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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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To cite this Article Xue, T. and Osseo-asare, K.(1988) 'Application of the pH-Stat Technique in Donnan Dialysis Effect of Anion Invasion in the $\text{CoSO}_4/\text{NAFION 117}/\text{H}_2\text{SO}_4$ System', *Separation Science and Technology*, 23: 12, 1825 — 1837

To link to this Article: DOI: 10.1080/01496398808075666

URL: <http://dx.doi.org/10.1080/01496398808075666>

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APPLICATION OF THE pH-STAT TECHNIQUE IN DONNAN DIALYSIS:
EFFECT OF ANION INVASION IN THE $\text{CoSO}_4/\text{NAFION 117}/\text{H}_2\text{SO}_4$ SYSTEM

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ABSTRACT

Cobalt transport during Donnan dialysis in the $\text{CoSO}_4/\text{Nafion 117}/\text{H}_2\text{SO}_4$ system was measured with a pH-stat technique. (i.e., the pH in the feed compartment was maintained constant). During the transfer process, Co^{2+} ions moved from the cobalt reservoir to the sink compartment, while hydrogen ions moved in the opposite direction. A standardized NaOH solution was used to neutralize the H^+ ions entering the reservoir compartment, and in the absence of anion invasion, the cobalt flux was determined as

$$J_{\text{Co}^{2+}} = \frac{1}{2} J_{\text{H}^+}$$

The experimental results indicate that for Donnan dialysis experiments involving high acid concentrations, the invasion of the membrane by the anions associated with the acid can be significant. Since anion transfer is accompanied by the cotransport of protons, it follows therefore that the anion invasion characteristics must be known before the pH-stat technique can be employed successfully. The transport of bisulfate ion (HSO_4^-) through Nafion 117 was measured with the pH-stat technique. An invasion-corrected cobalt flux was obtained by subtracting the hydrogen flux due to anion invasion from the cobalt flux determined with the above equation. The invasion-corrected flux was in substantial agreement with the flux obtained via cobalt analysis with atomic absorption spectrophotometry.

INTRODUCTION

Donnan dialysis is a potentially attractive membrane separation process for concentrating valuable materials in ionic form from dilute solutions or removing undesirable ionic species from solution (1). When cation exchange membranes are used, hydrogen ions, which exhibit relatively high diffusion rates, offer a convenient means of driving the dialytic process. Thus acids such as HCl and H₂SO₄ are often utilized as the stripping reagent. If a solution containing a low concentration of a divalent metal ion M²⁺ is placed on one side of the cation exchange membrane, while a second solution containing an acid is placed on the opposite side, both metal and hydrogen ions will diffuse through the membrane and the final distribution of ions between the two solutions can be predicted by the Donnan equilibrium equation (2)

$$\left(\frac{a_{M^{2+}}^I}{a_{M^{2+}}^{II}} \right) = \left(\frac{a_{H^+}^I}{a_{H^+}^{II}} \right)^2 \quad (1)$$

where I and II represent the metal ion reservoir and sink solutions respectively, and $a_{M^{2+}}$, a_{H^+} are the activities of the metal and hydrogen ions. Thus, thermodynamically, a high acid concentration in the sink compartment is desirable since the resulting large H⁺ concentration difference will effectively pump the metal ions into the second solution.

As a result of their excellent chemical and thermal stabilities, Nafion membranes, developed by Du Pont, have been considered as good candidate membrane materials for Donnan dialysis. In previous work (3,4) in which nickel and copper ions were stripped with sulfuric acid, Ng and Snyder found that when the metal ion concentration was low (e.g. 0.0017 mol dm⁻³ or 100 ppm) and the acid concentration was high (≥ 0.5 mol dm⁻³), the metal transport rate was controlled by aqueous boundary layer diffusion, and the disappearance of metal ions from the feed solution followed a first-order rate law.

For Donnan dialysis with cation exchange membranes, if the coions are assumed to be excluded by the membrane totally, i.e., only cation exchange occurs via Donnan dialysis, the mass balance between the hydrogen and divalent metal ions should satisfy the following relationship,

$$J_{M^{2+}} = \frac{1}{2} J_{H^+} \quad (2)$$

where $J_{M^{2+}}$ and J_{H^+} are the fluxes for M²⁺ and H⁺ respectively. This means that the metal ion concentration change can be derived directly from the pH change in the feed solution. However, at relatively high concentrations, the anions associated with the acid can also penetrate the cation-exchange membrane via simple diffusion; this effect is termed anion invasion. If anion invasion takes place during Donnan dialysis, the total hydrogen ion flux is:

$$J_{H^+}^T = J_{H^+}^E + J_{H^+}^I \quad (3)$$

where $J_{H^+}^T$ is the total H^+ flux and $J_{H^+}^E$ and $J_{H^+}^I$, the H^+ fluxes due to cation exchange and anion invasion respectively. Therefore, Equation 2 should be corrected as

$$J_{M^{2+}} = \frac{1}{2} \left(J_{H^+}^T - J_{H^+}^I \right) \quad (4)$$

i.e., the pH change in the feed solution cannot be utilized to determine the metal ion concentration change unless the anion invasion contribution is known.

The phenomenon of anion invasion of cation exchange materials has been recognized for some time. It is known that at high ionic strength, cation exchange resins can absorb anions strongly (5-7). For example, for Dowex 50 cation exchange resin, the distribution coefficient of HCl or $HClO_4$ initially decreases with increase of the solution concentration, then after a minimum it increases steadily (6). This behavior indicates that at high ionic strength the cation exchange material acquires an affinity for anions. This effect has been exploited in a number of schemes which separate or extract metal ions in anionic form by ion-exchange (5-7) and solvent extraction (8,9).

The effects of anion invasion in Nafion membrane systems have not been studied extensively. In the previous study of Ng and Snyder (3) involving the $NiSO_4$ - H_2SO_4 system, the feed compartment initially contained $0.0017 \text{ mol dm}^{-3}$ $NiSO_4$ (i.e., 100 ppm Ni) at pH 5.5, and the strip solution contained 0.5 mol dm^{-3} H_2SO_4 . After 3 hours, the feed compartment solution analyzed 5 to 50 ppm, depending on the hydrodynamic conditions (since the transport process was controlled by boundary layer diffusion) and the final pH was about 2.2. A simple calculation (assuming unit activity coefficient for H^+ , in view of the relatively low ionic strength) indicates that the final hydrogen ion concentration was about $0.006 \text{ mol dm}^{-3}$. This means that the final H^+ concentration was about three times higher than the initial Ni^{2+} concentration. This trend cannot be explained by the ion-exchange relation of Equation 2. A reasonable explanation can however be offered by considering the invasion by anions.

In the present work, the $CoSO_4$ /Nafion 117/ H_2SO_4 system was investigated in an effort to examine the possibility of using a pH-stat technique to monitor Donnan dialysis. When the pH value in the feed solution is fixed, the H^+ ions released during the ion exchange process can be neutralized with a standardized NaOH solution. Then if anion invasion can be ignored, Equation 2 can be used to calculate the metal ion flux. On the other hand, if anion invasion is significant, then the diffusion of the acid through the membrane should be investigated first so that Equation 4 may be used to determine the metal flux. The main advantage of the pH-stat technique is that it can provide a method to monitor the concentration change in the solutions continuously instead of taking samples at timed intervals. The pH-stat technique can also be used to measure the anion diffusion for acids. In this work, the diffusion of the bisulfate ion HSO_4^- , which is the main component in H_2SO_4 solution when $pH \leq 2.0$ is investigated with this technique. The equal-sized chambers are separated by a membrane; one of the

chambers contains distilled water and the other, H_2SO_4 solution. During the transfer process, when anion invasion takes place, HSO_4^- ions cross the membrane and enter the water chamber. At the same time, due to the requirement of electro-neutrality, each crossing HSO_4^- ion is accompanied by a H^+ ion so that the pH in the chamber changes. Again if a standardized NaOH is used to neutralize the H^+ ions, then the diffusion flux of HSO_4^- through the membrane can be readily calculated from the used NaOH volume and concentration.

EXPERIMENTAL

Double-distilled water and reagent grade H_2SO_4 , NaOH and CoSO_4 were used in this work. The ion exchange membrane was Nafion 117 (Du Pont) with a nominal capacity of 0.91 mequiv/g (EW 1100) and thickness of 0.017 cm. The as-received membrane was initially soaked in distilled water at room temperature for 24 hours. The membrane was subsequently soaked in 1 mol dm^{-3} H_2SO_4 for 12 hours followed by leaching and rinsing with distilled water for several times. The thickness of the treated membrane was measured with a micrometer as 0.022 cm.

The stirred diffusion cell employed in the present study consisted of two compartments; the left compartment was used for introducing the diffusant into the membrane and the other compartment for the titration measurement of the permeation rate. In principle, the present device is very similar to the electrochemical technique used by Yeo and McBreen (10). The membrane was held in place between plexiglass gaskets and clamped together. A silicon rubber ring surrounding the gasket was used to further prevent possible leakage. The exposed membrane area was 7.07 cm^2 . The Teflon stirring rod in each compartment was connected to a variable speed motor. A radiometer pH-stat apparatus consisting of a PHM84 pH meter with a combination electrode, an ABU 80 Autoburette and a TTT 80 titrator was used. An Apple IIe microcomputer was interfaced with the autoburette to record and treat the data.

After the membrane was fixed in the cell, 250 cm^3 distilled water or 0.0017 mol dm^{-3} CoSO_4 solution was put into the right (titration) compartment and the pH was adjusted to a preset value (i.e., 4.50) by the addition of small amounts of H_2SO_4 . After the pH was stable for one minute, 250 cm^3 of the relevant H_2SO_4 solution was quickly introduced into the left compartment, the rotating speeds on both sides were adjusted to a desired value and the computer program for data recording started. The computer took the signal every 10 seconds. The transfer experiments utilized two different modes of operation. In the first case, the pH-stat was not used and the pH of the right compartment was allowed to change with time from its initial value of 4.5. In the second case, i.e., the pH-stat mode of operation, the autotitrator was used to maintain a constant pH of 4.5 in the right compartment. In the pH-stat mode, the pH was controlled at 4.50 and therefore once a HSO_4^- ion crossed the membrane it was decomposed to SO_4^{2-} and H^+ , thus two H^+ ions were neutralized. The amount of HSO_4^- passing through the membrane at each time interval and the total accumulated HSO_4^- in the right compartment were recorded. For the CoSO_4 - H_2SO_4 system, a 0.1 cm^3 sample

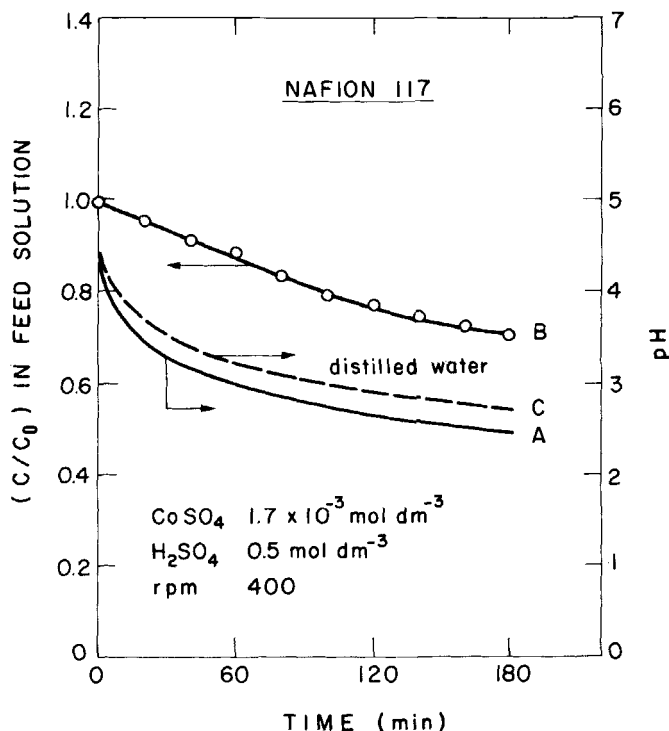


Figure 1. Time dependence of Co^{2+} concentration and pH during Donnan dialysis. A, B: $1.7 \times 10^{-3} \text{ mol dm}^{-3} \text{ CoSO}_4 / 0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; C: distilled water/ $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$; C_0 = initial cobalt concentration in the feed solution, C = Cobalt concentration in the feed chamber at time t .

from the right compartment was taken every 20 minutes with an Eppendorf digital pipette and the cobalt content was analyzed on a Perkin-Elmer Model 703 atomic absorption spectrophotometer. Since the sample volumes were very low, the associated volume changes in the cell compartment could be ignored. All experiments were conducted at room temperature ($22 \pm 2^\circ\text{C}$).

RESULTS AND DISCUSSION

Anion Invasion and Donnan Dialysis

In order to investigate the anion invasion effect, the feed compartment was initially filled with distilled water which contained no metal ions, while the strip compartment was filled with $0.50 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$. The pH change plotted in Figure 1 as dashed lines (Curve C) was obtained; the observed drop in pH clearly

indicates acid transfer from the strip to the feed chamber. A typical set of Donnan dialysis experimental data for the $\text{CoSO}_4\text{-H}_2\text{SO}_4$ system is plotted in Figure 1 (Curves A and B). Here the initial Co^{2+} concentration in the feed solution was $0.0017 \text{ mol dm}^{-3}$ (100 ppm) and H_2SO_4 concentration in the strip solution was 0.5 mol dm^{-3} . The pH of the feed solution changed from 4.50 to 2.50 in 180 minutes (Curve A); meanwhile about 30% of the Co^{2+} ions initially present in the feed chamber entered the strip solution (Curve B, atomic absorption data). The final pH of 2.5 (Curve A) means that the final hydrogen ion concentration in the feed chamber was about $3 \times 10^{-3} \text{ mol dm}^{-3}$ (assuming the activity coefficient of H^+ may be taken as unity), which is far higher than that expected from ion exchange with 30% of the cobalt ions originally present in the feed chamber. This result is attributable to the phenomenon of anion invasion.

If anion invasion is ignored during the Donnan dialysis process, and there are negligible solution volume changes in the cell compartments, then Curve A can be used directly to calculate the Co^{2+} concentration as:

$$C_{\text{Co}^{2+}} = J_{\text{H}^+} St/2V = C_{\text{H}^+}^A/2 \quad (5)$$

where $C_{\text{H}^+}^A$ is the hydrogen ion concentration determined from Curve A, S is the cross-sectional area of the membrane, t is time, and V is the volume of the solution in the cell compartment. On the other hand, if anion invasion is considered, then Curve A presents the pH change associated with the combined effects of cobalt transport and anion invasion. Thus, the difference in the hydrogen ion concentration represented by Curves A and C of Figure 1 should be used to estimate the Co^{2+} concentration in the feed chamber. That is,

$$C_{\text{Co}^{2+}} = \left(J_{\text{H}^+}^T - J_{\text{H}^+}^I \right) St/2V = \left(C_{\text{H}^+}^A - C_{\text{H}^+}^C \right)/2 \quad (6)$$

where $C_{\text{H}^+}^C$ is the hydrogen ion concentration determined from Curve C. The results obtained with Equation 6 are shown in Figure 2. Comparing curves A and B

which represent the data derived from Equations 5 and 6 respectively, it can be seen that the invasion-corrected Curve (B) is in good agreement with the atomic absorption Curve (C), at least in the first hour region. On the other hand, if anion invasion is ignored (i.e., Equation 5 is applied), the result is totally different from that obtained from atomic absorption. This means that in Donnan dialysis experiments involving high acid concentrations, pH measurement cannot yield accurate information on the metal ion concentration change unless the invasion of anions is also known.

Diffusion of HSO_4^-

A typical set of HSO_4^- diffusion data obtained with the pH-stat technique, and recorded and treated by the microcomputer is plotted in Figure 3. In these experiments, the left compartment was filled with $0.5 \text{ mol dm}^{-3} \text{ H}_2\text{SO}_4$ while the right compartment initially contained metal-free distilled water at pH 4.5. It can be seen that steady-state was achieved in about 1 minute, following which the HSO_4^-

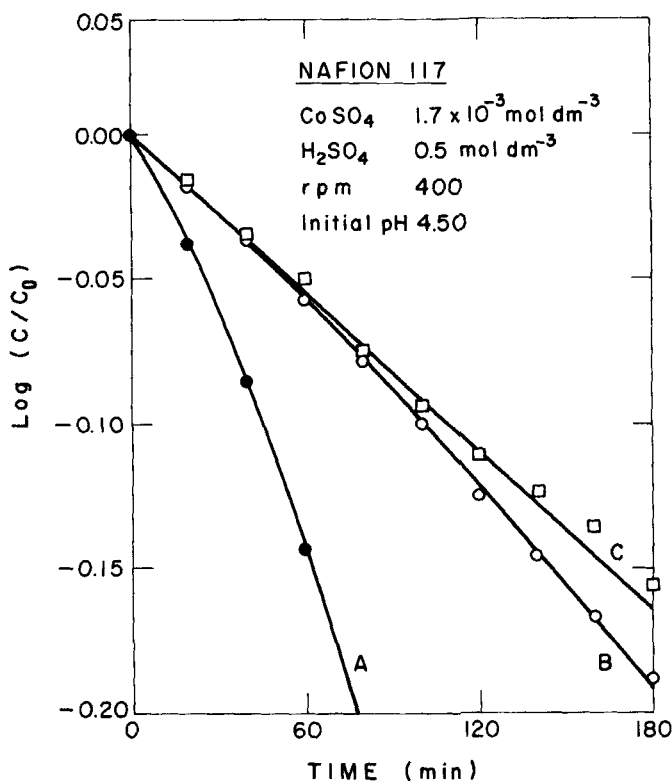


Figure 2. Plot of $\log (C/C_0)$ vs. time for the CoSO_4 - H_2SO_4 system; A: Co^{2+} determined from Eq. 2 (i.e., no correction for anion invasion); B: Co^{2+} determined from Eq. 4 (i.e., corrected for anion invasion); C: Co^{2+} obtained from atomic absorption spectrophotometry.

counting curve became practically a horizontal line. It was observed that if the reaction time was relatively long, e.g., $t > 30$ minutes, the slope of the counting curve gradually increased. This behavior is attributable to the transport of sodium ion. During the titration, more and more Na^+ ions went into the titration chamber and finally Na^+ - H^+ ion exchange took place resulting in an increase in the measured H^+ flux. To avoid or minimize such an ion exchange effect, the experiments were carried out for relatively short times, thereby ensuring that the Na^+ concentration in the titration chamber was maintained below $5 \times 10^{-4} \text{ mol dm}^{-3}$ (10 ppm). Therefore, the running time usually was 10 to 30 minutes depending on the H_2SO_4 concentration in the feed chamber. According to Figure 3, the flux of the HSO_4^- ion can be readily calculated from the slope of the plot of the total

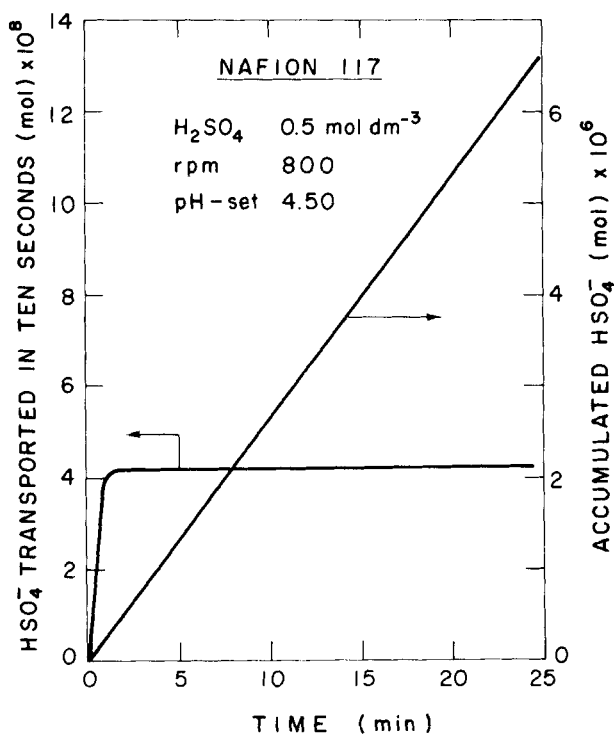


Figure 3. Effect of time on the instantaneous (pH-stat signal taken every 10 seconds) and cumulative transport of HSO_4^- .

accumulated amounts of HSO_4^- /unit area against time because this plot is a straight line.

The effect of rotating speed on HSO_4^- transfer is shown in Figure 4; when the rotating speed in both compartments increased from 400 to 800 min⁻¹, the flux remained practically constant. This means that in this range of stirring speed, the boundary layer effect was negligible and the process was only controlled by the membrane diffusion. Therefore, the membrane diffusion flux can be expressed as:

$$J_{\text{HSO}_4^-} = \frac{D}{d} \left(\bar{C}_{\text{HSO}_4^-}^L - \bar{C}_{\text{HSO}_4^-}^R \right) \quad (7)$$

where D is the diffusion coefficient of HSO_4^- through the membrane; d , thickness of

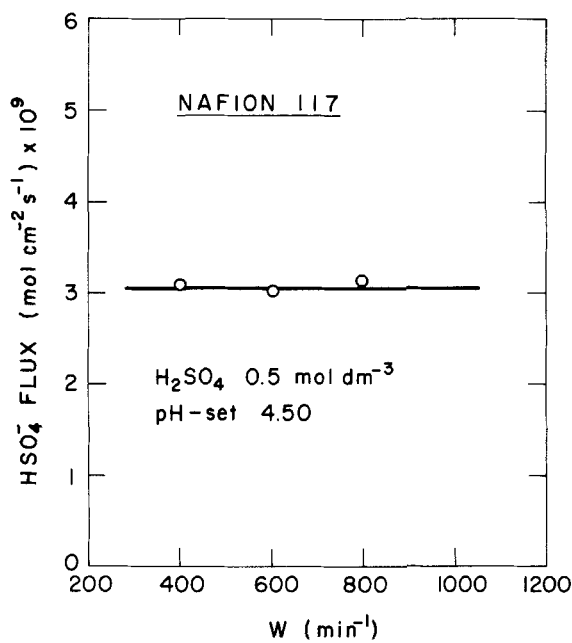


Figure 4. Effect of rotating speed on HSO_4^- flux.

the membrane and $\bar{C}_{\text{HSO}_4^-}^{\text{L}}$ and $\bar{C}_{\text{HSO}_4^-}^{\text{R}}$, the HSO_4^- concentrations in the membrane on the feed side (left) and receiving side (right) respectively. The distribution coefficient K_D can be defined as:

$$K_D = \bar{C}_{\text{HSO}_4^-} / C_{\text{HSO}_4^-} \quad (8)$$

where $C_{\text{HSO}_4^-}$ is the HSO_4^- concentration in the solution. Thus Equation 7 can be expressed as:

$$J_{\text{HSO}_4^-} = \frac{D'}{d} \left(\bar{C}_{\text{HSO}_4^-}^{\text{L}} - \bar{C}_{\text{HSO}_4^-}^{\text{R}} \right) \quad (9)$$

where $D' = DK_D$ is an apparent diffusion coefficient. This means the HSO_4^- flux is

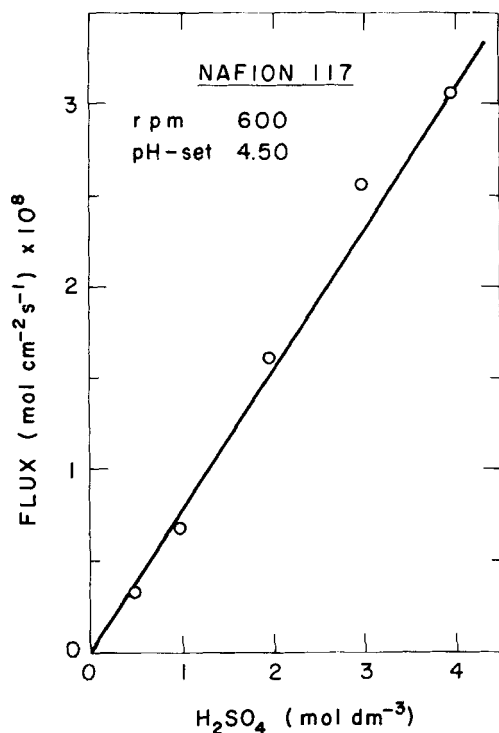


Figure 5. Effect of H₂SO₄ concentration on HSO₄⁻ flux.

proportional to the solution concentration difference. This expression is similar to those used by Yeo and McBreen (10) and Will (11) in their potentiostatic experiments for Cl⁻ and Br₃⁻.

Due to the fact that under the experimental conditions, $C^{\text{R}}_{\text{HSO}_4^-} \ll C^{\text{L}}_{\text{HSO}_4^-}$, Equation 9 can be simplified as:

$$J_{\text{HSO}_4^-} = \frac{D'}{d} C^{\text{L}}_{\text{HSO}_4^-} \quad (10)$$

Here Equation 10 is also similar to the limiting diffusion current measured by previous electrochemical methods (10,11). According to Equation 10, if a pair of values of $J_{\text{HSO}_4^-}$ and $C^{\text{L}}_{\text{HSO}_4^-}$ is available, then the value of D' can be calculated.

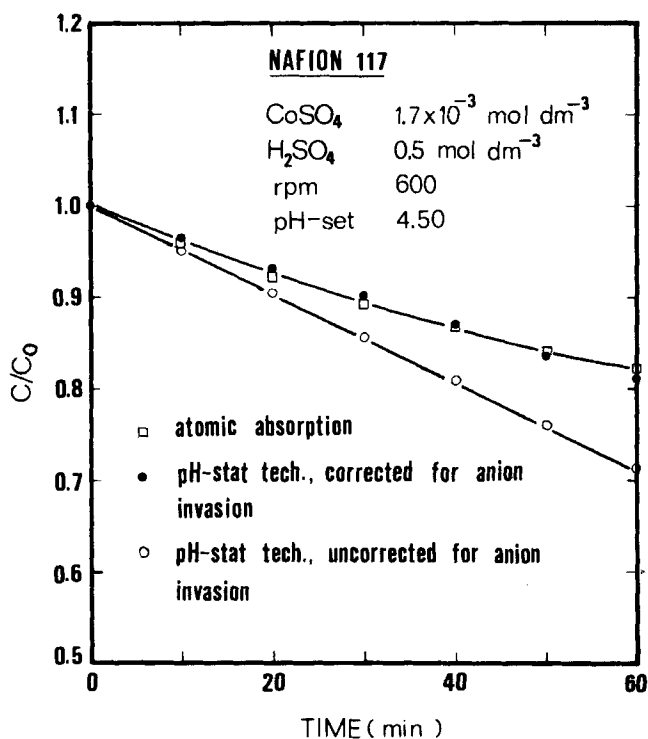


Figure 6. Effect of anion invasion on measurement of cobalt concentration with the pH-stat technique.

The effect of the H_2SO_4 concentration in the strip chamber on the flux of HSO_4^- through the membrane is presented in Figure 5. It can be seen that the diffusion flux increases linearly with H_2SO_4 concentration. Thus in a Donnan dialysis process, whenever the acid concentration increases, the invasion of anions through the membrane would be expected to become increasingly significant. Since the plot of the diffusion flux against H_2SO_4 concentration is a straight line, the apparent diffusion coefficient D' can be estimated from the slope in Figure 5 with the aid of Equation 10. A least squares method gives D' as $9.2 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The magnitude of this apparent diffusion coefficient for HSO_4^- is consistent with previous work (10,11).

Donnan Dialysis and the pH-Stat Technique

The application of the pH-stat technique in the CoSO_4 - H_2SO_4 system is shown in Figure 6. The pH of the cobalt reservoir compartment was set at 4.5. As expected, the cobalt concentrations measured from the pH-stat technique with consideration of anion invasion fit well with the atomic absorption analytical results, while the corresponding uncorrected data indicated a significant deviation from the atomic absorption analysis. The results further demonstrate that Equation 4 instead of Equation 2 should be used when the pH-stat technique is employed in Donnan dialysis experiments.

CONCLUSIONS

The main advantage of the pH-stat technique is that it provides a convenient microprocessor-based continuous monitoring of pH-sensitive ion-transfer processes. The results presented above demonstrate that anion invasion in Donnan dialysis can be significant if the acid strip solution concentration is high. The bisulfate ion has been shown to diffuse through Nafion membranes and the apparent diffusion coefficients and fluxes have been determined. It is demonstrated that the pH-stat technique can be an effective method for measuring anion flux. The application of this technique to Donnan dialysis experiments involving metal ions is feasible; however, it requires information on the anion invasion characteristics of the strip acid.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation under Grant No. R11-8311763.

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