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Mass Transport in Polyacetylene and Polypyrrole Measured by Ion Self-Exchange

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Abstract: The diffusional mass transport of ions in partially oxidized (doped) polyacetylene, $[CH]_x$, and polypyrrole, PPy, was studied using radioactive ClO_4^- self-exchange. In both cases, under the conditions used, exchange kinetics are described by finite, planar Fickian diffusion, which for $[CH]_x$ implies that ion transport is best represented by movement through a composite medium of $[CH]_x$ fibrils and electrolyte in voids. The diffusion coefficient for ClO_4^- in $[CH(ClO_4)_{0.054}]_x$ at 30 °C using propylene carbonate is $(2.8 \pm 0.3) \times 10^{-8}$ cm^2 s^{-1}, and is independent of sample thickness and solution ion concentration. The activation energy and entropy for diffusion in $[CH]_x$ are 6.4 kcal mol^{-1} and +20 cal K^{-1} mol^{-1}, respectively. Exchange kinetics for both polymers show a small dependence on anion but a very marked dependence on solvent. Perchlorate ion in polypyrrole has diffusion coefficients using H_2O, acetonitrile, and propylene carbonates of 4.2×10^{-8}, 3.6×10^{-10}, and 3×10^{-13} cm^2 s^{-1}, respectively, which are in agreement with diffusion coefficients previously obtained by other means in the presence and absence of an electric field.

Much work has been devoted to the study of electronic charge transport through polymeric materials containing extended π-conjugated backbones. Notable examples of these, so-called, "conducting" polymers include polyacetylene,[1] poly(*p*-phenylene),[2] and the more stable polypyrroles[3] and polythiophenes.[4] These polymers, having filled valence bands, acquire charge carriers upon oxidation or reduction by chemical or electrochemical means to attain electrical conductivities up to 10^3 Ω^{-1} cm^{-1}. Whereas a huge amount of work has been done to characterize the mobilities of these charge carriers under various conditions,[1,5] relatively little attention has been given to the process by which counterions, required for electroneutrality, move through the polymer bulk during the oxidation or reduction process. Many of the promising practical applications of conducting polymers take advantage of their reversible electrochemistry. Included in the possible uses for conducting polymers which involve redox reactions are battery electrodes, electrochromic displays,[6] "ion gate" membranes,[7] microelectronic devices,[5a,8] and media for controlled release.[9] Although each of these applications involves a very different conceptual approach, they all require the mass transport of counterions through the polymer matrix, which often proves to be the rate-limiting process.

Ion exchange of anion A in a partially oxidized conducting polymer, P, with anion B in solution is represented by

$$(PA_y)_x + xyB^- \rightleftharpoons (PB_y)_x + xyA^- \qquad (1)$$

Preliminary results using perchlorate-containing polyacetylene and hexafluoroarsenate as the exchanging ion showed that ion exchange was rapid, reversible, and quantitative if a large excess of B^- was used. These observations encouraged us to use ion self-exchange:

$$[PA_y{}^*]_x + xyA^- \rightleftharpoons [PA_y]_x + xyA^{-*} \qquad (2)$$

where A^{-*} is the radiolabeled counterion to address several questions regarding ion mobility in conducting polymers. First, there is confusion concerning the actual magnitude of the diffusion coefficient for ionic species in polyacetylene. Estimates range from 10^{-9} to 10^{-18} cm^2 s^{-1}.[10,11] The aim of the present work was to define the correct morphological picture for exchange in $[CH]_x$ and the appropriate mathematical expressions to describe the process. Burgmayer and Murray[7b] have made rough estimates of anion diffusion coefficients in polypyrrole by measuring permeation rates and dc conductivity through the polymer as a membrane. Better precision and sensitivity is offered by the simplicity of experimental technique and theoretical treatment of self-exchange. Second, in many cases there are several effects that obscure the picture of clear Fickian diffusion. For instance, there is a question as to whether ion movement is aided by the presence of an electric field.[12] This migration current has been invoked to explain higher-than-expected rates of polyacetylene discharge in batteries.[13] Further, if a reactive species, such as iodine, is used to follow diffusion, there is the added complication of simultaneous chemical reaction.[10] The zero-current technique of ion exchange,[14] in particular self-exchange, of unreactive anions avoids problems due to electric fields, electrochemical gradients, and simultaneous chemical reaction. Third, if conducting polymers are to be considered as media for the controlled release of drugs, as demonstrated by the release of glutamate ion from polypyrrole upon reduction of the polymer,[9] it is important that the ionic drug does not exchange spontaneously with other ions prior to the application of the drug-delivering electrochemical pulse.

Although ion transport in conducting polymers has been sparsely treated, much work has been done on mass and charge transport through electroactive or "redox" polymer films on electrodes[15,16]

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and other types of polymer-modified electrodes, such as those coated with the ion-exchanging Nafion.[17] It is of interest to compare ion transport in redox polymers and conducting polymers since, though both types of polymer show electrochemical activity, there are several important conceptual differences between them. For example, conducting polymers typically have a variable concentration of charge carriers on an extended, conjugated π-system along the backbone, whereas redox polymers, such as polyvinylferrocene,[15a,d] contain a fixed concentration of electroactive species anchored to the polymer backbone. The physical properties of the former depend to a great degree on the charge concentration.[5b,c] The conductivity in conducting polymers at high charge concentration is many orders of magnitude greater than in redox polymers, allowing free-standing films of conducting polymers to be used in electrochemical experiments. The mechanism of charge conduction (or propagation) is also different: contacts to metal are ohmic and conduction through bulk polymer is ohmic in conducting polymers[18,19] whereas charge transport through redox polymer films can be described by Fick's law[15a,d,16g,20] and only occurs if the potential of the supporting electrode is properly poised.[16h]

As a final incentive for this work on the novel use of conducting polymers as ion-exchange media with capacities that can be varied by changing the extent of oxidation, it was desired to examine the effect on conductivity of changing the counterion or "dopant" ion which can easily be done by immersing the polymer in solutions of different ions.

Experimental Section

Materials and Film Preparation. Neutral films of polyacetylene, $[CH]_x$, ca. 0.1 mm thick, were prepared by the method of Ito et al.[21] These films contain a loosely packed network of polyacetylene fibrils about 20 nm in diameter and have approximately 60% void volume. Propylene carbonate (Burdick and Jackson) and sulfolane (Aldrich) were vacuum distilled from calcium hydride and NaOH pellets, respectively. Acetonitrile, methylene chloride, and toluene (all Fisher, HPLC grade) were cryogenically distilled from 3A molecular sieves. Organic solvents were degassed on the vacuum line. Pyrrole monomer (Aldrich) was passed over neutral activated alumina prior to use. Water was of distilled, deionized grade. $LiClO_4$ (Aldrich) was melt-dried under vacuum. $LiAsF_6$ was used as received from U.S. Steel. $LiBF_4$ (Aldrich), $LiCF_3SO_3$, and Bu_4NClO_4 (both from Alfa) were vacuum-dried at 90 °C for 24 h. Organic electrolytes were prepared and stored in a Vacuum Atmospheres drybox containing argon. Polyacetylene was handled exclusively in the drybox except when aqueous electrolytes were used in which case an argon blanket was provided.

Radiolabeled electrolyte for $[CH]_x$ oxidation was made by adding an appropriate aliquot of 99% radioisotopically pure $Li^{36}ClO_4$ in water (ICN Radiochemicals) to $LiClO_4$ powder prior to drying, then adding propylene carbonate to give a 0.41 M $LiClO_4$ solution of specific activity 1.71 mCi/mol. Electrolyte for pyrrole polymerization contained perchlorate at 1.80 mCi/mol activity. Electrical conductivities were measured using the four-probe technique. Film thickness was determined, to ± 3 μm, with a micrometer.

Polyacetylene containing labeled perchlorate was typically prepared in the drybox by making electrical contact with the Pt wire to one end of a ca. 2 cm × 10 cm piece of *cis*-$[CH]_x$ film and oxidizing it at 4.0 V vs. Li in the above electrolyte using a PAR 173 potentiostat. A Li counter electrode separated by a glass frit was also used. A period of about 4 h was sufficient to ensure that $[CH]_x$ was oxidized homogeneously to the maximum level possible at this potential. Films were then rinsed with pure propylene carbonate, then toluene, and were then pumped dry under vacuum. The level of oxidation was 5.4 mol %, i.e., $[CH(ClO_4)_{0.054}]_x$, as determined separately to an accuracy of $\pm 5\%$ by elemental analysis and by counting dried films with gas proportional counter. The electrical conductivity of films after oxidation was about 800 Ω^{-1} cm^{-1}.

Pyrrole was electrochemically polymerized using a method adapted from that of Wynne and Street:[22] films were grown at 0 °C on vitreous carbon using an electrolyte of 0.15 M $(n\text{-}Bu_4N)ClO_4$, 0.2 pyrrole in propylene carbonate/1% water at a current density of 0.8 mA/cm^2 for 6 h. Strong, smooth films of PPy of about 60 μm thickness resulted. PPy polymerized thus is already in the partially oxidized form. The level of oxidation $[(C_4H_3N)(ClO_4)_{0.31}]_x$ was determined to within 5% both from the specific activity of the film and from elemental analysis. The conductivity ranged from 40 to 50 Ω^{-1} cm^{-1}. Since PPy is far more environmentally and thermally stable than polyacetylene, films were prepared and handled on the lab bench without special precautions to exclude air.

Ion-Exchange Procedure. Approximately 5 mg of labeled film was soaked for 15 min in pure solvent in order to ensure that the polymer was fully swollen before exchange. Films were then dabbed with a Kimwipe and immediately immersed in a 2-dram vial containing ca. 4 mL of unlabeled electrolyte and a magnetic stirbar. Ca. 200-μL aliquots of solution were then removed with a dropping pipet at various intervals and placed into preweighed scintillation vials. The exact volume was determined by weighing, and 5 mL of scintillation cocktail [4.0 g L^{-1} of 2,5-diphenyloxazole/0.2 g L^{-1} of 1,4-bis(5-phenyl-2-oxazolyl)benzene/80% toluene/20% propylene carbonate] was added. It was found that up to 10% of propylene carbonate significantly increased the counting efficiency, but the efficiency leveled off with more propylene carbonate. A Beckman LS100C scintillation counter was used for assay of ^{36}Cl by the ^{32}P channel (^{36}Cl is a β emitter, 0.7 MeV, $t_{1/2} = 3.1 \times 10^5$ yr); the counting error was usually less than 1%. In the cases where the fraction exchanged was less than about 0.1, the error ranged up to 3%. For exchanges in aqueous solution, the aliquots were taken to dryness in a vacuum oven at 150 °C before the addition of cocktail since water quenches the scintillation. When using volatile solvent it was essential to keep the exchange vial and scintillation vials capped to reduce its loss by evaporation. At the end of an exchange period the amount of labeled perchlorate remaining in films was determined by gas proportional counting. Exchanges were performed at 30 °C unless otherwise stated.

Theory

The exchange process across the polymer/electrolyte interface is considered to be non-rate-limiting.[14] The boundary conditions[14a] chosen for the present work are as follows: A^{-*} (labeled perchlorate) is initially uniformly distributed throughout the exchanging medium, the surface concentration of A^{-*} is maintained at zero, and the concentration ion of A^{-*} in the exchanger is zero as $t \rightarrow \infty$ since B^- is in infinite excess of A^-. The last two conditions were approximated by adding at least a 100-fold excess of B^- (or nonradiolabeled A^-). The fraction exchange, f, is defined by

$$f = \frac{\text{activity released at time } t}{\text{total activity in polymer at } t = 0}$$

The exact solution for the entire exchange, depending on the model chosen (see below), is

$$f = 1 - \frac{8}{\pi^2}\sum_{n=0}^{n=\infty}\frac{1}{(2n+1)^2}\exp\left[-\left(\frac{(2n+1)\pi}{h}\right)^2 Dt\right] \quad (3)$$

for planar geometry,[23] where h is the thickness of the film and n is an integer. For cylindrical geometry,[23]

$$f = 1 - \sum_{1}^{\infty}\frac{1}{E_v^{\,2}}\exp\left[-\frac{E_v^{\,2}Dt}{r^2}\right] \quad (4)$$

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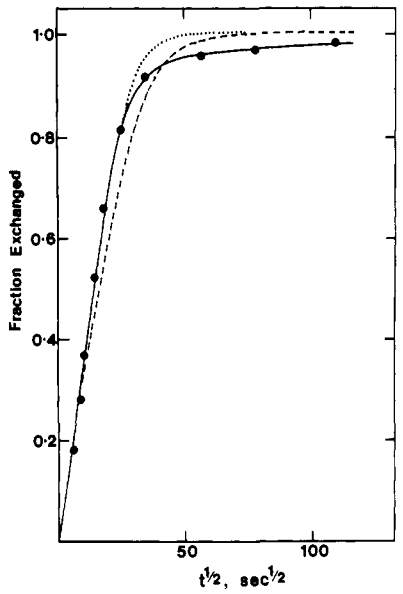

Figure 1. Self-exchange of $^{36}ClO_4^-$ in $[CH(ClO_4)_{0.054}]_x$ for unlabeled ClO_4^-, 1 M, in propylene carbonate at 30 °C as fraction exchanged vs. $t^{1/2}$: solid curve, experimental data; dashed curve, theoretical for finite cylindrical diffusion assuming average radius, 1.0×10^{-6} cm, $D = 2.6 \times 10^{-16}$ cm^2 s^{-1}; dotted curve, theoretical for finite planar diffusion assuming thickness 101×10^{-4} cm; $D = 2.6 \times 10^{-8}$ cm^2 s^{-1}.

where r is the radius of a polymer fibril and E_v's are the roots of the Bessel function of zero order. At short time, both eq 3 and 4 reduce to the form for semiinfinite planar diffusion:

$$f = \frac{4D^{1/2}t^{1/2}}{\pi^{1/2}(r,h)} \tag{5}$$

where the choice of h or r depends on the model. Diffusion coefficients are thus readily extracted from the slope of the initial portion of a plot of f vs. $t^{1/2}$.

Results and Discussion

Polyacetylene. The progress of self-exchange in polyacetylene using a 1 M $LiClO_4$/propylene carbonate electrolyte at 30 °C is illustrated by the f vs. $t^{1/2}$ plot in Figure 1. The general features are good linearity at short times, small scatter of experimental points (precison is estimated at ±3% or better), and nearly quantitative exchange within about an hour. Curves deviate from theoretical at high f because of a breakdown of the boundary condition that B^- is in infinite excess of A^-. Thus, there is typically ca. 3% residual A^- left in a 0.1-mm film after 20 h of exchange.

The correct dimension must be inserted into eq 5 to obtain meaningful diffusion coefficients. One reason there is such a discrepancy in reported diffusion coefficients stems from the choice of using film thickness[24] (ca. 100 μm) or fiber radius[11] (ca. 10 nm) as the appropriate dimension, which leads to eight orders of magnitude difference in the calculated diffusion coefficient.

Diffusion of anions from the interior of a $[CH]_x$ film to bulk solution can be described by two limiting mechanisms. The first supposes that solid-state diffusion through single polymer fibrils (10 nm) is extraordinarily slow (on the order 10^{-18} cm^2 s^{-1}), and once an anion leaves a polymer fibril it is swept into bulk solution by relatively rapid diffusion through void electrolyte. The void concentration of labeled perchlorate is therefore maintained at the external solution concentration, which is zero in the present case. The second mechanism considers diffusion through a macroscopic film (0.1 mm) comprised of a composite medium of polymer fiber and void electrolyte; anions encounter numerous polymer/electrolyte interfaces before arriving at bulk solution. The resulting effective diffusion coefficient represents the net effect of movement through these two media.

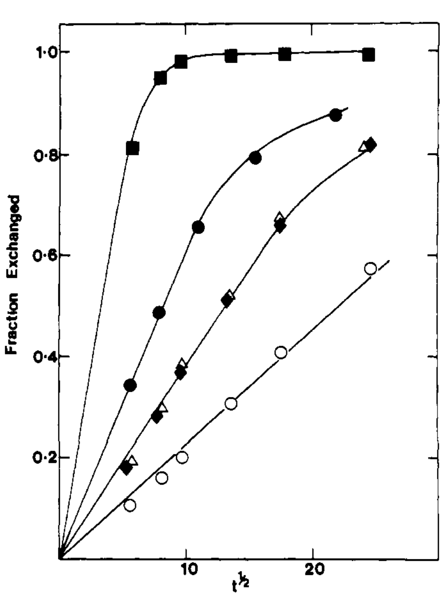

Figure 2. Self-exchange plot of fraction vs. $t^{1/2}$ for $[CH(^{36}ClO_4)_{0.054}]_x$ in 1 M $LiClO_4$/PC: film thickness (mm) 0.063 (●), 0.100 (♦), and 0.165 (○); in 0.2 M $LiClO_4$/PC, film thickness 0.101 mm (△). Exchange of $^{36}ClO_4^-$ in void space only, film thickness 0.150 mm (■).

Table I. Self-Exchange of Perchlorate in Polyacetylene at 30 °C

polymer	electrolyte	film thickness, mm	$D \times 10^8$, cm^2 s^{-1}
$[CH(ClO_4)_{0.054}]_x$	1 M $LiClO_4$/PC	0.063	2.8
$[CH(ClO_4)_{0.054}]_x$	1 M $LiClO_4$/PC	0.100	2.9
$[CH(ClO_4)_{0.054}]_x$	1 M $LiClO_4$/PC	0.165	2.7
$[CH(ClO_4)_{0.054}]_x$	0.2 M $LiClO_4$/PC	0.101	2.8
$[CH]_x$	1 M $LiClO_4$/PC	0.150	100

Although the second of these models is conceptually the correct one, since the probability that an anion will travel the tortuous path through the voids in the polymer matrix without encountering a fibril is infinitesimal, the correct model was determined unequivocally as follows. First, the data in Figure 1 were fit over the whole range using eq 3 and 4, which are for planar and cylindrical geometries corresponding to the geometries of the macroscopic film and the microscopic fibril, respectively (the expansion was limited to the first six terms). Better fit is obtained with the planar model in the region $f < 0.9$, where the boundary conditions are maintained. Second, the diffusion coefficient was determined as a function of film thickness, which yields more definitive support for the planar model than does the curve fitting. Figure 2 shows the results of exchange using film from 0.06 to 0.16 mm thick. Table I summarizes the findings that the diffusion coefficient has the same calculated value over the range when film thickness is used as the dimension parameter in eq 5. To rule out the possibility that fibril diameter changes in proportion to film thickness, as demonstrated in certain preparations of $[CH]_x$,[25] the specific surface area, A_s of $[CH]_x$ was determined as a function of film thickness. The average fibril diameter, d, is related to A_s by $d = 4/\rho A_s$, where ρ is the density (1.2 g cm^{-3}) of $[CH]_x$. Figure 3 demonstrates that specific surface area, determined by low-temperature BET, remains constant at 57 ± 4 m^2 g^{-1} over the whole range of thicknesses. The correct model is thus the planar one, and the appropriate dimension is the thickness of the film.

Rate-Limiting Component for Diffusion in the $[CH]_x$ Mixed-Medium. Ideally, one would like to know the individual coefficients for diffusion through each of the two components of the polyacetylene mixed medium. Since diffusion is a combination of parallel and series resistance to movement, in that ions can go through or around $[CH]_x$ fibrils on a microscopic scale, an explicit analytical expression involving individual coefficients is not

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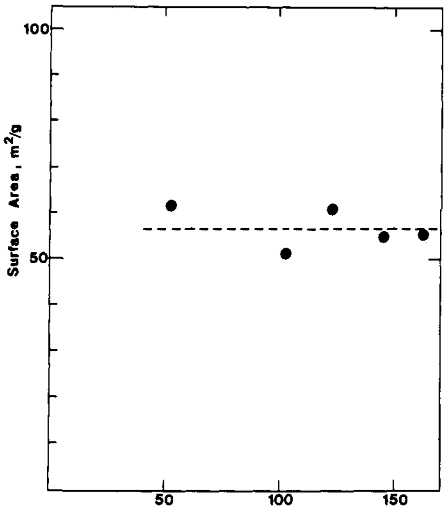

Figure 3. Variation of specific surface area of $[CH]_x$ with film thickness as determined by five-point BET.

available. However, the relative magnitudes can be estimated by performing exchange on $[CH]_x$ with ions that move through void spaces only. This is easily done by following self-exchange of undoped $[CH]_x$ soaked in electrolyte containing labeled perchlorate. Ions are excluded from $[CH]_x$ fibrils since there are no positive charges; 1 M $Li^{36}ClO_4$ in propylene carbonate electrolyte was imbibed into the ca. 60% void volume of undoped $[CH]_x$ by immersing the film into the electrolyte for a minute. The polymer absorbs electrolyte rapidly, as evidenced by the fact that the sample sinks in the electrolyte within a couple of seconds. The film was then removed, excess electrolyte was scraped off with a razor blade, and the sample was immersed into unlabeled 1 M $LiClO_4$ for exchange. The results for this exchange are given in Figure 2. The calculated diffusion coefficient is about 10^{-6} cm^2 s^{-1}, a reasonable value for D in an organic solvent. That both ions and solvent do not enter the polymer fibrils themselves is supported by the observation that undoped $[CH]_x$ does not swell at all (there is less than 0.2% change in length) when immersed in electrolyte. Dried films of doped $[CH]_x$, however, swell about 6% in volume when immersed in propylene carbonate. Diffusion through voids only is thus faster than diffusion in the mixed medium, which implies, not surprisingly, that diffusion through $[CH]_x$ fibrils is slower than through electrolyte.

Exchange in $[CH]_x$ is controlled by mass transport in the polyacetylene film mixed medium (referred to as "particle exchange" in the terminology of classical ion exchangers[14,26]) rather than solution transport of ions to the film, as prescribed[14] by the following evidence: (1) the expected dependence of f on $t^{1/2}$ rather than e^{-t}; (2) the inverse porportionality of f to h^2 rather than h; (3) the exchange rate being independent of solution concentration over the range 0.1 to 1.0 M, as shown in Figure 2 by the example of exchange using 0.2 M $LiClO_4$.

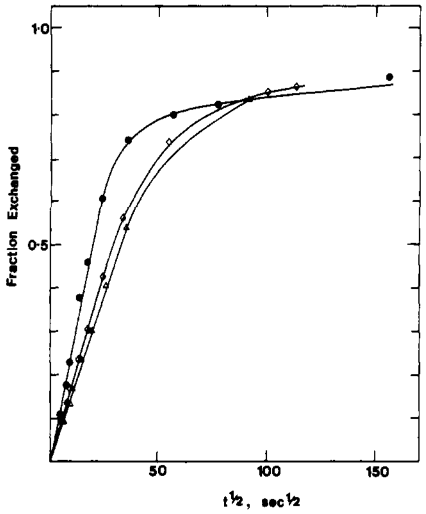

Figure 4. Plot of fraction exchanged against $t^{1/2}$ for $[CH(ClO_4)_{0.054}]_x$ using different anions in propylene carbonate. See Table II for conditions: AsF_6^- (△), BF_4^- (●), and $CF_3SO_3^-$ (◇) with thickness (mm) 0.125, 0.155, and 0.155, respectively.

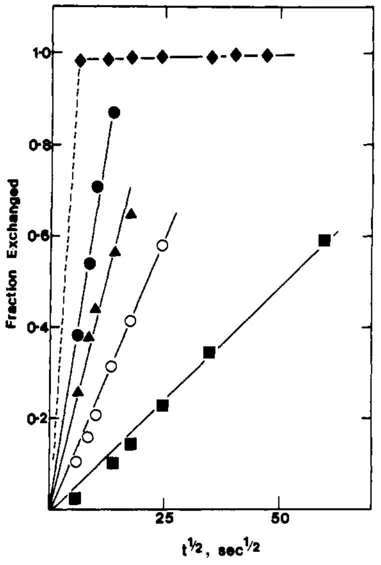

Figure 5. Plot of fraction exchanged against $t^{1/2}$ for perchlorate self-exchange in $[CH(ClO_4)_{0.054}]_x$ in different solvents. See Table II for conditions: H_2O (◆), acetonitrile (●), methylene chloride (▲), propylene carbonate (○), sulfolane (■); thickness (mm) 0.146, 0.150, 0.144, 0.165, 0.166, respectively.

Table II. Diffusion Coefficients of Ions in $[CH]_x$ and Polypyrrole Using Different Solvents, 30 °C

polymer[a]	electrolyte	ion	10^8D, cm^2 s^{-1}
$[CH]_x$	1 M $LiClO_4$/PC	ClO_4^-	2.8
$[CH]_x$	0.5 M $LiBF_4$/PC	BF_4^-	2.9
$[CH]_x$	0.5 M $LiCF_3SO_3$/PC	$CF_3SO_3^-$	1.3
$[CH]_x$	1 M $LiAsF_6$/PC	$LiAsF_6$	0.86
$[CH]_x$	1 M $LiClO_4$/SL	ClO_4^-	0.51
$[CH]_x$	1 M $LiClO_4$/PC	ClO_4^-	3.0
$[CH]_x$	0.5 M Bu_4NClO_4/$MeCl_2$	ClO_4^-	7.1
$[CH]_x$	0.5 M Bu_4NClO_4/ACN	ClO_4^-	19.7
$[CH]_x$	1 M $LiClO_4$/H_2O	ClO_4^-	>100
PPy	1 M $LiClO_4$/H_2O	ClO_4^-	4.2
PPy	1 M $LiClO_4$/PC	ClO_4^-	0.036
PPy	1 M $LiClO_4$/PC	ClO_4^-	3×10^{-5}

[a] $[CH]_x = [CH(ClO_4)_{0.054}]_x$; PPy $= [C_4H_3N)(ClO_4)_{0.31}]_x$.

Effect of Anion. Polyacetylene containing labeled perchlorate was exchanged with 0.5 or 1.0 M solutions of $LiCF_3SO_3$, $LiBF_4$, or $LiAsF_6$ in propylene carbonate. The progress of exchange as a function of $t^{1/2}$ is shown in Figure 4. The coupled interdiffusion of two different anions, A and B, diffusion coefficients D_A and D_B, can be described at any point in the exchange in terms of one diffusion coefficient, D_{AB}, by[27]

$$D_{AB} = \frac{D_A D_B (z_A^2 C_A + z_B^2 C_B)}{z_A^2 C_A D_A + z_B^2 C_B D_B} \qquad (6)$$

where z is the charge and C is the instantaneous concentration of anion in the exchanger. From eq 6 the ion present in smaller concentration has the stronger effect on interdiffusion. Thus, at the beginning of the exchange the interdiffusion coefficient will be purely that of the anion from solution. Diffusion coefficients were estimated from initial slopes in Figure 4 and are presented in Table II. Within experimental error, the diffusion coefficients

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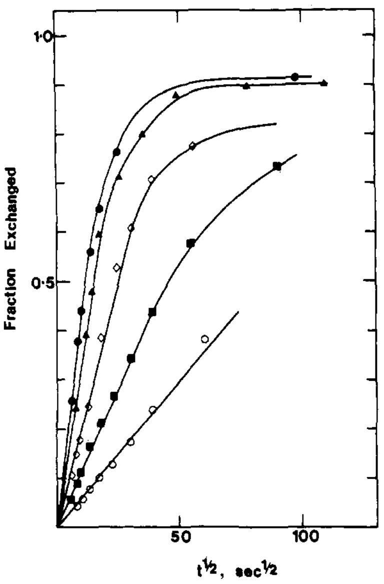

Figure 6. Dependence of exchange kinetics on temperature for self-exchange of perchlorate in $[CH(^{36}ClO_4)_{0.054})_x$ using $MeCl_2$: exchange at 30° (●), 10° (▲), −10° (◇), −30° (■), and −50 °C (○).

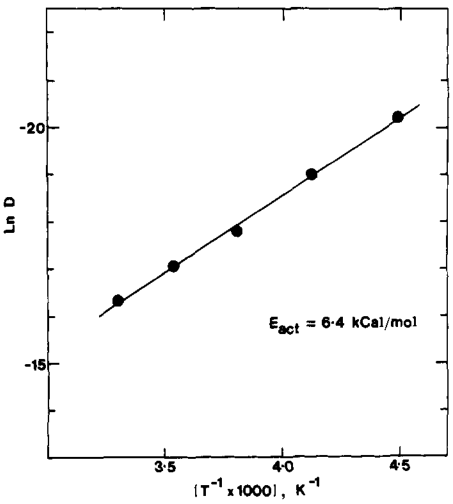

Figure 7. Arrhenius plot of variable-temperature exchange data from Figure 6.

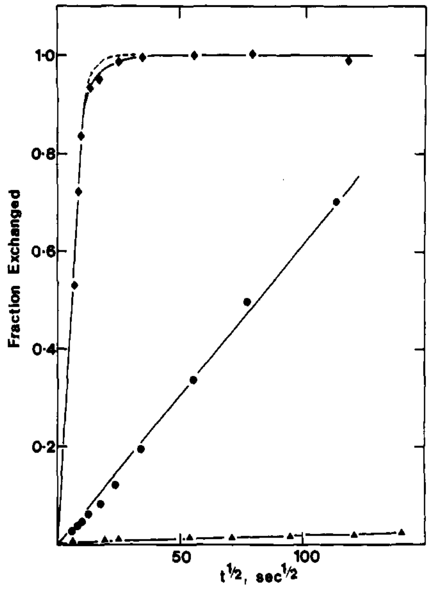

Figure 8. Fraction exchanged vs. $t^{1/2}$ plot of self-exchange of perchlorate in polypyrrole using water (♦), acetonitrile (●), and propylene carbonate (▲) electrolytes. Dotted line is theoretical for finite planar diffusion, D_{H_2O} = 4.2 × 10^{-8} cm^2 s^{-1}.

for ClO_4^- and BF_4^- are the same, whereas those for the larger AsF_6^- and $CF_3SO_3^-$ ions are smaller.

Effect of Solvent. The kinetics of exchange have a marked dependence on the solvent used. Polymer samples which were not preswollen with pure solvent had $t^{1/2}$ plots with nonzero intercepts. Figure 5 shows the effect of solvent on exchange performed on different samples of $[CH(^{36}ClO_4)_{0.054}]_x$ with perchlorate in propylene carbonate, sulfolane, acetonitrile, methylene chloride, and water. The electrolyte compositions and the calculated diffusion coefficients are given in Table II. Owing to the instability of polyacetylene in water,[28] the loss of labeled perchlorate includes, to some extent, loss by reaction of oxidized $[CH]_x$ with water. However, in the first few minutes, which is ample time for quantitative exchange as seen in Figure 5, the conductivity decreased less than 10%, demonstrating minimal degradation within this short time.

Temperature Dependence. A 0.5 M Bu_4NClO_4 in methylene chloride electrolyte was used to study the dependence of exchange kinetics on temperature from −50 to +30 °C. Exchanges were done in a 1-cm diameter tube fitted with a side arm so that a blanket of argon could be maintained during sampling. A circulating water bath or slush bath (nitromethane, *m*-xylene) was used to control temperature. Figure 6 shows the expected slowing of exchange kinetics with decreasing temperature. D follows an Arrhenius behavior:

$$D = D_0 \exp(-E_{act}/RT) \tag{7}$$

as plotted in Figure 7. An activation energy of 6.4 kcal/mol is obtained which falls in the range 6–8 kcal/mol determined for an anion exchanger based on polystyrene–divinylbenzene copolymers.[29] The preexponential factor, D_0, as formulated by Eyring,[30] is

$$D_0 = ed^2(kT/h) \exp(\Delta S^*/R) \tag{8}$$

where d is the diffusion jump distance, e is 2.71, and $\Delta S^*\phi$ is the entropy of activation. To estimate ΔS^* it is assumed that mass transport is limited mainly by diffusion through bulk polymer, density ca. 1.2 g/cm^3. The level of oxidation is 5.5 mol % which gives a concentration of 3.5 M and a value for d of 0.78 nm. Using D_0 = 4.3 × 10^{-3} cm^2 s^{-1}, obtained by extrapolating Figure 7, ΔS^* is determined to be +20 (K mol)$^{-1}$ at 303 K. This quite large and positive entropy of activation may be interpreted to result from the distortion of segments of ordered crystalline[31] $[CH]_x$ to accommodate ion movement.

Polypyrrole Exchange. Oxidized polypyrrole exhibits far greater environmental stability than oxidized polyacetylene,[3] thus allowing the study of exchange in aqueous solutions. The advantage to using water as a solvent is that many more common inorganic salts are soluble in it than are soluble in organic solvents. Since the properties of a conducting polymer are claimed to depend on the counterion,[3,32] it is of interest to compare, for example, the electrical conductivity of polypyrrole for the same sample that is exchanged with different anions. This approach eliminates the possibility that differences in conductivity are due to different conditions of polymerization.

Polypyrrole is space-filling[3,5b,6,7,22] and thus does not possess the large specific surface area of fibrillar $[CH]_x$. Since there are no voids, exchange in PPy can be modelled by planar, finite, solid-state diffusion using eq 3. It should be noted, however, that

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the polymer is reversibly swollen by solvent.[22] For example, the extent of swelling is 5 to 10% by weight when acetonitrile is used.

Self-exchange kinetics were determined for perchlorate using 1 M $LiClO_4$ in water, acetonitrile, and propylene carbonate. The f vs. $t^{1/2}$ plots are given in Figure 8. Diffusion coefficients obtained using eq 5 are $D_{H_2O} = 4.2 \times 10^{-8}$, $D_{ACN} = 3.6 \times 10^{-10}$, $D_{PC} = 3 \times 10^{-13}$ cm^2 s^{-1} in water, acetonitrile, H_2O, and propylene carbonate, respectively. These values may be compared with $D_{H_2O} \sim 2 \times 10^{-8}$ for Cl^- estimated by Burgmayer and Murray[7b] using Cl^- permeation and DC resistance measurements, and D_{ACN} for $ClO_4^- = 2$ to 10×10^{-10} cm^2 s^{-1} obtained by Genies and Pernaut[33] using a potential-step method. The latter result was obtained under conditions where any effect due to electric-field-assisted diffusion would be manifest. The fact that the results are similar to those seen here calls into doubt the importance of the electric field effect in ion transport.

A very strong dependence of diffusion rate on solvent is seen. Since "particle diffusion" is occurring under the conditions used herein (i.e., ion exchange is not limited by solution mass transport), these results imply that the particular solvent that swells the PPy plays a major role in the transport of ions through bulk polymer. Much faster electrochemical "switching"[5a,8] can be expected in aqueous media.

Exchange of Different Ions: Effect on Conductivity. It has often been noted that partially oxidized conducting polymers containing different anions have different conductivities;[34] this has been attributed either to a fundamental effect of the nature of the counterion on conductivity[32a,34b,35] or to the method of partial oxidation of the polymer.[36] Theoretical calculations on the electronic structure of conducting polymers suggest that the geometry of the counterions will have significant effect on electronic conductivity.[37] Ion exchange affords the possibility of rapidly changing the counterion in the same sample of polymer while retaining the same level of partial oxidation of reduction. The above-mentioned effects due to differences in sample preparation can therefore be eliminated.

Preliminary experiments on polypyrrole exchanged with 0.2 M solutions of sodium or potassium salts showed that chloride and fluoride could be exchanged with $^{36}ClO_4$ to 95% completion in 10 min, while larger anions, such as dodecyl sulfate and glutamate, exchanged to an extent of only 10% in the same time. Dichromate, a dianion, did not exchange at all. In all cases the conductivity measured on dried films remained the same (to ±5%) after the exchange regardless of the counterion.

Conclusions

The kinetics of ion exchange in two conducting polymers, polyacetylene and polypyrrole, were determined by self-exchange. Mass transport is limited by diffusion in the exchanging matrix, although the solvent has a strong effect on kinetics. Conducting polymers represent a new class of exchanger with variable capacity possessing the added dimension that the same polymer can be used for exchange in both aqueous systems and organic solvents with a wide range of polarities without the modifications that are necessary for classical ion-exchange resins.[38]

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Hydrogen Environments in Calcium Phosphates: ^1H MAS NMR at High Spinning Speeds[†]

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Abstract: High-resolution ^1H NMR spectra at 200 and 500 MHz of synthetic samples of biologically relevant calcium phosphates have been obtained by using magic-angle spinning (MAS) at spinning speeds up to 8 kHz. The use of high spinning speeds eliminates the need for either isotopic dilution of samples with deuterium or multiple-pulse line-narrowing methods and provides additional structural information, which is absent in the latter two approaches. Structural water molecules in brushite ($CaHPO_4{\cdot}2H_2O$), octacalcium phosphate ($Ca_8H_2(PO_4)_6{\cdot}5H_2O$), and the model compound gypsum ($CaSO_4{\cdot}2H_2O$) yield ^1H MAS NMR spectra with spinning sidebands extending over a 100-kHz range, reflecting the strong, largely inhomogeneous character of the homonuclear dipolar coupling. Structural hydroxyl groups in a series of solid solutions of fluorohydroxyapatites ($Ca_5F_x(OH)_{1-x}(PO_4)_3$) exhibit discrete peaks whose isotropic chemical shift values can be related to different hydrogen-bonding configurations. Surface-adsorbed water molecules in these samples give rise to a resolvable peak; the weakness of the spinning sidebands associated with this peak indicates substantial isotropic mobility of the water protons on the NMR time scale. The isotropic ^1H chemical shifts of protons in calcium phosphates are shown to correlate well with the strength of hydrogen bonding, as measured by O–H···O distances. A linear correlation is observed over a chemical shift range of 0–16 ppm; the accurate data reported here agree remarkably well with ab initio calculations of hydrogen-bonded OH groups reported by Ditchfield and co-workers.

Although calcium phosphates have received much attention in a variety of different disciplines, it is their central role in biomineralization that has provided the major impetus for extensive study of this class of compounds. Calcium hydroxyapatite (HAP, $Ca_5(OH)(PO_4)_3$) is particularly important in this regard, since the mineral phase of mature bone and teeth is believed to be a defect form of hydroxyapatite containing various substitutional impurities. However, other calcium phosphates have been pro-

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