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Controlling Catalytic Activity of a Polyion Scaffold on an Electrode via Microemulsion Composition

Christopher K. Njue and James F. Rusling*

Contribution from the Department of Chemistry, Box U-60, University of Connecticut, Storrs, Connecticut 06269-3060

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Abstract: Electrochemical and catalytic properties of vitamin B_{12} hexacarboxylate−polylysine films covalently immobilized onto pyrolytic graphite electrodes were controlled by microemulsion composition. Sodium dodecyl sulfate (SDS) in microemulsions and micellar solutions is incorporated to form micelles within the cationic films. This changes the net film charge from positive, characteristic of the protonated lysines, to negative, characteristic of SDS micelles. Micelle formation was supported by voltammetry and quartz crystal microbalance results, which also suggested that cationic surfactants do not enter the film. Catalytic turnover rates for the reduction of dibromocyclohexane to cyclohexene mediated by the film in SDS microemulsions were controlled by the difference between the reduction potential of the reactant and the catalyst $E^{\circ\prime}$ in the film. Thus, reaction rate in these systems is controlled by the intrinsic activation free energy. For a given reactant, catalyst $E^{\circ\prime}$, and consequently activation free energy, can be controlled by microemulsion composition via interactions of surfactant and salt with the polymer network. Fast catalyst turnover was also facilitated by high conductivity and low viscosity of the bulk microemulsion.

Introduction

Mediated electrochemical synthesis in low toxicity fluids provides an attractive approach to environmentally benign organic synthesis. Transition metal complexes mediate a versatile library of organic transformations.[1−3] To avoid toxic, expensive organic solvents, we have been exploring microemulsions as alternative fluid media for these reactions.[4,5] Microemulsions are thermodynamically stable, macroscopically homogeneous mixtures of oil, water, and surfactants with dynamic internal nanostructures.[6] Conductive oil-in-water (O/W) and bicontinuous microemulsions are directly applicable to electrosynthesis, are often cheaper than organic solvents, and can provide pathway control options not available with homogeneous solvents.[4,5−11]

Catalytic films of metal complexes on electrodes are desirable for synthesis because of ready reusability and more efficient use of catalyst compared to diffusing metal complexes. Microemulsions are such good solvents that covalent binding of catalytic films to electrodes is necessary for good stability. We recently attached the cobalt corrin vitamin B_{12} hexacarboxylic acid [(B_{12}(COOH)$_6$)] via amide linkages onto poly-L-lysine (PLL) which had been covalently bound to carbon electrodes,[7] providing catalytic films that were suitably stable in microemulsions. Turnover numbers for the catalytic conversion of *trans*-1,2-dibromocyclohexane to cyclohexene utilizing the Co^{II}/Co^{I} redox couple of this catalytic scaffold were 17-fold larger than those for vitamin B_{12} in microemulsions. The formal potential ($E^{\circ\prime}$) of the Co^{II}/Co^{I} redox couple in the films was influenced by microemulsion composition.

For dissolved cobalt complexes in microemulsions of sufficiently large oil/water interfacial area, the log of the apparent rate constant of catalytic and S_N2 reactions depended directly on the difference between the reduction potentials of catalyst and reactant,[4,5,8] just as in homogeneous solutions.[12] Thus, these electrochemically driven reactions are under control of the intrinsic activation free energy of the reaction, and specific rates can be increased by shifting the catalyst formal potential closer to that of the reactant. A similar relation between reaction rate and activation free energy might be found for catalytic films in microemulsions, if a means is available to systematically control catalyst formal potential. With the PLL-B_{12}(COOH)$_6$ films, we felt that systematic formal potential control would be available via microemulsion composition.

In this paper, we explore the control of catalytic activity of PLL-B_{12}(COOH)$_6$ in microemulsions. We show that interactions of the polycation network with anionic surfactant control the formal potentials of the Co^{II}/Co^{I} redox couple, which in turn

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Table 1. Microemulsion Properties and Compositions in Weight Percent

no.	surfactant[a]	pentanol	oil	water	type [ref]	η, cP	κ, mΩ^{-1} cm^{-1}
1	3.35 SDS	6.65	1.0 C12[b]	89	O/W [14]	3.74	4.52
2	3.35 SDS	6.65	1.0 C12	89/0.1 M NaCl	O/W [14]	4.12	10.5
3	13.3 SDS	26.7	8.0 C12	52	BC[e][16]	12.2	7.14
4	13.3 SDS	26.7	8.0 C12	52/0.1 M NaCl	BC [14]	12.5	6.04
5	16.6 SDS	45.5	5.0 C12	33.3	BC[e][16]	13.2	6.63
6	16.6 SDS	45.5	5.0 C12	33/0.1 M NaCl	BC [14]	13.1	6.07
7	20.1 SDS	40.0	5.9 C12	34	BC[e][16]	14.0	4.27
8	20.1 SDS	40.0	5.9 C12	34/0.1 M NaCl	BC [14]	14.4	3.79
9	5.0 CTAB	5.4	1.0 C16[c]	88.6	O/W [11]	5.66	4.07
10	17.5 CTAB	35	12.5 C14[d]	35	BC [11]	14.8	1.60

[a] SDS = sodium dodecyl sulfate, CTAB = hexadecyltrimethylammonium bromide. [b] Dodecane. [c] Hexadecane. [d] Tetradecane. [e] Confirmed by high conductivity accompanied by self-diffusion coefficients of oil-soluble ferrocene in the range 4×10^{-6} to 7×10^{-6} cm^2 s^{-1} consistent with bicontinuous fluids (see ref 15b).

control the catalytic efficiency for debromination of *trans*-1,2-dibromocyclohexane. Thus, catalytic efficiency of a polyion film can be controlled by microemulsion composition.

Experimental Section

Chemicals and Microemulsions. Synthesis of vitamin B_{12} hexacarboxylic acid ($B_{12}(COOH)_6$) was described previously.[13] Poly-L-lysine hydrobromide (PLL, MW 150000−300000) was from Sigma. Cetyltrimethylammonium bromide (CTAB, 99%) and sodium dodecyl sulfate (SDS, 99%) were from Acros. Water was >15 MΩ·cm, and other chemical sources were reported previously.[7,11] Characterized microemulsions were employed (Table 1).[14−16] A YSI model 35 meter was used to obtain conductivities. Ostwald viscometers were used for viscosities.

Equipment and Procedures. PLL-$B_{12}(COOH)_6$ films were prepared as described previously.[7] The procedure involves electrochemical oxidation of a carbon electrode, amide coupling of PLL to the surface using 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC), followed by coupling of $B_{12}(COOH)_6$ to PLL using EDC. Basal plane disk pyrolytic graphite (PG, $A = 0.016$ cm^2, Advanced Ceramics) electrodes for voltammetry were coated exactly as described previously.[7] Carbon cloth (CC, 1 in. × 2 in., Zoltek) electrodes were coated using concentrations decreased to 0.2 mM $B_{12}(COOH)_6$, 2.4 mM EDC, and 0.4 mequiv PLL with extensive water washing to make films thin enough for kinetic rather than internal mass transport control of electrolysis. Voltammetry and electrolysis utilized BAS and CH Instruments electrochemistry systems and previously reported procedures.[7] Rotating disk voltammetry (RDV) employed a Sargent Rotator (No. 3049087, type KYC-22) at 1800 rpm.

Electrolyses with stirring under nitrogen were continued for 0.5 h on 10 mM *trans*-1,2-dibromocyclohexane (DBCH) in 12 mL microemulsion, using a carbon rod counter electrode in 1 M KBr separated from the cathode compartment by an agar/KCl bridge behind a medium porosity grass frit, with an SCE reference. Current efficiencies were in the range 50−80%.

After electrolysis, a 0.2 mL reaction mixture was eluted with 5 mL of pentane on a silica gel column and analyzed by gas chromatography as described previously.[11] Results were reproducible to ±10%. Turnover numbers were referred to the amount of electroactive catalyst on electrodes, estimated by integrating cyclic voltammograms (CVs) in each microemulsion of 0.5 × 0.5 cm carbon cloth coated with catalytic film. CVs showed 70−80% of original Co^{II} after electrolyses.

For quartz crystal microbalance (QCM) studies, gold-quartz crystals (9 MHz) were coated with 3-mercaptopropionic acid. PLL-$B_{12}(COOH)_6$ films were made as usual[7] on these carboxylate-terminated surfaces. Mass estimates were made from QCM frequency changes (ΔF) on dry films as reported previously.[17]

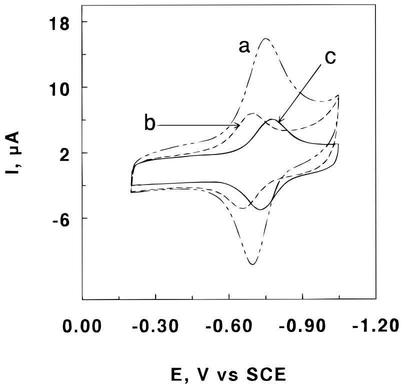

Figure 1. Cyclic voltammograms of PLL-$B_{12}(COOH)_6$ film at 50 mV s^{-1} in (a) pH 7.10 TRIS buffer in water, (b) SDS/pentanol/dodecane/water microemulsion **3**, and (c) CTAB/hexadecane/pentanol/water microemulsion **9**.

Results

Voltammetry. Cyclic voltammograms (CV) of PLL-B_{12}-$(COOH)_6$ films showed reversible Co^{II}/Co^{I} voltammetry in aqueous buffers and microemulsions (Figure 1). These CVs illustrate the influence of specific fluid composition on peak currents and formal potentials, the latter taken as the midpoint between the reduction and oxidation peaks. As a framework for analyzing the influence of fluid composition, we adapted a model for the influence of salt on formal potentials of redox sites in polyion-coated electrodes.[18] For positively charged PLL films, we use the simplified half-reaction:

$$\mathrm{Co^{II}L^{-n}} + (-\mathrm{NH_3}^{+}\mathrm{X}^{-})_{\mathrm{film}} + \mathrm{e}^{-} \rightleftharpoons \mathrm{Co^{I}L^{-n-1}} + (\mathrm{X}^{-})_{\mathrm{soln}} \quad (1)$$

where X$^-$ is an electroinactive counteranion that exits the film upon reduction of Co^{II}L^{-n} to maintain charge neutrality, and $-n$ is the total charge on the cobalt complex site. The apparent formal potential ($E^{\circ\prime}_{\mathrm{app}}$) of the Co^{II}/Co^{I} couple in the PLL film is predicted to be:

$$E^{\circ\prime}_{\mathrm{app}} = E^{\circ\prime}_{\mathrm{film}} + \frac{RT}{F}\ln\left(\frac{[\mathrm{X}^-]_{\mathrm{film}}}{[\mathrm{X}^-]_{\mathrm{soln}}}\right) \quad (2)$$

where $E^{\circ\prime}_{\mathrm{film}}$ is the formal potential of the redox sites in the film,

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Table 2. Influence of Anions on Electrochemical Characteristics of Co^{II}/Co^{I} in PLL-$B_{12}(COOH)_6$ Films

$[X^-]$, salt	linear range, mM	$dE^{\circ\prime}/d\ln[X^-]$, V/ln(M)	$d\Gamma_0/d\ln[X^-]$, nmol cm^{-2}/ln(M)	$dI_p/d\ln[X^-]$, μA/ln(M)
$[DS^-]$, SDS	0.34−2.59	−0.00543	−0.0156	−0.107
$[Cl^-]$, NaCl	0.00−11.8	−0.0173	−0.397	−2.20
$[Br^-]$, NaBr	0.00−17.0	−0.0119	−0.916	−4.57
$[I^-]$, NaI	0.00−11.8	−0.0302	−1.07	−6.95
$[I^-]$, KI	5.57−11.5	−0.0282	−1.03	−7.80
$[Br^-]$, CTAB	0.00−10.4	−0.0100	−1.49	−6.93

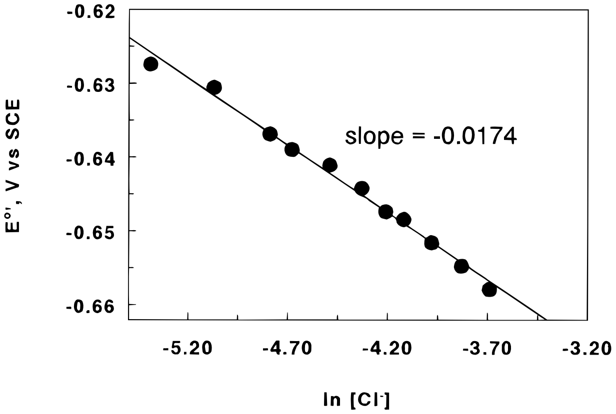

Figure 2. Influence of chloride ion concentration on the formal potential of PLL-$B_{12}(COOH)_6$ film in an aqueous 5 mM TRIS buffer, pH 7.1.

R, *T*, and *F* have their usual electrochemical meanings, and the concentration ratio refers to X^- in film and solution, respectively.

As predicted by eq 2, linearity of the measured $E^{\circ\prime}$ vs $\ln[X^-]$ was found when the concentration of salt was increased in dilute buffer solutions (Figure 2). Table 2 summarizes results of such studies for halide ions in pH 7.1 buffer, in a CTAB solution, and for $[DS^-]$ in a sub-micellar SDS solution. Buffers were used to avoid changes in PLL conformation with pH.[19] Slopes $dE^{\circ\prime}/d\ln[X^-]$ bracketed the theoretical value of −0.0257 V/ln$[X^-]$, but only the iodide salts gave good quantitative agreement. Increasing salt concentration also decreased the apparent amount of electroactive redox centers (Γ_o) in the films, as reflected in decreased peak currents (Table 2).

In SDS solutions, a negative linear shift in $E^{\circ\prime}$ vs $\ln[DS^-]$ was observed below the critical micelle concentration (CMC, 8 mM[20]). Above the CMC, the shift in $E^{\circ\prime}$ as $[DS^-]$ increased became positive (Figure 3a), suggesting a change in the net charge of the film from positive to negative. Consistent with this view, $E^{\circ\prime}$ shifted positive with increased total Na^+ concentration in aqueous micellar SDS solution (Figure 3b).

Microemulsions in Table 1 provide a regular series of total cation concentrations. $E^{\circ\prime}$ values of PLL-$B_{12}(COOH)_6$ films shifted positive in the SDS microemulsions with increasing total cation concentration $[M^+]$ (Figure 4), with a slope of 0.031 V/ln $[M^+]$ close to the theoretical value of 0.0257 V/ln$[M^+]$, and a correlation coefficient $R = 0.94$. $E^{\circ\prime}$ values in the CTAB microemulsions do not fall on this regression line, and show a trend in the opposite direction. Apparent surface concentrations of electroactive Co^{II} in these films also increased in the SDS microemulsion with slope 0.087 nmol cm^{-2}/ln$[M^+]$. Again, points for CTAB microemulsions fell off the regression line.

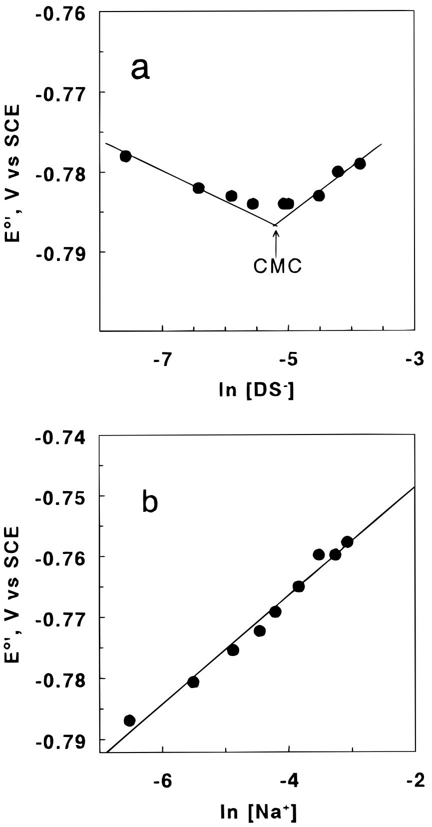

Figure 3. (a) Influence of SDS concentration on the formal potential of PLL-$B_{12}(COOH)_6$ film in an aqueous 5 mM TRIS buffer, pH 7.1. (b) Influence of NaCl concentration on the formal potential of PLL-$B_{12}(COOH)_6$ film in an aqueous 5 mM TRIS buffer, pH 7.1, containing 14 mM SDS.

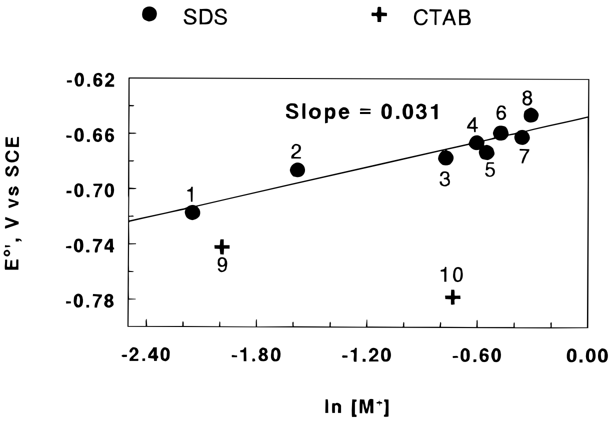

Figure 4. Influence of total cation concentration in the microemulsions on the formal potential of PLL-$B_{12}(COOH)_6$. (The numbers near points identify microemulsions in Table 1.)

Voltammetry was also used to investigate transport of ions and molecules through PLL-$B_{12}(COOH)_6$ films by comparing CVs of probes for coated and bare PG electrodes (see Supporting

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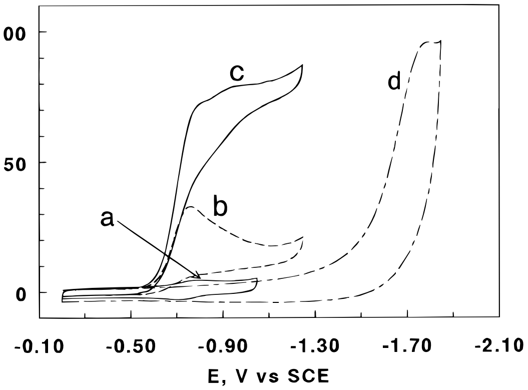

Figure 5. Representative voltammograms of PLL-$B_{12}(COOH)_6$ film at 50 mV s^{-1} in microemulsion **1**: (a) CV with no DBCH; (b) CV with 7 mM DBCH present (second scan); (c) RDV with 7 mM DBCH present; and (d) direct CV reduction of 7 mM DBCH on the PG/PLL electrode.

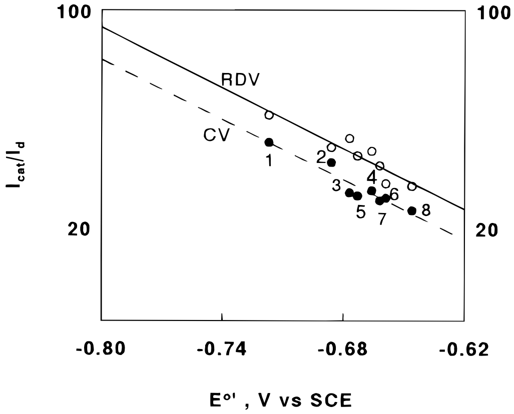

Figure 6. Influence of the formal potential of PLL-$B_{12}(COOH)_6$ films in SDS microemulsions on the voltammetric catalytic efficiency I_{cat}/I_d from CV and RDV at 50 mV s^{-1}. (The numbers near points identify microemulsions in Table 1.)

Table 3. Summary of Linear Regression Results for PLL-$B_{12}(COOH)_6$ Films in SDS Microemulsions

X	Y	$\lvert R\rvert^a$	slope, dY/dX^b	method
ln [M^+]	$E°'$	0.942	0.031	CV
$E°'$	log(I_{cat}/I_d)	0.950	−3.22	CV
$E°'$	log(I_{cat}/I_d)	0.926	−3.25	RDV
κ	I_{cat}/I_d	0.948	1.32	CV
κ	I_{cat}/I_d	0.642	1.26	RDV
η	I_{cat}/I_d	0.963	−1.08	CV
η	I_{cat}/I_d	0.745	−1.02	RDV
η	$E°'$	0.868	177	CV
κ	$E°'$	0.235	−23.4	CV
$E°'$	log(turnover no.)	0.892	7.4	electrolysis
κ	turnover no.	0.901	3.04×10^3	electrolysis
η	turnover no.	0.879	-4.67×10^3	electrolysis

[a] Absolute value of the correlation coefficient from linear regression. [b] See representative graphs for units.

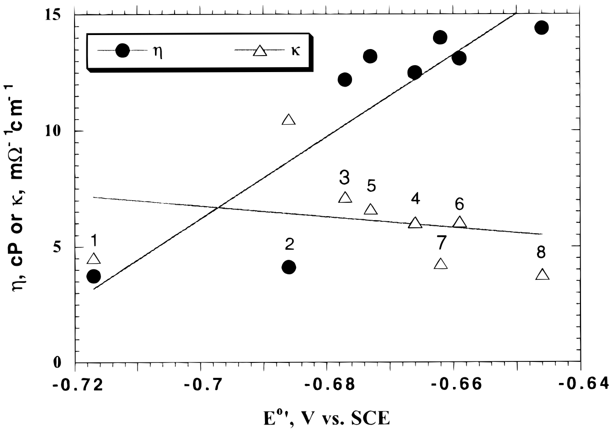

Figure 7. Correlation plots of viscosity and conductivity of microemulsions against $E°'$ of PLL-$B_{12}(COOH)_6$ films. (The numbers near points identify microemulsions in Table 1.)

Information). Negatively charged ferricyanide ($Fe(CN)_6^{3-}$) in SDS microemulsions gave peaks about 2-fold larger on PLL-$B_{12}(COOH)_6$ films than on a bare electrode, suggesting mild preconcentration of the electroactive ion in the film. $Ru(NH_3)_6^{3+}$ and ferrocene gave reversible, diffusion-controlled peaks roughly equal in height on bare and coated electrodes, suggesting nearly unrestricted access to the underlying electrode. Results are consistent with a rather open architecture of the polyion network.

When *trans*-1,2-dibromocyclohexane (DBCH) was added to a microemulsion, voltammetry of the PLL-$B_{12}(COOH)_6$ film featured a large reduction signal by CV or RDV close to the Co^{II}/Co^{I} reduction potential with disappearance of the oxidation peak (Figure 5). This well-known behavior is characteristic of electrochemical catalysis, in this case involving inner-sphere reduction of DBCH to cyclohexene. [7−9,21] The direct reduction of DBCH on a noncatalytic PLL coated electrode occurred at about −1.7 V, showing that the film catalysis with half-wave potentials at about −0.7 V decreases the overpotential required for the debromination by about 1 V.

The ratio of the film peak (CV) or limiting (RDV) current in the presence of DBCH (I_{cat}) to the peak current in the absence of DBCH (I_d) for the same catalytic electrode (cf. Figure 5) is a measure of catalytic efficiency. For PLL-$B_{12}(COOH)_6$ films, I_{cat}/I_d increased as $E°'$ became more negative with decreasing concentration of total Na^+ in SDS microemulsions (Figure 6). This is expected behavior for a catalytic reaction under intrinsic activation free energy control.[8,12a] Both RDV and CV data show the same trends, although RDV catalytic efficiencies are larger consistent with improved DBCH mass transport by convection. Correlation between I_{cat}/I_d and $E°'$ was shown by $R > 0.92$ (Table 3).

Voltammetric catalytic efficiencies increased with decreasing viscosity and increasing conductivity of SDS microemulsions (see Supporting Information). Correlation with conductivity was much better for CV data ($R = 0.95$) than for RDV ($R = 0.64$). Correlation coefficients for viscosity were similar (Table 3). Figure 7 shows no correlation of $E°'$ in the microemulsions with conductivity ($R = 0.24$), and a moderate correlation with viscosity ($R = 0.87$). Considerable scatter was observed in both plots. Since there is no intrinsic reason bulk fluid viscosity should influence the $E°'$ of the films, we consider the correlations of catalytic efficiency with $E°'$, κ, and η to be relatively independent of strong interparameter correlations.

Catalytic Turnover in Microemulsions. Turnover numbers for the catalytic reduction of DBCH to cyclohexene in the microemulsions were estimated as a measure of synthetic catalytic efficiency. Turnover numbers[22] increased as $E°'$ became more negative for bicontinuous SDS microemulsions (Figure 8), $R = 0.89$ indicating good correlation. The two O/W SDS microemulsions fell off of the regression line. Positive correla-

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(22) Turnover numbers were larger than those reported previously[7] because of improved cell design and decrease in film thickness allowing the system to operate under efficient kinetic control.

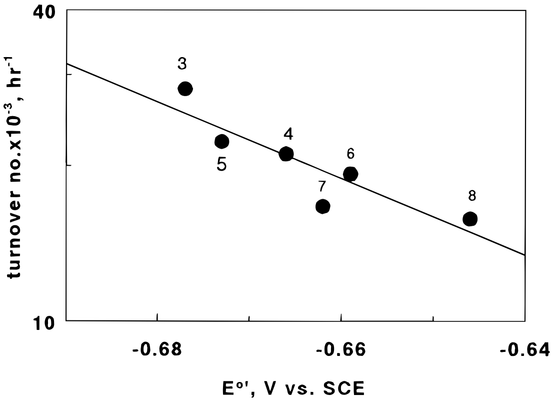

Figure 8. Influence of the formal potential of PLL-$B_{12}(COOH)_6$ films on the logarithm of turnover number from catalytic electrolyses of DBCH in bicontinuous SDS microemulsions. (The numbers near points identify microemulsions in Table 1.)

tions were also found between turnover number and increasing conductivity and decreasing viscosity of the SDS microemulsion (Table 3). Interestingly, thicker films made with 10-fold greater concentrations of PLL and catalyst gave no correlations with $E^{\circ\prime}$, conductivity, or viscosity. These results suggest that the activity of the thicker films may be under control of mass transport processes within the films, which is predicted as the thickness of catalytic films increases.[12b]

Microbalance Studies. QCM was undertaken to monitor weight changes of films soaked in microemulsions. Films were prepared on gold-coated quartz resonators, and QCM frequencies were measured on dry films before and after soaking. Film construction on the resonators resulted in $-\Delta F = 2163 \pm 178$ Hz, suggesting a mass increase of about 6000 ng cm^{-2}, and film thickness of roughly 35 nm assuming polymer density[17] of 1.2 mg mL^{-1}. Films soaked in 13% SDS microemulsion **3** for 1 h and dried gave $-\Delta F = 517 \pm 193$ Hz, or an average mass increase of 1400 ng cm^{-2}. Mass increases upon soaking films in 0.1 M NaCl or in 5% CTAB microemulsions were negligible.

Discussion

Data reported above clearly demonstrate that efficiency of a catalytic polyelectrolyte film on an electrode can be controlled by microemulsion composition. I_{cat}/I_d ratios from CV and RDV and turnover numbers for DBCH reduction, all measures of catalytic efficiency, were correlated with formal potentials of the PLL-$B_{12}(COOH)_6$ films in a series of SDS microemulsions (Figures 6 and 8). All measures of catalytic efficiency were also correlated with increasing conductivity and decreasing viscosity of the SDS microemulsions (Table 3). The main practical conclusion is that SDS microemulsions with lower cation concentrations and more negative formal potentials (Figure 4) facilitated catalytic efficiency. Other important attributes which improve catalyst turnover rates are high conductivity and low viscosity of the fluid.

Data in Figures 6 and 8 illustrate for the first time that the efficiency of a catalytic film in bicontinuous microemulsions can be controlled by the difference in reduction potential between the substrate and the catalyst in the film. This result is consistent with findings for homogeneous solutions,[12] and for microemulsions with dissolved catalysts.[8] It means that the reaction rate in these systems is controlled by the intrinsic activation free energy of the reaction. For a given reactant, activation free energy is governed by the SDS microemulsion composition, via control of the $E^{\circ\prime}$ of the catalyst redox couple in the film (Figure 4).

Data in Figures 2 and 3 and Table 2 provide insight into the nature of the control of the formal potential of the catalyst redox couple by the microemulsion. Figure 2 and similar data in aqueous and cationic micellar solutions (Table 2) are consistent with the influence of anions on the $E^{\circ\prime}$ of the catalyst film, as predicted by eq 2. However, when increasing the SDS concentration above the CMC, $E^{\circ\prime}$ shifts positive (Figure 3a). In micellar SDS solutions, addition of NaCl also shifts $E^{\circ\prime}$ in the positive direction (Figure 3b). These results are consistent with a change in the net charge on the polymeric network, suggesting the simplified reaction:

$$\mathrm{Co^{II}L^{-n} + (M^+)_{soln} + e^- \rightleftharpoons Co^{I}L^{-n-1} + (-SO_4^{\;-}M^+)_{film}} \qquad (3)$$

for which the apparent formal potential is predicted by:[18]

$$E^{\circ\prime}_{\mathrm{app}} = E^{\circ\prime}_{\mathrm{film}} + \frac{RT}{F}\ln\left(\frac{[\mathrm{M}^+]_{\mathrm{soln}}}{[\mathrm{M}^+]_{\mathrm{film}}}\right) \qquad (4)$$

This equation is also followed in the SDS microemulsions (Figure 4), where the slope of 0.031 is similar to the theoretical value of 0.0257.

Interactions between the cationic PLL and SDS seem to cause the formation of micelles within the polymer network, a well-known phenomenon.[23] This view is supported by the large weight gain observed by QCM when PLL-$B_{12}(COOH)_6$ films were placed in SDS microemulsions compared to negligible weight increase in salt solutions or CTAB microemulsions. The inclusion of SDS within the polymer film is in excess of charge neutralization because of the anionic micelle formation, and thus the net effective film charge becomes negative.

Conclusions

Catalytic efficiency of an electrochemically driven reaction mediated by a polycation network containing a redox couple was shown to be under control of the intrinsic activation free energy of the reaction. For a specific reactant, activation free energy was controlled by SDS microemulsion composition via interactions of negative surfactant with the cationic polymer which controlled the catalyst E°′. Rapid catalyst turnover was also facilitated by high conductivity and low viscosity of the bulk microemulsion.

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Supporting Information Available: Seven additional figures documenting probe voltammetry and correlations described in the text (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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