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Separation of Intrinsic and Electrostrictive Volume Effects in Redox Reaction Volumes of Metal Complexes Measured Using High-Pressure Cyclic Staircase Voltammetry

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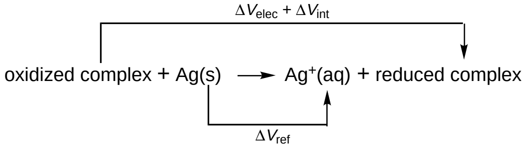
Redox reaction volumes, obtained by high-pressure cyclic voltammetry, are reported for a selection tris(diimine), tris(diamine), hexaammine, and hexaaqua couples of Fe(III/II), Cr(III/II), Ru(III/II), and Co(III/II). Separation of the intrinsic and electrostrictive volume contributions for these couples has been achieved, some in both aqueous and acetonitrile solutions. For the $Co(phen)_3^{3+/2+}$ system, the intrinsic volume change is estimated to be $+15.3 \pm 2.1$ cm^3 mol^{-1} (based on measurements in water) and $+16.5 \pm 2.0$ cm^3 mol^{-1} (in acetonitrile). For the $Co(bipy)_3^{3+/2+}$ system, values are $+12.7 \pm 1.4$ cm^3 mol^{-1} (in water) and $+15.5 \pm 2.5$ cm^3 mol^{-1} (in acetonitrile). Using these experimentally determined intrinsic contributions, a simple structural model suggests that the intrinsic volume change for these reactions can be described using the change in effective volume of a sphere with radius close to that of the coordinating-atom−metal bond length. Electrostrictive volume changes for the 3+/2+ complex-ion couples are a function of solute size and coordinated ligands. For $Ru(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ reduction, volume behavior is significantly different from that of the other systems studied and can be rationalized in terms of possible H-bonding interactions with surrounding solvent which affect the electrostrictive volume changes but which are not available for the ammine and other complexes studied.

Introduction

Recent interest in electrode kinetics at high pressures[1−5] and in the effects of pressure on redox equilibria, studied using cyclic voltammetry (CV)[6−11] and differential pulse voltammetry (DPV),[12] have yielded activation and reaction volumes which are important in mechanistic interpretation of heterogeneous or homogeneous electron transfer reactions[13] or as information for an improved understanding of changes in the structure of solute species and of solute−solvent interactions. Such information is finding application in describing various chemical processes from classical coordination chemistry[6−10] to reactions of proteins.[11,12]

For a series of low-spin Fe(III/II) couples reported previously,[7] molecular (intrinsic) volume changes, $\Delta V°_{int}$, associated with the redox process can be assumed to be negligible on the basis of crystallographic data for the oxidized and reduced forms of the compounds. In that series, we separated the contributions made by the electrostrictive volume change associated with reduction of the ionic complex, $\Delta V°_{elec}$, and the volume change for the reference half-cell, $\Delta V°_{ref}$, to the overall redox cell reaction volume, $\Delta V°_{cell}$. These contributions are summarized in eqs 1a and 1b. For the Ag/Ag$^+$(aq) reference half-cell, $\Delta V°_{ref}$ is -11.9 ± 0.5 cm^3 mol^{-1} ($I = 1.0$ M) or -13 cm^3 mol^{-1} ($I = 0.1$ M).[7] Extrathermodynamic assumptions of this type are common in studies of thermodynamic properties of ions in solution.[14a]

$$\Delta V°_{cell} = \Delta V°_{ref} + (\Delta V°_{int} + \Delta V°_{elec})_{complex} \tag{1a}$$



(1b)

In the present study we have applied high-pressure voltammetry to complex-ion redox couples $M(L)_6^{3+/2+}$ or $M(L\text{-}L)_3^{3+/2+}$ where M is Fe, Co, Cr, or Ru, L is NH_3 or H_2O, and L-L is 1,10-phenanthroline (phen), 2,2′-bipyridine (bipy), or 1,2-diaminoethane (en). For these couples, intrinsic contributions to the redox reaction volume may not be neglected because of significant changes in metal to ligand bond lengths during reduction. Although an estimate of $\Delta V°_{ref}$ is necessary for assignment of the molar volume change for the complex-ion couple (see eq 1a), for redox couples where $\Delta V°_{elec}$ and $\Delta V°_{ref}$ can be assumed to be constant for two systems being compared, the intrinsic volume change should be obtainable directly by difference in the measured cell reaction volumes.

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Ideally, the intrinsic volume change should correlate with an estimate based on the known structural change. For small monoatomic ions, reasonable estimates of the intrinsic volume can be made on the basis of a spherical volume with an appropriate choice of the ionic radius.[14b] For larger coordination complexes, such estimates of "effective radius" are inadequate. For example, it is well established that calculations of the intrinsic volume based on a sphere, using the furthest atomic position from the center of the ion as the radius, are clearly overestimates.[15,16] More sophisticated approaches based on a van der Waals volume or a solvent-excluded volume determined from the known structure of the compound have been developed.[17,18]

We have also set out to investigate the effects of ligand type and complex-ion size on electrostrictive volume changes in a more detailed manner than in the charge dependence study reported previously.[7] Redox reaction entropies have provided important information regarding local solvent reorganization and solute−solvent interactions for complex-ion couples.[19−22] Volume data therefore provide a useful additional tool to investigate such phenomena.

Experimental Section

Materials. $Co(en)_3Cl_3$,[23] $Co(bipy)_3(ClO_4)_3{\cdot}3H_2O$,[24] $Fe(phen)_3SO_4{\cdot}9H_2O$,[25] $Ru(NH_3)_6Cl_2$,[26] and $Ru(en)_3ZnCl_4$[27] were prepared according to literature methods without modification. $Fe(cp)_2$ (Strem, 99%) was used as supplied. $Co(phen)_3(ClO_4)_3$ was prepared by a method identical to that for the bipyridine analog by replacing 2,2′-bipyridine with an equivalent stoichiometric quantity of 1,10-phenanthroline. $Cr(bipy)_3(ClO_4)_3$ was prepared using the method similar to that described by Brunschwig and Sutin;[28] the only deviation from this procedure was the generation of a chromium(II) solution by dissolving chromium metal (New Metals and Chemicals, 99.99%) in 6 M $HClO_4$ under an argon atmosphere and, then, after dissolution, addition of argon-saturated water to lower the $HClO_4$ concentration to 1 M before proceeding according the literature method. *Caution: Perchlorate salts of complexes containing organic ligands are potentially explosive.* $Ru(H_2O)_6(tos)_3$ (tos = *p*-toluenesulfonate) was prepared using a combination of two procedures: RuO_4 was generated from $RuCl_3{\cdot}3H_2O$ (Aldrich) under an argon atmosphere according to the procedure outlined by Kallen and Earley;[29] then the volatile RuO_4 was isolated in three ice-cooled traps containing 1 M H_2SiF_6 using an argon gas carrier prior to oxidation of the Ru(II) to Ru(III) and ion exchange for the formation the hexaaqua complex as the toluenesulfonate salt using the method described by Bernhard *et al.*[30] Solutions of $Fe(H_2O)_6^{2+}$ were prepared by dissolving $(NH_4)_2SO_4{\cdot}FeSO_4{\cdot}6H_2O$ (BDH, AnalaR) in either 1.00 or 0.10 M $HClO_4$ such that the excess acid provided the supporting electrolyte for the electrochemical measurements. All compounds were characterized by UV−vis spectrophotometry and cyclic voltammetry using formal potentials reported in the literature.[31]

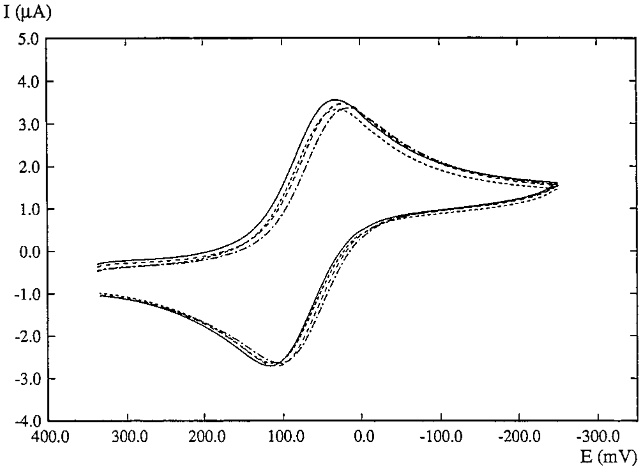

Figure 1. Voltammograms of the $Co(phen)_3^{3+/2+}$ couple in 0.1 M Et_4NClO_4/CH_3CN at 0.1 MPa (—), 30.7 MPa (- - -), 64.5 MPa (— — —), and 99.3 MPa (—˙—˙—) at a gold disk working electrode. Scan rate was 0.115 V s^{-1} and $T = 298$ K.

The $HClO_4$ (M&B, AR), $NaClO_4$ (Merck, AR), and KNO_3 (Ajax, AR) supporting electrolytes for measurements in aqueous solutions were all used as supplied. Either $AgNO_3$ (Ajax, LR) or $AgClO_4$ (BDH, 98%) was used as the source of Ag^+ for the reference cell. For the voltammetric measurements in acetonitrile (Millipore, HPLC), Et_4NClO_4 (Eastman, 95%) supporting electrolyte (TEAP) and $AgClO_4$ were used exclusively.

High-Pressure Voltammetric Measurements. The high-pressure voltammetric apparatus and technique have been described previously.[6,7] Concentrations of all complex-ion solutions were typically 0.001 M, except as discussed below. For all measurements, the three-electrode cell configuration consisted of either a 1.0 mm gold or gold amalgam disk working electrode, a 1.0 mm platinum wire auxiliary electrode, and a Ag/Ag^+ (0.01 M) reference electrode. The nature and concentration of the supporting electrolyte used in the reference cell were identical to those in the test solution except where noted.

For measurements in acetonitrile, the cell and all of the components required for its assembly were dried and stored in a desiccator over P_2O_5. A 1.0 mm gold disk working electrode, platinum wire auxiliary electrode, and $Ag/AgClO_4$ (0.01 M), 0.1 M TEAP reference electrode were used for all measurements. The Vycor frit junction was soaked in acetonitrile for at least 24 h prior to use.

With the exception of those of the ruthenium complexes, solutions were deoxygenated with solvent-saturated nitrogen before sealing the high-pressure cell. Solutions for both the $Ru(en)_3^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples were prepared by dissolving the Ru(II) salt in argon-saturated supporting electrolyte under an argon atmosphere. Although the dry $Ru(en)_3ZnCl_4$ and $Ru(NH_3)_6Cl_2$ salts are resistant to atmospheric oxidation for relatively lengthy periods (weeks) in the solid phase, they are much more susceptible to atmospheric oxidation and decomposition in solution.[26,27] Prior to sealing the cell, the solutions were again purged with solvent-saturated argon. The temperature for all electrochemical measurements was 25.0 ± 0.2 °C.

Results

The quality of the high-pressure CV data obtained in aqueous solution has been demonstrated elsewhere.[6,7] Cyclic voltammograms are presented at selected pressures for the $Co(phen)_3^{3+/2+}$ couple in acetonitrile /0.1 M TEAP in Figure 1. The pressure dependence of formal potential, $E^{\circ\prime}$ (Figure 2), provides a characteristic cell reaction volume of $+15.0 \pm 0.9$ cm^3 mol^{-1} for the couple. This treatment of the pressure dependence of $E^{\circ\prime}$ is typical of all of the systems to be discussed. A complete

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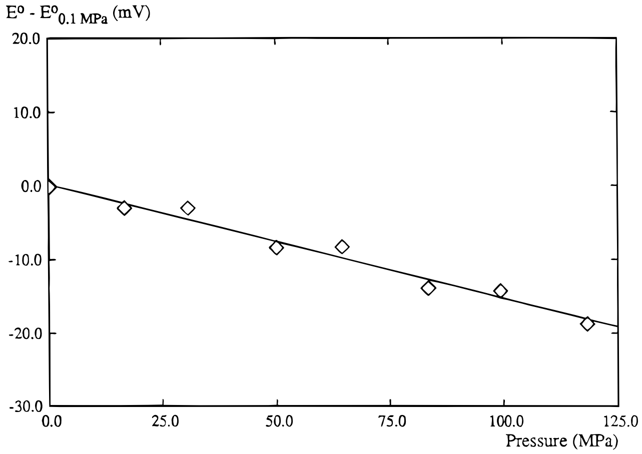

Figure 2. Shift in formal potential relative to the value at 0.1 MPa for $Co(phen)_3^{3+/2+}$ in 0.1 M Et_4NClO_4/CH_3CN as a function of pressure.

Table 1. Cell Reaction Molar Volumes and Electrochemical Parameters for Various Complex-Ion Couples in Aqueous Solution at 298 K

redox couple	supporting electrolyte[a]	working electrode	$E^{\circ\prime}_{0.1MPa}$[b] (mV)	ΔV°_{cell} ($cm^3\ mol^{-1}$)
$Fe(phen)_3^{3+/2+}$	KNO_3 (1.0)	Au	403.2	+6.7 (1.0)[c]
$Fe(phen)_3^{3+/2+}$	KNO_3 (0.25)	Au	445.1	+6.1 (0.3)[c]
$Fe(bipy)_3^{3+/2+}$	KNO_3 (1.0)	Au	381.5	+8.0 (0.3)[c]
$Fe(bipy)_3^{3+/2+}$	KNO_3 (0.1)	Au	413.9	+8.3 (0.5)[c]
$Cr(bipy)_3^{3+/2+}$	KNO_3 (0.1)	Hg(Au)	−895.1[d]	+8.1 (1.0)
$Co(phen)_3^{3+/2+}$	KNO_3 (0.1)	Au	−295.2[e]	+21.4 (1.1)
$Co(bipy)_3^{3+/2+}$	KNO_3 (0.1)	Au	−345.2[e]	+21.0 (0.9)
$Co(en)_3^{3+/2+}$	KNO_3, en (0.1, 0.01)	Hg(Au)	−828.1[e]	+26.9 (1.4)
$Ru(en)_3^{3+/2+}$	KNO_3 (0.1)	Hg(Au)	−481.0[d]	+14.0 (0.6)
$Ru(NH_3)_6^{3+/2+}$	KNO_3 (0.1)	Au	−592.3[d]	+17.3 (0.4)
$Ru(NH_3)_6^{3+/2+}$	$NaClO_4$ (0.1)	Hg(Au)	−559.9[d]	+16.8 (0.6)
$Ru(H_2O)_6^{3+/2+}$	$NaClO_4$ (0.1)	Au	−425.0[f]	−0.5 (0.7)
$Ru(H_2O)_6^{3+/2+}$	$HClO_4$ (0.1)	Au	−443.9[f]	+0.1 (0.6)
$Fe(H_2O)_6^{3+/2+}$	$HClO_4$ (1.0)	Au	64.6[d]	+1.7 (0.8)
$Fe(H_2O)_6^{3+/2+}$	$HClO_4$ (0.1)	Au	52.5[d]	−0.3 (1.4)

[a] Electrolyte concentration (M) shown in parentheses. [b] With respect to a $Ag/AgNO_3$ (0.01 M) reference electrode with ionic strength identical to that of the supporting electrolyte. [c] From ref 7. [d] Scan rate 0.115 V s^{-1}. [e] Scan rate 0.020 V s^{-1}. [f] Scan rate 0.075 V s^{-1}.

listing of formal potentials for each of the redox systems at all pressures is available as Supporting Information.

Measurements in Aqueous Solutions. Table 1 provides a summary of cell reaction volumes, formal potentials (at 0.1 MPa), and experimental details for each of the redox couples studied in aqueous solution. Quasi-reversible voltammograms for the $Co(bipy)_3^{3+/2+}$ and $Co(phen)_3^{3+/2+}$ couples were used to obtain reaction volumes of +21.0 ± 0.9 and +21.4 ± 1.1 $cm^3\ mol^{-1}$, respectively. The essentially identical results can be rationalized by the identical charge changes and similar structures and bond length changes upon reduction of the Co(III).[31] The reaction volume for the tris(bipyridine) couple is, however, substantially different from that recently reported by Cruañes[10] (+55.1 $cm^3\ mol^{-1}$ at zero pressure in 0.1 M KNO_3 using a Ag/AgCl, KCl (0.1 M) reference half-cell). Our previously reported value of +8.3 ± 0.5 $cm^3\ mol^{-1}$ (see Table 1)[7] for the $Fe(bipy)_3^{3+/2+}$ couple is also very different from the zero-pressure value of +39.5 $cm^3\ mol^{-1}$ reported by Cruañes *et al.*[10] However, as discussed below, the differences between the iron and cobalt couples are similar for both studies, perhaps suggesting the volume contributions for the different reference half-cells as a possible systematic source for the discrepancy. On the other hand, the excellent agreement between reaction volumes presented here and reported previously[6,7] (using a $Ag/AgNO_3$, KNO_3 (1.0 or 0.1 M) reference) with the corresponding measurements by Swaddle *et al.*[8] or Drickamer *et al.*[9] (but with a Ag/AgCl, KCl reference half-cell) discussed recently[12] suggests that the volume changes for the Ag/Ag^+ and Ag/AgCl/KCl reference half-cells are similar. Effects arising from other experimental differences, such as the use of ultramicro working electrodes and a much wider pressure range, may be operating. We have experiments currently underway to investigate these possibilities.

For the $Cr(bipy)_3^{3+/2+}$ couple, the cell reaction volume of +8.1 ± 1.0 $cm^3\ mol^{-1}$ in 0.1 M KNO_3 is in excellent agreement with the value we have reported[7] for $Fe(bipy)_3^{3+/2+}$. This is consistent with the minimal structural changes assumed for both of these couples.[31]

The $Co(en)_3^{3+/2+}$ couple was examined in the presence of 0.01 M excess ligand to suppress aquation of the labile high-spin Co(II) species. The voltammograms were quasi-reversible. Although there is the possibility of some ligand loss from the Co(II) state, the peak positions were well-defined. A reaction volume of +26.9 ± 1.4 $cm^3\ mol^{-1}$ was obtained. The cell reaction volume for the $Ru(en)_3^{3+/2+}$ couple in 0.1 M KNO_3 was +14.0 ± 0.6 $cm^3\ mol^{-1}$.

The $Ru(NH_3)_6^{3+/2+}$ couple was measured in two different supporting electrolytes (at constant ionic strength) to investigate any counterion effects on the reaction volume. The ΔV°_{cell} of +16.8 ± 0.6 $cm^3\ mol^{-1}$ in $NaClO_4$ was close to the value of +17.3 ± 0.4 $cm^3\ mol^{-1}$ obtained in KNO_3.

The $Fe(H_2O)_6^{3+/2+}$ couple was investigated under highly acidic conditions to prevent metal ion−hydroxo complex formation and polymerization. For measurements in 0.1 and 1.0 M $HClO_4$, reference half-cell solutions were prepared using $NaClO_4$ at a concentration identical to that of the perchloric acid in the test solution. Analyte concentrations were increased from the typical value of 0.001 M to improve peak resolution from the increased background current. For the 0.1 M perchloric acid solution the concentration of Fe(II) was 0.004 M and for 1.0 M perchloric acid solution the Fe(II) concentration was increased to 0.04 M. The cell reaction volumes for the $Fe(H_2O)_6^{3+/2+}$ couple in 0.1 and 1.0 M $HClO_4$ were −0.3 ± 1.4 and +5.4 ± 0.8 $cm^3\ mol^{-1}$, respectively. Although there appears to be some effect from the change in the acid concentration, the actual difference may be somewhat smaller. For the 1.0 M $HClO_4$ solution, a slight drift in the cell potential was observed over the 5 h period required to complete a series of pressure measurements, and the source of this drift appeared to be diffusion of some of the acid into the reference solution. The problem was most apparent for the last two pressure readings, and if these points were omitted from the linear fit, a reaction volume of +1.7 ± 0.8 $cm^3\ mol^{-1}$ was obtained. Overall, the data compare well with the published value of Swaddle *et al.*[8] of +5.0 ± 0.3 $cm^3\ mol^{-1}$ in 0.28 mol kg^{-1} CF_3SO_3H with respect to a Ag/AgCl, KCl (saturated) reference electrode. Slight differences here might be caused by the different volume contributions from the reference half-cells and/or specific anion effects. For the $Ru(H_2O)_6^{3+/2+}$ couple, such highly acidic conditions were not expected to be necessary; however reaction volumes were measured in both 0.1 M $HClO_4$ and 0.1 M $NaClO_4$ supporting electrolyte to investigate any pH effects. Cell reaction volumes of +0.1 ± 0.6 $cm^3\ mol^{-1}$ in 0.1 M $HClO_4$ and −0.5 ± 0.7 $cm^3\ mol^{-1}$ in 0.1 M $NaClO_4$ indicate that the ruthenium couple is unaffected by pH in this range. The results are very similar to the value obtained for the $Fe(H_2O)_6^{3+/2+}$ couple at the corresponding ionic strength and acidity.

Measurements in Acetonitrile. Many of the redox couples studied in aqueous solution could not be measured in acetonitrile

Table 2. Cell Reaction Molar Volumes and Electrochemical Parameters for Selected Complex-Ion Couples in Acetonitrile Using a Gold Disk Working Electrode and 0.1 M Et_4NClO_4 Supporting Electrolyte at 298 K

redox couple	$E°'_{0.1MPa}$[a] (mV)	$\Delta V°_{cell}$ (cm^3 mol^{-1})
$Fe(cp)_2^{+/0}$	103.2	−9.9 (0.5)
$Fe(phen)_3^{3+/2+}$	780.0	−1.5 (1.1)
$Co(phen)_3^{3+/2+}$	74.6	+15.0 (0.9)
$Co(bipy)_3^{3+/2+}$	17.7	+14.0 (1.4)

[a] With respect to a $Ag/AgClO_4$ (0.01 M in 0.1 M Et_4NClO_4) reference electrode with ionic strength identical to that of the supporting electrolyte in acetonitrile; scan rate 0.115 V s^{-1}.

due to low solubility. Redox reaction volumes for couples studied in acetonitrile are presented in Table 2. The $Fe(cp)_2^{+/0}$ couple is well-behaved and widely used and so was chosen as the most useful test system for high-pressure electrochemical studies in nonaqueous solvents. A cell reaction volume of −9.9 ± 0.5 cm^3 mol^{-1} was obtained. A more detailed study of the Ag/Ag^+ reference system in some common nonaqueous electrochemical solvents will be reported soon.[32]

For the $Co(phen)_3^{3+/2+}$ and $Co(bipy)_3^{3+/2+}$ couples the cell reaction volumes of +15.0 ± 0.9 and +14.0 ± 1.4 cm^3 mol^{-1} are quite different from those obtained in aqueous solution. However, like the corresponding measurements in aqueous solution, the volume changes are almost identical for the two couples. Measurement of the $Fe(phen)_3^{3+/2+}$ couple in acetonitrile provided a cell reaction volume of −1.5 ± 1.1 cm^3 mol^{-1}.

Discussion

Phenanthroline and Bipyridine Complexes. In a study of electron transfer reactivities, Hupp and Weaver[31] have summarized the differences in average metal to ligand bond lengths using crystallographic or EXAFS data[33] for many of the redox couples reported here. For the $Fe(phen)_3^{3+/2+}$ couple, the average metal-to-ligand bond length change is 0.0 ± 0.01 Å. The $Fe(bipy)_3^{3+/2+}$ and the $Cr(bipy)_3^{3+/2+}$ couples are expected to have minimal intrinsic and similar electrostrictive contributions to the measured volume changes. Supporting this, the reaction volume, $\Delta V°_{cell}$, for the $Cr(bipy)_3^{3+/2+}$ couple was found to be essentially identical to that for the $Fe(bipy)_3^{3+/2+}$ couple. On the basis of a typical M−N change of 0.19 ± 0.02 Å for $Co(phen)_3^{3+/2+}$ [31] a significant intrinsic volume change would also be anticipated for the $Co(bipy)_3^{3+/2+}$ couple. From the reaction volumes shown in Table 1, the intrinsic volume changes for the $Co(phen)_3^{3+/2+}$ and $Co(bipy)_3^{3+/2+}$ couples have substantial and similar effects on the overall reaction volume changes.

Using the relationship shown in eq 1, a measure of the intrinsic volume changes can be obtained from a direct comparison of cell reaction volumes for the corresponding iron and cobalt couples where values of $\Delta V°_{ref}$ and $\Delta V°_{elec}$ are assumed to be the same for both redox cells. By directly subtracting $\Delta V°_{cell}$ for the iron couples from those for the cobalt couples, one can assign intrinsic volume changes of +15.3 ± 1.4 and +12.7 ± 1.4 cm^3 mol^{-1} to the $Co(phen)_3^{3+/2+}$ and $Co(bipy)_3^{3+/2+}$ reductions. A treatment of this type can also be applied to the measurements made by Cruañes *et al.*,[10] who used a Ag/AgCl, KCl (0.1 M) reference half-cell. As has been pointed out, there are substantial differences in the absolute values, but by subtraction of the reaction volumes for the $Fe(bipy)_3^{3+/2+}$ and $Co(bipy)_3^{3+/2+}$ couples (both measured under identical experimental conditions), a difference in reaction volume of 15.6 cm^3 mol^{-1} is obtained, consistent with our data. In the same way, cell reaction volumes measured in acetonitrile can be compared for the iron and cobalt tris(phenanthroline) couples. By subtraction of the reaction volume of −1.5 ± 1.1 cm^3 mol^{-1} for the $Fe(phen)_3^{3+/2+}$ couple from that for the $Co(phen)_3^{3+/2+}$ couple (+15.0 ± 0.9 cm^3 mol^{-1}) directly, an estimate of the intrinsic volume change for the $Co(phen)_3^{3+/2+}$ couple of +16.5 ± 2.0 cm^3 mol^{-1} is obtained, in good agreement with the value of +15.3 ± 1.4 cm^3 mol^{-1} in aqueous solution though the separate overall volume changes differ substantially for the two solvents.

Table 3. Partial Molal Volumes and Average Metal to Nitrogen Bond Lengths, d_{M-N}, for Various $M(phen)_3^{2+}$ Complexes

complex ion	d_{M-N} (Å)	$V°_{M(phen)_3Cl_2}$[a] (cm^3 mol^{-1})
$Fe(phen)_3^{2+}$	1.973(5)[b]	445.1
$Ni(phen)_3^{2+}$	2.090(10)[c]	454.2
$Co(phen)_3^{2+}$	2.127(14)[d]	456.3

[a] Reference 15. [b] Reference 36. [c] Reference 37. [d] Reference 38.

Spin state changes on reduction of the Co(III) complexes are assumed to be central in the observed bond length changes. Activation volume studies on reactions of some $Co(N)_6$ systems have provided a recent discussion of this.[35] From the pressure dependence of the spin state equilibrium, which can be observed spectrophotometrically, Binstead and Beattie[34] assigned a molal volume change of 10.1 ± 0.4 cm^3 mol^{-1} to the low-spin to high-spin transition for $Co(terpy)_2^{2+}$. Although this equilibrium is suspected of being complicated by ligand dissociation processes,[35] the magnitude of the molal volume change is comparable to the intrinsic volume changes we obtain for the Co(III)/Co(II) tris(phenanthroline) and tris(bipyridyl) systems. The intrinsic volume change for the $Co(terpy)_2^{2+}$ spin system might also be affected by the quite different changes in central (0.21 Å) and distal (0.07 Å) bond lengths[34] resulting in a concentration of the expansion along one axis and a lower total change in intrinsic volume than the tris(diimine) complexes, where all six M−N bond lengths that change by an average 0.19 Å.

Partial molal volumes reported[15] for the tris(phenanthroline) compounds of Fe(II), Co(II), and Ni(II) show a clear empirical correlation between metal−ligand bond length and $V°$. Molal volumes for the chloride salts[15] and average metal−ligand bond lengths, d_{M-N}, for $Fe(phen)_3^{2+}$,[36] $Ni(phen)_3^{2+}$,[37] and $Co(phen)_3^{2+}$ [38] cations are summarized in Table 3 and presented in Figure 3. The volume contributions from the chloride counterion will be constant. Any ion−ion and electrostrictive components are anticipated to be similar due to the similar cation sizes and identical charges, so differences in the data should reflect only the differences in intrinsic volume for these M(II) compounds. On the basis of this correlation, we can therefore make an independent estimate of the intrinsic volume change for the cobalt tris(phenanthroline) couple. From the metal to nitrogen bond length change of 2.127 − 1.938 = 0.189 Å for the $Co(phen)_3^{2+/3+}$ complexes, we estimate an intrinsic volume for the Co(III) complex ion which is 13.7 ± 0.6 cm^3 mol^{-1} lower than that of the Co(II) complex ion. The error is derived

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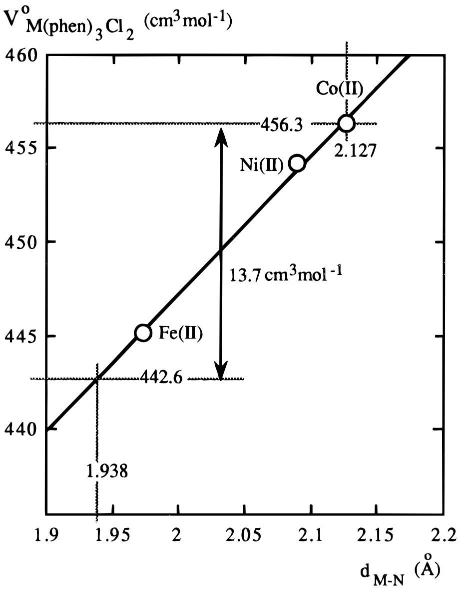

Figure 3. Plot of partial molal volumes, $V°$, for Fe(phen)$_3$Cl$_2$, Co(phen)$_3$Cl$_2$, and Ni(phen)$_3$Cl$_2$ as a function metal to ligand bond lengths, d_{M-N}.

from the uncertainty of the fitted gradient. The value is in good agreement with the 15.3 ± 1.4 and 16.5 ± 2.0 cm^3 mol^{-1} obtained from our electrochemical measurements in aqueous and acetonitrile solutions, respectively.

Ethylenediamine and Ammine Complexes. Unlike those of the diimine complexes, neither of the tris(ethylenediamine) redox couples measured here have nonzero intrinsic volume changes, although that of the Ru(III/II) system is expected to be small. However, taking some confidence from the relationship shown in Figure 3 for the tris(phenanthroline) complexes and the consistency of that prediction with other estimates of intrinsic change, a similar approach can be used, though only two partial molar volumes have been reported for tris(ethylenediamine) complexes.[40-43] From Glossop's data,[43] partial molar volumes for the Co(en)$_3$Cl$_3$ and Cr(en)$_3$Cl$_3$ salts are 186.6 and 193.7 cm^3 mol^{-1}, respectively. The average metal to nitrogen bond lengths have also been reported for these complex ions as 1.955 ± 0.006 Å for Co(III)−N[44] and 2.080 ± 0.008 Å for Cr(III)−N.[44] Assuming identical electrostrictive volumes for these complexes, this can be used to propose an intrinsic molar volume change/bond length change of 7.1/0.125 = 57 cm^3 mol^{-1} Å^{-1} for tris(ethylenediamine) complexes. For the cobalt tris(ethylenediamine) complexes, the Co(II)−N average bond length is 0.21 Å greater than the average Co(III)−N bond.[31,33] The intrinsic volume change for the reduction of Co(en)$_3^{3+}$ to Co(en)$_3^{2+}$ can therefore be estimated as +11.9 cm^3 mol^{-1}. The Ru(en)$_3^{3+/2+}$ reduction involves a bond length increase of 0.02 Å[31,33,45] and $\Delta V°_{int}$ estimated as +1.1 ± 1 cm^3 mol^{-1}. Combining these values for the $\Delta V°_{int}$ with the molar volume change for the reference half-cell at $\mu = 0.1$ M (−13 cm^3 mol^{-1}),[7] as in eq 1a, and taking into account the experimental uncertainties in the molar volumes and bond distances give the electrostrictive volume changes as +28 ± 2 cm^3 mol^{-1} for the reduction of Co(en)$_3^{3+}$ and +26 ± 2 cm^3 mol^{-1} for the reduction of Ru(en)$_3^{3+}$. The consistency in these values adds support to the approach. The greater electrostrictive volume changes for M(en)$_3^{3+/2+}$ compared to those for the larger M(phen)$_3^{3+/2+}$ and M(bipy)$_3^{3+/2+}$ couples would be expected from the size dependence predicted in, for example, the Drude−Nernst relationship.[46]

Table 4. Contributions to M(III/II) Reduction Volumes (cm^3 mol^{-1}) in Aqueous Solution at 298 K (Italicized Data Calculated from the Other Two Data for That System)

redox couple	$\Delta V°_{complex}$	$\Delta V°_{elec}$	$\Delta V°_{intr}$
Fe(phen)$_3^{3+/2+}$	+19.1[a]	*+19.1*	0
Fe(bipy)$_3^{3+/2+}$	+21.3[b]	*+21.3*	0
Cr(bipy)$_3^{3+/2+}$	+21.1[c]	*+21.1*	0
Co(phen)$_3^{3+/2+}$	+34.4[c,d]	+19.1[e]	*+15.3*
			+16.5[f]
	+34.4[c,d]	*+20.7*	+13.7[g]
Co(bipy)$_3^{3+/2+}$	+34.0[c,d]	+21.3[e]	*+12.7*
Co(en)$_3^{3+/2+}$	+39.9[c,d]	*+28.0*	+11.9[g]
Ru(en)$_3^{3+/2+}$	+27.0[c,d]	*+25.9*	+1.1[g]
Ru(NH$_3$)$_6^{3+/2+}$	+30.3[c,d,h]	*+27.7*	+2.6
Ru(NH$_3$)$_6^{3+/2+}$	+29.8[c,d,i]	*+27.2*	+2.6
Ru(H$_2$O)$_6^{3+/2+}$	+12.5 [d]	*+6.8*	+7.0
Ru(H$_2$O)$_6^{3+/2+}$	+13.[d,i]	*+6.4*	+7.0
Fe(H$_2$O)$_6^{3+/2+}$	+13.6[j]	*+4.0*	+7.1
Fe(H$_2$O)$_6^{3+/2+}$	+12.7[d,i]	*+3.1*	+7.1

[a] $I = 0.25$ M (KNO$_3$); ref 7. [b] $I = 0.10$ M (KNO$_3$), ref 7. [c] $I = 0.10$ M (KNO$_3$), this work. [d] Assumes $\Delta V°_{ref}$ of −13 cm^3 mol^{-1}. [e] Assumes Fe(III/II) value. [f] Based on difference in Co(III/II) and Fe(III/II) cell values in acetonitrile. [g] Assumes value based on molar volume data. [h] Using Au(Hg) working electrode. [i] $I = 0.1$ M (HClO$_4$). [j] $I = 1.0$ M (HClO$_4$) and assumes $\Delta V°_{ref} = -11.9$ cm^3 mol^{-1}.

A similar treatment of the ruthenium hexaammine couple is not possible, as the only hexaammine complex for which the partial molar volume has been reported is Co(NH$_3$)$_6$Cl$_3$.[41,43,47] However, if the correlations between intrinsic volume changes and bond length changes above (~57 cm^3 mol^{-1} Å^{-1} for M(en)$_3^{3+/2+}$, ~72 cm^3 mol^{-1} Å^{-1} for M(phen)$_3^{3+/2+}$) are used as a guide, a bond length change of 0.04 ± 0.01 Å for the Ru(NH$_3$)$_6^{3+/2+}$ couple[31,33,48] would produce a small $\Delta V°_{int}$ of around +2.6 cm^3 mol^{-1}. Hence, +27.7 cm^3 mol^{-1} of the total $\Delta V°_{complex}$ for the Ru(NH$_3$)$_6^{3+/2+}$ couple in 0.1 M KNO$_3$ is due to electrostrictive effects. This value is closer, as would be expected because of similarities in size, to the electrostrictive volume changes for the tris(ethylenediamine) couples than those for the tris(diimine) complexes. The ammine data continues the trend set by the tris(diimines) and tris(ethylenediamine) complexes towards slightly larger $\Delta V°_{elect}$ values for the smaller complexes.

Estimates of these contributions to the overall redox volumes, showing the consistency of the various approaches described, are summarized in Table 4.

Effective Radius Controlling $\Delta V°_{int}$. Modeling electron exchange processes for complex ions involves estimating the effective radius of the reactants in contact.[31,33] This distance, r_{vdW}, is taken as that from the center of the metal ion to the van der Waals limit of the outermost atom. However, as in other

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Table 5. Comparison of Electrochemically Determined Intrinsic Volume Changes for a Range of Complex-Ion 3+/2+ Redox Couples in Water

complex couple	$\Delta V°_{int}$ ($cm^3\ mol^{-1}$)	Δd[c] (Å)	r_{int} (Å)	$d_{M(III)-N}$ (Å)	r_{vdW}[c] (Å)
$Co(phen)_3^{3+/2+}$	+13.7[a]	0.19	2.99	1.94[d]	6.8
$Co(phen)_3^{3+/2+}$	+15.3[b]	0.19	3.17	1.94[d]	6.8
$Co(bipy)_3^{3+/2+}$	+12.7	0.19[h]	2.88	1.94[h]	6.8
$Co(en)_3^{3+/2+}$	+11.9[a]	0.21	2.63	1.96[e]	4.2
$Ru(en)_3^{3+/2+}$	+1.1[a]	0.02	2.69	2.09[f]	4.2
$Ru(NH_3)_6^{3+/2+}$	+2.5[a]	0.04	2.85	2.10[g]	3.35

[a] Data from the partial molal volume/d_{M-N} relationship. [b] Data from electrochemical measurements directly. [c] Reference 31 and 33. [d] Reference 39. [e] Reference 44. [f] Determined from data in refs 31, 33, and 45. [g] Reference 48. [h] Assumes Δd and d_{M-N} equal to those for the $Co(phen)_3^{3+/2+}$ system.

contexts,[15,16,34] to use these radii in conjunction with the known changes in metal to ligand bond distances would grossly overestimate the intrinsic volume and the intrinsic volume changes. The change in intrinsic volume may be visualized as the expansion by Δd (the change in metal to ligand bond length) of an effective intrinsic radius, r_{int}, as in eq 2, where $\Delta V°_{int}$ is

$$\Delta V°_{int} = {}^4/_3\pi(r_{int} + \Delta d)^3 - {}^4/_3\pi r_{int}{}^3 \qquad (2)$$

the experimentally based intrinsic volume change. Using our estimates of $\Delta V°_{int}$ and the reported values of Δd, the results summarized in Table 5 show that the effective radius, r_{int}, is very much smaller than the van der Waals radius, r_{vdW}, of the complex. For the tris-chelate complexes, the ligands form a chiral propeller structure with regions between the planes of the ligands, which will remain occupied by solvent as the metal to nitrogen bonds lengthen upon reduction. Recognizing that there is uncertainty of e.g. ±0.1Å in r_{int}, originating in the Δd and $\Delta V°_{int}$ data, there is remarkably little variation in r_{int} for the series of complexes.

Hexaaqua Couples. The iron and ruthenium hexaaqua couples have cell reaction volumes which are quite different from those of the other 3+/2+ systems reported (Table 1). The $Ru(H_2O)_6^{3+/2+}$ and $Ru(NH_3)_6^{3+/2+}$ couples, where the sizes are expected to be quite similar, show a difference in cell reaction volume of over 17 $cm^3\ mol^{-1}$. The significant difference in the reduction entropies for these systems (80 $J\ K^{-1}\ mol^{-1}$) has been explained[20] in terms of specific hydrogen-bonded interactions between the coordinated water ligands on the triply charged $Ru(H_2O)_6^{3+}$ and solvent water, resulting in a greater relaxation of solvent ordering on reduction than occurs for $Ru(NH_3)_6^{3+}$.

Using a reference half-cell value of −13 $cm^3\ mol^{-1}$ [7] at μ = 0.1M, $\Delta V°_{complex}$ values for the reduction of $Ru(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ in 0.1 M $HClO_4$ are estimated as +13.1 and +12.7 $cm^3\ mol^{-1}$, respectively. Metal to oxygen bond length changes for these couples (0.09 ± 0.02 Å for $Ru(H_2O)_6^{3+/2+}$ and 0.13 ± 0.01 Å for $Fe(H_2O)_6^{3+/2+}$ [31,33]) suggest that significant intrinsic volume changes should be expected. For some aquated M^{2+} ions (Mn^{2+}, Fe^{2+}, Co^{2+}, and Ni^{2+}) Atkinson[50] has reported a consistent set of molar volume data and Ohtaki[51] a set of $M-OH_2$ (solution) bond distances, which can be used to generate a molar volume/bond length relationship of the type used above to estimate $\Delta V°_{int}$ for the phenanthroline and ethylenediamine complexes. On this basis, the molar volume of $M^{2+}(aq)$ changes at a rate of 74 $cm^3\ mol^{-1}$ Å^{-1} and $\Delta V°_{int}$ would be estimated as around +6.7 $cm^3\ mol^{-1}$ for $Ru(H_2O)_6^{3+/2+}$ and +9.6 $cm^3\ mol^{-1}$ for $Fe(H_2O)_6^{3+/2+}$. These data are combined with $\Delta V°_{complex}$ to calculate the $\Delta V°_{elec}$ values in Table 4. In a molar volume study of aquated metal ions, Swaddle and Mak[52] derived a predictive expression which produced good agreement between calculated and experimental apparent molar volumes for a range of aquated metal ions. They used a Drude−Nernst relationship[46] to calculate the electrostrictive component of molar volume, given by $-417.5z^2/(r + 239)$, where z is the ion charge, r is the Shannon crystallographic radius,[53] appropriate to the spin state and coordination of the metal ion, and 239 pm is taken as the diameter of a coordinated water molecule. Using this expression, the reduction of $Fe^{3+}(aq)$ (r = 65 pm) to $Fe^{2+}(aq)$ (r = 78 pm) would produce a $\Delta V°_{elec}$ of +7.1 $cm^3\ mol^{-1}$. The corresponding calculation for Ru^{3+} (r = 68 pm) and an estimate for the 6-coordinate Ru^{2+} radius (r = 77 pm) suggest a $\Delta V°$ of 7.0 $cm^3\ mol^{-1}$. Recognizing that our experimentally derived $\Delta V°_{elec}$ for these systems are subject to an error of *ca.* ±2 $cm^3\ mol^{-1}$, the agreement is very satisfactory.

By this analysis, the differences between the hexaaqua complexes and the other systems studied in this work seem focused in the electrostrictive effects on the surrounding solvent. While all $\Delta V°_{elec}$ values are positive, those for $Ru(H_2O)_6^{3+/2+}$ and $Fe(H_2O)_6^{3+/2+}$ are very much less than those for the other systems, for the same change in charge. If the electrostrictive ordering of solvent around hexaaqua ions is a combination of specific hydrogen bonding to the immediate solvent layers and also longer range general ion−dipole interactions, the loss of highly structured H-bonded H_2O around $M(H_2O)_6^{3+}$ might be expected to lead to a reduction in volume as it collapses, offset or, as seems apparent, slightly outweighed by the longer range release of electrostricted solvent. While the immediate solvent layers around a structure-making[54] highly charged ion might be described as "icelike" and we do not suggest that the detailed properties of this region might be equivalent to ice, the volume occupied by specifically H-bonded H_2O may be close to that of ice. A simple but reasonable calculation, based on the molar volumes of ice (19.6 $cm^3\ mol^{-1}$ [55]) and water (18.0 $cm^3\ mol^{-1}$ [55]) and using a difference in $\Delta V°_{elec}$ of 21 $cm^3\ mol^{-1}$ between the hexaaqua− and hexaammine−Ru couples, suggests the formal release of around 13 additional "structured" water molecules per $M(H_2O)_6^{3+}$ on reduction. The immediate H-bonded region around the 3+ cation, though of much lower entropy than bulk solvent, would be expected to have access to vibrational and librational modes not available in the solid, which would make it more disordered than ice. Calculation based on ΔS_{sr} for the hexaaqua and hexaammine complexes[20] and the entropy of fusion of ice (22 $J\ K^{-1}\ mol^{-1}$ [55]) leads to around 4 additional H_2O molecules formally released on $M(H_2O)_6^{3+}$ reduction, as suggested, a lower value than that from the calculation based on volume.

Conclusions

Application of the high-pressure cyclic voltammetric technique has further illustrated how important structural information and insight can be obtained by direct measurement of volume changes for redox reactions in solution. Intrinsic volume contributions have been measured, compared with values determined using a partial molal volume/bond length relationship, and rationalized by a conceptually straightforward model

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incorporating the importance of the metal−ligand bond length changes on the overall reaction volume. Using this, it is proposed that for redox reactions involving ammine, diamine, and diimine ligands, intrinsic contributions to the reaction volume are not greatly affected by the ligand system. Estimates of the electrostrictive contributions on the overall complex ion volume change for $Fe(H_2O)_6^{3+/2+}$ and $Ru(H_2O)_6^{3+/2+}$ are very much lower than the values derived for the diimine, diamine, and ammine couples. When these are used in conjunction with reaction entropy measurements, a plausible description involving changes in solvent structure can be developed.

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Supporting Information Available: Listings of formal potentials and peak separations for redox couples at high pressure (4 pages). Ordering information is given on any current masthead page.

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