+/2+}$, $V_{aq}^{3+/2+}$, and $Fe_{aq}^{3+/2+}$, can be studied that exhibit widely varying formal potentials and yet are of similar size and structure so that the nature of the ion-solvent interactions, ¹¹ and therefore the solvent-reorganization process, should be similar in each case. Also, these couples exhibit relatively small heterogeneous electron-transfer rates so that measurements of α_{app} can be made over wide ranges of both cathodic and anodic overpotentials. An obvious difficulty faced with these systems is that the doublelayer corrections upon α_{add} are usually significant. These corrections are smallest and can be aplied with the greatest confidence for supporting electrolytes at high ionic strengths in the absence of specific ionic adsorption. 14,32 The reduction of Cr_{aq}^{3+} and Eu_{aq}^{3+} can be monitored at negative potentials at mercury electrodes where noncomplexing anions such as perchlorate are not significantly specifically adsorbed.³² However, the oxidations of Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} proceed at potentials positive of <u>ca</u>. -500 mV. vs. s.c.e. where most anions, including perchlorate, are strongly adsorbed. The required double-layer corrections

upon α_{app} can involve sizable uncertainties under these conditions as a result of the discrete nature of the specifically adsorbed anionic charge and its tendency to induce ligand-bridged reaction pathways.^{7,75} Therefore it is desirable to search for anions that are only weakly specifically adsorbed at potentials positive of the point of zero charge (p.z.c.) and which do not significantly complex with the cationic reactants. Suitable electrolytes are sparse. Although fluoride and hydroxide anions exhibit the smallest tendency to be specifically adsorbed at mercury,^{76,77} they both strongly complex aquo cations. However, hexafluorophosphate(V) anions have even less complexing ability than perchlorate⁷⁸ and yet are only weakly specifically adsorbed at potentials positive of the p.z.c. even in concentrated solutions.⁷⁹ Consequently, -q' ~ q^m, where q' and q^m are the specifically adsorbed and excess electronic charge densities, respectively.^{22,79,80}

In the present chapter, we report rate constants for the oxidation of Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} in KPF₆ and NaClO₄ supporting electrolytes at the mercury-aqueous interface over a wide range of electrode potentials (ca. -600 mV to +200 mV vs. s.c.e.) using normal pulse and d.c. polarography. Rate-potential data for the corresponding electroreduction reactions are also given. In addition, it was found that the electroreduction of Fe_{aq}^{3+} could be monitored in KPF₆ media at mercury electrodes. Taken together, these results strongly suggest that substantial decreases in the intrinsic transfer coefficient α_1 occur for aquo electrooxidation reactions with increasing anodic overpotentials. They also lead to a reinterpretation of the apparent failures of the Frumkin model in describing double-layer effects upon the electrooxidation of Eu_{aq}^{2+} and V_{aq}^{2+} which were reported recently.^{81,82}

EXPERIMENTAL

Stock solutions of Cr_{aq}^{3+} were prepared essentially as described in Ref. 32; Eu_{aq}^{3+} was made by dissolving Eu_2^{0} in a slight excess of either HC10₄ or HPF₆. Solutions of Cr_{aq}^{2+} , Eu_{aq}^{2+} , or V_{aq}^{2+} were prepared by exhaustive electrolyses of Cr_{ag}^{3+} , Eu_{ag}^{3+} , or $V0_2^+$ in the appropriate electrolyte at ca. -900 mV, -1000 mV, or -1100 mV vs. s.c.e., respectively, using a stirred mercury-pool cathode; V_{aq}^{3+} was obtained by reoxidation of V_{aq}^{2+} at -300 mV. Their electrode kinetics were examined immediately after preparation in the electrolysis cell to minimize reoxidation by trace impurities such as oxygen. The source of Fe_{aq}^{3+} was $Fe(C10_4)_3$ (G.F. Smith Co.). The supporting electrolytes contained sufficient concentrations of the appropriate acid, usually 5-10 mM, to suppress hydrolysis of the aquo reactants. Stock solutions of HPF₆ were prepared by adding concentrated $HC10_4$ to saturated (0.5 <u>M</u>) solutions of KPF_6 , cooling to 0°C and filtering off the KCl0₄. They were kept frozen prior to use to avoid any significant hydrolysis of $PF_{L}^{-,83}$ Sodium perchlorate, prepared from sodium carbonate and perchloric acid, and potassium hexafluorophosphate (Alfa Ventron Corp.) were recrystallized twice from water. The absence of significant amounts of F^{-} in PF_{6}^{-} solutions was confirmed using a fluoride-ion selective electrode (Orion Model 94-09A). Solutions were prepared using water purified by double distillation from alkaline permanganate followed by "pyrodistillation"¹¹ in order to remove trace organic impurities. All solutions were deoxygenated by bubbling with prepurified nitrogen, from which residual traces of oxygen were removed by passing through a column packed with B.A.S.F. R3-11 catalyst (Chemical Dynamics Corp. South Plainfield, N.J.) heated to 140° C. The electrolysis cell consisted of a working compartment of volume <u>ca</u>. 5-10 ml. which was separated from compartments containing the calomel reference and platinumwire counter electrodes by one and two glass frits, respectively ("very fine" grade Corning, Inc.). The working compartment was surrounded by a jacket through which was circulated water from a thermostat.

Normal pulse and d.c. polarograms were recorded at a dropping mercury electrode (flow rate 1.8 mg/sec) using a PAR 174A Polarographic Analyzer coupled with a Hewlett-Packard 7045A X-Y recorder. The kinetic analyses of these polarograms employed the methods due to Oldham and Parry.⁸⁴ Back-reaction corrections were applied where necessary as outlined in Ref. 32. All potentials are reported with respect to the saturated (KCl) calomel electrode (s.c.e.), and all kinetic parameters were obtained at 25.0 \pm 0.1^oC, unless otherwise stated.

RESULTS AND DATA ANALYSES

Figures 12-14 consist of typical rate data obtained for the oxidation of Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} in KPF₆ and NaClO₄ electrolytes at the mercury-aqueous interface expressed as (Tafel) plots of the logarithm of the observed (apparent) anodic rate constant log k_{app}^{a} ¹⁸ versus the electrode potential E. Apparent anodic



Figure 12. Rate-potential plots for the one-electron oxidation of Cr_{aq}^{2+} in KPF₆, NaClO₄, and KCl electrolytes at the mercury-aqueous interface. Key to symbols: 0.4 <u>M</u> KPF₆ (•); 0.1 <u>M</u> KPF₆ (•); 1 <u>M</u> NaClO₄ (Δ); 0.4 <u>M</u> NaClO₄ (\circ); 0.1 <u>M</u> NaClO₄ (\Box); 0.1 <u>M</u> KCl (\times).



Figure 13. Rate-potential plots for the one-electron oxidation of Eu_{aq}^{2+} in KPF₆, NaClO₄, and KCl electrolytes at the mercury-aqueous interface. Key to symbols: 0.4 M KPF₆ (\bullet); 0.1 M KPF₆ (\bullet); 1 M NaClO₄ (Δ); 0.4 M NaClO₄ (\circ); 0.1 M NaClO₄ (\Box); 0.1 M KCl (\times).



Figure 14. Rate-potential plots for the one-electron oxidation of V_{aq}^{2+} in KPF₆, NaClO₄, and KCl electrolytes at the mercury-aqueous interface. Key to symbols: 0.4 <u>M</u> KPF₆ (•); 0.1 <u>M</u> KPF₆ (•); 1 <u>M</u> NaClO₄ (Δ); 0.4 <u>M</u> NaClO₄ (\circ); 0.1 <u>M</u> NaClO₄ (\Box); 0.1 <u>M</u> KCl (\times). transfer coefficients α^a can be obtained from these plots using

$$\alpha_{app}^{a} = (2.303/f)(\partial \log k_{app}^{a} / \partial E)_{\mu}$$
 (5)

where μ is the ionic strength of the supporting electrolyte, and f = F/RT. Figures 12-14 exhibit two interesting features. Firstly, in KPF₆ electrolytes, values of α^a_{app} were obtained for Cr²⁺_{aq} and Eu²⁺_{aq} oxidation that markedly decrease with increasing anodic overpotential. Secondly, α^a_{app} is noticeably larger in NaClO₄ than in KPF₆ electrolytes so that k_{app} is markedly larger at higher anodic overpotentials in the former electrolyte. Values of α^a_{app} as a function of electrode potential in 0.4 <u>M</u> KPF₆ and 0.4 <u>M</u> NaClO₄ are summarized in Table 1. In order to obtain α^a_{app} over as wide a potential range as possible, values at potentials that are significantly more negative than the formal potentials E_f for Cr²⁺_{aq}, Eu²⁺_{aq}, and V²⁺_{aq} (-660 mV., -625 mV., and -475 mV., respectively¹⁵) were obtained from the slopes of the corresponding cathodic Tafel plots using

$$\begin{pmatrix} \alpha^{a} \\ app \end{pmatrix} = 1 - \begin{pmatrix} \alpha^{c} \\ app \end{pmatrix} E$$
 (6)

where α_{app}^{c} is the cathodic apparent transfer coefficient, equal to -(2.303/f)($\partial \log k_{app}^{c} / \partial E$) at the same electrode potential E. Eqn(6) follows from the Principle of Microscopic Reversibility. It is seen from Table 1 that α_{app}^{a} varies from about 0.35 to about 0.15 for Cr_{aq}^{2+} and Eu_{aq}^{2+} oxidation over the 900-1000 mV. observable potential ranges in 0.4 <u>M</u> KPF₆.

It is desired to extract from these results estimates of rate constants k_{corr} and transfer coefficients α_{corr} that are

Table 1.	Apparent	anodic	transfer	coefficien	ts α ^a app	for	Cr ²⁺ aq,	Eu ²⁺ aq,
	and V ²⁺	oxidati	ion as a	function of	electro	de po	otentia	al.

Electrolyte	E		a app	
	mV vs s.c.e.	Cr ²⁺ oxid [_]	Eu ²⁺ oxid ⁿ	V ²⁺ oxid ⁿ aq
	-900	0.38		
0.4 <u>m</u> KPF ₆	-800	0.38	0.33	
	-700	0.37	0.31	
	-600		0.24	0.34
	-500	0.24	0.19	0.33
	-400	0.19	0.18	0.30
	-300	0.18	0.17	0.24
	-200	0.175	0.15	0.21
	-100	0.175	0.14	
	0	0.175	0.135	
	+100	0.17		
0.4 <u>M</u> NaC10 ₄	-900	0.37		
	-700	0.37	0.35	
	-600		0.34	
	-500	0.34	0.34	0.42
	-400	0.32	0.31	0.38
	-300	0.29	0.26	
	-200	0.27		
	-100	0.25		

.

corrected for the influence of the ionic double layer. The relation between k_{corr}^{E} and k_{app}^{E} at a given electrode potential E can be written for one-electron reactions as (cf. Ref. 22)

$$\log k_{\text{corr}}^{\text{E}} = \log k_{\text{app}}^{\text{E}} - (f/2.303)(\alpha_{\text{corr}} \pm Z_r) \phi_{\text{rp}}$$
(7)

where Z_r is the reactant charge, ϕ_{rp} is the average potential on the reaction plane, and α_{corr} equals $\pm (2.303/f)(\partial \log k_{corr}/\partial E)_{\mu}$. The plus and minus signs in the second term of eqn (7) and in subsequent relations are appropriate to electrooxidation and electroreduction reactions, respectively. (Although α_{corr} is normally identified with α_1 , we shall distinguish between these quantities here in anticipation of other possible environmental influences upon α_{app} to be considered below.) The corresponding relation between α_{corr} and α_{app} can be obtained from eqn (7):

$$\alpha_{corr} = \frac{\alpha_{app} + Z(\partial \phi_{rp}/\partial E)_{\mu}}{1 - (\partial \phi_{rp}/\partial E)_{\mu}}$$
(8)

Although the application of eqn (7) and (8) is most straightforward in the absence of specific ionic adsorption, it turns out that reliable estimates of the required double-layer corrections in the presence of moderate amounts of PF_6^- and $C10_4^-$ specific adsorption can be ascertained in the following manner.

The simplest way of applying eqns (7) and (8) is to assume that $\phi_{rp} = \phi_d^{GCS}$ where ϕ_d^{GCS} is the diffuse-layer potential that is calculated from double-layer compositional data using the Gouy-Chapman-Stern (GCS) model.²⁹ However, for the reduction of Cr_{aq}^{3+} and Eu_{aq}^{3+} in NaClO₄ electrolytes at negative potentials (-E > 750 mV) where perchlorate specific adsorption is negligible,
it appears that $\phi_{rp} \approx 0.6 \phi_d^{GCS}$, at least for ionic strengths in the range $\mu = 0.3-1 \ \underline{M}$.¹⁶ The rate responses obtained upon the addition of specifically adsorbing halide anions at a constant ionic strength of 1 \underline{M} again yielded $\Delta \phi_{rp} \approx 0.6 \ \Delta \phi_d^{GCS}$, indicating that such discrete adsorbed charge q' has an effect similar to the electrode charge q^m itself.⁷⁵

On the other hand, it has been argued that specifically adsorbed perchlorate charge exerts a substantially smaller effect than the electrode charge upon the rates of Eu_{ac}^{2+} oxidation.⁸¹ If correct, this latter finding would severely complicate the application of double-layer corrections to kinetic data gathered in electrolytes containing PF_6^- as well as $C10_4^-$ in view of the structural similarity of these anions. However, the kinetic data in Figures 12-14 strongly indicate that the analysis employed in Ref. 81 is incorrect, as will now be demonstrated. By integrating the capacitance data for KPF_6 and HClO_4 electrolytes given in Refs. 79 and 85, the q^m -E curves for these two electrolytes at a given ionic strength were found to be closely similar. (Suitable data in $NaClO_{\underline{L}}$ electrolytes are unavailable.) Consequently, the large differences in log k_{app}^{E} observed for Eu_{aq}^{2+} oxidation between KPF₆ and NaClO₄ electrolytes at 0.1 and 0.4 \underline{M} ionic strengths (Figure 13) must be due to the greater specific adsorption of $C10_{4}^{-}$ compared with PF_{6}^{-} . It is convenient³³ to compute the difference in the potential at the reaction plane at a given electrode potential, $\Delta \phi = \frac{E}{rp}$, from the corresponding rate difference ($\Delta \log k_{app}$) for a pair of electrolytes using (cf. eqn (7)):

$$(\Delta \log k_{app})_{E} = -(f.2.303)(\alpha_{corr} + Z_{r}) \Delta \phi_{rp}$$
(9)

Table 2 summarizes some values of $\Delta \phi_{rD}$ for Eu²⁺_{a0}, Cr²⁺_{a0}, and V_{ac}^{2+} oxidation for pairs of KPF₆ and NaClO₄ electrolytes obtained from the data given in Figures 12-14 using eqn (9) and assuming that $\alpha_{corr} = 0.5$. (Although, as shown below, it is very likely that α^a < 0.5 for these reactions, such a choice has little effect on the resulting estimates of $\Delta \phi_{rp}$.) For comparison, the corresponding values of $\Delta \phi_{rp}$ are also given for the reduction of $Co(NH_3)_5 F^{2+}$, which were extracted from the rate data given in Ref. 22. This reaction was chosen because it has been shown to yield values of ϕ_{rp} in a range of supporting electrolytes, including KPF_{6} and $NaClO_{4}$, that are consistently close to the corresponding values of ϕ_d^{GCS} .²⁴ Inspection of Table 2 reveals that the values of - $\Delta \phi$ for Eu_{aq}²⁺ oxidation induced by replacing KPF_6 with $NaClO_4$ are almost as large as those for $Co(NH_3)_5 F^{2+}$ reduction. Also, it is interesting to note that a similar result holds for the replacement of 0.1 \underline{M} KPF₆ by 0.1 \underline{M} KCl (Table 2). The corresponding values of $\Delta \phi$ for the oxidation of Cr_{aq}^{2+} and V_{aq}^{2+} obtained from the kinetic data in Figures 12 and 14, respectively, are also given in Table 2. (Outer-sphere Cr_{aq}^{2+} oxidation cannot be studied in chloride electrolytes due to the presence of a more facile, chloride-bridged pathway⁷.) Somewhat smaller values of $\Delta \phi_{rp}$ for V_{aq}^{2+} and particularly Cr_{aq}^{2+} exidation are obtained in comparison with those for Eu_{aq}^{2+} oxidation. These variations may be due to differences in the plane of closest approach resulting from differences in the effective hydrated radii r_h of these cations.³³ Since the ionic radii increase in the sequence $Cr^{2+} < V^{2+} < Eu^{2+}^{32}$, r_b should increase in

Table 2. The effects of v plane ϕ_{rp} for (varying the elec Cr ²⁺ , Eu ²⁺ , and	ctrolyte compositic V ²⁺ oxidation and	m upon the avera Co(NH ₃) ₅ F ²⁺ redu	ge potential at ction, obtained	the reaction using eqn (5).
			- ∆¢ <mark>,1m</mark> V		
Electrolytes	ų	Cr ²⁺ oxid ^D	Eu ²⁺ oxid ⁿ	V ²⁺ oxid ⁿ	co(NH ₃) ₅ F ²⁺
	mV vs s.c.e.	-			1
0.1 <u>m</u> KPF ₆ /0.1 <u>m</u> Nacio ₄	200	16	27		33
	300	11.5	23		29
	4:00	7	16		≃ 2 4
0.4 <u>m</u> KPF ₆ /0.4 <u>m</u> Nacio ₄	200	18	25.5	19	25
•	300	14	21	16.5	22.5
	400	8.5	16	15.5	16
0.1 <u>M</u> KPF ₆ /1 <u>M</u> NaClO ₄	200	22	35	28	39.5
	300	15	29	24.5	33.5
	400	7	20	17	≃ 20
0.1 <u>m</u> KPF ₆ /0.1 <u>m</u> KCI	300		40		35
¹ Change in the average pote	ential at the re	saction plane at g	iven electrode po	tential brought	about by changing
the supporting electrolyte	from KPF ₆ to Na	aclo ₄ or KCl, as gi	iven in the far l	eft-hand column.	Obtained from
changes in log k _{app} at fix	ed electrode pot	tential using eqn ((9), assuming tha	t α _{corr} = 0.5 (see text). Rate
parameters for Cr ²⁺ , Eu ²⁺ ,	V ²⁺ oxidation 1	taken from Figures	12-14; for Co(NH	3)5 ^{F2+} reduction	n taken from
Figures 1, 2, & 4 in ref.	22.				

the sequence $\operatorname{Eu}_{aq}^{2+} < \operatorname{V}_{aq}^{2+} < \operatorname{Cr}_{aq}^{2+\frac{33}{aq}}$ so that $\operatorname{Eu}_{aq}^{2+}$ should be able to react closest to the electrode, yielding the largest values of $\Delta \phi_{rp}^{33}$. (Smaller, yet compatible differences in the rate responses to anion adsorption were also seen for $\operatorname{Eu}_{aq}^{3+}$ versus $\operatorname{Cr}_{aq}^{3+}$ reduction.⁷⁵)

It therefore appears to be very likely that the earlier assertion⁸¹ that adsorbed ClO_{4}^{-} induces anomalously small changes in ϕ_{rp} for Eu²⁺_{aq} oxidation is incorrect. The analysis employed in Ref. 81 consisted of comparing the experimental plots of log k_{app} versus E for Eu²⁺_{aq} oxidation with an estimate of the "double-layer corrected" plot of log k_{corr} versus E to obtain ϕ_{rp} using eqn (7). The latter plot was obtained by extrapolating rate data from markedly more negative potentials, where ClO_{4}^{-} is not adsorbed, by assuming that $\alpha_{corr} = 0.5$.⁸¹ The validity of this procedure relies critically upon the correctness of this assumption. Although α_{corr}^{c} was found to be close to 0.50 for Eu³⁺_{aq} reduction over the potential range -700 to -900 mV,³² any changes in α_{corr} at more positive potentials can lead to substantial errors in these estimates of log k_{corr} and therefore in the derived values of ϕ_{rn} using eqn (7).

Indeed, the values of α_{app}^{a} in KPF₆ electrolytes (Table 1) provide strong evidence that $\alpha_{corr}^{a} < 0.5$ for Eu_{aq}^{2+} and Cr_{aq}^{2+} oxidation over a wide range of anodic overpotentials. An extreme upper limit to α_{corr}^{a} under these conditions can be obtained by ignoring the effect of PF₆ specific adsorption. In the absence of specific ionic adsorption, the term $(\frac{\partial \phi}{rp}/\partial E)_{\mu}$ appearing in eqn (8) is equal to C_{dl}/C_{diff} , where C_{dl} and C_{diff} are the overall double-layer and diffuse-layer capacitances, respectively. For concentrated solutions of symmetrical electrolytes such as KPF₆, C_{diff} is calculated to be only weakly dependent upon the absolute value of q^m and independent of its sign.⁸⁸ Therefore the magnitude of ($\partial \phi_{rp} / \partial E$), should be approximately the same at a pair of electrode potentials on either side of the p.z.c. having similar values of $|q^m|$ and C_{d1} . By inspecting the published double-layer data,⁷⁹ such a circumstance is seen to be encountered for 0.4 <u>M</u> KPF₆ for E \simeq -200 mV and -700 mV vs. s.c.e. (where $|q^{m}|$ is approximately 6 μ C/cm² and C_{d1} \simeq 22 and 20 μ F/cm², respectively). However, PF_6^- is significantly adsorbed at -200 mV but not at -700 mV, 79 so that any effect of PF₆ adsorption will make ($\partial \phi_{rp} / \partial E$) smaller at -200 mV. At these two electrode potentials, α_{app}^{a} for Eu_{aq}²⁺ oxidation equals 0.15 and 0.31, respectively (Table 1). Since $\alpha_{corr}^{C} \simeq 0.50$ and therefore $\alpha_{corr}^{a} \simeq 0.50$ at E = -700 mV³² (eqn (6)), we conclude from eqn (8) that $\alpha \frac{a}{corr} < 0.35$ at -200 mV. Consequently it appears that the small values of α_{ann}^{a} seen for Eu_{an}²⁺ oxidation in KPF₆ at anodic overpotentials must be due to values of α^{a}_{corr} that are also well below 0.5. This finding leads to estimates of log k_{corr}^{a} for Eu_{ag}^{2+} oxidation, obtained by extrapolation from more negative potentials, that are markedly smaller than those given in Ref. 81, yielding estimates of $\phi_{\mbox{rn}}$ in perchlorate and chloride electrolytes that are much closer to the corresponding values of ϕ_d^{GCS} .

In view of these results and those presented in Table 2, it appears that semiquantitative estimates of log k_{corr}^{a} and α_{corr}^{a} can be obtained by using eqns (7) and (8), ϕ_{rp} being obtained

in the conventional manner from the net diffuse-layer charge density -(q_m + q'). Figure 15 contains plots of ϕ_d^{GCS} versus E in 0.1 and 0.4 \underline{M} KPF₆ which were obtained from the corresponding plots of $(q^m + q_{PF_c}^{\dagger})$ versus E derived from the double-layer data given in Ref. 79. It is seen that for 0.4 <u>M</u> KPF₆, $|\phi_d^{GCS}| < 5 \text{ mV}$ when -E < 450 mV. This is because $q'_{PF_{L}} \simeq -q^{m}$ at electrode potentials positive of the p.z.c.⁷⁹ In view of the relative values of $\Delta \phi_{rp}$ for Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} oxidation and $Co(NH_3)_5 F^{2+}$ reduction given in Table 2, together with the consistently good agreement between ϕ_{rp} and ϕ_{d}^{GCS} seen for the last reaction,²² rough estimates of ϕ_{rp} and hence $(\partial \phi_{rp} / \partial E)$ for Cr_{aq}^{2+} , Eu_{aq}^{2+} , and $V_{a\alpha}^{2+}$ oxidation in 0.4 <u>M</u> KPF₆ were obtained by assuming that ϕ_{rp} equals 0.6 ϕ_{d}^{GCS} , 0.9 ϕ_{d}^{GCS} , and 0.8 ϕ_{d}^{GCS} , respectively. The resulting estimates of ($\partial \phi_{rp} / \partial E$) μ were then inserted into eqn (8) along with the values of αa_{ADD}^{a} obtained in 0.4 <u>M</u> KPF₆ (Table 1) to yield the estimates of $\alpha \frac{a}{corr}$ given in Table 3. (Although this procedure is subject to sizable uncertainties, these are unlikely to affect greatly the derived values of α^{a} corr for -E < 450 mV since the double-layer corrections are quite small under those conditions.) Similar estimates of α^{a} were obtained from the values of α^{a}_{app} obtained in 0.1 <u>M</u> KPF₆, and also in $NaClO_{k}$ electrolytes using the published double-layer data for $HC10_L$.⁸⁸ However, the double-layer corrections are larger and more uncertain in perchlorate media as a result of the substantially greater specific adsorption of $C10_4^-$.

Inspection of Table 3 reveals that indeed α^{a}_{corr} for Cr^{2+}_{aq} and Eu²⁺_{aq} oxidation decreases markedly as the electrode potential



Figure 15. Plots of the potential across the diffuse-layer $\phi \frac{GCS}{d}$ against the electrode potential E for 0.4 <u>M</u> and 0.1 <u>M</u> KPF₆. Key to symbols: 0.4 <u>M</u> (\bullet), 0.1 <u>M</u> (\bullet)

CO	efficients (α ⁻) _{ca}	ilc calculate	ed from the hai	monic oscil	lator model.		
ш	$\frac{\partial \phi_{d}^{GCS}}{\partial E}$	Cr ²⁺ o	k i dat i on	Eu ²⁺ ox	ki dat i on	V ²⁺ ox i	dat i on
mV vs s.c.e.		α ^a 2 corr	s (α <mark>a</mark>) _{calc}	α ^a 2 corr	s (α ^a) _{calc}	α ^a 2 corr (ς α ^a) l calc
-900	0.080	0.50	0.55 ₅				
-800	0.085	0.50	0.53 ₅	0.52	0.54 ₅		
-700	0.10	0.52	0.51	0.54	0.52		
-600	0.115			0.49		0.57	0.54
-500	0.12	0,40	0.46 ₅	0.47	0.47	0.57	0.51
-400	0.075	0.29	0.44	0.34	0.44	0.45	0.48
-300	0.025	0.21	0.42	0.22	0.41 ₅	0.29	0.44 ₅
-200	0.02	0.20	0.39 ₅	0.20	0.39	0.24	0.41 ⁵
-100	0.02	0.20	0.37	0.18	0.36 ₅		n
0	0.015	0.20	0.35	0.17	0.34		
100	0.015	0.19	0.32 ₅		0.31		

Double-layer corrected anodic transfer coefficients α_{corr}^a for Cr_{aq}^2 , Eu_{aq}^{2+} , and V_{aq}^{2+} oxidation as a function of electrode potential, compared with the corresponding intrinsic transfer • ł u u -. à . Table 3.

Notes for Table 3.

¹Variation of diffuse-layer potential ϕ_d^{GCS} with electrode potential E in 0.4 <u>M</u> KPF₆, obtained from slopes of plot in Figure 15.

²Anodic transfer coefficient at stated value of E, corrected for the effect of the ionic double layer. Obtained from values of α_{app}^{a} in 0.4 <u>M</u> KPF₆ given in Table 1 from eqn (8) using the listed values of ($\partial \phi \frac{GCS}{d} / \partial E)_{\mu}$, assuming that $(\partial \phi_{rp} / \partial E)_{\mu}$ equals x($\partial \phi \frac{GCS}{d} / \partial E)_{\mu}$, where x = 0.6, 0.9, and 0.8 for Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} oxidation, respectively (see text).

³Intrinsic anodic transfer coefficient, calculated using eqns (11) and (12) (see text).

E becomes less negative so that $\alpha_{corr}^{a} < 0.2$ for -E < 300 mV. These data are also presented as plots of log k_{corr}^{a} versus E in Figures 16-18, which were obtained by inserting the appropriate estimates of ϕ_{rp} together with log k_{app}^{a} in 0.4 <u>M</u> KPF₆ from Figures 12 and 14 into eqn (7). The corresponding cathodic segments log k_{corr}^{c} versus E that were obtained from measurements of k_{app}^{c} in 0.4 <u>M</u> KPF₆ are also included in Figures 16-18.

Although the large positive formal potential for $Fe_{aq}^{3+/2+}$ (+500 mV at an ionic strength of 0.2¹¹) precludes monitoring the kinetics of Fe_{aq}^{2+} oxidation at mercury electrodes, it turns out that the kinetics of Fe_{aq}^{3+} reduction in KPF₆ electrolytes are sufficiently slow so that pulse polarography can be used to obtain cathodic Tafel plots in the potential range <u>ca</u>. 300 to 0 mV. In 0.4 <u>M</u> KPF₆, k_{app}^{c} is 1.3 x 10⁻² cm/sec at a potential of +100 mV, and α_{app}^{c} is 0.50 ± 0.04 for potentials between 200 and 50 mV. Consequently, from eqn (6), $\alpha_{app}^{a} \approx 0.50$ under these conditions. Applying the same double-layer correction as for Cr_{aq}^{2+} oxidation using eqn (8) yields $\alpha_{corr}^{a} \approx 0.55$ for Fe_{aq}^{2+} oxidation at a potential of +100 mV.

Rate measurements were also made as a function of temperature in the range $15^{\circ} - 45^{\circ}$ C for Cr_{aq}^{2+} and Eu_{aq}^{2+} oxidation in 0.4 <u>M</u> KPF₆. Using a nonisothermal cell arrangement with the reference electrode held at room temperature, ^{11,89} so-called "ideal" enthalpies of activation $\Delta H_{ideal}^{\dagger}$ were obtained from the Arrhenius slopes. ^{17,89} Values of $\Delta H_{ideal}^{\dagger}$ close to zero (0-2 kcal/mole) were obtained over a wide range of anodic overpotentials (+100 $\leq E \leq -450$ mV); i.e., the anodic rate constants were found to be almost independent Figure 16. Plots of the logarithm of the rate constant corrected for ionic double-layer effects log k for Cr^{3+/2+} against the electrode potential E at the mercury-aqueous interface. Key: Solid lines are experimental values. Anodic

Key: Solid lines are experimental values. Anodic rate constants shown for $-E < -E_f$, cathodic rate constants shown for $-E > -E_f$. Values of log k_{corr} obtained from corresponding values of log k_{app} in 0.4 <u>M</u> KPF₆ (Figure 12) using eqn (7), assuming that ϕ_{rp} equals 0.6 ϕ_d^{GCS} for $Cr_{aq}^{3+/2+}$. Values of ϕ_d^{GCS} for 0.4 <u>M</u> KPF₆ taken from Figure 15. The dashed lines are the theoretically predicted curves from the harmonic oscillator model which were obtained using eqns (10) and (11). The dotted lines are the anodic Tafel plots obtained by assuming that $\alpha = 0.50$ at all potentials.



Figure 17. Plots of the logarithm of the rate constant corrected for ionic double-layer effects log k for Eu $\frac{3+/2+}{aq}$ against the electrode potential E at the mercury-aqueous interface.

> Key: Solid lines are experimental values. Anodic rate constants shown for $-E < -E_f$, cathodic rate constants shown for $-E > -E_f$. Values of log k_{corr} obtained from corresponding values of log k_{app} in 0.4 <u>M</u> KPF₆ (Figure 13) using eqn (7), assuming that ϕ_{rp} equals 0.9 ϕ_d^{GCS} for $Eu_{aq}^{3+/2+}$. Values of ϕ_d^{GCS} for 0.4 <u>M</u> KPF₆ taken from Figure 15. The dashed lines are the theoretically predicted curves from the harmonic oscillator model which were obtained using eqns (10) and (11). The dotted lines are the anodic Tafel plots obtained by assuming that $\alpha = 0.50$ at all potentials.



Figure 18. Plots of the logarithm of the rate constant corrected for ionic double-layer effects log k for $V_{aq}^{3+/2+}$ against the electrode potential E at the mercury-aqueous interface.

> Key: Solid lines are experimental values. Anodic rate constants shown for $-E < -E_f$, cathodic rate constants shown for $-E > -E_f$. Values of log k corr obtained from corresponding values of log k app in 0.4 <u>M</u> KPF₆ (Figure 14) using eqn (7), assuming that ϕ_{p} equals 0.8 ϕ_{d}^{GCS} for $V_{aq}^{3+/2+}$. Values of ϕ_{d}^{GCS} for 0.4 <u>M</u> KPF₆ taken from Figure 15. The dashed lines are the theoretically predicted curves from the harmonic oscillator model which were obtained using eqns (10) and (11). The dotted lines are the anodic Tafel plots obtained by assuming that $\alpha = 0.50$ at all potentials.



of temperature. The corresponding "ideal" entropies of activation $\Delta S_{ideal}^{\dagger}$ were found to change from <u>ca</u>. -30 to -20 e.u. with increasing anodic overpotential over the same potential range. DISCUSSION

The very marked decreases of αa_{corr}^{a} seen for Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} oxidation with increasing "formal" anodic overpotential $n^{a}(=E-E_{f}^{4})$ contrast with the approximate constancy of αc_{corr}^{c} seen previously for Cr_{aq}^{3+} reduction¹⁴ over a substantial range (100 - 500 mV) of formal cathodic overpotential $n^{c}(=E_{f}^{-}E)$. Decreases in the intrinsic transfer coefficient α_{l} with increasing overpotential are indeed predicted by contemporary theories of electron transfer, arising from the expected curvature of the reactant and product free-energy surfaces in the intersection region.^{10,63} However, the theoretically predicted variations in the anodic and cathodic transfer coefficients (αa_{l}^{a}) calc and (αc_{l}^{c}) calc with increasing anodic and cathodic overpotentials are very similar to, and markedly smaller than, the experimental variations in αa_{corr}^{a} at anodic overpotentials. Using the harmonic oscillator model, $\frac{1}{(\alpha l)}$ calc is obtained from*

$$(\alpha_{I})_{calc} = 0.5 + \frac{F(E_{f}-E)}{2\lambda}$$
 (10)

where λ is the Marcus intrinsic reorganization term. (Forms of eqn (10) have been written with either 2λ or 4λ in the denominator of the last term.¹⁰ As explained in Ref. 14, the form of eqn (10) written here follows from the definition of the electrochemical transfer coefficient at a given electrode potential E in terms of the <u>tangent</u> to the Tafel plot at E, i.e., α is taken as +(2.303/f)($\partial \log k/\partial E$), and is therefore consistent with the experimental values of $\alpha \frac{a}{app}$ which were obtained using eqn (5).) λ is related to the double-layer corrected rate constant k_{corr}^{s} at the formal ("standard") potential by¹⁰

$$RT \ln(\frac{k_{corr}^{s}}{Z}) = -\lambda$$
(11)

where Z is the heterogeneous collision frequency, which is usually calculated from 1 Z = $(kT/2 \pi m)^{\frac{1}{2}}$. Taking the effective mass m of the present reactants equal to 200 yields Z = 5 x 10³ cm/sec. Values of k_{corr}^{s} were obtained from eqn (7) using k_{app} obtained in 0.4 <u>M</u> KPF₆: for $Cr_{aq}^{3+/2+}$, $k_{corr}^{s} \approx 3 \times 10^{-6}$ cm.s.⁻¹; $Eu_{aq}^{3+/2+}$, 3.5 x 10⁻⁵ cm.s.⁻¹; $V_{aq}^{3+/2+}$, 7.5 x 10⁻⁴ cm.s.⁻¹. (Although these values naturally depend somewhat upon the assumptions used in applying the double-layer corrections, the uncertainties in this procedure do not significantly affect the resulting values of (α_{1})_{calc} obtained from eqn (10).)

The values of $(\alpha_{1}^{a})_{calc}$ obtained from eqn (10) for Cr_{aq}^{2+} , Eu_{aq}^{2+} , and V_{aq}^{2+} exidation are listed in Table 3 along with the corresponding values of α_{corr}^{a} . It is seen that $\alpha_{corr}^{a} < (\alpha_{1}^{a})_{calc}$ over a wide range of anodic overpotentials. On the other hand, for electrode potentials negative of E_{f} , little change in α_{corr}^{a} (and therefore α_{corr}^{c}) is observed, and $\alpha_{corr} \simeq (\alpha_{1})_{calc} \simeq 0.5$. The predictions of eqn (10) are also expressed as dashed lines in Figures 16-18. For comparison, Tafel plots generated by assuming that $\alpha = 0.50$ at all potentials are given in Figures 16-18 as dotted lines. The experimental double-layer corrected Tafel plots clearly exhibit markedly more curvature than the theoretical plots at anodic overpotentials, whereas the opposite appears to be true at cathodic overpotentials, at least for Cr_{aq}^{3+} reduction.¹⁴ In order to unravel the physical reasons responsible for these unexpectedly large variations in α_{corr}^{a} , it is instructive to ascertain whether they arise as a consequence of a given anodic overpotential for the reaction under consideration or from the particular electrode potential region where the effect is observed. The latter situation would be expected if there are sizable contributions to the double-layer corrections beyond the averaged coulombic terms considered in eqn (8), so that α_{corr} differs from the required intrinsic transfer coefficient α_{1} . Such contributions could arise from differences in reactant-solvent interactions in the bulk solution and in the interphase or from discretenessof-charge effects. All these double-layer influences can generally be taken into account by expressing them as "thermodynamic" work terms (c.f. refs. 7 and 90):

$$\alpha_{app} = \alpha_{I} \pm \frac{\alpha_{I}}{F} \left(\frac{\partial w^{p}}{\partial E}\right)_{\mu} \pm \left(\frac{1-\alpha_{I}^{a}}{F}\right) \left(\frac{\partial w^{r}}{\partial E}\right)_{\mu}$$
(12)

where w^r and w^p are the work required to transport the reactant and product, respectively, from the bulk solution to the reaction site. If these work terms arise solely from averaged coulombic effects so that $\alpha_{corr} = \alpha_{1}$, then w^r = ZF ϕ_{rp} and w^p = $(Z \pm \alpha_{1})F\phi_{rp}$; and eqn (12) reduces to eqn (8). In all probability, the work terms ($\partial w^{p}/\partial E$)µ in eqn (12) will be approximately the same for the redox couples under scrutiny here for a given electrolyte and electrode potential, irrespective of their origin; the same is true of ($\partial w^{r}/\partial E$)µ. From the form of eqn (12), if α_{app}^{a} (or α_{corr}^{a}) values for a pair of aquo oxidation reactions are markedly different at a given electrode potential, this difference must at least partly arise from differences in α_{1}^{a} for the two reactions. Also, if $(\partial w^p / \partial E) \mu \simeq (\partial w^r / \partial E) \mu$, the magnitude of the double-layer corrections will be approximately independent of α_1^a anyway.

The relative values of α_{corr}^{a} for Fe_{aq}^{2+} and Cr_{aq}^{2+} oxidation at a given electrode potential are of particular interest in this connection since E_f for $Fe_{aq}^{3+/2+}$ (500 mV) is substantially more positive than E_f for $Cr_{aq}^{3+/2+}$ (-660 mV). In the region of electrode potential (+100 to 0 mV) where kinetic data for both reactions are available, α_{corr}^{a} for Fe_{aq}^{2+} oxidation (\approx 0.5) is substantially larger than for Cr_{aq}^{2+} oxidation (\approx 0.20). In view of eqn (12), α_1^{a} is also substantially larger for the former reaction, even if $\alpha_{corr} \neq \alpha_1$. From eqn (10), the corresponding values of (α_1^{a})_{calc} at E = +100 mV are 0.60 and 0.33, respectively. (An estimate of k_{corr}^{s} for Fe_{aq}^{2+} of $\approx 1 \times 10^{-5}$ cm/sec was obtained by linearly extrapolating the cathodic Tafel plots to the formal potential.)

The relative values of α_{aq}^{a} for V_{aq}^{2+} oxidation in comparison with those for Cr_{aq}^{2+} and Eu_{aq}^{2+} oxidation are also instructive since E_{f} for $V_{aq}^{3+/2+}$ oxidation (-475 mV) is significantly more positive than for $Cr_{aq}^{3+/2+}$ and $Eu_{aq}^{3+/2+}$ (-660 and -625 mV). It is seen (Table 3) that at a given electode potential, α_{corr}^{a} for the former reaction tends to be larger than for the latter two reactions. However, at given values of n^{a} , all three reactions exhibit closely similar values of α_{corr}^{a} . It therefore appears that the observed marked dependence of α_{corr}^{a} upon electrode potential arise from variations α_{l}^{a} as a consequence of the anodic overpotential itself. Assuming then that the plots of log k_{corr} against anodic and cathodic overpotential for $Cr_{aq}^{3+/2+}$, $Eu_{aq}^{3+/2+}$, and $V_{aq}^{3+/2+}$ given in Figures 16-18 approximate the desired plots after correction for all environmental effects, it remains to consider possible ways in which such asymmetry in the dependence of α_1 upon the anodic and cathodic overpotentials could be generated. Some asymmetry will appear when the vibrational force constants for the reduced and oxidized species differ.^{10,91} However, this effect is predicted to be small.¹⁰ Another way in which such asymmetry can arise is when the work terms w^r and w^p markedly differ. Then if $(\partial_w^r/\partial_E)\mu$ and $(\partial_w^p/\partial_E)\mu$ equal zero, it can be shown (eqn (87b) of Ref. 10) that instead of eqn (10) we should write

$$(\alpha_{l})_{calc} = 0.5 \pm (F/2\lambda)(E_{f}-E) + (w^{P}-w^{r})/2\lambda$$
 (13)

Physically, the final term in eqn (13) accounts for the difference between the thermodynamic driving force $F(E_f-E)$ for the overall reaction and the driving force associated with the free-energy barrier for the elementary electron-transfer step which determines α_{1} . Consequently, a possible explanation of the observation that $\alpha_{corr}^{a} < (\alpha_{1}^{a})_{calc}$ (Table 3) is that there is at least one component of the work terms w^r and w^p other than the coulombic terms so that w^r >> w^p. However, in order to fit the values of α_{corr}^{a} in Table 2 with $(\alpha_{1}^{a})_{calc}$ obtained from eqn (13), values of $(w^{p}-w^{r}) \approx 11$ kcal/mole are required. Such large differences in work terms between M_{aq}^{3+} and M_{aq}^{2+} seem unlikely.

It is interesting to note that the observed shapes of the anodic and cathodic Tafel plots closely resemble those which are obtained from a theoretical nonadiabatic model involving

resonance tunneling via a localized electronic state in a surface film.⁹² Although such films are absent from the mercury-aqueous interface, the inner-layer solvent could conceivably act in a similar fashion. However, the physical nature of the localized electronic states in this case are unclear.

The remaining explanation for the observed behavior is that the free-energy surfaces which provide the elementary Franck-Condon barrier to electron transfer are inherently nonsymmetrical or of complex shape. An important property of M_{aq}^{2+} oxidation reactions that may be responsible for such a circumstance is the substantial increase in solvent ordering that apparently attends the conversion of M_{ac}^{2+} to M_{ac}^{3+} , which is manifested in extremely large "reaction entropies" ΔS_{rc}^{o} for such $M_{aq}^{3/2+}$ couples (where ΔS_{rc}^{O} equals the difference between the ionic entropies of the reduced and oxidized halves of the redox $couple^{11}$). At the formal ("standard") potential for the redox couple, the freeenergy driving force ΔG° equals zero¹⁰ so that $T \Delta S^{\circ} = \Delta H^{\circ}$.¹⁷ Since ΔS_{rc}^{o} for $Cr_{aq}^{3+/2+}$ and $Eu_{aq}^{3+/2+}$ equals <u>ca</u>. 50 e.u.,¹¹ then ΔH^{O} for Cr_{aq}^{2+} and Eu_{aq}^{2+} oxidation equals ca. -15 kcal. mol.⁻¹ at their respective formal potentials. Consequently, these oxidations are highly exothermic so that the potential energy surfaces will be highly nonsymmetrical, and increasingly so as the anodic overpotential is increased, since $-\Delta H^{\circ} = T\Delta S_{rc}^{\circ} + F(E-E_{f})$. As explained in detail in Ref. 92, the measured "ideal" activation parameters are approximately equal to the actual enthalpic and entropic barriers to electron transfer. The finding that $\Delta H_{ideal}^{\dagger} \simeq 0$ for Cr_{aq}^{2+} and Eu_{aq}^{2+} oxidations at anodic overpotentials therefore

indicates that those reactions are sufficiently exothermic so that the reactant's and product's potential-energy surfaces intersect close to the reactant's energy well. Admittedly, the dependence of the free energy of activation upon the overpotential (i.e., upon the free-energy driving force ΔG^{O}) should be given by eqn (10) irrespective of the individual enthalpy and entropy of activation, providing that the resulting free-energy surfaces are parabolic. In the present case, the observed small values of $\triangle H^{\dagger}$ would be expected to be accompanied by small values of Δ S⁺ because the transition-state structure should closely resemble that of the reactants. Instead, substantial values of ΔS^{\dagger} are obtained for the oxidation reactions so that $\triangle S^{\dagger} = 0.5 \triangle S^{\circ}$ even when $\Delta H \stackrel{\dagger}{\cong} 0$. This anomaly may arise from the need for the solvent molecules in the immediate vicinity of the $M_{a\alpha}^{2+}$ reactant to be oriented strongly via hydrogen bonding with the aquo ligands¹¹ in the configuration similar to that appropriate for the solvent "structure-making" M_{ad}^{3+} product prior to formation of the transition state. These solvent structural changes may be envisaged as occurring in a separate step prior to the normal inner-shell reorganization and long-range (dielectric-continuum) solvent polarization leading to the formation of the transition state.¹⁰ Such a mechanism would indeed lead to the observed asymmetric shape of the anodic and cathodic Tafel plots since one can show that $\left(\begin{array}{c} \alpha \\ 1 \end{array} \right)_{calc}$ would then be given by a relation similar to eqn (13), only with $(w^{p}-w^{r})$ replaced by the free energy required for the prior solvent-reorganization step.

Irrespective of the detailed reasons for the observed behavior, it seems likely that the observed Tafel plot asymmetry is associated with major differences in short-range solvent polarization between the reduced and oxidized aquo species. The electrochemical reactivities of these aquo redox couples also exhibit anomalously large dependences upon the nature of the electrode material, which have been ascribed to varying interactions between the aquo ligands and inner-layer water molecules.⁹³

The present conclusion that adsorbed perchlorate as well as halide anions induce changes in ϕ_{rp} for Eu²⁺ oxidation that are comparable to the effect of the electrode charge removes the puzzling anomaly arising from the earlier conclusion of Ref. 81, being in harmony with the similar results seen for the effects of a number of anionic adsorbates upon the outer-sphere reduction rates of Co(III) ammine complexes.^{22,23} Taken together, these results demonstrate that the simple Frumkin model embodied in eqn (7), if generalized to take into account differences between ϕ_{rn} and ϕ_{rn} arising from the possible noncoincidence of the reaction plane and the o.H.p., has so far been consistently and surprisingly successful in describing the effects of specific anionic adsorption upon the electrode reaction rates of simple cationic metal complexes. Although individual discreteness-ofcharge effects could well play an important role, their net influence appears to be relatively small for these outer-sphere reactions. Substantial differences have been reported between the prediction of eqn (7) and the experimental double-layer influences upon the rates of Eu_{aq}^{2+} and V_{aq}^{2+} oxidation in extremely dilute (millimolar)

supporting electrolytes. However, these discrepancies partly arise from the use of the same double-layer analysis as in ref. 81, i.e., from assuming that $\alpha^{a}_{corr} = 0.50$ for Eu_{aq}^{2+} and V_{aq}^{2+} oxidation at all electrode potentials.

ADDENDUM

As a complement to studies on (structuring) aquo complexes in structured solvents such as H_2^{0} , the electroreduction kinetics of $Co(NH_3)_5 F^{2+}$ was examined over several orders of magnitude in rate to see if the lack of curvature in reduction Tafel plots in water is specific to (structuring) complexes with water in the primary coordination sphere. Results described in Chapter III indicated that reliable rate data could be obtained for this complex in neutral 1 <u>M</u> KF from pulse-polarographic data taken at sampling times as short as 300 µsec. Pulse measurements in the range of 500 µsec to 50 msec were coupled with dc measurements, including foot-of-the-wave (activation-controlled) measurements on concentrated solutions.

A 30 mM solution was prepared by dissolving solid $[Co(NH_3)_5F](Cl0_4)_2$ in 1 M KF. Its dc polarogram was well behaved until close to the top of the wave, which at about -400 mV against SCE is very close to the pzc. Pronounced depression in the currents was observed for more negative potentials, making rate measurements unreliable. (However the kinetic parameters are to be derived, the limiting current must be known, even if only aproximately: use of 90% of the wave (in terms of i/i_{1im}) requires accurate knowledge, and the applicability of the assumption that the current is activation-controlled relies on the current being less than

15 to 20% of the limiting value.) The use of a pulse-polarographic limiting current in conjunction with previously characterized ratios of pulse to dc limiting currents was vitiated by the observation of similar, albeit less extreme, behaviour in the pulse polarogram. A tenfold dilution of this solution by supporting electrolyte produced well-behaved dc and pulse polarograms; the poor limitingcurrent behaviour of the concentrated solutions is probably due to base-induced precipitation which results from the release of ammine ligands at the electrode surface from the labile reduced cobalt molety. However, kinetics analysis of the concentrated-solution polarograms using limiting-current values which were ten times larger than those obtained from the diluted solution produced rate constants and apparent transfer coefficients which were significantly disparate from those of the dilute solution. The roughly 8% difference in ionic strength due to concentrated complex may be responsible for this. Use of limiting-current estimates from the original concentrated-solution data prior to the onset of current depression yielded kinetic parameters which agreed well with values from the dilute solutions in the potential regions where kinetic parameters are accessible from both data sets.

The Tafel plot for the system, shown in Figure 19, spans more than four orders of magnitude in rate and shows upward concavity, in contrast to the plots for aquo oxidations and to theoretical predictions. Essentially linear behaviour was seen at the highest rates, rather than downward curvature. Because the smallest rate constants were obtained from concentrated solutions prepared from the perchlorate salt, the possiblity exists that the upward









curvature of the Tafel plot results from a rate enhancement which is produced by anion adsorption, particularly the specific adsorption of perchlorate.

An ion-exchange technique was used to make a stock solution of $Co(NH_3)_5 F^{2+}$ which was ostensibly free of perchlorate. An anion-exchange column of AG 1-X2 in the fluoride form was made from enough resin to present an approximately ten-fold excess of exchange capacity over the amount of perchlorate in the sample. The solution of the prechlorate salt (enough to make 5 ml of a 15 mM stock solution) was introduced into the column and eluted by water. The absence of perchlorate was inferred from the lack of a precipitate produced by a drop of eluate in 2 M KF; since a saturated potassium perchlorate solution is about 30 mM at room temperature, the residual perchlorate concentration was less than 0.5 mM. The complex-containing eluate was reduced in volume by vacuum distillation, enough solid KF having been added to make a 1 M solution, and diluted to volume.

Both the stock solution and a solution diluted tenfold by electrolyte gave reasonable pulse and dc polarograms. The footof-the-wave kinetic parameters obtained from the dc polarogram of the stock solution produced less curvature in the Tafel plot than those from solutions containing perchlorate, but again upward concavity is present.

It remained to correct the rates for coulombic double-layer effects; corrected transfer coefficients were obtained from $(\partial \phi / \partial E)\mu$ and the apparent transfer coefficient. Values of this derivative were approximated from capacitance ratios by assuming that (1) there is no specific adsorption of electrolyte or reactant; (2) the Galvani potential at the reaction site is given by the Gouy-Chapman theory; and (3) the inner-layer capacitance depends only on the electrode charge. Using double-layer capacitance and electrode-charge values from Parsons⁹⁴ for 0.79 <u>M</u> NaF, and diffuselayer capacitances from GCS theory, the inner-layer capacitance as a function of electrode charge was calculated. These values, coupled with diffuse-layer capacitances calculated for 1 <u>M</u> solutions, produced the necessary transfer-coefficient corrections. The corrected values of the transfer coefficient showed even more disparity from the theoretical predictions. It would seem that the specific solvent-structuring argument for the pattern of the potential dependence of the transfer coefficient continues to be appropriate.

CHAPTER V. SOLVENT ISOTOPE EFFECTS UPON THE KINETICS

OF SOME SIMPLE ELECTRODE REACTIONS

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INTRODUCTION

It has been known for some time that sizable changes in the rate constant of homogeneous electron transfer reactions between transition-metal complexes occur when heavy water (D_2^{0}) is substituted for H_{20} .⁹⁵⁻⁹⁷ These solvent isotope effects have been attributed to "secondary" isotope effects arising from differences in reactantsolvent interactions as well as to "primary" isotope effects arising from the replacement of hydrogen by deuterium in the coordination sphere of the reacting cations.⁹⁶⁻⁹⁸ Studies of deuterium-isotope effects in electrode kinetics have largely been limited to the important but atypical cases of hydrogen and oxygen evolution, 99,100 and no isotope effects upon the kinetics of simple outer-sphere electrode reactions have apparently been reported. Nevertheless, it is anticipated that such studies could shed light on the role of the solvent in outer-sphere processes. In particular, the dielectric properties of H_2^{0} and D_2^{0} are almost identical; and yet the mass difference between H and D yields significantly different hydrogen-bonding properties, so that these measurements could in principle provide a means of assessing the importance of specific solute-solvent interactions to the kinetics of electron transfer. In some respects, electrode reactions are more suitable than homogeneous redox processes for such fundamental studies since the former type involves the thermal activation of only a single redox center. Also, the comparison between the solvent isotope effects observed for corresponding homogeneous and electrochemical reactions involving transition-metal complexes could provide clues as to the similarities and differences between

the reactant-solvent interactions in the bulk and interphasial redox environments.

For this reason, we have examined the effect of replacing $H_{2}O$ solvent with $D_{2}O$ upon the electrode kinetics of a number of aquo and ammine complexes for which the solvent isotope effects upon outer-sphere homogeneous reactions involving these complexes have previously been scrutinized. 96,98,101-103 These reactions include $Fe_{an}^{3+/2+}$ self-exchange^{96,101} and the reduction of Co(III) ammines by V_{ag}^{2+} and Cr_{ag}^{2+} 102,103 Although the sizable (factor of two) ratio of the rate constants in $\rm H_20$ and $\rm D_20~(k^{H}/k^{D})$ for $Fe_{a0}^{3+/2+}$ self-exchange was originally attributed to the presence of a hydrogen-atom transfer mechanism, ¹⁰¹ similarly large values of $\boldsymbol{k}^{H}/\boldsymbol{k}^{D}$ have been observed for cross-reactions involving aquo complexes for which this mechanism is ruled out. 96,102,103 We have recently measured the solvent isotope effect upon the formal electrode potentials E_{f} of a number of transition-metal redox couples.¹⁰⁴ For couples containing aquo or hydroxo ligands, large differences in E_f between H_00 and D_00 were observed that appear to be at least partly due to hydrogen bonding between these ligands and the surrounding solvent.¹⁰⁴ It is of interest to determine how these thermodynamic differences are reflected in the electrode kinetics of such complexes. Studies of isotope effects for substitutionally inert ammine and ethylenediamine complexes are also of particular interest since, in contrast to aquo complexes, the deuteration of the ligands and the solvent, i.e., the primary and secondary isotope effects, can be investigated

separately. 105,106 The results of these experiments are reported in the present chapter.

EXPER IMENTAL

The Co(III) and Cr(III) complexes were synthesized as solid perchlorate salts using the procedures noted in refs. 23 and 33, respectively. Stock solutions of Eu_{an}^{3+} were prepared by dissolving Eu_2O_3 in a slight excess of perchloric acid, and those of Cr_{aq}^{3+} as described in ref. 32. Solutions of Eu_{aq}^{2+} , Cr_{aq}^{2+} , and V_{aq}^{2+} were obtained in the appropriate electrolytes by electrolyzing solutions of Eu_{aq}^{3+} , Cr_{aq}^{3+} , and V(V), respectively, over a stirred mercury pool at -1100 mV. vs. s.c.e.; V_{ag}^{3+} was formed by reoxidizing V_{ac}^{2+} at -300 mV. vs. s.c.e. The source of Fe_{aq}^{3+} was $Fe(C10_4)_3$ (G.F. Smith Co.). Potassium hexafluorophosphate (Alfa Ventron Corp.) was thrice recrystallized from water. Sodium perchlorate was prepared from sodium carbonate and perchloric acid and recrystallized prior to use. Stock solutions of lanthanum perchlorate were prepared by dissolving La_2O_3 in a slight excess of perchloric acid. The use of aqueous reagents such as 70% perchloric acid generally introduced only small (<1%) amounts of water into the resulting D_20 solutions. The Co(III) and Cr(III) ammine and ethylenediamine complexes were deuterated by dissolving the protonated perchlorate salts in the minimum amount of D₂O containing 1 mM hydroxide ions. The amine hydrogens are rapidly deuterated under these conditions.¹⁰⁵ These stock solutions were then added to the appropriate electrolyte in H_20 or D_20 acidified with sufficient perchloric acid (usually 5-10 mM) to suppress completely the exchange of amine hydrogens on the timescale of the kinetics

experiments. Water was purified either by means of a "MilliQ" purification system (Millipore Corp.) or by distillation from alkaline permanganate followed by "pyrodistillation", ¹¹ with identical results. Deuterium oxide (99.8%, Stohler Isotope Chemicals) was used either directly or following distillation from alkaline permanganate, again with identical results. All solutions for electrochemical scrutiny were deoxygenated by bubbling with prepurified nitrogen, from which residual traces of oxygen were removed by passing through a column packed with B.A.S.F. R3-11 catalyst heated to 140° C, and then humidified by bubbling through either H₂O or D₂O, as appropriate.

Kinetic parameters were obtained at a dropping mercury electrode (flow rate 1.8 mg/sec, mechanically controlled drop time 2 sec) by means of normal pulse and d.c. polarography using a PAR 174A Polarographic Analyzer coupled with a Hewlett-Packard 7045A X-Y recorder. The kinetic analyses of these irreversible polarograms employed the methods due to Oldham and Parry,⁸⁴ which allowed rate constants in the range <u>ca</u>. 10^{-4} to 4×10^{-2} cm/sec to be evaluated reliably. The electrochemical cell used for the kinetic measurements consisted of a working compartment containing ca. 5 ml of the solution of interest in either H_20 or D_20 , which was separated from the reference compartment by means of a glass frit ("very fine" grade, Corning, Inc.). For experiments where bulk electrolyses were performed, the platinum-wire counter electrode was located in a third compartment which was also separated from the working compartment by a glass frit. The reference compartment was filled with an aqueous solution of the same ionic composition

as in the working compartment, in which was immersed a commercial saturated calomel electrode (s.c.e.). When using strongly acidic electrolytes, the reference compartment was filled instead with saturated aqueous NH_LC1 in order to minimize the liquid-junction potential.¹⁰⁴ The solvent liquid-junction potential between the H₂O and D₂O solutions is probably negligible (\leq 1-2 mV) using this cell arrangement , as evidenced by the essentially identical formal potentials obtained in H_20 and D_20 for ferrocene/ferrocinium and $Fe(bpy)_{3}^{3+/2+}$ (bpy = 2,2'-bipyridine) redox couples.¹⁰⁴ (Both these couples are expected to exert only a small, nonspecific influence upon the surrounding solvent.) Consequently, a given cell potential E measured in a given electrolyte in H_00 and D_00 will correspond to essentially the same, albeit unknown, value of the Galvani metal-solution potential difference ϕ_m in both solvents. (See ref. 104 for a detailed discussion of this point.) All electrode potentials are therefore quoted versus an aqueous s.c.e. using this cell arrangement, unless otherwise noted. All kinetic parameters were obtained at 25.0 \pm 0.1 $^{\circ}$ C.

RESULTS

Aquo Complexes

Since large differences in the formal potential, ΔE_f^{D-H} , are observed for redox couples containing aquo ligands when changing from H₂0 to D₂0 solvent, ¹⁰⁴ it is of particular interest to examine the corresponding differences in their electrode kinetics. Reactions that have been found to be suitable for scrutiny at the mercury-aqueous interface are $Fe_{aq}^{3+/2+}$ at cathodic overpotentials, and $Cr_{aq}^{3+/2+}$, $V_{aq}^{3+/2+}$, and $Eu_{aq}^{3+/2+}$ at both cathodic and anodic

overpotentials; "aq" denotes OH_2 or OD_2 ligands in the appropriate solvents. (Although the formal potential for $Fe_{aq}^{3+/2+}$ [495 mV, μ = 0.5(H_20)] is positive of the potential where mercury dissolution occurs in noncomplexing media (>350 mV), we have found that well-defined normal pulse and dc polarograms can be obtained for Fe_{aq}^{3+} reduction in acidified KPF₆ or NaClO₄ over the potential range ca. 300 to -100 mV. on account of apparently very slow exchange kinetics for $Fe_{aq}^{3+/2+}$. To our knowledge, no previous measurements of $Fe_{aq}^{3+/2+}$ kinetics at the mercury-aqueous interface have been reported.) When comparing electrochemical rate constants in H_00 and D_00 , it is desirable to correct the relative rates for differences in the ionic double-layer effect between these solvents. By assuming that this correction can be calculated using the simple electrostatic (Frumkin) model, we can express the ratio of the observed (apparent) rate constant for a given one-electron reaction in H_2^0 to that in D_2^0 , $(k^H/k^D)_{app}$, as (cf. ref. 22):

 $\log(k^{H}/k^{D})_{app} = \log(k^{H}/k^{D})_{corr} - (f/2.303)(\alpha_{corr} + Z)\Delta\phi_{rp}^{D-H}$ (14) where $(k^{H}/k^{D})_{corr}$ is the corresponding isotopic rate ratio corrected for ionic double-layer effects, $^{22} \Delta \phi_{rp}^{D-H}$ is the alteration in the average potential on the reaction plane in changing from H₂0 to D₂0, Z is the reactant charge, α_{corr} is the double layercorrected transfer coefficient, and f=F/RT. (The plus/minus sign in eqn (14) refers to electrooxidation and electroreduction reactions, respectively.) In order to estimate $\Delta \phi_{rp}^{D-H}$, plots of the excess electrode charge density q^m against the electrode potential E are required in both H₂0 and D₂0. Figure 20 consists


Figure 20. The excess electronic charge density q^{m} of mercury in contact with 1 <u>M</u> KF(H₂0) and 1 <u>M</u> KF(D₂0) electrolytes versus the electrode potential E.

of a pair of such plots for 1 \underline{M} KF. These were obtained by inte grating the capacitance-electrode potential curves for these electrolytes^{94,107} along with the following values of the potential of zero charge that were determined by the streaming potential method:⁷⁷ 1 \underline{M} KF(H₂0), -434 mV; 1 \underline{M} KF(D₂0), -440 mV vs aqueous s.c.e.

It is seen from Figure 20 that the q^m -E plots for H₂O and ${\rm D}_{2}{\rm O}$ are quite similar, although it is interesting to note that the plot for D_20 is displaced significantly relative to H_20 at the most negative potentials. Since fluoride anions are not significantly specifically adsorbed within this potential range, ⁷⁶ these electrode-charge displacements at fixed values of E, $(\Delta q^m)_F^{D-H}$, presumably arise from differences in the inner-layer structure between H_00 and D_00 . For most of the reactions considered here, either 0.4 <u>M</u> KPF₆ or 40 m<u>M</u> La(ClO₄)₃, rather than fluoride, supporting electrolytes were used in order to minimize the extent of ionpairing and to enable acidic solutions to be used; there is extensive information available on the magnitude of the double-layer corrections for the present reactants in these electrolytes. 15,22,23,32,33 Although both 0.4 <u>M</u> KPF₆ and 40 m<u>M</u> La(ClO₄)₃ exhibit significant anion specific adsorption at positive electrode charges, the extent of adsorption is small at potentials more negative than ca. -500 mV and -650 mV, respectively. Under these latter conditions, the relative q^{m} -E curves for these electrolytes in H₂0 and $D_{2}0$ will be closely similar to those given in Figure 20, so that the required double-layer corrections to the observed rate ratios $(k^{H}/k^{D})_{app}^{E}$ could be obtained to a reasonable approximation

in the following manner. The value of $(\Delta q^m)_F^{D-H}$ at the appropriate value of E was read from Figure 20 and the corresponding difference in the diffuse-layer potentials ϕ_d between D₂O and H₂O in a given electrolyte, ($\Delta \phi_{d}$) $_{E}^{D-H}$, obtained using Gouy-Chapman theory. The corresponding values of ($\Delta \phi = \frac{D-H}{d} = \frac{D-H}{E}$ were obtained by assuming that $\Delta \phi_{rp} = 0.7 \Delta \phi_{d}$ and $\Delta \phi_{rp} = \Delta \phi_{d}$ for 0.4 <u>M</u> KPF₆ and 40 mM La(C10₄)₃, respectively, as indicated from earlier studies. 15,32 These values of $(\Delta \phi_d)_E^{D-H}$ were then inserted into eqn (14) to obtain the required values of $(k^{H}/k^{D})_{corr}^{E}$. (Fortunately the extent of these double-layer corrections is small for most reactants.) Some reactions required scrutiny at positive electrode charges (corresponding to -E < 450 mV) where PF_6^- and particularly $C10_4^$ supporting electrolytes exhibit significant anion specific adsorption, so that ϕ_{rn} will be influenced by the adsorbed anionic charge density q'. However, the use of 0.4 \underline{M} KPF₆ minimized the extent of the diffuse-layer corrections since $q^{\,\prime\,\,\simeq}\,\,q^m$ at potentials positive of the p.z.c. in aqueous solution so that $\phi_{rp} \simeq 0.22,79$ A similar circumstance is expected in D₂0, so that $\Delta \phi \frac{D-H}{rp} \simeq 0$ under these conditions.

Table 4 summarizes representative electrode kinetic parameters for the reduction of Fe_{aq}^{3+} , Cr_{aq}^{3+} , V_{aq}^{3+} , and Eu_{aq}^{3+} at the Hg/H₂O and Hg/D₂O interfaces. The rate parameters were all found to be independent of pH below <u>ca</u>. pH 2.5 where hydrolysis of the aquo cations is suppressed. Essentially linear Tafel plots were obtained for each reaction over the observable span (200-300 mV) of cathodic overpotentials, ^{15,32} so that the cathodic rate parameters can conveniently be expressed as a value of k_{app} at a

Table 4.	Solvent Isotope Ef at the Mercury-Aqu	ifects Upon the Elec leous Interface.	troreduction Kinetics	s of Some Transit 2	tion-Metal 3	Complexes 1
Reactant	Solvent	Electrolyte ¹	E mV vs. H ₂ 0 s.c.e.	k ^E app cm. sec. ⁻¹	dde _v	(k ^H /k ^D)corr
Fe ³⁺	H ₂ 0	0.4 <u>m</u> KPF ₆	200	2.25×10 ⁻³	0.48	r 0
•	D20	=	=	3.3×10 ⁻³	0.48	
Cr ³⁺ cr ^{aq}	Η ₂ 0	40 mM ra(c104) ³	-850	7.9×10 ⁻⁴	0.57	1
:	D20	Ξ	=	6.8×10 ⁻⁴	0.57	
=	H ₂ 0	0.4 <u>m</u> KPF ₆	-	2.5×10 ⁻³	0.63	1
=	D20	=	=	2.1×10 ⁻³	0.63	~
v ³⁺ aq	Η ₂ 0	0.4 <u>m</u> KPF ₆	-500	3.5×10 ⁻³	0.67	۲ ۲
=		=	=	4.4×10 ⁻³	0.67	
Eu ³⁺	H ₂ 0	40 m <u>M</u> La(ClO ₄) ₃	-750	5.8×10 ⁻³	0.57	0
=	D20	=	Ξ	5.8×10 ⁻³	0.57	cć.u
¹ Acidifie ² Cathodic	ed with 5-10 mM HClo : apparent rate cons	<pre>h to suppress hydro itant at stated elec </pre>	lysis of aquo reactan trode potential, obta	ined from k _{app} =	- 1/FC ^b , wh	ere i is
3 Cathodic	: apparent transfer	coefficient, obtain	ed from app = -(f/2		(Celler Beron	
⁻ Ratio of potential	<pre>f double-layer corre l in same supporting</pre>	cted rate constant electrolyte; obtai	k _{corr} measured in D ₂ 0 ned from correspondin) to that in H ₂ O ig quoted values	at fixed e of k _{app} us	lectrode ing eqn (14).

selected electrode potential and an apparent cathodic transfer coefficient α_{app} , found from $\alpha_{app} = -(f/2.303)(\partial \log k_{app}/\partial E)\mu$. The corresponding double-layer corrected rate ratios at a fixed electrode potential, $(k^{H}/k^{D})_{corr}^{E}$, are also given in Table 4. (Since essentially identical values of α and hence α corr were measured for a given system in H_00 and D_00 , these rate ratios will be approximately independent of the value of E chosen.) It is seen that the values of $(k^{H}/k^{D})_{corr}^{E}$ are comparable to, or somewhat less than, unity. However, a given electrode potential corresponds to larger cathodic overpotentials in $D_{2}O$ than in $H_{2}0$ since values of E_{f} for these couples are markedly less negative in the former solvent.¹⁰⁴ The cathodic Tafel plots were therefore extrapolated to the appropriate formal potentials for each couple measured in H_20 and D_20^{104} to obtain the "standard" apparent rate constants $\binom{k}{s}$ listed in Table 5. These results are also presented as ratios of $(k_s)_{app}$ for a given redox couple in H₂0 and D₂0, $(k_s^H/k_s^D)_{aDD}$. These rate ratios were corrected for the effect of the ionic double layer as noted above, except that values of $(\Delta q^m)^{D-H}$ and hence $\Delta \phi \frac{D-H}{r_D}$ between the respective formal potentials in D_20 and H_20 were inserted into eqn (14) to obtain the values of $(k_s^H/k_s^D)_{corr}$ given in Table 5. For $Fe_{aq}^{3+/2+}$, the listed estimate of $(k_s^H/k_s^D)_{corr}$ was obtained by assuming that $\Delta \phi_d^{D-H} = 0$ in 0.4 <u>M</u> KPF₆, and that $\alpha_{corr} = 0.5$. It is seen that the values of $(k_s^H/k_s^D)_{corr}$ as well as $(k_s^H/k_s^D)_{app}$ are substantially greater than unity, particularly for $Cr_{ac}^{3+/2+}$ which also exhibits the largest value of ΔE_{f}^{D-H} .104

Table 5.	Solvent Isotope Metal Aquo Coup	Effects upon les.	the Standard	i Electrochemical F	late Constant 3	s of Some Trar 4	ısition− 4
Redox Coup le	e Solvent	E 1 mV vs. H ₂ 0 s.c.e.	E D-H ² f mV	Electrolyte	k ^s app	(k ^H /k ^D) s app cm sec ⁻¹	(k ^H /k ^D) corr
Fe ^{3+/3+}	H ₂ 0	495	43	0.4 <u>m</u> KPF ₆	9×10 ⁻⁶	1 66	и -
=	D20	538	f	Ξ	5.9×10 ⁻⁶		2
Cr ^{3+/2+} cr ^{aq}	Η20	-655	1	40 m <u>M</u> La(ClO ₄) ₃	1.0×10 ⁻⁵	r	ر م
=	D20	-600	ŝ	-	2.7×10 ⁻⁶	1.0	0.7
=	H ₂ 0	-655	£5	0.4 <u>M</u> KPF ₆	2.0×10 ⁻⁵	ЧЧ	с Д
=	D20	-600	2	=	4.5×10 ⁻⁶	r r	0.1
v ^{3+/2+} aq	H ₂ 0	-472		0.4 <u>m</u> KPF ₆	1.7×10 ⁻³	0	4
=	D20	-439	ĉ	Ξ	9.0×10 ⁻⁴	<u>.</u>	2
Eu ^{3+/2+} eu ^{aq}	H ₂ 0	-622	đ	40 mM La(ClO ⁴)3	3.4×10 ⁻⁴	- -	
=	D20	-613	n	-	2.8×10 ⁻⁴	7.1	-
Formal pote	ential for redox	couple at app	ropriate ion	nic strength, from	ref. 104.		
² Change in f	E _f in substituti	ng D ₂ 0 for H ₂ 0	solvent. 1	laken from ref. 104	-		

³Apparent "standard" rate constant, obtained by extrapolating plots of log k_{app} versus E to the appropriate ' value of E_f. 4 Ratio of apparent standard rate constant in $\mathrm{H_20}$ to that in $\mathrm{D_20}$.

 5 Ratio of standard rate constant in H_{2}^{0} and $D_{2}^{\overline{0}}$, corrected for the effect of the ionic double layer using eqn (14) (see text).

Ammine and Ethylenediamine complexes

The effects of separately deuterating the coordinated ligands and the solvent upon the irreversible electroreduction kinetics 23 of various Co(III) ammine and ethylenediamine complexes are summarized in Table 6. Some corresponding kinetic data for several Cr(III) ammine and ethylenediamine complexes are given in Table 7. Since essentially linear Tafel plots were obtained over the measurable overpotential range (ca. 300 mV) for each system, the kinetic parameters are again conveniently summarized as values of k app at a selected electrode potential along with the corresponding values of α_{app} . The listed isotopic rate ratios $(k^{NH}/k^{ND})_{corr}^{E}$ and $(k^{H_20}/k^{D_20})^{E}_{corr}$ resulting from deuterating the ligands and the solvent, respectively, were obtained from the appropriate pair of apparent rate constants. As before, the latter ratios were corrected for the differences in double-layer structure between H₂0 and D₂0 using eqn (14), assuming that $\Delta \phi_{rp} = \Delta \phi_d$. Unfortunately, the values of ${\rm E}_{\rm f}$ and hence ${\rm k}_{\rm S}$ for the ammine couples are unknown on account of the lability and thermodynamic instability of the reduced complexes.

Inspection of Tables 5 and 7 reveals that separate deuteration of the solvent and the reactant's coordination sphere can both have substantial influences upon the electroreduction rates measured at a fixed electrode potential. The latter effects are largest for the reduction of $Co(NH_3)_6^{3+}$ and $Cr(NH_3)_6^{3+}$, where deuteration of the ammine ligands produced isotopic rate ratios $(k^{NH}/k^{ND})_{corr}^E$ that are around two in both H_2^0 and D_2^0 solvents. Values of $(k^{NH}/k^{ND})_{corr}^E$ considerably greater than unity are also seen for other Co(111) ammines and $Co(en)_3^{3+}$ (Table 6). On the other

Table 6.	Primary and and Ethylen	1 Secondary Isoto ediamine Complex	pe Effects es.	upon the f	Electro	reduction Kinet	ics of some Co(II L	i) Ammine r
Reactant	Solvent	Electrolyte	E mV vs H ₂ O s.c.e.	k app cm sec 1	dde	(k ^{NH} /k ND) ^E corr	(k ^H 2 ⁰ /k ^D 2 ⁰) ^E corr	R Corr Corr
$c_{0}(NH_{3})_{6}^{3+}$	H ₂ 0	0.4 <u>m</u> KPF ₆	-300	5.4×10 ⁻⁴	0.76	2.36	8,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	
=	D20	:	=	7.2×10 ⁻⁴	0.76	2.07	c/.n	
co(ND ₃) ³⁺	H ₂ 0	:	:	2.3×10 ⁻⁴	0.76		61, 0	1.50
' =	D20	:	=	3.6×10 ⁻⁴	0.76			
со(NH ₃) ₅ 0H ³	+ H ₂ 0	0.4 <u>m</u> KPF ₆	-300	2.9×10 ⁻²	0.63	1.45 ⁶	8,0	
. co(NH ₃) ₅ 00 ³	+ D ₂ 0	=	=	3.6×10 ⁻²	0.62	1.45 ⁷	-0.0	L • •
Co(ND ₃) ₅ 0H ³	+ H ₂ 0	Ξ	=	2.0×10 ⁻²	0.63		600 0	<u>.</u>
$c_0(ND_3)_50D_2^3$	+ 0 ₂ 0	=	=	2.5×10 ⁻²	0.62		0.00	
co(NH ₃) ₅ F ²⁺	H ₂ 0	0.4 <u>m</u> KPF ₆	-300	1.0×10 ⁻³	0.66	1.8 ⁶	8-0 0	
Ξ	D20	Ξ	=	1.15×10 ⁻³	0.66	1.65 ⁷	/0.0	L 4 •
co(ND ₃) ₅ F ²⁺	H20	=	=	5.5×10 ⁴	0.66	610 0		. 40
Ξ	D20	Ξ	=	6.9×10 ⁻⁴	0.66	40 ° N		
со(ин ₃) ₅ 0н ²	.+ H ₂ 0	1 M KF+1 mM KOH	-500	2.4×10 ⁻³	0.65			L (
$c_{0}(ND_{3})_{5}OD^{2}$	+ D ₂ 0	=	=	9.5×10 ⁻⁴	0.58			C•7

Table 6 (conti	nued)			-	2	3	4 5	S
Reactant	Solvent	Electrolyte	E mV vs H ₂ 0 s.c.e.	k app cm sec ⁻¹	app	(k ^{NH} /k ^{ND) E} corr	(k ^H 2 ⁰ /k ^D 2 ⁰) ^E R ^E corr ^{corr}	۲
co(en _H) ³⁺	H ₂ 0	0.4 <u>m</u> KPF ₆	-300	4.6×10 ⁻⁴	0.98	1.6 ⁶	n 78 ⁸	
=	D20	=	=	5.9×10 ⁻⁴	0.98	1.457		:
co(en _D)3 ⁺	H ₂ 0	Ξ	=	2.9×10 ⁻⁴	0.98		915 0	2
=	D20	=	=	4.1×10 ⁻⁴	0.98			
Notes for Tabl	es 6 and	7.						
Observed (app.	arent) ca	thodic rate co	nstant at st	ated electr	ode pot	tential E.		
² Apparent cath	odic tran	sfer coefficie	nt, obtained	from eqn (5).			
³ Ratio of doub	le-layer	corrected rate	constants k	corr for co	rrespo	nding protonate	d and deuterated comple	lexes
at electrode p	otential	and in support	ing electrol	ytes indica	ited in	columns at lef	t, measured in either	
H ₂ 0 or D ₂ 0 as in same suppor	indicated ting elec	. Obtained fr trolyte (k ^{NN} /k ¹	om correspon ND)E (k corr = (k	ding listed NH _{/k} ND ₎ E app [•]	l value:	s of k _{app} since		
⁴ Ratio of k _{cor}	r for eit	her protonated	or deuterat	ed complexe	s in H.	2 ⁰ to that in D	$_2^0$ at electrode potenti	tial
and in support	ing elect	rolytes indica	ted in colum	ns at left.	Obta	ined from k _{ann}	using eqn (14).	

⁵Ratio of k_{corr} for protonated complex in H₂O to that for deuterated complex in D₂O, $(k^H/k^D)_{corr}^E$. Obtained from corresponding listed values of k_{app} using eqn (14) as outlined in the text. $\begin{cases} n & H_2O\\ n & D_2O\\ protonated complex \end{cases}$

Table 7, Pr an	imary and d Ethylen	<pre>1 Secondary Isotope lediamine Complexes.</pre>	Effects	upon the 1	Electro 2	reduction Kinet 3	ics of some Cr(111 4)Ammine 5
Reactant	Solvent	Electrolyte mV	E vs H ₂ 0 s.c.e.	k app cm sec ⁻¹	dde	(k ^{NH} /k ND) ^E corr	(k ^H 2 ⁰ /k ^D 2 ⁰) ^E corr	REcorr
$cr(NH_3)_6^{3+}$	H ₂ 0	40 mM La(C104)3	-900	1.1×10 ⁻³	0.82	2.0 ⁶	6 8 9	
Ξ	D20	÷	=	1.9×10 ⁻³	0.82	2.1 ⁷		1 16
cr(ND ₃) ₆	H ₂ 0	=	=	5.5×10 ⁻⁴	0.82		n £8 ⁹	2
=	D20	=	=	9.0×10 ⁻⁴	0.82			
с-Сг(NH ₃)4(ОН ₂	$)_{2}^{3+}$ H ₂ 0	40 m <u>M</u>	006-	7.0×10 ⁻³	0.73		0 78 ⁸	
с-Сг(NH ₃)4(0D ₂	$)_{2}^{3+} p_{2}^{0}$	=	=	8.5×10 ⁻³	0.73			
Cr(en _H) ³⁺	H ₂ 0	40 m <u>M</u> La(ClO ₄) ₃	006-	2.2×10 ⁻³	0.90		η 7 ^μ 8	
=	D20	=	=	2.8×10 ⁻³	06.0			
$cr(NH_3)_5NCS^{2+}$	H ₂ 0	40 mM LaCl ₃	006-	1.4×10 ⁻³	0.45		0 ¢08	
=	D20	=	=	2.2×10 ⁻³	0.43			

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hand, substitution of H_2^0 by D_2^0 solvent for a reactant with either protonated or deuterated ligands generally resulted in noticeable rate decreases, so that the listed values of $(k^{H_2^0}/k^{D_2^0})^{E}_{corr}$ are uniformly less than unity (Tables 6 and 7). Also listed in Tables 5 and 7 are the net isotopic rate ratios $(k^{H}/k^{D})^{E}_{corr}$ resulting from deuterating both the ligands and the surrounding solvent. It is seen that in every case $(k^{H}/k^{D})^{E}_{corr} > 1$.

Nearly all the reactions listed in Tables 6 and 7 are believed to occur via outer-sphere mechanisms.^{23,33} The one exception is the reduction of $Cr(NH_3)_5NCS^{2+}$, which probably occurs via a thiocyanate-bridged pathway.³³ It is interesting to note that there were virtually no variations in a_{app} observed for a given system as a result of deuteration of either the ligands or the solvent, at least within the experimental reproducibility of a_{app} ($\pm 0.01-0.02$). The notable exception is $Co(NH_3)_5OH^{2+}$ reduction, which exhibits significantly smaller values of a_{app} in D_2O than in H_2O . Unfortunately, basic solutions (pH 9) were required for this reactant in order to suppress the protonation of the hydroxo ligand; this prevented the separate study of primary and secondary effects since the ammine hydrogens are rapidly exchanged with the solvent under these conditions.¹⁰⁵

The diffusion coefficients D obtained from the polarographic limiting currents were generally smaller for a given complex in D_2^0 than in H_2^0 . The diffusion coefficient ratios $D^{H_2^0}/D^{D_2^0}$ were typically 1.35 ± 0.05 for M_{aq}^{3+} complexes and 1.2-1.25 for Co(III) and Cr(III) ammine complexes. Deuterated ammine complexes also exhibited significantly (3-8%) smaller diffusion coefficients than the corresponding protonated complexes in both H_2^0 and D_2^0 . The observed $D^{H_2^0/D^{D_2^0}}$ ratios are roughly consistent with the higher viscosity of D_2^0 (1.107 cP) compared to H_2^0 (0.8903 cP):¹⁰⁸ inserting this viscosity ratio into the Stokes-Einstein equation¹⁰⁹ yields $D^{H_2^0/D^{D_2^0}} = 1.24_3$.

DISCUSSION

Interpretation of observed isotopic rate ratios

In order to interpret the substantial kinetic isotope effects presented in Tables 4-7, it is useful at the outset to consider the fundamental significance of the isotopic rate ratios $(k^{H}/k^{D})_{corr}^{E}$ and $(k^{H}_{s}/k^{D}_{s})_{corr}$.

Consider the generalized electrochemical reaction

$$ox + e^{-}(\phi_{m}) = red \qquad (15)$$

We can express the free energies of the thermodynamic states prior to, and following, electron transfer (labeled states I and II, respectively) as¹¹⁰

$$G_{I}^{O} = \overline{G}_{OX}^{O} + \mu_{e}^{O} - F \phi_{m}$$
(16)

$$G_{II}^{O} = \overline{G}_{red}^{O}$$
(17)

where \bar{G}_{0x}^{O} and \bar{G}_{red}^{O} are the partial molal free energies of the oxidized and reduced species, respectively, and μ_{e}^{O} - is the chemical potential of the reacting electron. Since the overall free energy of reaction $\Delta G^{O}(=G_{11}^{O}-G_{1}^{O})$ for eqn. (15) will by definition equal zero when $\phi_{m} = \phi_{m}^{O}$ (the standard Galvani potential corresponding to the experimental formal potential for the redox couple), then

$$\bar{G}_{red}^{o} - \bar{G}_{ox}^{o} = -F\phi_{m}^{o}$$
(18)

Although neither absolute nor even relative values of ϕ_m^{O} in

different solvents are strictly thermodynamically accessible quantities, as noted above the electrochemical cell arrangement used here allows the measured differences in formal potentials in D₂O and H₂O, ΔE_f^{D-H} , to be equated to a very good approximation (±1 mV.) with corresponding difference in ϕ_m^o , ($\Delta \phi_m^o$)^{D-H}, between the two solvents. Therefore, from eqn. (18) we can evaluate the difference in ($\bar{G}_{red}^o - \bar{G}_{ox}^o$) between D₂O and H₂O, $\Delta (\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H}$, using (eqn. (15) of ref. 104)

$$\Delta (\bar{g}_{red}^{o} - \bar{g}_{ox}^{o})^{D-H} = -F \Delta E_{f}^{D-H}$$
(19)

An analogous relationship for kinetic isotope effects can also be derived by noting that the activation free energy corrected for double-layer effects $\Delta G_{corr}^{\dagger} = G_{corr}^{\dagger} - G_{l}^{\circ}$ can be separated into a potential-dependent ("electrical") part $(G_{corr}^{\dagger} - G_{l}^{\circ})_{e}$ and a potential-independent ("chemical") part $(G_{corr}^{\dagger} - G_{l}^{\circ})_{c}$.²⁷ The former component is related²⁷ to the potential-dependent part of ΔG° , $(G_{ll}^{\circ} - G_{l}^{\circ})_{e}$, by

$$(G_{corr}^{\dagger} - G_{I}^{o})_{e} = \alpha_{corr}(G_{II}^{o} - G_{I}^{o})_{e}$$
(20)

Although equivalent to the corresponding relations given in ref. 110, eqn. (20) differs in that the transition-state free energy used here is presumed to be corrected for the effect of the ionic double-layer, so that the free energies of the <u>bulk</u> reactant and product ground states appear in eqn. (20), rather than those for the corresponding states within the double layer.¹¹⁰ Since from eqns. (16) and (17), $(G_{11}^{\circ} - G_{1}^{\circ})_{e} = F \phi_{m}^{\circ}$, then

 $(G_{corr}^{\dagger} - G_{I}^{o})_{e} = \alpha_{corr}^{F\phi}$ (21)

The isotopic rate ratio $(k^{H}/k^{D})_{corr}^{E}$ can be expressed in terms of the corresponding activation free energies for the same reaction in D₂O and H₂O as

$$RTln(k^{H}/k^{D})_{corr}^{E} = (\Delta G_{corr}^{\dagger})^{D} - (\Delta G_{corr}^{\dagger})^{H}$$
(22)

Since the condition of constant E also essentially maintains constancy of ϕ_m^{-} , we can write

$$RTln(k^{H}/k^{D})_{corr}^{E} = (G_{corr}^{\dagger} - G_{I}^{o})_{c}^{D} - (G_{corr}^{\dagger} - G_{I}^{o})_{c}^{H}$$
(23)
$$= \Delta(G_{corr}^{\dagger} - \overline{G}_{ox}^{o})_{c}^{D-H}$$

where the subscript "c" again refers to the potential-independent part of G_{corr}^{\dagger} . The rate ratios $(k^{H}/k^{D})_{corr}^{E}$ [or the constituent ratio $(k^{H}2^{0}/k^{D}2^{0})_{corr}^{E}$] therefore provides a measure of the influence of solvent deuteration upon the relative stabilities of the reacting species within the reactant and activated states.

The significance of the rate ratio (k_s^H/k_s^D) can be seen by noting that for cathodic reactions

$$lnk_{corr}^{E} = ln(k_{s})_{corr} - \alpha_{corr}f(E-E_{f})$$
(24)

so that

$$\ln(k^{H}/k^{D})_{corr}^{E} = \ln(k_{s}^{H}/k_{s}^{D})_{corr} - \alpha_{corr}f^{\Delta} E_{f}^{D-H}$$
(25)

By combining eqns. (19), (23), and (25), we obtain

$$RTln(k^{H}/k^{D})_{corr}^{E} = \Delta(G_{corr}^{\ddagger} - \bar{G}_{ox}^{o})_{c}^{D-H} \propto_{corr} \Delta(\bar{G}_{red}^{o} - \bar{G}_{ox}^{o})^{D-H} (26)$$

The first and second terms on the right-hand side of eqn. (24) constitute the so-called "intrinsic" and "thermodynamic" contributions to the overall redox reactivity.^{8,111,112} Thus $(k_s)_{corr}$ is related to the intrinsic electrochemical free energy of activation ΔG_{ie}^{\dagger} by -RTin $[(k_s)_{corr}/Z^e] = \Delta G_{ie}^{\dagger}$. (Z^e is the electrochemical collision frequency.) This intrinsic barrier ΔG_{ie}^{\dagger} (labeled $\lambda^{el}/4$ in the Marcus treatment¹¹³) is equal to the work-corrected free energy activation when the ground states immediately preceding and succeeding the transition state have equal free energies.^{8,111-113} The rate ratio $(k_s^H/k_s^D)_{corr}$ therefore provides a measure of the change in the intrinsic barriers resulting from isotopic substitution, i.e.,

$$RTln(k_{s}^{H}/k_{s}^{D})_{corr} = (\Delta G_{ie}^{\dagger})^{D} - (\Delta G_{ie}^{\dagger})^{H}$$
(27)

From the form of eqn. (26) it is seen that $(k_s^H/k_s^D)_{corr}$ will equal unity when

$$\Delta (\mathbf{G}_{\text{corr}}^{\dagger} - \bar{\mathbf{G}}_{\text{ox}}^{\mathbf{o}})_{\text{c}}^{\mathbf{D}-\mathbf{H}} = \alpha_{\text{corr}} \Delta (\bar{\mathbf{G}}_{\text{red}}^{\mathbf{o}} - \bar{\mathbf{G}}_{\text{ox}}^{\mathbf{o}})^{\mathbf{D}-\mathbf{H}}$$

i.e., when the change in the potential-independent part of the transition-state free energy $(\Delta G_{corr}^{\dagger})^{D-H}$ is equal to that expected for a (hypothetical) stable species having a structure and charge appropriately intermediate between ox and red. Therefore values of (k_s^H/k_s^D) differing from unity result from changes in G_{corr}^{\dagger} upon isotopic substitution that are not reflected in corresponding changes in \overline{G}_{ox}^{O} and \overline{G}_{red}^{O} , i.e., are unique ("intrinsic") to the transition state.

The observation that $(k_s^H/k_s^D)_{corr}^E \simeq 1$ for the aquo couples (Table 4) arises from an approximate compensation between the intrinsic and thermodynamic contributions (eqn. (25)) inasmuch as $(k_s^H/k_s^D)_{corr}^E > 1$ and $\Delta E_f^{D-H} < 0$ for each of these reactions (Table 5). The latter result indicates that $\Delta (\bar{g}_{red}^O - \bar{g}_{ox}^O)^{D-H}$ is negative (eqn. (19)) [e.g. for $Cr_{aq}^{3+/2+}$, $\Delta (\bar{g}_{red}^O - \bar{g}_{ox}^O)^{D-H}$ is -1.3 kcal/mole]. This finding has been interpreted in terms of the relative destabilization of the oxidized species M_{aq}^{3+} in D_2^{0} resulting not only from deuteration of inner-shell water molecules but also from the greater "solvent-ordering" tendency¹¹⁴ of M_{aq}^{3+} in D_2^{0} compared to H_2^{0} .¹⁰⁴ Evidence supporting this latter contention includes the especially large values of reaction entropies ΔS_{rc}^{0} for these $M_{aq}^{3+/2+}$ couples;¹¹ this result probably arises from hydrogen bonding between the M_{aq}^{3+} aquo ligands which is partly dissipated when the cation is reduced to M_{aq}^{2+} . A significantly larger value of ΔS_{rc}^{0} for $Fe_{aq}^{3+/2+}$ is observed in D_2^{0} (45.4 e.u., μ =0.2) than in H_2^{0} (43.2 e.u.)¹⁰⁴ which is consistent with the expected greater extent of hydrogen bonding in D_2^{0} and H_2^{0} .¹⁰⁴

The observation that $(k_s^H/k_s^D)_{corr} > 1$ for each of the four aquo couples given in Table 5 indicates that the intrinsic barriers for these reactions are significantly larger in D₂O than in H₂O (eqn (27)). In particular, for $Cr_{aq}^{3+/2+}$, $[(\Delta G_{1e}^+)^D - (\Delta G_{1e}^+)^H]$ is 0.7 kcal/mole. The intrinsic barrier is usually separated into an "inner-shell" component $(\Delta G_{1e}^+)_{1s}$ arising from intramolecular reactant reorganization (particularly from changes in metal-ligand bond lengths), and an "outer-shell" component $(\Delta G_{1e}^+)_{os}$ arising from reorganization of the surrounding solvent.¹¹³ The observed values of $(k_s^H/k_s^D)_{corr}$ may arise from either or both of these contributions. Thus the stretching of the metal-oxygen bonds that is required in order for the tripositive aquo cations M_{aq}^{3+} to accept an electron to form the corresponding M_{aq}^{2+} species may well require significantly greater energy when the oxygen is bound to deuterium rather than to hydrogen as a result of coupling between the vibrations of the M-O and O-H (or O-D) bonds. By taking such inner-shell contributions into account, Newton^{115,116} has calculated that the ratio of the rate constants (k_h^H/k_h^D) for homogeneous $Fe_{aq}^{3+/2+}$ self-exchange in H₂O and D₂O would be no greater than 1.15. Since the inner-shell contribution to the intrinsic barrier for homogeneous self-exchange is generally predicted to be twice that for the corresponding electrochemical exchange reaction¹¹³ (<u>vide infra</u>), it follows that the corresponding prediction for electrochemical $Fe_{aq}^{3+/2+}$ exchange is $(k_s^H/k_s^D)_{corr}$ is about (1.15)^{1/2} or 1.07.

It therefore seems quite likely that the markedly larger observed value of (k_s^H/k_s^D) seen for $Fe_{aq}^{3+/2+}$ (ca. 1.5, Table 5) is at least partly due to contributions from water molecules beyond the primary coordination sphere. In view of the close similarity in the change in metal-oxygen bond distances $\Delta \bar{a}$ for Fe_{aq}^{2+} versus $Fe_{aq}^{3+}(\bar{a}=0.14\ \text{Å})$ and V_{aq}^{2+} versus $V_{aq}^{3+}(\Delta \bar{a}=0.15\ \text{Å})^{35}$ together with the involvement of a t_{2g} electron in both $Fe_{aq}^{3+/2+}$ and $V_{aq}^{3+/2+}$ exchange reactions, it seems likely that such a calculation for $V_{aq}^{3+/2+}$ would also yield $(k_s^H/k_s^D)_{corr} \cong 1.0-1.1$, in contrast to the observed value of 1.5.

The simplest approach to the estimation of the outer-shell contribution (ΔG_{ie}^{\dagger}) involves treating the surrounding solvent as a dielectric continuum.³¹ By inserting the known values¹⁰⁸ of the optical and static dielectric constants ε_{op} and ε_{s} for liquid H₂0 [ε_{op} = (refractive index)² = 1.777, ε_{s} = 78.3] and liquid D₂0 at 25°C (ε_{op} = 1.764, ε_{s} = 77.95) into the relationship for (ΔG_{ie}^{\dagger}) derived by Marcus (eqn. (90) of ref. 113) leads via eqn. (27) to the prediction that $(k_s^H/k_s^D)_{corr} = 1.06$ (using the typical reactant radius of 3.5 Å and a reactant-electrode distance of 7 Å).

Consequently this dielectric-continuum model for the solvent is also unable to explain the observed values of $(k_s^H/k_s^D)_{corr}$. However, it seems feasible that the substantial differences in <u>short-range</u> solvent polarization between the oxidized and reduced forms of the $M_{aq}^{3+/2+}$ couples could provide a much larger contribution to the increased intrinsic barriers in D_2^0 . Thus the formation from M_{aq}^{2+} of the transition state in D_2^0 is expected to involve a greater increase in the extent of solvent ordering induced by hydrogen bonding compared with the corresponding process in H_2^0 . Similarly, the formation of the transition state from M_{aq}^{3+} will require a greater dissipation of this hydrogen-bonded solvent in D_2^0 than in H_2^0 . These differences will not affect the intrinsic barrier if

$$\Delta(\mathbf{G}_{corr}^{\mathsf{T}} - \bar{\mathbf{G}}_{ox}^{\mathsf{O}})^{\mathsf{D}-\mathsf{H}} = \alpha_{corr} \Delta(\bar{\mathbf{G}}_{red}^{\mathsf{O}} - \bar{\mathbf{G}}_{ox}^{\mathsf{O}})^{\mathsf{D}-\mathsf{H}} (cf. eqn. (26))$$

i.e., when the isotope influence upon the transition-state stability is that expected for a cation with a structure identical to that of the transition state but having the charge $(3-\alpha_{\rm corr})$. However, in actuality the transition state is reached via the reorganization of nuclear coordinates while the reactant charge <u>remains fixed</u>, the electron transfer occurring rapidly ($\simeq 10^{-16}$ sec) once the transition state is formed.¹¹³ The solvent reorientation required for transition-state formation will therefore be unaided by concomitant variations in the cation charge so that the required solvent structural changes should involve an additional component of the activation energy which will form part of the intrinsic barrier. Consequently, the larger structural differences between M_{aq}^{3+} and M_{aq}^{2+} in D_2^{0} compared with those in H_2^{0} are also expected to yield larger intrinsic barriers in D_2^{0} , in harmony with the experimental results. However, it is difficult to estimate quantitatively the magnitude of this contribution.

It is interesting to note that the magnitude of $(k_s^{H}/k_s^{D})_{corr}$ for $Cr_{aq}^{3+/2+}$ (2.8) is substantially larger than for the other two hexacoordinate aquo couples $Fe_{aq}^{3+/2+}$ and $V_{aq}^{3+/2+}$ [≈ 1.5 (Table 5)]. This difference parallels the markedly larger values of both ΔS_{rc} and ΔE_f^{D-H} observed for $Cr_{aq}^{3+/2+}$ (50 e.u. and 55 mV, $\mu = 0.1$) compared with $Fe_{aq}^{3+/2+}$ (43 e.u. and 43 mV.) and $V_{aq}^{3+/2+}$ (37 e.u., 33 mV.).^{11,104} These correlations are compatible with the notion that an important component of the observed values of $(k_s^{H}/k_s^{D})_{corr}$ arises from specific solvent polarization. However, the intrinsic barrier to $Cr_{aq}^{3+/2+}$ exchange should also contain the largest innershell contribution since in this case the electron is transferred into an e_g orbital; at least part of the especially large value of $(k_s^{H}/k_s^{D})_{corr}$ for this couple may arise from this source.

It remains to rationalize the sizable isotope effects seen for the reduction of the Co(III) and Cr(III) amine complexes that are summarized in Tables 6 and 7. Since $\triangle E_f^{D-H}$ values for these reactions are unknown (except for Co(en) $\frac{3^{+/2^{+}}}{3}$), it is not possible to make a complete experimental separation of the observed values of $(k^{NH}/k^{ND})_{corr}^{E}$ and $(k^{H}2^{0}/k^{D}2^{0})_{corr}^{E}$ into intrinsic and thermodynamic factors (eqn. (24)). Nevertheless, approximate limits can be placed on ΔE_f^{D-H} which allow the intrinsic part to be estimated.

The effects upon E_f of deuterating separately the ligands and the solvent have been examined 104 for Ru(111)/(11) amine couples that are structurally similar to the Co(III) and Cr(III) reactants considered here; the inertness of both Ru(II) and Ru(III) to substitution allows E_{ϵ} to be evaluated accurately using cyclic voltammetry.¹⁰⁴ Deuteration of the ligands was found to have only a very small effect upon $E_f (\Delta E_f^{ND-NH} \le 2 \text{ mV}^{104})$; deuteration of the solvent also yielded small positive shifts in $E_{f} (\Delta E_{f}^{D} 2^{0-H} 2^{0})$ is less than 10 mV 104). The net effect of deuterating both the ligands and the solvent, $\Delta E_f^{D-H} \leq 10 \text{ mV}$, is therefore typically smaller than for $M_{aq}^{3+/2+}$ couples. This behavioral difference is probably due to the apparently smaller solvent "structuremaking" ability of tripositive ammine complexes compared with otherwise similar aquo species,³³ presumably arising from the smaller tendency of the less acidic ammine hydrogens to engage in hydrogen bonding with surrounding water molecules.¹¹

It is quite likely that the (experimentally inaccessible) behavior of the Co(III)/(II) and Cr(III)/(II) amine couples is not greatly different from that for the corresponding Ru(III)/(II) couples. A clue to the probable values of ΔE_f^{ND-NH} for (Co(III)/(II) ammines is given by the observation¹¹⁸ that the deuteration of the ammine ligands increases the equilibrium constant for the dissociation reaction

$$Co(NH_3)_5OD_2^{3+} + D_2O = Co(NH_3)_5OD^{2+} + D_3O^+$$

in D_20 by a factor of 1.3. This finding can be rationalized

by the greater decrease in the zero-point vibrational energy¹¹⁹ of the N-D bonds compared with the weaker¹¹⁸ N-H bonds in the conjugate base resulting from its smaller cationic charge.^{120,121} A similar charge effect upon the redox thermodynamics of Co(111)/(11) ammine complexes is therefore expected; a corresponding change in the relative stability of the oxidized and reduced forms leads to the estimate $\Delta E_f^{ND-NH} \approx 7 \text{ mV}$. In any event, it seems very likely that the values of ΔE_f^{ND-NH} for the Co(111)/(11) ammine and ethylenediamine couples and probably also the Cr(111)/(11) couples are small and positive. Therefore from eqn (18), the values of $(k^{NH}/k^{ND})_{corr}^{E}$ greater than unity observed for these reactions are probably associated with still larger values of $(k_s^{NH}/k_s^{ND})_{corr}^{E}$. For example, if $\Delta E_f^{ND-NH} = 7 \text{ mV}$ for Co(NH₃)^{3+/2+}, then since $(k^{NH}/k^N)_{corr}^{E} \approx 2.0$ in both H₂0 and D₂0 (Table 6) and $\alpha_{corr}^{c} = 0.5^{13}$, from eqn (19) $(k_s^H/k_s^N)_{corr}^{c} \approx 2.3$.

It therefore appears that deuteration of amine ligands yields noticeable increases in the intrinsic electrochemical barrier for Co(111)/(11) and Cr(111)/(11). This effect probably is at least in part an inner-shell effect arising from coupling between the symmetrical M-N stretching vibration and the stretching and bending modes of the N-H (or N-D) bonds.¹¹⁶ (Such coupling has been estimated theoretically to be much stronger than that between M-O and O-H bonds in aquo complexes¹¹⁶). Additionally, there may be a contribution to $(k_s^H/k_s^D)_{corr}$ from the expected greater interaction between the ammine hydrogens and solvating water molecules when the former are deuterated (see below). However, this latter contribution is likely to be less significant than for aquo couples in view of the apparently weaker ligand-solvent interactions for the ammine complexes. ¹⁰⁴

Since the effect of separate deuteration of the solvent upon the Co(III) and Cr(III) amine reduction rates yields values of $(k^{H_20}/k^{D_20})^{E}_{corr}$ that are less than unity (Tables 6 and 7), given that the values of $\Delta E_f^{D_2 0-H_2 0}$ are probably small and positive it is quite possible that this thermodynamic factor could account partly or even entirely for the observed isotope effect (eqn. (18)). Thus since $(k^{H_20}/k^{D_20})^{E}_{corr}$ is about 0.7 for $Co(NH_3)^{3+}_{6}$ and $Co(ND_3)^{3+}_{6}$ reduction (Table 6), if for example $\Delta E_f^{D_2 O-H_2 O}$ is 20 mV, then from eqn. (19) $(k_s^{H_20}/k_s^{D_20})_{corr} \approx 1.0$. Although there are several factors that could produce larger intrinsic barriers in D_2O compared with H_2^0 solvent $[(k_s^{H_2^0}/k_s^{D_2^0})_{corr} > 1]$, the opposite situation is unexpected and would be without an obvious explanation. It therefore seems most likely that the values of $\Delta E_f^{D_2 0-H_2 0}$ for the (Co(111)/(11)) and Cr(111)/(11) amine couples are sufficiently large (ca. 10-20 mV) so to offset the observed values of $(k^{H_20}/k^{D_20})^{E}_{corr}$ yielding $(k_s^{H_20}/k_s^{D_20})_{corr} \simeq 1$ (eqn. (18)). In any case, the observation of non-unit values of $(k^{H_20}/k^{D_20})^{E}_{corr}$ is intriguing. Since the interactions between the ammine hydrogens and the oxygen of the solvating water molecules should be very similar in H_20 and $D_{2}O$, this result suggests that there are significant differences in the long-range solvent polarization induced by the ammine reactants in H_2^0 and D_2^0 . These differences are likely due to "specific" (hydrogen-bonding) differences between these solvents; the Born model predicts only negligible (< 0.5 mV) values of $^{\Delta} E_{f}^{D} 2^{O-H} 2^{O}$ since the dielectric constants of liquid H₂O and D_2^{0} are almost identical (78.3 and 77.95, respectively, at 25°C¹⁰⁸).

The equal value of α_{app} observed in H₂0 and D₂0 for each of the electrode reactions, except for $Co(NH_3)_5 0H^{2+}$ reduction, indicates that the position of the reaction site in the interphase 14 is normally unaffected by isotopic substitution. The origin of the smaller value of α_{app} observed for Co(NH₃)₅0H²⁺ reduction in D_20 compared to that in H_20 (Table 6) may well be the same as that responsible for the anomolously small values of α_{ann} for this reaction in ${\rm H_20}$ which have been found to increase with increasing temperature. This latter result has been attributed to stabilizing hydrogen bonding between the oxygen of the hydroxo ligand and the inner-layer water molecules which diminishes as the electrode potential becomes more negative due to the tendency of the inner-layer water to become polarized with the hydrogens pointing towards the metal under these conditions.⁸⁹ This effect is expected to diminish with increasing temperature since the extent of hydrogen bonding should then decrease. On the other hand, the substitution of D_20 for H_20 should increase the extent of hydrogen bonding at a given temperature, in harmony with the observed smaller value of α_{add} in 0.0 at 25° C. Comparisons between isotope effects for corresponding electrochemical

and homogeneous reactions.

The foregoing suggests that a substantial part of the rate changes observed upon replacing hydrogen with deuterium in the reactant's coordination sphere as well as the surrounding solvent can arise from the influence of water molecules beyond the coordination sphere, i.e., from secondary as well as primary isotope effects. Additional evidence favoring such an interpretation is obtained by comparing the isotope effects for corresponding electrochemical and homogeneous reactions. By assuming that the reorganizational barriers consist of independent, additive contributions from each reactant, it has been shown that^{113,122}

$$(k_{s}^{e}/Z^{e}) = (k_{ox}^{h}/Z^{h})^{\frac{1}{2}}$$
 (28)

where k_s^e and k_{ox}^h are the (work-corrected) rate constants for the electrochemical and homogeneous exchange reactions involving a given redox couple, and Z^h is the homogeneous collision frequency.

It has recently been shown 123,124 that eqn. (28) can be generalized to include heteronuclear (cross-) reactions, expressed by

$$(k_{s}^{e}/Z^{e}) = (k_{12}^{h}/Z^{h})^{\frac{1}{2}}$$
 (29)

where k_{12}^{h} is the rate constant for the homogeneous cross-reaction, and where k_{12}^{e} is the rate constant at the intersection of the (double-layer corrected) cathodic and anodic Tafel plots for the two constituent electrochemical reactions. Eqn. (29) has been found to be in approximate accordance with experimental rate data for various ammine and aquo couples, although significant behavioral differences between these two reactant types were observed.¹²⁴ From eqn. (29), the following predicted relationship between the isotope effects for corresponding electrochemical and homogeneous reactions is obtained:

$$(k_{12}^{H}/k_{12}^{D})_{corr}^{e} = [(k_{12}^{H}/k_{12}^{D})_{corr}^{h}]^{\frac{1}{2}}$$
 (30)

Table 8 contains comparisons between $(k_{12}^{H}/k_{12}^{D})_{corr}^{e}$ and $(k_{12}^{H}/k_{12}^{D})_{corr}^{h}$ resulting from solvent deuteration for four redox reactions involving Co(III) ammines and aquo complexes. The electrochemical rate ratios were obtained from the rate constants at the intersection

Table 8.	Comparison of Solvent Isotope E	ffects	for	Corresponding
	Electrochemical and Homogeneous	Reacti	ons	•

	1	2
Reactant Pair	(k <mark>H</mark> /kD)e (k12/k12)corr	(k ^H /k ^D)h 12 ^{/k} 12 ⁾ corr
$Co(NH_3)_6^{3+} - Cr_{aq}^{2+}$	1.9	1.3 ³
$Co(NH_3)_6^{3+} - V_{aq}^{2+}$	3.0	1.7 ³
$Co(NH_3)_5 OH_2^{3+} - V_{ag}^{2+}$	2.4	2.6 ³
$Fe_{aq}^{3+} - Fe_{aq}^{2+}$	1.6	2 4

¹Ratio of rate constants at the intersection of the (cathodic and anodic) Tafel plots for the constituent electrochemical half-reactions obtained in H_20 and D_20 using acidified 0.4 <u>M</u> KPF₆ as supporting electrolyte (see text and refs. 123 and 124), after correction for double-layer effects using eqn (5) as indicated in the text.

 2 Ratio of rate constants for listed homogeneous rection in H₂0 to that in D₂0 in same supporting electrolyte, from literature source indicated.

³ref. 103.

⁴ref. 101.

in 0.4 \underline{M} KPF₆; the (small) double-layer corrections were applied as outlined above. The homogeneous rate ratios were taken from the literature as indicated (note that the work terms are expected to cancel in such homogeneous rate ratios if the same supporting electrolyte is used in D_20 and H_20). Contributions to these rate ratios arise from differences in thermodynamic as well as intrinsic factors in H_20 and D_20 .¹⁰ In contrast to the prediction of eqn (30), it is seen from Table 8 that $(k_{12}^{H}/k_{12}^{D})_{corr}^{e} \ge (k_{12}^{H}/k_{12}^{D})_{corr}^{h}$. It is expected that eqn (30) would apply if the solvent isotope effect arises solely from changes in the inner-shell reorganization energy since this contribution should be insensitive to the surrounding environment. The unexpectedly larger electrochemical rate ratios implicate the involvement of surrounding (outer-shell) water molecules. Given that the cationic complexes in Table 8 undoubtedly exert a substantial influence on the structure of the surrounding solvent, it would be expected that V_{aa}^{2+} , for example, would experience a significantly different solvent environment when involved in a homogeneous electron-transfer reaction with $Co(NH_3)_6^{3+}$ compared with its environment at the mercury-aqueous interface. This difference could account for the markedly larger value of $(k_{12}^{H}/k_{12}^{D})_{corr}^{e}$ (3.0) compared with $(k_{12}^{H}/k_{12}^{D})_{corr}^{h}$ (1.7) for this reaction (Table 8) inasmuch as the surrounding solvent structure (the extent of hydrogen bonding, etc.) could be quite different in the two environments.

It has been pointed out that no significant solvent isotope effect has been observed upon the rates of homogeneous outersphere processes for reactants that do not contain coordinated water.⁹⁶ This finding has been used to support the contention that the often large isotope effects observed for reactions involving aquo complexes are chiefly or even entirely due to deuteration of the aquo ligands.⁹⁶ However, only two homogeneous reactions involving reactants not containing replaceable protons appear to have been studied: $Co(NH_3)_6^{3+} + Cr(bpy)_3^{2+}$, and $Co(phen)_3^{3+/2+}$ self-exchange.⁹⁶ The significant solvent isotope effects observed for the electrochemical kinetics of ammine and ethylenediamine complexes (Tables 6 and 7), illustrate the more general occurrence of this effect beyond aquo complexes.

It is interesting to note that deuteration of the ammine ligands yields sizable decreases in the rates of electrochemical and homogeneous processes involving $Co(NH_3)_6^{3+}$ or $Co(NH_3)_5OH_2^{3+}$ in either H₂O or D₂O. Thus $Co(NH_3)_6^{3+}$ reacts a factor of 2.3 times slower than $Co(NH_3)_6^{3+}$ at a given electrode potential (Table 6) and a factor of 1.35 times slower for its homogeneous reduction by $Cr(bpy)_3^{2+}$.¹⁰² However, again the relative electrochemical and homogeneous isotope effects differ from expectations since equal rate decreases are predicted theoretically under those conditions.¹¹³ This discrepancy between theory and experiment may again be due to an environmental solvent effect arising from the difference in the interactions between NH₃ and ND₃ ligands and surrounding water molecules.

CONCLUSIONS

Taken together, the foregoing results provide fairly convincing of the Tafel plots for the constituent half-reactions obtained evidence that the deuteration of solvating water molecules can induce substantial changes in the electrochemical kinetics as well as thermodynamics of transition-metal aquo, ammine, and ethylenediamine redox couples. As such, they furnish an illustration of the limitations of the conventional dielectric-continuum model in describing the role of the surrounding solvent in the activation process leading to electron transfer and suggest that an additional component of the activation barrier may arise from extensive changes in short-range solvent polarization associated with the formation and fission of hydrogen bonds. Since there is reason to believe that 0...D hydrogen bonds in D_20 are significantly ($\simeq 0.25$ kcal/mole), stronger as well as more extensive than 0...H bonds 16,125 in H₂0, larger intrinsic barriers in D₂0 would generally be expected for redox couples whenever the electron transfer entails an alteration in the hydrogen-bonded structure of the surrounding solvent. The present approach of employing electrochemical cells where both the kinetic and thermodynamic parameters in D_20 and H_20 can be compared at a constant Galvani potential (constant free energy of the reacting electron) provides additional experimental information beyond that which is accessible to homogeneous redox systems, and illustrates the virtues of electrochemical systems in exploring the fundamental influences of the solvent upon redox processes.

CHAPTER VI. THE UTILITY OF PULSE-POLAROGRAPHIC ANALYSIS TECHNIQUES IN THE ASSESSMENT OF ELECTROCHEMICAL KINETIC PARAMETERS FROM TOTALLY IRREVERSIBLE CHRONOAMPEROMETRIC TRANSIENTS

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INTRODUCTION

The analysis of the current transients which result from potential-step perturbations is a well-established route to the determination of heterogeneous charge-transfer rate parameters. Both chronoamperometric¹²⁶ and normal pulse-polarographic^{84,127} data-analysis methods have been utilized. The former analysis considers the dependence at a fixed potential of current upon the time following the application of the potential step (i-t plane), whereas the latter analysis is concerned with the variation with potential-step amplitude of the current at a constant time into the pulse (i-E plane). Figure 21 illustrates the bailiwick of each analysis technique on the current-time-potential surface. These large-amplitude methods are particularly suitable for assessing rate information as a function of overpotential, including that for reactions which are totally irreversible from a chemical as well as electrochemical standpoint. A major preoccupation in our laboratory is the acquisition of quantitative rate data, often for irreversible electrode reactions, at solid and mercury electrodes over wide ranges of overpotential and hence rate constants. These studies are performed in order to probe correlations between electrochemical reactivity and surface structure. Since we frequently utilize potential-step techniques for this purpose, we have been concerned with establishing clearly the experimental upper limits to the magnitude of the rate constant that can be reliably evaluated.

Although the question of the measurability of large standard rate constants (i.e. for chemically reversible redox couples at small overpotentials) has been extensively considered, the





equally important question of the measurability of rapid rate constants when the reverse reaction rate is negligible (i.e. at large overpotentials) has been relatively neglected. Regardless of the analysis method employed, it is neccessary for this purpose to ascertain from empirical evidence a minimum time following the potential step for which the mathematical analysis used is valid inasmuch as the extent of kinetic information will generally be greater at shorter times. 84,126 Although the analysis of individual current-time curves has been most commonly employed, we have preferred to employ a pulse-polarographic readout, i.e. to display the current at a fixed time following the potential step as a function of the step size. The immediate advantage of this approach is that the simple explicit mathematical analysis due to Oldham and Parry 84 can be utilized. In contrast, the mathematical analysis of chronoamperometric transients is complicated when the rate constants become large. ¹²⁶ Moreover, chronoamperometric transients demonstrate an essentially featureless decay of current. One is less likely to observe consequences of nonidealities of the experimental potential-control and current-measurement equipment in a collection of current-time curves measured in response to various potential steps than in the ensemble of pulse polarograms which can be generated from the same data. Although some attempts have recently been made to account for the effect of potentiostat nonidealities upon chronoamperometric transients, ^{128,129} they are approximate at best. Quantitative calculations have apparently been limited to small-amplitude steps.¹²⁸

We have utilized a microcomputer-based electrochemical data acquisition and analysis system to gather extensive current-timepotential data for irreversible electrode reactions in order to make a direct comparison of the effectiveness of pulse-polarographic and chronoamperometric data analysis methods for reliably evaluating rapid rate constants. In this chapter experimental results are reported for the one-electron reductions of $Cr(0H_2)_6^{3+}$ and $Co(NH_3)_F^{2+}$ at the mercury-aqueous interface. These reactions were chosen since they are mechanistically simple, following outer-sphere pathways in concentrated fluoride of perchlorate electrolytes. In these solutions, the reactant is either not adsorbed or only slightly adsorbed at the reaction plane via the influence of the diffuse layer. 22,23,32 We also compare the experimental data with the results of digital simulations of the distortion in current-potential-time data arising both from reactant adsorption and from nonidealities in the potential-step waveform. These results illustrate the importance of such effects in determining the upper limit to the rate constants that can be reliably evaluated and demonstrate the important advantages of pulse-polarographic readout for diagnosing, by simple means, the presence of these effects.

EXPERIMENTAL

Reagents

All solutions were prepared in distilled water which was deionized by a "Milli-Q" water-purification system (Millipore Corporation). Solutions of 1 \underline{M} KF supporting electrolyte were prepared by dissolution of recrystallized salt; solutions of

1 <u>M</u> NaClO₄ were made by diluting a stock solution which resulted from neutralizing concentrated perchloric acid with solid sodium carbonate. Solid $[Co(NH_3)_5F](ClO_4)_2$ was synthesized as described previously. ¹³⁰ Stock solutions of acidified Cr(III) perchlorate were obtained by reducing CrO₃ with excess hydrogen peroxide in perchloric acid.³²

All potentials are quoted relative to a NaCl-saturated calomel reference electrode. This electrode has a potential in contact with 1 <u>M</u> electrolytes which is 5 mV more negative than the conventional s.c.e. The flow rate of the dropping mercury electrode (dme) employed for these measurements was 1.3 mg/sec.

Measurement System

The electrochemical measurements were performed with a conventionally designed three-electrode potentiostat¹³¹ whose control amplifier is capable of providing ± 100 V at 1 A. For the more sensitive ranges (cell current below 1 mA), the current-to-voltage converter (IEC) is a low-bias, high-speed (18 MHz gain-bandwidth product) operational amplifier. A slightly slower (4 MHz) amplifier is used in conjunction with an emitter-follower Darlington buffer for larger cell currents. The stability of the IEC in response to the charging-current transient was improved considerably by the simple expedient of placing in the feedback loop of the IEC back-to-back low-leakage zener diodes the sum of whose reverse-breakdown voltage (V_z) and forward-bias voltage (V_f) were less than the supply voltage.¹³³ This IEC is represented schematically in Figure 22. Whereas a large potential step applied to the cell could cause the basic IEC to oscillate for as much



Figure 22. Transient stabilization of current-to-voltage

converter.

as a millisecond, the transient-stabillized IEC avoids oscillation by providing a feedback current through the diodes whenever the cell current was large enough to drive the IEC output to $\pm (V_f$ $\pm V_z)$. Figure 23 shows the first hundred microseconds of representative current-time responses to potential-step perturbations of various magnitudes. The measurements were made a 50-nsec intervals by a Biomation Model 820 transient recorder (Gould-Biomation Inc.). (For clarity, not all data are shown.)

The potentiostat system was placed under the control of a laboratory microcomputer which performed the functions of potential control, measurement timing, data acquisition and management, and real-time graphic display of averaged signals. Several chronoamperometric transients were sampled and digitized for each potentialstep value, averaged, and plotted in pulse-polarographic format. Background currents were measured for solutions of supporting electrolyte alone under identical conditions. Of some significance in this regard is the use of the same IEC sensitivity for solutions with and without depolarizer because of disparities at different sensitivities in amplifier offsets which result from the sight leakage current through the zener diodes. Positive-feedback iR compensation was used; its effect was slight because of the substantial (1 molar) supporting-electrolyte concentration. RESULTS

Plots in pulse-polarographic format of background-corrected chronoamperometric transients at a dme in response to potential steps from -600 mV applied to cells containing $2 \text{ mM} \text{ Cr}(0\text{H}_2)_6^{3+}$ and $2 \text{ mM} \text{ H}^+$ in $1 \text{ M} \text{ NaClO}_4$ are shown for multiples of 2 milliseconds


FIGURE 23

Figure 23. Current-time transient responses to potential steps for $Cr(OH_2)_6^{3+}$ reduction.

and 100 microseconds in Figures 24 and 25 respectively. While the expected sigmoidal shape is observed⁸⁴ for the longer time values, as the sampling time decreases below 2 msec the polarograms develop a progressively more peaked shape ("maximum"), even to the extent that a limiting-current region is not observed prior to the onset of proton reduction. On the other hand, dc polarograms for this solution at identical drop times do not show maxima.

Similar observations were made for the reduction of $Co(NH_3)_5 F^{2+}$ in neutral 1 <u>M</u> KF. Figures 26 and 27 show the background-corrected normal pulse polarograms derived from the chronoamperometric data obtained for the electroreduction of this complex. These polarograms differ from those for $Cr(0H_2)_6^{3+}$ reduction in that at a given sampling time, the size of the peak is smaller for $Co(NH_3)_5 F^{2+}$ reduction. Again, maxima are absent from dc polarograms for $Co(NH_3)_5 F^{2+}$ reduction.

Limiting-current values (i_{lim}) obtained from pulse polarograms from which maxima are absent agree quite well with the Cottrell equation. Plots of i_{lim} vs. $t^{-\frac{1}{2}}$ (where t is the time following the potential step) are linear without a systematic pattern of residuals from the regression line. The intercept of the line is not statisitcally different from zero. Extrapolation of this plot to the sampling times where the polarograms exhibit maxima produces estimates of the limiting current which are substantially less (by as much as 20%) than the experimental values.

Rate constants determined from the monotonic polarograms by the pulse-polarographic technique 84 agree well with published values 22,23,32 and are internally consistent in that polarograms



FIGURE 24







Figure 25. Pulse polarograms for Cr_{aq}^{3+} reduction at 0.1 msec intervals.



FIGURE 26

Figure 26. Pulse polarograms for $Co(NH_3)_5 F^{2+}$ reduction at 2 msec intervals.



FIGURE 27

Figure 27. Pulse polarograms for $Co(NH_3)_5 F^{2+}$ reduction at 0.2 msec intervals.

sampled at different times in the pulse yield essentially identical rate constants.

DISCUSSION

A Comparison of Chronoamperometric and Pulse-Polarographic Data Analyses

It could be argued that potential-step chronoamperometry and pulse polarography should produce identical rate constants because they are derived from the same set of data. However, a crucial difference between the two techniques is that they employ different groupings of the data. Chronoamperometric analysis makes use of any current-time (i-t) curve for which the currents are less than their counterparts measured at potentials where the reaction is diffusion-limited. As noted above, the essentially featureless morphology of the i-t curves provides no obvious clue of unexpected behavior. A pulse polarogram, on the other hand, offers a built-in diagnostic capability because the electrode behavior at a fixed time following the potential steps is shown as the reaction passes from activation control to the diffusion limit. For electrochemical systems such as $Co(NH_3)_5 F^{2+}$ reduction whose polarograms should have a predictably simple shape, then, the pulse polarogram shows at a glance whether the boundary conditions of simple theory have been satisfied when the i-t transient does not.

The factors which produce the anomalous pulse-polarographic currents (i > i_{lim}) can presumably also operate in the potential region where i < i_{lim} . The shape of the polarogram suggests to the experimenter that simple theory should not be used on these data, but no such admonition is inherent in the chronoamperometric curve. It is of interest, therefore, to compare the rate parameters derived by both techniques from the identical set of currenttime-potential data for those circumstances where the data indicate that both analyses are possible.

Some attention must be paid to the details of the chronoamperometric analysis. Rather than risk introducing artifacts into the kinetic parameters through the use of approximations to the exact equation, ^{126,127} we attempted a nonlinear regression analysis¹³⁴ based upon the explicit formalism.¹²⁶ The analysis could not be conducted successfully in large part due to difficulties in evaluation of the function

$$y(x) = \exp(x^{2})\operatorname{erfc}(x)$$
(31)

A numerical integration technique for calculating the error-function complement

$$\operatorname{erfc}(x) = 1 - \operatorname{erf}(x) = 1 - \frac{2}{\pi \frac{1}{2}} \int_{0}^{x} \exp(-u^{2}) du$$
 (32)

is of no avail for large values of the argument because a computer maintains a floating-point representation of a real number with a finite precision characteristic of the size of the number. As x increases, erf(x) approaches 1; even when multiple-precision arithmetic is employed, the significance of the digits supplied by the computer in calculating [1 - erf(x)] consequently becomes vanishingly small. The failure of this numerical-integration calculation of y(x) to agree with approximate values of y(x) determined for large x by series approximation^{36,126} (which can actually be shown to be divergent for large values of the argument) renders impossible the task of fine-tuning the rate parameters to minimize the residuals in the nonlinear regression.

Analysis can be performed in Laplace space³⁷ without such a calculational difficulty. Exponential interpolation³⁷ between data points was used in determining the Laplace transform of the experimental current-time curve. That this approximation itself produced no spurious results was evidenced by its rendering within 2% the anticipated rate constant from a set of test data which were generated by a digital simulation. 26,135 The results of a Laplace analysis of $Cr(OH_2)_6^{3+}$ reduction data, shown in Table 9, demonstrate the effect on the derived rate constants of the shorttime current enhancements. The values of k_f agree well at -975 and -1000 mV with those obtained from pulse-polarographic analysis of monotonic polarograms; but as the potential becomes more negative, the disparity becomes greater. (The procedure of extrapolating the pulse-polarographic Tafel plot (log k_f vs. E) beyond -1075 mV is justified in the light of the observation that the apparent electrochemical transfer coefficient (α_{app}) is independent of the potential in this region.)¹⁴ The distortion produced in the Laplace-analysis plot for -1175 mV can be seen in Figure 28, where the curvature at low abscissa values is pronounced. The derived rate constants for potentials beyond -1000 mV are too small, in keeping with the notion that the exponential nature of the Laplace transform emphasizes the currents at the beginning of the pulse, 3^7 which are abnormally enhanced.

The Maximum Reliable Rate Constant

That the reduction of $Co(NH_3)_5 F^{2+}$ proceeds <u>via</u> a simple mechanism without specific adsorption of the reactant has been established.^{22,23} The theory of irreversible pulse polarography⁸⁴ predicts that

E, mV vs. Na s.c.e.	Slope ^{a,b} sec/coul	Intercept ^{a, c} 	k calc' cm/sec	k _{ex} , cm/sec
-1000	18030	68610	.0174	.0180 ^e
-1025	11490	55280	.0273	.0355 ^e
-1050	7140	64010	.0440	.0533 ^e
-1075	4720	66510	.0665	.0947 ^e
-1100	3360	64800	.0935	.161 ^f
-1125	2420	64470	.130	.279 ^f
-1150	2740	44520	.115	.481 ^f
-1175	1940	57360	. 162	.831 ^f
-1200	1450	63110	.217	1.44 ^f

Table 9. Laplace analysis of chronoamperometric data obtained for reduction of 2 mM Cr^{3+} in 1 M NaClO_L/2 mM H⁺.

^a Linear-regression parameters for a plot of $1/(\overline{i}(p) \ge p^{\frac{1}{2}})$ vs. $p^{\frac{1}{2}}$, where p is the Laplace-transform variable and $\overline{i}(p)$ is the Laplace transform of the time-dependent cell current i(t).

- ^b Slope = $1/(nFAk_{calc}C)$, where F is the Faraday, A the electrode area, k_{calc} the calculated heterogeneous charge-transfer rate constant, and C the bulk concentration of reactant (ref. 37). Here, A = .0165 cm² and C = 2 x 10⁻⁶ moles/cm³.
- ^c Intercept = $1/nFAD^{\frac{1}{2}}C$, where D is the diffusion coefficient, and other symbols as in Note b. (ref. 37). Here, D = 5.9 x 10^{-6} cm²/sec.
- d Rate constant derived either from monotonic pulse polarograms according to the method in ref. 17 or from extrapolation of the experimental Tafel plot (see text).

e Denotes experimental value.

f

Denotes extrapolated value.

Figure 28. Laplace-space analysis of current-time transient for Cr_{aq}^{3+} reduction (-1200 mV).

.



FIGURE 28

for such kinetically uncomplicated electrode reactions the faradaic current sampled at a fixed time following the application of potential steps should vary monotonically with the overpotential. The reliability of rate parameters for $Co(NH_3)_5 F^{2+}$ reduction should therefore be called into question if the voltammetric data from which they are derived show peaks when displayed as pulse polarograms. The shortest sampling time for which the pulse polarograms for this system are monotonic is 400 microseconds.

How many of the pulse-polarographic data are to be used for rate-constant calculations depends on the precision desired for the results. One can derive by standard propagation-of-error mathematics the effects that the rational function for k_f has on the uncertainty in the rate constant:^{84,132}

$$\Delta k_{f}^{\prime}/k_{f}^{\prime} = \left| \frac{-20x^{3} + 16x^{2} - 21x + 14}{2(7 + 4x^{2})(1 - x)} \right| \frac{\Delta x}{x}$$
(33)

where $\Delta k_f/k_f$ and $\Delta x/x$ are the respective relative uncertainties in the rate constant and in x (the ratio of the current to the limiting value). Assuming that one can measure x to within 1%, the relative uncertainty in the calculated rate constant will be below 5% for x < 0.92. The use of a diffusion coefficient of 8.3 x 10^{-6} cm²/sec (refs. 22 and 23) suggests that rate constants as large as 0.33 cm/sec can be considered reliably evaluated. For Cr(OH₂)³⁺₆ reduction, however, this limit is only 0.14 cm/sec because the diffusion coefficient of Cr(OH₂)³⁺₆ is only 5.9 x 10^{6} cm²/sec,³² and because pulse polarograms for Cr(OH₂)³⁺₆ reduction show maxima for sampling times below 1.5 msec. 142

Chemical Causes of the Polarographic Peaks

It remains to determine the causes of the peaks in the pulse polarograms. It is tempting to consider that the shape of the curves, which is strongly reminiscent of conventional polarographic maxima, is ascribable to the same causes. However, tangential motion of the mercury surface introduced by differences in surface tension at various points of the cathode figures prominently in the explanation of such maxima.¹³⁶ Such conditions are unlikely to exist in the $Cr(OH_2)_6^{3+}$ solution inasmuch as $Cr(OH_2)_6^{3+}$ is not specifically adsorbed at Hg^{32} and as the rest potential (-600 mV) is close to the potential of zero charge (pzc), which is about -520 mV. The contribution of the reactant to the surface tension is therefore negligible, and electrolysis of the $Cr(0H_2)_6^{3+}$ during the first millisecond of the pulse should affect the surface tension imperceptibly. In addition, the extent of electrolysis increases with the sampling time and is its greatest in the dc polarograms. In these cases, however, no peaks are seen.

Peaked shapes have been observed previously for pulse polargrams in two different circumstances: reactant depletion at an unrenewed (solid) surface¹³⁷ and adsorption of electroactive species where the electrode reaction is reversible.¹³⁸ One feature which distinguishes depleted-reactant polarograms from those in Figures 24-27 is that the plateau currents are less than the "true" limiting currents. These "true" values are ascertained by increasing the wait time between pulses to alleviate concentration polarization.¹³⁷ Neither the theory nor the experimental results from studies of reactant depletion suggest the incidence of currents greater than the "true" limiting values. Furthermore, the peak in the polarogram is both predicted and observed in the case of reactant depletion to disappear as the wait time between pulses is increased or the pulse width decreased.¹³⁷ The behaviour shown in Figures 24-27 is seen regardless of the drop time or the duration of the pulse, albeit that in the former instance a greater current is produced as a result of the larger electrode area.

The digital simulation of reversible pulse polarograms of adsorbed reactants also predicts plateau currents less than the "true" limiting values.^{135,138} Empirical observations bear this out when the "true" limiting currents are determined by deliberately excluding adsorption-inducing anions from the solution.¹³⁸ It should be pointed out that a difficulty with this adsorption calculation is that the size of the Henry's-Law adsorption coeffecient necessary to produce pulse polarograms of the shape seen here and in the reversible-reaction study is quite large--about 0.05 cm.²⁰ This implies for the conditions employed in that study (100-micromolar iodide concentration) the surface charge of iodide ions is 500 microcoulombs/cm², about 1.5 monolayers. This value is unrealistically large and certainly beyond the realm where Henry's Law could be expected to apply.

Nonetheless, digital simulation can be used to expose the role of adsorption in irreversible pulse-polarographic phenomena. Values of π_2 obtained from double-layer data 32,85 produce estimates of the diffuse-layer adsorption coefficients (cf. Equation 4) from $Cr(0H_2)_6^{3+}$ at -600 mV (K_{ads} = 10^{-6} cm) and -1200 mV (K_{ads} = 10^{-5} cm) for a reactant radius of 3.5 angstroms. A simulation performed

with reactant adsorption of this magnitude yields polarograms with peaks 10% or less above the limiting current and a shape which agrees qualitatively with the experimential results here.²⁶ The simulation predicts even larger peaks (25% above the limiting current at 100 microseconds) if the adsorption is strong (K_{ads} = 1.4×10^{-5} cm) throughout the wave. This prediction is borne out by the time-resolved pulse-polarograms for $Cr(NH_3)_{\varsigma}(NCS)^{2+}$, a complex whose adsorption constants exceed 2 x 10^{-5} cm over much of its polarographic wave. The polarograms have peaks 40% in excess of the limiting current at a sampling time of 300 microseconds, and the peaks persist until 5 msec into the pulse. A more sophisticated weak-adsorption calculation using diffuselayer profiles and Φ_2 values for 1 <u>M</u> KF electrolytes and ratepotential parameters characteristic of $Co(NH_3)_5 F^{2+}$, however, shows no maxima.²⁶ The simulation results are nevertheless valuable in that they suggest that experimental conditions which tend to produce or keep the reactant near the electrode longer than simple theory assumes can be responsible for producing peak-shaped polarograms.

The Effect of Instrument Performance on Pulse Polarograms

The causes of peaks in pulse polarograms can be electronic as well as chemical. Examination of the simple electronic schematic representations of an electrochemical cell and the potentiostat (Figures 29 and 30, respectively) indicates that the dynamic characteristics of both the control amplifier (CA) and the IEC will have an effect on the shape of the applied-potential waveform. The system must be considered in toto because the electronic



Figure 29. Schematic representation of an electrochemical cell.



Figure 30. Schematic representation of the potentiostat circuity.

information fed back to the CA from the reference electrode is on a potential-difference scale which depends crucially on the maintenance of the working electrode at virtual ground by the IEC. To the extent that the latter is incapable of performing this task in the face of the charging-current transient produced by a potential step, the actual applied cell potential--that is, the voltage difference between the summing point of the IEC and the output of the reference-electrode buffer amplifier--will be at variance with the theoretical (instantaneous) ideal. The customary criterion of potentiostat performance is the rise time of the reference buffer, but a condition necessary for this to reflect the applied potential is that the IEC feedback to the working electrode at its input a current of identical magnitude but opposite in sign to the cell current provided by the CA. If an integrated-circuit operational amplifier forms the IEC, a situation commonly encountered in electrochemical instrumentation, it can provide only 10 to 20 mA to its summing point. To match the charge produced by the CA for a 1-V step into a one-microfarad double-layer capacitance would require 50 to 100 microseconds. Indeed, without a nonlinear feedback element such as in Figure 22, the maximum output current is never reached for IEC sensitivities above 1 mA/V, protracting system response time even further.

It is possible to characterize the IEC summing-point and reference-buffer behavior and determine the actual applied potential. Additional buffering (shown inside the dashed lines in Figure 30) was installed since it was observed that the potentiostat could oscillate if a probe from a voltage-measuring device were attached

to the reference buffer and that the magnitude of the noise in the IEC output depended critically upon the length of the cable connecting it to the microcomputer's analog-to-digital converter. (This is understandable in view of the fact that the cables present capacitive loads to these amplifiers, which will unintentionally contribute to their output characteristics and thereby affect the behavior of the entire cell-potential control loop.) To provide a quantitative description of the time-dependence of the applied potential, one needs data taken at rates greater than the computer system is capable; the Biomation transient recorder was employed to sample circuit voltages with 8-bit (1 part in 256) resolution at intervals as small as 50 nsec.

Measurements were made of both the IEC summing-point and the reference-electrode voltages during potential steps for the reduction at Hg of 2 mM $Cr(OH_2)_6^{3+}$ in 1 M $NaClO_4$. The former, an example of which is shown in Figure 31, are triangular in shape, ranging from 10 to 40 mV at maximum excursion. The situation can be much worse for solid electrodes; Figure 32 shows the behavior for a polycrystalline silver electrode of large area (0.5 sq cm). The reference potentials were approximately exponentially damped square waves with time constats of eight to ten microseconds. Nonlinear regression¹³⁴ applied to the reference signals using a single time-constant produced residuals of the same sign in a cluster at the beginning of the step, suggesting that the signal rises less quickly than exponential damping predicts. Use of two time constants in the model reduced the chi-squared value considerably, with essentially random distribution of residual



Summing-point behaviour

Figure 31. Summing-point deviations for $\operatorname{Cr}_{aq}^{3+}$ reduction at Hg.



FIGURE 32

Figure 32. Summing-point deviations for $Co(NH_3)_5 F^{2+}$ reduction

signs for data at short times. There is a trend to the two time constants: one remains fixed at about 3.5 microseconds irrespective of potential-step size, while the other varies from 0.1 nanosecond for a 125-mV step to about 1.2 microseconds for a 750-mV step. This is encouraging in that the slew rates of potentiostat amplifiers should provide an exponential damping more or less without regard to step size, while the time constant of the load (the cell) should increase, mainly as a manifestation of integral capacitance. However, the value of the varying time constant at low overpotentials seems unrealistically small. The maximum summing-point excursions increase with step size, again in harmony with larger electrode capacitances.

The results of the foregoing analysis allowed the mathematical description of the time dependence of the applied potential throughout the polarographic wave, the results of which are summarized in Figure 33. When the effect of a time-dependent heterogeneous charge-transfer rate constant derived from the substitution of the potential-time curve into the Tafel equation was simulated digitally, peak-shape polarograms resulted (Figure 34) which were in qualitative agreement with the experimental data. The use of slightly larger deviations from instantaneous potential application gave results closer to experimental performance. This is not surprising inasmuch as the calculation does not allow for iR drop. Simulations demonstrate that peaks a few percent above the limiting current can be introduced into the short-time pulse polarograms by an uncompensated solution resistance as low as 50 ohms.



Applied potential waveforms

Figure 33. Applied-potential waveforms for Cr_{aq}^{3+} reduction at Hg.



FIGURE 34

CONCLUSIONS

Pulse-polarographic data analysis is at least under some circumstances a clearly more efficacious method than chronoamperometric analysis for the determination of electrochemical kinetic parameters from current-time-potential data. The utilization of a pulsepolarographic display format for irreversible chronoamperometric transients can provide information as to the presence in the data of effects due to instrumental performance which cannot be seen in the transients themselves. Chronoamperometric analysis, which assumes that any deviation from limiting-current behavior is due to slow electrode reactions, cannot show that it could also be due to adsorption phenomena or slow instrumentation. In addition, the display features of pulse polarography allow the calculation of the reliability limits to rate data measured by a given instrument for a specified electrode reaction. Rate parameters determined from monotonic submillisecond pulse polarograms agree with previously reported values, in sharp contrast to those rendered by a chronoamperometric analysis of the same currentpotential-time data.

Adsorption phenomena can contribute to the appearance of maxima in pulse polarograms sampled rapidly after the application of the potential step. Even the very weak but inevitable diffuselayer adsorption imposes a limit on the maximum rate constant which can be reliably determined by equations derived from simple models for large-amplitude potential-step techiques.

Total potentiostat-system response time, rather than just that of the reference-electrode monitoring circuitry, is a determining

criterion of fast-rate reliability, particularly for solid-electrode measurements. Deviations from virtual ground by the currentto-voltage converter summing point can have a large effect on the shape of the potential-time waveform applied to the cell. To obtain information about faster rates free of distortion produced by instrument-response time, current-to-voltage converter enhancements which inject charge of the appropriate sign into the amplifier's summing point during the charging-current transients must be employed.

CHAPTER VII. THE ACCESSIBILITY OF ELECTROCHEMICAL CHARGE-TRANSFER RATE INFORMATION FROM TIME-RESOLVED, DIRECT-CURRENT POLAROGRAPHIC DATA

INTRODUCTION

In recent years, a number of reports have been made of the applications in analytical chemistry of direct-current polarographic currents sampled rapidly after the fall of the previous drop from a dropping mercury electrodes. 30,52,54,139-143 Both naturally flowing capillary electrodes, some with subsecond drop times, and electrodes whose drops are forcibly dislodged by a mechanical knocking device which operates at frequencies between 1 and 100 Hz have been used. 52,139,140 Among the advantages offered by such an approach are the decrease in the amount of time required for a complete polarographic scan and the suppression or elimination of polarographic maxima. 30, 143 Conventional sampling times (ca. 1 to 10 seconds) have been utilized innumerably in the acquisition of current-potential data from which electrochemical -reaction rate information is derived; but the use of subsecond sampling times, particularly those below 0.5 sec, for the same purpose is much less widespread.

The simplest method for extracting this rate information is to determine the ratio i/i_{lim} of the current i at a fixed sampling time t to the current i_{lim} in the diffusion-limited region and to use the analysis method due to Koutecky.²⁹ According to this description, the current ratio for a totally irreversible polarographic wave is given by:

$$\frac{1}{1} = \phi(\lambda) \tag{34}$$

Where $\lambda = k(t/D)^{\frac{1}{2}}$, k is the heterogeneous charge-transfer rate constant, D is the diffusion coefficient of the reactant, and Φ (z) is a transcendental infinite-series function. A rational-

function description of the relationship has been given 84

$$\frac{2x(3 - x)}{5(1 - x)} = 1.35k(t/D)^{\frac{1}{2}}$$
(35)

where $x = i/i_{\lim}$. A distinction between reversible and irreversible electrode reactions can thus be made on the basis of a time dependence to x (at a given potential) for the latter case.

Three advantages of shorter sampling times are suggested by the predicted time behavior of kinetically controlled polarographic waves. First, a fixed value of i/i lim for different sampling times is produced by a rate constant which varies as the inverse square-root of t.²⁹ This is important in that it promises access to rate constants that are too large for conventional polarography in redox systems not amenable to either large-amplitude pulse techniques or small-amplitude perturbation methods. The lack of a potential region in which the electrode is ideally polarizable precludes the use of the former class of methods, whereas the latter category of techniques cannot be used if there are additional chemical reactions following the electron transfer which consume the electrochemical-reaction product on a time scale comparable to that of the small-amplitude perturbation. Neither of these complications affects dc-polarographic measurements adversely. Second, decreasing the sampling time at a fixed potential decreases the value of i/i_{lim} , thereby shifting the wave along the potential axis. One could therefore hope to separate a kinetically controlled wave of interest from an interfering wave by decreasing the measurement time. Finally, a shorter sampling time implies that less electroactive material has been electrolyzed in the vicinity of the electrode

surface. Were the electroactive species to contribute significantly to the double-layer composition at the electrode-solution interface, the moving drop would exhibit differences in surface tension at various points of the drop, progressively more so as the time after drop birth increases. Circumstances such as these contribute to the appearance of polarographic maxima, which distort the polarographic wave.¹³⁶ Polarograms obtained at short sampling times thus are less likely to be complicated by maxima, particularly if the sampling time is less than the time characteristic of the undesired electrode movement.^{136,144} Consequently, we decided to monitor the time dependence of dc polarographic current-potential curves for the mechanistically simple electroreductions of $Cr(OH_2)_6^{3+}$ and $Co(NH_3)_5 F^{2+}$ in order to evaluate rapid dc polarography as a method for the determination of electrochemical charge-transfer rate parameters. Each of the predictions described above will be explored in turn in the present chapter.

It is essential to consider the experimental ramifications of the boundary conditions assumed in solving the convectiondiffusion equation whose solution provides the link between polarographic data and the electrochemical rate parameters which produce them. First, the concentration is assumed to be spatially invariant and equal to the bulk value at the instant of drop birth. Second, only radial velocity components (that is, those in the direction of the movement of the drop issuing forth from the dme capillary) are present in the mercury drop. Tangential components, which entrain solution in their direction of movement and thereby create additional convection, are assumed to be negligible. Finally, the solution is taken to be quiescent except for the movement produced by the (radially) growing drop.^{29,136} Several tests can be applied to polarographic data to determine whether or not these conditions have been met. Mechanistically simple electrode processes whose reactants do not constitute a significant portion of the ions in the double layer must yield monotonic polarograms.²⁹ The calculated rate constants derived at a given electrode potential from sampled-current polarograms should be independent of the value of the sampling time. Furthermore, the limiting currents must not exceed the values predicted by the likovic equation:

$$I_{\rm lim} = 706 \, {\rm nm}^{2/3} {\rm t}^{1/6} {\rm D}^{1/2} {\rm C}$$
(36)

where n is the number of electrons transferred in the electrode reaction, m is the Hg flow rate in mg/sec, t is the sampling time, D is the diffusion coefficient of the reactant in cm²/sec, C is the concentration in moles/cm³, and i_{lim} is the limiting current in microamperes. This equation represents the asymptotic limit of kinetically controlled polarograms.¹⁴⁵

Polarography is actually practiced under circumstance which may be quite different from those which have been assumed in the mathematical model. Electrolysis of solution which occurred during the previous drop produces a concentration distribution whose nonuniformity is at least partially compensated by the motion introduced into the solution when that drop fell from the dme.¹⁴⁶ The commonly employed experimental expedient of mechanically dislodging a drop before its natural drop time provides a more convenient data-acquisition procedure, but introduces additional stirring into the solution. It is therefore imperative that conditions be ascertained for which the reactant depletion and solution stirring nullify each other sufficiently so that the boundary conditions described above are satisfied. Polarographic data acquired under a variety of experimental circumstances were examined by the tests previously mentioned in order to test the accuracy of the assumptions and to assess the suitabilty of the data for providing electrochemical rate information <u>via</u> the Koutecky model.

EXPERIMENTAL

The $Cr(0H_2)_6^{3+}$ and $Co(NH_3)_5 F^{2+}$ reagents and KF and NaClO₄ supporting electrolytes were prepared as described in previous chapters. KBrO₄ was obtained from Research Inorganic Chemicals Corp., and Professor F. C. Anson kindly provided samples of $[cis-Co(en)_2(N_3)_2](ClO_4)$. Solid K₃ $[Cr(NCS)_6]$ and reagentgrade NH₄F (J. T. Baker Inc.) were used without further purification. Reagent-grade NaNO₃ was thrice recrystallized from deionized distilled water prior to use.

The microcomputer-controlled electrochemical data-acquisition system documented in Chapter II was used for all polarographic measurements except for preliminary studies. In those cases, a Princeton Applied Research Model 174A polarographic analyzer, modified to allow for programmable sampling-time resolution, was employed.²⁸ Synchronization of experimental timing circuitry with natural drop fall or dislodgment was accomplished through detection and interface circuitry discussed in Chapter III. All measurements were made at ambient temperature (23 + 1°C), and potentials are reported relative to a NaCl-saturated calomel electrode (see note in Chapter VI).

RESULTS AND DISCUSSION

This section presents a description of the search for the experimental conditions for which the Koutecky analysis can be use to extract electrode-reaction rate information from timeresolved dc polarograms. The effect of Hg flow rate through the dme is examined first, followed by a comparison among natural, forced, and first-drop techniques under conditions where rate information is accessible. The utility of rapid current sampling is then demonstrated for situations in which complications obscure necessary polarographic information at conventional sampling times.

The Effect of Large flow Rates

There are several motivations for choosing a flow rate which is as large as is practicable. The current will always be larger at a given potential and time into the drop life for a larger flow rate. One would therefore expect to enhance the signalto-noise ratio for current measurements made shortly after the birth of a new drop (when the currents are always relatively small) if one increases the flow rate. In addition, subsecond natural drop times can be achieved for dme capillaries in contact with molar halide or perchlorate electrolyte solutions when the flow rate is above about 15 mg/sec.⁵⁴ Under these circumstances, rapid polarographic-current monitoring can be performed with freely flowing capillaries without the need for additional circuitry not ordinarily found in polarographic instruments (see Chapter III). Alternatively, equipped with such enhanced instruments, one could improve the precision of current measurements sampled at times before drop fall occurs.

A special, high flow-rate capillary was fabricated from a section of a Fahrenheit thermometer and attached to a Hg-delivery system to provide a high-speed dme. Time-resolved polarographic currents for the reduction of $Cr(0H_2)_6^{3+}$ in 1 <u>M</u> NaClO₄ solution (pH 2) were measured at this capillary for flow rates of 10.3 and 17.0 mg/sec under conditions of natural drop fall. The results for the higher flow rate are shown in Figure 35. While the polarograms themselves show no unexpected features in their shapes, the rate constants derived from these data show a systematic and significant increase as the sampling time is increased at a given potential. This time dependence suggests that the assumed boundary conditions have not been satisfied.

An additional demonstration of this conclusion is seen in the limiting-current behavior for these two flow rates which, along with the time variation predicted by the llkovic equation, is shown in Figure 36. The experimental values clearly exceed the calculated ones for all sampling times, and the discrepancy is more pronounced for the larger flow rate. Tangential velocity components have been found to be non-zero for drops growing from a dme into $1 \ M$ KCl solutions between -250 and -1250 mV (vs. sce) for flow rates larger than 10 mg/sec.¹⁴⁷ It would not be unreasonable to suggest that some tangential velocity components are present in drops growing into $1 \ M$ NaClO₄ electrolytes, for the following reason: the potentials employed here are substantially



Figure 35. Time-resolved dc polarograms for Cr_{aq}^{3+} reduction (m = 17 mg/sec).


Figure 36. Comparison of Ilkovic-equation predictions and experimental results.

negative of the potential of zero charge. Neither cation exhibits specific adsorption, and the anion adsorption should be negligible for large negative rational potentials.¹⁹ Consequently, the conditions at the Hg/solution interface should be similar in both KCl and NaClO₄ solutions for the potentials employed here. Clearly, the strong possiblitiy of tangential velocity components in the drop and the observation of behavior deviant from the prediction of the model preclude the use of flow rates above 10 mg/sec in the determination of electrochemical reaction rates from polarographic data.

The Effect of Intermediate Flow Rates

The $Cr(0H_2)_6^{3+}$ electroreduction reaction was also studied at intermediate values of the flow rate. Figures 37, 38, and 39 show the time-resolved polarographic data for forcibly dislodged drops for flow rates of approximately 1.8, 3 and 4 mg/sec, respectively, Data for natural drops under corresponding conditions of Hg flow are shown in Figures 40, 41, and 42. All of the polarograms in Figures 38, 39, 41, and 42 show a severe shape distortion: rather than attaining a limiting value, the currents begin to decrease as the poential becomes very negative.

A shape such as this is characteristic of a situation in which stirring of the solution from the falling of the previous drop and from capillary movement (when induced) has failed to eradicate the concentration polarization created by electrolysis at the previous drop. ^{137,148} The depletion exhibits both potentialdependent and potential-independent characteristics. Naturally falling drops do not have the benefit of the additional stirring



FIGURE 37

Figure 37. Knocked-drop dc polarograms for Cr_{aq}^{3+} reduction (1.8 mg/sec).



FIGURE 38

Figure 38. Knocked-drop dc polarograms for Cr_{aq}^{3+} reduction (3 mg/sec).



Figure 39. Knocked-drop dc polarograms for Cr_{aq}^{3+} reduction (4 mg/sec).



FIGURE 40

Figure 40. Natural-drop dc polarograms for Cr_{aq}^{3+} reduction (1.8 mg/sec).



Figure 41. Natural-drop dc polarograms for Cr_{aq}^{3+} reduction (3 mg/sec).



Figure 42. Natural-drop dc polarograms for Cr_{aq}^{3+} reduction (4 mg/sec).

produced by the drop knocker and consequently show currents that are always less than the values for knocked drops at all potentials. However, the peak-shaped polarogram results from the depletion being larger for potentials at the top of the wave, where the cell current is not dependent on the rate of the electrode reaction, than it is at the foot of the wave, where the extent of concentration polarization created by the previous drop is substantially smaller as a consequence of kinetic control of the current.¹³⁷

That the peaks are more pronounced for larger flow rates is additional corroboration of this point. The cell current, and hence concentration depletion, will be larger for a greater flow rate even though the smaller drop time which accompanies a larger flow rate opposes this depletion increase somewhat. Since the mass of the falling drop at a given potential is essentially independent of the flow rate,¹⁴⁹ the amount of stirring due to the fall of the drop is roughly the same regardless of the flow rate. More depletion remains uncompensated by solution movement at the higher flow rates, and the size of the peak is therefore expected to be larger for a larger rate of Hg flow.

The data obtained at 1.8 mg/sec (Figures 37 and 40) are encouraging in that they show the anticipated monotonic polarograms for knocked drops and potential-dependent deletion effects which seem just barely unaccepatable for naturally falling drops. These results suggest that some electrochemical reactions may produce naturaldrop polarograms of a shape appropriate to Koutecky analysis for flow-rate values around 2 mg/sec. This point will be examined in further detail later in this chapter.

The Effect of Small Flow Rates

It is also interesting to determine the accessibility of rate information from polarographic data obtained at a flow rate of around 1 mg/sec. Figure 43 shows time-resolved polarographic data obtained for forcibly dislodged drops from a dme whose flow rate was 0.97 mg/sec. The corresponding natural-drop data were of poor quality owing to a low signal-to-noise ratio, predominantly because of concentration depletion. The extent of this depletion at this small flow rate can be appreciated by considering the limiting-current behavior for the knocked drops shown in Figure 44 along with the llkovic-equation prediction. Only for sampling times around 2 seconds do the experimental values approach the calculated ones. Despite the depletion the short sampling times may yet yield kinetic information because the Koutecky analysis is sensitive to the <u>ratio</u> of a current to its limiting value for fixed sampling time.

Indeed, if one compares rate constants derived from the 50msec polarogram with those from the 2-second polarogram (Figure 45), one can see that the two values agree where the two analyses overlap and that the former values lie on a linear extrapolation of the Tafel plot for the latter rate constants. This behavior is consistent with that previously derived from conventional pulse-polarographic data (Chapter VI). Dc-polarographic data taken at sampling times two orders of magnitude lower than conventional times can indeed extend the accessible rate information by a factor of ten under these capillary conditions, in keeping with the prediction of Koutecky's equations. These results show that



FIGURE 43

Figure 43. Knocked-drop dc polarograms for Cr_{aq}^{3+} reduction (0.97 mg/sec).







FIGURE 45

Figure 45. Tafel plots derived from 50 msec and 2 sec knocked-drop polarograms for Cr_{aq}^{3+} reduction (0.97 mg/sec).

rate constants approaching 0.1 cm/sec can be measured reliably by rapid-sampling polarography.

A Comparison of Techniques

The preceding section demonstrated that even though absolute current values at short sampling times may be different from the predictions of the Koutecky model, there are circumstances where currents are affected equally throughout the wave such that the i/i lim ratios are close to the predicted values. It is interesting to compare the conventional and first-drop varieties of the polarographic technique at naturally falling and forcibly dislodged drops to determine the circumstances under which polarograms from all four methods would yield identical rate constants. The reduction of $Co(NH_3)_5 F^{2+}$ in 1 <u>M</u> KF was chosen as the electrode reaction for the investigation of the time dependence of polarographic currents for the four experimental variations. Admittedly, the first-drop method is difficult to implement on commercial instruments and is not applicable to electrode reactions for which there is no potential at which the electrode is ideally polarizable; but the advantages of the technique here are two-fold. First, in the case of natural drops, the solution conditions represent most closely those which have been assumed as boundary values, namely uniform concentration distribution and unstirred solution. Second, the comparison between natural first-drop results and those of conventional natural and forced drops shows directly both the concentration depletion and the extent to which the depletion is diminished by the solution stirring introduced by the drop knocker.

Polarograms measured at sampling times of 50 and 500 msec are shown for the four techniques in Figures 46 and 47, respectively. In the first-drop experiments, the electrode potential was held at 0 V, where the rate of $Co(NH_3)_5 F^{2+}$ reduction is negligible, throughout three drop lifetimes prior to polarization to allow restoration of the concentration distribution. The magnitudes of the currents appear in the anticipated order: first-drop results are greater than the conventional results, especially for short sampling times. Beyond a time of around half a second, all four techniques provide essentially the same current, confirming the expected short-duration nature of depletion effects. The i/i_{lim} ratios are shown in Table 10 for the first six 50-msec intervals for all four methods. For sampling times 150 msec or larger, the four techniques yield essentially the same ratio (and hence rate constant). At 50 msec, however, the conventional natural-drop results are much closer to the natural first-drop ratios than values for either of the knocked-drop experiments.

The reason for this short-term disparity can be seen in Figures 48 and 49, which are the current-time traces in the limiting-current region for the reduction of $KBrO_4$ in 1 <u>M</u> NH_4F for two different drop-knocker solenoid displacements. (Identical results were obtained for the reduction of $Co(NH_3)_5F^{2+}$. The $KBrO_4$ reduction data are shown only for convenience.) The former shows the results of a larger displacement: the time between the trigger signal (zero time) and the fall of the drop is about 6 msec, and oscillations in the current-time trace are apparent for the next 80 msec. The latter demonstrates that the oscillations can be diminished





Figure 46. Comparison of polarographic techniques for $Co(NH_3)_5 F^{2+}$ reduction (50 msec).



Figure 47. Comparison of polarographic techniques for $Co(NH_3)_5 F^{2+}$ reduction (0.5 msec).

Table 10. Values of i/i_{lim} for four polarographic techniques for the reduction of Co(NH₃)₅F²⁺ in 1 <u>M</u> KF. ^a Denotes natural drops. ^b Denotes natural first drops. ^c Denotes knocked drops. ^d Denotes knocked first drops.

	a	Ь	с	d	а	Ь	с	d
	.05 sec				.1 sec			
200								
225				0.012				
250		0.002		0.014	0.012	0.0047	0.001	0.014
275		0.006	0.009	0.018	0.019	0.016	0.010	0.025
300	0.041	0.017	0.014	0.027	0.029	0.024	0.017	0.034
325	0.073	0.031	0.025	0.033	0.035	0.044	0.026	0.057
350	0.13	0.059	0.046	0.054	0.063	0.078	0.046	0.095
375	0.18	0.11	0.075	0.090	0.11	0.15	0.083	0.17
400	0.27	0.20	0.13	0.15	0.18	0.26	0.15	0.28
425	0.38	0.33	0.22	0.25	0.29	0.41	0.45	0.44
450	0.54	0.50	0.38	0.39	0.44	0.59	0.40	0.62
475	0.71	0.68	0.50	0.55	0.62	0.74	0.59	0.78
500	0.88	0.83	0.68	0.72	0.81	0.81	0.72	0.90
525	0.92	0.92	0.81	0.84	0.96	0.93	0.86	0.94
550	0.97	0.96	0.87	0.92	1.00	0.97	0.91	0.97
	.15 sec				.2 sec			
200	0.006	0.004			0.005			
225	0.017	0.004	0.004	0.017	0.011	0.005	0.006	
250	0.022	0.005	0.009	0.018	0.019	0.013	0.014	0.014
275	0.035	0.019	0.021	0.030	0.025	0.024	0.028	0.032
300	0.061	0.031	0.034	0.036	0.039	0.036	0.036	0.037
325	0.11	0.055	0.059	0.063	0.065	0.064	0.058	0.069
350	0.20	0.10	0.097	0.12	0.13	0.12	0.12	0.13
375	0.32	0.18	0.18	0.20	0.22	0.20	0.20	0.23
400	0.50	0.30	0.29	0.33	0.35	0.34	0.34	0.36
425	0.67	0.47	0.46	0.47	0.52	0.51	0.51	0.54
450	0.84	0.65	0.63	0.68	0.69	0.69	0.67	0.71
475	0.95	0.79	0.77	0.82	0.84	0.82	0.80	0.84
500		0.90	0.88	0.91	0.93	0.91	0.90	0.92
	.25 sec				.3 sec			
200					0.0087			
225	0.006		0.005	·	0.0099	0.0081	0.0066	0.018
250	0.019	0.014	0.016	0.017	0.022	0.013	0.013	0.025
275	0.027	0.024	0.023	0.025	0.031	0.030	0.025	0.030
300	0.041	0.045	0.045	0.046	0.038	0.041	0.042	0.044
325	0.074	0.072	0.073	0.079	0.079	0.084	0.071	0.081
350	0.13	0.13	0.13	0.14	0.15	0.14	0.14	0.15
375	0.24	0.23	0.22	0.25	0.25	0.24	0.24	0.26
400	0.37	0.37	0.36	0.39	0.40	0.40	0.39	0.41
425	0.55	0.54	0.54	0.56	0.58	0.58	0.56	0.59
450	0.71	0.73	0.70	0.73	0.72	0.75	0.73	0.74
475	0.84	0.85	0.83	0.80	0.84	0.86	0.84	0.86
500	0.92	0.92	0.92	0.92	0.91	0.94	0.92	0.94



FIGURE 48

Figure 48. Effect of drop-knocker solenoid response time and displacement on polarographic current-time curves (large displacement).



FIGURE 49

Figure 49. Effect of drop-knocker solenoid response time and displacement on polarographic current-time curves (small displacement).

by a smaller travel, but at the expense of more than doubling the delay due to the response time of the solenoid.

The complications caused by the experimentally convenient drop knocker impose a lower limit at this flow rate of about 150 msec for artifact-free current-time data. Nevertheless, this represents access to a two-fold larger rate constant than can be measured at half a second, the fastest available sampling time on conventional instruments in our laboratory. Comparison of Limiting Currents With Reported Behavior

The limiting-current data described above stand in sharp contrast to published reports of high-speed polarographic behavior.³⁶ The results of Bond and O'Halloran show limiting currents less than those predicted by the llkovic equation for end-of-drop measurements at freely flowing capillaries with flow rates above 10 mg/sec.³⁶ These authors, however, show no distortion of the shapes of polarographic waves for the reversible reduction of Cd^{2+} in 1 M HCl. It is possible that the response time of their current-measuring equipment may be responsible for the disparity between their results and those of the present study. Their currents were measured with an x-y recorder,³⁶ a device which typically has a slewing speed less than 30 in/sec. Since the pen takes at least 30 msec to travel an inch, it is likely that the subsecond currents are not accurately represented by the recorder trace. Not suprisingly, the reported measurements³⁶ show a larger negative deviation from llkovic behavior as the flow rate is increased (sampling time decreased). The measurement system used in the present study is fully capable of representing

the currents at short times because the amplifiers used have power bandwidths in excess of 10 kHz.¹³¹ As a consequence, the limiting-current data reported here are far less likely to have been distorted by the speed of the measurement equipment. The previous study made no measurements at short times and small flow rates, ³⁶ so there is no basis for comparison of such results. The Effect of Sampling Time of Polarographic Maxima

Figure 50 shows two sampled-current polarograms for the reduction of $Cr(NCS)_6^{3-}$, dissolved in 1 <u>M</u> NaClO₄ at pH 2.7, at a dme with a flow rate of 2.0 mg/sec. The explanation of the polarographic shapes lies in the interactions between the redox center and the electrode. Complexes of Cr(111) containing isothiocyanate ligands have been shown to exhibit strong adsorption at Hg electrodes.¹⁸ The hexaisothiocyanate complex in particular has a Henry's-Law adsorption constant of about 0.03 cm.¹⁸ Because of this strong adsorption, the reduction of the complex at the growing drop can produce uneven concentration distributions at the surface, leading to additional drop movement and producing a maximum.¹³⁶

Currents sampled shortly into drop life thus have a better chance of "outrunning" the drop movement, and the results in Figure 50 clearly indicate this. The current peak is six times as large as the limiting current at 400 msec, but just over twice as large at 50 msec. The feature of greatest importance in the 50-msec polarogram, however, is the definition of a limitingcurrent region for potentials <u>positive</u> of those where the maximum appears. All of the current-potential data between -400 and





-700 mV can be taken with justifiable confidence as being uncomplicated by the maximum, and this renders the rate information accessible. The lack of an inflection makes the same assessment unreliable for the 400-msec polarogram.

On the other hand, high-speed current sampling presents no such advantages to the study of the reduction of $[cis-Co(en)_2(N_3)_2]^+$ in neutral 1 <u>M</u> KF. While an inflection is seen in the polarograms (Figure 51), complications presumably due to the adsorption of released azide ions preclude determination of the requisite limiting current.

The Effect of Sampling Time on Kinetically Controlled Waves

The determination of a limiting current for the reduction of perbromate in concentratied nitrate or mixed nitrate/fluoride electrolytes is virtually impossible at conventional times because of the onset of kinetically controlled bromate reduction at extremely negative potentials.²⁶ Figure 52 shows the effect of diminishing the sampling time from 900 msec to 100 msec in the reduction of perbromate in 1 <u>M</u> NaNO₃ at a 2 mg/sec flow rate. Kinetic parameters derived from the polarograms obtained at conventional times would be of questionable reliability because of the uncertainty in the limiting-current value. The most rapidly sampled polarogram, however, does not suffer from this limitation.

The benefits of time resolution do not always accrue to the study of kinetically controlled polarograms. The reduction of perbromate in 1 \underline{M} NH₄F produced the time-resolved polarograms shown in Figure 53. The rapid current sampling is not fast enough



Figure 51. Dc polarograms for the reduction of cis-Co(en) $_2(N_3)_2^+$ in 1 <u>M</u> KF.





Figure 52. Dc polarograms for the reduction of $KBrO_4$ in 1 <u>M</u> NaNO₃.



FIGURE 53

Figure 53. Dc polarograms for the reduction of $KBrO_4$ in 1 <u>M</u> NH_4F .

to shift the perbromate wave far enough negative of the reversible Hg-oxidation wave to provide a region of potential where the electrode is ideally polarizable. Therefore, the data measured at positive potentials always contains some current-diminishing contribution from the oxidation reaction. It remains a question of judgment, then, how far negative the potential must be so that the currents in 1 M NH₄F result only from perbromate reduction. CONCLUSIONS

Rapidly sampled polarographic data have been shown to be capable under appropriate circumstances of producing clear advantages, over data measured at conventional times, for the assessment of electrochemical-reaction rates. The complications due to polarographic maxima or to interference waves can sometimes be eliminated through the use of short sampling times.

Not all flow rates can be used for such studies, nor can all technique variations and sampling times be utilized at a given flow rate. Specifically, flow rates above 3 mg/sec produce severe depletion effects or undesirable tangential mercury-drop velocity components. For flow rates around 2 mg/sec, sampling times below 150 msec produce spurious results for knocked drops as a consequence of mechanical response times and stirring complications. Below 1 mg/sec, natural drops cannot be used reliably, whereas knocked-drop polarograms allow the determination of rate constants as large as 0.07 cm/sec which agree with values measured by normal pulse polarography.

CHAPTER VIII. SUGGESTIONS FOR FURTHER STUDY

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Research endeavors can be rewarded not only with answers to questions posed as the research was conceived but also with the additional problems which emanate from those answers. This section presents suggestions for further investigation which are based upon the conclusions of the previous chapters.

MEASUREMENT-SYSTEM IMPROVEMENTS

There are several ways in which the measurement system described in Chapter II could be enhanced, based upon the experience of this study. First, the signal-to-noise ratio can be improved both in general and for specific types of experiments. While the electronic noise present in the laboratory environment, particularly within the computer itself, does not completely vitiate the use of the mainframe A/D converter, there is little doubt that digitization of the measured signals as close as possible to their sources would improve the signal-to-noise ratio of the measurements, particularly for low-level voltages. A battery-powered, remote sampling head containing the sample-and-hold amplifier and A/D converter would permit information transmission in the digital domain.⁴⁷ Optical isolation of the domain converter from the (digital) DMA interface would decrease the noise induced by highspeed logic-gate transitions.

In addition, the potentiostat circuitry was optimized more for speed than for sensitivity, the best performance being obtained for currents in the 0.1 to 10 mA range. For the dc-polarographic studies, which occur on more protracted time scale than the pulse experiments and in which the currents are smaller, a programmable gain stage in the analog-measurement subsystem would enable current

sampling even closer to drop birth than the measurements described in Chapter VII.

Finally, greater computational throughput could be realized by interfacing the data-acquisition timing with the operating system's resident-monitor code through pseudo-device handler programs. In this way, the real-time, dual-task capability of RT-11⁴² could be utilized, allowing the use of the computer by two operators: one who performs time-critical measurements without compromise in timing integrity and one who executes data-analysis or software-development programs with nearly imperceptible delays.

The results of Chapter VI show that the speed of the potentialcontrol circuitry clearly establishes upper limits to the electrochemical rate measurements which can be made reliably with the use of simple models. Several changes can be made to improve the response time of the potentiostat. One method is to inject charge of a sign opposite to the control-amplifier current into the summing point of the current-to-voltage converter. This charge could come either from an amplifier which differentiates electronically the output of the control amplifier or from a current source which is switched on momentarily when the cell potential is stepped. Alternatively, one could eliminate the need for a current-tovoltage converter by designing a control amplifier which contains a linear transconductance stage. This portion would provide a voltage output which is proportional to the output current of the amplifier. There is also the intriguing prospect of controlling the cell potential solely by programmed charge injection.¹⁵¹ This technique is considerably more complicated to implement

than conventional (completely analog) control, and its original configuration¹⁵¹ is probably too slow for most electrode-kinetics measurements. Nonetheless, the method is capable of producing potential changes in cells containing concentrated aqueous electrolytes much faster than voltage-control amplifiers.

The versatility of the measurement system will be increased through the creation of additional applications software. Conventional charge-based experiments such as chronocoulometry are now in progress, not only for the customary mercury-electrode studies but also for those at solid electrodes. A novel automated differentialcapacitance technique based upon small potential-step chronocoulometry is also currently under development.

STUDIES OF SOLVENT STRUCTURING

Chapters IV and V presented results which demonstrate further the applicability of a model which includes secondary solvent structuring engendered by reactant ions in solution. It would be interesting to expand the study of the potential dependence of the electrochemical transfer coefficient to include the reductions of substituted Co(III) ammine complexes in electrolytes such as $0.4 \ M \ KPF_6$ where the requisite double-layer corrections are small. In particular, the transfer-coefficient variations of the Co(III) analogs of the Ru(III) amine complexes scrutinized in the half-cell reaction entropy study¹¹ could shed additional light on the role of hydrogen bonding between solvent molecules and reactant ligands in electron-transfer processes.

In addition, the isotope-substitution studies suggest that larger intrinsic energy barriers would generally be expected

in D₂O whenever the electron transfer entails an alteration in the hydrogen-bonded structure of the surrounding solvent. To explore this prediction further, it would be desirable to select chemically reversible redox couples which exhibit significant values of ΔE_f^{D-H} and yet do not contain replaceable protons so that the secondary isotope effect upon the electrochemical kinetics would provide the sole contribution to $(k_s^H/k_s^D)_{corr}$. Examples include hexachloroiridate (IV/II) and hexacyanatoferrate (III/II), as well as oxalato complexes.

Furthermore, it would be interesting to determine ΔE_f^{D-H} for the Co(III) amine complexes studied in Chapter V in order to scrutinize changes in the intrinsic barrier heights for electron transfer to these complexes, similar to the treatment of the aquo-complex results. The use of very high-speed, double-pulse coulostatics to determine formal potentials by the Tafel-plot intersection method (see Chapter IV) is possible for those complexes whose reduced forms aquate slowly enough to be seen on the reverse pulse. An added benefit of these formal-potential measurements is that their temperature dependence would provide the half-cell entropy changes which attend the electron-transfer reaction.¹¹

DC-POLAROGRAPHIC MEASUREMENTS

Chapter VII demonstrated the limits to the accessibility of electrochemical rate information derived from rapidly sampled dc polarograms. The application of this method to kinetic-probe experiments involving perbromate reduction would provide information to complement that produced by the outer-sphere, cationic Co(III) ammine probes. It would also be of interest to determine the effect of a variable forced drop time on the polarographic limiting currents at a fixed flow rate and sampling time to see what additional complications are introduced by the added stirring.

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