

Reaction Entropy Measurements for Transition-Metal Ions Bound to Nafion-Coated Electrode Surfaces

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Reaction entropies, ΔS°_{rc} , have been determined for a series of transition-metal ions electrostatically bound into Nafion films. Complexes with hydrophobic, "shielding" ligands such as $\text{Ru}(2,2'\text{-bipyridine})_3^{3+/2+}$ and $\text{Co}(2,2'\text{-bipyridine})_3^{3+/2+}$ yield similar ΔS°_{rc} values in Nafion films and in aqueous solution, indicating that the electrochemically active probes reside in a predominantly waterlike local environment in the polymer film. Complexes containing aquo and ammine ligands yield markedly lower ΔS°_{rc} values in Nafion than in aqueous media ($\mu = 0.1 \text{ M}$). The ΔS°_{rc} values for these Nafion-bound systems are similar to values measured for the $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ system in concentrated aqueous salt solutions (5 M LiCl). The ΔS°_{rc} measurements imply that the outer-sphere electron-transfer work terms for polymer bound ions may be lower than those observed in typical aqueous solutions. Differential free energies, enthalpies, and entropies of transfer for the redox reaction $\text{M(III)} + e^- \rightarrow \text{M(II)}$ from aqueous media to Nafion have also been determined.

Introduction

Attention has recently been devoted to the application of spectroscopic techniques which can elucidate the local environment in polymer-modified electrodes.¹⁻⁵ For many polymer/probe systems, a direct correlation of spectroscopic information with electrochemical reactivity is not straightforward, especially in situations where the probe molecules are not electrochemically active or when the electrochemically detectable molecules are bound at only a small subset of the equilibrium binding sites. As pointed out by Weaver and co-workers,⁶ electrochemical reaction entropy measurements are particularly sensitive to local environmental effects around metal ion sites. We report here ΔS°_{rc} values for several transition-metal complexes bound into recast Nafion films.

These measurements are of particular interest to our laboratory because studies of ligand substitution kinetics⁷ of $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ have provided evidence for pronounced local solvation effects in recast Nafion. Thus, the reaction entropy measurements should provide a confirmation of this hypothesis. Additionally, substantial information is now available correlating solution phase ΔS°_{rc} measurements with solvent acceptor number, hydrogen-bonding effects, and other local environmental parameters.⁸ To date, only one ΔS°_{rc} measurement is available in Nafion,⁸ and it is difficult to ascertain which molecular factors (i.e., polymer structural changes, polymer/solution junction potentials, ion pairing, etc.) contribute to the observed temperature dependence of E° for this system. The ΔS°_{rc} measurements performed here on a series of metal ion systems should provide direct information regarding the solvation sphere of the electrochemically detectable

ions in the polymer phase. These measurements are also valuable in correlating apparent electron diffusion rates for polymer-confined ions with electron self-exchange rates.

Experimental Section

ΔS°_{rc} measurements of transition-metal complexes incorporated in Nafion films were performed using the nonisothermal technique described by Weaver and co-workers.^{6c} Our ΔS°_{rc} values were obtained by temperature-dependent measurements of $E_{1/2}$ values from cyclic voltammetry, using a cell design similar to that described for experiments with complexes in aqueous solution.^{6c} Measurements were made at 10° intervals from 5 to 45°C . The data were collected with both increasing and decreasing temperature to confirm that the changes in $E_{1/2}$ were not due to changes of the polymer film with time.

Metal complexes were incorporated into recast Nafion films⁹ ($0.4\text{--}0.6\text{-}\mu\text{m}$ swollen film thickness) by immersion of the polymer-coated electrodes (pyrolytic graphite, edge-plane exposed) in $0.1\text{--}0.5 \text{ mM}$ aqueous solutions of the complexes. All electrodes were thoroughly rinsed with deionized water after immersion in the incorporation solutions, and ΔS°_{rc} measurements were then performed in solutions containing only supporting electrolyte.

Most electrolyte solutions contained $0.1 \text{ M NaCF}_3\text{SO}_3$ and were buffered to pH 7.0 (5 mM phosphate). Data for $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$ were obtained at pH 3 to avoid interference from acid-base equilibria of the aquo ligand. $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ (Strem) and $\text{Ru}(\text{bpy})_3\text{Cl}_2$ (G. Frederick Smith), $\text{bpy} = 2,2'\text{-bipyridine}$, were used as received. $\text{Co}(\text{bpy})_3\text{Cl}_2$ was a gift from H. Taube, and $\text{Fe}(\text{bpy})_3^{3+}$ was generated in solution by addition of an acidified $\text{Fe}(\text{ClO}_4)_3$ solution to a solution of excess bpy . $\text{Ru}(\text{NH}_3)_5(\text{pyr})^{3+/2+}$ was generated electrochemically in the Nafion film by reducing incorporated $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$ in the presence of pyridine. $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{2+}$ was made from $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ according to literature procedures.^{7,10}

Results

Cyclic voltammograms for the $\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+/2+}$ and $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ redox couples in Nafion show behavior characteristic of an ideal one-electron process for a surface-confined species, i.e. the separation of the anodic and cathodic peak potentials, E_{pa} and E_{pc} , is less than 10 mV and the full width at half-maximum is approximately $90\text{--}100 \text{ mV}$. In accord with the ideal model for a nondiffusive species, the peak currents are observed to be linearly dependent on scan rate ($10\text{--}200 \text{ mV/s}$). These observations demonstrate that the voltammograms are equilibrium measurements and indicate that a good approximation of E° for the surface confined species can be obtained from the

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TABLE I: Redox Potentials, Reaction Entropies, and Differential Free Energies for Metal Ions in Nafion Films

complex	Nafion		μ , M	solution		Nafion - solution		
	$E_{1/2}$, V vs. SCE ^a	ΔS°_{rc} , ^a eu		$E_{1/2}$, V vs. SCE ^b	ΔS°_{rc} , ^b eu	$\Delta\Delta G$, ^c kcal/mol	$T\Delta\Delta S$, kcal/mol	$\Delta\Delta H$, kcal/mol
Fe(bpy) ₃ ^{3+/2+}	0.801 ± 0.002	2 ± 1	0.1	0.832	2 ± 1	0.71 ± 0.26	0.00 ± 0.42	0.71 ± 0.49
Ru(bpy) ₃ ^{3+/2+}	1.000 ± 0.005	0 ± 1	0.1	1.027	1 ± 1	0.62 ± 0.26	0.00 ± 0.42	0.62 ± 0.49
Co(bpy) ₃ ^{3+/2+}	0.053 ± 0.002	24 ± 3	0.1	0.070 ^d	22 ± 3	0.39 ± 0.26	0.60 ± 1.26	0.99 ± 1.28
Ru(NH ₃) ₆ ^{3+/2+}	-0.332 ± 0.005	5.7 ± 1.4	0.1	-0.178 ^e	19 ± 1	3.55 ± 0.26	-3.97 ± 0.51	-0.42 ± 0.57
Ru(NH ₃) ₆ ^{3+/2+}			5.0	-0.210 ^f	7.0 ± 1 ^f	0.74 ± 0.26	-3.58 ± 0.42	-2.84 ± 0.49
Ru(NH ₃) ₅ (pyr) ^{3+/2+}	-0.037 ± 0.003	10 ± 1	0.1	0.058	17 ± 1	2.19 ± 0.26	-2.09 ± 0.42	0.10 ± 0.49
Ru(NH ₃) ₅ (H ₂ O) ^{3+/2+} g	-0.256 ± 0.003	7.5 ± 1	0.1	-0.157	25 ± 2	2.28 ± 0.26	-5.22 ± 0.67	-2.94 ± 0.72

^a Determined by cyclic voltammetry. Electrolyte is 0.1 M NaCF₃SO₃ at pH 7.0 (buffered) except where indicated otherwise. $E_{1/2}$ values in solution are ±0.010 V. ^b Values are taken from ref 6; measurements in this work have verified these data for several of the redox systems.

^c Calculated from $\Delta E_{1/2} = [E_{1/2}(\text{Nafion}) - E_{1/2}(\text{H}_2\text{O})]$; $\Delta\Delta G = -nF\Delta E_{1/2}$; $\Delta\Delta G = \Delta\Delta H - T\Delta\Delta S$. ^d Determined in 0.1 M LiClO₄; ref 6d.

^e Determined in 0.1 M NaClO₄; ref 6e. Values for $\mu \leq 0.8$ M are available;^{6e} at $\mu = 0.8$ M (CF₃CO₂Na) $\Delta S^\circ_{rc} = 14$ eu. ^f Determined in 5.0 M LiCl.

^g Determined at pH 3 to avoid hydrolysis.

average of the anodic and cathodic peak potentials.

Cyclic voltammograms for the other complexes bound in Nafion, Co(bpy)₃^{3+/2+}, Ru(bpy)₃^{3+/2+}, and Fe(bpy)₃^{3+/2+}, typically exhibit E_{pa} - E_{pc} separations of more than 60 mV (at 200 mV/s) and peak currents which are not directly proportional to the scan rate (20–200 mV/s). The Ru(NH₃)₅(pyr)^{3+/2+} redox system exhibited voltammetric characteristics which were closer to ideal behavior than observed for the M(bpy) systems, with E_{pa} - E_{pc} values of 15–30 mV. Similar behavior for some of these complexes has been reported by other workers using slightly different Nafion samples (equiv wt = 970 g).¹¹ This behavior has been associated with mixed thermodynamic and kinetic control of the voltammograms. Scan rates as slow as 50 mV/s still yielded appreciable peak separation for these couples; however, the ratio of i_{pa}/i_{pc} was always close to unity. Under these conditions, the formal potential was approximated by the average of the anodic and cathodic peak positions. Inspection of the entire voltammograms as a function of temperature indicates that any reasonable procedure to yield $E_{1/2}$ values from the cyclic voltammetric data would produce similar values of ΔS°_{rc} to the procedure used here. Reaction entropies and other relevant thermodynamic quantities for all of the ions investigated in this study are compiled in Table I.

Discussion

Weaver and co-workers have demonstrated that ΔS°_{rc} can be correlated with solvent acceptor number and local hydrogen-bonding effects.⁶ Typically, in aqueous solution, the one-electron reduction of tripositively charged aquo and ammine complexes will result in a large positive reaction entropy, because there is a substantial decrease in the solvent ordering associated with the dipositive species. Also, complexes with hydrophobic ligands, such as Ru(bpy)₃^{3+/2+}, yield very low ΔS°_{rc} values. This has been ascribed to the absence of increased solvent structure in the tripositive state due to shielding of the metal cation from the surrounding water.¹²

The ΔS°_{rc} values are similar in aqueous solution and in Nafion films for the Co(bpy)₃^{3+/2+}, Fe(bpy)₃^{3+/2+}, and Ru(bpy)₃^{3+/2+} couples (Table I). Substantial differences in ΔS°_{rc} are observed for these ions when dissolved in other solvents, such as CH₃CN and (CH₃)₂SO.⁶ Thus, the close accord between our ΔS°_{rc} values and those reported in aqueous solution suggests a local solvent acceptor number in Nafion which is very close to that of water. This conclusion is confirmed by luminescence data for Ru(bpy)₃²⁺ in recast Nafion films which have indicated that this ion is located in a water-like environment.^{4,5}

The Co(III/II) systems typically exhibit ΔS°_{rc} values which are 15–20 eu greater than Ru(III/II) based systems due to the unique electronic configuration of the Co ions;⁶ thus, the similarity of the Nafion phase and aqueous phase ΔS°_{rc} values for all of these M(bpy)₃^{3+/2+} complexes clearly eliminates the possibility

of substantial systematic errors in our ΔS°_{rc} data due to temperature-dependent junction potentials at the Nafion/solution interface. Furthermore, the different ΔS°_{rc} values for the various ions indicates that the temperature dependence of $E_{1/2}$ for the polymer-confined species is not dominated by temperature-dependent changes in the polymer morphology.

A comparison of the ΔS°_{rc} values in Nafion with those determined in aqueous electrolytes ($\mu = 0.1$ M) indicates that pronounced differences in ΔS°_{rc} are present for the "unshielded" probe species used in this study (Table I). For the Ru(NH₃)₅(H₂O)^{3+/2+} and Ru(NH₃)₆^{3+/2+} ions, we observe much lower ΔS°_{rc} values in Nafion films than are observed in aqueous solution ($\mu = 0.1$ M). Ion pairing effects and local solvation shell structure will lead to reduced ΔS°_{rc} values; consistently, the measured values for the Ru-ammine complexes in Nafion are close to ΔS°_{rc} values obtained for the Ru(NH₃)₆^{3+/2+} system in concentrated aqueous salt solutions (Table I). Notably, structural data on intact Nafion membranes indicates that an upper limit on the effective ionic strength is 2 M,¹³ and the ionic strength in recast Nafion films is likely to be lower than this value. It would thus appear that a combination of ion pairing and local solvent order contributes to the low ΔS°_{rc} values for the Ru-ammine complexes in Nafion.

Also of note are the $\Delta E_{1/2}$ values ($\Delta E_{1/2} = E_{1/2}(\text{Nafion}) - E_{1/2}(\text{H}_2\text{O})$) for the redox systems under study (Table I). The negative $\Delta E_{1/2}$ indicates a more favorable partition coefficient into Nafion for the more highly charged member of the redox pair.⁸ This is expected from stronger electrostatic interactions with the negatively charged film. Consistently, $\Delta E_{1/2}$ is reduced when the solution ionic strength is increased (i.e., Ru(NH₃)₆^{3+/2+} in 5 M LiCl).

The large reaction entropy differences observed in this study between aqueous solutions ($\mu = 0.1$ M) and Nafion films correlate well with kinetic results on Nafion-bound metal ion substitution reactions,⁷ and these data suggest that pronounced reactivity differences can be expected as a result of electrocatalyst immobilization on many chemically modified electrode surfaces. In particular, the correlation of the reaction entropy with the solvent reorganization energy for outersphere electron-transfer processes¹⁴ implies that several of the ions studied here could exhibit higher electron self-exchange rates in Nafion films than in aqueous solution. This observation may be relevant to the unusual effective diffusion coefficient behavior observed for several systems in Nafion films.¹⁵ Experiments designed to test this prediction, and the application of these ΔS°_{rc} techniques to other polymer-coated electrode systems, are currently being investigated.

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