Multiply charged electroactive anions [IrCl$_6^{2-}$, Fe(CN)$_6^{3-}$, and W(CN)$_6^{4-}$] are electrostatically incorporated in polymeric films of tris(4-vinyl-4'-methyl-2,2'-bipyridine) ruthenium(II) [poly-Ru(vbpy)$_3^{2+}$] from aqueous trifluoroacetate solution. Values of apparent diffusion coefficients ($D_{at}$) and heterogeneous electron transfer rates ($k_{et}$) are measured for these anions as a function of their relative concentration ($I_M/I_{Ru}$) in the film. $D_{at}$ and $k_{et}$ decrease systematically as $I_M/I_{Ru}$ increases in a manner that is independent of charge and chemical identity of the ion. This result suggests that a nonchemical process, presumably electrostatic cross-linking, limits diffusional motion and is responsible for the decrease in $D_{at}$ and $k_{et}$ with increasing anion content. Protonated polyvinylpyridine films exhibit similar ranges and variations in $D_{at}$ and $k_{et}$, which suggest similar structures and mechanisms of charge transport for these films and poly-Ru(vbpy)$_3^{2+}$.

KEY WORDS: Bipyridine ruthenium complexes; electroactive ions; polymeric films; electron transfer kinetics; polyvinylpyridine.

INTRODUCTION

Polymeric films of tris(4-vinyl-4'-methyl-2,2'-bipyridine) ruthenium(II), [poly-Ru(vbpy)$_3^{2+}$], [1] have many applications as electrocatalysts, electron transfer mediators, and molecular devices based on their redox properties [2–8]. We are interested in using these films to incorporate...
electroactive and catalytic reagents by means of ion exchange. Electrostatic partitioning of redox active ions into polymer films is a versatile means of confining molecules to electrode surfaces [9-14] and has application in electroanalysis [15], catalysis [16], and examination of molecules of biological interest [17]. Although the ion exchange properties of [poly-Ru(vbpy)$_3$]$_2^{2+}$ were recognized almost immediately after its preparation [1], it has not been widely used for this purpose. Its advantages in this regard include ease of preparation, chemical robustness, high charge density per monomeric site, and a wide electrochemical window (ca. 2.5 V) between its potentials of metal-centered oxidation and ligand-centered reduction.

This paper reports the incorporation and electrochemical behavior of redox active IrCl$_6^{2-}$, Fe(CN)$_6^{3-}$, and W(CN)$_4^{4-}$ anions in poly-Ru(vbpy)$_2^{2+}$ films on glassy carbon electrodes. Rates of diffusional charge transport ($D_{ct}$) and of heterogeneous electron transfer ($k_{et}$) are measured for these ions within the film in aqueous trifluoroacetate electrolyte. In addition, we have measured the charge transfer rate of the fixed Ru(vbpy)$_2^{2+}$ sites in the film. Besides illustrating the ion-exchange properties of poly-Ru(vbpy)$_3^{2+}$, these results provide insight to the dynamics of ionic and electrochemical charge transport in redox polymer films, a topic of continuing interest [18-30].

**EXPERIMENTAL**

**Materials.** The monomeric reagent, Ru(vbpy)$_3^{2+}$, was prepared from RuCl$_3$ and 4-vinyl-4'-methyl-2,2'-bipyridine(vbpy) following the procedure of Braddock and Meyer [31] and isolated as the hexafluorophosphate salt. The vbpy ligand was prepared by the procedure of Abrufia et al. [32] and characterized by $^1$H NMR spectroscopy. The reagents K$_2$IrCl$_6$ (Aldrich), K$_3$Fe(CN)$_6$ (J. T. Baker), and CF$_3$COONa (Aldrich) were commercial products and were used as received. K$_4$W(CN)$_8$ was synthesized as described by Heintz [33].

**Methods.** Poly-Ru(vbpy)$_3^{2+}$ films were prepared by cycling the potential of a glassy carbon disk electrode (0.071 cm$^2$; Bioanalytical Systems) between $-0.9$ and $-1.9$ V vs Ag/AgCl in an acetonitrile solution containing 1-2 mM Ru(vbpy)$_3$(PF$_6$)$_2$ plus 0.1 M Bu$_4$NPF$_6$. Scans were carried out at a sweep rate of 200 mV s$^{-1}$ for a period of ca. 8 min, which resulted in electrodes with surface coverages of 4 to $9 \times 10^{-9}$ mol Ru/cm$^2$.

Incorporation of anions was carried out by soaking poly-Ru(vbpy)$_3^{2+}$-coated electrodes in aqueous solutions containing 0.2 M CF$_3$COONa and