

drophilic) in the interior of a globular protein.

For a proper study on denaturation the influence of denaturant molecules on both the native and the denaturated state has to be considered. When DMF is a reasonable model for the interior of a protein in the native state, we may conclude from the arguments given in this paper that, disregarding steric influences, strong urea-CONH interactions may occur in the inside of a native protein, whereas in the denaturated state (aqueous environment) this interaction is of much less importance. Unfortunately no data are available on the Gibbs energy of transfer of urea from water to an amidic solvent. However the change in enthalpy of this process is clearly negative.³⁶ This seems to indicate that direct urea-CONH interaction would stabilize the native structure rather than the denaturated state. Therefore, it may be concluded that the disruption of the water structure by urea, leading to a reduced hydrophobic interaction,^{5,37} is the dominating process in denaturation. With respect to alkyl-substituted urea compounds, it is clear that they will stabilize the denaturated state by hydrophobic interactions and show small stabilizing influences in the native state. On the other hand, they do not have the same influence on the water structure as urea. These counteracting influences of alkyl-substituted urea compounds may be the cause of the contradictory conclusions in reports on the denaturing effectiveness of these compounds. Whether alkyl substitution in urea leads to a more effective denaturing agent will be highly protein dependent, and conclusions about the hydrophobicity or hydrophilicity of proteins on basis of the relative denaturation effec-

tiveness of (substituted) urea compounds must be taken with great care.

Conclusions

The enthalpy of interaction between urea molecules in DMF is exceptionally large. The pairwise and higher enthalpic interaction coefficients largely exceed any value measured before. These anomalies disappear gradually upon subsequent introduction of methyl groups in the solute molecules. Strong solute-solvent association by hydrogen bonding can account for these features. In water the enthalpies of interaction are smaller. Considering DMF as a model for the native state of a globular protein and recalling that in the denaturated state the groups of a protein are in an aqueous environment, it can be concluded that the denaturation of proteins by urea is not caused by stabilization of the denaturated state by urea-peptide binding as is often suggested. Since alkyl-substituted urea compounds have counteracting effects on the denaturation of globular proteins, conclusions on the hydrophobicity of a protein on basis of the denaturing activities of a series of substituted ureas as suggested by Feinstein¹⁶ are cumbersome.

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Stable Composite Polyelectrolyte Electrode Coatings with Morphologies That Yield Large Ion-Exchange Capacities and High Cross-Coating Charge Propagation Rates

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Abstract: A new material for preparing polyelectrolyte coatings on electrode surfaces is described. A random ternary copolymer containing two types of hydrophilic cationic groups and hydrophobic styrene groups was mixed with a variety of conventional polycationic electrolytes to obtain coatings with exceptional properties. These include large ion-exchange capacities, remarkably high effective diffusion coefficients of incorporated counterions, and prolonged retention of multiply charged counterions. Electron microscopy revealed that the coatings spontaneously segregate into discrete hydrophilic and hydrophobic domains. The properties of these new composite coatings are especially attractive for applications in electrocatalysis.

Adsorbed polyelectrolytes are attractive as a simple means for endowing electrode surfaces with high affinities for ionic reactants that can be incorporated into the polyelectrolyte coatings¹⁻³ by ion exchange. Although electrodes coated with polyelectrolytes loaded with redox reactants have been exploited in a variety of applications,³⁻⁹ the number of useful polyelectrolyte systems that

are presently available is limited because all common polyelectrolytes lack one or more of the essential properties required for

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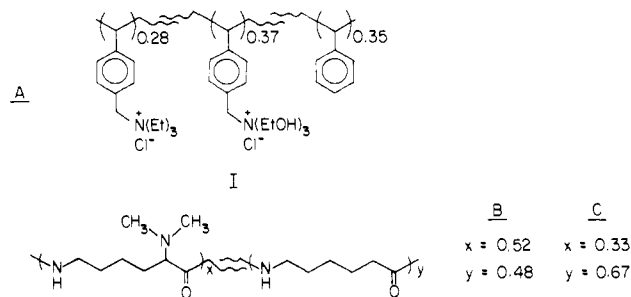


Figure 1. Structures of new copolymers employed in this study. (A) Random ternary copolymer, I. The proportions of the three groups present in the copolymer were calculated from the percentages of chloride and nitrogen it contained. (B, C) Random binary copolymers of nylon and a dimethylamino nylon derivative. The values of x and y were determined from elemental analysis.

use as effective electrode coatings. These include strong, irreversible binding of the polyelectrolyte to electrode surfaces, reasonable ion-exchange capacities of the coatings, retention by the coatings of counterionic reactants for long periods in solutions containing none of the counterions, rapid charge propagation rates within the coatings, and reasonable chemical and mechanical stability.

Of the polyelectrolytes that have been applied to electrode surfaces in order to bind electroactive counterions, the one which has exhibited the most of these desired properties is a block copolymer based on poly(*l*-lysine), PLC.^{6f-i} For example, PLC provides much higher charge propagation rates than are available with otherwise attractive coatings prepared from Nafion,^{5,6b,e} and coatings of protonated or quaternized poly(4-vinylpyridine), PVP or QPVP, are less adherent than PLC and much inferior in retaining incorporated anions when transferred to pure supporting electrolyte solutions. The latter shortcoming is also shared by non-cross-linked polystyrene sulfonate.^{1c,3,9}

In this report we describe a new composite coating that exhibits properties superior even to those of PLC.¹⁰ The new coating consists of a mixture of a random ternary copolymer containing cationic sites with any one of a series of cationic homopolymers. The copolymer, which contains both hydrophobic styrene groups and hydrophilic quaternized amino styrene groups, yields films having an internal morphology characterized by segregated hydrophobic and hydrophilic domains. By means of electron microscopy it was possible to show that the self-segregating tendency of the copolymer causes it to exert a strong influence on the internal structures of coatings prepared from its mixtures with auxiliary polyelectrolytes. The copolymer appears to act as a template that defines the internal morphology of the composite coating. Mixtures of the copolymer with a variety of homopolyelectrolytes yield coatings with essentially identical structures, ion-exchange and charge-propagation properties. The results strongly suggest that internal morphology, far more than chemical composition, is the dominant factor that determines the behavior of the coatings.

Experimental Section

Materials. The random ternary copolymer, I, shown in Figure 1A, was prepared as follows: A benzene solution containing 0.6 M styrene, 2.4 M chloromethylstyrene, and 6×10^{-2} M 2,2'-azobis(isobutyronitrile) (AIBN) was degassed on a vacuum line according to standard procedures.¹¹ The polymerization was allowed to proceed for 24 h at 60 °C which consumed about 70% of the monomers. The resulting random binary copolymer was isolated and purified by reprecipitation from *n*-hexane. The Menschutken reaction¹² was employed to convert the

chloromethyl groups in the copolymer to quaternary amine groups, using first triethylamine and subsequently tris(hydroxyethyl)amine. The resulting ternary copolymer was dissolved in concentrated HCl and dialyzed against water for 2 days to remove unreacted amine and other low molecular weight impurities. The aqueous polyelectrolyte solution became quite turbid during the course of the dialysis, and THF was added at this point to improve the solubility of the polyelectrolyte. The resulting solvent ratio (THF:H₂O) for the slightly turbid (1.0 wt.%) solution of the polyelectrolyte was ca. 1:1. The final 0.5 wt. % polyelectrolyte solution from which the coatings were prepared was approximately 25% H₂O by volume (0.67 M THF/1.0 M H₂O) and remained slightly turbid. The composition of the ternary copolymer was determined by elemental analysis for Cl and N as well as infrared spectroscopy. Its molecular weight was not estimated. Poly(*N*-vinyl-2-methylimidazole) of average molecular weight 7×10^4 daltons and the functionalized nylons (Figure 1, B and C) were prepared by standard procedures.^{13,14} All other polyelectrolytes employed were commercially available samples that were used as received.

Supporting electrolyte solutions consisted of 0.1 M sodium acetate adjusted to pH 4.5 with glacial acetic acid. Laboratory distilled water was purified by passage through a purification train (Barnstead Nanopure). Solutions of K₄Fe(CN)₆ were prepared from the analytical grade salt immediately prior to the experiment in which they were employed.

Apparatus and Procedures. Glassy carbon electrodes (Tokai Electrode Manuf. Co., Ltd., Tokyo) having an area of 0.34 cm² were mounted and prepared as previously described.^{1b} The hanging mercury drop electrode was conventional (Brinkmann Instruments, Inc.) and was filled with triply distilled mercury (Bethlehem Instruments Co.).

Cyclic voltammetry was conducted with conventional previously described procedures and instrumentation.^{1b,d} The quantities of electro-oxidizable Fe(CN)₆⁴⁻ incorporated by electrode coatings were measured coulometrically after transfer of the electrode to the pure supporting electrolyte solution. The potential was scanned immediately at 2 mV s⁻¹ to a potential well beyond the peak potential and maintained at that point until the current had decreased to background levels (10–20 s). The total charge passed during the experiment was measured and used to calculate the total quantity of Fe(CN)₆⁴⁻ in the coating. The slopes of chronocoulometric charge-(time)^{1/2} plots were used to evaluate diffusion coefficients of Fe(CN)₆⁴⁻ incorporated in electrode coatings.^{1b,6e} The data were obtained with an Electrochemical Analyzer (Bioanalytical Systems, Model 100) and analyzed graphically. Relatively long measurement times were employed (25 ms) in order to avoid possible non-linearities arising from the uncompensated resistance presented by the coatings. Composite coatings were cast by mixing 1 μL of a 0.5 wt. % solution of I in 1:3 H₂O-THF with 1 μL of a 0.5 wt. % solution of the auxiliary polyelectrolyte in methanol, transferring the mixture to a freshly polished glassy carbon electrode and allowing the solvent to evaporate at room temperature. Coatings of a single polyelectrolyte were cast from a mixed solvent of the same composition as used with the composite coatings: CH₃OH:THF:H₂O = 4:3:1. Coating thicknesses were estimated by micrometric measurements on coatings prepared from 10 to 20 times more polyelectrolyte than was used in the experiments with the assumption that the thickness was a linear function of the quantity of polyelectrolyte employed.^{6b}

Solutions were deaerated with prepurified argon. Experiments were conducted at ambient temperatures (22 ± 2 °C). Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode.

Transmission electron micrographs were obtained with a Phillips EM 201 instrument. Coatings were cast on 400-mesh copper minigrids (Ted Pella, Inc.) that were first coated with a thin layer of carbon by a conventional procedure.²³ Aliquots (1 μL) of 0.005 wt. % solutions of the

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Table I. Retention Ratios and Diffusion Coefficients for $\text{Fe}(\text{CN})_6^{4-}$ and Other Multiply Charged Counterions Incorporated in Electrode Coatings Prepared from Single Polyelectrolytes

coating material ^a	$10^7 \Gamma_p^b$ mol cm ⁻²	counterion	$10^8 \Gamma_{os}^c$ mol cm ⁻²	$\Gamma_{45}/\Gamma_{os}^d$	$Z\Gamma_o/\Gamma_p^e$	$10^6 D_{E}^f$ cm ² s ⁻¹
I	0.45	$\text{Fe}(\text{CN})_6^{4-g}$	0.37	0.73	0.33	<i>k</i>
PVI	1.55	$\text{Fe}(\text{CN})_6^{4-g}$	0.39	0.54	0.10	<i>k</i>
PVP	5.37	$\text{Fe}(\text{CN})_6^{4-h}$	10.3		0.77	0.0038
PLC	2.8	$\text{Mo}(\text{CN})_6^{4-i}$			0.70	0.76
Nafion		$\text{Ru}(\text{NH})_6^{3+j}$				0.002

^a Abbreviations: I, see Figure 1A; PVI = poly(*N*-vinyl-2-methylimidazole); PVP = poly(4-vinylpyridine); PLC, a block copolymer of lysine;^{6h} Nafion, see ref 5. ^b Total quantity of fixed charge sites in the polyelectrolyte coating. ^c Quantity of counterion incorporated by the coating as measured coulometrically immediately after transfer to pure supporting electrolyte. ^d Retention ratio: fraction of the initially incorporated counterion that was retained after 45 min of exposure to pure supporting electrolyte solution. ^e Fraction of the fixed charge sites occupied by the electroactive counterions of charge *Z*. ^f Effective diffusion coefficient of the multiply charged counterions incorporated in the coating as measured chronocoulometrically in pure supporting electrolyte.^{1b} ^g Supporting electrolyte: 0.1 M $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$ (pH 4.5); this study. ^h Supporting electrolyte: 0.1 M $\text{CF}_3\text{COONa} + \text{CF}_3\text{COOH}$ (pH 1.8).¹⁷ ⁱ Supporting electrolyte: 0.2 M $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$ (pH 5.5).^{6h} ^j Supporting electrolyte: 0.5 M Na_2SO_4 .^{6c} ^k Uncertainty in coating thickness prevented evaluation of D_E .

polyelectrolyte of interest in the mixed THF-H₂O-CH₃OH solvent were carefully applied to the coated minigrids (with a 10- μL syringe) and allowed to dry for 30 min. To stain the resulting coatings 1 μL of a 10^{-7} M solution of IrCl_6^{3-} in a 0.1 M acetate buffer (pH 4.5) was syringed onto the coating and time was allowed for the coating to swell and incorporate the IrCl_6^{3-} . The coatings were then dried at room temperature for at least 2 h. Next, 1.5 μL of water was applied to the coating, allowed to stand for 5 min, and then carefully wicked away with the fine point of a triangular sliver of filter paper. The coatings were then allowed to dry again for several hours before they were used. This final step proved necessary in order to remove most of the residual supporting electrolyte which otherwise tended to form microcrystals that obscured morphological features resulting from the IrCl_6^{3-} staining.

For purposes of comparison, micrographs were also taken of unstained coatings treated with a solution of pure supporting electrolyte and with coatings in which ferrocene was used in place of IrCl_6^{3-} to provide a stain. The procedure was identical with that used to obtain the IrCl_6^{3-} stained coatings in both cases.

Results

The structure of the random ternary copolymer examined in this study, I, is given in Figure 1A. Glassy carbon electrodes were coated with polyelectrolyte films by evaporation of aliquots of solutions containing (i) poly(*N*-vinyl-2-methylimidazole), PVI; (ii) I; and (iii) a mixture of I and PVI. In each case the solvent was a 1:1 mixture of aqueous tetrahydrofuran and methanol. The ion-exchange and retention capabilities of the resulting coatings were tested by measuring the quantities of $\text{Fe}(\text{CN})_6^{4-}$ they incorporated, Γ_{os} , from a 10^{-4} M solution of the multiply charged counteranion and also the quantity of the incorporated $\text{Fe}(\text{CN})_6^{4-}$ that was retained 45 min after the electrode was transferred to a pure supporting electrolyte solution, Γ_{45} .

The set of the steady-state cyclic voltammograms in Figure 2 compares the responses obtained immediately after each coating (previously equilibrated in 10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$) was transferred to the pure supporting electrolyte solution with those that resulted 45 min later. The coatings prepared from pure PVI (Figure 2A) or I (Figure 2C) incorporate relatively little $\text{Fe}(\text{CN})_6^{4-}$ and much of what is incorporated is lost within 45 min (Figure 2, B and D; Table I). The results obtained with the composite coating are dramatically different (Figure 2, E and F). Much more $\text{Fe}(\text{CN})_6^{4-}$ is incorporated by the composite coating, and it is lost much more slowly when the coating is transferred to a pure supporting electrolyte solution (Table II). The composite coating exhibits properties that would not be expected on the basis of the behavior of its two components alone, clearly displaying synergistic enhancements of both ion-exchange capacity and retention ratio. Indeed, the retention ratio of 0.93 for the composite coating prepared from PVI and I (Table II) is the largest we have measured for any cationic polyelectrolyte and is all the more remarkable in view of the unusually high diffusion coefficients

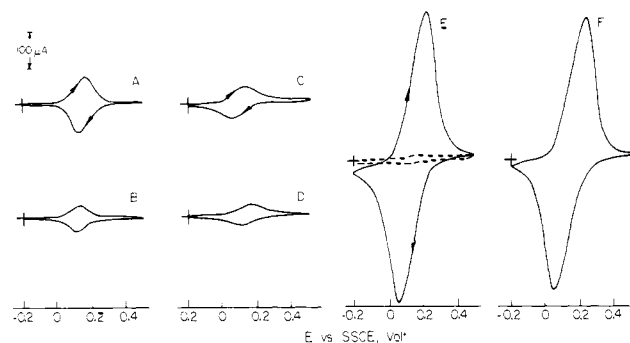


Figure 2. Steady-state cyclic voltammograms for $\text{Fe}(\text{CN})_6^{4-}$ incorporated in pure and composite polyelectrolyte coatings on a glassy carbon electrode (0.34 cm²). Coating compositions: A, B., pure PVI; C, D., pure copolymer I; E, F. PVI + copolymer I. All curves were recorded in pure supporting electrolyte (0.1 M $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH}$; pH 4.5) where the electrode was transferred after it was equilibrated with 10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ in the same electrolyte for the 5–10 min required for a stable response to be obtained. Curves A, C, and E were recorded immediately after the transfer. Curves B, D, and F were recorded 45 min after the transfer. The dashed curve in E is the voltammogram for 10^{-4} M $\text{Fe}(\text{CN})_6^{4-}$ at the uncoated electrode. Scan rate 100 mV s⁻¹.

Table II. Retention Ratios and Diffusion Coefficients for $\text{Fe}(\text{CN})_6^{4-}$ Incorporated in Electrode Coatings Prepared from Composite Polyelectrolyte Systems

coating material ^a	$10^7 \Gamma_p^b$ mol cm ⁻²	$10^8 \Gamma_{os}^c$ mol cm ⁻²	$\Gamma_{45}/\Gamma_{os}^d$	$4\Gamma_o/\Gamma_p^e$	$10^4 \phi_p^f$ cm	$10^6 D_E^g$ cm ² s ⁻¹
PVI + I ^h	1.99	2.40	0.93	0.48	1.0	1.6
PVP + I ⁱ	1.85	2.27	0.84	0.49	1.0	1.4
PVP + I ^j	1.85	2.32	0.82	0.50	0.9	1.1
PVP + I ^k	1.85	2.12	0.85	0.46	1.1	1.5
ND1 + I	1.39	2.18	0.88	0.63	0.8	1.5
ND2 + I	0.99	1.90	0.92	0.77	0.9	1.9
ND3 + I	0.83	1.12	0.84	0.54	1.2	4.9
PEI + I ^l	3.87	3.96	0.82	0.41	1.1	3.6
1-PEI + I	3.87	4.64	0.87	0.48	1.1	2.9
PLL + I ^m	1.16	2.15	0.83	0.74	1.1	2.1
PVI + I ⁿ	7.22	8.30	0.91	0.46	0.3	1.4

^a Abbreviations: I, see Figure 1A; PVI = poly(*N*-vinyl-2-methylimidazole); PVP = poly(4-vinylpyridine); ND1, first nylon derivative = $-(\text{N}(\text{H})(\text{CH}_2)_4-\text{CH}(\text{N}(\text{CH}_2)_2)-\text{C}(=\text{O})-)_n$; ND2, second nylon derivative (Figure 1B); ND3, third nylon derivative (Figure 1C); PEI = branched poly(ethyleneimine); 1-PEI = linear poly(ethyleneimine); PLL = poly(*l*-lysine). ^b Total quantity of fixed charged sites in the polyelectrolyte coating. I contributed 0.45×10^7 mol cm⁻² to the value of Γ_p in each case. ^c Quantity of $\text{Fe}(\text{CN})_6^{4-}$ incorporated by the coating upon equilibration with a 10^{-4} M solution as measured coulometrically immediately after transfer to pure supporting electrolyte solution. ^d As in Table I. ^e As in Table I. ^f Coating thickness. ^g Calculated from eq 1. ^h $\overline{\text{MW}}$ of PVI = 7×10^4 daltons. ⁱ $\overline{\text{MW}}$ of PVP = 7.5×10^5 daltons. ^j $\overline{\text{MW}}$ of PVP = 7×10^4 daltons. ^k $\overline{\text{MW}}$ of PVP = 1×10^4 daltons. ^l $\overline{\text{MW}}$ of PEI = 1.8×10^3 daltons. ^m $\overline{\text{MW}}$ of PLL = 1.8×10^5 daltons. ⁿ Experiment performed with a hanging mercury drop electrode: surface area 2.22×10^{-2} cm²; total amount of 0.5 wt % coating solution was 0.25 μL .

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of the incorporated $\text{Fe}(\text{CN})_6^{4-}$ anions in the composite coating (Table II).

Charge Propagation Rates. The larger peak current obtained in Figure 2F reflects not only greater incorporation of $\text{Fe}(\text{CN})_6^{4-}$ but also a larger effective diffusion coefficient for the anion. The significance of diffusion coefficients for reactants confined within electrode coatings has been extensively discussed,^{6b,e,15,16} and several methods for their evaluation are available.^{1b,15,17} We employed potential-step chronocoulometry and measured the slopes, S , of the linear charge-(time)^{1/2} plots recorded after the loaded coating was transferred to a pure supporting electrolyte solution and allowed to stabilize for 45 min. The total quantity of $\text{Fe}(\text{CN})_6^{4-}$ present in the coating at this point, Γ_{45} , was also measured just prior to the chronocoulometric measurements. The diffusion coefficient, D_E , is given by eq 1:¹⁷

$$D_E = \pi S^2 \phi^2 / 4F^2 \Gamma^2 \quad (1)$$

where ϕ is the coating thickness and F is Faraday's constant. To evaluate ϕ , coatings ten to twenty times thicker than those employed experimentally were prepared and their thicknesses estimated with the aid of a micrometer. This procedure is most satisfactory with composite coatings such as PVI and I which swell by factors of at least 100-fold. The values of ϕ measured in this way for the composite coatings employed in this work are given in Table II. Values of D_E obtained with a series of composite coatings are listed in the final column of Table II. These may be compared with the values given in Table I for coatings prepared from single polyelectrolytes. The D_E values for $\text{Fe}(\text{CN})_6^{4-}$ in the composite polyelectrolytes are the largest yet reported for multiply charged counterions in any polyelectrolyte. The largest value of D_E , obtained with the composite coating containing the third nylon derivative (ND3 + I in Table II), is within a factor of 1.5 of the diffusion coefficient of $\text{Fe}(\text{CN})_6^{4-}$ in solution ($D = 6.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$).¹⁸ Thus, these composite coatings offer remarkably low barriers for the diffusion of the counterions that they incorporate despite their abilities to retain the counterions for long periods. These two properties might have reasonably been regarded as mutually incompatible, but they are both exhibited by all of the composite coatings listed in Table II. The fact that the same combination of properties is highly desirable for catalytic applications of electrodes modified with polyelectrolyte coatings adds to the significance of the data summarized in Table II.

The Roles of the Components of the Composite Coatings. Although the quantities of $\text{Fe}(\text{CN})_6^{4-}$ incorporated by the various coatings in Table II vary over a considerable range, the retention ratios, Γ_{45}/Γ_0 , and the D_E values are all surprisingly insensitive to changes in the identity and molecular weight of the auxiliary polyelectrolyte that is combined with copolymer I (Table II). It seems evident that the properties of copolymer I are primarily responsible for the behavior of the composite coatings.

Of all the auxiliary polyelectrolytes employed in the experiments that are summarized in Table II, only PVI yielded sufficiently stable coatings when used alone under our experimental conditions to permit reliable evaluation of its behavior (Table I). Thus, copolymer I is responsible for the stability of the composite coatings as well as the other desirable properties that they exhibit.

The stabilizing effect of copolymer I allows long-lived coatings to be applied to a wide variety of electrode materials. Thus, in addition to glassy carbon and pyrolytic graphite, satisfactorily stable coatings have also been produced on gold, tin oxide, platinum, and even a hanging mercury drop electrode (Table II). In the latter case the coated mercury drop was readily transferred between solutions without dislodging the drop from the capillary tube from which it was suspended, a much more difficult challenge with uncoated hanging mercury drops.

The values of Γ_0 in Table II are all well below the limit calculated from the number of cationic sites, Γ_p , provided by the composite coatings. It was of interest to determine the relative importance of the two components in the composite coatings in the electrostatic binding of the $\text{Fe}(\text{CN})_6^{4-}$ anions to the coating. This was possible in cases where the cationic sites in the auxiliary polyelectrolytes were provided by protonation of basic sites because

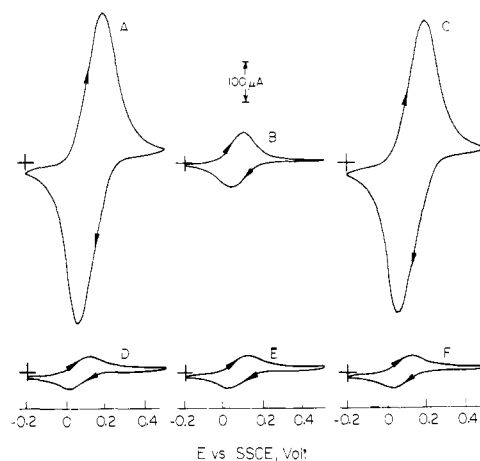


Figure 3. pH dependence of steady-state cyclic voltammograms for $\text{Fe}(\text{CN})_6^{4-}$ incorporated in a composite coating of copolymer I + PVI (A, B, C) and in copolymer I alone (D, E, F). Curves A, C, D, and F were recorded in a 10^{-4} M solution of $\text{Fe}(\text{CN})_6^{4-}$ at pH 4.5. For curves B and E the pH was 10.0. Other conditions as in Figure 2.

the positive charges could be removed at sufficiently high pH values. Of course, the quaternary ammonium groups responsible for the cationic sites in I retain their charge at all pH values. An example of the use of pH to alter the number of fixed charge sites within a coating consisting of a mixture of I and PVI is shown in Figure 3. At pH 4.5 the imidazole groups in PVI ($pK_a = 8.5$) are protonated, both components of the coating are polycationic, and the coating readily incorporates $\text{Fe}(\text{CN})_6^{4-}$ (Figure 3A). If the experiment is repeated at pH 10 the coating shows a greatly attenuated response (Figure 3B) despite the fact that the cationic sites carried by polyelectrolyte I are still present. Transfer of the electrode back to the pH 4.5 solution of $\text{Fe}(\text{CN})_6^{4-}$ restores most of the original response (Figure 3C), showing that the coating remains on the electrode surface and regains its high ion-exchange capacity upon reprotonation. These results indicate that the auxiliary polyelectrolyte in the mixed coatings is primarily responsible for the incorporation of $\text{Fe}(\text{CN})_6^{4-}$. This conclusion is also consistent with the results summarized in Table I which show that I alone has a rather low capacity for incorporating $\text{Fe}(\text{CN})_6^{4-}$ anions.

Electron Microscopy of Mixed Polyelectrolyte Coatings. The behavior of composite coatings prepared from the mixture of copolymer I with various auxiliary polyelectrolytes suggested that morphology might be at least as important as chemical identity in determining the important properties of the coatings, i.e., ion-exchange capacity, retention ratios, D_E values, and stability. To examine this proposition more directly, transmission electron microscopy was employed to examine coatings cast on carbon layers that were deposited on copper minigrad supports. The resulting coatings were swollen and stained with IrCl_6^{3-} which was incorporated and retained by the hydrophilic portions of the polycationic coatings when they were washed with distilled water (see the Experimental Section).

Micrographs obtained for three types of coatings are shown in Figure 4. The coating in Figure 4A was prepared from pure PVP. It exhibits an almost homogeneous appearance with little evidence of segregated domains. Similar structures resulted with all coatings prepared from the pure auxiliary polyelectrolytes examined. Figure 4B is a micrograph of a coating prepared from the ternary copolymer, I. The film appears much less homogeneous with segregation into what appears to be two types of domains. Coatings prepared from mixtures of PVP and I (Figure 4C) resemble those containing only I, indicating that, in mixtures, I acts as a template to induce the added polyelectrolyte to adopt a similar structure. The two types of structure evident in the micrographs of parts B and C in Figure 4 seem likely to arise from spontaneous segregation of the coatings into hydrophilic and hydrophobic domains. The ternary copolymer, I, was synthesized to contain both hydrophobic and hydrophilic groups, and there is precedent for such materials' separating into different domains

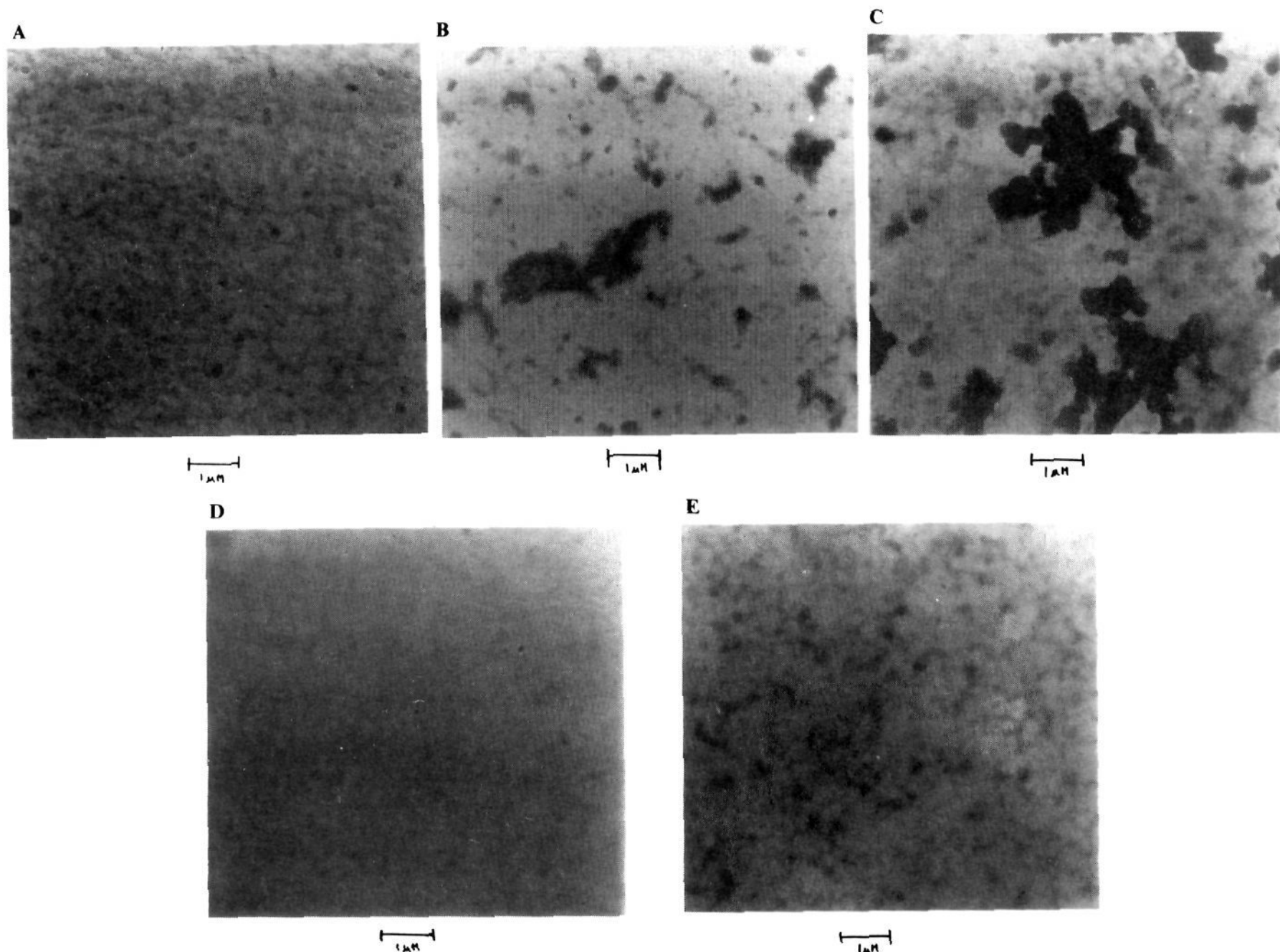


Figure 4. Transmission electron micrographs of polyelectrolyte coatings on carbon-coated copper grids. Preparations of the samples is given in the Experimental Section: A, pure PVP ($MW = 7.5 \times 10^5$ daltons), B, pure copolymer I, C, composite coating prepared from PVP + I, D, repeat of C with the use of only pure supporting electrolyte during the sample preparation, E, repeat of C substituting ferrocene for $IrCl_6^{3-}$ as the staining agent.

when cast as films or membranes.¹⁹ The more or less spherical domains which aggregate together in the micrographs are believed to be stained by $IrCl_6^{3-}$ and represent the hydrophilic portions which are dispersed in the hydrophobic matrix that constitutes the remainder of the coatings. In isolation, the hydrophilic domains appear to have average diameters of ca. 1000 Å in coatings prepared from I alone (Figure 4B), but this dimension increases to ca. 3000 Å when I is mixed with PVP or similar polyelectrolytes (Figure 4C). We suggest that this increase results from the ability of the added polyelectrolyte to induce an expansion of the hydrophilic domains generated by the structure of I. The expansion may well result from the preferential association of the added polyelectrolyte with the hydrophilic portions of I.

A pair of coatings was prepared by using supporting electrolyte alone (Figure 4D) and a 1×10^{-7} M solution of ferrocene in supporting electrolyte (Figure 4E) to assure that the structural features seen in Figure 4, A–C, were a result of the incorporation of $IrCl_6^{3-}$ ions into charged hydrophilic domains and were not an artifact of the staining procedure. The featureless micrograph exhibited in Figure 4D indicates that the supporting electrolyte is completely removed during the staining procedure and that without a staining agent there are no observable features in the film. Figure 4E indicates that a neutral molecule with considerable hydrophobic character, ferrocene, is unable to stain the coating effectively. Thus, it appears that the features which result when the coatings are stained with $IrCl_6^{3-}$ represent hydrophilic domains containing a large number of charged sites.

Discussion

One of the most intriguing and appealing properties of the composite coatings is the high values of D_E they provide for the

incorporated counterions (Table II). Similarly large values were also observed previously for the diffusion of $[Fe(edta)]^-$ within a poly(*l*-lysine) copolymer⁶⁸ that may well have adopted the type of domain structure revealed in Figure 4C. The very large values of D_E make it highly unlikely that electron exchange between pairs of the oxidized and reduced reactants could contribute significantly to the measured diffusional rates in the way proposed by Dahms and Ruff^{20,21} and observed for $Co(bpy)_3^{2+}$ (*bpy* = 2,2'-pyridine) incorporated in Nafion.^{6c} Thus, the rate constant for self-exchange between $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ would have to be ca. $10^9 M^{-1} s^{-1}$ in the composite coatings where the concentration of incorporated $Fe(CN)_6^{4-}$ was ca 0.1 M in order for self-exchange to contribute even 10% to a D_E value as large as $2 \times 10^{-6} cm^2 s^{-1}$. The value of $10^9 M^{-1} s^{-1}$, calculated from the equation of Dahms and Ruff,^{6c,10,21} is an unreasonably large rate constant for self-exchange between these two highly charged anions²² and is the basis for our doubting that self-exchange makes a substantial contribution to the diffusional process measured by D_E . One is therefore led to the conclusion that the $Fe(CN)_6^{4-}$ anions confined electrostatically to the "Donnan domains" within the composite polyelectrolyte coating⁶⁸ are able to move surprisingly rapidly across the coating. A kind of hopping of the bound, and possibly less than fully hydrated, counterions from charged site to charged site within the Donnan domains has been previously suggested as a possible origin of large values of D_E .⁶⁸ The present results are consistent with such an interpretation.

The electron micrographs in Figure 4 illustrate clearly the morphological differences between coatings cast from homopolyelectrolytes on the one hand and polyelectrolyte I, containing both charged, hydrophilic groups and hydrophobic groups, on the other: Coatings of the homopolyelectrolytes appear largely fea-

tureless and homogeneous while polyelectrolyte I yields coatings that appear segregated into two types of domains. Of even greater importance to the present study was the observation that polyelectrolyte I appears to retain its domain-forming tendency when mixed with auxiliary polyelectrolytes. The resulting coatings assume structures in which polyelectrolyte I apparently serves as a template that controls the morphology adopted by the composite coating. Coatings with structures similar to that in Figure 4C developed when polyelectrolyte I was mixed with several other auxiliary polyelectrolytes, indicating that the spontaneous tendency of I to form segregated domains dictates the morphologies adopted by the mixtures. However, the second polyelectrolyte in the mixtures is not an inert component. Its presence is essential to produce highly swollen coatings that exhibit hydrophilic domains with ion-exchange capacities much greater than those of polyelectrolyte I alone. The sizes of the hydrophilic domains obtained with the composite coatings are approximately two orders of magnitude larger than those that have been reported for the rather dissimilar and relatively permselective polyelectrolyte Nafion.¹⁹ The much more highly swollen nature of the composite coatings we have prepared and their larger hydrophilic domains may result in rather low permselectivity.

Mixing polyelectrolyte I with the auxiliary polyelectrolytes also yields coatings that are much longer lived than those obtained from the auxiliary polyelectrolytes alone. The greater coating stability probably results from some form of association of the polymeric chains of the two components in the mixtures coupled with a strong hydrophobic interaction between the electrode surface and the styrene groups of polyelectrolyte I. Whatever the molecular basis of the greater stability of the composite coatings, the data collected in Tables I and II show clearly that a property other than chemical composition must be important in determining the ion-exchange capacities and diffusional rates of counterions incorporated by the composite coatings. However, a two-domain structure alone is not adequate to ensure these attractive properties: Coatings prepared from polyelectrolyte I alone exhibit a two-domain structure (Figure 4B) but have much lower ion-exchange

capacities and retain incorporated reactants rather poorly when transferred to pure supporting electrolyte solutions (Table I). Thus, the presence of segregated domains within polyelectrolyte coatings appears to be a necessary but not sufficient condition for obtaining the desirable properties we have described.

The idea that certain types of polyelectrolyte coatings on electrodes are made up of two (or more) domains has been suggested in previous studies,^{6e,8} and considerable evidence supporting a segregated domain structure for Nafion membranes is available.¹⁹ However, the notion that useful domain structures can be induced in polyelectrolyte coatings by using a strong domain-forming polymer as a template that controls the structure of coatings obtained from mixtures containing other components that have desirable properties is new. The examples offered in this study demonstrate the concept, but the full range of its applicability remains to be explored. The potential of composite coatings in which templating polymers define the overall morphology and auxiliary polyelectrolytes establish the electrostatic and chemical environment experienced by incorporated reactants seems broad and appealing. The flexibility such a strategy introduces for tailoring the properties of coatings to meet specific requirements should prove valuable both in practical applications and in fundamental investigations of the behavior of polyelectrolyte-coated electrodes.

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Registry No. PVI, 26983-77-7; ND1, 96164-78-2; PEI, 26336-38-9; PLL, 25104-18-1; PVP, 25232-41-1; Fe(CN)₆⁴⁻, 13408-63-4; IrCl₆³⁻, 14648-50-1; Hg, 7439-97-6; C, 7440-44-0; ferrocene, 102-54-5.

Quenching and Possible Coulombic Complexation of the Pyrene-*N,N*-Dimethylaniline Exciplex by Tetraalkylammonium Salts

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Abstract: Tetraalkylammonium salts are shown to quench the fluorescence of the pyrene-*N,N*-dimethylaniline exciplex in solvents of low dielectric constant. Linear Stern-Volmer plots are obtained for quenching of both lifetime and intensity in dioxane. However, mechanistic complications are implied by intercepts exceeding unity and by the unequal slopes of these plots. Qualitatively similar behavior is observed when the solvents and electrolytes are varied. Historic conductivity data indicate that the quenching species Q in dioxane are aggregates of electrolyte ions, probably ion pairs or quadrupoles. A proposed kinetic model is both qualitatively consistent with the experimental observations and quantitatively self-consistent. An emitting complex formed at a diffusion-controlled rate by an encounter between Q and an exciplex is postulated. The emitting complex is apparently quenched by subsequent encounters with additional Q at rates considerably below the encounter-limited value.

Since the discovery of polar exciplexes by Leonhardt and Weller,¹ there has been particular interest in these aggregates of unlike molecules that exhibit stable binding in excited electronic states but repulsive interactions in the ground state.²⁻⁷ Many

feature strong charge-transfer character and are bound essentially by Coulombic forces between the positive and negative moieties. Ample evidence has accumulated to indicate their general im-

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