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Electrochemical Kinetics of Cyanometalate Complexes in Aqueous Solution at High Pressures

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For the aqueous couples $Os(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $W(CN)_8^{3-/4-}$, volumes of reaction $\Delta V_{Ag/AgCl}$ relative to Ag/AgCl/4.0 mol L^{-1} KCl and volumes of activation $\Delta V_{el}^{\ddagger}$ for the electrode reactions are reported. Values of $\Delta V_{Ag/AgCl}$ are consistent with a very small increase in the metal−carbon bond length on reduction in each case, the main component of $\Delta V_{Ag/AgCl}$ (other than that of the reference electrode) being electrostrictive solvation change. For media in which the cation is 0.5 mol L^{-1} K^+ or (for Mo) Na^+, $\Delta V_{el}^{\ddagger}$ is strongly positive (+9.4 ± 0.7, +7.3 ± 0.7, and +10.8 ± 0.4 cm^3 mol^{-1} for $Os(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $W(CN)_8^{3-/4-}$, respectively, at 25 °C), whereas the theoretical expectation for a mechanism involving only the cyanometalate anions is −3 ± 1 cm^3 mol^{-1}. For $Mo(CN)_8^{3-/4-}$ in Et_4NCl, however, $\Delta V_{el}^{\ddagger}$ is −4.2 ± 0.2 cm^3 mol^{-1}. In all cases, $\Delta V_{el}^{\ddagger}$ is just one-half of the corresponding parameter $\Delta V_{ex}^{\ddagger}$ for the homogeneous (bimolecular) self-exchange reaction of the same couple, giving strong confirmation of the "fifty-percent rule" (Fu, Y.; Swaddle, T. W. *J. Am. Chem. Soc.* **1997**, *119*, 7137). These and related results are interpreted in terms of a mechanism for both electrode and homogeneous electron-transfer reactions of cyanometalates in which the counterion mediates the electron-transfer process. For alkali metal cations, partial deaquation to permit this mediation results in positive $\Delta V_{el}^{\ddagger}$ values, whereas for tetraalkylammonium counterions, there are no aqua ligands to be removed and $\Delta V_{el}^{\ddagger}$ is "normal".

Introduction

We have described elsewhere[1,2] a correlation that exists between volumes of activation for homogeneous outer-sphere self-exchange reactions of metal complex couples of the type $ML_n^{(z+1)+/z+}$ and those for reactions of the same couples at an electrode ($\Delta V_{ex}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$, respectively), in aqueous solutions

$$\Delta V_{el}^{\ddagger} = {}^1/_2\Delta V_{ex}^{\ddagger} \qquad (1)$$

As this correlation is remarkably precise and apparently of general applicability, we refer to it as the "fifty-percent rule". Since $(\partial G/\partial P)_T = V$, its origin can be understood through a simple extension of Marcus' prediction[3−7] that the Marcus free energies of activation ΔG^* for homogeneous (bimolecular) electron transfer and electrode reactions should be similarly related:

$$\Delta G_{el}^* \geq {}^1/_2\Delta G_{ex}^* \qquad (2)$$

In simple terms, ΔG_{el}^* reflects solvational and M−L bond length reorganization in just *one* ML_n complex at an electrode to a configuration halfway between $ML_n^{(z+1)+}$ and ML_n^{z+}, whereas ΔG_{ex}^* comprises contributions from *two* ML_n complexes going to the common configuration in a bimolecular process, so ΔG_{ex}^* can be expected to be twice ΔG_{el}^*. The inequality in eq 2 would apply if, in the electrode reaction, a layer of intervening material were present on the electrode such that the M−electrode distance were more than half the M−M distance in homogeneous self-exchange. In fact, eq 1 holds precisely, implying that eq 2 is also an equality for the systems tested to date and that any adsorbed layers on the electrode either are penetrated by the electroactive species or else simply move the plane of effective electrical contact outward.

Attempts to test eq 2 through rate constants k_{el} and k_{ex} as such have generally been unsuccessful because the corresponding frequency factors Z_{el} and Z_{ex} cannot easily be related—indeed, they do not even have the same dimensions (cm s^{-1} and L mol^{-1} s^{-1}, respectively).

$$k_{el} = Z_{el}\exp(-\Delta G_{el}^*/RT) \qquad (3)$$

$$k_{ex} = Z_{ex}\exp(-\Delta G_{ex}^*/RT) \qquad (4)$$

$$k_{el}/Z_{el} = (k_{ex}/Z_{ex})^{1/2} \qquad (5)$$

Z_{el} and hence k_{el} are very dependent upon the nature and mode of preparation of the electrode surface as well as double-layer effects.[2] The nature of the electrode and the condition of its surface, however, are not perceptibly affected by pressures of a few hundred megapascals. Thus, Z_{el} is essentially independent of pressure, as is Z_{ex},[1,2] and since $\Delta V^{\ddagger}$ is given by $-RT(\partial \ln k/\partial P)_T$, eq 1 follows from eq 5.

We report here measurements of $\Delta V_{el}^{\ddagger}$ as well as volumes of reaction $\Delta V_{Ag/AgCl}$ (relative to the Ag/AgCl/4.0 mol L^{-1} KCl electrode) for the aqueous couples $Os(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $W(CN)_8^{3-/4-}$. Complementary studies of the corresponding self-exchange reactions[8] have shown that the exchange rates

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k_{ex} are strongly and linearly dependent upon the nature and concentration, respectively, of the cations present. Furthermore, when the counterion is an alkali metal ion, $\Delta V_{ex}^{\ddagger}$ is unexpectedly strongly positive (on the order of +20 cm^3 mol^{-1}, as first noted for the $Fe(CN)_6^{3-/4-}$ couple[9]), yet with tetraalkylammonium counterions, $\Delta V_{ex}^{\ddagger}$, is moderately negative and close to the value expected for simple anion–anion electron transfer (−6 ± 2 cm^3 mol^{-1}).[8] It is therefore important to check these $\Delta V_{ex}^{\ddagger}$ values by an independent method, in this case through $\Delta V_{el}^{\ddagger}$ and application of eq 1; conversely, successful application of eq 1 would confirm the validity of the fifty-percent rule and also the common basis of electrode and outer-sphere electron-transfer processes proposed by Marcus.[3–7]

Experimental Section

$K_4Os(CN)_6 \cdot 3H_2O$, $K_4Mo(CN)_8 \cdot 2H_2O$, $[(C_2H_5)_4N]_4Mo(CN)_8 \cdot 2H_2O$, and $K_4W(CN)_8 \cdot 2H_2O$ were prepared by Metelski as described elsewhere.[8] The W and especially the Mo complexes are photosensitive, particularly in the oxidized forms, and were handled in the dark or under a red safelight. In all cases, solutions were purged with water-saturated N_2 prior to voltammetric measurements. Distilled water was passed through a Barnstead NANOpure train before use. Inorganic supporting electrolytes (KCl, NaCl; BDH Assured) were used as received, but tetraethylammonium chloride (Eastman) was purified by recrystallization from water and its purity verified by CHN analysis.

Electrochemical procedures and the high-pressure electrochemical apparatus were as described previously.[1,2] All measurements were made on solutions thermostated at 25.0 ± 0.1 °C. Half-wave potentials $E_{1/2}$ were determined from cyclic voltammograms (CVs), and electrode reaction rate constants k_{el} were obtained from alternating current voltammograms (ACVs). The cyanometalate complexes were found to cause contamination of electrode surfaces, and consequently the key to obtaining reproducible k_{el} values, particularly after a pressure change, was the regeneration of a clean working electrode surface in situ by cycling the applied potential several times between hydrogen evolution and the most positive potential to be scanned in the actual measurements.[1,2] Of the high-pressure measurements, only those sets for which the readings at the end of the pressure cycle agreed with those at the beginning to within the experimental uncertainty (±2 mV) for a given pressure were accepted. Thus, stability of reagents and electrode response over the 8–10 h of a pressure cycle was required.

In this article, concentrations are given in units of mol L^{-1} valid at 22 °C and 0.1 MPa.

Results

The $Os(CN)_6^{3-/4-}$ Couple. Solutions of $K_4Os(CN)_6 \cdot 3H_2O$ were stable for at least 1 week in stoppered vessels and were not affected by room lighting. CVs obtained using Pt wire working and counter electrodes referred to Ag/AgCl/4.0 mol L^{-1} KCl were accurately reproducible over several hours, but the $E_{1/2}$ value obtained from them (615 ± 5 mV) lies close to the potential at which Pt oxide films may form, and the definitive kinetic measurements were therefore made with a glassy carbon disk working electrode. Comparison of $E_{1/2}$ from CVs with the peak potential from the ACVs[1,2] showed that the transfer coefficient α was 0.50. For 1.51 mmol L^{-1} $K_4Os(CN)_6$ in 0.61 mol L^{-1} KCl, k_{el}^0 (the value of k_{el} at ambient pressure) was 0.0194 cm s^{-1} at glassy carbon and 0.035 cm s^{-1} at Pt; Oyama et al.[10] used CV peak separation to obtain $k_{el}^0 = 0.15 \pm 0.11$ cm s^{-1} at a carbon fiber microelectrode for a different, highly acidic medium (0.1 mol L^{-1} CF_3COONa + 0.1 mol L^{-1} CF_3COOH) in which the electroactive hexacyanoosmate species would have been protonated.[11] The pressure dependences of $E_{1/2}$ and ln k_{el} were linear within the experimental uncertainty over the range 0–200 MPa, as shown in Figures 1 and 2,[12] and the corresponding values of $\Delta V_{Ag/AgCl}$ and $\Delta V_{el}^{\ddagger}$ are given in Tables 1 and 2, respectively. Table 2 also records the measured value of the diffusion coefficient D, which was taken to be the same for the oxidized and reduced species.

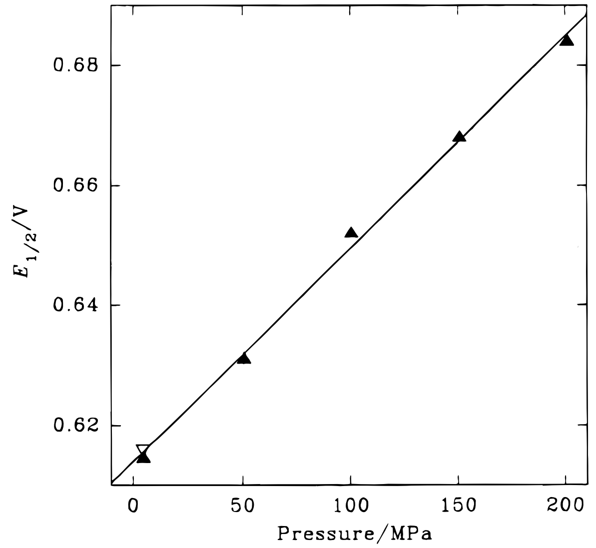

Figure 1. Pressure dependence of the half-wave potential for $Os(CN)_6^{3-/4-}$ relative to Ag/AgCl/4.0 mol L^{-1} KCl in an aqueous K^+ medium; $[K_4Os(CN)_6]$ = 1.91 mmol L^{-1}; [KCl] = 0.70 mol L^{-1}.

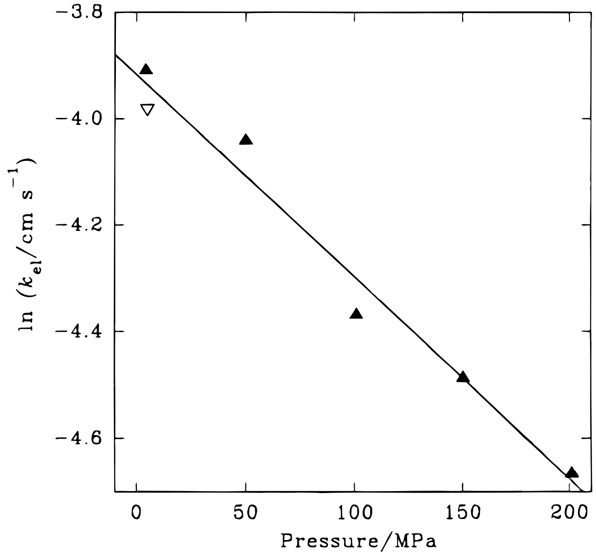

Figure 2. Pressure dependence of the rate constant for $Os(CN)_6^{3-/4-}$ in an aqueous K^+ medium at a glassy carbon disk electrode. $[K_4Os(CN)_6]$ = 1.51 mmol L^{-1}; [KCl] = 0.607 mol L^{-1}.

The $Mo(CN)_8^{3-/4-}$ Couple. A report on our study of this couple in aqueous Na^+ and K^+ media has been given elsewhere;[2] the results are summarized in Tables 1 and 2. When Et_4N^+ was the only cation present, Pt electrodes became poisoned even more rapidly than in K^+ solutions. With a glassy carbon disk as the working electrode, the oxidative wave of the first CV scan was typically distorted, but after further cycling of the potential, the electrode response became highly reversible and reproducible over several hours. As noted previously,[2] k_{el}^0

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Table 1. Pressure Dependence of Half-Wave Potentials from Cyclic Voltammetry ($\alpha = 0.50$)

couple, electrode	medium, c/mol L^{-1}	$E_{1/2}{}^{a}$/mV	$\Delta V_{\mathrm{Ag/AgCl}}{}^{a}$/ cm^3 mol^{-1}
$\mathrm{Os(CN)_6}^{3-/4-}$, Pt	KCl, 0.70	615	-34.3 ± 0.8
$\mathrm{Os(CN)_6}^{3-/4-}$, $\mathrm{C_{gl}}$	KCl, 0.61	626	-33.4 ± 0.9
$\mathrm{Mo(CN)_8}^{3-/4-}$, Au^{b}	$\mathrm{NaClO_4}$, 0.5	618	-29.8 ± 1.0
$\mathrm{Mo(CN)_8}^{3-/4-}$, $\mathrm{C_{gl}}$	$\mathrm{Et_4NCl}$, 0.5	645	-33.6 ± 0.9^{c}
$\mathrm{W(CN)_8}^{3-/4-}$, Pt	KCl, 0.5	320	-27.5 ± 0.8

[a] Relative to Ag/AgCl/4.0 mol L^{-1} KCl, ±5 mV, in neutral solution except as noted. [b] pH 2.7; ref 2. [c] Mean of three independent runs.

values for $\mathrm{Mo(CN)_8}^{3-/4-}$ in the literature vary widely with the medium and the nature of the electrode;[10,13-16] nevertheless, it should be noted that $k_{\mathrm{el}}{}^{0}$ was found to be markedly faster in $\mathrm{Et_4NCl}$ at glassy carbon than in $\mathrm{NaClO_4}$ at gold (Table 2). The pressure dependences of $E_{1/2}$ and ln k_{el} were linear within the experimental uncertainty, 0−200 MPa (Supporting Information, Figures S1 and S2), and the corresponding values of $\Delta V_{\mathrm{Ag/AgCl}}$ and $\Delta V_{\mathrm{el}}{}^{\ddagger}$ from replicate runs are given in Tables 1 and 2.

The $\mathbf{W(CN)_8}^{3-/4-}$ Couple. Since the $E_{1/2}$ value for $\mathrm{W(CN)_8}^{3-/4-}$ in KCl media (320 mV) lies at a much less oxidizing potential than that for the Mo analogue or $\mathrm{Os(CN)_6}^{3-/4-}$, Pt working electrodes were entirely satisfactory in this case. Because the rate constants k_{ex} for the homogeneous self-exchange reactions of cyanometalate complexes show a linear dependence on the concentration of an added electrolyte (actually, on the concentration of the cation),[8] the relationship between k_{el} and the concentration of added KCl was investigated. As in the self-exchange case,[8] k_{el} was found to be directly proportional to [KCl], within the experimental uncertainty, with a slope of 0.32 ± 0.02 (Supporting Information, Figure S3). Oyama et al.[10] found $k_{\mathrm{el}} = 0.44 \pm 0.28$ cm s^{-1} for $\mathrm{W(CN)_8}^{3-/4-}$ in a $\mathrm{CF_3COONa/CF_3COOH}$ medium of pH 1.0 by a CV method, but as noted above for the hexacyanoosmate case, it is likely that protonation of the reactants would complicate interpretation of this result.

The pressure dependences of $E_{1/2}$ and ln k_{el} for $\mathrm{W(CN)_8}^{3-/4-}$ in KCl were accurately linear (Supporting Information, Figures S4 and S5), and the derived quantities are listed in Tables 1 and 2.

Discussion

Volumes of Reaction. The cell reaction volumes $\Delta V_{\mathrm{Ag/AgCl}}$ for the $\mathrm{Fe(CN)_6}^{3-/4-}$, $\mathrm{Os(CN)_6}^{3-/4-}$, $\mathrm{Mo(CN)_8}^{3-/4-}$, and $\mathrm{W(CN)_8}^{3-/4-}$ couples in $\mathrm{K^+}$ or $\mathrm{Na^+}$ media (0.5 mol L^{-1}) are −37,[17,18] −33, −30, and −28 cm^3 mol^{-1}, respectively (Table 1). It is worth noting that $\Delta V_{\mathrm{Ag/AgCl}}$ for $\mathrm{Mo(CN)_8}^{3-/4-}$ is less than 4 cm^3 mol^{-1} more negative for tetraethylammonium than for sodium ion media; this stands in sharp contrast to the large differences seen in the corresponding volumes of *activation* (Table 2), adding credence to the view[8] that the counterion plays an important *mechanistic* role in anion−anion electron transfer but has only a secondary influence on the overall thermodynamics of the redox process. We have reviewed ion association in aqueous cyanometalates elsewhere.[8] A quantitative analysis is not feasible because of the possibility of multiple ion association and the dependence of ion pair formation constants K_{IP} themselves on ionic strength I, but a Fuoss-type calculation[19] of K_{IP} values for a generic $\mathrm{M(CN)}_n{}^{4-}$ of radius 460 pm with $\mathrm{K^+}$ in 0.5 mol L^{-1} aqueous KCl over the pressure range 0−200 MPa at 25 °C indicates that the volume change ΔV_{IP} accompanying ion pair formation is less than +2 cm^3 mol^{-1}. In other words, the effects of ion association on $\Delta V_{\mathrm{Ag/AgCl}}$ are small, and the $\Delta V_{\mathrm{el}}{}^{\ddagger}$ data show that the role of the counterion in the kinetics goes beyond mere ion pairing.

Tregloan and co-workers[18,20] have shown that, for couples such as $\mathrm{Fe(CN)_6}^{3-/4-}$, in which the metal−ligand bond length d_0 is essentially the same in both the oxidized and reduced species, the observed $\Delta V_{\mathrm{Ag/AgCl}}$ comprises solely a contribution ΔV_{ref} from the reference electrode (for Ag/AgCl/4 mol L^{-1} KCl, this has been estimated to be −9.0 cm^3 mol^{-1} [18,20]) and another arising from the electrostrictive solvational change that accompanies reduction:

$$\Delta V_{\mathrm{Ag/AgCl}} = \Delta V_{\mathrm{ref}} + B\Delta z^2/r \qquad (6)$$

where Δz^2 is the square of the charge number of the oxidized partner minus the square of the charge number of the reduced form, r is the effective radius of the reacting ions, and B is a constant. For reactants of the approximate size of the cyanometalate complexes considered here, B/r is about 4.0 cm^3 mol^{-1}. Correlation of the $\Delta V_{\mathrm{Ag/AgCl}}$ data with crystallographic (i.e., solid-state) d_0 values may not be quantitatively significant, since the EXAFS study by Brunschwig et al.[21] showed d_0 for $\mathrm{Fe(CN)_6}^{3-}$ and $\mathrm{Fe(CN)_6}^{4-}$ in solution to be equal and significantly shorter (188 pm) than had been reported for the solid state (192.6 and 190.0 pm, respectively).[22] Furthermore, not all metal−cyanide bond lengths in crystalline solids are equal.[23] Nevertheless, crystallographic measurements[22-31] indicate $\Delta d_0 = 4$ pm for the $\mathrm{Mo(CN)_8}^{3-/4-}$ and $\mathrm{W(CN)_8}^{3-/4-}$ couples, and Macartney[11] argues for a similar Δd_0 for $\mathrm{Os(CN)_6}^{3-/4-}$, so that, in contrast to the $\mathrm{Fe(CN)_6}^{3-/4-}$ case, where Δd_0 is zero, a small, positive, "intrinsic" (i.e., molecular volume change) contribution to $\Delta V_{\mathrm{Ag/AgCl}}$ may be expected to accompany reduction in these couples and to increase with increasing d_0. For $\mathrm{Fe(CN)_6}^{4-}$, $\mathrm{Os(CN)_6}^{4-}$, $\mathrm{Mo(CN)_8}^{4-}$, and $\mathrm{W(CN)_8}^{4-}$, d_0 in solids is typically 193, 204, 216, and 218 pm, respectively,[23-31] and so the trend Fe < Os < Mo < W in $\Delta V_{\mathrm{Ag/AgCl}}$ may be qualitatively understood. Corresponding increases in the overall effective radii r of the reactants will also make minor contributions to this trend through eq 6.

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Table 2. Diffusion Coefficients, Rate Constants at Ambient Pressure, and Volumes of Activation for Cyanometalate Couples in Water at 25.0 °C

couple, electrode	medium,[a] c/mol L^{-1}	D/10^{-6} cm^2 s^{-1}	k_{el}^0/cm s^{-1}	$\Delta V_{el}^‡$/cm^3 mol^{-1}	$\Delta V_{ex}^‡$/cm^3 mol^{-1}
$Fe(CN)_6^{3-/4-}$, Pt[b]	KCl, 0.50	7.63	0.072 ± 0.005	+11.9 ± 1.3	+ 21.8 ± 1.7[c]
$Os(CN)_6^{3-/4-}$, C_{gl}	KCl, 0.61	6.78	0.020 ± 0.001	+9.4 ± 0.7	+18.5 ± 0.8[d]
$Mo(CN)_8^{3-/4-}$, Au[e]	$NaClO_4$, 0.5	5.47	0.053 ± 0.001	+7.3 ± 0.7[f]	+14.7 ± 0.6[g]
$Mo(CN)_8^{3-/4-}$, C_{gl}	Et_4NCl, 0.5	4.88	0.18 ± 0.03	−4.2 ± 0.2[f]	−8.2 ± 0.6[h]
$W(CN)_8^{3-/4-}$, Pt	KCl, 0.5	5.08	0.16 ± 0.01	+10.8 ± 0.4[f]	+22.5 ± 1.1[i]

[a] For electrode processes only; does not apply to $\Delta V_{ex}^‡$. [b] Reference 2. [c] Reference 9; $[K_4Fe(CN)_6] = 0.08$ mol L^{-1}; $[K_3Fe(CN)_6] = 0.002$ mol L^{-1}. [d] Reference 8; $[K_4Os(CN)_6] = 0.189$ mol L^{-1}; $[K_3Os(CN)_6] = [K_3IrCl_6] = 0.010$ mol L^{-1}. [e] Reference 2; pH 2.7. [f] Average of two independent runs. [g] Reference 8; $[K_4Mo(CN)_8] = 0.0785$ mol L^{-1}; $[K_3Mo(CN)_8] = 0.0485$ mol L^{-1}. [h] Reference 8; $[(Et_4N)_4Mo(CN)_8] = 0.069$ mol L^{-1}; $[(Et_4N)_3Mo(CN)_8] = 6.7$ mmol L^{-1}. [i] Reference 8; $[K_4W(CN)_8] = 0.23$ mol L^{-1}; $[K_3W(CN)_8] = 0.014$ mol L^{-1}.

Electrode Reaction Kinetics. Electrochemical rate constants measured in different media or at different electrodes[2] (or even at the same electrode with different modes of preparation[32]) can vary widely. There is therefore little to be gained by comparing the k_{el} data presented here with literature values. The essential proportionality of k_{el} to [KCl] for the $W(CN)_8^{3-/4-}$ couple, however, deserves comment, as a generally similar phenomenon was reported by Campbell and Peter[33] for the $Fe(CN)_6^{3-/4-}$ couple and is also strongly evident in the self-exchange reactions of all the couples considered here in homogeneous alkali metal ion-containing solutions.[8] It is evident that the alkali metal salt (more specifically, its cation[8,33]) is intimately involved in the electron-transfer process, not only in bulk solution but also at electrode surfaces. This commonality of mechanism between corresponding electrode and homogeneous solution processes is further demonstrated by the success of the fifty-percent rule linking the two modes of electron transfer, as noted below.

Volumes of Activation. The most striking results arising from the high-pressure electrode kinetics are (1) that $\Delta V_{el}^‡$ is strongly *positive* for all the cyanometalate couples studied to date when the cation present is an alkali metal cation yet moderately *negative* when it is a quaternary ammonium ion and (2) that the fifty-percent rule relating $\Delta V_{el}^‡$ to $\Delta V_{ex}^‡$ applies with striking accuracy *regardless of the sign and magnitude of* $\Delta V_{el}^‡$. The latter point is given further emphasis in Figure 3, which combines the results of Table 2 with those obtained previously.[2] Conversely, if we accept that the fifty-percent rule is applicable, the present $\Delta V_{el}^‡$ measurements authenticate the $\Delta V_{ex}^‡$ values for self-exchange reactions of the cyanometalate couples obtained from NMR line-broadening by Metelski and Swaddle.[8] The remarkable consistency of these data for two different reaction modes, measured by completely unrelated techniques, demonstrates a fundamental mechanistic commonality between outer-sphere self-exchange reactions in homogeneous solution and electron transfer at an electrode, for a given couple. This commonality of mechanism is implicit in Marcus' theory of electrode reactions,[3−7] and the fact that the slope of the regression line in Figure 3 is precisely one-half (0.50 ± 0.02) provides a quantitative vindication of Marcus' theory.

For the aqueous $Mo(CN)_8^{3-/4-}$ couple, both $\Delta V_{el}^‡$ and $\Delta V_{ex}^‡$ change dramatically in sign and magnitude on going from alkali metal ion (M^+) to tetraalkylammonium ion (R_4N^+) media (Table 2), and our studies[8] of the self-exchange reactions of the other cyanometalate couples indicate that this is likely to be a general phenomenon in this class of complexes. This effect cannot be attributed to ion pairing as such, because K_{IP} values for R_4N^+ with cyanometalate anions are similar to those for alkali metal ions,[8] and furthermore, as noted above, the expected contributions of ion pairing to volumes of activation are too small. Since $\Delta V_{el}^‡$ for the $Mo(CN)_8^{3-/4-}/Et_4N^+$ system is close to the value predicted[8] ($^1/_2\Delta V_{ex}^{‡calc} = -3 \pm 1$ cm^3 mol^{-1}) for a simple outer-sphere electron-transfer mechanism involving only the anions, it is tempting to conclude that the cation is involved in electron transfer in the M^+ but not the R_4N^+ cases; the strongly positive $\Delta V_{el}^‡$ for M^+ can be attributed to a partial deaquation of the cation that enables it to facilitate electron transfer.[8] In fact, however, the self-exchange reactions of aqueous cyanometalate couples are more strongly facilitated by R_4N^+ than by any but the heaviest M^+.[8] For electrode reactions, k_{el} is too dependent on the nature of the electrode surface to permit rate comparisons of this kind to be made with certainty, but k_{el} for $Mo(CN)_8^{3-/4-}$ in aqueous Et_4NCl at glassy carbon is indeed much faster than that in aqueous $NaClO_4$ at Au (Table 2), despite the general observation for the benchmark $Fe(CN)_6^{3-/4-}$ couple that glassy carbon electrodes give slower reaction rates than do the noble metals.[32]

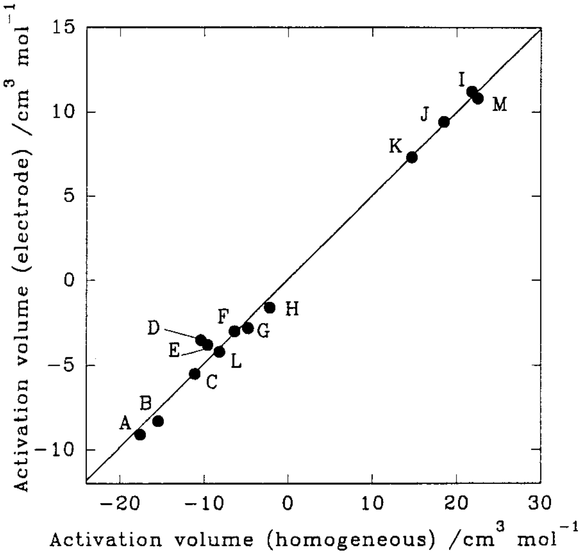

Figure 3. Relationship between $\Delta V_{el}^‡$ and $\Delta V_{ex}^‡$. (A) $Co(phen)_3^{3+/2+}$; (B) $Co(en)_3^{3+/2+}$; (C) $Fe(H_2O)_6^{3+/2+}$; (D) $Co(diamsar)^{3+/2+}$; (E) $Co(diamsarH_2)^{5+/4+}$; (F) $Co(sep)^{3+/2+}$; (G) $Co(ttcn)_2^{3+/2+}$; (H) $Fe(phen)_3^{3+/2+}$; (I) $Fe(CN)_6^{3-/4-}/K^+$; (J) $Os(CN)_6^{3-/4-}/K^+$; (K) $Mo(CN)_8^{3-/4-}/K^+$; (L) $Mo(CN)_8^{3-/4-}/Et_4N^+$; (M) $W(CN)_8^{3-/4-}/K^+$. Data were taken from ref 2 (couples A−I) and Table 2 (couples J−M).

Thus, the difference in $\Delta V_{el}^‡$ values is more likely attributable to the absence of coordinated aqua ligands in R_4N^+, so that the deaquation that is presumed to be necessary to secure participation of M^+ in the electron-transfer process is not required for R_4N^+. The sequence of self-exchange rate constants (k_{ex} for $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+ \sim R_4N^+$) is certainly consistent with the deaquation model, as the energy input required for deaquation must decrease in that order.[8] The linear dependence of k_{el} on [KCl] for the $W(CN)_8^{3-/4-}$ electrode reaction implies

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(32) McCreery, R. L. *Electroanal. Chem.* **1991**, *17*, 221 and references therein.

(33) Campbell, S. A.; Peter, L. M. *J. Electroanal. Chem. Interfacial Electrochem.* **1994**, *364*, 257.

that the same kind of M^+ effect found[8] for k_{ex} also affects k_{el}. It may therefore be inferred that the M^+ and R_4N^+ effects established[8] for k_{ex} also apply to k_{el} and may be similarly explained.

Conclusions

We present here, for several aqueous cyanometalate couples, $\Delta V_{el}^{\ddagger}$ data that serve to verify the fifty-percent rule[1,2] and conversely to authenticate the $\Delta V_{ex}^{\ddagger}$ data reported previously[8] for the self-exchange reactions of the same couples in homogeneous solution. The values of $\Delta V_{el}^{\ddagger}$ and other related observations are interpreted in terms of mechanisms for both electrode and homogeneous electron-transfer reactions of cyanometalates in which the counterion mediates the electron-transfer process. For alkali metal cations M^+, it is argued that the partial deaquation of $M(H_2O)_n^+$ necessary to permit this mediation results in anomalously positive $\Delta V_{el}^{\ddagger}$ values, whereas for R_4N^+ counterions, there are no aqua ligands to be removed and $\Delta V_{el}^{\ddagger}$ is negative and "normal".

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Supporting Information Available: Figures S1−S5, showing pressure dependence plots for $E_{1/2}$ and k_{el}. This material is available free of charge on the Internet at http://pubs.acs.org.

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