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Solvent Isotope Effects upon the Thermodynamics of Some Transition-Metal Redox Couples in Aqueous Media

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The effects of substituting D_2O for H_2O as solvent upon the formal potentials of a number of transition-metal redox couples containing aquo, ammine, and simple chelating ligands have been investigated with the intention of evaluating the importance of specific solvation factors in the thermodynamics of such couples. The solvent liquid junction formed between H_2O and D_2O was shown to have a negligible effect on the measured formal potentials. Substantial solvent isotope effects were observed for a number of these systems, particularly for couples containing aquo ligands. The effects of separately deuterating the ligands and the surrounding solvent were investigated for some ammine couples. Possible origins of the solvent isotope effects are discussed in terms of changes in metal–ligand and ligand–solvent interactions. It is tentatively concluded that the latter influence provides the predominant contribution to the observed effects for aquo couples arising from increases in the extent of hydrogen bonding between the aquo ligands and surrounding solvent when D_2O replaces H_2O. The implications of these results in unraveling the solvent isotope effects upon the kinetics of simple redox reactions are also considered.

Introduction

The effect of substituting heavy water (D_2O) for H_2O, i.e., the solvent isotope effect, upon the thermodynamics and kinetics of ionic reactions in aqueous media has been actively pursued over the years with the aim of unraveling some influences of the solvent upon these processes.[1,2] Some time ago, it was found that the kinetics of a number of simple inorganic redox reactions exhibited large solvent isotope effects, which stimulated some discussion on the nature of transition states for electron transfer in aqueous media.[3] This flurry of experimental activity receded when it became apparent that the explanations for the results were not straightforward.[3] However, the interpretation of these results has been severely limited by an absence of experimental information on the solvent isotope effects upon the redox thermodynamics.

We have recently been employing the solvent isotope effect as a means of exploring the influences of the solvent structure upon the electrochemical reactivity of simple inorganic reactants in aqueous media.[4] In connection with these studies we have measured the formal potentials, E_f, for a number of transition-metal redox couples of kinetic significance in D_2O and H_2O. These results are reported in the present paper. The magnitude of the solvent isotope effect has been found to be substantial and sensitive to the nature of the coordinated ligands, with large differences in E_f between D_2O and H_2O being observed for redox couples containing aquo ligands.

The possible origins of these differences will be discussed in the light of our recent measurements of the reaction entropies $\Delta S_{rc}°$ of redox couples containing aquo, ammine, and other simple ligands in aqueous media, which suggest the importance of hydrogen bonding between aquo ligands and the surrounding solvent to the thermodynamics of such redox couples.[5] Since D_2O appears to have a greater tendency to form hydrogen bonds (it is "more structured"[1]) and yet has almost identical dielectric properties with those of H_2O,[1] the scrutiny of solvent isotope effects upon E_f may provide a useful means of evaluating the importance of such "specific solvation" upon redox thermodynamics. The implications of these results in understanding the origins of the observed solvent isotope effects upon the kinetics of some simple redox reactions will also be considered.

Experimental Section

Techniques: Solvent Isotope Effect upon Formal Potentials. It is desired to compare directly the thermodynamics of a given redox couple in H_2O and D_2O. In a given solvent, the difference ($\bar{G}_{Red}° - \bar{G}_{Ox}°$) between the partial molal free energies of the reduced and oxidized halves of a one-electron redox couple in a given electrolyte is related to the measured formal potential E_f by eq 1, where ϕ_f is the Galvani

$$\bar{G}_{Red}° - \bar{G}_{Ox}° = -F\phi_f = -F(E_f - \phi_{ref} - \phi_{lj}) \qquad (1)$$

metal-solution potential difference at the working electrode which corresponds to the formal ("standard") cell potential E_f, ϕ_{ref} is the Galvani potential difference formed at the reference electrode, ϕ_{lj} is any liquid junction potential that may be formed in the cell, and F is the faraday. Of these potentials, only E_f is an experimentally accessible quantity. When D_2O (or another solvent) is substituted for H_2O, the observed changes in E_f can arise from variations in ϕ_{ref} and ϕ_{lj} as well as from ϕ_f and hence ($\bar{G}_{Red}° - \bar{G}_{Ox}°$); in fact, the experimental separation between these two effects is not possible on a purely thermodynamic basis.[6] Nevertheless, it turns out that useful estimates of the required change in ϕ_f, $\Delta\phi_f^{D-H}$, resulting from the substitution of D_2O for H_2O can be made by using the following approaches.

If the nature of the reference electrode is fixed as D_2O is substituted for H_2O in the working compartment (e.g., an aqueous calomel electrode is used), then ϕ_{ref} will remain constant. Although ϕ_{lj} can easily be arranged to be essentially zero in the all-aqueous cell by the use of a salt bridge, etc., a finite value of ϕ_{lj} may be present in the cell containing D_2O due to dissimilar values of the surface potentials χ_{D_2O} and χ_{H_2O} at the solvent junction. By measuring the real free energy of solvation of chloride ions in D_2O and H_2O, Case and Parsons[7] estimated that $\chi_{D_2O} - \chi_{H_2O} \approx 7$ mV when both solvents form surfaces with air. This estimate is compatible with the probable orientation of water molecules at the water–air interface.[7,8]

However, smaller values of $\chi_{D_2O} - \chi_{H_2O}$ might be expected at surfaces formed directly between these solvents since there would be little tendency for either the H_2O or D_2O molecules to preferentially orientate in the interphasial environment. This expectation is supported by the observation (vide infra) that the ferrocinium/ferrocene redox

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(1) E. M. Arnett and D. R. McKelvey in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, Chapter 6.

(2) P. M. Laughton and R. E. Robertson, "Solute-Solvent Interactions", J. F. Coetzee and C. D. Ritchie, Eds., Marcel Dekker, New York, 1969, Chapter 7.

(3) (a) J. Halpern, *Q. Rev., Chem. Soc.*, **15**, 207 (1961); (b) H. Taube, *Can. J. Chem.*, **37**, 129 (1959); (c) N. Sutin, J. K. Rowley, and R. W. Dodson, *J. Phys. Chem.*, **65**, 1248 (1961); (d) H. Taube, "Electron Transfer Reactions of Complex Ions in Solution", Academic Press, New York, 1970, pp 34, 37.

(4) P. D. Tyma, S. M. Nettles, and M. J. Weaver, submitted for publication.

(5) E. L. Yee, R. J. Cave, K. L. Guyer, P. D. Tyma, and M. J. Weaver, *J. Am. Chem. Soc.*, **101**, 1131 (1979).

(6) For example, see O. Popovych, *Crit. Rev. Anal. Chem.*, **7**, 73 (1970).

(7) B. Case, R. Parsons, *Discuss. Faraday Soc.*, **39**, 102 (1965); *Trans. Faraday Soc.*, **63**, 1224 (1967).

(8) The surface potential χ is the potential drop due to orientated solvent dipoles and will attain positive values when the positive end of the dipole is preferentially orientated toward the bulk solution.

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couple exhibits essentially identical formal potentials in H_2O and D_2O with respect to an aqueous reference electrode. Ferrocene and ferrocinium should exhibit weak and largely compensatory interactions with the surrounding solvent, so that $\Delta(\bar{G}_{Red}^\circ - \bar{G}_{Ox}^\circ)$ for the couple between different solvents should be small and roughly in accordance with the predictions of the dielectric-continuum Born model.[6] Since the dielectric properties of D_2O and H_2O are almost identical,[1] then probably $\Delta\phi_f^{D-H} \approx 0$ so that the observation that $\Delta E_f = 0$ (±1–2 mV) indicates that the solvent junction potential $\phi_{lj} \approx 0$ (eq 1). (From the Born model, $\Delta\phi_f^{D-H} \approx 0.15$ mV for ferrocinium/ferrocene.)

Consequently, the cell arrangement employed in the present work consisted of a reference compartment containing aqueous solution and a working compartment containing the redox couple in either D_2O or H_2O which was separated from the reference compartment by means of a glass frit ("very fine" grade, Corning, Inc.). A commercial aqueous saturated calomel electrode (SCE) was immersed in the reference compartment. For redox couples that could be examined in supporting electrolytes where hydrogen or hydroxide ions made only a minor (<5%) contribution to the total ionic strength, the reference compartment was filled with an aqueous solution of the same ionic composition as the H_2O and D_2O solutions in the working compartment. For some reactants it was necessary to employ strongly acidic or basic electrolytes in order either to suppress or to promote hydrolysis. Since the ionic mobilities of the proton and deuteron in H_2O and D_2O differ significantly,[9] under these circumstances the reference compartment contained a concentrated "salt bridge" solution of either saturated aqueous KCl or NH_4Cl in order to minimize the liquid junction potential. (The latter solution was used in place of KCl when concentrated perchlorate or hexafluorophosphate electrolytes were being scrutinized in order to avoid precipitation of $KClO_4$ or KPF_6 in the liquid junction.) The success of this tactic in minimizing ϕ_{lj} was evidenced by the similar values of E_f that were obtained as the acid concentration was varied at a constant ionic strength for reactants where the extent of hydrolysis is negligible.

Some formal potential measurements were made as a function of temperature in D_2O and H_2O in order to evaluate the reaction entropy of the redox couple, ΔS_{rc}°.[5] A nonisothermal cell arrangement was used.[5] For measurements in D_2O, the reference compartment was filled with D_2O solution so that the solvent liquid junction formed in these cells was maintained at a fixed temperature and did not contribute to the temperature dependence of E, and therefore to ΔS_{rc}°.

Formal potentials were evaluated for most systems by using cyclic voltammetry from the average of the cathodic and anodic peak potentials. Electrolyte conditions were chosen so that reversible or near-reversible voltammetric response was obtained; i.e., the cathodic–anodic peak separation was ca. 60–80 mV. Such reversibility was encouraged where necessary by employing noncomplexing electrolytes that also exhibit extensive anion-specific adsorption. Since most of the redox couples that were scrutinized consisted of multicharged cations, markedly accelerated electrochemical reactivities (i.e., more reversible behavior) typically resulted from the large and negative diffuse-layer potentials that are thereby produced.[10] For the $Cr_{aq}^{3+/2+}$ couple (where "aq" represents aquo ligands), the heterogeneous electron-transfer rates were too small to allow E_f to be satisfactorily evaluated by using cyclic voltammetry. For this system, E_f was determined potentiometrically by electrolytically generating solutions containing both halves of the redox couple, measuring the potential corresponding to zero current on the resulting cathodic–anodic dc polarogram,[11] and inserting this potential into the Nernst equation along with the concentration ratio of the oxidized to reduced species. This ratio was obtained from the relative sizes of the cathodic and anodic limiting currents. Strictly speaking, both this approach and cyclic voltammetry yield "half-wave" potentials $E_{1/2}$ which differ from E_f by $E_{1/2} = E_f + RT/F[\ln (D_{Red}/D_{Ox})^{1/2}]$, where D_{Red} and D_{Ox} are the diffusion coefficients of the reduced and oxidized species, respectively.[12] Fortunately, D_{Red}/D_{Ox} is usually close to unity so that the correction only amounts to 2–3 mV. Although significantly (10–30%) smaller values of D_{Red} and D_{Ox} were observed in D_2O compared to those in H_2O by using polarography,[4] the ratios D_{Red}/D_{Ox} were typically found to be very similar (within ca. 5%) in the two solvents, so that the required relative values of E_f will be almost identical (±1 mV) to the measured relative values of $E_{1/2}$ in H_2O and D_2O.

Consequently, in view of eq 1 an observed shift in $E_{1/2}$ for a given couple, $\Delta E_{1/2}^{D-H}$, in changing from H_2O to D_2O is related to a good approximation (±1–2 mV) to the required change in $\bar{G}_{Red}^\circ - \bar{G}_{Ox}^\circ$, $\Delta(\bar{G}_{Red}^\circ - \bar{G}_{Ox}^\circ)^{D-H}$, by eq 2.

$$\Delta(\bar{G}_{Red}^\circ - \bar{G}_{Ox}^\circ)^{D-H} = -F\Delta\phi_f^{D-H} \approx -F\Delta E_{1/2}^{D-H} \qquad (2)$$

Apparatus. The electrochemical cells and electrodes used were substantially the same as those described in ref 5. Either a hanging mercury drop electrode (HMDE) or a platinum "flag" electrode was used for cyclic voltammetry, depending on the potential region being scrutinized. (As expected, these electrodes yield identical results for reversible couples having values of E_f where either electrode could be used.) Both cyclic voltammograms and dc polarograms were obtained by using a PAR 174A polarographic analyzer (Princeton Applied Research) coupled with a Hewlett-Packard 7045A X-Y recorder. Cyclic voltammograms were recorded by using sweep rates in the range 50–500 mV s^{-1}. All electrode potentials are quoted vs. an aqueous SCE.

Materials. Most analytical grade reagents were used without further purification. Water was purified by using a MilliQ purification system (Millipore Corp.). Deuterium oxide (99.8%, Stohler Isotope Chemicals) was used either directly or following distillation from alkaline permanganate with identical results. Descriptions of or sources for syntheses of most of the complexes used in the present work are given in ref 5. Ferrocinium picrate was prepared as described in ref 13. Solutions of U_{aq}^{3+} were prepared by electrolyzing uranyl perchlorate (G. F. Smith Co.) in 0.5 M $HClO_4$ at −1000 mV by using a stirred mercury pool.

Results

Table IA summarizes values of $E_{1/2}$ obtained at 25 °C in H_2O and D_2O, labeled $E_{1/2}^H$ and $E_{1/2}^D$, respectively, for nine transition-metal redox couples of the general form $M^{III} + e^- \rightleftharpoons M^{II}$ containing ammine, ethylenediamine, or simple aromatic ligands. Table IB contains corresponding data for nine redox couples containing aquo or hydroxo ligands. It is seen that significant and even large differences, $\Delta E_{1/2}^{D-H}$, between $E_{1/2}^D$ and $E_{1/2}^H$ were observed for a number of the redox couples containing aquo ligands. The most dramatic effect is seen for $Cr_{aq}^{3+/2+}$, where $\Delta E_{1/2}^{D-H} = 57$ mV, although large values of $\Delta E_{1/2}^{D-H}$ were also observed for $Fe_{aq}^{3+/2+}$ and $V_{aq}^{3+/2+}$ (43 and 33 mV, respectively). Substantial values of $\Delta E_{1/2}^{D-H}$ were also seen for $U_{aq}^{4+/3+}$ (28 mV) and $Tl_{aq}^{3+/+}$ (~20 mV). The changes in $E_{1/2}$ observed for $Fe_{aq}^{3+/2+}$ in various D_2O–H_2O mixtures compared to pure H_2O were found to be approximately proportional to the mole fraction of D_2O present. The magnitude of $\Delta E_{1/2}^{D-H}$ was typically found to be essentially independent of the ionic strength μ, at least in the range $\mu \approx 0.05$–0.5.

In contrast, small or negligible values of $\Delta E_{1/2}^{D-H}$ were observed for most of the couples not containing aquo ligands, although significant values of $\Delta E_{1/2}^{D-H}$ were seen for $Co(bpy)_3^{3+/2+}$ (5 mV), $Co(phen)_3^{3+/2+}$ (8 mV), and $Ru(en)_3^{3+/2+}$ (10 mV). Also, negative values of $\Delta E_{1/2}^{D-H}$ were found for $Ru(NH_3)_5OH^{2+/+}$ (−13 mV) and $Co(en)_3^{3+/2+}$ (−8 mV).

For aquo complexes, the substitution of H_2O by D_2O as solvent will also yield an unavoidable corresponding change in the composition of the aquo ligands. However, although the hydrogen atoms bound to coordinated nitrogen in ammine and ethylenediamine complexes are rapidly exchanged with the solvent in neutral and basic solutions, the exchange rates typically become slow in acidic media.[14,15] Consequently, it

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Table I

couple	medium[j]	$E_{1/2}^{H}$,[a] mV vs. aq SCE	$E_{1/2}^{D}$,[b] mV vs. aq SCE	$\Delta E_{1/2}^{D-H}$,[c] mV
A. Solvent Isotope Effect upon the Formal Potentials for Various Transition-Metal Redox Couples Containing Amine or Aromatic Ligands at 25 °C				
ferricinium/ferrocene	0.05 M $NaClO_4$	−125	−125	0
	0.2 M $NaClO_4$	−124	−124	0
$Fe(bpy)_3^{3+/2+}$ [f]	0.05 M KCl	844	844	0
$Co(bpy)_3^{3+/2+}$ [f]	0.05 M KCl	78	83	5
$Co(phen)_3^{3+/2+}$ [g]	0.05 M KCl	138	146	8
$Ru(NH_3)_6^{3+/2+}$	0.1 M KPF_6	−177		
	0.1 M NapTS	−180		
	0.09 M NapTS + 0.01 M HpTS	−180	−176	4
$Ru(ND_3)_6^{3+/2+}$	0.1 M KPF_6		−177	
	0.1 M NapTS		−177	
	0.09 M NapTS + 0.01 M HpTS	−179	−176	3
$Ru(en_H)_3^{3+/2+}$ [h]	0.1 M KPF_6	−65		
	0.1 M NapTS	−75		
	0.09 M NapTS + 0.01 M HpTS	−75	−65	10
$Ru(en_D)_3^{3+/2+}$ [h]	0.1 M KPF_6		−57	
	0.1 M NapTS		−65	
	0.09 M NapTS + 0.01 M HpTS	−75	−65	10
$Ru(NH_3)_5NCS^{2+/+}$	0.1 M KPF_6	−135		
$Ru(ND_3)_5NCS^{2+/+}$	0.1 M KPF_6		−135	0
$Ru(NH_3)_5NCS^{2+/+}$	0.09 M NapTS + 0.01 M HpTS	−138	−138	0
$Co(en_H)_3^{3+/2+}$	0.2 M KPF_6 + 0.05 M en	−445		
$Co(en_D)_3^{3+/2+}$	0.2 M KPF_6 + 0.05 M en		−453	−8
$Co(sepulchrate)^{3+/2+}$ [i]	0.1 M $NaClO_4$	−539	−538	1
B. Solvent Isotope Effect upon the Formal Potentials for Various Redox Couples Containing Aquo or Hydroxo Ligands at 25 °C				
$Ru(NH_3)_5OH^{2+/+}$	0.1 M KPF_6 + 0.2 M KOH	−650		−13
$Ru(ND_3)_5OD^{2+/+}$	0.1 M KPF_6 + 0.2 M KOH		−663	
$c\text{-}Ru(NH_3)_4(OH_2)_2^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$	−130		13
$c\text{-}Ru(NH_3)_4(OD_2)_2^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$		−117	
$Cr(OH_2)_6^{3+/2+}$	0.08 M $NaClO_4$ + 0.02 M HpTS	−651[d]		57
$Cr(OD_2)_6^{3+/2+}$	0.08 M $NaClO_4$ + 0.02 M HpTS		−594[d]	
$Fe(OH_2)_6^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$	495		43
$Fe(OD_2)_6^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$		538	
$V(OH_2)_6^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$	−472		33
$V(OD_2)_6^{3+/2+}$	0.16 M $NaClO_4$ + 0.04 M $HClO_4$		−439	
$Eu(OH_2)_n^{3+/2+}$	0.1 M NapTS + 1 mM HpTS	−622		9
$Eu(OD_2)_n^{3+/2+}$	0.1 M NapTS + 1 mM HpTS		−613	
$U(OH_2)_n^{4+/3+}$	0.5 M $HClO_4$	−867		28
$U(OD_2)_n^{4+/3+}$	0.5 M $HClO_4$		−839	
$Tl(OH_2)_n^{3+/+}$	0.5 M $HClO_4$	1005		~20
$Tl(OD_2)_n^{3+/+}$	0.5 M $HClO_4$		~1025[e]	
$UO_2^{2+/+}$	0.19 M $NaClO_4$ + 0.01 M $HClO_4$	−177	−165	12

[a] "Half-wave" potential for stated redox couple in H_2O using the supporting electrolyte listed obtained, unless otherwise stated, from the average of the cathodic and anodic peak potentials by using cyclic voltammetry. The precision of these and other potentials listed is generally ca. ±1 mV. [b] "Half-wave" potential obtained in D_2O. [c] Difference between half-wave potentials in D_2O and H_2O, $E_{1/2}^{D} - E_{1/2}^{H}$. [d] Determined by using potentiometry (see text). [e] Approximate value due to unavoidably large (~100 mV) cathodic-anodic peak separation observed for cyclic voltammograms with a Pt electrode. [f] bpy = 2,2′-bipyridine. [g] phen = 1,10-phenanthroline. [h] en = ethylenediamine. Subscripts H and D refer to protonated and deuterated amine hydrogens, respectively. [i] Sepulchrate = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane. See I. I. Creaser, J. M. Harrowfield, A. J. Herlt, A. M. Sargeson, and J. Springborg, *J. Am. Chem. Soc.*, 99, 3181 (1977). [j] pTS = *p*-toluenesulfonate.

is often possible to examine independently the effects of deuterating the aqueous solvent and the amine ligands. Such examinations were made for $Ru(NH_3)_6^{3+/2+}$, $Ru(en)_3^{3+/2+}$, and $Ru(NH_3)_5NCS^{2+/+}$. Solutions of the deuterated complexes $Ru(ND_3)_6^{3+}$ and $Ru(en_D)_3^{3+}$ were prepared by adding concentrated (30 mM) stock solutions of $Ru(NH_3)_6(ClO_4)_3$ and $Ru(en_H)_3(ClO_4)_3$ in neutral D_2O to solutions containing 10^{-2} M acid in H_2O or D_2O as appropriate and were examined immediately (within ~30–60 s). Under these conditions the exchange of the amine hydrogens is slow (half-lives of ca. 30 and 15 min for the ammine and ethylenediamine complexes, respectively),[15] so that the complexes remain essentially deuterated. (The corresponding Ru(II) complexes formed during the cyclic voltammetric sweeps are similarly inert to hydrogen exchange.[15]) The protonated complexes were also examined in H_2O and D_2O by using a similar procedure.

Inspection of Table I reveals that substitution of deuterium for hydrogen in the coordination sphere produces little change in $E_{1/2}$ for $Ru(NH_3)_6^{3+/2+}$ or $Ru(en)_3^{3+/2+}$ in either H_2O or D_2O. However, the substitution of D_2O for H_2O solvent yielded small yet significant values of $\Delta E_{1/2}^{D-H}$ for $Ru(NH_3)^{3+/2+}$ and $Ru(ND_3)_6^{3+/2+}$ (3–4 mV) and larger values for $Ru(en_H)_3^{3+/2+}$ and $Ru(en_D)_3^{3+/2+}$ (10 mV).

It is of interest to apportion the large values of $\Delta E_{1/2}^{D-H}$ and hence $-\Delta(\bar{G}_{Red}^{\circ} - \bar{G}_{Ox}^{\circ})^{D-H}$ (eq 2) observed for aquo couples into the corresponding enthalpic and entropic components $\Delta(\bar{H}_{Red}^{\circ} - \bar{H}_{Ox}^{\circ})^{D-H}$ and $\Delta(\bar{S}_{Red}^{\circ} - \bar{S}_{Ox}^{\circ})^{D-H}$. We have recently pointed out[5] that absolute values of $\bar{S}_{Red}^{\circ} - \bar{S}_{Ox}^{\circ}$

= $\Delta S_{rc}°$ (the "reaction entropy"[5]) in a given solvent can be obtained directly from the temperature dependence of $E_{1/2}$ by using nonisothermal cells. Determination of $\Delta S_{rc}°$ for $Fe_{aq}^{3+/2+}$ in H_2O and D_2O using a supporting electrolyte of 0.16 M $NaClO_4$ and 0.04 M $HClO_4$ yielded values of 43.2 and 45.4 eu, respectively (both ca. ±0.3 eu, taken over the temperature range 3–60 °C). Since $\Delta E_{1/2}^{D-H} = 43$ mV under these conditions at 25 °C, then from eq 2 $\Delta(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H} = -1.0$ kcal mol^{-1} and $T\Delta(\bar{S}_{Red}° - \bar{S}_{Ox})^{D-H} = 0.65$ kcal mol^{-1} at 25 °C, and it therefore appears that the solvent isotope effect upon $\Delta(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H}$ for this system arises from reinforcing contributions from both the entropic and the enthalpic components. Unfortunately, the determination of $T\Delta(\bar{S}_{Red}° - \bar{S}_{Ox}°)^{D-H}$ for other aquo couples was curtailed by the extremely accurate measurements of $\Delta S_{rc}°$ that are required for this purpose.

Discussion

Solvent Isotope Effects. The substantial changes in $E_{1/2}$ seen for some aquo couples by substituting D_2O for H_2O show that the solvent isotope effect can yield surprisingly large shifts in redox equilibria. For instance, the value of $\Delta E_{1/2}^{D-H}$ for $Cr_{aq}^{3+/2+}$ (57 mV) corresponds to $\Delta(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H} = -1.35$ kcal mol^{-1} (eq 2) or a change in the redox equilibrium constant of about one order of magnitude, so that Cr_{aq}^{2+} is a substantially less powerful reducing agent in D_2O than in H_2O. These results may arise from (i) differences in the electrostatic interactions between the metal redox center and the aquo ligands when the latter are changed from H_2O to D_2O and/or (ii) differences in the interaction between the D_2O ligands and surrounding D_2O solvent as compared to H_2O ligands and surrounding H_2O solvent.

Effect i has previously been invoked to explain the significant isotope effects seen for some complexation equilibria.[3c,16] It also predicts isotope effects upon redox equilibria that are in qualitative accordance with the present results. Thus it is expected that the enhancement of the field within the coordination sphere caused by an increase in the charge of the metal cation will yield a decrease in the zero point energy difference between OD_2 and OH_2 ligands, as a result of a lowering of the stretching vibrational frequencies.[16] Consequently, deuteration of the aquo ligands in the tripositive complex is expected to lead to a smaller energy stabilization than deuteration of the corresponding divalent state, leading to positive values of $\Delta E_{1/2}^{D-H}$, as observed. However, the expected magnitude of this effect is not easy to assess. One argument against the importance of effect i to the present results is that this simple electrostatic model might also be expected to predict significant values of $\Delta E_{1/2}^{D-H}$ for ammine couples in view of the rough similarities in size and structure of NH_3 and OH_2. In contrast, virtually identical values of $E_{1/2}$ were observed for $Ru(NH_3)_6^{3+/2+}$ and $Ru(ND_3)_6^{3+/2+}$ in both H_2O and D_2O (Table IA). Also, effect i is expected to be purely enthalpic in nature, whereas the observed value of $(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H}$ at least for $Fe_{aq}^{3+/2+}$ contains a major entropic contribution.

On the other hand, effect ii can provide a reasonable explanation of this last result. Thus it is likely that aquo couples $M_{aq}^{3+/2+}$ induce a substantial degree of hydrogen bonding between the aquo ligands and surrounding water molecules, especially in the higher oxidation state where such solvent "structure making" will be aided by the tripositive charge.[5] This effect is partly responsible for the observed values of $\Delta S_{rc}°$ for a number of $M(OH_2)_6^{3+/2+}$ couples that are substantially larger than $\Delta S_{rc}°$ for otherwise similar $M(NH_3)_6^{3+/2+}$ couples as well as the theoretical estimates obtained from the Born model.[5] It is known that D_2O tends to engage in hydrogen bonding to a significantly greater extent than H_2O,[1] so that the solvent "structure-breaking" or "structure-making" abilities of ions are accentuated in the former medium.[1] Consequently, the replacement of H_2O by D_2O in the coordination sphere of $M_{aq}^{3+/2+}$ couples is anticipated to result in an increase in the extent of solvent ordering via hydrogen bonding with these ligands, and this is expected to occur to a greater extent in the higher oxidation state. This expectation is in harmony with the observed positive value of $\Delta(\bar{S}_{Red}° - \bar{S}_{Ox}°)^{D-H}$ for $Fe_{aq}^{3+/2+}$. This effect might also be expected to yield positive values of $\Delta(\bar{H}_{Red}° - \bar{H}_{Ox}°)^{D-H}$ since O–D···O hydrogen bonds appear to be slightly stronger than O–H···O bonds.[1,17] The values of $\Delta(\bar{S}_{Red}° - \bar{S}_{Ox}°)^{D-H}$ and $\Delta(\bar{H}_{Red}° - \bar{H}_{Ox}°)^{D-H}$ would then counteract each other to yield smaller values of $\Delta(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H}$. Such compensation effects are often observed in aqueous media.[18] In contrast, a negative value of $\Delta(\bar{H}_{Red}° - \bar{H}_{Ox}°)^{D-H}$ (ca. −0.35 kcal mol^{-1}) is actually observed for $Fe_{aq}^{3+/2+}$. This may arise because the greater polarization of solvating water molecules in the higher oxidation state could nonetheless result in a slightly smaller *overall* number of hydrogen bonds within the surrounding solvent compared with those formed in the lower oxidation state. Alternatively, there could be a significant negative contribution to $\Delta(\bar{H}_{Red}° - \bar{H}_{Ox}°)^{D-H}$ from effect i.

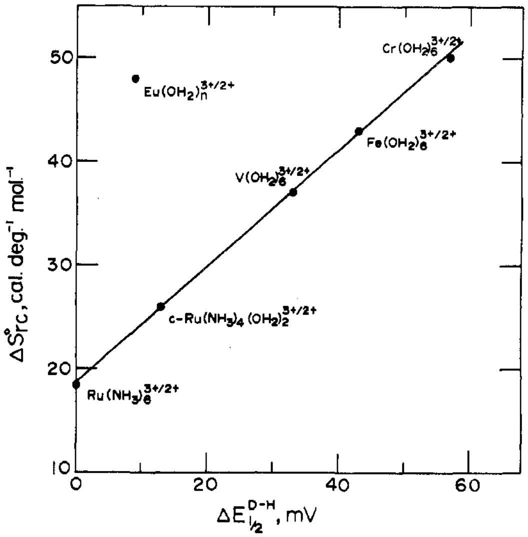

Figure 1. Reaction entropies $\Delta S_{rc}°$ for six $M^{3+/2+}$ redox couples plotted against the corresponding measured shift in half-wave potential between H_2O and D_2O solvent, $\Delta E_{1/2}^{D-H}$. Values of $\Delta E_{1/2}^{D-H}$ were taken from Table IA,B. Values of $\Delta S_{rc}°$ were measured at or extrapolated to an ionic strength of 0.1 and are taken from ref 5.

Further evidence supporting the interpretation of $\Delta H_{1/2}^{D-H}$ for aquo couples primarily in terms of effect ii is obtained by comparing the corresponding values of $\Delta S_{rc}°$ in H_2O and $\Delta E_{1/2}^{D-H}$ for a series of related redox couples. Figure 1 is such a plot for six $M^{3+/2+}$ couples containing aquo and/or ammine ligands. It is seen that an excellent linear correlation is obtained between $\Delta S_{rc}°$ and $\Delta E_{1/2}^{D-H}$ for five of these couples which are all hexacoordinate in both oxidation states. (The line drawn through these points has a slope, expressed as the dimensionless ratio $-Td\Delta S_{rc}°/d\Delta(\bar{G}_{Red}° - \bar{G}_{Ox}°)^{D-H}$, equal to 7.0.) Inasmuch as the marked variations of $\Delta S_{rc}°$ in Figure 1 almost certainly arise from the influence of the coordinated ligands upon the surrounding solvent,[5,19] this correlation suggests that a major part of the observed values of $\Delta E_{1/2}^{D-H}$ for aquo couples also arises from the same source. The marked deviation from the correlation seen for the $Eu_{aq}^{3+/2+}$ couple

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(Figure 1) may be due to complications from the probable difference in the number of coordinated aquo ligands between Eu_{aq}^{3+} and Eu_{aq}^{2+}. It is interesting to note that large variations in $\Delta S_{rc}°$ have also been observed between a number of redox couples not containing aquo ligands for which relatively small values of $\Delta E_{1/2}^{D-H}$ were obtained. For example, $Fe(bpy)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Co(en)_3^{3+/2+}$ yield $\Delta S_{rc}°$ values of 2, 22, and 37 eu,[5] whereas $\Delta E_{1/2}^{D-H}$ equals 0, 5, and −8 mV, respectively (Table IA). These findings are in harmony with a recent suggestion[19] that the observed values of $\Delta S_{rc}°$ may arise from two distinct sources, only one of which contributes to $\Delta S_{rc}°$ for nonaquo couples and both of which contribute to $\Delta S_{rc}°$ for aquo couples. The large values of $\Delta S_{rc}°$ seen for the Co(III)/Co(II) couples have been ascribed to the solvation changes induced by the expansion of the metal center upon reduction.[19] This effect probably also contributes to the large observed values of $\Delta S_{rc}°$ for aquo couples along with the influence of hydrogen bonding noted above.

It remains to consider the possible origins of the appreciable values of $\Delta E_{1/2}^{D-H}$ observed for some redox couples not containing aquo ligands (Table IA). The negative value of $\Delta E_{1/2}^{D-H}$ (−13 mV) seen for $Ru(NH_3)_5OH^{2+/+}$ is interesting in the light of the unusually small value of $\Delta S_{rc}°$ (~0 eu) observed for this couple in H_2O which was attributed to hydrogen bonding in the Ru(II) state between the hydroxo ligand and the surrounding solvent. This explanation is also nicely compatible with the negative value of $\Delta E_{1/2}^{D-H}$ provided that the predominant contribution arises from a net entropic destabilization of the divalent oxidation state. The values of $\Delta E_{1/2}^{D-H}$ seen for $Ru(en)_3^{3+/2+}$ and $Co(en)_3^{3+/2+}$ (+10 and −8 mV, respectively) are somewhat surprising. It is interesting to note that the former value arises purely from a *solvent* isotope effect since $Ru(en_H)_3^{3+/2+}$ and $Ru(en_D)_3^{3+/2+}$ yield identical results. It seems likely that these effects reflect alterations in solvent structure resulting from changes in the conformation in the chelating ligands[20] upon electron transfer.

Implications for Isotope Effects in Redox Kinetics. The data in Table IA,B show that substantial changes in the equilibrium constants K of redox reactions involving aquo couples result from changing the solvent from H_2O to D_2O. In the light of this information, it is of interest to reexamine the available data for the solvent isotope effect upon the kinetics of simple cross reactions. Upon consideration of structural influences upon redox reactivity such as those that give rise to a difference between the rate constants k^H and k^D for a given reaction in H_2O and D_2O, it is convenient to distinguish between the so-called "intrinsic" and "thermodynamic" contributions.[21-23] The latter contribution includes the overall driving force as measured by the equilibrium constant K. For cross reactions having small or moderate driving forces, a given ratio of equilibrium constants measured in H_2O and D_2O (K^H/K^D) will generally be expected to give rise to a corresponding ratio of rate constants (k^H/k^D) according to $k^H/k^D \approx (K^H/K^D)^{1/2}$.[21] Table II summarizes the available experimental values of k^H/k^D for cross reactions involving the same or similar reactants for which values of $\Delta E_{1/2}^{D-H}$ are listed in Table I. The estimates of $(K^H/K^D)^{1/2}$ given for each reaction in Table II were obtained from eq 3, where $(\Delta E_{1/2}^{D-H})_{Red}$ and

$$K^H/K^D = \exp[(F/RT)[(\Delta E_{1/2}^{D-H})_{Red} - (\Delta E_{1/2}^{D-H})_{Ox}]] \tag{3}$$

$(\Delta E_{1/2}^{D-H})_{Ox}$ refer to the couples undergoing net one-electron reduction and oxidation, respectively. Since the values of $\Delta E_{1/2}^{D-H}$ for some of these couples are unknown, they were either roughly estimated by assuming that $\Delta E_{1/2}^{D-H}$ equals zero for couples not containing OH_2 or OH^- ligands or set equal to the values of $\Delta E_{1/2}^{D-H}$ for structurally similar couples to those given in Table I.

Table II. Solvent Isotope Effects upon the Kinetics of Some Cross Reactions

reactants	k^H/k^D [a]	$(K^H/K^D)^{1/2}$ [b]	pathway[c]	ref
(1) $Co(NH_3)_6^{3+} + Cr(bpy)_3^{2+}$	0.98	1.0	os	*d*
(2) $Co(NH_3)_6^{3+} + Cr_{aq}^{2+}$	1.3	3.0	os	*d*
(3) $Co(NH_3)_6^{3+} + V_{aq}^{2+}$	1.7	1.9	os	*d*
(4) $Co(NH_3)_5OH_2^{3+} + Cr(bpy)_3^{2+}$	2.6	0.8	os	*d*
(5) $Co(NH_3)_5OH_2^{3+} + V_{aq}^{2+}$	2.6	1.6	os	*d*
(6) $Co(NH_3)_5OH^{2+} + Cr_{aq}^{2+}$	2.6	4.0	is	*e*
(7) $Co(NH_3)_5Cl^{2+} + V_{aq}^{2+}$	2.2	1.9	os?	*d*
(8) $Cr(NH_3)_5Cl^{2+} + Cr_{aq}^{2+}$	1.3	3.0	is	*f*
(9a) $Pu_{aq}^{4+} + PuO_2^{+}$	0.58	0.7	os?	*g*
(9b) $PuO_2^{2+} + Pu_{aq}^{3+}$	1.79	1.4	os?	*g*

[a] Ratio of measured rate constant in H_2O to that in D_2O under the same conditions. Compositions of ammine ligands remain unchanged in H_2O and D_2O. [b] Square root of ratio of estimated equilibrium constant for reaction in H_2O to that in D_2O. Obtained from eq 3 by using data in Table I (see text for details). [c] Probable reaction pathway: os denotes outer sphere; is denotes inner sphere. [d] A. Zwickel and H. Taube, *J. Am. Chem. Soc.*, **83**, 793 (1961). [e] A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959). [f] A. E. Ogard and H. Taube, *ibid.*, **80**, 1084 (1958). [g] S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

Inspection of Table II reveals that the kinetic isotope effects observed for the majority of these reactions are due in large part to the influence of the thermodynamic driving force. Undoubtedly other factors contribute to the observed kinetic effects, such as variations in the "thermodynamic" contribution arising from the work terms required to form the binuclear intermediate prior to electron transfer.[24]

It therefore appears that specific solvation arising from hydrogen-bonding interactions can play a significant and even important role in determining the thermodynamics and kinetics of redox reactions involving aquo complexes. It is surprising that virtually no previous attempts have been made to explore the solvent isotope effect upon redox thermodynamics. In view of the present results, such measurements may provide a valuable method of probing the influence of specific solvation upon the thermodynamics of more complex systems such as metalloprotein redox reactions, particularly when combined with measurements of the reaction entropies.[25] When coupled with the corresponding thermodynamic data, studies of the solvent isotope effect upon the kinetics of simple redox reactions may yet provide a useful way of probing the influences of the surrounding solvent upon such processes. We shall report elsewhere the results of a study of solvent isotope effects upon the electrochemical kinetics of simple inorganic reactants.[4]

Acknowledgment. Robert Cave and Edmund Yee performed some additional experiments. Dr. Gilbert Brown and Professor John Endicott kindly supplied some of the complexes used in this study. This work is supported by the Air Force Office of Scientific Research.

Registry No. Ferrocenium, 12125-80-3; ferrocene, 102-54-5; $Fe(bpy)_3^{3+}$, 18661-69-3; $Fe(bpy)_3^{2+}$, 15025-74-8; $Co(bpy)_3^{3+}$, 19052-39-2; $Co(bpy)_3^{2+}$, 15878-95-2; $Co(phen)_3^{3+}$, 18581-79-8; $Co(phen)_3^{2+}$, 16788-34-4; $Ru(NH_3)_6^{3+}$, 18943-33-4; $Ru(NH_3)_6^{2+}$, 19052-44-9; $Ru(ND_3)_6^{3+}$, 73117-29-0; $Ru(ND_3)_6^{2+}$, 73117-30-3; $Ru(en_H)_3^{3+}$, 21393-87-3; $Ru(en_H)_3^{2+}$, 21393-86-2; $Ru(en_D)_3^{3+}$, 73117-31-4; Ru-

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$(en_D)_3^{2+}$, 73117-32-5; $Ru(NH_3)_5NCS^{2+}$, 44819-58-1; $Ru(NH_3)_5NCS^+$, 73117-33-6; $Ru(ND_3)_5NCS^{2+}$, 73117-34-7; $Ru(ND_3)_5NCS^+$, 73117-35-8; $Co(en_H)_3^{3+}$, 14878-41-2; $Co(en_H)_3^{2+}$, 23523-25-3; $Co(en_D)_3^{3+}$, 23420-60-2; $Co(en_D)_3^{2+}$, 73117-16-5; Co(sepulchrate)$^{3+}$, 72496-77-6; Co(sepulchrate)$^{2+}$, 63218-22-4; $Ru(NH_3)_5OH^{2+}$, 38331-41-8; $Ru(NH_3)_5OH^+$, 73117-17-6; $Ru(ND_3)_5OD^{2+}$, 73117-18-7; $Ru(ND_3)_5OD^+$, 73117-19-8; *c*-$Ru(NH_3)_4(OH_2)_2^{3+}$, 38139-18-3; *c*-$Ru(NH_3)_4(OH_2)_2^{2+}$, 29946-00-7; *c*-$Ru(NH_3)_4(OD_2)_2^{3+}$, 73117-20-1; *c*-$Ru(NH_3)_4(OD_2)_2^{2+}$, 73117-21-2; $Cr(OH_2)_6^{3+}$, 14873-01-9; $Cr(OH_2)_6^{2+}$, 20574-26-9; $Cr(OD_2)_6^{3+}$, 44437-80-1; $Cr(OD_2)_6^{2+}$, 73117-22-3; $Fe(OH)_6^{3+}$, 15377-81-8; $Fe(OH)_6^{2+}$, 15365-81-8; $Fe(OD)_6^{3+}$, 73117-23-4; $Fe(OD)_6^{2+}$, 69701-34-4; $V(OH_2)_6^{3+}$, 21374-21-0; $V(OH_2)_6^{2+}$, 15696-18-1; $V(OD)_6^{3+}$, 73117-24-5; $V(OD)_6^{2+}$, 73117-25-6; Eu^{3+}, 22541-18-0; Eu^{2+}, 16910-54-6; U^{4+}, 16089-60-4; U^{3+}, 22578-81-0; Tl^{3+}, 14627-67-9; Tl^+, 22537-56-0; UO_2^{2+}, 16637-16-4; UO_2^+, 21294-41-7.

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Gallium Complexes of Multidentate Ligands in Aqueous Solution

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Gallium(III) was equilibrated in dilute aqueous solution at 25 °C, $\mu = 0.100$ M, with ten multidentate ligands containing combinations of phosphonate, acetate, phenolate, and tertiary amino donor groups, and hydrogen ion concentrations were determined potentiometrically as a function of added standard alkali. Stability constants, chelate protonation constants, hydrolysis constants, and formation constants were calculated for all systems, thus providing a quantitative description of the concentrations of gallium–ligand species present as a function of hydrogen ion concentration. Correlations of stability constants with basicities of the ligands and of chelate hydrolysis constants with stability constants are provided for the present work and for previously published values of related ligands. Probable coordinate bonding sites and the stereochemistry of metal–ligand interactions are inferred from the thermodynamic data.

Introduction

Harris and Martell[1] described the interactions of gallium(III) with 16 multidentate ligands and reported the equilibrium constants involving the presence of protonated chelates, olated chelates, and some polynuclear species. Letkeman et al.[2] extended the study to the interaction of gallium(III) with several phenolic and 1,2-dihydroxy aromatic ligands. Apart from these two definitive studies no other comprehensive work on gallium(III) and its interaction with multidentate ligands has become available.

It was found by Harris and Martell[1] that the equilibrium constants for the reactions of Ga(III) with certain strongly binding ligands could not be measured potentiometrically, since even at the lowest measurable pH, Ga(III) ion is 100% complexed. These cases were solved by a novel experimental approach—the measurement of metal or ligand displacement reactions. Metal–metal competitive equilibria were determined spectrophotometrically, and ligand–ligand competition reactions were followed potentiometrically. In the present paper, a completely new competitive equilibrium technique is employed—the displacement of strongly bound ligands from the coordination sphere of the Ga(III) ion by hydroxide ions. The very strong tendency of the Ga(III) ion to undergo hydrolysis to $Ga(OH)_4^-$ turns out to be an asset which makes possible potentiometric measurements of stability constants that could not be determined any other way. As the pH is increased, virtually every multidentate ligand dissociates from gallium and is replaced by four hydroxide ions. Therefore this new method has wide application to many chelates of Ga(III) and is now offered as a powerful technique for measurement of chelate equilibria of amphoteric metal ions. One of the ligands that has been determined by this new method in the present study is triethylenetetraminehexaacetic acid (TTHA), a decadentate ligand for which no satisfactory competing chelating was found by Harris and Martell.[1]

The multidentate ligands which form the basis of this study and their abbreviations in parentheses are *N*-(2-hydroxy-5-sulfobenzyl)ethylenediamine-*N*,*N*′-bis(methylenephosphonic) acid (MSHBEDPO), triethylenetetraminehexaacetic acid (TTHA), tetraethylenepentamineheptaacetic acid (TPHA), ethylenediamine-*N*,*N*′-diacetic-*N*,*N*′-bis(methylenephosphonic) acid (EDDADPO), glycine-*N*,*N*-bis(methylenephosphonic) acid (GDPO), ethylenediamine-*N*,*N*′-bis(methylenephosphonic) acid (EDDPO), 1-hydroxyethane-1,1-diphosphonic acid (HEDPO), (2-hydroxybenzyl)iminobis(methylenephosphonic) acid (HBIDPO), ethylenediamine-*N*,*N*,-*N*′,*N*′-tetrakis(methylenephosphonic) acid (EDTPO), and *N*-(phosphonomethyl)iminodiacetic acid (PMIDA). For each of the above ligands, the stability constant of the gallium(III) chelates and all other significant related equilibrium constants are now reported.

Experimental Section

Reagents. EDDPO was synthesized from ethylenediamine, formaldehyde, and phosphorus acid in aqueous hydrochloric acid medium as outline by Moedritzer and Irani.[3] The ligands GDPO and PMIDA were prepared by a similar method from glycine and iminodiacetic acid, respectively. The chelating agent HBIDPO was prepared by the alkylation of iminobis(methylenephosphonic) acid (IDPO) with *o*-acetoxybenzyl bromide with the method described by Harris et al.,[4] while IDPO was prepared by the procedure of Moedritzer.[5] The ligand MSHBEDPO was prepared by the reaction of *p*-hydroxyphenylsulfonic acid and formaldehyde with EDDPO as outlined by Kroll et al.[6] Only monosubstitution products could be isolated in pure form. TPHA was synthesized by alkylation of a purified sample of tetraethylenepentamine with chloroacetic acid.[7] The decadentate polyaminopolycarboxylic acid TTHA was obtained commerically from Dojindo Pharmaceutical Laboratories, Japan. The chelating agent HEDPO was kindly supplied by the Monsanto Chemical Co. The ligand EDTPO was synthesized by the method described by Motekaitis et al.,[8] while EDDADPO was prepared by alkaline bromoacetic acid alkylation of EDDPO.

Procedure. The potentiometric equilibrium measurements were performed by using the procedure outlined previously.[1] All constants

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