

will cause the L_{β} to " L_c " transition, which can be observed from the changes of C-H stretching ratios but not from changes in O-H band intensities.

We find that the structure of water between fully hydrated bilayers of multilamellar dispersions is similar to that of bulk water. As the water concentration in the lipid is reduced, the intensity distribution of the OH band moves to lower frequencies, which indicates that the remaining waters form a stronger hydrogen bonded structure with the lipid than the OH-O hydrogen bonds of bulk water.

The intensities of the C-N "totally" symmetric stretching band and the OH stretching band are directly correlated. The "totally"

symmetric C-N stretching band is very sensitive to the water content of the bilayer and can change even with slight differences in hydration. The frequency of this band increases primarily during the L_{β} to " L_c " transition, whereas the intensity decrease is greatest across the L_{α} to L_{β} transition. The decrease in intensity between 10 and 0% RH (4 and 2 water molecules/lipid molecule) probably indicates a structural rearrangement in the head-group. This band intensity should not be used as an internal standard for spectral normalization unless the precise lipid/water concentration is known and held constant.

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Association of Electroactive Counterions with Polyelectrolytes. 4. Coordinative Binding of Ru(edta) to Poly(4-vinylpyridine)

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The coordination of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ (edta = ethylenediaminetetraacetate) to poly(4-vinylpyridine) (PVP) dissolved in aqueous acid was investigated with electrochemical techniques. Rotating disk voltammetry provided estimates of the diffusion coefficients of the polymer-metal complex. The diffusional rate of the $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ complex, but not the $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ complex, is enhanced substantially by homogeneous electron transfer between $\text{Ru}^{\text{III}}(\text{edta})$ centers bound to the PVP and $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ complexes generated at the electrode surface. The diffusion coefficient measured for the $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ complex, $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, provides an estimate of the diffusion coefficient for the protonated PVP chains themselves.

Previous studies in this series have involved water-soluble polyelectrolytes based on a polysiloxane¹⁻³ or polystyrenesulfonate.⁴ The present study employs protonated poly(4-vinylpyridine) (PVP) as the water-soluble cationic polyelectrolyte and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ (edta = ethylenediaminetetraacetate) as electroactive counterions. The issues we wanted to consider included the possible competition between coordination and electrostatic association of the counterions with the pyridine or with the pyridinium sites, respectively, the effect of varying the proportions of protonated and unprotonated pyridine groups on the diffusional rates of the PVP-counterion complexes, and the effects of electron transfer between bound and unbound counterions on their measured diffusion coefficients.

The enhancement of the diffusional rates of $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ complexes by electron transfer proved to be substantial while no apparent enhancement was observed with $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ complexes. The likely reasons for this marked difference in behavior are presented in this report.

Experimental Section

Materials. Poly(4-vinylpyridine) obtained from Polysciences, Inc., was fractionated according to molecular weight by partial precipitation from methanol-ether mixtures. The fraction employed in this study had a molecular weight of ca. 126 000 Da corresponding to ca. 120 monomer units per polymer chain. $\text{HRu}^{\text{III}}(\text{edta})\text{OH}_2^-$ was prepared as previously described.⁵ Solutions of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ were prepared by reduction of the $\text{Ru}^{\text{III}}(\text{edta})$ complex with Zn(Hg) under an argon atmosphere. Other chemicals were reagent grade and were used as received. Solutions were prepared from laboratory distilled water which had been further purified by passage through a purification train (Sybron Barnsted-Nanopure).

Apparatus and Procedures. The electrochemical instrumentation and procedures employed were described previously.² The edge plane pyrolytic graphite (EPG) electrode employed had an area of 0.32 cm^2 and was polished with 0.3- μm alumina and sonicated in pure water before each experiment. Experiments were conducted at ambient laboratory temperature, $22 \pm 2^\circ\text{C}$. Potentials were measured and are reported with respect to a saturated calomel electrode (SCE).

Results and Discussion

Protonation and Dissolution of PVP. The poly(4-vinylpyridine) employed in this study became soluble in aqueous solutions when ca. 35% of the pyridine sites were protonated. This feature restricted the pH range within which the PVP-counterion complexes could be investigated. A titration of a solution of PVP with CF_3COOH is shown in Figure 1A. The titration began with ca. 35% of the pyridine groups protonated and was terminated near pH 3 where further additions of the titrant produced only small decreases in pH. The fraction of protonated pyridine groups in the PVP at each pH was calculated from the data in Figure 1A and is plotted in Figure 1B. The behavior shown in Figure 1B is very different than that obtained during the titration of monomeric pyridine (py) with acid in that the range of pH values over which the protonation of the PVP proceeds is much more extended and there is no inflection in the titration curve. These features are expected during the protonation of the increasingly positively charged poly(4-vinylpyridinium) molecules.⁶ At pH 3.2 only ca. 72% of the pyridine groups of the PVP are protonated while monomeric pyridine is over 99% protonated at pH 3.2 (the $\text{p}K_a$ of pyH^+ is 5.3).

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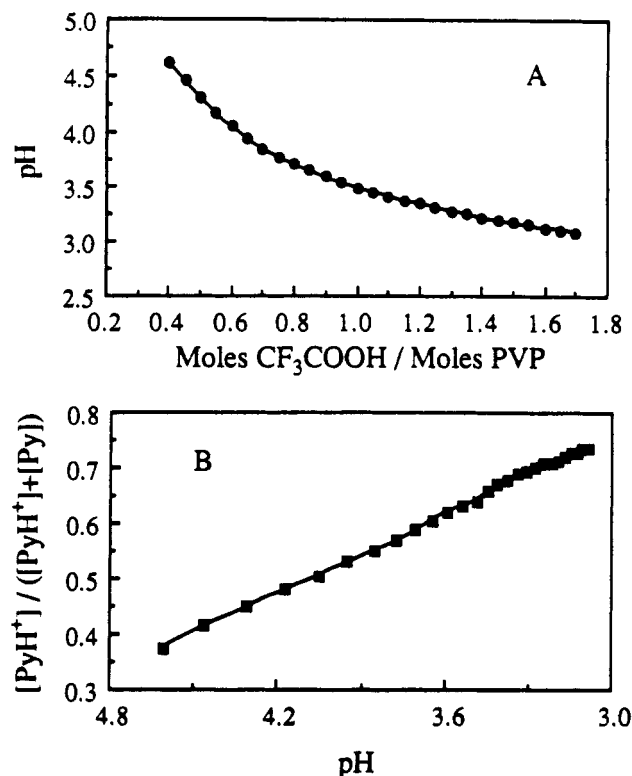


Figure 1. (A) Titration of 10 mL of a solution of PVP, 1 mM in pyridine groups, with 10 mM CF_3COOH . Supporting electrolyte: 0.1 M CF_3COONa . Thirty-five percent of an equivalent quantity of CF_3COOH was added at the start of the titration to dissolve the PVP. (B) Fraction of the pyridine groups which are protonated as a function of pH.

This significant difference in the protonation equilibria for PVP compared with monomeric pyridine produces corresponding differences in the equilibria between the two types of pyridine ligand and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$. The association between $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and py to form $\text{Ru}^{\text{III}}(\text{edta})\text{py}^-$ is governed by an association constant of 10^5 M^{-1} .⁷ Thus, at pH 3.2 in the presence of 5 mmol per liter of py + pyH^+ only about 80% of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ is converted to $\text{Ru}^{\text{III}}(\text{edta})\text{py}^-$ (with $[\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-] + [\text{Ru}^{\text{III}}(\text{edta})\text{py}^-] \ll [\text{py}] + [\text{pyH}^+]$). By contrast, at the same pH and concentration of pyridine groups in a solution of PVP, over 99% of the $\text{Ru}^{\text{III}}(\text{edta})$ would be present as $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ if the equilibrium association constant had the same value as it has for monomeric pyridine as ligand. One of the results of the present experiments was an estimate of the equilibrium constant for the association of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ with PVP.

Association of $\text{Ru}^{\text{III}}(\text{edta})$ with PVP. The addition of PVP to acidic solutions of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ produces several changes in the electrochemical response of the anion as shown in Figure 2A. The cyclic voltammetric peak potential is shifted to a more positive value because the greater back-bonding involved in the coordination of pyridine to $\text{Ru}(\text{II})$ than to $\text{Ru}(\text{III})$ ⁸ causes the complex with $\text{Ru}(\text{II})$ to be more stable. PVP tends to adsorb on the surface of the EPG electrodes and carries with it the $\text{Ru}^{\text{III}}(\text{edta})$ complex to which it is coordinated. This adsorption causes the voltammetric peak currents for the reduction of $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ to be enhanced by the contribution from the adsorbed complex. The effect is clearly evident at a PVP concentration of 0.5 mM (Figure 2A, curve 2). However, at higher concentrations of PVP more of the $\text{Ru}^{\text{III}}(\text{edta})$ complex is coordinated to unadsorbed PVP molecules and the peak currents become smaller because of the smaller contribution from the adsorbed complex and the decrease in the diffusion coefficient of the unadsorbed $\text{Ru}^{\text{III}}(\text{edta})$ centers which results from their coordination to the PVP chains (Figure 2A, curve 3). There is a corresponding decrease in the reduction

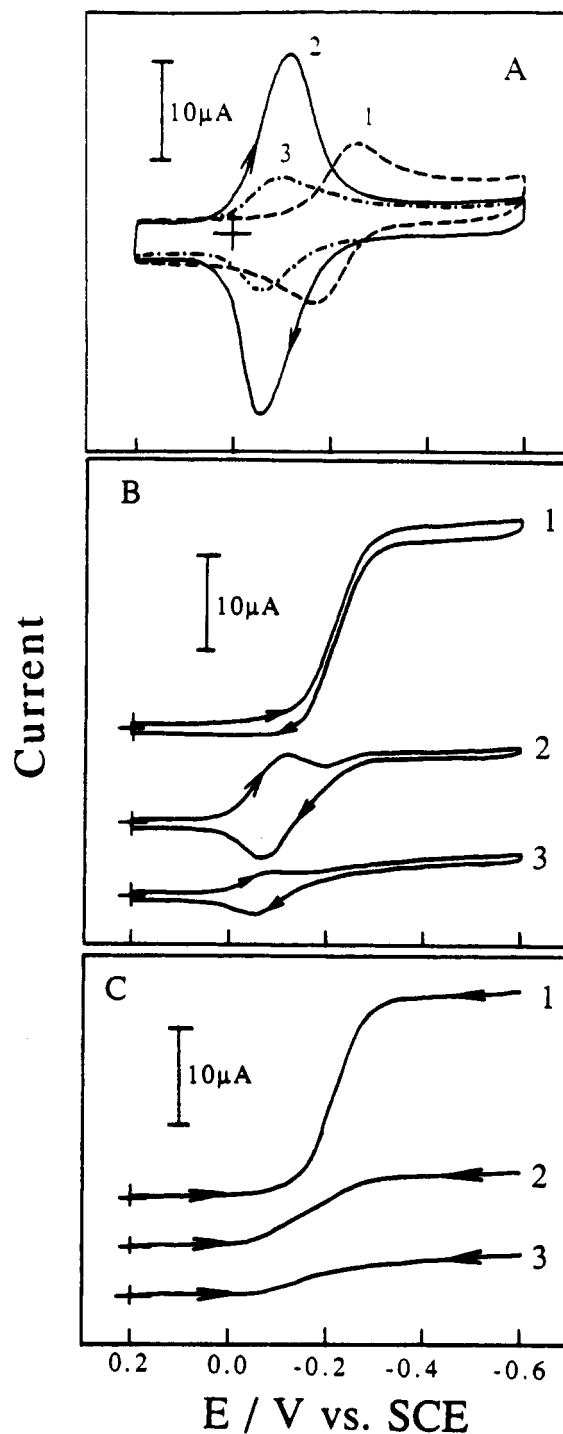


Figure 2. (A) Cyclic voltammetry for 0.2 mM $\text{Ru}^{\text{III}}(\text{edta})^-$ (1) in the absence of PVP, (2) in the presence of 0.5 mM PVP, and (3) in the presence of 2.0 mM PVP. Supporting electrolyte: 0.1 M CF_3COONa adjusted to pH 3.0–3.3. Scan rate: 50 mV/s. (B) Rotating disk voltammetry with the solutions from A. Electrode rotation rate: 900 rpm; scan rate: 10 mV s^{-1} . (C) Repeat of B under true steady-state conditions (i.e., scan rate = 0 mV s^{-1}).

currents on the plateau of current–potential curves recorded at a rotating disk electrode (Figure 2B). The peaks in the rotating disk voltammograms in curves 2 and 3 of Figure 2B arise from the $\text{Ru}^{\text{III}}(\text{edta})$ that is coordinated to the adsorbed PVP. These peaks disappear when true steady-state currents are measured by maintaining the electrode at each potential until the current becomes constant (curves 2 and 3 in Figure 2C).

The extensive adsorption of the electroactive complexes in the presence of PVP interfered with the evaluation of the formal potential of the dissolved $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}/\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ couple from cyclic voltammetric peak potentials which were dominated

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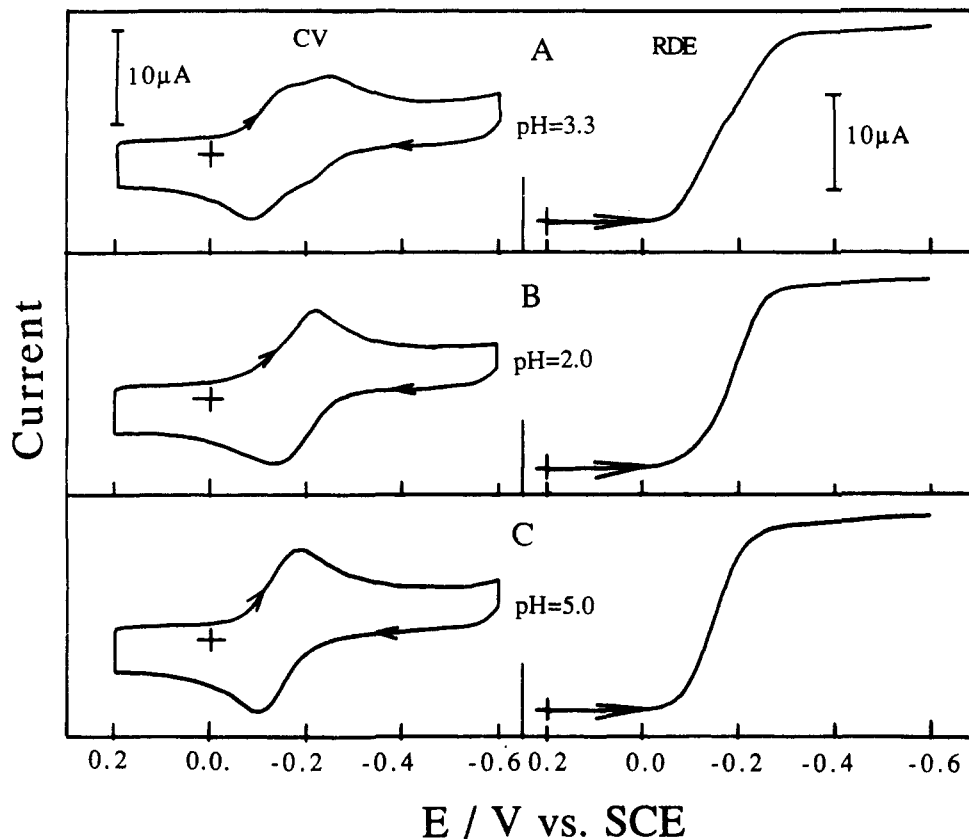


Figure 3. Cyclic and rotating disk voltammetry with 0.2 mM $\text{Ru}^{\text{III}}(\text{edta})^-$ in the presence of 1.0 mM pyridine. Supporting electrolyte: 0.1 M CF_3COONa adjusted to the indicated pH values. Cyclic voltammetric scan rate: 50 mV s^{-1} . Rotating disk rotation rate: 900 rpm; potential scanned at 10 mV s^{-1} .

by the response of the adsorbed complex. The formal potentials of the dissolved couple were therefore estimated from the half-wave potentials of curves such as 2 and 3 in Figure 2C. The value obtained, -0.15 V , was very close to the value for the $\text{Ru}(\text{edta})\text{py}^-/\text{Ru}(\text{edta})\text{py}^{2-}$ couple.

The contribution to the currents arising from the adsorbed $\text{Ru}(\text{edta})\text{PVP}$ complex also made it difficult to determine if solutions of PVP and $\text{Ru}(\text{edta})\text{OH}_2^-$ exhibited a single reduction wave or two closely spaced waves. The latter pattern is obtained with mixtures of $\text{Ru}(\text{edta})\text{OH}_2^-$ and monomeric pyridine at pH values where the complex formation reaction is incomplete. For example, the cyclic voltammogram and rotating disk voltammogram shown in Figure 3A both contain two waves which correspond to the reduction of the $\text{Ru}(\text{edta})\text{py}^-$ complex followed by the reduction of the $\text{Ru}(\text{edta})\text{OH}_2^-$ complex. At pH 2 only the latter wave is present (Figure 3B) because the $\text{Ru}(\text{edta})\text{py}^-$ complex is unstable at low pH while at pH 5 the pyridine complex is dominant and only the first wave remains (Figure 3C). The presence of two waves in Figure 3A (instead of a single wave at an intermediate potential) shows that the time required for the association of the pyridine ligand with the $\text{Ru}(\text{edta})\text{OH}_2^-$ anions is longer than the time required for the reactants to cross the diffusion layers at the electrode surfaces (ca. 0.1 s in rotating disk voltammetry at 900 rpm). This result is consistent with the rate constant reported for this coordination reaction by Matsubara and Creutz,⁷ which corresponds to a reaction half-life of ca. 10 s at pH 3.3 with 1 mM pyridine. The likely presence of two waves in the cyclic voltammetry of the corresponding $\text{PVP-Ru}(\text{edta})\text{OH}_2^-$ system is obscured by the large adsorption wave and the steady-state current-potential curves at rotating disk electrodes (Figure 2C, curves 2 and 3) were not sufficiently well defined to distinguish two closely spaced waves. However, on the basis of the result with monomeric pyridine complexes it seems reasonable to assume that the coordination equilibria for the $\text{PVP-Ru}(\text{edta})\text{OH}_2^-$ system are also frozen during the electrochemical measurements.

Addition of PVP to solutions of $\text{Ru}(\text{edta})\text{OH}_2^-$ produces major

decreases in the cathodic plateau currents at the rotating disk electrode. The dependence of the plateau current on the concentration of PVP is shown in Figure 4A. The decrease in the current could be the result of several effects in addition to the decrease in the effective diffusion coefficient of the $\text{Ru}^{\text{III}}(\text{edta})$ produced by its electrostatic and coordinative binding to the polycationic PVP chains: the viscosity of the solution could be increased by the addition of the PVP, the adsorbed layer consisting of PVP and the $\text{PVP-Ru}(\text{edta})$ complex could prevent the unadsorbed $\text{Ru}(\text{edta})\text{PVP}$ complex from reaching the electrode surface at the convection-diffusion-controlled rate, and the transfer of electrons between the (reduced) adsorbed layer and the $\text{Ru}(\text{edta})\text{PVP}$ complex that arrives at the boundary between the adsorbed layer and the solution could be slow.

The effect of PVP on the plateau currents for the reduction of $\text{Ru}(\text{NH}_3)_6^{3+}$ cations, which do not associate with the polycationic PVP molecules, is shown in Figure 4B. The relatively small change in current indicates that changes in viscosity contribute very little to the current decreases obtained with $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$.

Small decreases in plateau currents resulted when $\text{Fe}^{\text{III}}(\text{edta})\text{OH}_2^-$, which exhibits no tendency to coordinate to pyridine ligands, is substituted for $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ (Figure 4B). This result indicates that electrostatic association of these anionic complexes with the polycation could play only a small role in diminishing the diffusion coefficient of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ in solutions of PVP.

The possible influence of the adsorbed layer on the plateau currents for reduction of $\text{Ru}(\text{III})$ at rotating disk electrodes in mixtures of PVP and $\text{Ru}(\text{edta})\text{OH}_2^-$ was examined by means of Levich plots of current vs (rotation rate)^{1/2}.⁹ The plots were linear at rotation rates below 1000 rpm with slopes that corresponded to the apparent diffusion coefficients calculated from the plateau currents plotted in Figure 4A. This behavior showed that the adsorbed layer of PVP on the surface of the rotating disk did not

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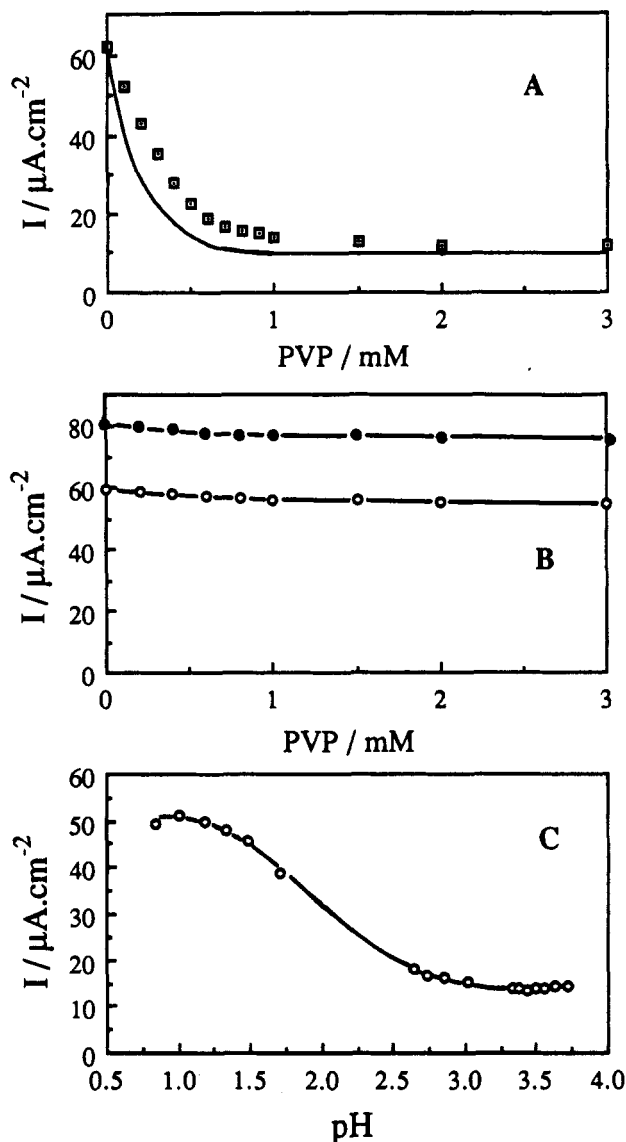


Figure 4. (A) Rotating disk plateau currents for the reduction of 0.2 mM $\text{Ru}^{\text{III}}(\text{edta})^-$ in the presence of PVP. Supporting electrolyte: 0.1 M CF_3COONa adjusted to pH 3.0–3.3. Electrode rotation rate: 900 rpm. The solid line gives the calculated currents which would be observed in the absence of enhancement by electron transfer via reaction 4 (see text). (B) Behavior of $\text{Ru}(\text{NH}_3)_6^{3+}$ (●) and $\text{Fe}(\text{edta})\text{OH}_2^-$ (○) under the same conditions. (C) pH dependence of the plateau current for the reduction of a mixture of 0.2 mM $\text{Ru}^{\text{III}}(\text{edta})^-$ and 1.0 mM PVP. Other conditions as in part A.

retard the reduction of $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ complexes arriving at the electrode surface.

The decrease in reduction current for $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ produced by the addition of PVP depends upon pH as shown in Figure 4C. These data suggest that the coordination of $\text{Ru}^{\text{III}}(\text{edta})$ to PVP is largely eliminated in the presence of 0.1 M H^+ . Any electrostatic association is surely absent at pH 1 because $\text{Ru}(\text{edta})\text{OH}_2^-$ is converted into the neutral $\text{Ru}(\text{Hedta})\text{OH}_2$ complex below pH 2.⁷

Thus the primary cause of the large decreases in current shown in Figure 4A is the decrease in the diffusion coefficient of $\text{Ru}^{\text{III}}(\text{edta})$ produced by its coordination to the PVP molecules. In suitable circumstances,^{2–4,10,11} the changes in plateau currents can provide a convenient means for monitoring the extent of this association. To estimate the quantities of the $\text{Ru}(\text{III})$ complex that are associated with the polycation at each concentration of

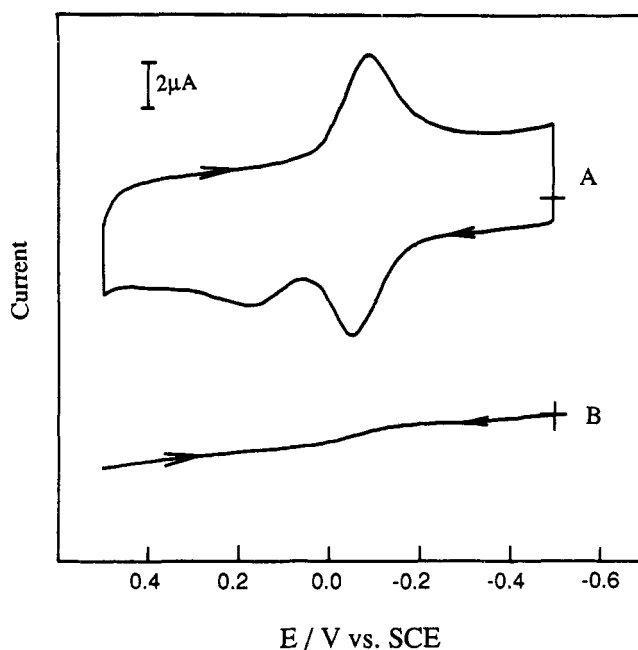


Figure 5. (A) Cyclic voltammogram for 0.2 mM $\text{Ru}^{\text{II}}(\text{edta})^{2-}$ in the presence of 1.5 mM PVP. Supporting electrolyte: 0.1 M CF_3COONa adjusted to pH 3.0–3.3. Scan rate: 50 mV s^{-1} . (B) Rotating disk voltammogram with the solution from A. Electrode rotation rate: 900 rpm. Scan rate: 0 mV s^{-1} .

PVP, it is necessary to know the diffusion coefficient of the $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ complex, D_b , and any coupling of the diffusion of the associated and unassociated counterions must be taken into account.^{3,4,12} A convenient method for estimating D_b was to examine the corresponding complex of $\text{Ru}^{\text{II}}(\text{edta})$ with PVP because the reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ with pyridine is more nearly quantitative.⁷

Coordination of $\text{Ru}^{\text{II}}(\text{edta})$ to PVP. The driving force for the coordination of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ to pyridine is greater than that for $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$, but the rate of the reaction is much larger for the latter complex.⁷ However, the coordination reactions of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ are catalyzed by $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ through an electron-transfer mechanism.⁷ This property was exploited in experiments directed at examining the coordination of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ to PVP by carrying out the measurements in the presence of small quantities of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$. Cyclic voltammograms for solutions of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ in the presence of PVP exhibit a second, smaller, anodic peak at potentials ~ 150 mV more positive than the first anodic peak (Figure 5). The smaller anodic peak has little or no cathodic counterpart. This behavioral pattern was observed in a previous study in which $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ interacted with PVP adsorbed on the surface of graphite electrodes.¹³ It results from the substitution of a second pyridine ligand on the $\text{Ru}(\text{II})$ center by the displacement of a coordinated carboxylate group of the edta ligand.^{7,13} The second pyridine ligand is replaced by the carboxylate group at an appreciable rate when the Ru center is oxidized to $\text{Ru}(\text{III})$, which accounts for the lack of a cathodic counterpart to the second anodic peak in the voltammogram in Figure 5.

It is interesting to note that the coordination of a second pyridine group to the $\text{Ru}^{\text{II}}(\text{edta})$ center in mixtures of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ and monomeric pyridine requires a much higher concentration of the ligand than is required when PVP is the ligand. Pyridine concentrations greater than 0.1 M are needed to produce two sets of waves in the voltammetry of $\text{Ru}^{\text{II}}(\text{edta})$. This striking difference is probably a reflection of the much higher "local concentration" of pyridine groups experienced by the $\text{Ru}(\text{edta})$ center when it is coordinated to a PVP chain than when it is coordinated to a pyridine ligand in solutions containing excesses of the monomer.

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An additional complication encountered in experiments with $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ at concentrations of PVP above ca. 2 mM was a significant time dependence of the anodic plateau currents. The currents continued to decrease for 20–40 min after addition of the PVP. The $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$ complex exhibited no similar time-dependent reduction currents. The unusual behavior of the $\text{Ru}^{\text{II}}(\text{edta})$ complex may result from the coordination of a second PVP chain to the $\text{Ru}^{\text{II}}(\text{edta})$ centers because of the higher affinity of $\text{Ru}(\text{II})$ for pyridine ligands.⁷ Measurements of anodic plateau currents for $\text{Ru}^{\text{II}}(\text{edta})$ were restricted to concentrations of PVP below 2 mM to avoid this complication.

A typical current–potential curve recorded at a rotating disk electrode under true steady-state conditions (i.e., at a scan rate of 0 mV s^{-1}) is shown in Figure 5B. The plateau current is much smaller than expected from the peak currents in Figure 5A because the latter are dominated by the contribution from the adsorbed complex, which is absent from the steady-state response of Figure 5B. The presence of the second anodic wave in the voltammetry of $\text{Ru}^{\text{II}}(\text{edta})$ –PVP mixtures required that anodic plateau currents at rotating disk electrodes be measured at potentials sufficiently positive to encompass both waves in order to measure plateau currents which corresponded to the oxidation of all forms of $\text{Ru}^{\text{II}}(\text{edta})$ present. A potential of 0.2 V proved suitable for this purpose and in Figure 6A are shown the effects of additions of PVP on the plateau currents for the oxidation of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ at a rotating disk electrode. The decrease in current is more abrupt and more linear than is obtained with $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$ (Figure 4A) and the intersection of the two straight lines drawn through the initial and final current values occurs close to the point expected for a quantitative reaction between the two reactants. A similar conclusion results from spectral measurements of mixtures of PVP with $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$. The intensity of an absorption band at 412 nm, which has been assigned to the $\text{Ru}^{\text{II}}(\text{edta})\text{py}_2^{2-}$ complex,⁷ increases linearly with the concentration of PVP until a stoichiometric quantity is added (Figure 6B). The equilibrium constant for the reaction between $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ and monomeric pyridine is $7 \times 10^6 \text{ M}^{-1}$.⁷ If the same constant applied to the reaction with PVP, a negligible quantity of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ would remain unbound to the PVP in a 1 mM solution of the polymeric ligand even at pH 3 where only 25% of the pyridine groups remain unprotonated (Figure 1B).

The limiting values of the anodic plateau currents in Figure 6A (for $[\text{PVP}] = 1.5$ and 2.0 mM) were therefore assumed to reflect the diffusion coefficient of the $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ complex. Contributions to the current from uncoordinated $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ were initially assumed to be negligible because of its low concentration and the lack of dependence of the limiting current on the concentration of PVP above ca. 1.0 mM (Figure 6A) or upon the solution pH between pH 1.5 and 3.5 (Figure 6C). The diffusion coefficient calculated from the limiting plateau current of $6.6 \mu\text{A cm}^{-2}$ was $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which was assumed to apply to $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ as well. This value of the diffusion coefficient, D_b , was then utilized with the current data in Figure 4A to estimate an equilibrium constant for the association of PVP with $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$.

Equilibrium Binding Constant for Association between PVP and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$. The decrease in the cathodic plateau currents for the mixtures of PVP and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$ shown in Figure 4A reflects changes in the quantities of bound and unbound counterions in the solution. As described above, when the time required for attainment of the association–dissociation equilibria is large compared with the time the reactants spend crossing the diffusion layer at rotating disk electrodes, separate waves for the reduction of the bound and unbound counterions are expected and were observed in mixtures of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^{2-}$ with monomeric pyridine (Figure 3A). Under these conditions, the total current on the plateau of the second wave is given by eq 1, where G is

$$I = GC_T(X_f D_f^{2/3} + X_b D_b^{2/3}) \quad (1)$$

a combination of known constants, C_T is the total concentration of $\text{Ru}^{\text{III}}(\text{edta})$ present, X_f and X_b ($= 1 - X_f$) are the fractions of free and bound $\text{Ru}^{\text{III}}(\text{edta})$, respectively, and D_f and D_b are the

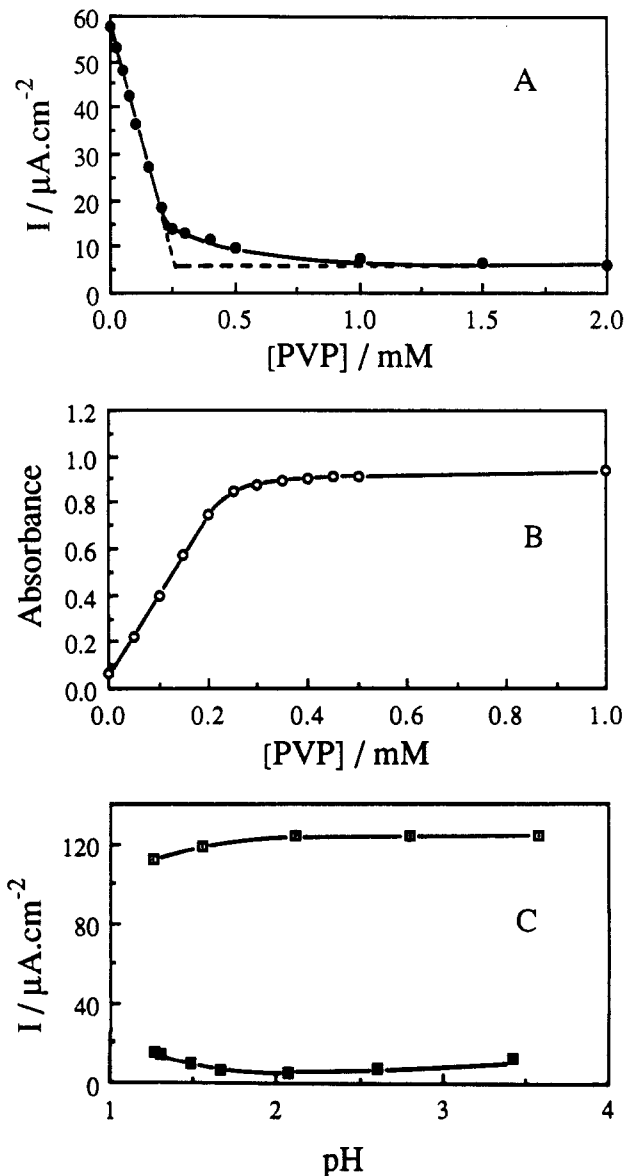


Figure 6. (A) Rotating disk plateau currents for the oxidation of $0.2 \text{ mM Ru}^{\text{II}}(\text{edta})^{2-}$ in the presence of PVP. Experimental conditions as in Figure 5B. (B) Absorbance at 412 nm for mixtures of $0.2 \text{ mM Ru}^{\text{II}}(\text{edta})^{2-}$ and PVP in $0.1 \text{ M CF}_3\text{COONa}$ adjusted to pH 3. (C) pH dependence of plateau currents for the oxidation of $0.4 \text{ mM Ru}^{\text{II}}(\text{edta})^{2-}$ in the absence (top curve) and the presence (bottom curve) of 1.5 mM PVP .

corresponding diffusion coefficients.^{3,4,10,11} The relation between K_b and X_f and X_b is given in eq 2. Substitution and rearrangement

$$X_f = \frac{1}{K_b[\text{PVP}] + 1} = 1 - X_b \quad (2)$$

of eqs 1 and 2 leads to eq 3, where I_0 is the current measured in the absence of PVP and I_b is the current to be expected when all of the $\text{Ru}^{\text{III}}(\text{edta})$ is coordinated to the PVP as calculated from the value of D_b obtained from the data in Figure 6A ($1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$).

$$\frac{I_0 - I}{I - I_b} = K_b[\text{PVP}] \quad (3)$$

An assumption made in writing eqs 2 and 3 is that the binding of $\text{Ru}^{\text{III}}(\text{edta})$ to PVP can be regarded as analogous to the binding of the complex to monomeric pyridine in that the equilibrium binding constant is independent of the concentration of PVP. This assumption is not likely to be true because of the mutual repulsion of the polycationic chains of PVP. At concentrations of PVP where most of the $\text{Ru}^{\text{III}}(\text{edta})$ is coordinated to the polymer chains, the

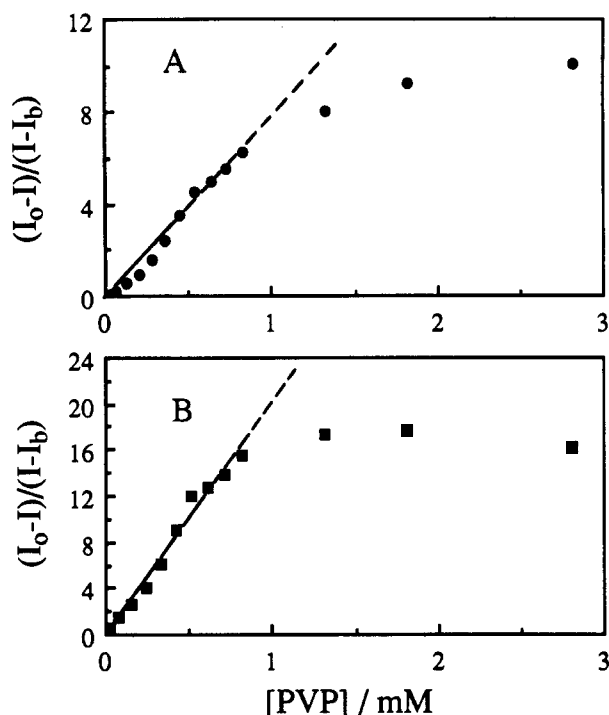
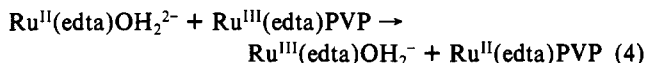


Figure 7. (A) Plot of the left-hand side of eq 3 vs [PVP] for the data points in Figure 4A. (B) Same plot after the values of I were corrected for the current enhancement produced by reaction 4 (see text).

local concentration of pyridine sites encountered by a $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ complex is unlikely to increase linearly with the bulk concentration of PVP. For this reason, significant deviations from the behavior predicted by eq 3 might be anticipated. A plot of the left-hand side of eq 3 versus the concentration of PVP for the plateau currents of Figure 4A is shown in Figure 7A. The plot is reasonably linear at low concentrations of PVP but increasing deviations from the extrapolated line are present at higher concentrations where repulsion between the polycationic chains would be expected to increase. The slope of the initial linear portion of the plot corresponds to a value of K_b of $8.5 \times 10^3 \text{ M}^{-1}$.

Because the association–dissociation equilibria between $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and PVP are believed to be established slowly, electron transfer between reduced, unbound $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^-$ and $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ (reaction 4) will produce an enhancement in the plateau currents at rotating disk electrodes.^{4,12} The appropriate



value of I to use in preparing the plot in Figure 7 in order to estimate K_b is the unenhanced current. We therefore adopted an iterative procedure to obtain a plot of eq 3 with corrected values of I .

The extent of the enhancement of plateau currents by electron transfer can be calculated from a knowledge of the concentrations of bound and unbound $\text{Ru}^{\text{III}}(\text{edta})$, the diffusion coefficients for these two species, and the equilibrium constant, K_{et} , for the electron transfer reaction between them (reaction 4). The value of K_b obtained from the slope of the plot in Figure 7A was used with eq 2 to estimate the concentrations of bound and unbound $\text{Ru}^{\text{III}}(\text{edta})$. Their diffusion coefficients were taken as $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ (from Figure 5A) and $3.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ (from Figure 4A), respectively. The difference in the formal potentials of the $\text{Ru}(\text{edta})\text{OH}_2^{2-}/\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ and $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}/\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ couples corresponds to $K_{\text{et}} = 73$ (at pH 3.3). These parameters were employed in a calculation similar to that described by Andrieux et al.¹⁴ as adapted for rotating disk voltammetry.^{4,12} The resulting set of calculated current enhancement factors was applied to the

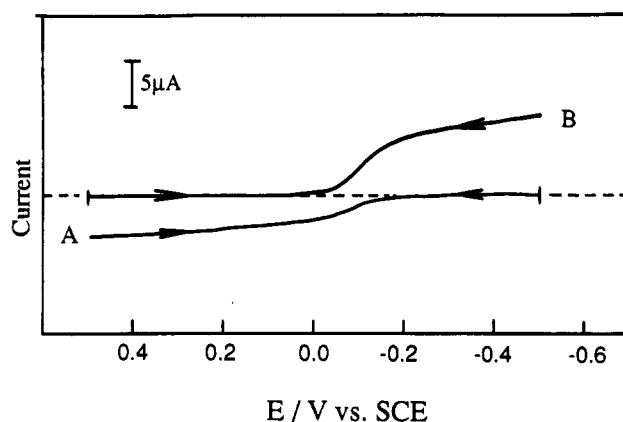


Figure 8. Current–potential curves at a rotating disk electrode for a solution containing 2 mM PVP and (A) 0.4 mM $\text{Ru}^{\text{II}}(\text{edta})^{2-}$ or (B) 0.4 mM $\text{Ru}^{\text{III}}(\text{edta})^-$. Supporting electrolyte: 0.1 M CF_3COONa adjusted to pH 3. Rotation rate: 900 rpm. Scan rate: 0 mV s^{-1} .

measured values of I at each concentration of PVP and a “corrected” plot similar to Figure 7A was prepared. The slope of the linear plot was then used to obtain an improved value of K_b and the process was repeated until a constant value of K_b was obtained. The resulting plot of eq 3, which became invariant after two iterations, is shown in Figure 7B. Its slope corresponds to $K_b = 2.0 \times 10^4 \text{ M}^{-1}$.

Attempts to measure K_b independently by equilibrium dialysis, as in previous studies,^{3,4} were thwarted by the formation of precipitates as the ratio of the concentrations of $\text{Ru}^{\text{III}}(\text{edta})$ to PVP increased within the dialysis bag which caused us to abandon this approach. The spectral changes produced by the reaction between $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and PVP are too small to allow K_b to be evaluated from spectroscopic measurements,⁷ so that the estimate of K_b obtained from Figure 7B is the only value available.

The experiments upon which Figure 7 is based were carried out at pH 3.3 where 70% of the pyridine groups of PVP are protonated (Figure 1B). Taking this factor into account leads to a pH independent value for K_b of $7.5 \times 10^4 \text{ M}^{-1}$, which is close to the known value for the constant governing the reaction between monomeric pyridine and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$, $1 \times 10^5 \text{ M}^{-1}$.⁷ Thus, the affinity of $\text{Ru}^{\text{III}}(\text{edta})$ for pyridine appears to be diminished only moderately when the pyridine ligands are linked together in PVP.

The continuous decrease in the basicity of the pyridine groups in PVP as the fraction which is protonated increases (Figure 1B) is not paralleled by a decreased affinity of the pyridine groups for $\text{Ru}^{\text{III}}(\text{edta})$. On the other hand, the electrostatic repulsion which controls the acid–base chemistry does not translate into sufficient electrostatic attraction between protonated pyridine groups and negatively charged $\text{Ru}^{\text{III}}(\text{edta})^-$ anions to produce a dramatic enhancement in K_b for the PVP– $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ system compared with the py– $\text{Ru}(\text{edta})\text{OH}_2^-$ system.

Current Enhancement by Electron Transfer with Mixtures of $\text{Ru}(\text{edta})$ and PVP. Reaction 4 produces significant enhancements in the plateau currents measured with mixtures of $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ and $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$. This enhancement is particularly clear when the anodic plateau current for the oxidation of $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ (Figure 8A) is compared with the cathodic plateau current for the reduction of the same quantity of $\text{Ru}^{\text{III}}(\text{edta})$ in the presence of the same concentration of PVP (Figure 8B).

The assumption that the limiting anodic plateau currents for the oxidation of $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ in Figure 6A can be used to obtain the value of D_b for $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ depends upon the absence of significant enhancement of the plateau currents for the oxidation of $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ by electron transfer via the reverse of reaction 4. Calculations showed that this condition is realized because the value of the equilibrium constant for the reaction of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ with PVP (obtained from K_b and the difference in formal potentials of the bound and unbound couples) corresponds to very small concentrations of $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^{2-}$ in the presence of excess PVP and because the unfavorable equilibrium constant for the

(14) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. *J. Electroanal. Chem.* 1984, 172, 49.

reverse of reaction 4 acts to diminish the extent of the current-enhancing electron-transfer reaction. For example, the current-enhancement factors calculated for concentrations of PVP between 0.5 and 2.0 mM in Figure 6A were between 0.99 and 1.00. The corresponding current-enhancement factors calculated for the reduction of $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ ranged between 1.3 and 1.6. When the appropriate factors were applied to the measured currents for the reduction of $\text{Ru}^{\text{III}}(\text{edta})$ to calculate the currents that would have resulted in the absence of the enhancement by electron transfer, currents much closer to those in Figure 6A were obtained, which lends support to the model we have employed of slow ligand exchange coupled to rapid electron-transfer cross-reactions in the $\text{Ru}^{\text{III}}(\text{edta})$ -PVP system. This is the result to be anticipated if the rates of diffusional motion of $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ and $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ were essentially equal and determined by the mobility of the polymer chains to which the $\text{Ru}(\text{edta})$ centers are bound. There is extensive protonation of the pyridine sites of the PVP chains at pH 3.2 (>70%) and relatively few of the sites have $\text{Ru}(\text{edta})$ centers coordinated to them at concentrations of PVP above 1 mM (<20%). Under these conditions, the structural changes that no doubt occur when the coordinated $\text{Ru}(\text{edta})$ centers have their negative charges increased from -1 to -2 are apparently not large enough to produce large changes in the diffusion coefficients of the polymer-metal complexes so that both the oxidized and reduced forms of the complexes exhibit the same rates of diffusional motion.

It is worth noting that the plateau currents in Figure 4A at PVP concentrations of 1 mM and above do not decrease significantly as the concentration of PVP is increased even though the concentration of the more rapidly diffusing $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$ complex continues to decline as the concentration of PVP increases. The plateau currents in Figure 4A are enhanced by the occurrence of reaction 4 at all concentrations of PVP but the extent of the enhancement becomes virtually independent of the ratio of free to bound $\text{Ru}^{\text{III}}(\text{edta})$ for the particular values of K_b , K_{et} , and diffusion coefficients which apply to the $\text{Ru}^{\text{III}}(\text{edta})$ -PVP system. For the same reason, the plateau currents in Figure 4C are insensitive to changes in pH between pH 2.5 and 3.8 despite the resulting changes in the concentrations of bound and unbound complex. Only at lower pH values do the currents increase when the binding of $\text{Ru}^{\text{III}}(\text{edta})$ to PVP is largely eliminated.

It was of interest to assess the effect of the extent of protonation on the diffusion coefficient for PVP. To do so, the $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$

complex was employed because of its greater resistance to dissociation and the lack of enhancement of its diffusional rate by electron transfer. The data in Figure 6C show that little or no change in the diffusion coefficient occurs between pH 1 and 3.3. (The small apparent changes in Figure 6C lie within the range of experimental reproducibility.) Extrapolation of the data in Figure 1B indicates that the extent of protonation of the PVP chains decreases from near 100% to ca. 70% in this pH range. That no substantial change in diffusion coefficient results from the relatively small decrease in protonation is not surprising because the highly positively charged polyelectrolyte chains probably remain fully extended to minimize electrostatic repulsions throughout the range of pH values investigated. The formation of precipitates at higher pH values prevented measurements under conditions where the majority of the pyridine groups were not protonated.

Conclusions

This study and its predecessors²⁻⁴ have illustrated some of the ways in which electrochemical measurements can be used to study the mobilities of polyelectrolytes and polymeric ligands in solution. The important role that homogeneous electron-transfer reactions can play in enhancing the apparent diffusion coefficients of polymer-metal complexes is particularly clear with mixtures of PVP and $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$. Extensive adsorption on the electrode surfaces, frequently encountered with solutions of polymers and metal complexes with which they interact, poses difficulties in evaluating diffusional rates by cyclic voltammetry. The use of rotating disk voltammetry under truly steady-state conditions often allows these difficulties to be circumvented as illustrated in this study. The diffusion coefficients of the $\text{Ru}^{\text{III}}(\text{edta})\text{PVP}$ and $\text{Ru}^{\text{II}}(\text{edta})\text{PVP}$ complexes are equal and the measured value for the latter complex, $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, should represent a reasonable estimate of the diffusion coefficient of the protonated PVP chains themselves.

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Registry No. PVP, 25232-41-1; $\text{Ru}^{\text{III}}(\text{edta})\text{OH}_2^-$, 68122-22-5; $\text{Ru}^{\text{II}}(\text{edta})\text{OH}_2^-$, 70208-95-6; CF_3COOH , 76-05-1; CF_3COONa , 2923-18-4; $\text{Ru}^{\text{III}}(\text{edta})^-$, 93983-46-1; $\text{Ru}(\text{NH}_3)_6^{3+}$, 18943-33-4; $\text{Fe}(\text{edta})\text{OH}_2^-$, 28784-18-1; graphite, 7782-42-5; pyridine, 110-86-1.