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Electrode Films of Porous Agarose Impregnated with Nafion. Structural Heterogeneity and its Effects on Electron Transport

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Abstract

Inert, porous gels of agarose can be coated onto electrodes. Impregnation of Nafion into agarose coatings creates porous matrices capable of incorporating and retaining electroactive species. Chronocoulometric measurements of film porosity showed that both agarose and Nafion/agarose films are quite permeable, with porosities of 92% and 62%, respectively. Diffusion coefficients measured for methyl viologen in Nafion/agarose matrices are more than an order of magnitude higher than those in Nafion. The variation of diffusion coefficient with methyl viologen concentration in these films also differs: in Nafion, the diffusion coefficient decreases with increasing methyl viologen concentration, while in Nafion/agarose the opposite dependence is observed. The faster rate of electron transport in Nafion/agarose films is related to the heterogeneous structure of these films and the coupling of the diffusion pathways between the solution and the polymer phases within the electrode films.

Much of the recent interest in chemical modification of electrodes has been spurred by potential applications in electrocatalysis [1]. Immobilization of electrocatalysts results in numerous advantages over homogeneous catalysis, such as easily attainable high concentration of a catalyst near the electrode surface and the elimination of the need for separation of the products from the catalyst. Furthermore, appropriately designed electrocatalytic assemblies allow an expansion of the region of electrochemical reactions from the two-dimensional plane of the electrode surface into a multimolecular layer with a suitable molecular organization. The design of this sort of electrode assemblies has to include elements fulfilling both the chemical and the structural needs of its function. Regardless of the type of electrocatalytic reaction to be carried out, an electrode film immobilizing a catalyst and/or electron transfer mediator should provide means for fast electron propagation between the catalyst sites and the electrode surface. It should also exhibit physical permeability to allow efficient transport of reactants to all electrocatalytic centers. In numerous published reports, polymeric electrode films incorporating electroactive species showed negligible permeability [2-15]. This deficiency demands improvements in the design of the films' physical structure.

We have recently described two novel designs of electrode catalytic films [16-18]. In both cases the porous structure of these matrices was for the first time purposefully included in the design of the films and emphasized in the studies of their behavior. One of them consists of aluminum oxide of very regular porosity [16]; densely packed cylindrical pores of uniform pore diameter (in the range of 100 - 1500) penetrate the entire thickness of the film perpendicular to its surface. The other one is a cross-linked copolymeric gel of acrylamide/ vinylpyridine [17]. Its porous structure

consists of polymer bundles and aqueous microscopic (20 - 100 diameter) pools.

In the present work we describe another type of porous polymer matrix as well as its properties and application for reagent immobilization at electrodes. We have taken advantage of the porous, gel structure of agarose and used it as a matrix for immobilization of Nafion, a well known ionophore. Electrode films of agarose impregnated with Nafion remain physically porous and therefore permeable to all monomeric species.

Agarose is a naturally occurring polysaccharide widely used in affinity chromatography and electrophoresis [19,20]. Agarose gel formation is the result of multiple hydrogen-bonding of double-stranded helices of polysaccharide chains which leads to the formation of polymeric bundles separated by aqueous channels [21]. Gels form upon cooling of hot aqueous solutions of agarose. The process is thermally reversible. Highly swelled agarose gels are commonly made from 0.5% to 4% solutions. Increasing the agarose solution concentration results in decrease of the average pore diameter of the gel [19]. The diameter of individual pores is typically on the order of a few hundred angstroms [19]. Tight structure of the polysaccharide bundles is responsible for the mechanical rigidity of the agarose gels. Also due to their rigidity, these gels withstand transfer to solvents of low polarity such as acetonitrile and methylene chloride. Transfers between solvents of different polarity are reversible and do not result in readily apparent changes in the gel microscopic or macroscopic dimensions or structure.

Nafion, a highly perm-selective perfluorinated sulfonated polymer, is known for its ability to incorporate and retain multiply charged cations [22]. Although Nafion has been proposed as an electrocatalyst support, it is

practically impermeable to anions and uncharged species. Permeability to dioxygen molecules is a noteworthy exception [23]. Furthermore, Nafion electrode films containing electroactive cations exhibit very slow electron transport rates, with diffusion coefficients in the range of 10^{-9}-10^{-10} cm^2/s [22]. Despite these disadvantages Nafion has been studied extensively as an electrode coating material because of its intricate microscopic structure and the related remarkably stable retention of electroactive (cationic) species [24,25].

With the goal of combining the ion exchange properties of Nafion with the permeability of agarose films, desirable in electrocatalytic applications, we have impregnated electrode films of agarose gel with Nafion. The resulting composite films indeed remain permeable and retain ion exchange characteristics analogous to those of plain Nafion. In addition, the electron transport diffusion coefficients measured for methyl viologen in agarose/Nafion films are as much as two orders of magnitude higher than those in plain Nafion. While this research was in progress, Penner and Martin published their preliminary findings of similar increase of the diffusion coefficients observed for Gore-Tex (commercially available porous Teflon) membranes impregnated with Nafion [26].

We present here the results of our studies of the structure of the agarose/Nafion films and a quantitative examination of the factors leading to the observed increase of the electron transport rates. Based on these studies we can relate the observed effect to the internal mediation process and the heterogeneous structure of these composite films.

Experimental

Materials. A 2 wt. % solution of agarose (standard grade, low $-m_r$) as

received from Bio-Rad Corp., was prepared by dissolution of the dry material in doubly distilled and deionized (Barnstead Nanopure) water at 100 °C. The solution was then cooled and thermostated at 65 °C in a sealed container until the time of electrode coating. A 5 wt. % solution of Nafion in alcohols (1100 E.W., Solution Technology Inc,) was diluted as necessary with ethanol. Na_2SO_4, methyl viologen dichloride and benzoquinone were recrystallized prior to use. All other chemicals were reagent grade and used as received.

Nearly optically flat films of Nafion and agarose were cast at electrodes by spin coating at controlled rotation rate (motor and controller, E552-MG; E552-M, Electrocraft Corp.). Electrodes (0.55 cm^2 area) were prepared by vapor deposition of approximately 1500 thick gold films onto 2.54 x 2.54 cm^2 float glass slides. (A 100 chromium layer was always deposited first through the same stainless steel mask to improve the adhesion of the gold.)

Film thickness measurements were made with a stylus profilemeter (Alpha Step 100, Tenor Inc.,).

Electrochemical measurements were done with a PAR model 173/179 potentiostat/galvanostat and PAR model 175 universal programmer. Chronoamperometric data were collected and processed on an Apple IIe computer equipped with a commercial interface card (Adalab Data Acquisition System with fast A/D converter, Interactive Microware Inc.). Chronocoulometric experiments were done with a BAS 100 (Bioanalytical Systems Inc.) electrochemical analyzer. All potentials are reported vs. Ag/AgCl/KCl (0.1M) reference electrode. Supporting electrolyte was 0.2 M Na_2SO_4 in all experiments.

Results and Discussion

Film Properties. Thin films of agarose gel can be cast on electrodes by spin-coating. To form a film, a drop of hot (65 °C) 2 wt. % agarose solution is placed on an electrode substrate positioned on the rotating plate of a spin coater. Spinning results in rapid cooling of the agarose solution which causes the film to gel. By varying the rotation rate during spin-coating, agarose coatings can be produced with swelled thicknesses from 1 m to 100 m. Agarose adheres well to metal surfaces, producing stable electrode films. Freshly produced films were kept moist until they were used in further treatments or in electrochemical measurements. After drying, reswelling of agarose films does not restore their original structure or thickness, as is the case with bulk gels.

Porous Nafion/agarose films (Naf/AG) are produced by impregnation of agarose films with an alcoholic solution of Nafion. After coating electrode substrates with agarose films, a small quantity of a Nafion solution (10-20 L) is placed on the electrode surface. The solution spreads across the entire surface of the electrode substrate assuring an even distribution of Nafion in the agarose film. Immediately, the electrode substrate is transferred into a sealed chamber through which water saturated nitrogen is passed in a steady stream. After approximately 30 minutes the solvent exchange process is complete. Since Nafion is not soluble in water, the solvent exchange leads to uniform precipitation of Nafion in the agarose matrix producing a composite Naf/AG film. Increase of Nafion aliquot volume or repeated aliquots had little influence on the final Nafion content in the Naf/AG films. The factor that determines the Nafion content in Naf/AG films is the Nafion concentration of the impregnating solution. 5% Nafion solutions have been used in all experiments. While formation of agarose films of a

given thickness is very reproducible (± 5%), the impregnation process results in a variation of the amount of Nafion in the matrix of approximately ± 16%, depending primarily on the completeness of alcohol removed in the solvent exchange step. The quantity of Nafion in an agarose matrix was inferred from the reduction charge of methyl viologen incorporated into the film under specific conditions as described in the second section.

To measure the thickness of these highly swelled films with a stylus profilometer, it was necessary to develop a method of preventing extensive film damage due to the stylus plowing through the swelled films in the course of the measurement. We have used thin films (0.5 m - 1.0 m) of porous aluminum oxide (formed electrolytically at Al substrates) which have a rigid structure that provides the required mechancial support for the stylus, while their porosity assures adherence to the wet agarose and Naf/AG films (see Figure 1A). The methodology of film preparation and properties of these films have been described elsewhere. With the stylus force adjusted to a low value (2 mg - 5 mg), there was no evidence of any film damage or even of film compression during the thickness measurements. A typical surface profile of fully swelled Naf/AG film overcoated with a 0.6 m thick porous Al_2O_3 film (recorded on an electrode) is shown in Figure 1B. After the measurement of the wet film thickness, the measurement is repeated once the film has dried (Figure 1C). The dry thickness of the uncoated gel film subtracted from the total dry thickness of the assembly gives the exact thickness of the oxide film. The oxide thickness is then used to calculate the swelled thickness of the gel film from the first measurement.

Using the oxide technique we found, over a wide range of thicknesses, that agarose gel films coated from 2 wt. % solutions are 49 ± 3 times thicker when wet than after they have dried. When wetted again their thicknesses

increase only by a factor of 4 to 6. As expected, swelled agarose films have uniform thickness across the entire electrode area. The 2% agarose films impregnated with 5.0% Nafion solution had the same swelled thickness as the plain agarose matrices before impregnation. Depending on the content of Nafion in the Naf/AG films, these films collapse to 12% - 29% of their swelled thickness when dried ($d_{swelled}/d_{dry}$ of 3.4 - 8.3). As for plain agarose, Nafion impregnated agarose films do not return to their original structure or thickness once dried; their reswelling factor is less than 2. Uniform thickness of the dry Naf/AG films across the entire electrode area indicates uniform lateral impregnation of agarose matrices with Nafion. Using the oxide technique, the swelling factor for plain Nafion films was found to be 16%.

Initial voltammetric experiments showed little difference between uncoated electrodes and those coated with agarose or Naf/AG films (8.5 m thick) when anionic electroactive species were involved. In those instances ($Fe(CN)_6^{4-}$, $IrCl_6^{3-}$ in Na_2SO_4 solutions) peak currents decreased by less than 5% and the anodic to cathodic peak potential difference increased by 10 mV (20 mV for Naf/AG films) compared to the uncoated gold electrodes. Similar behavior was typical for cationic electroactive species on agarose coated electrodes. These observations demonstrate the substantial porosity of agarose and also of Naf/AG films, which stems from their heterogeneous structure.

Chronocoulometry was used to calculate the porosity of our films. Knowing that structure of these films consists of tightly coiled polysaccharide bundles and interdispersed polymer-free solution, we can assume that the diffusion coefficient of an electroactive reagent that is not attached to the polymer phase within the agarose films is the same as the bulk solution diffusion coefficient. Conventional chronocoulometric charge vs. $t^{1/2}$ plots were recorded under identical conditions for an electrode before and

after it was coated with a film. The duration of the potential pulse in these experiments was made sufficiently short (25 ms) that the diffusion layer thickness did not exceed the thickness of the electrode films (typically 50 m). The ratio of the slopes of the forward Anson plots obtained for the coated and bare electrodes can be interpreted, under these circumstances, as the solution volume fraction of the entire film volume or, in other words, the porosity factor, P. These experiments, as shown in Table 1, were repeated for a variety of electroactive species both for the plain agarose and the Naf/AG films. The apparent porosity of plain agarose films based on these data is approximately 91%, a value somewhat smaller than the one which could be calculated from the swelling factor of 49 obtained from thickness measurements. The difference is likely due to internal hydration and swelling of the agarose bundles.

The analogous measurements conducted with Naf/AG films (Table 1) gave an apparent porosity of approximately 62%, a value qualitatively consistent with the presence of the Nafion precipitate in these films. Our measurements in this case were restricted to the anionic species, since even uncharged electroactive probes such as benzoquinone partitioned to some extent into Nafion, giving slope ratios greater than one.

In order to substantiate our experimental approach in the measurements of film porosity, long potential pulse experiments were performed in ferrocyanide solution on a bare electrode and later on the same electrode coated with a Naf/AG film. Chronoamperometry was used this time. The Cottrell plots from both experiments are shown in Figure 2. As expected, a linear plot for the entire duration of a 2.0 s pulse was obtained in the first experiment for the bare electrode. Under identical conditions, the Naf/AG coated electrode gave a Cottrell plot with a slope of about 62% of the slope value from the first

experiment for the initial short part of the potential pulse. Subsequently, the slope of this plot increased, approaching the value from the first experiment towards the end of the 2.0 s potential pulse. This behavior is consistent with the expansion of the diffusion layer far beyond the thickness of the porous electrode film. Under these circumstances the current-time characteristic reflects the solution conditions unperturbed by the presence of the electrode film [27].

As in the case of plain Nafion films, the Naf/AG films readily incorporate and retain cationic species by ion-exchange. This behavior is illustrated in Figure 3, where voltammograms of methyl viologen (MV^{2+}) are shown on a bare gold electrode and after incorporation of MV^{2+} into a Naf/AG film. Retention of MV^{2+} in the Naf/AG films is only slightly less permanent than in plain Nafion. Typically, less than 20% of the incorporated methyl viologen is lost in 30 min of electrochemical experiments in MV^{2+}-free solution. Chronocoulometric experiments done after medium transfer to a MV^{2+}-free electrolyte solution produced linear Anson plots with a slope value independent of the time length of the potential pulse in the range of 100 ms to 1 s. This indicates again that methyl viologen, and by implication the Nafion precipitate is uniformly distributed across the thickness of the film.

Electron Transport. The diffusion coefficients of electron transport D_{app} in the Naf/AG films loaded with MV^{2+} were measured by chronoamperometry in a MV^{2+}-free solution of 0.2 M Na_2SO_4. Since the electrode films were relatively thick (5 m - 10 m), current-time data were collected over 250 to 500 ms time intervals in these measurements. The well behaved Cottrell plots obtained from these experiments were used to calculate the D_{app} values. The diffusion coefficients are significantly larger than those for plain Nafion film. Their

average value is $1.3 \pm 0.2 \times 10^{-8}$ cm^2/s for the Naf/AG films initially equilibrated with 1.0 mM MV^{2+} solution in 0.2 M Na_2SO_4. This value is independent of the film thickness and varied only slightly with the amount of Nafion in the agarose matrix.

The effect of the MV^{2+} concentration in polymer films on apparent diffusion coefficients was investigated for the Naf/AG and plain Nafion films. Methyl viologen was incorporated into these films to different extents by equilibrating the coated electrodes with MV^{2+} solutions of different concentrations. Chronoamperometric data were obtained in supporting electrolyte solutions free of MV^{2+}. The results are collected in Table 2. The decrease of D_{app} with increasing MV^{2+} concentration in plain Nafion is not surprising. Gaudiello et al. recently demonstrated in their simultaneous electrochemical and electron spin resonance studies that physical diffusion of methyl viologen, rather than electron exchange, contributes predominantly to the charge transport through Nafion films [27]. The slow rate of electron-exchange for $MV^{2+}/MV^{+\cdot}$ in Nafion is presumably due to the partitioning of the oxidized and the reduced forms of methyl viologen into domains of different polarity within the Nafion film [27]. The diffusion coefficient of electron transport in Nafion has been shown to decrease with increasing concentration of electroactive centers in cases where electroactive species exhibited a relatively slow rate of electron-exchange [25]. Such behavior is characteristic, for example, of the $Co(bpy)_3^{3+/2+}$ couple (bpy is 2,2'-bipyridyl) as demonstrated by Buttry and Anson, and can be attributed to the competition of the diffusing centers for the sites of attachment within the interfacial region of Nafion [25]. This effect, sometimes referred to as "single file diffusion," is likely to account for the behavior we have observed in the present case of $MV^{2+}/MV^{+\cdot}$ diffusion in Nafion (Table 2).

The electron transport characteristics of Naf/AG films contrast sharply with those of plain Nafion. As shown in Table 2, the diffusion coefficient of MV^{2+} increases with increasing concentration of methyl viologen in a film. The diffusion coefficients are also close to two orders of magnitude higher than those in plain Nafion. Can these differences be explained in view of the heterogeneous structure of the composite Naf/AG films?

Note that the Naf/AG films, although not as permeable as agarose films, still exhibit substantial porosity. Nafion must therefore be dispersed in an agarose matrix as small aggregates; the size of these aggregates is probably similar to the average pore diameter of the agarose gel (i.e. a few hundred). This assessment is supported by our observation that the equilibration time necessary to incorporate MV^{2+} into Nafion/AG films is twenty times shorter than that for a 5000 thick plain Nafion film. Let us recall also that the retention of methyl viologen in the Naf/AG films, while good, is not as permanent as observed for plain Nafion films which experience very little loss of MV^{2+} upon prolonged soaking in a solution of supporting electrolyte. Based on this evidence, we can presume that the aqueous phase interdispersed within the electrode films contains some methyl viologen in quasi-equilibrium with MV^{2+} in the Nafion aggregates. It seems plausible then that the solution phase methyl viologen participates in the overall electron transport process in our composite films. Having a substantially larger diffusion coefficient than D_{app} of MV^{2+} in Nafion, the solution phase methyl viologen can accelerate the overall electron propagation. This scheme is analogous to the Buttry-Anson model of the two-phase internal structure of Nafion [25]. They demonstrated how only a small amount of $Ru(bpy)_3^{3+/2+}$ species present in hydrophilic domains of Nafion (characterized by a larger diffusion coefficient) can dramatically accelerate the overall electron transport as

long as the diffusion processes in the hydrophilic and the hydrophobic domains are coupled by rapid cross-phase electron and/or material exchange [25].

Thus, the key issue in the studies of our system was to determine whether solution phase methyl viologen affects the rate of electron transport through Naf/AG films. With our porous Naf/AG films, the solution-phase MV^{2+} concentration within the films can be varied simply by changing the bulk MV^{2+} concentration. We have taken advantage of this characteristic of our system to analyze the role of solution phase MV^{2+} in the electron transport within Naf/AG films.

The equations describing the relationship between the apparent diffusion coefficient in a two-phase system and the individual diffusion coefficients for each of the two phases are the same as those used by Buttry and Anson [25]. Recently, we dealt with a different type of a two phase system which more directly resembles the present system. The derivation scheme for the equations used below was given in the account of those studies [18].

If the diffusion in the solution phase of the Naf/AG films is coupled to that in the Nafion phase then the observed diffusion coefficient, D_{app}, can be expressed by the following equation:

$$D_{app} = D_p x_p + D_s x_s \tag{1}$$

where D_p and D_s are the diffusion coefficients of MV^{2+} in Nafion and in the aqueous solution, and x_p and x_s are the MV^{2+} mole fractions in the polymer and the solution phase. If, however, the diffusional pathways in both phases are not coupled the corresponding relationship is:

$$D_{app}^{1/2} = D_p^{1/2} x_p + D_s^{1/2} x_s \tag{2}$$

As shown previously, in both cases the following substitutions can be made [18]:

$$x_p = \frac{Q_p}{Q_p + Q_s} \tag{3}$$

$$x_s = \frac{Q_s}{Q_p + Q_s} \tag{4}$$

where Q_p and Q_s are the equivalent charges of methyl viologen present in the two phases of the Naf/AG film. In the present case, due to the strong partitioning of methyl viologen into the Nafion phase, Q_p is always much greater than Q_s. This implies that $Q_p + Q_s \quad Q_p$. Q_s can be related to the bulk concentration of MV^{2+}, C^* by the following equation:

$$Q_s = nFAdPC^* \tag{5}$$

where P is the solution phase fraction or the porosity factor of the Naf/AG film, and d is the swelled thickness of the film. With these substitutions, equations 1 and 2 become:

$$D_{app} = D_p + nFAD_s dPC^*/Q_p \tag{6}$$

$$D_{app}^{1/2} = D_p^{1/2} + nFAD_s^{1/2}\, dPC^*/Q_p \tag{7}$$

By plotting D_{app} and $D_{app}^{1/2}$ vs. C^*/Q_p, we can determine whether one of the two models describes the electron transport in the Naf/AG films. In addition, the slope of a straight line plot would allow us to calculate the film porosity factor, P, which can then be compared with the porosity value determined in the previous section. The intercept should give us the diffusion coefficient for MV^{2+} in plain Nafion.

Experimentally, the apparent diffusion coefficients were obtained from the chronoamperometric Cottrell plots. The series of experiments were done with 8.5 m thick Naf/AG films. The bulk solution MV^{2+} concentration was varied from 0.05 mM to 1.0 mM. Q_p was determined in the MV^{2+} solutions by integration of slow scanned cathodic voltammograms, followed by correction for the solution contribution to the measured charge as described below. Due to the proximity of the second electron reduction potential of methyl viologen the potential scan was stopped 150 mV negative of the first electron reduction peak potential and held there until the reduction current decayed to the background level. (The recorder was operated in a y-t mode in these experiments.) The charges thus obtained were subsequently corrected for the solution component by subtracting the charge value obtained under identical conditions at an uncoated electrode. Typical results, plotted in the format of equations 6 and 7, are shown in Figure 4. In five series of such experiments the data fit the coupled diffusional pathways model (equation 6) with correlation coefficients exceeding 0.99. The slope of the five plots gave an average porosity factor of 0.66 ± 0.05 (The experimentally determined solution MV^{2+} diffusion coefficient of 7.24×10^{-6} cm^2/s was used.) The porosity factor obtained here is in very good agreement with the porosity measurements described in the previous section.

The average intercept of $4 \pm 3 \times 10^{-9}$ cm^2/s appears, at first glance, higher than typical diffusion coefficients for MV^{2+} in Nafion. We must consider, however, the increase of the MV^{2+} diffusion coefficient in Nafion with decreasing MV^{2+} concentration (see Table 2). Despite the rather large variation of the experimental intercepts obtained from the plots like that in Figure 4A, their average value seems reasonable as a limiting D_p as the Nafion concentration of MV^{2+} is extrapolated to zero. It is also important to note

that the variation of D_p with MV^{2+} concentration in Nafion is small relative to the variation of D_{app} with the methyl viologen concentration in solution. Thus, in equation 6 the D_p can be considered to be independent of the solution concentration of MV^{2+}.

These results demonstrate that the behavior of our system follows the coupled diffusion pathways model. (The experimental data fit equation 6 and not equation 7).

Conclusions.

Porous agarose gels are useful as electrode matrices for immobilization of Nafion. Composite films of Nafion impregnated agarose retain the advantageous features of Nafion and in addition show substantial porosity, a very desirable characteristic for electrode films in electrocatalytic applications. Electron transport measurements revealed another desirable feature of these composite materials: the diffusion coefficient of methyl viologen immobilized in the Naf/AG films is more than an order of magnitude higher than it is in plain Nafion. This significant increase in the apparent rate of electron propagation is a result of the coupling of the diffusional pathways of MV^{2+} in the finely dispersed Nafion aggregates and the solution phase of the composite films. Due to the large difference between the diffusion coefficients in the solution and the Nafion phase, only a small fraction of all the methyl viologen centers must be present in the solution phase in order to produce a significant increase in the overall rate of electron transport. For example, plain Nafion and Naf/AG films equilibrated in 1 mM MV^{2+} solution and then transferred to pure supporting electrolyte gave D_{app} of 8.0×10^{-10} cm^2/s and 1.3×10^{-8} cm^2/s respectively. For the latter case (Naf/AG), using equation 1 one can calculate that only 0.2% of all the MV^{2+} centers had to partition back into the solution phase to account for this increase in the electron transport rate.

Despite the repartitioning of MV^{2+} from the Nafion phase into the solution phase, the observed stability of incorporated material in Naf/AG films is only somewhat poorer than that in plain Nafion. This is most likely due to the exceedingly high interdispersion of the polymer and solution phases.

We have developed a new technique for thickness measurements of these highly swelled gel films by stylus profilometry. By using porous aluminum oxide films to protect the surface of the soft, swollen polymer films, highly accurate measurements are routinely possible.

The use of agarose for entrapment of other polymers, solid particles, etc. in electrode films can be easily envisioned. Structural stability of agarose gels in nonaqueous solvents as well as the possibility of chemical derivatization of the polysaccharide hydroxyl groups warrant further research with this material.

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References

1. R.W. Murray in A.J. Bard (Ed.), Electroanalytical Chemistry Vol. 13, M. Dekker: New York 1984, p. 191 (and references therein).

2. C. Degrand and L.L. Miller, J. Am. Chem. Soc., 102 (1980) 5728.

3. N. Oyama and F.C. Anson, Anal. Chem., 52 (1980) 1192.

4. P. Daum and R.W. Murray, J. Phys. Chem., 85 (1981) 389.

5. R.D. Rocklin and R.W. Murray, J. Phys. Chem., 85 (1981) 2104.

6. N. Oyama, K. Shigehara and F.C. Anson, Inorg. Chem., 20 (1981) 518.

7. S. Ahahoshi, S. Toshima and K. Itaya, J. Phys. Chem., 85 (1981) 818.

8. T. Ikeda, C.R. Leidner and R.W. Murray, J. Electroanal. Chem., 138 (1982) 343.

9. P. Martigny and F.C. Anson, J. Electroanal. Chem., 139 (1982) 383.

10. K.N. Kuo and R.W. Murray, J. Electroanal. Chem., 131 (1982) 37.

11. J. Facci and R.W. Murray, Anal. Chem., 54 (1982) 772.

12. R.M. Buchanan, G.S. Calabrese, T.J. Sobieralski and M.S. Wrighton, J. Electroanal. Chem., 153 (1983) 129.

13. F.C. Anson, Y-M. Tsou and J.M. Saveant, J. Electroanal. Chem., 178 (1984) 113.

14. D.J. Harrison, K.A. Daube and M.S. Wrighton, J. Am. Chem. Soc., 106 (1984) 6947.

15. M. Krishnan, X. Zhang and A.J. Bard, J. Am. Chem. Soc., 106 (1984) 7371.

16. C.J. Miller and M. Majda, J. Am. Chem. Soc., 107 (1985) 1419.

17. J.E. Van Koppenhagen and M. Majda, J. Electroanal. Chem., 189 (1985) 379.

18. C.J. Miller and M. Majda, J. Electroanal. Chem., submitted.

19. R.R. Walters, Anal. Chem., 57 (1985) 1099A.

20. W.H. Scouten, Affinity Chromatography, J. Wiley and Sons, N.Y. 1981.

21. S. Arnott, A. Fulmer, W.E. Scott, I.C.M. Dea, R. Moorhouse and D.A. Rees, J. Mol. Biol., 90 (1874) 269.

22. I. Rubinstein, J. Electroanal. Chem., 188 (1985) 222 (and references therein).

23. F.C. Anson, C-L. Li and J.M. Saveant, J. Am. Chem. Soc., 107 (1985) 3442.

24. H.L. Yeager and A. Steck, J. Electrochem. Soc., 128 (1981) 1880.

25. D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 105 (1983) 685.

26. R.M. Penner and C.R. Martin, J. Electrochem. Soc., 132 (1985) 514.

27. D. Shoup and A. Shabo, J. Electroanal. Chem., 160 (1984) 19.

28. J.G. Gaudiello, P.K. Ghosh and A.J. Bard, J. Am. Chem. Soc., 107 (1985) 3027.

Table 1

Porosity of Agarose and Naf/AG Films Based on Chronocoulometric Measurements

Probe Species[a]	% Relative Porosity	
	Agarose[b]	Naf/AG[b]
$Fe(CN)_6^{4-}$	92±2	60±3
$Fe(CN)_6^{3-}$	91±4	-
$IrCl_6^{2-}$	92±2	62±1
Benzoquinone[c]	90±2	d
Methyl viologen	95±1[e]	d
Hydroxyferrocene	90±2	d

a. Concentration of the electroactive species was 1.0 mM.

b. 2% Agarose films; Naf/AG films were prepared from 2% Agarose films and 5% Nafion solution as described in text.

c. 1M phosphate buffer, pH 7.0 was used as a supporting electrolyte.

d. Erroneous data were obtained due to partitioning of the probe species into Nafion.

e. High value of film porosity is due to weak partitioning of MV^{2+} induced by a residual quantity of sulfonate and pyruvate sites in agarose.

Table 2

Effect of MV^{2+} Concentration on its Diffusion Coefficient in Nafion and Naf/AG films.[a]

Nafion		Naf/AG[b]	
$[MV^{2+}]_{film}$(M)	$10^{10}D_{app}$(cm^2/s)	$[MV^{2+}]_{film}$(M)	$10^{8}D_{app}$(cm^2/s)
0.30	14.6	0.0066	0.56
0.50	9.3	0.027	0.73
0.58	8.4	0.054	0.94
0.60	8.0	0.062	1.3
0.70	5.5	0.072	1.5

a. The diffusion coefficients reported in each row of the table were obtained by equilibrating film coated electrodes in the same MV^{2+} solution; MV^{2+} solutions in the concentration range of 0.01 M to 5.0 mM were used.

b. The electrode films were of the same type as those described in Table 1.

Figure Captions

Figure 1. Thickness measurements of agarose films impregnated with Nafion. (A) Schematic representation of a relative position of a polymer film and the porous aluminum oxide overlayer used in the thickness measurements. (B) Representative thickness profile of a swollen assembly. (C) Thickness profile of the same assembly after drying.

Figure 2. Chronoamperometric Cottrell plots obtained at a bare Au electrode (A) and at the same electrode coated with a 50 μm Naf/AG film (B) in 1.0 mM $K_4Fe(CN)_6$, 0.2 M Na_2SO_4 solution. Length of the potential pulse, 2s.

Figure 3. Steady-state cyclic voltammograms of methyl viologen recorded at a gold electrode (A = 0.55 cm^2). (A) 1.0 mM MV^{2+}, 0.2 M Na_2SO_4, v = 50 mV/S. (B) The electrode was coated with 50 m thick Naf/AG film and then equilibrated with 1.0 mM MV^{2+} solution; the voltammogram was recorded in 0.2 M Na_2SO_4, v = 50 mV/S.

Figure 4. Plots of D_{app} vs. C^*/Q_p according to equations 6(A) and 7(B) testing whether the electron transport pathways in the solution and the polymer phase are coupled (A) or uncoupled (B).

Thickness Measurements of Agarose Films Impregnated with Nafion

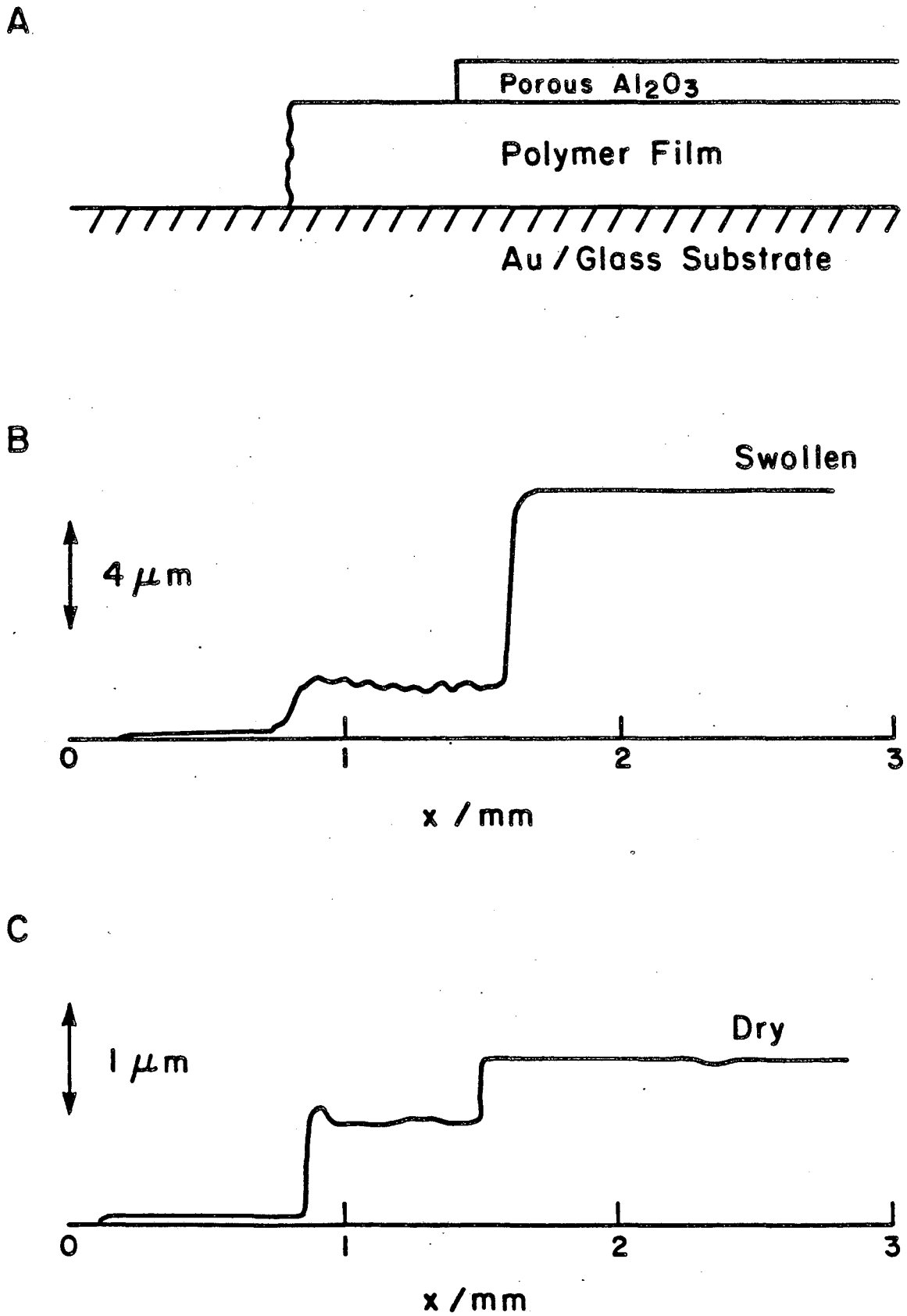

Figure 1

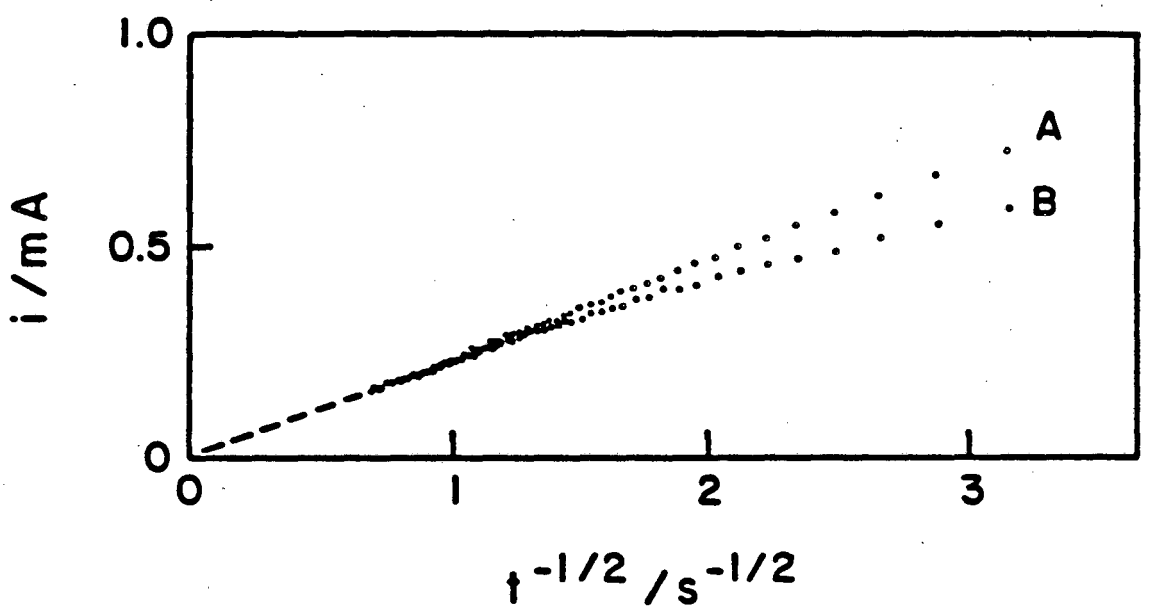

Figure 2

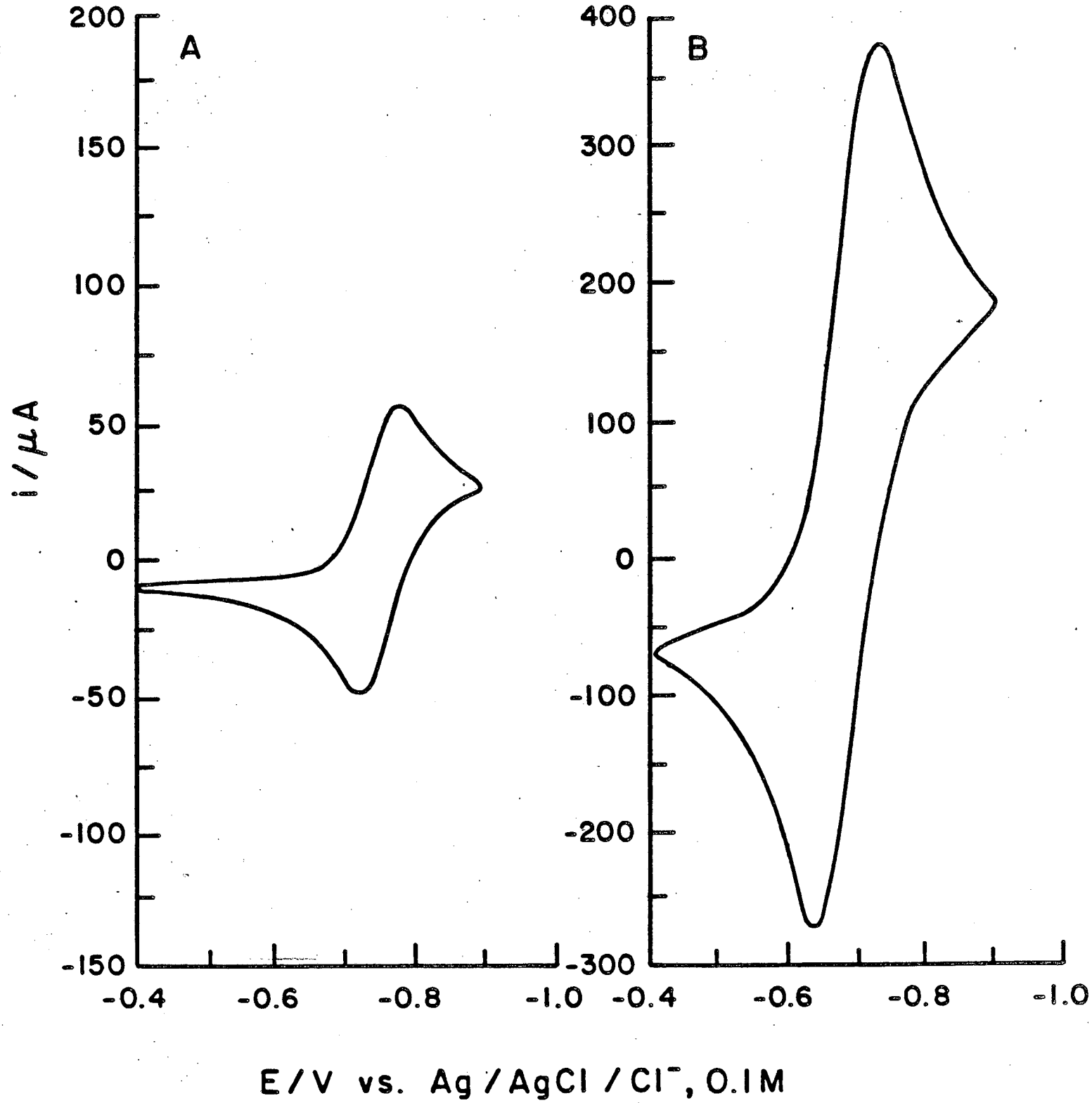
A
B
200
150
100
50
0
-50
-100
-150
400
300
200
100
0
-100
-200
-300
i / μA
-0.4
-0.6
-0.8
-1.0
E / V vs. Ag / AgCl / Cl⁻, 0.1M

Figure 3

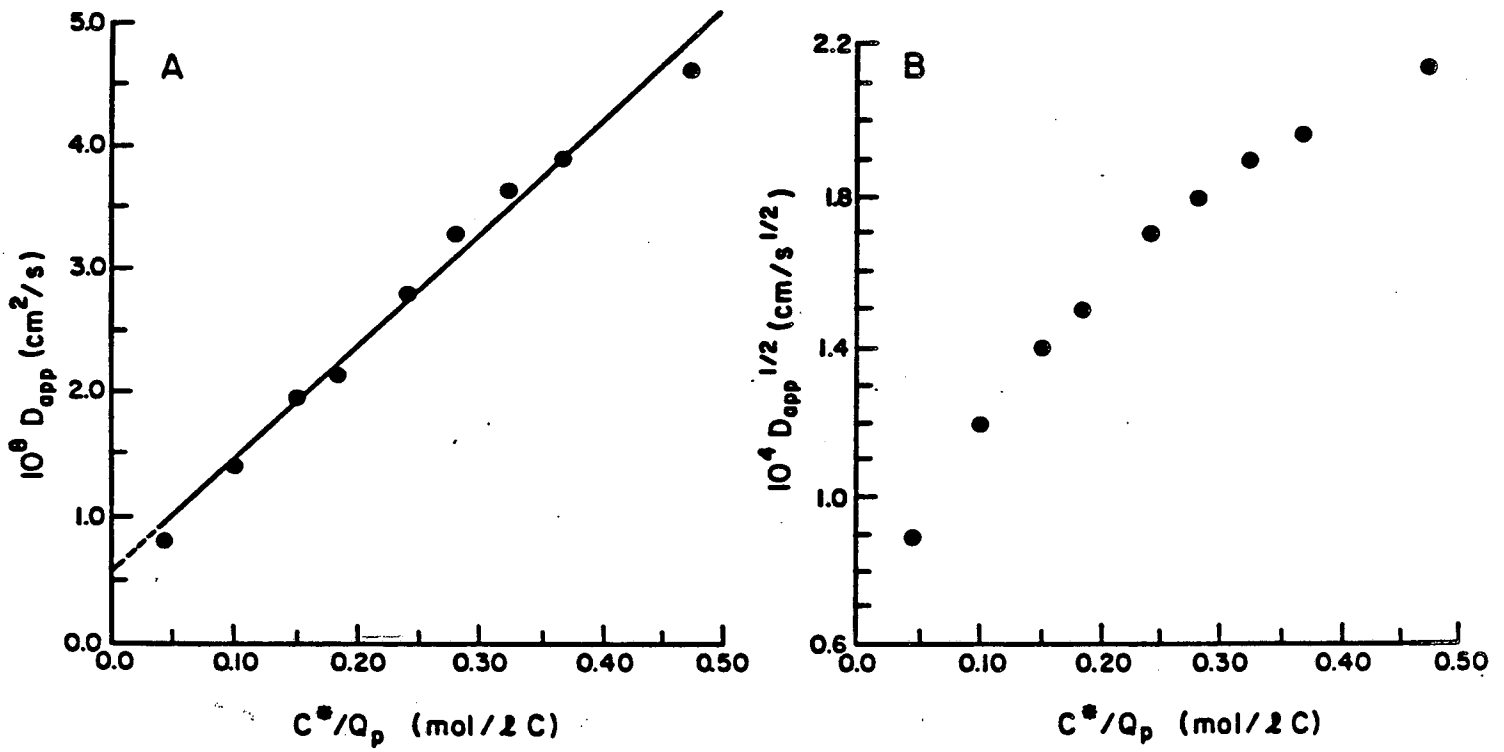
A
B
$10^8 D_{app}$ (cm²/s)
$10^4 D_{app}^{1/2}$ (cm/s$^{1/2}$)
C*/Q$_p$ (mol/ℓ C)
C*/Q$_p$ (mol/ℓ C)
0.0
1.0
2.0
3.0
4.0
5.0
0.6
1.0
1.4
1.8
2.2
0.10
0.20
0.30
0.40
0.50

Figure 4

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