Electrochemical Studies on Ion Transport in Gels with Scanning Electrochemical Microscopy

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Ion transport properties of two gels made from polyacrylate and polyacrylamide (PAAM) were studied with scanning electrochemical microscopy (SECM) by using three ferrocene derivatives, which carry different charges, as the probe molecules. Ion diffusion in these gels could be nearly as fast as in aqueous electrolytes and did not adhere to the Stokes–Einstein equation. Passivation of the electrode surface in polyacrylate gels reported previously was mainly caused by the electrophoretic deposition of gel particles on the surface of the electrode. The deposited gel film can act as a cation-exchange membrane and shows permselectivity, which affects both the electrochemical and SECM behavior. No detectable film formation was found in the PAAM gel perhaps because of its neutral charge and rigid three-dimensional network structure. The small change in diffusion coefficients as a function of PAAM gel concentration and charges of the probe molecules suggest much of the transport in the gel occurs via a water-filled domain. The transient (chronoamperometric) SECM response could be used to determine diffusion coefficients from the critical transient time as a function of tip displacement without knowing the concentration of the redox mediator, the tip radius, and the number of electrons transferred in the electrode reaction.

Introduction

Electrochemical (EC) techniques that can be utilized to characterize microscale systems have been the subject of recent interest. For example, SECM can be used for EC studies with high spatial resolution.[1] Among microsystems of interest, polymer films (electronically and ionically conductive) and gels have been the subject of considerable activity. Gels have been applied as thickening agents for cosmetics and pharmaceuticals and as media for drug delivery systems.[2] Gels serve as convenient immobilizing media for the analyses of biological molecules. For example, the detection of individual DNA strands during capillary electrophoresis[3] and the detection of individual single-fluorophore-labeled protein molecules in a PAAM gel matrix[4] were achieved by observing the fluorophores diffuse through the local volume with spectroscopic techniques. Gel electrolytes have also been used as media for certain EC devices, such as electrochromic displays,[5] EC diodes or transistors,[6] and sensors,[7] because they are more easily contained than conventional liquids. These applications require gel systems that are able to support rapid movement of active species or counterions necessary for rapid electron-transfer reactions. Although numerous EC investigations have dealt with electrodes modified by layers of polymers,[8] EC studies in gels are still relatively scarce. Among them, steady-state voltammetry, impedance measurements, and transient generation–collection methods are the most commonly used EC techniques for the investigation of the transport properties.[9] In a previous report, SECM was employed to probe inside a PAAM film by measuring the transient current[10] to gain information about the diffusion coefficient and the concentration of a redox species in the film without knowing film thickness or density. This approach is based on the difference in the dependence of the transient and steady-state currents on the diffusion current.[11]

In this report, the EC and SECM behavior of two gels made from polyacrylate and PAAM is compared by using three ferrocene derivatives, which carry different charges, as probe molecules. Diffusion measurements were made at microelectrodes using transient or steady-state techniques with an SECM. Passivation of the electrode surface in the polyacrylate gels reported previously[9c] was associated with the electrophoretic deposition of gel particles on the electrode surface. The deposited film can act as a cation-exchange membrane and show permselectivity, which is reflected in both EC and SECM behavior. Different from polyacrylate gels, no appreciable permselectivity and passivation were found for PAAM gels, suggesting that no deposition of a gel film occurred on the electrode surface. Consistent with previous studies, the diffusion coefficients measured in both gel systems at a gel concentration as high as 20 wt % were only slightly smaller than those measured in fluid solution.

Experimental Section

Chemicals. Poly(acrylic acid)s were obtained as Carbopol 940 (B. F. Goodrich Co.). Acrylamide (AAM), *N,N′*-methylenebis(acrylamide) (X-AAM) (Aldrich), and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (Sigma) were electrophoresis grade and were used as received. All other chemicals were reagent grade and were used as received. All aqueous solutions were prepared with deionized water (Milli-Q, Millipore Corp.).

Gel Preparation. *Polyacrylate Gel.* Polyacrylate gels were prepared based on the procedures reported previously.[9c] Upon neutralization, the cloudy, colorless, somewhat viscous poly-(acrylic acid) solution became a highly viscous, clear gel. For preparation of gels for EC and SECM measurements, the redox species was added prior to neutralization.

PAAM Gel. PAAM gels (19.48% AAM, 0.52% X-AAM, ca. 20 wt % polymer or 2.38% AAM, 0.12% X-AAM, ca. 2.5 wt % polymer) were prepared[12] by room-temperature radical polymerization of ca. 10 mL of a deaerated aqueous 0.1 M $NaClO_4$ solution of AAM and X-AAM with TMEDA (0.005
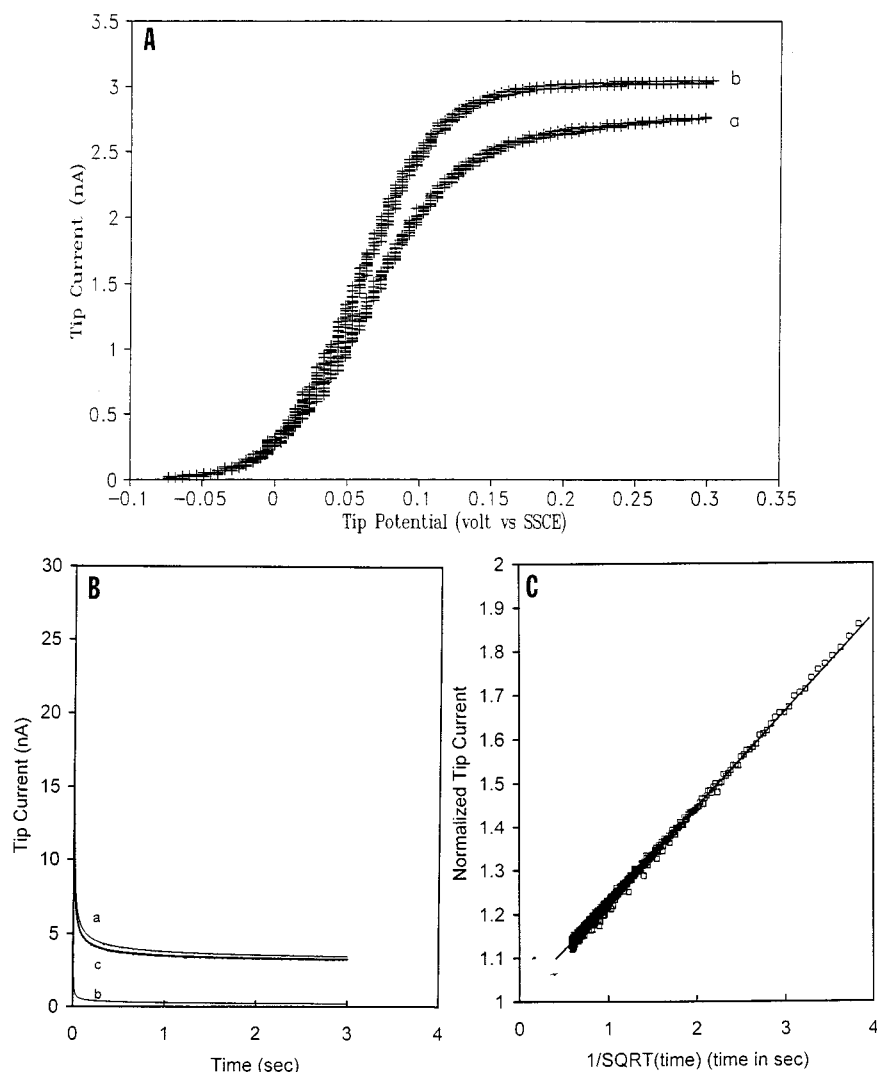
Figure 1. (A) Cyclic voltammograms at a scan rate of 2 mV/s on a Pt MD having a nominal radius of 12.5 μm in (a) 0.5% C940 gel containing 0.89 mM Fc(CH$_2$OH)$_2$ and (b) 0.1 M NaClO$_4$ containing 0.89 mM Fc(CH$_2$OH)$_2$. (B) Chronoamperometric curves on the same Pt tip in (a) 0.5% C940 gel containing 0.89 mM Fc(CH$_2$OH)$_2$, (b) 0.5% C940 gel only, and (c) the difference between (a) and (b). (C) A plot of the tip current shown in curve c of Figure 1B, normalized with respect to $i_{d,ss}$ vs $t^{-1/2}$. A linear regression straight line is also shown.

mL) and ammonium persulfate (0.15 wt %). The gels were then soaked and washed thoroughly with 0.1 M NaClO$_4$ to remove residual electroactive ammonium persulfate.

Electrodes and Apparatus. The SECM tip was a Pt microdisk (MD), with a nominal diameter of 25 μm, encased in glass; its construction followed the procedures reported previously.[1a,b] Before each experiment, the tip was polished with 0.05 μm alumina. A Pt wire was used as a quasi-reference electrode (PtQRE), or a sodium-saturated calomel electrode (SSCE) was used as the reference electrode. A Pt foil served as the counter electrode. Polyacrylate gel was placed in a glass cell for EC and SECM measurements. PAAM gels were cut into 5 × 5 × 1 mm^3 flat slabs, which could then be pressed and immobilized in an opening of similar size in a Macor plate. The Macor support and gel slab were then immersed in a solution containing a suitable redox couple for EC and SECM measurements. Details of the construction[13] and operation of the SECM[1a,b] have been described elsewhere.

Data Treatment. Chronoamperometric data are the average of 10 trials after background subtraction from the average of five trials in the blank solution (i.e., a solution containing no redox couple). To analyze the MD chronoamperometric response, the equation for the normalized diffusion-controlled current to a MD of radius a was used:[11b]

$$i_d(t)/i_{d,ss} = (\pi^{1/2}/4)a(Dt)^{-1/2} + 1 \tag{1}$$

where $i_{d,ss}$ is the steady-state current which is given by

$$i_{d,ss} = 4nFDCa \tag{2}$$

where D is the diffusion coefficient of a redox species, C is its concentration, n is the number of electrons transferred in the electrode reaction, and F is the Faraday constant.

From eqs 1 and 2, the following relation is obtained

$$D = (\pi^{1/2}i_{d,ss}/(16nFCS))^{2/3} \tag{3}$$

where S is the slope of the $i_d(t)/i_{d,ss}$ vs $t^{-1/2}$ plot. Thus, D can be determined from S and $i_{d,ss}$ without knowing the effective tip radius a if C is known (method 1).

Alternatively, D can be determined from the chronoamperometric SECM responses for different values of tip displacement, Δd, based on the following approximate analytical relation for a conducting substrate:[14]

Ion Transport in Gels

J. Phys. Chem. B, Vol. 102, No. 49, 1998 **9779**

$$(Dt_c)^{1/2} = 0.66 \, \Delta d + \text{a term independent of } \Delta d \quad (4)$$

where t_c is the critical time that defines when the SECM undergoes a transition from the MD regime to the thin layer cell (TLC) regime. Equation 4 can be used to determine D and can be evaluated from a series of plots of the normalized tip current against $t^{-1/2}$ at various Δd, without knowing C and a (method 2).

Results and Discussion

Comparison of Diffusion Coefficients of Electroactive Species in Aqueous Electrolytes and Gels. *Polyacrylate Gels.* Cyclic voltammograms obtained with a Pt tip having a nominal radius of 12.5 μm in a 0.5% C940 gel containing 0.89 mM Fc(CH$_2$OH)$_2$ and in a 0.1 M NaClO$_4$ solution containing the same concentration of Fc(CH$_2$OH)$_2$ are shown in Figure 1A. The $i_{d,ss}$ in the gel is only ca. 10% smaller than that in aqueous NaClO$_4$. If the Fc(CH$_2$OH)$_2$ molecules in the gel are assumed to stay in the less viscous continuous H$_2$O phase,[15] the concentration of Fc(CH$_2$OH)$_2$ in the H$_2$O phase is very close to that in the aqueous solution used for the preparation of gel, although the total volume (gel particles plus H$_2$O phase) might change during gel preparation. This is a reasonable assumption for small neutral electroactive species such as Fc(CH$_2$OH)$_2$, since the permselectivity of the charged gel particles only plays a minor role in the determination of the local concentration of Fc(CH$_2$OH)$_2$ (see discussion below). The continuous water-filled domains in the gel are expected to be much larger than the size of the individual Fc(CH$_2$OH)$_2$ molecule when the concentration of polyacrylate is low. In Figure 1B, three chronoamperometric curves are shown for 0.5% C940 gel containing 0.89 mM Fc(CH$_2$OH)$_2$ (curve a), 0.5% C940 gel alone (curve b), and their difference (curve c). The tip current shown in curve c after normalization with respect to $i_{d,ss}$ plotted against $t^{-1/2}$ is shown in Figure 1C. A linear regression of the data points was used to compute the slope with an intercept very close to unity (within ± 0.5%) as suggested by eq 1. Assuming that the concentrations of Fc(CH$_2$OH)$_2$ in gel and in aqueous solution are both 0.89 mM, the gel $D = 6.3 \times 10^{-6}$ cm^2/s based on eq 3. Similar experiments carried out for 0.89 mM Fc(CH$_2$OH)$_2$ in aqueous NaClO$_4$ solution give $D = 6.4 \times 10^{-6}$ cm^2/s. This D value is very close to that $(6.5 \times 10^{-6}$ cm^2/s) calculated from $i_{d,ss}$ based on eq 2 by taking $C = 0.89$ mM and $a = 12.5$ μm.

Consistent with previous observations,[9c] the diffusion coefficient of Fc(CH$_2$OH)$_2$ in 0.5% polyacrylate is much larger than the D predicted by the Stokes−Einstein equation for an ideal solution of comparable viscosity. The small decrease in D for the gel vs fluid with such a large increase in viscosity has been attributed to the two-phase structure of the gel (a highly viscous discontinuous phase, the gel particles, and a continuous aqueous phase).[15] The continuous aqueous phase allows for high diffusivity. The diffusion coefficient in gels, as expected, becomes smaller with an increased concentration of polyacrylate; e.g., the D of Fc(CH$_2$OH)$_2$ decreases from 6.3×10^{-6} cm^2/s in 0.5% C940 gel to 5.2×10^{-6} cm^2/s in 2.5% C940 gel.

An independent measurement of the D of Fc(CH$_2$OH)$_2$ in 2.5% C940 gel was also carried out based on eq 4 (method 2). Figure 2A shows a series of chronoamperometric curves at different tip−substrate distances above a conducting substrate (e.g., indium tin oxide, ITO). Figure 2B shows the corresponding normalized tip currents as a function of the inverse square root of time. Since it is difficult to observe true MD behavior at very short times, the short time line used to determine t_c was
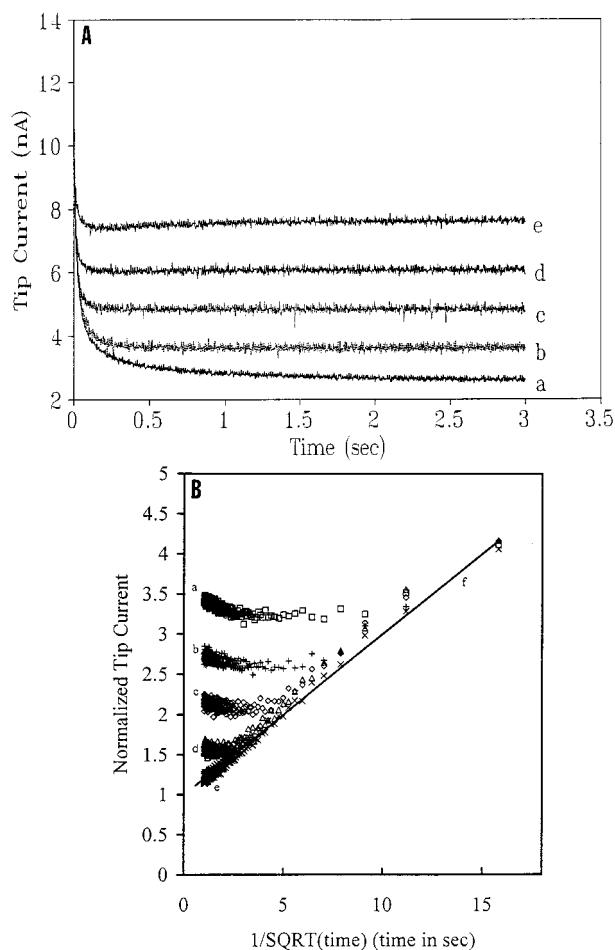

Figure 2. (A) A series of chronoamperometric curves on a Pt MD having a nominal radius of 12.5 μm in a 2.5% C940 gel containing 0.89 mM Fc(CH$_2$OH)$_2$ and 10 mM NaClO$_4$ at different tip−substrate distances above an ITO substrate. With (a) the tip far away from substrate and with a steady-state tip current of (b) 3.5, (c) 5.0, (d) 6.0, and (e) 7.3 nA. (B) The corresponding normalized tip currents as functions of the inverse square root of time. Straight line f is constructed from the linear regression of the data points shown in curve e.

obtained from the current transient recorded when the tip was far away from the substrate (curve e). A linear regression of the data points in curve e was used to construct the MD transient as shown in the straight line f that can be used for the determination of the experimental critical time. By applying eq 4, $D = 5.3 \times 10^{-6}$ cm^2/s for Fc(CH$_2$OH)$_2$ in a 2.5% C940 gel. This value is in very good agreement with that determined from method 1.

PAAM Gels. The diffusion coefficients of three ferrocene derivatives in PAAM gel films were determined by method 1. PAAM films containing redox species were produced by immersing the blank PAAM films, prepared and cleaned as described in the Experimental Section, in 0.1 M NaClO$_4$ solution containing the desired redox species. Figure 3A shows the cyclic voltammograms on a Pt tip of nominal radius of 12.5 μm taken at a scan rate of 2 mV/s in 2.5% PAAM (AAM: X-AAM = 20:1) gel containing 0.9 mM [(trimethylammonio)-methyl]ferrocene (FcTMA$^+$) and 0.1 M NaClO$_4$. The $i_{d,ss}$ in the gel (curve b) is ca. 12% smaller than that in aqueous NaClO$_4$ (curve a). In Figure 3B, the tip current normalized with respect to $i_{d,ss}$ is plotted against $t^{-1/2}$. A linear regression of the data points gives a straight line with a slope of 0.276 and an intercept of 0.998. Based on eq 3, $D = 5.4 \times 10^{-6}$ cm^2/s for FcTMA$^+$, assuming its concentration in the gel is 0.9 mM. Similar
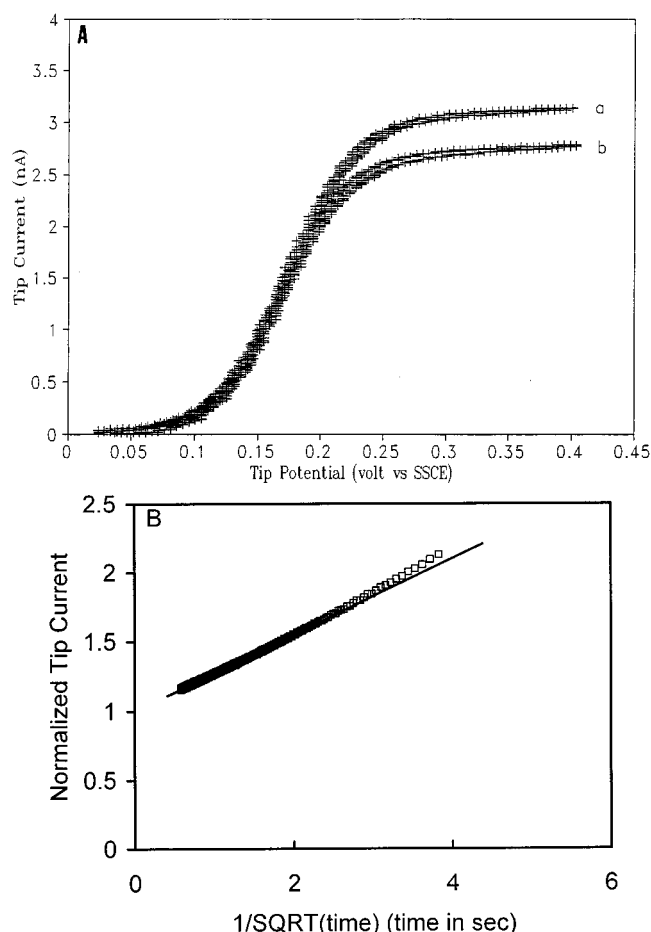
Figure 3. (A) Cyclic voltammograms at a scan rate of 2 mV/s on a Pt tip having a nominal radius of 12.5 μm in (a) 2.5% PAAM gel containing 0.9 mM FcTMA$^+$ and 0.1 M NaClO$_4$ and (b) 0.1 M NaClO$_4$ solution containing 0.9 mM FcTMA$^+$. (B) Normalized transient tip current plotted vs $t^{-1/2}$ on the same MD in 2.5% PAAM gel containing 0.9 mM FcTMA$^+$ and 0.1 M NaClO$_4$. The straight line constructed from the linear regression of the data points is also shown.

TABLE 1: Diffusion Coefficients D (10^{-6} cm^2/s) of Various Redox Species in Various Media

redox species	medium	D	eq
Fc(CH$_2$OH)$_2$	0.1 M NaClO$_4$	6.4	3
Fc(CH$_2$OH)$_2$	0.1 M NaClO$_4$	6.5	2
Fc(CH$_2$OH)$_2$	0.5% C940 gel	6.3	3
Fc(CH$_2$OH)$_2$	2.5% C940 gel	5.2	3
Fc(CH$_2$OH)$_2$	2.5% C940 gel and 10 mM NaClO$_4$	5.3	4
Fc(CH$_2$OH)$_2$	2.5% PAAM gel and 0.1 M NaClO$_4$	5.5	3
Fc(CH$_2$OH)$_2$	20% PAAM gel and 0.1 M NaClO$_4$	4.5	3
FcTMA$^+$	0.1 M NaClO$_4$	6.6	2
FcTMA$^+$	2.5% PAAM gel and 0.1 M NaClO$_4$	5.4	3
FcTMA$^+$	20% PAAM gel and 0.1 M NaClO$_4$	4.3	3
FcCOO$^-$	0.1 M NaClO$_4$	6.7	2
FcCOO$^-$	2.5% PAAM gel and 0.1 M NaClO$_4$	5.8	3
FcCOO$^-$	20% PAAM gel and 0.1 M NaClO$_4$	4.9	3

techniques carried out for 0.9 mM Fc(CH$_2$OH)$_2$ and 0.9 mM ferrocenecarboxylate (FcCOO$^-$) in 2.5% PAAM give $D = 5.5 \times 10^{-6}$ and 5.8×10^{-6} cm^2/s, respectively. These values of D are close to those observed previously for other small redox species, such as Ru(NH$_3$)$_6^{3+}$, in a PAAM film of similar composition.[10] Similar to polyacrylate gels, the diffusion coefficients in PAAM gels decreased with an increased concentration of PAAM. As summarized in Table 1, the D of FcTMA$^+$ decreased from 5.4×10^{-6} cm^2/s in 2.5% PAAM (AAM: X-AAM = 20:1) gel to 4.3×10^{-6} cm^2/s in 20% PAAM (AAM: X-AAM = 37:1) gel; likewise, D dropped somewhat from 5.5
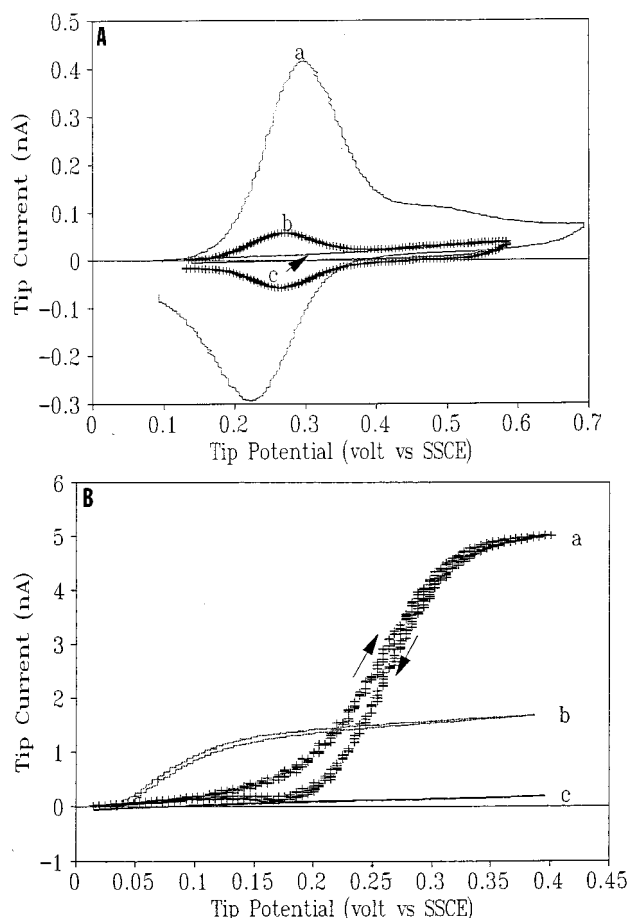

Figure 4. (A) Cyclic voltammograms in 0.1 M NaClO$_4$ solution on three polyacrylate-coated Pt microelectrodes, biased at $E_T = 0.35$ V vs PtQRE for 30 min, after incorporation with Os(bpy)$_3^{2+}$ for ca. 1 h: (a) 2.5% C940 gel containing 0.9 mM Fc(CH$_2$OH)$_2$, (b) 2.5% C940 gel containing 0.9 mM Fc(CH$_2$OH)$_2$ and 10 mM NaClO$_4$, and (c) 2.5% C940 gel only. In all three experiments, a Pt MD having a nominal radius of 12.5 μm was polished before deposition. (B) Cyclic voltammograms for three different ferrocene derivatives in 10 mM NaClO$_4$ on a gel-coated Pt MD. The deposition of polymer was carried out in 2.5% C940 gel containing 0.9 mM Fc(CH$_2$OH)$_2$ by biasing the tip at $E_T = 0.35$ V vs Pt QRE for 30 min: (a) 10 mM NaClO$_4$ solution containing 1.2 mM FcTMA$^+$, (b) 10 mM NaClO$_4$ solution containing 0.89 mM Fc(CH$_2$OH)$_2$, and (c) 10 mM NaClO$_4$ solution containing 1.0 mM FcCOO$^-$.

$\times 10^{-6}$ to 4.5×10^{-6} cm^2/s for Fc(CH$_2$OH)$_2$ and from 5.8×10^{-6} to 4.9×10^{-6} cm^2/s for FcCOO$^-$ as the PAAM concentration increased from 2.5% to 20%. These small changes in D as a function of gel concentration again suggest a continuous water-filled network structure of the gel, which is different from an ideal polymer film of comparable viscosity.

Formation of Thin Films on Electrodes and Their Permselectivity. The long-term bias of a microelectrode in C940 gel solution containing a redox species caused the tip current to decrease continuously with time. The tip current also decreased over the course of several cyclic voltammograms on a freshly polished microelectrode. These results suggest some degree of passivation of the surface of the microelectrode due to film formation. The current decrease can be attributed to a decrease in the effective electrode area and the permselectivity of the polymer film (see discussion below). Similar passivation behavior was observed for other redox species, e.g., Fc(CH$_2$-OH)$_2$, although the apparent passivation rate was different. To verify that a thin polymer film was formed on the surface of the electrode after long-term bias, electrophoretic deposition of
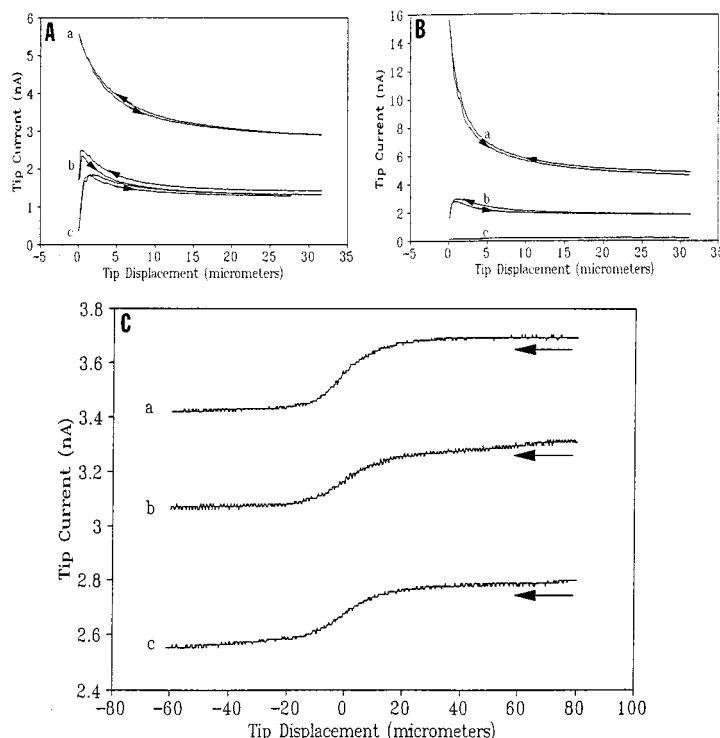
Figure 5. (A) (a) Typical SECM approach curve for a Pt microelectrode having a nominal radius of 12.5 μm over an ITO substrate in 1 M NaClO$_4$ solution containing 0.89 mM Fc(CH$_2$OH)$_2$; E_T = 0.35 V and E_S = -0.2 V vs PtQRE. (b) The first approach curve for the same microelectrode over the same ITO substrate at the same biases in a 2.5% C940 gel solution containing 0.89 mM Fc(CH$_2$OH)$_2$. (c) The second approach curve carried out in the same gel solution. (B) SECM approach curves for a polyacrylate-coated Pt MD over an ITO substrate in 10 mM NaClO$_4$ solution containing (a) 1.2 mM FcTMA$^+$, (b) 0.89 mM Fc(CH$_2$OH)$_2$, or (c) 1.0 mM FcCOONa. The polyacrylate film was deposited on the electrode surface according to the procedure described above. (C) SECM approach curves for 0.9 mM of (a) Fc(CH$_2$OH)$_2$, (b) FcTMA$^+$, or (c) FcCOO$^-$ in 0.1 M NaClO$_4$ and 2.5% PAAM gel. Curves b and c are shifted downward 0.4 and 0.8 nA, respectively, relative to curve a. The Pt tip of nominal radius of 12.5 μm was moved from aqueous solution toward the (solution/PAAM gel) interface and into the gel film.

the polymer in various C940 gel solutions was carried out. The relative amount of polymer film deposited on the electrode surface can then be determined by monitoring the incorporation of a charged redox species in the film. For example, Os(bpy)$_3^{2+}$ can be used as the probe molecule, if the polymer is negatively charged. Figure 4A shows cyclic voltammograms carried out in 0.1 M NaClO$_4$ solution on three polyacrylate-coated microelectrodes after incorporation of Os(bpy)$_3^{2+}$ (ca. 1 mM concentration) by soaking for ca. 1 h. For a microelectrode biased at E_T = 0.35 V vs PtQRE for ca. 30 min in a 2.5% C940 gel solution containing only 0.9 mM Fc(CH$_2$OH)$_2$, a significant amount of Os(bpy)$_3^{2+}$ was incorporated into the surface film formed (curve a of Figure 4A). The addition of 10 mM NaClO$_4$ into the above gel solution reduced the amount of Os(bpy)$_3^{2+}$ incorporated (curve b of Figure 4A), indicating the rate of film formation was retarded. In a gel solution containing no redox species, film formation was essentially eliminated, as manifested by negligible oxidation of Os(bpy)$_3^{2+}$ (curve c of Figure 4A). These results suggest that a large and sustained current density is required for significant electrophoretic deposition of gel particles from a gel electrolyte.

Three ferrocene derivatives with different charges, i.e., Fc-(CH$_2$OH)$_2$ (a neutral species), FcTMA$^+$ (a positively charged species), and FcCOO$^-$ (a negatively charged species), were employed as probe molecules to study the permselectivity of the polymer film deposited on the surface of a Pt microelectrode. Figure 4B shows the cyclic voltammograms for these three ferrocene derivatives in 10 mM NaClO$_4$ on a polymer-coated microelectrode. The deposition of polyacrylate was carried out in a 2.5% C940 gel solution containing 0.9 mM Fc(CH$_2$OH)$_2$ based on the procedure stated above. The steady-state tip

current on a polyacrylate-coated microelectrode for a neutral species, such as Fc(CH$_2$OH)$_2$, is ca. 50% smaller than that on a bare electrode (compare curve b of Figure 4B with curve b of Figure 1A). The decrease in $i_{d,ss}$ is mainly associated with a decrease in the effective area of the microelectrode due to polymer coating. For a positively charged redox species, such as FcTMA$^+$, $i_{d,ss}$ on the same polyacrylate-coated electrode is substantially enhanced as compared to that on a bare electrode (compare curve a of Figure 4B with curve a of Figure 3A). For a negatively charged redox species, such as FcCOO$^-$, $i_{d,ss}$ on the same polyacrylate-coated electrode drops to a very small value. These results suggest that the surface polyacrylate film not only changes the effective area of the electrode but also acts as a cation-exchange membrane and shows permselectivity. The film formation is also reflected in the SECM behavior in C940 gel solution, as described below.

SECM Approach Curves. A record of the tip current, $i_{d,ss}$, against tip–substrate separation, d, as the tip is moved toward a substrate is called an approach curve. In polyacrylate gel, the shape of an approach curve is dependent on the redox species present in the gel due to film formation. In Figure 5A, curve a shows a typical approach curve for a microelectrode over an ITO substrate in 1 M NaClO$_4$ solution containing 0.89 mM Fc(CH$_2$OH)$_2$. As expected, a monotonic increase in current is observed with a decrease in d. Curve b shows the first approach curve for the same electrode over the same ITO in a 2.5% C940 gel solution containing 0.89 mM Fc(CH$_2$OH)$_2$. Much less positive feedback is observed as compared with that observed in the absence of gel, and the current reaches a maximum before it starts to drop as d decreases. In the reverse scan, a similar shape of the current vs d curve is observed. This type of

approach curve is frequently observed for a wax or polymer insulated tip, and the drop in current is mainly attributed to the contact of the insulating film to the substrate which causes a decrease in the effective tip area as the tip is pressed against the substrate.[16] Curve c shows the second approach curve recorded in the same gel solution. A similar shape is observed, although curve c shows less positive feedback as compared to curve b. A close look at these two curves also reveals that the tip current at a given *d* decreases with time. These results suggest that slow passivation of the electrode surface takes place due to progressive growth of an insulating polymer film on the electrode surface. To verify that the characteristic approach curve shown in curve b or c of Figure 5A is associated with film formation on the electrode surface, a polymer layer was electrophoretically deposited on the tip surface from a 2.5% C940 gel solution containing only 0.9 mM $Fc(CH_2OH)_2$ based on the procedure stated above. The approach curve was then carried out on this polymer-coated electrode in 10 mM aqueous $NaClO_4$ containing 0.9 mM $Fc(CH_2OH)_2$. The result is shown in curve b of Figure 5B. The similarity between this curve and curves b and c of Figure 5A is obvious. This strongly indicates that the observed approach curves b and c shown in Figure 5A are associated with film formation on the tip surface. The permselectivity of this polymer layer (presumably negatively charged) results in different shapes of the approach curves for redox species having different types of charge. As shown in curve a of Figure 5B for a positively charged species, e.g., $FcTMA^+$, not only was an enhanced steady-state tip current observed (as compared to a bare electrode), but an approach curve showing positive feedback over a conductive substrate was also obtained due to enhanced effective concentration. For a negatively charged species, e.g., $FcCOO^-$, the steady-state tip current, as shown in curve c of Figure 5B, is dramatically reduced, and an approach curve showing slight negative feedback even over a conductive substrate is obtained. Thus, the polymer film formed on the tip surface acts as a cation-exchange membrane, which can either gather positively charged species or repel negatively charged species. Different from polyacrylate gel, PAAM gel apparently shows neither electophoretic deposition on the tip nor permselectivity, perhaps because it is a neutral gel having a rigid three-dimensional network covalently connected by a cross-linking agent.[12] As shown in Figure 5C, irrespective of the types of charges on the three ferrocene derivatives, similar SECM approach curves were obtained as the tip was moved from aqueous solution toward the solution/PAAM gel interface and into the 2.5% PAAM gel film containing 0.9 mM redox species and 0.1 M $NaClO_4$. The tip current shows a smooth decrease when the tip approaches the solution/PAAM gel interface. It then attains a steady-state value as the tip continues to penetrate the film. The $i_{d,ss}$ in the gel is steady with time and is ca. 10% smaller than that in aqueous $NaClO_4$ solution. As long as the tip penetrates deeply enough inside the film, the value of $i_{d,ss}$ is independent of the position. These results suggest that, in the dimension of the tip size, the electroactive species is uniformly distributed within the gel. The PAAM gel shows no permselectivity, and no obvious film formation on the tip is observed.

Conclusions

Electrochemical and SECM measurements of the diffusion coefficients, *D*, of three ferrocene derivatives having different types of charges in polyacrylate and polyacrylamide gels were presented. Diffusion in the gel was nearly as fast as in aqueous electrolytes, consistent with the results reported previously. In polyacrylate gels, passivation of the electrode surface occurs due to electrophoretic deposition of a thin gel film, which can act as a cation-exchange membrane and which shows permselectivity. No detectable film formation was found in a PAAM gel perhaps because of its neutral charge and rigid three-dimensional network structure. The transient (chronoamperometric) SECM response can be used to determine *D* from the critical transient time as a function of tip displacement without knowing the concentration of a redox species in the film, *C*, the number of electrons transferred in the electrode reaction, and the radius of the tip electrode, *a*. There are, however, some limitations in the accuracy of diffusion coefficients determined by eq 3 if there are uncertainties in the assumed values of *a* and *C*.

References and Notes

(1) See, e.g.: (a) Bard, A. J.; Fan, F.-R. F.; Kwak, J.; Lev, O. *Anal. Chem.* **1989**, *61*, 132. (b) Bard, A. J.; Fan, F.-R. F.; Mirkin, M. V. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 243. (c) Mirkin, M. V. *Anal. Chem.* **1996**, *68*, 177A.

(2) See, e.g.: (a) Deasy, P. B.; O'Neill, C. T. *Pharm. Acta Helv.* **1989**, *64*, 231. (b) Gourlay, S. J.; Rice, R. M.; Hegyeli, A. F.; Wade, C. W. R.; Dillon, J. G.; Jaffe, H.; Kulkarni, R. K. *J. Biomed. Mater. Res.* **1978**, *12*, 219. (c) Davis, F. F.; Abuchowski, A.; Van Es, T.; Palczuk, N. C.; Savoca, K.; Chen, R. H.-L.; Pyatak, P. In *Biomedical Polymers: Polymeric Materials and Pharmaceuticals for Biomedical Use;* Goldberg, E. P., Nakajima, A., Eds.; Academic Press: New York, 1980; p 441. (d) Hershfield, M. S.; Buckley, R. H.; Greenberg, M. L.; Melton, A. L.; Schiff, R.; Hatem, C.; Kurtzberg, J.; Markett, M. L.; Kobayashi, R. H.; Kobayashi, A. L.; Abuchowski, A. *New Engl. J. Med.* **1987**, *316*, 589.

(3) Haab, B. B.; Mathies, A. *Anal. Chem.* **1995**, *67*, 3253.

(4) Dickson, R. M.; Norris, D. J.; Tzeng, Y.-L.; Moerner, W. E. *Science* **1996**, *274*, 966.

(5) See, e.g.: Stinson, S. *Chem. Eng. News* **1992**, *70* (17), 20.

(6) See, e.g.: (a) Chao, S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1987**, *109*, 6627. (b) Talham, D. R.; Crooks, R. M.; Cammarata, V.; Leventis, N.; Schloh, M. O.; Wrighton, M. S. In *Low-Dimension Systems and Molecular Electronics*; Metzger, R. M., Day, P., Papavassiliou, G., Eds.; NATO ASI Series B 248; Plenum Press: New York, 1990.

(7) See, e.g.: (a) Geng, L.; Reed, R. A.; Longmire, M.; Murray, R. W. *J. Phys. Chem.* **1987**, *91*, 2908. (b) Schloh, M. O. Ph.D. Thesis, Massachusetts Institute of Technology, Jan 1990.

(8) See, e.g.: (a) *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Wiley: New York, 1992. (b) Inzelt, G. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, 1994; Vol. 18, p 89.

(9) (a) Van Koppenberg, J. E.; Majda, M. *J. Electroanal. Chem.* **1985**, *189*, 379. (b) Oliver, B. N.; Egekeze, J. O.; Murray, R. W. *J. Am. Chem. Soc.* **1988**, *110*, 2321. (c) Tatistcheff, H. B.; Fritsch-Faules, I.; Wrighton, M. S. *J. Phys. Chem.* **1993**, *97*, 2732. (d) Silva, F.; Sousa, M. J.; Pereira, C. M. *Electrochim. Acta* **1997**, *42*, 3095.

(10) Pyo, M.; Bard, A. J. *Electrochim. Acta* **1997**, *42*, 3077.

(11) (a) Winlove, C. P.; Parker, K. H.; Oxenham, R. K. C. *J. Electroanal. Chem.* **1984**, *170*, 293. (b) Denuault, G.; Mirkin, M. V.; Bard, A. J. *J. Electroanal. Chem.* **1991**, *308*, 27.

(12) (a) *Gel Electrophoresis of Proteins: A Practical Approach*, 2nd ed.; Hames, B. D., Rickwood, D., Eds.; Oxford University Press: New York, 1990. (b) Allen, R. C.; Budowle, B. *Gel Electrophoresis of Proteins and Nucleic Acids*; Walter de Gruyter: Berlin, 1994.

(13) Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1989**, *136*, 3216.

(14) Bard, A. J.; Denuault, G.; Friesner, R. A.; Dornblaser, B. C.; Tuckerman, L. S. *Anal. Chem.* **1991**, *63*, 1282.

(15) Taylor, N. W.; Bagley, E. B. *J. Appl. Polym. Sci.* **1974**, *18*, 2747.

(16) Fan, F.-R. F.; Kwak, J.; Bard, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 9669.