POLYMER FILMS ON ELECTRODES

PART XVIII. DETERMINATION OF HETEROGENEOUS ELECTRON TRANSFER KINETICS AT POLY(VINYLFERROCENE) AND NAFION/ Ru(bpy)$_3^{2+}$ POLYMER-MODIFIED ELECTRODES BY CONVOLUTION VOLTAMMETRY

JOHNA LEDDY and ALLEN J. BARD*

Department of Chemistry, University of Texas at Austin, Austin, TX 78712 (U.S.A.)

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ABSTRACT

Convolution voltammetry was used to evaluate the rates of heterogeneous charge transfer to ferrocene groups in poly(vinylferrocene) and to Ru(bpy)$_3^{2+}$ in Nafion-modified electrodes under semi-infinite conditions. This technique allows correction for uncompensated resistance and double layer capacitance, as well as determination of the diffusion coefficient, D, transfer coefficient, α, and half-wave potential, $E_{1/2}$, from a single cyclic voltammogram. Vinylferrocene in solution and a bound copolymer of vinylferrocene and styrene in a ratio of 58:42 were also examined. For the polymer films, the heterogeneous charge transfer rate constants, $k°$, are $10^{-4} \geq k° \geq 10^{-5}$ cm/s; these values are about two order of magnitude smaller than those for the similar species in homogeneous solution. The values of $k°/D^{1/2}$, however, are comparable to those in solution; $10 > (k°/D^{1/2}) > 0.1$ s$^{-1/2}$.

INTRODUCTION

The question addressed is how the rate of heterogeneous charge transfer at the electrode surface is affected by the incorporation of the electroactive species into a polymer layer; comparison is made to the same or similar species in solution. Two types of polymer systems are considered: those in which the electroactive moieties are attached to the polymer backbone, typified by poly(vinylferrocene), and those in which the species is held by electrostatic interactions or is extracted into the polymer, for example, ions incorporated into Nafion or poly(vinylpyridine). Measurements of the heterogeneous charge transfer rate to electroactive species in a polymer layer on the electrode surface are complicated by two properties of the film. First, the film resistance and charging currents at a polymer-modified electrode are frequently higher than those in solution. Current responses are affected by both the uncompensated resistance (R_u) and slow heterogeneous charge transfer. Thus, determination of the heterogeneous rate constant requires correction for R_u, e.g., by ac impedance measurements or transform techniques. The second difficulty arises

because rates of heterogeneous charge transfer can only be measured when they are slower than or comparable to the rate of mass transfer. The effective diffusion coefficients in a polymer are 10^3 to 10^6 times slower than those in solution; this drastically reduces the window over which a given heterogeneous rate can be determined. The convolution [1,2] or semi-integral [3] voltammetric technique allows correction for uncompensated resistance and charging current [1a,3a,4a] and has been used for the determination of heterogeneous rate constants for charge transfer to a solution species [1-3]. By digital convolution of a single cyclic voltammogram, the standard heterogeneous rate constant, k°, [1a-1e,2b,3a,3d] the transfer coefficient, α, and the reversible half-wave potential, $E_{1/2}$, [1c] can be determined for a quasi-reversible charge transfer. If the film thickness, l, can be determined, convolution can be used to find the effective diffusion coefficient of charge, D, in the polymer. Here, convolution cyclic voltammetry is used to evaluate these parameters for vinylferrocene in solution and in two polymers matrices, as well as for $Ru(bpy)_3^{2+}$ (bpy = 2,2'-bipyridine) bound electrostatically in Nafion.

Linear potential sweep voltammetry under thin layer conditions can be used to determine k° from the difference between anodic and cathodic peak potentials, ΔE_p [5,6]. Sharp et al. attempted to use this technique to measure k° for silane-and alkylamine-ferrocenes covalently bound to platinum [7]. However, Roullier and Laviron [8] have suggested that an uncompensated resistance of 4 to 10 Ω would also account for the peak splitting ascribed to charge transfer kinetics in these films. Recently, Oyama and co-workers used normal pulse voltammetry to measure the heterogeneous charge transfer rate to $Fe(CN)_6^{4-/3-}$, $Fe(CN)_5^{3-/2-}$, and $Mo(CN)_8^{4-/5-}$ bound by coordination or electrostatically in poly(vinylpyridine) [9]. In these cases, conditions of semi-infinite diffusion, small charging currents, and a rate of charge transfer comparable to mass transport were satisfied for a time window between 2 and 16 ms. Positive feedback techniques were used to compensate for film and solution resistance. The time window for convolution voltammetry is longer. Although conditions of semi-infinite diffusion must be maintained and positive feedback can be used, uncompensated resistance and charging currents can be corrected directly using convolution [1b,3a]. This lengthens the time window for measurement to earlier times, which is important when charge transfer is fast or mass transport is slow.

CONVOLUTION OR SEMI-INTEGRAL VOLTAMMETRY

The application of convolution voltammetry requires a semi-infinite system, where the reaction at the electrode surface is eventually diffusion-limited, and mass transport is via a diffusion process described by Fick's laws [1,3,4a]. A polymer-modified electrode can satisfy these conditions if the data are taken at a sufficiently rapid scan rate or a sufficiently early time to confine the diffusion layer to the film, and if the charge transport within the film can be described by an effective diffusion coefficient. For the reaction $O + n\ e^- \rightarrow R$, the convolution technique allows one to obtain the concentration of O at the electrode surface, $c_0(0, t)$, from the measured

current, $i(t)$. For initial concentrations of the oxidized and reduced species, $c_0(x, 0) = c^*$ and $c_r(x, 0) = 0$ [1,3,4a]:

$$c_0(0, t) = c^* - I(t)/nFAD_0^{1/2} \tag{1}$$

where $I(t)$ is the convolution integral:

$$I(t) = \pi^{-1/2} \int_0^t \frac{i(u)du}{(t-u)^{1/2}} \tag{2}$$

n, F, A, and c^* are the number of electrons transferred, Faraday's constant, the electrode area, and the bulk concentration, respectively. Once the current becomes diffusion limited, $(c_0(0, t) \to 0)$, and $I(t)$ reaches a maximum value, I_{lim}. For a species in solution:

$$I_{lim} = nFAD_0^{1/2}c^* \tag{3}$$

If Q_{film} is the charge required to oxidize completely or reduce the electroactive species in a polymer layer, $c^* = Q_{film}/nFAl$, and,

$$I_{lim} = Q_{film}D_0^{1/2}/l \tag{4}$$

As $c_0(0, t) + c_r(0, t) = c^*$,

$$c_0(0, t) = \left[I_{lim} - I(t)\right]/nFAD_0^{1/2} \qquad c_r(0, t) = I(t)/nFAD_r^{1/2} \tag{5}$$

The potential establishes the relationship between $c_0(0, t)$ and $c_r(0, t)$, such that these equations can be used to express the relationship between the current and the potential directly. For a Nernstian charge transfer, the potential, E, is related to $I(t)$ by [1a]:

$$E = E_{1/2} + (RT/nF) \ln\left[(I_{lim} - I(t))/I(t)\right] \tag{6}$$

where $E_{1/2} = E^{o'} - (RT/nF) \ln [\xi]$, $E^{o'}$ is the formal potential and $\xi = [D_0/D_r]^{1/2}$.

All of the above equations apply for any potential perturbation which eventually leads to a diffusion-limited current. The potential perturbation of interest is the triangular wave of cyclic voltammetry. Savéant and Tessier [1c] have shown that for the convolution of a cyclic voltammogram under quasi-reversible conditions:

$$E_{1/2} = E_{i=0} - (RT/F) \ln\left[(I_{lim} - I_{i=0})/I_{i=0}\right] \tag{7}$$

where $E_{i=0}$ and $I_{i=0}$ are the potential and the convoluted current when the current, $i(t)$, passes through zero on the reverse scan. They have also shown [1a] that $k_f(E)$, the potential dependent rate constant for the forward charge transfer reaction, can be obtained from the equation:

$$\ln\left[\frac{D_o^{1/2}}{k_f(E)}\right] = \ln\left[\frac{I_{lim} - I(t)\{1 + \xi \exp[(nF/RT)(E - E^{o'})]\}}{i(t)}\right] \tag{8}$$

Butler–Volmer kinetics have not been assumed in deriving this equation.

The potential and the current at any time can be corrected [1b] for uncompensated resistance and the double layer capacitance, C_{dl}, by the following equa-

tions:

$$E = E_{\text{applied}} + i_{\text{meas}} R_u \tag{9}$$

$$i = i_{\text{meas}} - C_{\text{dl}} v + C_{\text{dl}} R_u \, \mathrm{d}i_{\text{meas}} / \mathrm{d}t \tag{10}$$

where E is the corrected potential, E_{applied} is the experimentally applied potential, t
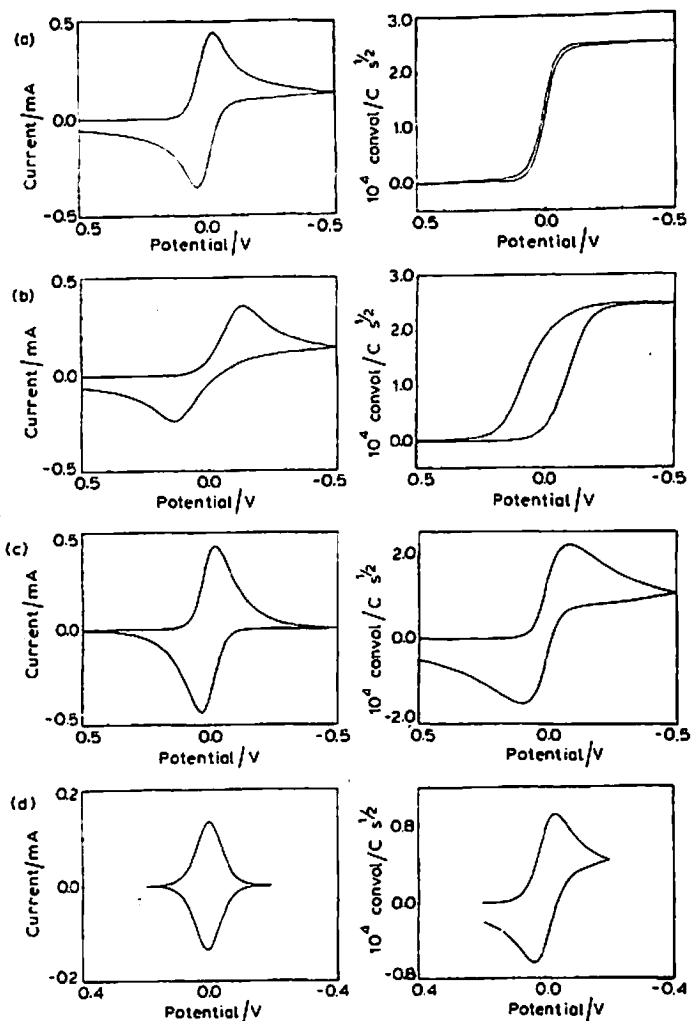

Fig. 1. Left, computer generated cyclic voltammograms; right, the convoluted voltammograms computed with eqn. (11) for (a) Nernstian system under semi-infinite conditions; $\lambda = k^\circ/(DvnF/RT)^{1/2} = 20$; (b) semi-infinite system under quasireversible conditions; $\lambda = 0.01$; (c) system approaching thin layer behavior, under reversible conditions; $\lambda = 20$ and $lv^{1/2}D^{-1/2} = 0.34$; (d) system at thin layer behavior, under reversible conditions; $\lambda = 20$ and $lv^{1/2}D^{-1/2} = 0.086$.

is the time, v is the scan rate, i_{meas} is the measured current, and i is the faradaic current.

One algorithm used to compute the convolution integral from the digitized current is [10]:

$$I(t) = I(k\Delta t) = \left[\frac{\Delta t}{\pi}\right]^{1/2} \sum_{j=1}^{k} \frac{i(j\Delta t)}{(k-j+0.5)^{1/2}} \tag{11}$$

The time given as $(j\Delta t)$ in the numerator of eqn. (11) is more precisely represented as $(j\Delta t - \Delta t/2)$. However, for a sufficiently large value of k, the effect of neglecting the $(\Delta t/2)$ term is negligible. The total voltammetric time span is divided into k intervals of width, Δt. Computer simulated cyclic voltammograms [4b] and their convolutions are shown in Fig. 1. The convoluted voltammograms in Fig. 1a (Nernstian) and 1b (quasi-reversible) attain a limiting value, consistent with a semi-infinite system. The forward and reverse branches of the convoluted voltammogram in Fig. 1a are superimposable, while hysteresis is observed in Fig. 1b; these behaviors are characteristic of reversible and quasi-reversible charge transfers, respectively. A cyclic voltammogram for a system approaching thin layer behavior [11] (i.e., where the semi-infinite condition is not satisfied) is shown in Fig. 1c; a system exhibiting true thin layer behavior is shown in Fig. 1d. Here, the convoluted currents do not attain a limiting value, and the resulting I vs. E plot has the shape of a diffusion-controlled cyclic voltammogram. In these latter cases, although the charge transfers are reversible, hysteresis is observed. For a diffusion-limited process, $k°$ can be calculated from eqn. (8) at $E = E°'$. If Butler–Volmer kinetics [1a] apply, α is a potential-independent parameter, and a plot of the r.h.s. of eqn. (8) vs. the potential will be linear, with a slope of $-\alpha nF/RT$.

Several systems were examined using convolution voltammetry; in most cases ferrocene/ferrocenium was the couple of interest. Vinylferrocene, VF, was examined in solution. Poly(vinylferrocene) (PVF) and a copolymer of vinylferrocene and styrene in a ratio of 58 : 42 (PVF58) were electroprecipitated and examined as bound films. A thin layer of the ion exchange membrane, Nafion (equivalent weight 970), containing $Ru(bpy)_3^{2+}$, denoted $Naf/Ru(bpy)_3^{2+}$ [12] was also examined.

EXPERIMENTAL

Film preparation

PVF and PVF58 were oxidatively electroprecipitated [13] from dichloromethane (Matheson, Coleman, and Bell) containing tetrabutylammonium tetrafluoroborate (TBABF$_4$) (Southwestern Analytical Chemicals) onto a platinum disk (area = 0.022 cm^2). The platinum electrode was prepared by polishing with 0.5 μm alumina; rinsing with water; soaking in concentrated HNO_3; rinsing again; and air drying. VF and PVF were examined in acetonitrile (MeCN) (MCB) containing 0.1 M TBABF$_4$; VF was also tested in MeCN + 0.1 M LiClO$_4$. MeCN was dried over 4Å molecular

sieves. PVF58 was studied in LiClO$_4$ solution because of its limited stability in the presence of TBABF$_4$. These films were prepared by oxidation in CH$_2$Cl$_2$ + TBABF$_4$, transferred to MeCN + 0.1 M LiClO$_4$, and reduced immediately after being immersed; this tended to force the BF$_4^-$ from the film. PVF58 was prepared by Pittman et al. [14]; PVF was prepared by Smith et al. [15].

The Nafion films were deposited on a glassy carbon electrode (area = 0.458 cm^2) by evaporation from an 8% (wt/v) ethanol solution of the 970 equivalent weight polymer [12]. The dried films were soaked for 15 min in 1 mM Ru(bpy)$_3^{2+}$, and examined in 0.1 M Na$_2$SO$_4$ in water.

Thickness

The thicknesses of the PVF and PVF58 films were determined by monitoring the rate of solvent evaporation from a solvent-soaked film on a Mettler microbalance (Model M5) by the method discussed in ref. 16. Q_{film} was determined by integration of the cathodic wave of a cyclic voltammogram taken at 2 mV/s. For the vinylferrocene polymers, the density was taken as 1.25 g/cm^3 [17] and the molar mass was taken as $(213x + 101(1 - x))/x$, where x is the mole fraction of ferrocene in the polymer; the molar masses of ferrocene and styrene are 213 g and 101 g. These results are expressed as a value of Al/Q_{film}. For PVF, $Al/Q_{film} = 3.179 \times 10^{-3}$ cm^3 C^{-1}, and for PVF58, 6.523×10^{-3} cm^3 C^{-1}. These values indicate the solvent-saturated films were 1.8 (PVF) and 2.8 (PVF58) times as thick as the dry films.

Electrochemical measurements

The electrochemical measurements employed a Princeton Applied Research Model 173 potentiostat, Model 175 universal programmer, and Model 179 digital coulometer. Positive feedback was used to compensate solution resistance. Feedback was adjusted such that the current transient produced by a small potential step in a non-faradaic region decayed as sharply as possible without oscillation. Cyclic voltammograms and potential steps were recorded on a Norland 3001 digital oscilloscope. The digitized voltammograms were transferred to a Digital Equipment Corporation Minc 11 minicomputer, where the convolution and analysis were performed. The remaining incompensated resistance and the capacitance were determined by applying small potential steps (50 to 200 mV) in the region at the foot of the wave where negligible faradaic current flows. The determination of R_u and C_{dl} was based on a series RC circuit, characterized by the equation:

$$i(t) = (\Delta V/R) \exp(-t/R_u C_{dl}) \qquad (12)$$

where ΔV is the size of the potential step. Plots of $\ln[i(t)]$ vs. t were linear with correlation coefficients generally better than 0.999, for t between one and 2 to 3 time constants ($R_u C_{dl}$). A typical analysis, for PVF58, is shown in Fig. 2. In all cases, the values of R_u and C_{dl} found from repetitive trials showed standard deviations of less
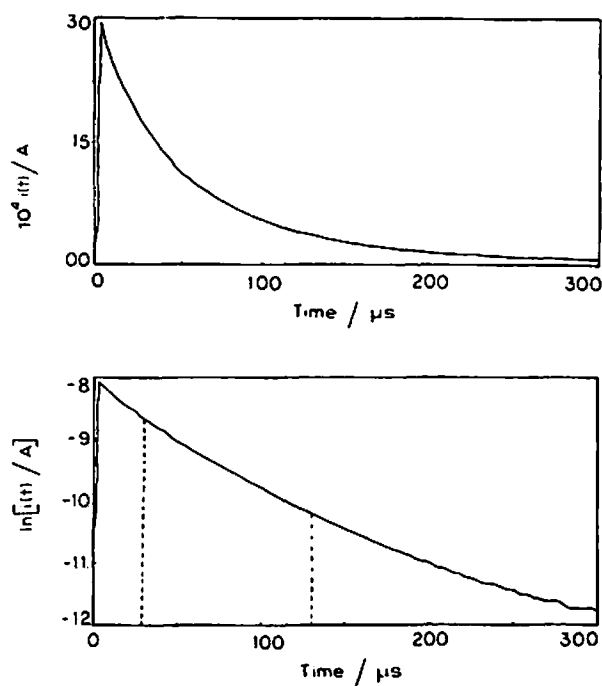
Fig. 2. Method of determination of R_u and C_{dl}. A potential step ($0.8 \to 0.7$ V vs. Ag R.E.) in the non-faradaic region produced the transient shown in (a) at a PVF58 modified electrode; (b) a plot of $\ln[i(t)]$ vs. t (eqn. 12), yields a slope, $1/R_u C_{dl}$ and intercept, $\Delta V/R_u$. The linear region between 30 and 130 μs yielded $R_u = 383 \, \Omega$ and $C_{dl} = 1.67 \times 10^{-7}$ F (correlation coefficient of 0.999).

than 10% and were taken as constants over the potential range examined. Average values of R_u and C_{dl} are listed in Table 1. Potential steps were applied and R_u and C_{dl} measurements were made in the non-faradaic region of both the reduced and oxidized forms of PVF and PVF58. R_u and C_{dl} for the $\text{Naf/Ru(bpy)}_3^{2+}$ are based on the film containing Ru(bpy)_3^{2+}, because oxidation of the solvent limits the available non-faradaic region at potentials where the complex is in the oxidized state. For PVF and PVF58, $E^{\circ\prime}$ was determined from the null potential of a half-oxidized film. For $\text{Naf/Ru(bpy)}_3^{2+}$ and VF, $E^{\circ\prime}$ was taken as the potential midway between the peak potentials of a cyclic voltammogram taken at a scan rate of 0.1 V/s. A silver wire quasi-reference electrode (Ag R.E.) was employed in MeCN, and a saturated NaCl calomel electrode (SSCE) was used in water. The convolutions were calculated using approximately 500 time intervals in each voltammogram. Useful scan rates were typically between 0.1 and 10 V/s. We assumed that α is potential-independent, and $k_f(E)D^{-1/2}$ and α were calculated from eqn. (8). The slope was taken from values about a potential midway between E_{peak} on the reverse scan and $E^{\circ\prime}$.

TABLE 1

Results of the convolution analysis for all the systems examined

Sample			$k^\circ D^{-1/2}$ /s$^{-1/2}$	$D^{1/2}l^{-1}$ /s$^{-1/2}$	$l/\mu m$	$D/cm^2\ s^{-1}$	$k^\circ/cm\ s^{-1}$	α	$E^{\circ\prime}/V$ vs. Ag R.E.	$E_{1/2}/V$ vs. Ag R.E.	R_u/Ω	$10^7\ C_{dl}/F$
VF	R → O	LiClO$_4$[a]	3.59			3.22×10^{-5}	0.024	0.62	0.307	0.312	41.8±3.3	2.96±0.17
	R → O	LiClO$_4$[a]	1.88			2.51×10^{-5}	0.0093	0.71	0.317	0.305	55.6±6.4	2.54±0.28
	R → O	TBABF$_4$[a]	1.41			2.52×10^{-5}	0.007	0.56		0.638	48.8±5.3	2.50±0.11
PVF	R → O	TBABF$_4$[a]	3.42	0.246	1.13	0.77×10^{-9}	9.4×10^{-5}	0.61	0.726	0.734	92.3±5.7	2.15±0.11
	R → O	TBABF$_4$[a]	1.95	0.189	2.48	2.21×10^{-9}	9.1×10^{-5}	0.46	0.841	0.836	41.6±3.7	3.08±0.20
	O → R	TBABF$_4$[a]	0.82	0.306	1.13	1.19×10^{-9}	2.8×10^{-5}	0.77	0.726	0.702	92.3±5.7	2.15±0.11
	O → R	TBABF$_4$[a]	0.66	0.282	2.48	4.91×10^{-9}	4.5×10^{-5}	0.58	0.841	0.782	41.6±3.7	3.08±0.20
PVF58	O → R	LiClO$_4$[a]		0.287	3.00	7.41×10^{-4}			0.348	0.356	384 ±11	1.67±0.04
Naf/Ru(bpy)$_3^{2+}$	R → O	Na$_2$SO$_4$[b]	5.38	0.904	0.22[c]	4×10^{-10}[c]	10^{-4}[c]	0.61	1.032[d]	1.053[d]	56.0±2.7	76.0 ±3.7

[a] 0.022 cm^2 platinum working electrode.

[b] 0.458 cm^2 glassy carbon working electrode.

[c] D was taken from Reference [12], and used to calculate l and k°.

[d] vs. SSCE.

RESULTS

The determinations of k°, α, and D for the polymer species and vinylferrocene (VF) in MeCN are discussed below; results for all the systems examined are summarized in Table 1. Each value in Table 1 represents the average of results for four to six scan rates. The standard deviation is ± 10 to 15%, and in most cases, a slight systematic dependence on scan rate was observed for both the polymer and solution species. $E_{1/2}$ is the half-wave potential determined from the convoluted voltammograms according to eqns. (6) or (7). For PVF and the first VF sample, $\ln[D^{1/2}/k_f(E)]$ was calculated using $E^{\circ\prime}$; $E_{1/2}$ was used in the other cases. ξ was usually taken as 1. The values reported for k° and D depend on the concentration in the film, c^*, and, thus, their accuracy depends on the value of l. To the extent l is accurate, D and k° can be determined from $D^{1/2}/l$ and $k^\circ D^{-1/2}$. In all cases, α, as determined from plots of $k_f(E)$ vs. E, was between 0.4 and 0.8.

Vinyl ferrocene

The cyclic voltammogram and its convolution for a 1 V/s sweep rate are shown in Fig. 3. The values of k° cited in Table 1 are essentially the same as those found directly from the cyclic voltammogram by Nicholson's method [18]; $k^\circ \sim 0.01$ to 0.03 cm/s. Based on the variation of ΔE_p with V, Diggle and Parker [19] report a standard heterogeneous rate constant of 0.044 cm/s for ferrocene in TBAP/MeCN, while Sharp et al. [7b] report 0.22 cm/s for the same system. A diffusion coefficient of 2.0×10^{-5} cm^2/s [20] has also been reported. The reference potential of the Ag R.E., and, thus, the $E^{\circ\prime}$ values reported for VF, change with supporting electrolyte. The convoluted voltammogram is not a closed loop as shown in Fig. 3b, because the concentration of VF$^+$ is depleted by slow reaction with trace water in the MeCN. The 2 values of $k^\circ/D^{1/2}$ reported for VF in LiClO$_4$ were determined under the same conditions. The factor of 2 difference in these values may be ascribable to small differences in the water content of the MeCN.

Poly(vinylferrocene)

The results for the reduction of a 1.13 μm thick film of PVF are shown in Fig. 4. A peak splitting in the cycle voltammogram (Fig. 4a) in excess of 60 mV and hysteresis in the convoluted voltammogram (Fig. 4b) are indicative of a quasi-reversible charge transfer under semi-infinite conditions. The convolution attains a limiting value and the loop is closed, showing the measurements are made under semi-infinite conditions without any chemical reaction or convection. The I_{lim} values for the oxidation and the reduction yield $\xi \sim 1.4$. The value found for the diffusion coefficient of the oxidized moieties, 3.0×10^{-9} cm^2 s^{-1}, agrees well with the value we found by chronoamperometry, 2.8×10^{-9} cm^2 s^{-1}. A plot of $\ln[D^{1/2}/k_f(E)]$ vs. E for several scan rates is shown in Fig. 4c. From Nicholson's method, $k^\circ \sim 3 \times 10^{-5}$ cm/s, a value in the same range as those found by convolution. Using potential step
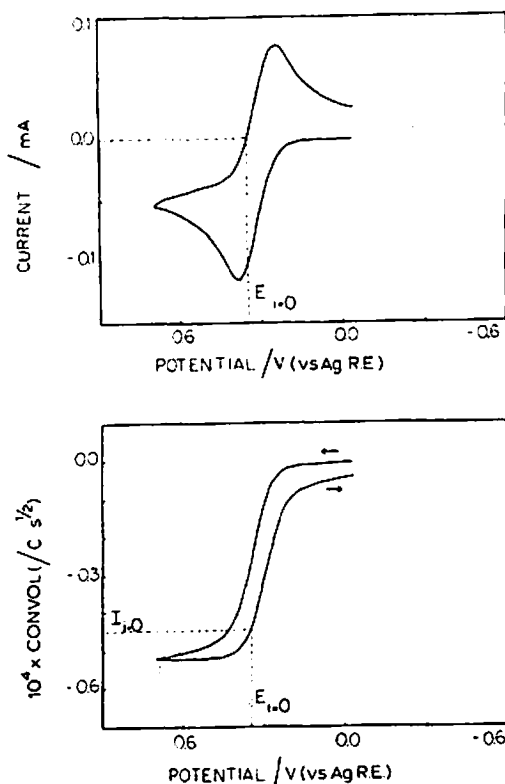
Fig. 3. Cyclic (a) and convoluted (b) voltammograms for 4.67 mM vinylferrocene in 0.1 M $LiClO_4$ + MeCN; $v = 1$ V/s. The hysteresis in the convolution loop indicates quasireversible charge transfer. $I_{lim} = -5.23 \times 10^{-5}$ C s$^{-1/2}$, and $D = 2.4 \times 10^{-5}$ cm^2 s^{-1}. $E_{i=0}$, the potential at which the current is zero on the reverse scan, is marked in (a); $I_{i=0}$ is marked on (b). $E_{i=0}$ and $I_{i=0}$ are used in conjunction with eqn. (7) to calculate $E_{1/2} = 0.302$ V.

chronocoulometry [21], we found $k^\circ \sim 10^{-4}$ cm/s and $\alpha \sim 0.35$ starting with the reduced form of PVF. This value of α was determined by assuming the transfer coefficient is potential independent. The slight curvature of the $\ln[D^{1/2}/k_f(E)]$ plot suggests α may be slightly potential-dependent [1]. A previous study [16] of PVF has shown diffusion coefficients of a solution soluble species within the film are high (10^{-7} cm^2/s) and the uncompensated resistance and capacitance are low. Thus, measurement of the charge transfer rate to PVF should not be complicated by high uncompensated resistance of sluggish counterion mobility. The average value we found for R_u was 66 Ω. For a system where $k^\circ D^{-1/2} = 3$ and $i_p = 1$ mA, an uncompensated resistance of 55 Ω would be necessary to diminish the measured value of $k^\circ D^{-1/2}$ to 1.5. As a factor of two is the order of the error in these measurements and the uncompensated resistance is known within approximately 5 Ω, the values of $k^\circ D^{-1/2}$ found here are probably not significantly affected by uncompensated resistance.
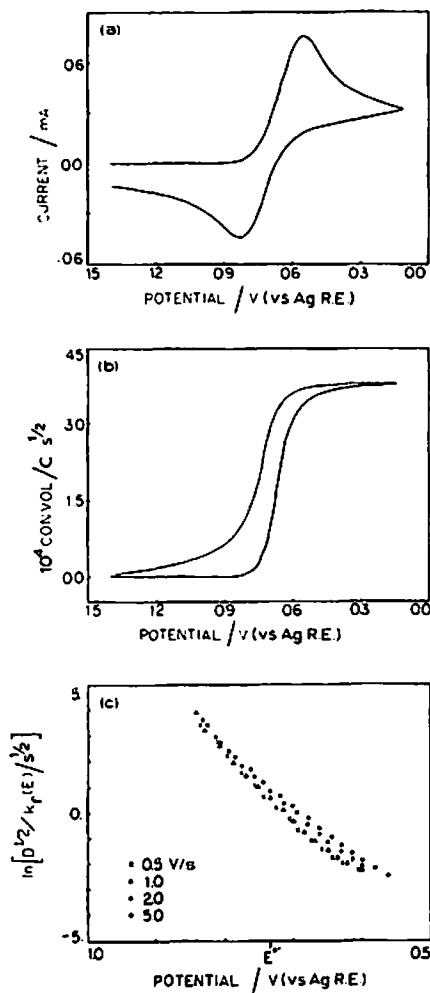
Fig. 4. Cyclic (a) and convoluted (b) voltammograms for the reduction of a 1.13 μm thick PVF film at 1.0 V/s in 0.1 M TBABF$_4$ + MeCN. Both peak splitting in (a) and the hysteresis in (b) are indications of quasi-reversible behavior. (c) Plot of $\ln[D^{1/2}/k_f(E)]$ vs. E over the potential range about $E^{o\prime} = 0.726$ V vs Ag R.E. wire for several scan rates. $k^{o\prime}$ is determined from the value of $\ln[D^{1/2}/k_f(E)]$ at $E^{o\prime}$. The limiting value of the convolution indicates $D \sim 1.2 \times 10^{-9}$ cm^2/s.

PVF58

Reliable values of k^o could not be obtained for the copolymer of vinyl ferrocene and styrene. Convolutions for PVF58 at different scan rates achieve the same limiting value, and the effective diffusion coefficient of the oxidized moieties was found to be 7.8 ± 0.4 × 10^{-9} cm^2/s. However, the relative positions of the forward and reverse branches of the convolution are not consistent with Nernstian, quasi-re-
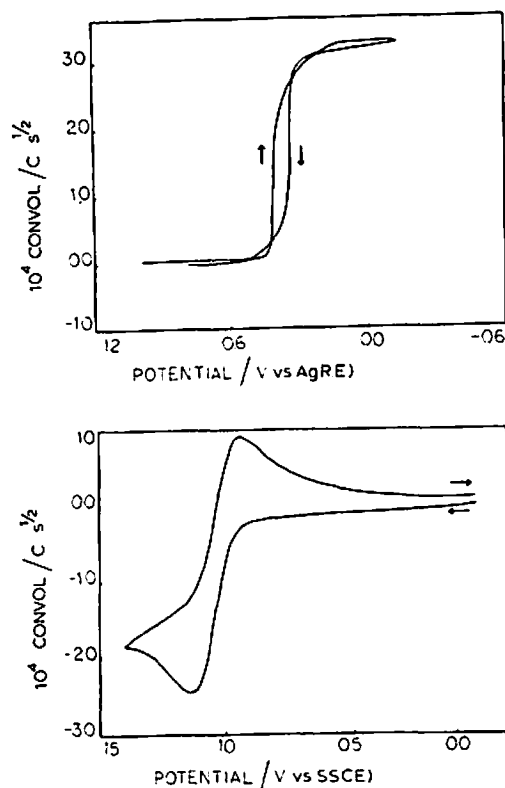
Fig. 5. (a) Convolution of a 3.0 μm thick PVF58 film taken at 10 V/s. The limiting value indicates $D \sim 3.3 \times 10^{-9}$ cm^2/s. No information about k° can be obtained. (b) Convolution of a 0.22 μm thick Nafion film containing Ru(bpy)$_3^{2+}$ taken at 0.1 V/s. The convolution peaks and then decays because the scan rate was not high enough to maintain semi-infinite diffusion. For this system, $I_{\lim}$ was achieved at higher scan rates.

versible, or thin layer behavior (Fig. 5a). Plots of $\ln[D^{1/2}/k_f(E)]$ vs. E are linear but yield an α value in excess of 1. This type of behavior can occur when the determined values of R_u and C_{dl} are seriously in error or when strong interactions exist within the film. The value found for $k^\circ D^{-1/2}$ for PVF58 based on peak splittings only reflects the uncompensated resistance (384 Ω).

$Naf / Ru(bpy)_3^{2+}$

For Ru(bpy)$_3^{2+}$ in Nafion, values found for k° and D are somewhat uncertain because only an approximate value of the swollen film thickness was known. $k^\circ D^{-1/2}$ was 5.4; the diffusion coefficient has been determined previously [12]. With $D = 4 \times 10^{-10}$ cm^2/s, k° is approximately 10^{-4} cm/s. Nicholson's method indicated $k^\circ = 6 \times 10^{-5}$ cm/s, again, reasonably consistent with the values found from the convolution analysis. A k° value of ~ 0.07 cm/s has been reported for

TABLE 2

Summary of average k° and D values and a comparison of $k^{\circ}/D^{1/2}$ determined for solution and polymer bound moieties

Couple	System	$k^{\circ a}$/cm s^{-1}	D/cm^2 s^{-1}	$k^{\circ} D^{-1/2}$/s$^{-1/2}$
VF$^{\circ/+}$	MeCN + LiClO$_4$	0.013	2.8×10^{-5}	2.5
PVF R → O	MeCN + TBABF$_4$	9.2×10^{-5}	1.5×10^{-9}	2.4
O → R	MeCN + TBABF$_4$	3.6×10^{-5}	3.0×10^{-9}	0.7
Ru(bpy)$_3^{2+/3+}$	H$_2$O	0.07 [22]	8×10^{-6} [12]	25
Naf/Ru(bpy)$_3^{2+}$	H$_2$O + Na$_2$SO$_4$	10^{-4}	4×10^{-10} [12]	5.4
Mo(CN)$_8^{4-/3-}$	H$_2$O	0.5 [23]	b	22
	PVP [9b] c	2×10^{-4}	2.5×10^{-9}	4
Fe(CN)$_6^{4-/3-}$	H$_2$O	0.01 [24]	b	5.0
	PVP [9c]	32 to 1.6×10^{-4}	420 to 1×10^{-9}	4.5
Fe(CN)$_5^{3-/2-}$				
	PVP [9c]	15 to 1×10^{-4}	420 to 1×10^{-9}	2.3 to 3.2

a As determined by convolution voltammetry or normal pulse voltammetry. Direct determination of k° from ΔE_p of cyclic voltammograms [18], yielded the following values (cm s^{-1}): VF, 0.02; PVF, 3.5×10^{-5}; NaF/Ru(bpy)$_3^{2+}$, 6×10^{-5}.

b The diffusion coefficient in solution was taken as 5×10^{-6} cm^2/s.

c PVP = poly(vinylpyridine)

Ru(bpy)$_3^{2+}$ oxidation at a glassy carbon electrode in water based on potential step and cyclic voltammetric measurements [22]. The convolution shown in Fig. 5b is for a cyclic voltammogram taken at 0.1 V/s, and the effects of a finite film thickness can be seen. The convolutions attain the anticipated limiting behavior at higher scan rates.

The average values of k° and D found by the convolution technique, and k° values by Nicholson's method for all species are summarized in Table 2.

DISCUSSION

The determination of k° by convolution analysis was successful for PVF, but not for PVF58. Determination of k° by convolution analysis requires that no interactions exist between the oxidized and reduced forms of the electroactive species. Although PVF is known to have several states within the film [11], the rate of change between the states is slow. As a result, interconversions of these states are usually observed at slow scan rates (of the order of mV/s), as shown by the distorted tailing for $v = 2$ mV/s (Fig. 6a). The narrow anodic peak observed at 2 mV/s is indicative of interactions within the film. However, for a film ~ 1 μm thick, cyclic voltammograms taken at 0.1 V/s or faster give a diffusional response with no evidence of interaction (Fig. 6a, $v = 0.1$ V/s). Stronger interactions within the PVF58 films are evident in the 2 mV/s scans shown in Fig. 6b, and can be observed at scan rates up to 0.05 V/s. These strong interactions are reflected in the poor results of the convolution analysis for PVF58.
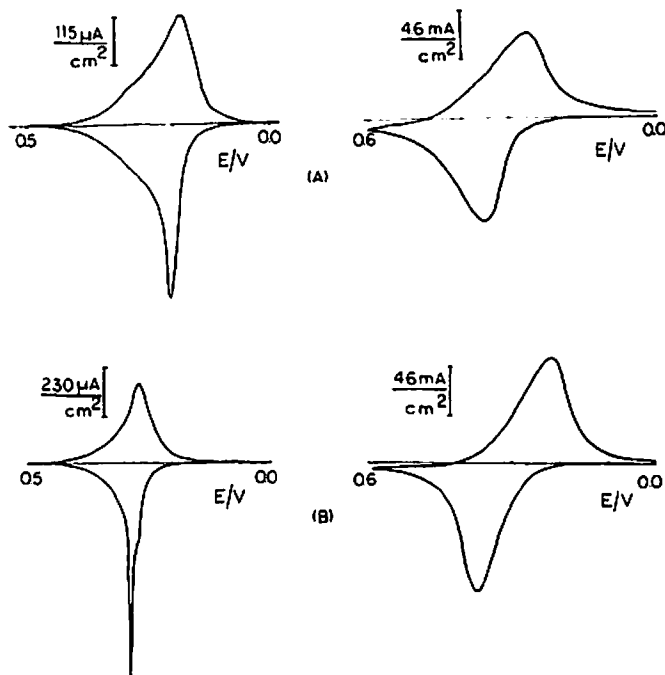
Fig. 6. Cyclic voltammograms taken at (left) 2 mV/s and (right) 0.1 V/s from 0.0 to 0.6 V vs. AgR.E. For (A) PVF and (B) PVF58 in LiClO$_4$/MeCN. Evidence for strong interactions within the PVF film can be seen at 2 mV/s, where a diffusional wave, typical of a single electroactive species, is observed at 0.1 V/s for PVF. PVF58 shows stronger interactions within the films.

For PVF, the $k°$ found starting with the oxidized state is approximately three times smaller than that found starting with the reduced state. Although this is of the order of the error in the measurements, a possible alternative explanation exists. A computer simulation of PVF's cyclic voltammetry is based on a square reaction scheme [11]. A simplified representation of the scheme is:

$$PVF_a^o \overset{E_a^o}{\rightleftharpoons} PVF_a^+$$

$$k_{-1} \uparrow \qquad \downarrow k_1$$

$$PVF_p^o \underset{E_b^o}{\rightleftharpoons} PVF_b^+$$
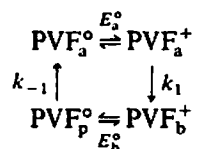
where E_a^o and E_b^o are separated by a few millivolts and k_{-1} and k_1 are fairly slow, having a discernible effect only at slow scan rates. a and b represent different states within the film. For a cyclic voltammetric oxidation, the polymer begins in state a; if the scan rate is rapid compared to k_1, the voltammogram and, thus, the value found for $k°$ is characteristic of state a. If the voltammetry is performed with the polymer initially in the ferrocenium state and the scan rate is rapid compared to k_{-1}, the convolution and $k°$ will be characteristic of state b.

The results of these studies comparing k° and D in a polymer film with the values of monomeric species in solution, as well as results of previous studies [9b,c] are summarized in Table 2. Note that the k° values for species in solution are typically 10^2 to 10^3 times higher than for virtually the same species in a polymer matrix. $k^\circ/D^{1/2}$ values for the polymer and solution species, however, are comparable, i.e., within a factor of 5. This relation between k° and D is also apparent in the previously reported polymer results [9b,c] and in the trends of D and k° with increased loading of the electroactive material in the PVP in the latter work. This relationship between k° and D is not predicted by most of the usual models for electron transfer either under homogeneous or heterogeneous conditions, when the reaction rate is not near diffusion control [25–27]. We have found, in preliminary experiments involving ferrocene oxidation in DMSO + TBABF$_4$ solutions whose viscosity (and D for ferrocene) was varied by addition of sucrose, a similar variation of k° with D [28], so the situation involving the polymer films is not unique. One explanation for this dependency could be that the same solvent properties that affect viscosity also affect modes important in electron transfer kinetics, e.g., λ_0 [25]. However, because of the apparent generality of the effect, we do not feel that this is the major contribution and we are currently searching for a more direct relationship.

The smaller k° in the polymer (and its relationship with D) can alternatively be explained by assuming that the actual active area of the electrode at which the electron transfer occurs is much smaller than the geometric electrode area. As discussed by Savéant et al. [29] for cyclic voltammetry, when the electrode reaction occurs only at microscopic active sites distributed homogeneously on the electrode surface, the actual current density at a given potential will be much larger than the apparent one calculated from the geometric area, with the overall result that the voltammogram appears less reversible and a small apparent k° is found. The voltammograms can have a quasireversible appearance with no diminution of the peak currents as compared to those at the bare electrode. The measured value of the heterogeneous rate constant under these conditions is the product of $(1 - \theta)$ and k° at the active sites, where θ is the surface coverage. For the values in Table 2, if the actual k° at the active sites is the same as k° at the bare electrode, then this suggests 99 to 99.9% of the surface is blocked. If the polymer film also causes a diminution in D, an apparent relation between the apparent k° and D could be found. However, this effect would require almost complete electrode blockage by very different kinds of polymers [e.g., poly(vinylferrocene), Nafion, and poly(vinylpyridinium)]. Moreover, it would not account for the effects seen in viscous homogeneous solutions.

One could also invoke uncompensated resistance effects in the polymer film for the smaller apparent k°. If k° in the polymer had been as high as in the solution, D in the polymer would have forced the value measured, $k^\circ/D^{1/2}$, into a range where resistance would have severely complicated most electrochemical measurements of k°. However, we believe that positive feedback techniques with correction for uncompensated resistance by the convolution procedure minimized effects of resistance on the determination of k°. For PVF and Naf + Ru(bpy)$_3^{2+}$, the total resistance is not high and k° is fairly low; standard electrochemical techniques

operating under semi-infinite conditions give results for k° within half an order of magnitude of those found by convolution (Table 2). The magnitude of resistance in these systems, if not compensated, would introduce approximately half an order of magnitude error into the value found for k°.

Convolution voltammetry is a good method of characterizing polymer-modified electrodes when the electrochemical reactions are uncomplicated and linear diffusion is maintained. When these two conditions were met, the results for the polymers studied here were closer to ideality than those of the solution species. All of the polymers' non-idealities have been previously observed for solution species; none can be ascribed to the nature of the film. Convolution voltammetry is sensitive to deviations from the conditions of diffusion control and absence of associated chemical reactions. Convection, which is not a severe problem in a polymer film, disturbs the diffusion profile and distorts the convoluted voltammogram. More importantly for polymers, interactions between the oxidized and reduced forms of the electroactive species that occur on the time scale of the measurement are difficult to interpret, as, for example, in the PVF58 films (Fig. 5a). Chemical reactions can also perturb the convoluted voltammograms, as seen in Fig. 3b for VF undergoing slow reaction with water. Thin layer effects also distort the convoluted voltammogram as in Fig. 5b. If these difficulties are avoided, convolution voltammetry is an excellent technique for correcting for R_u and C_{dl}. Within polymer layers, the time window for measurement is limited at higher scan rates only by the ability to determine R_u and C_{dl}. A single scan can yield D, k°, $E_{1/2}$, and α. It is a particularly good method for determining $D^{1/2}/l$ because the shape of the convoluted voltammogram insures semi-infinite conditions are maintained.

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