The rate constant for the dimerization/dehydration of nitroxyl is of interest in biochemistry, because there is reason to believe that denitrifying bacteria may form N_2O by dimerization/dehydration of nitroxyl produced in the reduction of nitrite and/or NO.[8,30]

Acknowledgment. This work was supported by a grant from the National Science Foundation (PCM 82-18000) and Biomedical Research Support Grant S07 RR 07044 from the National Institutes of Health. We thank Francis Bonner for useful discussions and information on the trioxodinitrate system and Joanne Goretski for having synthesized the $Na_2N_2O_3$.

Registry No. $N_2O_3^{2-}$, 15435-67-3; NO^-, 14967-78-3; ^{15}NO, 15917-77-8.

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Electrostatic Binding of Bicarbonate and Formate in Viologen-Based Redox Polymers: Importance in Catalytic Reduction of Bicarbonate to Formate

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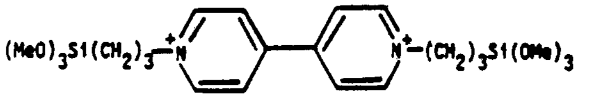
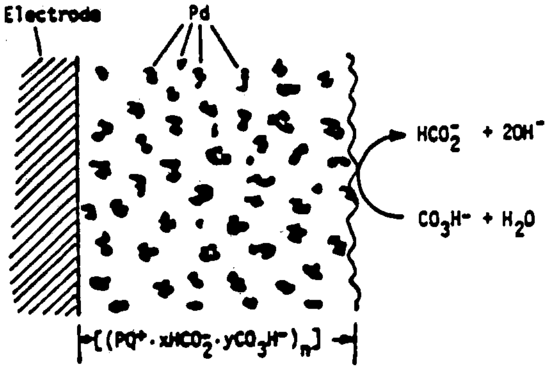
The relative importance of electrostatic binding of CO_3H^- and HCO_2^- in a redox polymer derived from an *N,N'*-dialkyl-4,4'-bipyridinium monomer has been investigated by Fourier transform infrared (FTIR) spectroscopy. At 298 K and a total concentration of C-containing species of 0.1 M the two species are equally firmly bound in a polymer immobilized on a single-crystal Si electrode surface. When the concentration of C-containing species is 1.0 M, the CO_3H^- ion is more firmly bound by about a factor of 2.5, and at a total concentration of 3.0 M the CO_3H^- ion is about 7 times more firmly bound than the HCO_2^- ion. The HCO_2^- and Cl^- anions are equally firmly bound at 1.0 M total anion concentration. On the basis of the lack of change in the cyclic voltammetry response of a derivatized electrode in 1.0 M Na[CO_3H] or Na[HCO_2] compared to 1.0 M NaCl, the exchange rate of the C-containing anions does not appear to be a factor that would limit the rate of reduction of the CO_3H^- ion at an electrode modified with the polymer and impregnated with Pd(0).

We wish to report results relating to the electrostatic binding of CO_3H^- and HCO_2^- to the polysiloxane polymer derived from the hydrolysis of the viologen derivative represented by I. This work was undertaken with the aim of adding to the characterization of catalytic electrodes for the reduction of CO_3H^- to HCO_2^- (Scheme I).[1-3] It is well-known that ions can be more and less firmly bound into electrode-confined polymers,[4-8] including the $[(PQ^{2+/+})_n]_{surf}$ polymer derived from I.[9] Since the heterogeneous rate constant for the reduction of CO_3H^- at Pd(0) is relatively modest,[2] it is important to be able to take advantage of the three-dimensionality of the polymer/Pd(0) assembly to achieve useful rates of reduction. The point is that there is a potential advantage in terms of efficiency for HCO_2^- formation when Pd(0) and CO_3H^- are concentrated in the redox polymer. Accordingly, the kinetics and thermodynamics associated with binding of the CO_3H^-/HCO_2^- redox reagents and other anions are important in achieving the optimum catalyst system.



I

Scheme I. Catalytic Electrode for the Reduction of CO_3H^- to HCO_2^- [3]



There is a variety of physical techniques that can be useful in establishing the relative concentration of anionic species bound to a surface-immobilized polymer. In this work we have used Fourier transform infrared (FTIR) spectroscopy to establish the relative importance of the binding of CO_3H^- and HCO_2^- from aqueous solutions of various concentration ratios of these two

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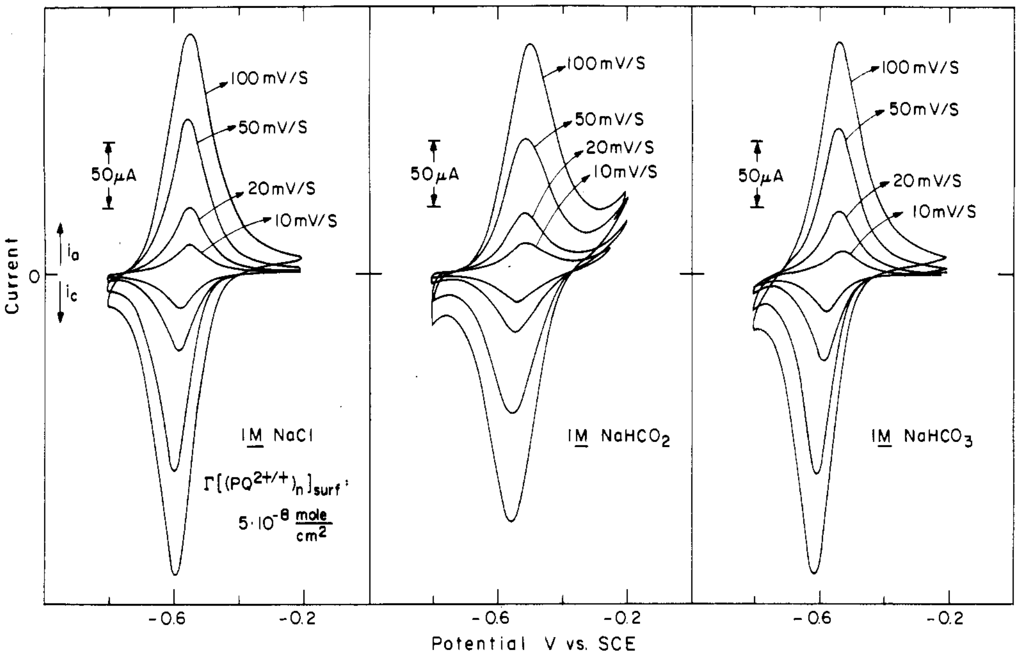

Figure 1. Cyclic voltammetry response of a Pt electrode derivatized with reagent I. The cyclic voltammetry as a function of sweep rate and supporting electrolyte is shown and illustrates that the electrochemical response of the polymer from I is largely unaffected by variation in the electrolyte among the three shown.

anions. Quantitative data can be obtained, by assuming that the surface-immobilized polymer is fully charge-compensated by CO_3H^- or by HCO_2^- when the surface is equilibrated with a solution containing only CO_3H^- or HCO_2^-, respectively. FTIR has been demonstrated to be a viable technique for such studies, as evidenced by the consistency of electrochemical and FTIR determinations of the relative binding of various anionic metal cyanide complexes into the polymer derived from I.[9,10] The assumption that the $[(PQ^{2+})_n]_{surf}$ system can be fully charge-compensated by equilibration with only one anion in solution has been verified for metal cyanide complexes by a combination of FTIR, Auger, and electrochemical measurements.[9,10] For nonelectroactive anions such as Cl^- complete charge compensation of the polymer has been established by Auger spectroscopy.[9]

A recent study of the relative binding of Cl^-, CO_3H^-, and HCO_2^- to alkylammonium and alkylpyridinium reagents covalently anchored to silica shows that there can be substantial differences in the binding strengths.[11] Accordingly, there may be significant differences in the binding of these anions to the polymer derived from I. We now report findings relating to the kinetics and thermodynamics of anion exchange involving $[(PQ^{2+})_n]_{surf}$ and Cl^-, CO_3H^-, and HCO_2^-.

Experimental Section

Electrodes and Derivatization with I. The electrodes used in this work were IR-transparent, single-crystal, n-type Si fashioned in such a way that the electrodes could be derivatized with I, equilibrated with aqueous solutions of electrolyte, and then suspended in the beam of an FTIR spectrometer for analysis to determine the distribution of charge-compensating anions in the cationic polymer. The n-type Si wafers were obtained from Monsanto Co., Palo Alto, CA, as 0.37 mm thick material with the ⟨111⟩ face exposed. The resistivity of the P-doped wafers was 3–7 Ω/cm. Electrodes were fabricated from pieces of the wafer with about 5 cm² of exposed area on one face. On one of the two faces exposed, a Ga–In eutectic was rubbed around the perimeter, leaving clean Si in a circle in the middle of the electrode so that the IR beam could be passed through the electrode. A Cu foil with a circular hole was contacted to the Ga–In eutectic with Ag epoxy, and a Cu wire lead was connected to the Cu foil. The Cu wire lead was encases in a glass tube so that the electrode could be easily mounted. All surfaces except the circular region in the center of the electrode were coated with ordinary epoxy to define a two-sided Si electrode that is IR transparent. The two sides of the Si were each about 0.8 cm² in exposed area. The IR beam exposed approximately 0.3 cm² of the derivatized electrode.

The derivatizing reagent (I) has been described previously,[12] and the material used in this work was available from previous work in this laboratory. The n-type Si was pretreated prior to derivatization by first etching with HF to remove the thick air-grown oxide. Then the electrode was washed with H_2O, dipped into alkaline base, washed again with H_2O, and rinsed with acetone and dried.[13] The electrode was then derivatized by electrochemically assisting the polymerization of I as previously described for metallic electrodes.[12] The electrochemical interconversion of $[(PQ^{2+})_n]_{surf}$ and the reduced form occurs in the dark on n-type Si because the potential of the redox couple is more negative than the conduction band edge of the semiconductor; for the purposes of the experimentation described here the n-type Si behaves as a metallic electrode.[13] Derivatization of the n-type Si was carried out until the desired coverage was achieved. The coverage was determined by integrating the cyclic voltammograms for the interconversion of the redox states of the polymer. The coverage of PQ^{2+} units used was in the range $(2–10) \times 10^{-8}$ mol/cm² on each of the two exposed surfaces.

Ion-Exchange Procedure. After derivatization the n-type Si electrodes were stored in saturated aqueous KCl prior to use. This procedure resulted in assurance that the polymer was initially charge-compensated only by Cl^-. All ion-exchange processes were carried out in HPLC grade, deoxygenated H_2O under N_2 with the appropriate electrolyte. The electrolytes used were NaCl, $Na[CO_3H]$, $Cs[CO_3H]$, or $Na[HCO_2]$, obtained from commercial sources as reagent grade and used as received. In some experiments 99% ^{13}C-enriched $Na[CO_3H]$ or $Na[HCO_2]$ was used; these materials were obtained from Cambridge Isotope Lab, Cambridge, MA, and used as received. In a typical experiment a derivatized electrode is removed from the KCl storage medium, rinsed liberally with H_2O, and then immersed into a solution containing the C-containing ions. The electrode has an insignificant anion-binding capacity compared to the amount of anion in the solution, and the anion concentration in the solution is unaffected by the binding to the electrode. The electrode is equilibrated with the anions for 35 min at 298 K. After equilibration the electrode is removed from the solution and rinsed first with H_2O for 5 s and then with dry EtOH for 5 s. The electrode is then completely dried by placing it in a vacuum (about 10^{-3} torr) at 298 K for 20 min. The electrode is then analyzed by FTIR.

FTIR Spectroscopy. All IR spectra were recorded by using a Nicolet 7199 Fourier transform IR spectrometer. The optical bench and the sample chamber were continously purged with N_2 during measurements

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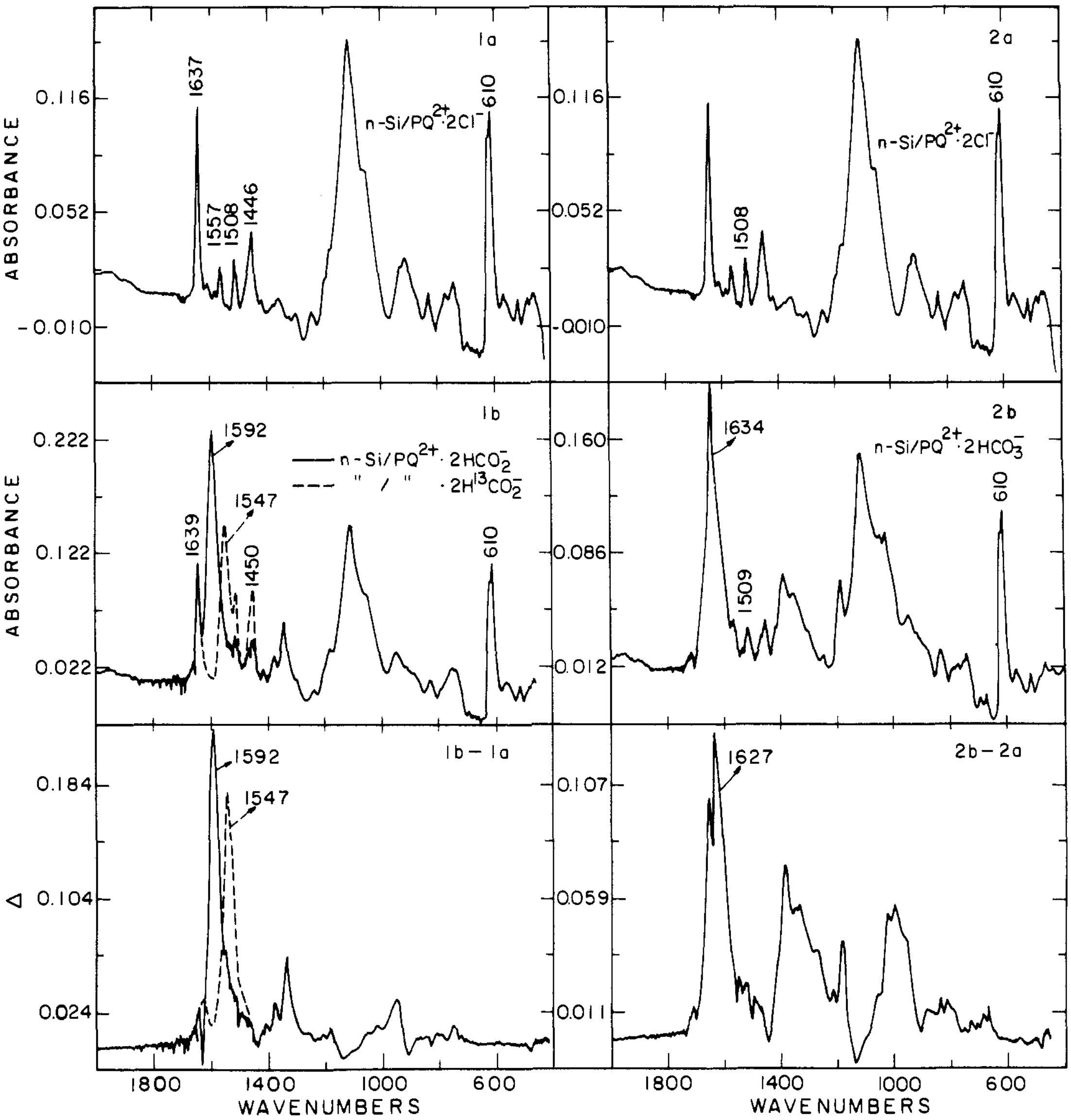

Figure 2. FTIR spectra of n-Si[$(PQ^{2+}{\cdot}2Cl^-)_n$] (top right and left), n-Si[$(PQ^{2+}{\cdot}2HCO_2^-)_n$] (middle left; 99% ^{13}C-enriched HCO_2^- is shown in the dashed curve), and n-Si[$(PQ^{2+}{\cdot}2CO_3H^-)_n$] (middle right). The bottom spectra are difference spectra showing the difference between the Cl^--compensated and HCO_2^--compensated polymer (left) and the difference between the Cl^--compensated the CO_3H^--compensated polymer (right).

and at least 30 min prior to data acquisition. Typically, 512 interferograms at 2-cm^{-1} resolution were collected. Prior to transforming, the interferograms were corrected for problems stemming from the mismatch of the refractive index of the sample and N_2.

Results and Discussion

Figure 1 shows the cyclic voltammetry responce response of a Pt electrode derivatized with about 5 × 10^{-8} mol/cm^2 of PQ^{2+} from reagent I. Data are given for three electrolytes in Figure 1, showing that the cyclic voltammetry response associated with the interconversion of the PQ^{2+} and PQ^+ states of the immobilized polymer is essentially unaffected by the variation in anion among CO_3H^-, HCO_2^-, and Cl^-. Both the peak shapes and the peak currents at a given sweep rate are nearly the same for the three-electrolyte systems. These data lead to the conclusion that the anions under consideration are capable of rapidly moving in and out of the immobilized polymer. The crucial fact is that the sweep rate dependence of the cyclic voltammograms is nearly the same for the three electrolytes shown, meaning that the overall kinetics associated with polymer oxidation and reduction are the same. The reduction of $(PQ^{2+})_n$ to $(PQ^+)_n$ must be accompanied by the movement of anions out of, or cations into, the immobilized polymer in order to maintain charge balance in the polymer coating. Experiments with anionic metal cyanide complexes in the electrolyte show that the cyclic voltammetry waves of the polymer are severely distorted when a charge-compensating anion does not move in and out of the polymer with good kinetics.[9,10] Lack of an effect on the cyclic voltammetry upon variation in the anion among Cl^-, CO_3H^-, and HCO_2^- is in accord with the conclusion that the charge-transport properties of $[(PQ^{2+/+})_n]_{surf}$ are the same in the three media considered. Thus, it can be concluded that all three anions can move in and out of the polymer with facility. The rate of oxidizing and reducing the polymer is known to be fast for weakly bound anions, e.g. Cl^-,[9,10] and HCO_2^- and CO_3H^- appear to be no exception.

The similarity in the average positions of the cathodic and anodic current peaks in the three different electrolytes shown in Figure 1 permits an important conclusion regarding the anion binding. The average position of the anodic and cathodic current peaks is taken to be the formal potential of the immobilized polymer. For the three electrolytes illustrated the formal potential is thus nearly the same. This fact is consistent with the conclusion that the three anions considered are equally firmly bound in the two redox levels of the polymer, the 2+ and 1+ states. Accordingly, we have made quantitative studies of the relative binding of the anions to the 2+ state of the polymer. Direct studies of the 1+ state are not possible, owing to the extreme O_2 sensitivity of the reduced polymer.

FTIR spectroscopy of derivatized n-type Si has been used to establish the relative importance of anion binding in $[(PQ^{2+})_n]_{surf}$ for the anions Cl^-, CO_3H^-, and HCO_2^-. Figure 2 illustrates spectra for relevant electrodes. The top spectra show the transmission of n-Si/$[(PQ^{2+}\cdot 2Cl^-)_n]_{surf}$ with N_2 as the reference. Since the Cl^- ion is IR-silent, the transmission spectrum of such an assembly is that of the polymer and Si. The Si itself shows no absorption, but Si is known to have an oxide layer between the Si and the polymer. The oxide absorption is associated with the 610-cm^{-1} absorption band. For a given electrode this band is regarded as a standard. The sharp and relatively strong feature at 1637 cm^{-1} is an absorption of the polymer. Assuming that the IR spectrum of the polymer is not significantly affected by the nature of the charge-compensating anion(s), the differences between spectra of the Cl^--compensated assembly and an assembly with IR-active anions must be due to anions. Thus, the difference in the spectrum of the n-Si/$[(PQ^{2+}\cdot 2HCO_2^-)_n]_{surf}$ and that of the Cl^--compensated polymer shows the strong absorption of HCO_2^- at 1591 cm^{-1} (Figure 2). The actual transmission spectrum of the HCO_2^--compensated polymer shows the HCO_2^- absorption very clearly. Additionally, if the polymer is charge-compensated with 99% ^{13}C-enriched HCO_2^-, the strong absorption is at 1548 cm^{-1}, consistent with the mass effect on the C–O stretch. Unfortunately, the IR spectrum of the CO_3H^--compensated material does not clearly show the absorption of the charge-compensating anion; the 1637-cm^{-1} absorption of the polymer is in the same region as the strong absorption of CO_3H^-. Moreover, the absorption of CO_3H^- is not as strong as that of HCO_2^-, and quantitative measurements are difficult to obtain. Nonetheless, when a given electrode is measured with HCO_2^- compensation vs. CO_3H^- compensation, the differences are clear, and good, quantitative data can be obtained with respect to the quantity of one ion vs. another in the polymer.

One issue that is difficult to resolve is whether the binding of CO_3H^- into the cationic polymer changes the pK_a and/or the hydrogen ion activity to a degree sufficient to change the distribution of CO_3H^- and CO_3^{2-} compared to that in solution. Study of the binding of CO_3^{2-} is not possible owing to the fact that the polymer is not durable in basic media. At this point we shall assume that the distribution of CO_3H^- and CO_3^{2-} in the polymer is the same as in solution, mainly CO_3H^-. This assumption appears to be valid because the IR spectrum of the charge-compensating ion from equilibration of the polymer in $Na[CO_3H]$ closely resembles that of $Na[CO_3H]$ examined as a KBr pellet. The spectrum of the bound material differs considerably from that of $Na_2[CO_3]$, also recorded as a KBr pellet. Thus, IR spectroscopy confirms that the charge-compensating ion is CO_3H^- when derivatized electrodes are equilibrated with aqueous $Na[CO_3H]$.

Figure 3 is representative of the quantitative FTIR spectroscopy that can be done to assess the relative binding of CO_3H^- and HCO_2^-. The spectrum at the bottom is for an assembly equilibrated with Cl^-, and the others are for the same assembly equilibrated with different solutions. The spectra in Figure 3 labeled b–f are for an electrode equilibrated in an aqueous solution containing a total concentration of CO_3H^- and HCO_2^- of 1.0 M. The mole fraction of HCO_2^- in solution is denoted by X_f. As shown by the spectra, the absorption associated with HCO_2^- grows in strength as the mole fraction of HCO_2^- in the solution increases. Quantitative evaluation of the spectral changes allows a determination of the relative amounts of CO_3H^- and HCO_2^- in the polymer. The experiment was also done with a total concentration of 0.1 and 3.0 M of the C-containing anions. All experiments involved the use of the Na^+ salts of the anions except for the experiments at 3.0 M, where the Cs^+ salt of CO_3H^- is required to achieve the high concentration. The quantitative data are summarized by the graphs in Figure 4, which show the relationship between the mole fraction of HCO_2^- in solution, X_f, and the mole fraction of HCO_2^- in the polymer, Γ_f. The data points for Figure 4 are determined from data like those shown in Figure 3. The data in Figure 3 allow determination of Γ_f. The values of Γ_f for Figure 4 are determined by measuring the absorbance at 1590 cm^{-1}, an isosbestic point (cf. Figure 3), for various values of X_f used. Since both $X_f = 0$ and $X_f = 1.0$ give defined values of Γ_f, 0 and 1.0, respectively, intermediate values of Γ_f at various values of X_f can be quantitatively measured. Figure 4 shows graphs of data from experiments involving the equilibration of electrodes in solutions of CO_3H^- and HCO_2^-. Similar data have also been obtained for the equilibration of electrodes in solutions of Cl^- and HCO_2^-, and the results at an ionic strength of 1.0 M are included in Figure 4.

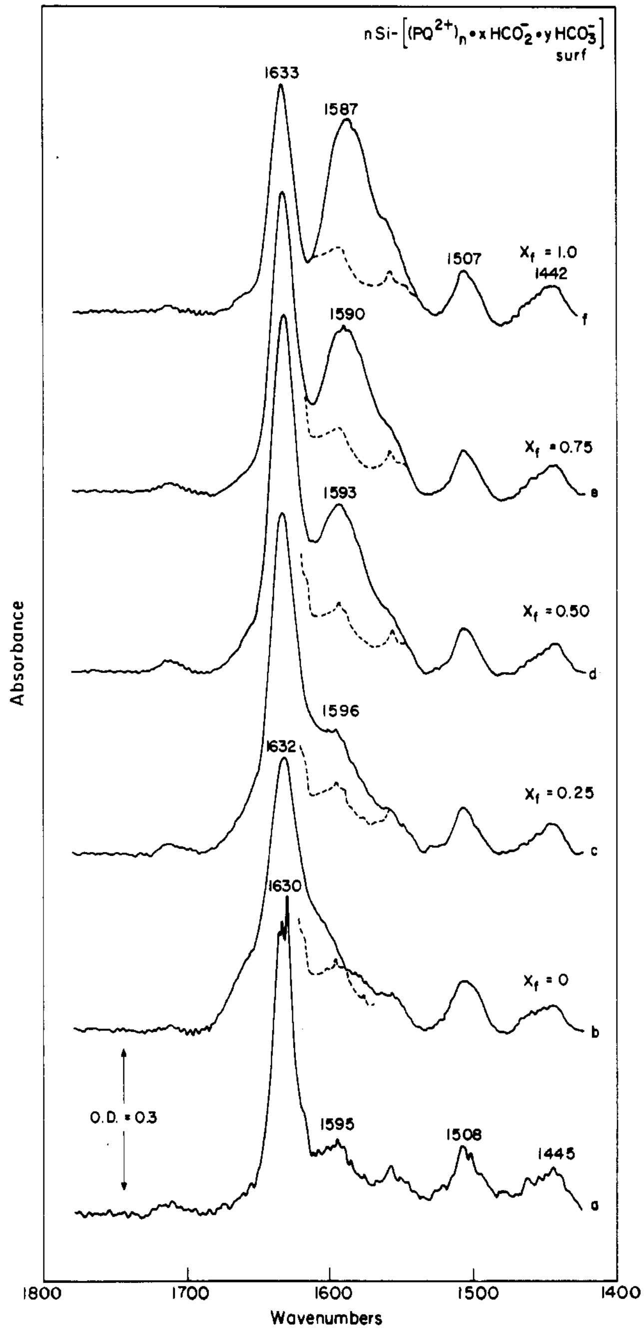

Figure 3. FTIR spectra of n-Si$[(PQ^{2+})_n]$ equilibrated in (a) 1.0 M NaCl, (b) 1.0 M $Na[CO_3H]$, (c) 0.75 M $Na[CO_3H]$/0.25 M $Na[HCO_2]$, (d) 0.50 M $Na[CO_3H]$/0.50 M $Na[HCO_2]$, (e) 0.25 M $Na[CO_3H]$/0.75 M $Na[HCO_2]$, and (f) 1.0 M $Na[HCO_2]$. The mole fraction of HCO_2^- in the polymer can be determined by measuring the absorbance difference at the maximum of the HCO_2^- absorbance where the Cl^-- and the CO_3H^--compensated polymers absorb nearly the same.

The plots in Figure 4 stem from the observation of the mole fraction of HCO_2^- in the polymer at a given value of X_f. The exchange equilibrium is represented by eq 1, where A_s and B_s are

$$A_s + B_p \rightleftarrows A_p + B_s \qquad (1)$$

the monoanions in solution and A_p and B_p are the charge-compensating monoanions bound in the polymer. The equilibrium constant for the process is given by eq 2[14] when the activity

$$K_{eq} = [A_p][B_s]/[A_s][B_p] \qquad (2)$$

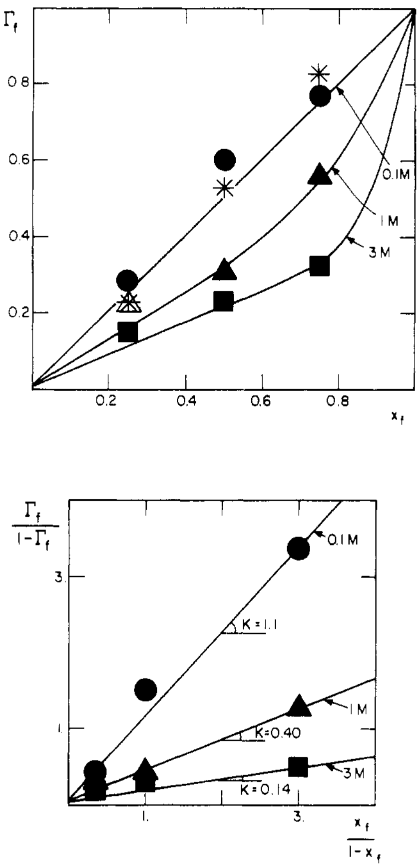

Figure 4. Relationships of the mole fraction of HCO_2^- bound in the polymer vs. the mole fraction of HCO_2^- in solution X_f. The circles, triangles, and squares are data for the uptake of HCO_2^- against CO_3H^- at a total anion concentration of 0.1, 1.0, and 3.0 M, respectively. The asterisks are data for a separate experiment involving the uptake of HCO_2^- against Cl^- at 1.0 M total anion concentration in the solution.

coefficients are 1 for the various species. Experimentally, we have determined the mole fraction of HCO_2^- in the polymer, Γ_f, as a function of the mole fraction of HCO_2^- in solution (Figure 4). It can be shown that K_{eq} is also given by eq 3; the plots in the

$$K_{eq} = [(1 - X_f)/X_f][\Gamma_f/(1 - \Gamma_f)] \quad (3)$$

lower half of Figure 4 thus give the values of the equilibrium constants for the binding of the monoanions considered. As can be seen, the HCO_2^- and Cl^- ions bind equally firmly at a total ionic strength of 1.0 M. Within experimental error the value of K_{eq} is 1. However, the binding of CO_3H^- is superior to that of HCO_2^- at 1.0 M and even more so at 3.0 M. At the lowest ionic strength the equilibrium data show no preference for binding any one of the three ions. Variation in the selectivity of ion binding with variation in ionic strength is commonly encountered for ion-exchange systems.[14]

The equilibrium constants given in Figure 4 are for the uptake of HCO_2^- into the polymer against polymer-bound CO_3H^-. Despite the fact that the formation of the polymer from I is a complicated process, we find little variation from electrode to electrode in terms of the relative binding of ions. The procedures used produce polymers having reproducible ion-binding properties. At high ionic strength there is clearly a tendency to charge compensate the polymer with CO_3H^-. This fact suggests there is consequence in the use of high concentrations of CO_3H^- in electrochemical reduction of aqueous CO_2 with electrodes represented by Scheme I.[3] The selective binding of the oxidized form of the redox couple provides a relatively high activity of redox-active material in the catalytic zone up to large extent conversions to HCO_2^-, but of course, the firmer binding of the oxidized species means that the reducing power required is somewhat greater. The preference for binding, though, is less than a factor of 10 in favor of CO_3H^- and adds relatively little to the reduction voltage needed in the production of HCO_2^-. There would appear to be value, especially in photoelectrochemical reduction of CO_3H^-, in maintaining as high a concentration of the redox-active species as long into the reaction as possible. This is especially important in a photoelectrochemical reduction, because the aim is to produce reduction products at a rate only controlled by the light intensity even though the process is carried out at controlled potential. In conventional controlled-potential processes the current goes down as the redox reagent is consumed. The energy conversion efficiency does not suffer because the current goes down with declining concentration of redox reagent. In photoconversion processes there is loss in optical energy conversion efficiency when the observed rate becomes controlled by reagent concentration and not by the photoexcitation rate. The fast rate of exchange of the HCO_2^- and CO_3H^- anions, inferred from the sweep rate independence of the cyclic voltammetry in various media, and the slight preference for the CO_3H^- ion are positive features of the $[(PQ^{2+}\cdot Pd(0))_n]$ catalyst assembly[3] for the reduction of aqueous CO_2.

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. J.-F.A. was a Postdoctoral Fellow supported by the Swiss National Science Foundation, 1983–1985.

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