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THE DIFFUSION OF FERRICYANIDE THROUGH PERFLUORINATED IONOMER (NAFION) MEMBRANES

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ABSTRACT

The diffusion coefficient for ferricyanide anion in perfluorinated ionomer films (Nafion) have been measured. They are low enough to permit the use of ferricyanides to detect the presence of defects in such films.

INTRODUCTION

While the diffusion coefficients (*D*) and partition coefficients (*K*) of cations are usually determined in films or thin layers of the cation-exchange polymer Nafion (PFI) [1-4], those of anions are also of interest. For example, highly charged anions, such as $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$, are used as probes for determining the quality of cast PFI films on electrode surfaces, i.e., the freedom of such films from pinholes and other defects [5]. This is accomplished by measuring the current for the electrochemical oxidation of $Fe(CN)_6{}^{4-}$ or reduction of $Fe(CN)_6{}^{3-}$, e.g., at a rotating-disk electrode, with the assumption that the flux of these ions through the film approaches zero, so that the only current observed is that attributable to gaps or holes in the film. There is also interest in using PFI as a matrix for carrying out syntheses or depositions. For example, CdS can be precipitated within a PFI film by placing the film between two solutions, one containing Cd^{2+} and the other a sulfide species [6, 7]. Similarly, Prussian blue can be produced in PFI films by codiffusion of Fe^{2+}

and $Fe(CN)_6^{3-}$ [8]. The location of the precipitate layer within the film in these cases, as well as the interesting Liesegang ring structures that are sometimes observed [9], depend upon the rate of diffusion of the anionic species in the film. We thus thought it of interest to determine D for $Fe(CN)_6^{3-}$ within PFI.

EXPERIMENTAL

The diffusion coefficient of $Fe(CN)_6^{3-}$ in Nafion 115 membranes was measured by a previously described method [10]. Nafion membranes (1100 equivalent weight, 0.13 mm thick; E. I. du Pont de Nemours, Inc., Wilmington, Delaware) were cleaned by boiling in concentrated HNO_3 for 1 h and then in milli-Q reagent grade water (Continental Water Systems, El Paso, Texas) for 1 h. The membrane was clamped between two half-cells, one containing 0.10 *M* $Fe(CN)_6^{3-}$ ($K_3Fe(CN)_6$, Aldrich Chemical Co., Milwaukee, Wisconsin) and the other, an isotonic solution of 0.3 *M* KCN (Fisher Scientific, Fair Lawn, New Jersey). The molar absorptivity of $Fe(CN)_6^{3-}$, determined spectrophotometrically at 306 nm with duplicate measurements of four standard solutions ranging in concentration from 0.05 to 0.50 m*M*, was 1270 (± 60). The concentration of $Fe(CN)_6^{3-}$ in the KCN compartment was monitored until it reached 0.11 m*M*.

RESULTS AND DISCUSSION

Under these conditions, the following boundary conditions hold:

$$C_{Fe(CN)_6^{3-}} = 0 \text{ at } 0 < x < d; \text{ for } t > 0, \quad (1)$$

$$= 0 \text{ at } x = 0; \text{ for } t > 0, \quad (2)$$

$$= C_0 \text{ at } x = d, \text{ for } t > 0, \quad (3)$$

and the solution for steady-state flux under linear diffusion becomes

$$J = DKC_0/d, \quad (4)$$

where K is the partition coefficient of $Fe(CN)_6^{3-}$ between the aqueous solution and the PFI membrane, d is the membrane thickness (0.13 mm), D is

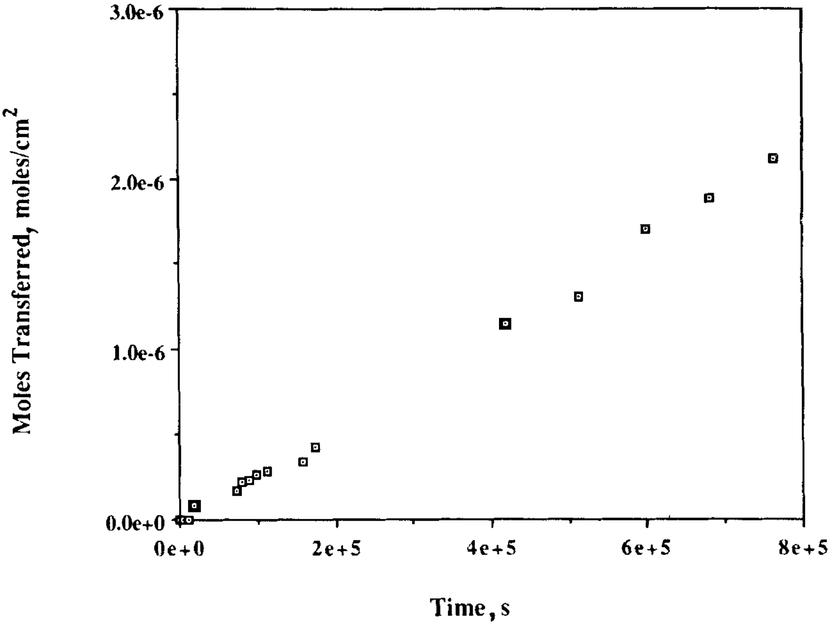

FIG. 1. Data used in calculation of flux of $Fe(CN)_6^{3-}$ through PFI membrane. The configuration was 0.1 *M* $K_3Fe(CN)_6$/PFI/0.3 *M* KCN.

the diffusion coefficient of $Fe(CN)_6^{3-}$ in the membrane, and C_0 is the concentration of $Fe(CN)_6^{3-}$ in solution ($x > d$), 0.1 *M*. Figure 1 shows a plot of moles $Fe(CN)_6^{3-}$ transported per unit area of membrane vs time. The linear portion represents steady-state conditions, and the slope of the line is the steady-state flux, *J*, which was calculated by a linear regression as 2.8×10^{-12} $mol \cdot cm^{-2} \cdot s^{-1}$. The partition coefficient, *K*, for $Fe(CN)_6^{3-}$ between PFI and aqueous solution was also measured spectrophotometrically, after soaking a membrane in 0.10 *M* $Fe(CN)_6^{3-}$ for 48 h. If the molar absorptivity of $Fe(CN)_6^{3-}$ in the PFI is taken as the same value as that in water, 1270 at 306 nm, the equilibrium concentration is 1.9 m*M*, and the partition coefficient,

$$K = [Fe(CN)_6^{3-}]_{PFI}/[Fe(CN)_6^{3-}]_{aq} \qquad (5)$$

is 0.019. The diffusion coefficient (*D*) calculated from these data and Eq. (4) is 1.9×10^{-8} cm²/s.

TABLE 1. Diffusion Coefficients of Anionic Species through PFI Membranes

Membrane type	Ion	D, cm^2/s	Reference
125	Cl^-	9×10^{-7}	3
125		1.6×10^{-6} [a]	2
125/127	I^-	9×10^{-8}	4
115	$PtCl_6^{2-}$	1×10^{-8}	10
125	SO_4^{2-}	4.4×10^{-7} [a]	2
115	$Fe(CN)_6^{3-}$	2×10^{-8}	This study

[a] 80°C (3 M NaCl + 0.1 M Na_2SO_4).

The diffusion coefficient reported for anionic species in PFI membranes are collected in Table 1. As noted in previous studies of diffusion [1, 11], the diffusion coefficients of most anions in PFI are significantly smaller than those of cations (e.g., Na^+, $D = 10^{-6}$ cm^2/s). This has been ascribed to differences in the diffusion paths of these species in the clustered structure of these ionomers. The small value of D for $Fe(CN)_6^{3-}$, coupled with the small value of K, suggests that low concentrations of $Fe(CN)_6^{3-}$ can be used to test the integrity of PFI films. On the other hand, D and K are sufficiently large that $Fe(CN)_6^{3-}$-based structures can be formed in PFI membranes by soaking them in more highly concentrated solutions.

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