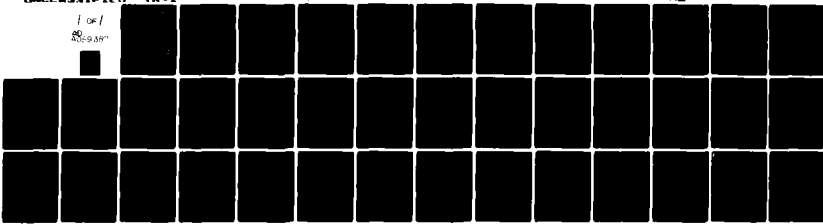AD-A089 387 MICHIGAN STATE UNIV EAST LANSING DEPT OF CHEMISTRY F/G 7/4
SOLVENT ISOTOPE EFFECTS UPON THE KINETICS OF SOME SIMPLE ELECTR--ETC(U)
AUG 80 M J WEAVER, P D TYMA, S M NETTLES N00014-79-C-0670
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OFFICE OF NAVAL RESEARCH

Contract N00014-79-C-0670

(15)

(9) TECHNICAL REPORT NO. 1   (14) TR-1

6 SOLVENT ISOTOPE EFFECTS UPON THE KINETICS

OF SOME SIMPLE ELECTRODE REACTIONS

by

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Prepared for Publication

in the

Journal of Electroanalytical and Interfacial Electrochemistry

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REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
1	AD-A089 387	

4. TITLE (and Subtitle)	5. TYPE OF REPORT & PERIOD COVERED
SOLVENT ISOTOPE EFFECTS UPON THE KINETICS OF SOME SIMPLE ELECTRODE REACTIONS.	Technical Report #1
	6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)	8. CONTRACT OR GRANT NUMBER(s)
M. J. Weaver, P. D. Tyma, S. M. Nettles.	N00014-79-C-0670

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Dept. of Chemistry, Michigan State University East Lansing, Mich. 48824	

11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE
Office of Naval Research Dept. of the Navy Arlington, Virginia 22217	August 15, 1980
	13. NUMBER OF PAGES
	35

14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)	15. SECURITY CLASS. (of this report)
	Unclassified.
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

SOLVENT ISOTOPE EFFECT, DEUTERIUM OXIDE, ELECTROCHEMICAL KINETICS, COBALT(III), CHROMIUM(III).

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(continued on next page)

20. (cont.)

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Solvent Isotope Effects upon the Kinetics of some Simple Electrode Reactions

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ABSTRACT

The effects of replacing H_2O with D_2O solvent upon the electrochemical
kinetics of simple transition-metal redox couples containing aquo, ammine, or
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of exploring the possible contribution of ligand-aqueous solvent interactions
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typically markedly larger than those predicted by the Marcus model from the
homogeneous rate ratios. These discrepancies appear to arise from differences
in the solvent environments in the transition states for electrochemical and
homogeneous reactions.

INTRODUCTION

It has been known for some time that sizable changes in the rate constants of homogeneous electron transfer reactions between transition-metal complexes occur when heavy water (D_2O) is substituted for H_2O.[1-3] These solvent isotope effects have been attributed to "secondary" isotope effects arising from differences in reactant-solvent interactions as well as to "primary" isotope effects arising from the replacement of hydrogen by deuterium in the coordination sphere of the reacting cations.[2-4] Studies of deuterium-isotope effects in electrode kinetics have largely been limited to the important but atypical cases of hydrogen and oxygen evolution,[5,6] 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_2O and D_2O 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_2O solvent with D_2O 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.[2,4,7-9] These reactions include $Fe_{aq}^{3+/2+}$ self-exchange[2,7] and the reduction of Co(III) ammines by V_{aq}^{2+} and Cr_{aq}^{2+}.[8,9] Although the sizable (factor of two) ratio of the rate constants in H_2O and D_2O (k^H/k^D) for $Fe_{aq}^{3+/2+}$ self-exchange was originally attributed to the presence of a hydrogen-atom transfer mechanism,[7] similarly large values of k^H/k^D have been observed for cross-reactions involving aquo complexes for which this mechanism is ruled out.[2,8,9] We have recently measured the solvent isotope effect upon the formal electrode potentials E_f of a number of transition-metal redox couples.[10] For couples containing aquo or hydroxo ligands, large differences in E_f between H_2O and D_2O were observed that appear to be at least partly due to hydrogen bonding between these ligands and the surrounding solvent.[10] 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.[11,12] The results of these experiments are reported in the present paper.

EXPERIMENTAL

The Co(III) and Cr(III) complexes were synthesized as solid perchlorate salts using the procedures noted in refs. 13 and 14, respectively. Stock solutions of Eu_{aq}^{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. 15. 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_{aq}^{3+} was formed by reoxidizing V_{aq}^{2+} at -300 mV. vs. s.c.e. The source of Fe_{aq}^{3+} was $Fe(ClO_4)_3$ (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_2O solutions. The Co(III) and Cr(III) ammine and ethylene-diamine complexes were deuterated by dissolving the protonated perchlorate salts in the minimum amount of D_2O containing 1mM hydroxide ions. The amine hydrogens are rapidly deuterated under these conditions.[11] These stock solutions were then added to the appropriate electrolyte in H_2O or D_2O acidified with sufficient perchloric acid (usually 5-10mM) 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",[16] 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 $140^\circ C$, and then humidified by bubbling through either H_2O or D_2O, as appropriate.

Kinetic parameters were obtained at a dropping mercury electrode (flow rate 1.8 mg. sec.$^{-1}$, mechanically controlled drop time 2 secs.) 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,[17] which allowed rate constants in the range ca. 10^{-4} to 4×10^{-2} cm. sec.$^{-1}$ to be

evaluated reliably. The electrochemical cell used for the kinetic measurements consisted of a working compartment containing ca. 5 mls. of the solution of interest in either H_2O or D_2O, 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_4Cl in order to minimize the liquid-junction potential.[10] The solvent liquid-junction potential between the H_2O and D_2O solutions is probably negligible ($<$1-2 mV.) using this cell arrangement, as evidenced by the essentially identical formal potentials obtained in H_2O and D_2O for ferrocene/ ferrocinium and $Fe(bpy)_3^{3+/2+}$ (bpy = 2,2'bipyridine) redox couples.[10] (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_2O and D_2O will correspond to essentially the same, albeit unknown, value of the Galvani metal-solution potential difference ϕ_m in both solvents. (See ref. 10 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 ± 0.1°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 H_2O to D_2O solvent,[10] 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). When comparing electrochemical rate constants in H_2O and D_2O, 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_2O to that in D_2O, $(k^H/k^D)_{app}$, as (c.f. ref. 18):

$$\log(k^H/k^D)_{app} = \log(k^H/k^D)_{corr} - (f/2.303)(\alpha_{corr} \pm Z)\Delta\phi_{rp}^{D-H} \qquad (1)$$

where $(k^H/k^D)_{corr}$ is the corresponding isotopic rate ratio corrected for ionic double-layer effects,[18] $\Delta\phi_{rp}^{D-H}$ is the alteration in the average potential on the reaction plane in changing from H_2O to D_2O, Z is the reactant charge, α_{corr} is the double layer-corrected transfer coefficient, and $f=F/RT$. (The plus/minus

---

*Although the formal potential for $Fe_{aq}^{3+/2+}$ [495 mV., $\mu \sim 0.5(H_2O)$] is positive of the potential where mercury dissolution occurs in noncomplexing media ($\gtrsim 350$ mV.), we have found that well-defined normal pulse and d.c. polarograms can be obtained for Fe_{aq}^{3+} reduction in acidified KPF_6 or $NaClO_4$ 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.

sign in eqn (1) 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 H_2O and D_2O. Fig. 1. consists of a pair of such plots for $1\underline{M}$ KF. These were obtained by integrating the capacitance-electrode potential curves for these electrolytes[19,20] along with the following values of the potential of zero charge that were determined by the streaming potential method:[21] $1\underline{M}$ KF(H_2O), -434 mV; $1\underline{M}$ KF(D_2O), -440 mV vs aqueous s.c.e.

It is seen from fig. 1 that the q^m-E plots for H_2O and D_2O are quite similar, although it is interesting to note that the plot for D_2O is displaced significantly relative to H_2O at the most negative potentials. Since fluoride anions are not significantly specifically adsorbed within this potential range,[22] these electrode charge displacements at fixed values of E, $(\Delta q^m)_E^{D-H}$, presumably arise from differences in the inner-layer structure between H_2O and D_2O. For most of the reactions considered here, either $0.4\underline{M}$ KPF_6 or $40m\underline{M}$ $La(ClO_4)_3$, rather than fluoride, supporting electrolytes were used in order to minimize the extent of ion-pairing 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.[13,14,15,18,23] Although both $0.4\underline{M}$ KPF_6 and $40m\underline{M}$ $La(ClO_4)_3$ 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 H_2O and D_2O will be closely similar to those given in fig. 1, 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 $(\Delta q^m)_E^{D-H}$ at the appropriate value of E was read from fig. 1 and the corresponding difference in the diffuse-layer

potentials ϕ_d between D_2O and H_2O in a given electrolyte, $(\Delta\phi_d)_E^{D-H}$, obtained using Gouy-Chapman theory. The corresponding values of $(\Delta\phi_{rp})_E^{D-H}$ were obtained by assuming that $\Delta\phi_{rp} = 0.7\Delta\phi_d$ and $\Delta\phi_{rp} = \Delta\phi_d$ for $0.4\underline{M}$ KPF_6 and $40m\underline{M}$ $La(ClO_4)_3$, respectively, as indicated from earlier studies.[15,23] These values of $(\Delta\phi_{rp})_E^{D-H}$ were then inserted into eqn (1) 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 $-E \lesssim 450$ mV.) where PF_6^- and particularly ClO_4^- supporting electrolytes exhibit significant anion specific adsorption, so that ϕ_{rp} will be influenced by the adsorbed anionic charge density q'. However, the use of $0.4\underline{M}$ KPF_6 minimized the extent of the diffuse-layer corrections since $q' \sim q^m$ at potentials positive of the p.z.c. in aqueous solution so that $\phi_{rp} \approx 0$.[18,24] A similar circumstance is expected in D_2O, so that $\Delta\phi_{rp}^{D-H} \approx 0$ under these conditions.

Table I 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/H_2O and Hg/D_2O interfaces. The rate parameters were all found to be independent of pH below ca. 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,[15,23] so that the cathodic rate parameters can conveniently be expressed as a value of k_{app} at a 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 I. (Since essentially identical values of α_{app} and hence α_{corr} were measured for a given system in H_2O and D_2O, 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_2O than in H_2O since values of E_f for these couples are markedly less negative in the former solvent.[10] The cathodic Tafel plots were therefore extrapolated to the appropriate formal potentials for each couple measured in H_2O and D_2O[10] to obtain the "standard" apparent rate constants $(k_s)_{app}$ listed in Table II. These results are also presented as ratios of $(k_s)_{app}$ for a given redox couple in H_2O and D_2O, $(k_s^H/k_s^D)_{app}$. 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 $\Delta\phi_{rp}^{D-H}$ between the respective formal potentials in D_2O and H_2O were inserted into eqn (1) to obtain the values of $(k_s^H/k_s^D)_{corr}$ given in Table II. [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 $0.4\underline{M}$ KPF_6, 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 $Cr_{aq}^{3+/2+}$ which also exhibits the largest value of ΔE_f^{D-H}.[10]

Ammine and ethylenediamine complexes

The effects of separately deuterating the coordinated ligands and the solvent upon the irreversible electroreduction kinetics[13] of various Co(III) ammine and ethylenediamine complexes are summarized in Table III. Some corresponding kinetic data for several Cr(III) ammine and ethylenediamine complexes are given in Table IV. 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 $(k^{H_2O}/k^{D_2O})_{corr}^E$ 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 H_2O and D_2O using eqn (1), assuming that $\Delta\phi_{rp} = \Delta\phi_d$.[13,14] Unfortunately, the values of E_f and hence k_s for the ammine couples are unknown on account of the lability and thermodynamic instability of the reduced complexes.

Inspection of Tables III and IV 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_2O and D_2O solvents. Values of $(k^{NH}/k^{ND})_{corr}^E$ considerably greater than unity are also seen for other Co(III) ammines and $Co(en)_3^{3+}$ (Table III). On the other hand, substitution of H_2O by D_2O solvent for a reactant with either protonated or deuterated ligands generally resulted in noticeable rate decreases, so that the listed values of $(k^{H_2O}/k^{D_2O})_{corr}^E$ are uniformly less than unity (Tables III and IV). Also listed in Tables III and IV are the net isotopic rate ratios $(k^H/k^D)_{corr}^E$ resulting from deuterating both the ligands and the surrounding solvent. It is seen that in every case $(k^H/k^D)_{corr}^E > 1$.

Nearly all the reactions listed in Tables III and IV are believed to occur via outer-sphere mechanisms.[13,14] The one exception is the reduction of $Cr(NH_3)_5NCS^{2+}$, which probably occurs via a thiocyanate-bridged pathway.[14] It is interesting to note that there were virtually no variations in α_{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 α_{app} (± 0.01–0.02). The notable exception is $Co(NH_3)_5OH^{2+}$ reduction, which exhibits significantly smaller values of α_{app} in D_2O than in H_2O. Unfortunately, basic solutions ($pH \gtrsim 9$) were required for this reactant in order to suppress the protonation

of the hydroxo ligand; this prevented the separate study of primary and second-ary effects since the ammine hydrogens are rapidly exchanged with the solvent under these conditions.[11]

The diffusion coefficients D obtained from the polarographic limiting currents were generally smaller for a given complex in D_2O than in H_2O. The diffusion coefficient ratios D^{H_2O}/D^{D_2O} were typically 1.35±0.05 for M_{aq}^{3+} com-plexes 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_2O and D_2O. The observed D^{H_2O}/D^{D_2O} ratios are roughly consistent with the higher viscosity of D_2O (1.107 cP) compared to H_2O (0.8903 cP):[25] inserting this viscosity ratio into the Stokes-Einstein equation[26] yields $D^{H_2O}/D^{D_2O} = 1.24_3$.

DISCUSSION

Interpretation of observed isotopic rate ratios

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

Consider the generalized electrochemical reaction

$$ox + e^-(\phi_m) \rightleftharpoons red \qquad (2)$$

We can express the free energies of the thermodynamic states prior to, and following, electron transfer (labeled states I and II, respectively) as[27]

$$G_I^o = \bar{G}_{ox}^o + \mu_{e^-}^o - F\phi_m \qquad (3)$$

$$G_{II}^o = \bar{G}_{red}^o \qquad (4)$$

where $\bar{G}_{ox}^o$ and $\bar{G}_{red}^o$ are the partial molal free energies of the oxidized and reduced species, respectively, and $\mu_{e^-}^o$ is the chemical potential of the reac-ting electron. Since the overall free energy of reaction $\Delta G^o (= G_{II}^o - G_I^o)$ for

eqn. (2) 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

$$\bar{G}_{red}^o - \bar{G}_{ox}^o = -F\phi_m^o \qquad (5)$$

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 D_2O and H_2O, ΔE_f^{D-H}, to be equated to a very good approximation (± 1 mV.) with the corresponding difference in ϕ_m^o, $(\Delta\phi_m^o)^{D-H}$, between the two solvents. Therefore, from eqn. (5) we can evaluate the difference in $(\bar{G}_{red}^o - \bar{G}_{ox}^o)$ between D_2O and H_2O, $\Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H}$, using (eqn. (2) of ref. 10)

$$\Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H} = -F\Delta E_f^{D-H} \qquad (6)$$

An analogous relationship for kinetic isotope effects can also be derived by noting that the activation free energy corrected for double-layer effects $\Delta G_{corr}^{\ddagger}$ $[= G_{corr}^{\ddagger} - G_I^o)]$ can be separated into a potential-dependent ("electrical") part $(G_{corr}^{\ddagger} - G_I^o)_e$ and a potential-independent ("chemical") part $(G_{corr}^{\ddagger} - G_I^o)_c$.[27] The former component is related[27] to the potential-dependent part of ΔG^o, $(G_{II}^o - G_I^o)_e$, by*

$$(G_{corr}^{\ddagger} - G_I^o)_e = \alpha_{corr}(G_{II}^o - G_I^o)_e \qquad (7)$$

Since from eqns. (3) and (4), $(G_{II}^o - G_I^o)_e = F\phi_m^o$, then

$$(G_{corr}^{\ddagger} - G_I^o)_e = \alpha_{corr}F\phi_m \qquad (8)$$

The isotopic rate ratio $(k^H/k^D)_{corr}^E$ can be expressed in terms of the

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*Although equivalent, eqn. (7) differs from the corresponding relations given in ref. 27 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 *bulk* reactant and product ground states appear in eqn. (7), rather than those for the corresponding states within the double layer.[27]

corresponding activation free energies for the same reaction in D_2O and H_2O as

$$RT\ln(k^H/k^D)^E_{corr} = (\Delta G^{\ddagger}_{corr})^D - (\Delta G^{\ddagger}_{corr})^H \tag{9}$$

Since the condition of constant E also essentially maintains constancy of ϕ_m, we can write

$$RT\ln(k^H/k^D)^E_{corr} = (G^{\ddagger}_{corr} - G^o_I)^D_c - (G^{\ddagger}_{corr} - G^o_I)^H_c$$
$$= \Delta(G^{\ddagger}_{corr} - \bar{G}^o_{ox})^{D-H}_c \tag{10}$$

where the subscript "c" again refers to the potential-independent part of $G^{\ddagger}_{corr}$. The rate ratio $(k^H/k^D)^E_{corr}$ [or the constituent ratio $(k^{H_2O}/k^{D_2O})^E_{corr}$] 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 $(k^H_s/k^D_s)_{corr}$ can be seen by noting that *for cathodic reactions*

$$\ln k^E_{corr} = \ln(k_s)_{corr} - \alpha_{corr} f(E-E_f) \tag{11}$$

so that

$$\ln(k^H/k^D)^E_{corr} = \ln(k^H_s/k^D_s)_{corr} - \alpha_{corr} f\Delta E^{D-H}_f \tag{12}$$

By combining eqns. (6), (10), and (12), we obtain

$$RT\ln(k^H_s/k^D_s)_{corr} = \Delta(G^{\ddagger}_{corr} - \bar{G}^o_{ox})^{D-H}_c - \alpha_{corr} \Delta(\bar{G}^o_{red} - \bar{G}^o_{ox})^{D-H} \tag{13}$$

The first and the second terms on the right-hand side of eqn. (11) constitute the so-called "intrinsic" and "thermodynamic" contributions to the overall redox reactivity.[28-30] Thus $(k_s)_{corr}$ is related to the intrinsic electrochemical free energy of activation $\Delta G^{\ddagger}_{ie}$ by $-RT\ln[(k_s)_{corr}/Z^e] = \Delta G^{\ddagger}_{ie}$. ($Z^e$ is the electrochemical collision frequency.) This intrinsic barrier $\Delta G^{\ddagger}_{ie}$ (labeled $\lambda^{el}/4$ in the Marcus treatment[31]) is equal to the work-corrected free energy of activation when the ground states immediately preceding and succeeding

the transition state have equal free energies.[28-31] *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.,

$$RTln(k_s^H/k_s^D)_{corr} = (\Delta G_{ie}^{\ddagger})^D - (\Delta G_{ie}^{\ddagger})^H \tag{14}$$

From the form of eqn. (13) it is seen that $(k_s^H/k_s^D)_{corr}$ will equal unity when $\Delta(G_{corr}^{\ddagger} - \bar{G}_{ox}^o)_c^{D-H} = \alpha_{corr} \Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H}$; i.e., when the change in the potential-independent part of the transition-state free energy $(\Delta G_{corr}^{\ddagger})^{D-H}$ 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 $G_{corr}^{\ddagger}$ upon isotopic substitution that are not reflected in corresponding changes in $\bar{G}_{ox}^o$ and $\bar{G}_{red}^o$, i.e., are unique ("intrinsic") to the transition state.

The observation that $(k^H/k^D)_{corr}^E \sim 1$ for the aquo couples (Table I) arises from an approximate compensation between the intrinsic and thermodynamic contributions (eqn. (12)) inasmuch as $(k_s^H/k_s^D)_{corr} > 1$ and $\Delta E_f^{D-H} > 0$ for each of these reactions (Table II). The latter result indicates that $\Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H}$ is negative (eqn. (6)) [e.g. for $Cr_{aq}^{3+/2+}$, $\Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H} = -1.3$ kcal.mol.$^{-1}$] This finding has been interpreted in terms of the relative destabilization of the oxidized species M_{aq}^{3+} in D_2O resulting not only from deuteration of inner-shell water molecules but also from the greater "solvent-ordering" tendency[32] of M_{aq}^{3+} in D_2O compared to H_2O.[10] Evidence supporting this latter contention includes the especially large values of reaction entropies ΔS_{rc}^o for these $M_{aq}^{3+/2+}$ couples;[16] 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}^o for $Fe_{aq}^{3+/2+}$ is observed in D_2O (45.4 e.u., $\mu=0.2$) than in H_2O (43.2 e.u.)[10] which is consistent with the

expected greater extent of hydrogen bonding in D_2O than in H_2O.[10]

The observation that $(k_s^H/k_s^D)_{corr} > 1$ for each of the four aquo couples given in Table II indicates that the intrinsic barriers for these reactions are significantly larger in D_2O than in H_2O (eqn (14)). In particular, for $Cr_{aq}^{3+/2+}$, $[(\Delta G_{ie}^{\ddagger})^D - (\Delta G_{ie}^{\ddagger})^H] = 0.7$ kcal.mol.$^{-1}$ The intrinsic barrier is usually separated into an "inner-shell" component $(\Delta G_{ie}^{\ddagger})_{is}$ arising from intra-molecular reactant reorganization (particularly from changes in metal-ligand bond lengths), and an "outer-shell" component $(\Delta G_{ie}^{\ddagger})_{os}$ arising from reorganiza-tion of the surrounding solvent.[31] 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[33,34] has calculated that the ratio of the rate constants (k_h^H/k_h^D) for homogeneous $Fe_{aq}^{3+/2+}$ self-exchange in H_2O and D_2O 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 reaction[31] *(vide infra)*, it follows that the corresponding prediction for electrochemical $Fe_{aq}^{3+/2+}$ exchange is $(k_s^H/k_s^D)_{corr} \approx (1.15)^{\frac{1}{2}} = 1.07$.

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 II) 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+} ($\Delta \bar{a} = 0.14$ Å) and V_{aq}^{2+} versus V_{aq}^{3+} ($\Delta \bar{a} \approx 0.15$ 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 $(k_s^H/k_s^D)_{corr} \approx 1.0\text{-}1.1$, in contrast to the observed value of 1.5.

The simplest approach to the estimation of the outer-shell contribution $(\Delta G_{ie}^{\ddagger})_{os}$ involves treating the surrounding solvent as a dielectric continuum.[31] By inserting the known values[25] of the optical and static dielectric constants ε_{op} and ε_s for liquid H_2O [ε_{op} = (refractive index)^2 = 1.777, ε_s = 78.3] and liquid D_2O at 25°C (ε_{op} = 1.764, ε_s = 77.95) into the relationship for $(\Delta G_{ie}^{\ddagger})_{os}$ derived by Marcus (eqn. (90) of ref. 31) leads via eqn. (14) 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 *short-range* 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_2O. Thus the formation from M_{aq}^{2+} of the transition state in D_2O is expected to involve a greater increase in the extent of solvent ordering induced by hydrogen bonding compared with the corresponding process in H_2O. Similarly, the formation of the transition state from M_{aq}^{3+} will require a greater dissipation of this hydrogen-bonded solvent in D_2O than in H_2O. These differences will not affect the intrinsic barrier if $\Delta(G_{corr}^{\ddagger} - \bar{G}_{ox}^o)_c^{D-H} = \alpha_{corr} \Delta(\bar{G}_{red}^o - \bar{G}_{ox}^o)^{D-H}$ (eqn. 13)), 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 $(3-\alpha_{corr})$. However, in actuality the transition state is reached via the reorganization of nuclear coordinates *while the reactant charge remains fixed*, the electron transfer occurring rapidly ($\sim 10^{-16}$ sec) once the transition state is formed.[31] 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_2O compared with those in H_2O are also expected to yield larger intrinsic barriers in D_2O, 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 II). 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., μ=0.1) compared with $Fe_{aq}^{3+/2+}$ (43 e.u. and 43 mV.) and $V_{aq}^{3+/2+}$ (37 e.u., 33 mV.).[10,16] 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 inner-shell 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 III and IV. Since ΔE_f^{D-H} values for these reactions are unknown (except for $Co(en)_3^{3+/2+}$[10]), it is not possible to make a complete experimental separation of the observed values of $(k^{NH}/k^{ND})_{corr}^E$ and $(k^{H_2O}/k^{D_2O})_{corr}^E$ into intrinsic and thermodynamic factors (eqn. (11)). 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[10] for Ru(III)/(II) 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_f to be evaluated accurately using cyclic voltammetry.[10] Deuteration of the ligands was found to have only a very small effect upon E_f ($\Delta E_f^{ND-NH} \lesssim 2$ mV.[10]); deuteration of the solvent also yielded small positive shifts in E_f ($\Delta E_f^{D_2O-H_2O} \lesssim 10$ mV.[10]). The net effect of deuterating both the ligands and the solvent, $\Delta E_f^{D-H} \lesssim 10$ mV., is therefore typically smaller than for $M_{aq}^{3+/2+}$ couples. This behavioral difference is probably due to the apparently smaller solvent "structure-making" ability of tripositive ammine complexes compared with otherwise similar aquo species,[14] presumably arising from the smaller tendency of the less acidic ammine hydrogens to engage in hydrogen bonding with surrounding water molecules.[16]

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 observation[36] that the deuteration of the ammine ligands increases the equilibrium constant for the dissociation reaction $Co(NH_3)_5OD_2^{3+} + D_2O \rightleftharpoons Co(NH_3)_5OD^{2+} + D_3O^+$ in D_2O by a factor of 1.3. This finding can be rationalized by the greater decrease in the zero-point vibrational energy[37] of the N-D bonds compared with the weaker[36] N-H bonds in the conjugate base resulting from its smaller cationic charge.[38,39] A similar charge effect upon the redox thermodynamics of Co(III)/(II) ammine complexes is therefore expected; a corresponding change in the relative stability of the oxidized and reduced forms leads to the estimate $\Delta E_f^{ND-NH} \approx 7$ mV. In any event, it seems very likely that the values of ΔE_f^{ND-NH} for the Co(III)/(II) ammine and ethylenediamine couples and probably

also the Cr(III)/(II) couples are small and positive. Therefore from eqn (5), the values of $(k^{NH}/k^{ND})^E_{corr}$ greater than unity observed for these reactions are probably associated with still larger values of $(k_s^{NH}/k_s^{ND})^E_{corr}$. For, example, if $\Delta E_f^{ND-NH} = 7$ mV. for $Co(NH_3)_6^{3+/2+}$, then since $(k^{NH}/k^{ND})^E_{corr} \approx 2.0$ in both H_2O and D_2O (Table III) and $\alpha_{corr} = 0.5$[13], from eqn (6) $(k_s^H/k_s^D)_{corr} \approx 2.3$.

It therefore appears that deuteration of amine ligands yields noticeable increases in the intrinsic electrochemical barrier for Co(III)/(II) and Cr(III)/(II). 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.[34] (Such coupling has been estimated theoretically to be much stronger than that between M-0 and 0-H bonds in aquo complexes[34]). 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.[10]

Since the effect of separate deuteration of the solvent upon the Co(III) and Cr(III) amine reduction rates yields values of $(k^{H_2O}/k^{D_2O})^E_{corr}$ that are less than unity (Tables III and IV), given that the values of $\Delta E_f^{D_2O-H_2O}$ 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. (5)). Thus since $(k^{H_2O}/k^{D_2O})^E_{corr} \approx 0.7$ for $Co(NH_3)_6^{3+}$ and $Co(ND_3)_6^{3+}$ reduction (Table III), if for example $\Delta E_f^{D_2O-H_2O} = 20$ mV., then from eqn. (6) $(k_s^{H_2O}/k_s^{D_2O})_{corr} \approx 1.0$. Although there are several factors that could produce larger intrinsic barriers in D_2O compared with H_2O solvent $[(k_s^{H_2O}/k_s^{D_2O})_{corr} > 1]$, the opposite situation is unexpected and would be without an obvious explanation. It therefore seems most likely that the values of $\Delta E_f^{D_2O-H_2O}$ for the

Co(III)/(II) and Cr(III)/(II) amine couples are sufficiently large

(ca. 10-20 mV.) so to offset the observed values of $(k^{H_2O}/k^{D_2O})^E_{corr}$ yielding

$(k_s^{H_2O}/k_s^{D_2O})_{corr} \approx 1$ (eqn. (5)). In any case, the observation of non-unit values

of $(k^{H_2O}/k^{D_2O})^E_{corr}$ is intriguing. Since the interactions between the ammine

hydrogens and the oxygen of the solvating water molecules should be very

similar in H_2O and D_2O, this result suggests that there are significant dif-

ferences in the long-range solvent polarization induced by the ammine reactants

in H_2O and D_2O. These differences are likely due to "specific" (hydrogen-

bonding) differences between these solvents; the Born model predicts only

negligible (<0.5 mV.) values of $\Delta E_f^{D_2O-H_2O}$ since the dielectric constants of

liquid H_2O and D_2O are almost identical (78.3 and 77.95, respectively, at

25°C [25]).

The equal values of α_{app} observed in H_2O and D_2O for each of the electrode

reactions, except for $Co(NH_3)_5OH^{2+}$ reduction, indicates that the position of

the reaction site in the interphase[14] is normally unaffected by isotopic sub-

stitution. The origin of the smaller value of α_{app} observed for $Co(NH_3)_5OH^{2+}$

reduction in D_2O compared to that in H_2O (Table III) may well be the same as

that responsible for the anomolously small values of α_{app} for this reaction

in H_2O 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.[40] 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_2O for H_2O

should increase the extent of hydrogen bonding at a given temperature, in

harmony with the observed smaller value of α_{app} in D_2O 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[31,41]

$$(k_s^e/Z^e) = (k_{ox}^h/Z^h)^{1/2} \tag{15}$$

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.

We have recently shown[42,43] that eqn. (15) can be generalized to include heteronuclear (cross-) reactions, expressed by

$$(k_{12}^e/Z^e) = (k_{12}^h/Z^h)^{1/2} \tag{16}$$

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. (16) has been found to be in approximate accordance with experimental rate data for various amine and aquo couples, although

significant behavioral differences between these two reactant types were observed.[43] From eqn. (16), the following predicted relationship between the isotope effects for corresponding electrochemical and homogeneous reactions is obtained:

$$(k_{12}^H/k_{12}^D)_{corr}^e = [(k_{12}^H/k_{12}^D)_{corr}^h]^{1/2} \tag{17}$$

Table V 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 of the Tafel plots for the constituent half-reactions obtained in $0.4\underline{M}$ KPF_6; 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_2O and H_2O). Contributions to these rate ratios arise from differences in thermodynamic as well as intrinsic factors in H_2O and D_2O.[10] In contrast to the prediction of eqn. (17), it is seen from Table V that $(k_{12}^H/k_{12}^D)_{corr}^e \gtrsim (k_{12}^H/k_{12}^D)_{corr}^h$. It is expected that eqn. (17) 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 V undoubtedly exert a substantial influence on the structure of the surrounding solvent, it would be expected that V_{aq}^{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 V) 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 outer-sphere processes for reactants that do not contain coordinated water.[2] 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.[2] 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.[2] The significant solvent isotope effects observed for the electrochemical kinetics of ammine and ethylenediamine complexes (Tables III and IV), 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 H_2O or D_2O. 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 III) and a factor of 1.35 times slower for its homogeneous reduction by $Cr(bpy)_3^{2+}$.[8] However, again the relative electrochemical and homogeneous isotope effects differ from expectations since *equal* rate decreases are predicted theoretically under these conditions.[31] This discrepancy between theory and experiment may again be due to an environmental solvent effect arising from the difference in the interactions between the NH_3 and ND_3 ligands and surrounding water molecules.

CONCLUSIONS

Taken together, the foregoing results provide fairly convincing 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 O...D hydrogen bonds in D_2O are significantly (~ 0.25 kcal.mol^{-1}), stronger as well as more extensive than O...H bonds[44,45] in H_2O, larger intrinsic barriers in D_2O would generally be expected for redox couples 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 $(k_s^H/k_s^D)_{corr}$.

The present approach of employing electrochemical cells where both the kinetic and thermodynamic parameters in D_2O and H_2O 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. The utilization of this "extrathermodynamic" approach to unraveling solvent effects upon redox kinetics on a more general basis is the subject of a forthcoming paper.[46]

ACKNOWLEDGEMENTS

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TABLE I. Solvent Isotope Effects upon the Electroreduction Kinetics of some Transition-Metal Aquo Complexes at the Mercury-Aqueous Interface.

Reactant	Solvent	Electrolyte[a]	E mV. vs. H_2O s.c.e.	k_{app}^E [b] cm. sec.$^{-1}$	α_{app} [c]	$(k^H/k^D)_{corr}^E$ [d]
Fe_{aq}^{3+}	H_2O	0.4$\underline{M}$ KPF_6	200	2.25×10^{-3}	0.48	≈ 0.7
"	D_2O	"	"	3.3×10^{-3}	0.48	
Cr_{aq}^{3+}	H_2O	40m$\underline{M}$ $La(ClO_4)_3$	-850	7.9×10^{-4}	0.57	1.09
"	D_2O	"	"	6.8×10^{-4}	0.57	
"	H_2O	0.4$\underline{M}$ KPF_6	"	2.5×10^{-3}	0.63	1.09
"	D_2O	"	"	2.1×10^{-3}	0.63	
V_{aq}^{3+}	H_2O	0.4$\underline{M}$ KPF_6	-500	3.5×10^{-3}	0.67	0.8
"	D_2O	"	"	4.4×10^{-3}	0.67	
Eu_{aq}^{3+}	H_2O	40m$\underline{M}$ $La(ClO_4)_3$	-750	5.8×10^{-3}	0.57	0.95
"	D_2O	"	"	5.8×10^{-3}	0.57	

[a]Acidified with 5-10m$\underline{M}$ $HClO_4$ to suppress hydrolysis of aquo reactants.

[b]Cathodic apparent rate constant at stated electrode potential, obtained from $k_{app} = i/FC^b$, where i is current density corrected for diffusion polarization and C^b is the bulk reactant concentration.

[c]Cathodic apparent transfer coefficient, obtained from $\alpha_{app} = -(f/2.303)(\partial\log k_{app}/\partial E)_\mu$.

[d]Ratio of double-layer corrected rate constant k_{corr} measured in D_2O to that in H_2O at fixed electrode potential in same supporting electrolyte; obtained from corresponding quoted values of k_{app} using eqn (1) as outlined in the text.

TABLE II. Solvent Isotope Effects upon the Standard Electrochemical Rate Constants of some Transition-Metal Aquo Couples.

Redox Couple	Solvent	E_f^a mV vs H_2O s.c.e.	$\Delta E_f^{D-H\,b}$ mV	Electrolyte	$k_{app}^{s\,c}$ cm sec^{-1}	$(k_s^H/k_s^D)_{app}^d$	$(k_s^H/k_s^D)_{cor}^e$
$Fe_{aq}^{3+/2+}$	H_2O	495		$0.4\underline{M}$ KPF_6	9×10^{-6}		
"	D_2O	538	43	"	5.9×10^{-6}	1.55	≈ 1.5
$Cr_{aq}^{3+/2+}$	H_2O	-655		$40m\underline{M}$ $La(ClO_4)_3$	1.0×10^{-5}		
"	D_2O	-600	55	"	2.7×10^{-6}	3.7	2.8
"	H_2O	-655		$0.4\underline{M}$ KPF_6	2.0×10^{-5}		
"	D_2O	-600	55	"	4.5×10^{-6}	4.4	2.8
$V_{aq}^{3+/2+}$	H_2O	-472		$0.4\underline{M}$ KPF_6	1.7×10^{-3}		
"	D_2O	-439	33	"	9.0×10^{-4}	1.9	≈ 1.5
$Eu_{aq}^{3+/2+}$	H_2O	-622		$40m\underline{M}$ $La(ClO_4)_3$	3.4×10^{-4}		
"	D_2O	-613	9	"	2.8×10^{-4}	1.2	1.1

[a] Formal potential for redox couple at appropriate ionic strength, from ref. 10.

[b] Change in E_f in substituting D_2O for H_2O solvent. Taken from ref. 10.

[c] Apparent "standard" rate constant, obtained by extrapolating plots of

log k_{app} versus E to the appropriate value of E_f.

[d] Ratio of apparent standard rate constant in H_2O to that in D_2O.

[e] Ratio of standard rate constant in H_2O and D_2O, corrected for the effect of the ionic double layer using eqn. (1) (see text).

TABLE III. Primary and Secondary Isotope Effects upon the Electroreduction Kinetics of some Co(III) Ammine and Ethylenediamine Complexes.

Reactant	Solvent	Electrolyte	E mV vs H$_2$O s.c.e.	k_{app} cm sec^{-1} [a]	α_{app} [b]	$(k^{NH}/k^{ND})E_{corr}$ [c]	$(k^{H_2O}/k^{D_2O})E_{corr}$ [d]	$(k^H/k^D)E_{corr}$ [e]
Co(NH$_3$)$_6^{3+}$	H$_2$O	0.4M̲ KPF$_6$	-300	5.4×10^{-4}	0.76	2.3 [f]	0.75 [h]	
"	D$_2$O	"	"	7.2×10^{-4}	0.76	2.0 [g]		1.50
Co(ND$_3$)$_6$	H$_2$O	"	"	2.3×10^{-4}	0.76		0.64 [i]	
"	D$_2$O	"	"	3.6×10^{-4}	0.76			1.15
Co(NH$_3$)$_5$OH$_2^{3+}$	H$_2$O	0.4M̲ KPF$_6$	-300	2.9×10^{-2}	0.63	1.45 [f]	0.81 [h]	
Co(NH$_3$)$_5$OD$_2^{3+}$	D$_2$O	"	"	3.6×10^{-2}	0.62	1.45 [g]		1.15
Co(ND$_3$)$_5$OH$_2^{3+}$	H$_2$O	"	"	2.0×10^{-2}	0.63		0.80 [i]	
Co(ND$_3$)$_5$OD$_2^{3+}$	D$_2$O	"	"	2.5×10^{-2}	0.62			
Co(NH$_3$)$_5$F^{2+}	H$_2$O	0.4M̲ KPF$_6$	-300	1.0×10^{-3}	0.66	1.8 [f]	0.87 [h]	
"	D$_2$O	"	"	1.15×10^{-3}	0.66	1.65 [g]		1.45
Co(ND$_3$)$_5$F^{2+}	H$_2$O	"	"	5.5×10^{-4}	0.66		0.84 [i]	
"	D$_2$O	"	"	6.9×10^{-4}	0.66			
Co(NH$_3$)$_5$OH^{2+}	H$_2$O	1M̲ KF + 1mM̲ KOH	-500	2.4×10^{-3}	0.65			
Co(ND$_3$)$_5$OD^{2+}	D$_2$O	"	"	9.5×10^{-4}	0.58			2.5

TABLE III. (continued)

Reactant	Solvent	Electrolyte	E mV vs H$_2$O s.c.e.	k_{app}[a] cm sec^{-1}	α_{app}[b]	$(k^{NH}/k^{ND})E_{corr}$[c]	$(k^{H_2O}/k^{D_2O})E_{corr}$[d]	$(k^H/k^D)E_{corr}$[e]
Co(en$_H$)$_3^{3+}$	H$_2$O	0.4M KPF$_6$	-300	4.6×10^{-4}	0.98	1.6[f]		
"	D$_2$O	"	"	5.9×10^{-4}	0.98	1.45[g]	0.78[h]	
Co(en$_D$)$_3^{3+}$	H$_2$O	"	"	2.9×10^{-4}	0.98			1.12
"	D$_2$O	"	"	4.1×10^{-4}	0.98		0.71[i]	

TABLE IV. Primary and Secondary Isotope Effects upon the Electroreduction Kinetics of some Cr(III) Ammine and Ethylenediamine Complexes.

Reactant	Solvent	Electrolyte	E mV vs H$_2$O s.c.e.	k_{app}^{a} cm sec^{-1}	α_{app}^{b}	$(k^{NH}/k^{ND})E_{corr}^{c}$	$(k^{H_2O}/k^{D_2O})E_{corr}^{d}$	$(k^{H}/k^{D})E_{corr}^{e}$
Cr(NH$_3$)$_6^{3+}$	H$_2$O	40mM La(ClO$_4$)$_3$	-900	1.1×10^{-3}	0.82	2.0 f	0.55 h	
"	D$_2$O	"	"	1.9×10^{-3}	0.82	2.1 g		1.16
Cr(ND$_3$)$_6^{3+}$	H$_2$O	"	"	5.5×10^{-4}	0.82		.0.58 i	
"	D$_2$O	"	"	9×10^{-4}	0.82			
c-Cr(NH$_3$)$_4$(OH$_2$)$_2^{3+}$	H$_2$O	40mM La(ClO$_4$)$_3$	-900	7×10^{-3}	0.73		0.78 h	
c-Cr(NH$_3$)$_4$(OD$_2$)$_2^{3+}$	D$_2$O	"	"	8.5×10^{-3}	0.73			
Cr(en$_H$)$_3^{3+}$	H$_2$O	40mM La(ClO$_4$)$_3$	-900	2.2×10^{-3}	0.90		0.74 h	
"	D$_2$O	"	"	2.8×10^{-3}	0.90			
Cr(NH$_3$)$_5$NCS^{2+}	H$_2$O	40mM LaCl$_3$	-900	1.4×10^{-3}	0.45		0.60 h	
"	D$_2$O	"	"	2.2×10^{-3}	0.43			

Notes for Tables III and IV.

[a]Observed (apparent) cathodic rate constant at stated electrode potential E.

[b]Apparent cathodic transfer coefficient, obtained from
$$\alpha_{app} = -(f/2.303)(\partial \log k_{app}/\partial E)_{\mu}.$$

[c]Ratio of double-layer corrected rate constants k_{corr} for corresponding protonated and deuterated complexes at electrode potential and in supporting electrolytes indicated in columns at left, measured in either H_2O or D_2O as indicated. Obtained from corresponding listed values of k_{app} since $(k^{NH}/k^{ND})^E_{corr} = (k^{NH}/k^{ND})^E_{app}$ in same supporting electrolyte.

[d]Ratio of k_{corr} for either protonated or deuterated complexes in H_2O to that in D_2O at electrode potential and in supporting electrolytes indicated in columns at left. Obtained from corresponding listed values of k_{app} using eqn (1) as outlined in the text.

[e]Ratio of k_{corr} for protonated complex in H_2O to that for deuterated complex in D_2O. Obtained from corresponding listed values of k_{app} using eqn (1) as outlined in the text.

[f]in H_2O.

[g]in D_2O.

[h]protonated complex.

[i]deuterated complex.

TABLE V. Comparison of Solvent Isotope Effects for Corresponding Electrochemical and Homogeneous Reactions.

Reactant Pair	$(k_{12}^H/k_{12}^D)_{corr}^e$ [a]	$(k_{12}^H/k_{12}^D)_{corr}^h$ [b]
$Co(NH_3)_6^{3+} - Cr_{aq}^{2+}$	1.9	1.3 [c]
$Co(NH_3)_6^{3+} - V_{aq}^{2+}$	3.0	1.7 [c]
$Co(NH_3)_5OH_2^{3+} - V_{aq}^{2+}$	2.4	2.6 [c]
$Fe_{aq}^{3+} - Fe_{aq}^{2+}$	≈ 1.6	≈ 2 [d]

[a]Ratio of rate constants at the intersection of the (cathodic and anodic) Tafel plots for the constituent electrochemical half-reactions obtained in H_2O and D_2O using acidified $0.4\underline{M}$ KPF_6 as supporting electrolyte (see text and refs. 42 and 43), after correction for double-layer effects using eqn (1) as indicated in the text.

[b]Ratio of rate constants for listed homogeneous reaction in H_2O to that in D_2O in same supporting electrolyte, from literature source indicated.

[c]ref. 9.

[d]ref. 7.
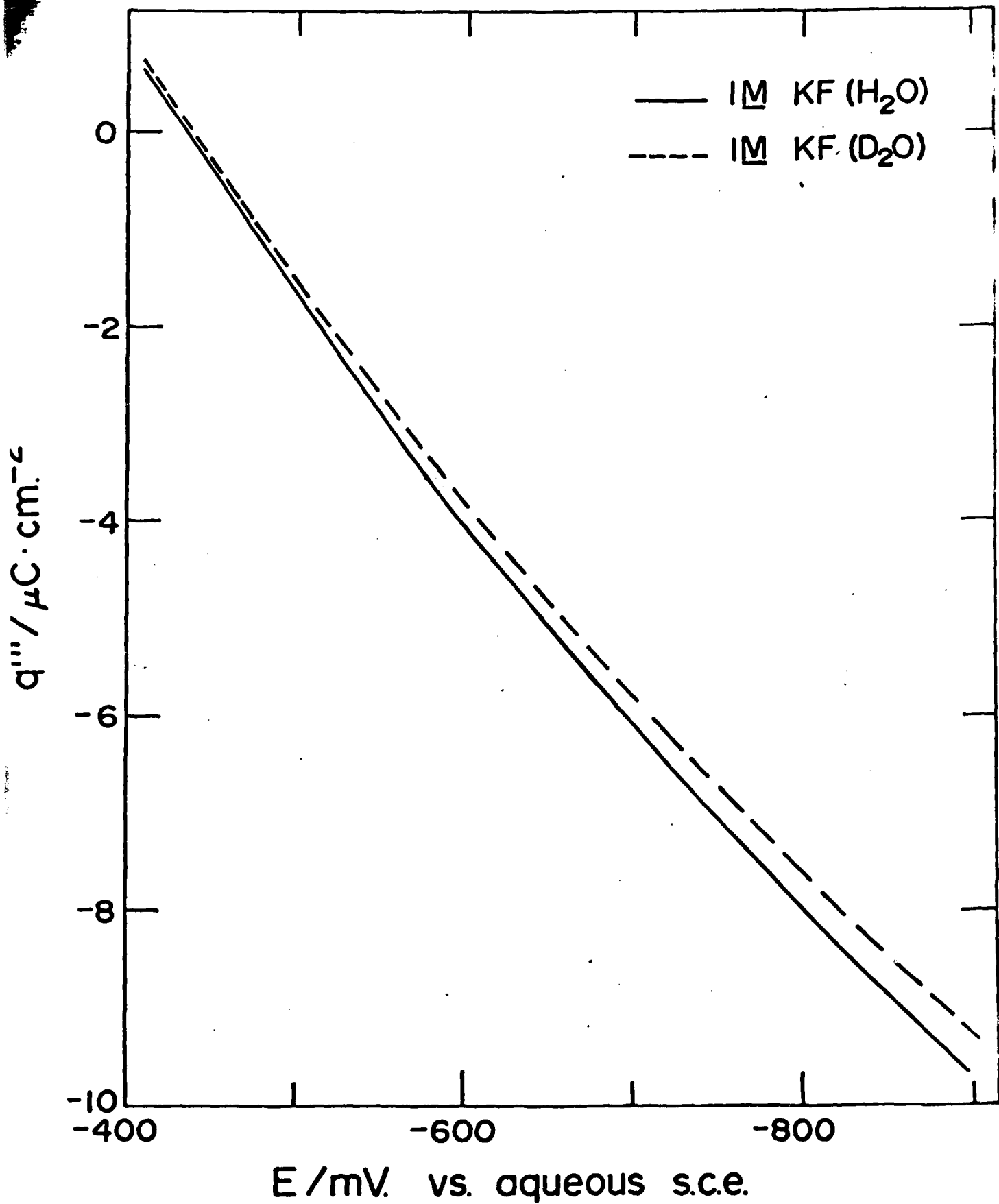
Caption to Fig. 1

The excess electronic charge density q^m of mercury in contact with 1$\underline{M}$ KF(H_2O) and 1$\underline{M}$ KF(D_2O) electrolytes plotted against the electrode potential E versus an aqueous s.c.e.