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

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Reaction entropies, $\Delta S^{\circ}$, have been determined for a series of transition-metal ions electrostatically bound into Nafion films. Complexes with hydrophilic, "shielding" ligands such as Ru(2,2'-bipyridine)$_2$ and Co(2,2'-bipyridine)$_2$ yield similar $\Delta S^{\circ}$ values in Nafion films and in aqueous solution, indicating that the electrochemically active probe resides in a predominantly waterlike local environment in the polymer film. Complexes containing aquo and ammine ligands yield markedly lower $\Delta S^{\circ}$ values in Nafion than in aqueous media ($\mu = 0.1 \, \text{M}$). The $\Delta S^{\circ}$ values for these Nafion-bound systems are similar to values measured for the Ru(phen)$_3$ system in concentrated aqueous salt solutions (5 M LiCl). The $\Delta S^{\circ}$ 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 M(III) + e$^- \rightarrow$ 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. 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, electrochemical reaction entropy measurements are particularly sensitive to local environmental effects around metal ion sites. We report here $\Delta S^{\circ}$ 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 kinetics of Ru(NH$_3$)$_5$(H$_2$O)$_2^+$ have provided evidence for pronounced solvent-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 $\Delta S^{\circ}$ measurements with solvent acceptor number, hydrogen-bonding effects, and other local environmental parameters. To date, only one $\Delta S^{\circ}$ measurement is available in Nafion, 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 $E^\circ$ for this system. The $\Delta S^{\circ}$ 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

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

Metal complexes were incorporated into recast Nafion films by immersion of the polymer-coated electrodes (pyrolytic graphite, edge-plane exposed) in 0.1–0.5 mM aqueous solutions of the complexes. All electrodes were thoroughly rinsed with deionized water after immersion in the incorporation solutions, and $\Delta S^{\circ}$ measurements were then performed in solutions containing only supporting electrolyte.

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

Results

Cyclic voltammograms for the Ru(NH$_3$)$_5$(H$_2$O)$_2^+$ and Ru(NH$_3$)$_5$Cl$_2^+$ 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, $E_p$ and $E_m$, is less than 10 mV and the full width at half-maximum is approximately 90–100 mV. In accord with the ideal model for a nondiffusive species, the peak currents are observed to be linearly dependent on scan rate (10–200 mV/s). These observations demonstrate that the voltammograms are equilibrium measurements and indicate that a good approximation of $E^\circ$ for the surface confined species can be obtained from the

average of the anodic and cathodic peak potentials. Cyclic voltammograms for the other complexes bound in Nafion, Co(bpy)$_2$($\text{H}_2\text{O}$)$_2$Ru($\text{NH}_3$)$_6^{2+/+},$ Fe(bpy)$_3^{2+/+},$ and Fe(bpy)$_3^{3+/+},$ 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(NH$_3$)$_6^{2+/+}$ 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 approximately 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 $\Delta S_{oc}^o$ 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 $\Delta S_{oc}^o$ can be correlated with solvent acceptor number and local hydrogen-bonding effects. Typically, in aqueous solution, the one-electron reduction of tripositionally 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)$_3^{2+/+},$ yield very low $\Delta S_{oc}^o$ 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 $\Delta S_{oc}^o$ values are similar in aqueous solution and in Nafion films for the Co(bpy)$_2$($\text{H}_2\text{O}$)$_2$Ru($\text{NH}_3$)$_6^{2+/+},$ Fe(bpy)$_3^{2+/+},$ and Ru(bpy)$_3^{3+/+}$ couples (Table I). Substantial differences in $\Delta S_{oc}^o$ are observed for these ions when dissolved in other solvents, such as CH$_3$CN and (CH$_3$)$_2$SO. Thus, the close accord between our $\Delta S_{oc}^o$ values and those reported in aqueous solution suggests a local solvent structure breaking and the solvent polarization term, has been presented.$^{6a}$

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

<table>
<thead>
<tr>
<th>Complex</th>
<th>Nafion</th>
<th>Solution</th>
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<tbody>
<tr>
<td></td>
<td>$E_{1/2}, V$ vs. SCE$^o$</td>
<td>$\Delta S_{oc}^o, eu$</td>
</tr>
<tr>
<td>Fe(bpy)$_3^{2+/+}$</td>
<td>0.801 ± 0.002</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>Ru(bpy)$_3^{3+/+}$</td>
<td>1.000 ± 0.005</td>
<td>0 ± 1</td>
</tr>
<tr>
<td>Co(bpy)$_3^{3+/+}$</td>
<td>0.053 ± 0.002</td>
<td>24 ± 3</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{2+/+}$</td>
<td>-0.332 ± 0.005</td>
<td>5.7 ± 1.4</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+/+}$</td>
<td>5.0</td>
<td>-0.210</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+/+}$ (pyr)</td>
<td>-0.037 ± 0.003</td>
<td>10 ± 1</td>
</tr>
<tr>
<td>Ru(NH$_3$)$_6^{3+/+}$ (H$_2$O)</td>
<td>-0.256 ± 0.005</td>
<td>7.8 ± 1.4</td>
</tr>
</tbody>
</table>

$^a$Determines by cyclic voltammetry. Electrolyte is 0.1 M NaCF$_2$SO$_4$ 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 $\Delta E_{1/2} = (E_{1/2}(\text{Nafion}) - E_{1/2}(\text{H}_2\text{O}))$; $\Delta \Delta G = nF\Delta E_{1/2}$; $\Delta \Delta G = \Delta H - T\Delta S$. $^d$Determined in 0.1 M LiClO$_4$; ref 6d. $^e$Determined in 0.1 M NaClO$_4$; ref 6e. **TABLE II: Redox Potentials, Reaction Entropies, and Differential Free Energies for Metal Ions in Nafion Films**

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