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Decontamination of Nitrate Polluted Water[1]

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ABSTRACT

Nitrate can be extracted from water at any pH below 10 by a water-insoluble quaternary ammonium 2,4,6-trimethylphenate or N-benzyl-4-methylbenzenesulfonamidate dissolved in trioctylphosphate (TOP). Membranes were prepared by taking up TOP solutions of the quaternary ammonium bases in porous polypropylene (Celgard^{R}-2400). These membranes were used in a modified dialysis cell to transfer NO_3^- from near-neutral water to stripping solutions of pH, 12-14. Specific rate constants, $\underline{k}$, in excess of 10^{-4} cm s^{-1} were observed for nitrate removal under a wide variety of loading and stripping conditions. This is sufficient to project a practical device for the decontamination of nitrate-polluted water.

When the hydrodynamic resistances in both the feed and the strip are removed by pumping these solutions through static mixers adjacent to the membrane, $\underline{k}$ is reduced by making the stripping solution less basic or by increasing its nitrate concentration. These observations suggest that the disassembly of the carrier of the NO_3^- and H^+ at the stripping interface is a stepwise process, involving energetically unfavorable, charge-separated species.

INTRODUCTION

Pollution of ground and surface water by nitrates is a widespread problem in the United States (2,3), and even more serious in

Europe (4,5), where population densities are higher. Nitrate pollution results from oxides of nitrogen in automobile exhausts, from industrial activity, and especially from intensive agricultural application of nitrogenous fertilizers (3-6). In an earlier paper (7) it was shown that nitrate could be removed from near-neutral water by a solid-supported liquid membrane, in which the active, liquid phase was didodecylamine dissolved in trioctylphosphate (TOP). The nitrate is deposited, along with a proton derived from the treated water or a buffer, in a stripping solution at a pH of about 13. The liquid phase served to couple the transfer of the nitrate ion, which is the least hydrophilic ion commonly occurring in domestic water (8), to the transfer of the proton (9). The criterion of thermodynamic spontaneity is that the product $(H^+)(NO_3^-)$, should be larger in the treated water than in the stripping solution (9). (The quantities in parenthesis should be activities, but these are usually approximated by concentrations.) However, the flux was marginal for practical application, and was not improved by using primary or tertiary amines.

We have now improved the performance of such membranes by replacing the amine with a quaternary ammonium phenate or sulfonamidate, which are stronger bases than the amines, and, therefore reduce the internal resistance. The simplest acid-base reaction of these substances in a two-phase system is shown in eq. 1. The overbar

$$H^+ + NO_3^- + \overline{R_3NCH_3^+B^-} \rightleftharpoons \overline{R_3NCH_3^+NO_3^-} + \overline{HB} \qquad (1)$$

indicates a substance in the organic phase. The groups, R, of the quaternary ammonium cation are mixtures of $n\text{-}C_8H_{17}$ and $n\text{-}C_{10}H_{21}$, in equal amounts. Two substances, 2,4,6-trimethylphenol and N-benzyl-4-methylbenzenesulfonamide were used as HB. The latter ionizes by losing a proton from nitrogen (10). The non-aqueous solvent used was TOP.

Separatory funnel experiments showed that the mass-action quotient, Q, for the extraction of nitric acid by $R_3NCH_3^+B^-$ was considerably more complicated than suggested by eq. 1, and we were unable to arrive at an analytical expression for it. As a result, we were unable to distinguish clearly, between the internal resistance and the feed-side interfacial resistance. However we were able to isolate the stripping-side interfacial resistance. This paper describes a stripping mechanism which is consistent with the dependence of the stripping resistance on the composition of the stripping solution. It also describes the dependence of the nitrate transfer rate on the composition of the loading solution.

EXPERIMENTAL

Membrane transfer experiments were carried out in a cell which has been previously described (11,12), by the previously described techniques (12). For membrane experiments, nitrate concentration was usually determined from its U.V. absorption (13). This was occasional-

ly confirmed electrometrically, with a nitrate-sensitive electrode, previously calibrated with solutions of known composition. For separatory funnel extraction experiments nitrate was determined electrometrically, because the final solutions could not be made sufficiently haze-free for reliable optical measurements. The membrane support was a porous polypropylene, Celgard^{R}-2400 (14,15).

In all the membrane transfer experiments the decay of $\underline{A}$, the optical absorbance at 232 nm in the loading solution was fitted to the pseudo first-order rate law (12), in which $\underline{k}$ is a rate constant, with

$$\frac{\underline{k}\underline{a}}{\underline{v}} = \frac{\ln(\underline{A}_0/\underline{A}_t)}{\underline{t}} \quad , \tag{2}$$

units of cm s^{-1}, $\underline{a}$ is the area of the working membrane, 6.5 cm^2, $\underline{v}$ is the volume of the loading solution, and $\underline{t}$ is time. The subscripts of $\underline{A}$ indicate the time of measurement. Typically, semilogarithmic plots of $\underline{A}$ as a function of $\underline{t}$ were linear from 5% to about 90% transfer. Multiple repetition gave an average deviation from the mean of ~10% for $\underline{k}\underline{a}/\underline{v}$ for serial experiments. Larger discrepancies were sometimes observed for experiments repeated after long time lapses and/or with new batches of reagent.

Quaternary ammonium bases were prepared by dissolving .024 moles of the corresponding chloride (Aliquat^{R}-336[16]) and the phenol or sulfonamide in a minimum volume of dichloromethane, then shaking three times with fresh, 65 cm^3 portions of 0.5 $\underline{M}$ NaOH. The organic layer was separated, washed with water, dried with anhydrous magnesium sulfate, and the dichloromethane was removed under vacuum. The residues were viscous liquids which gave only the faintest precipitate when they were dissolved in alcohol, acidified with glacial acetic acid, and alcoholic silver nitrate was added.

N-Benzyl-4-methylbenzenesulfonamide was prepared by dropping 20 g (.105 moles) of 4-methylbenzenesulfonyl chloride, dissolved in 50 cm^3 of anhydrous pyridine, slowly, with stirring, into 5 g (.047 moles) of benzylamine dissolved in 50 cm^3 of anhydrous pyridine. The mixed solution was allowed to stand for one hour. Then 50 cm^3 of water was added with stirring to hydrolyze the excess 4-methylbenzenesulfonyl chloride and 50 cm^3 of dichloromethane was added to induce separation. The organic layer was washed twice with 50 cm^3 portions of 10% aqueous HCl, some additional dichloromethane being added to solubilize any precipitate which formed. The organic layer was dried with anhydrous magnesium sulfate and the dichloromethane removed under vacuum. The residual solid, N-benzyl-4-methyl-benzenesulfonamide, was recrystallized from an ethanol-water mixture. It had m.p., 113° (previously reported, 114° (17) and gave appropriate IR and ^{1}H-NMR spectra.

Trioctylphosphate was distilled under vacuum before use. It, and other materials were of the best quality commerically available, and were obtained from standard sources. Other materials were used as supplied.

RESULTS

A series of separatory funnel equilibrations were carried out with the quaternary ammonium sulfonamidate in an attempt to determine the form of the mass action expression, and, thereby, the composition of the nitrate carrying species. However, at higher NO_3^- and/or H^+ concentrations, more than one mole of NO_3^- was extracted per mole of quaternary ammonium base, so that no single form of mass action expression is valid over a wide range of concentrations. Typical results are shown in Table I.

Membrane experiments were carried out to test the utility of a solid-supported membrane device using these reagents in removing nitrate from near-neutral water. We also probed the interfacial resistances in order to suggest a mechanism for the interfacial reaction. Using 2,4,6-trimethylphenol as HB, the pumping rate was varied in order to find a range of pumping rates within which the aqueous hydrodynamic resistances were negligible. Experiments in which the composition of the stripping solution was varied were carried out with the sulfonamidate. Less extensive experiments of this sort, carried out with the phenate, suggest that it behaves similiarly. The rate constants for nitrate transfer, $\underline{k}$, that were obtained in these experiments, are shown in figs. 1-3.

If there is no significant accumulation of NO_3^- in the membrane, and the overall process is spontaneous, $\underline{k}$ should be governed by eq. 3 (12,17,18).

$$\frac{1}{\underline{k}} = \frac{1}{\underline{k}_1} + \frac{1}{\underline{k}_2} + \frac{1}{\underline{k}_3} + \frac{1}{\underline{k}_4} + \frac{1}{\underline{k}_5} \qquad (3)$$

Table I
Equilibrium Loading of Nitrate by Quaternary Ammonium Sulfonamidate[a,b]

Initial ($R_3NCH_3^+A^-$),M	Final Aq.(NO_3^-),M	Final pH	Final Org.(NO_3^-),M
0.80	2.1×10^{-4}	7.3	0.19
0.20	3.3×10^{-4}	7.8	0.097
0.054	1.3×10^{-3}	11.7	0.048
0.81	3.7×10^{-3}	7.3	0.84
0.52	5.9×10^{-3}	7.3	0.73
0.51	3.1×10^{-3}	7.6	0.62

[a]The organic solvent was TOP. The ratio of aqueous to organic volumes was 50 except where otherwise given.
[b]The ratio of aqueous to organic volumes was 20.

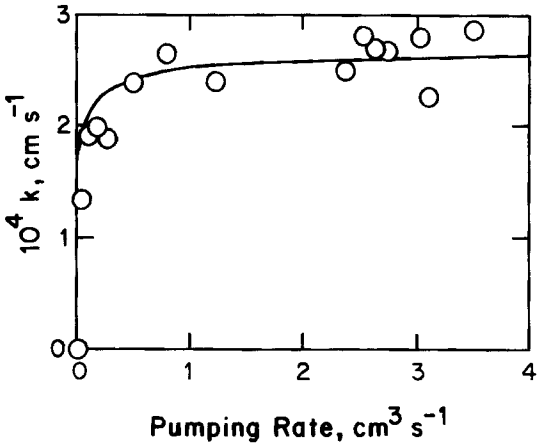


Figure 1. The variation of $\underline{k}$ with pumping rate, $\underline{r}$. The membrane reagent was the quaternary ammonium phenate, 0.8 $\underline{M}$ in TOP. The loading solutions were buffered to a pH of 7.3 with a phosphate buffer. The stripping solution contained 0.1 $\underline{M}$ NaOH. Both loading and stripping solutions initially contained 10^{-3} $\underline{M}$ $NaNO_3$. The solid line shows the values of $\underline{k}$ derived from eq. 3, with values of $\underline{k}_1$ given by eq. 4, $(1/\underline{k}_2 + 1/\underline{k}_3 + 1/\underline{k}_4)$ taken as $(2.7 \times 10^{-4})^{-1}$ and $1/\underline{k}_5$ assumed to be negligible.

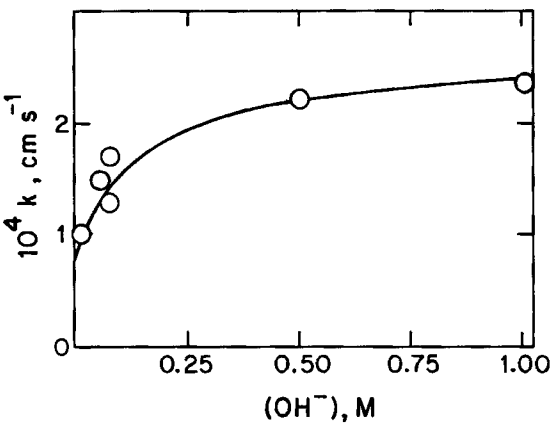


Figure 2. The response of $\underline{k}$ to the OH^- concentration of the stripping solution. The feed initially contained 10^{-3} $\underline{M}$ NO_3^- and was buffered to a pH of 7.3 with a phosphate buffer. The stripping solutions all contained 1×10^{-3} $\underline{M}$ $NaNO_3$ and varying NaOH concentrations, as shown. The membrane solution was 0.8 $\underline{M}$ quaternary ammonium N-benzyl-4-methylbenzenesulfonamidate in TOP. The solid line is the prediction of eq. 8, with parameters given in the text.

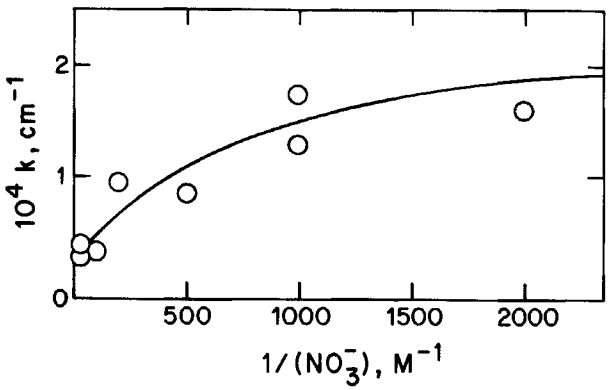


Figure 3. The response of $\underline{k}$ to the NO_3^- concentration of the stripping solution. The OH^- concentration of the strip was 0.1 $\underline{M}$. Other conditions are the same as those for fig. 2. The solid line is again the prediction of eq. 8.

Equation 3 is obtained from a steady-state treatment of the membrane transport process. It is a specialized form of the general expression for pseudo-first order processes in sequence. The individual terms are called resistances, and the equation has the same form as the equation for electrical reistances in series. If the aqueous solutions are well buffered and the carrier is in substantial excess, each $\underline{k}$ can be approximated by imagining that the system is in equilibrium up to that point, calculating the flux per unit area, and dividing it by the (NO_3^-) of the feed. Thus, for $\underline{k}_5$, we imagine that the only significant resistance is diffusion of NO_3^- away from the stripping interface. The flux, $\underline{j}_5$, is given by $\underline{D}\{(NO_3^-)_i - (NO_3^-)_s\} / \underline{l}$, where $\underline{D}$ is the diffusion coefficient of NO_3^- in the aqueous phase, $(NO_3^-)_i$ is the interfacial NO_3^- concentration, subscript s indicates a concentration in the bulk of the stripping solution, and $\underline{l}$ is the thickness of the semi-stagnant Nernst layer, adjacent to the membrane. If $(NO_3^-)_i >> (NO_3^-)_s$, which is reasonable if the transport is strongly spontaneous, then $\underline{j}_5$ is, simply, $\underline{D}(NO_3^-)_i / \underline{l}$. Since all processes up to process 5 are imagined to be in equilibrium, $(NO_3^-)_i$ is given its value at equilibrium with the feed, $(NO_3^-)_f(H^+)_f / (H^+)_s$ (9), where subscript f indicates a concentration in the feed. Thus, $\underline{k}_5$ is approximated by eq. 4. It should be emphasized that eq. 4 does not

$$\underline{k}_5 = \underline{D}(H^+)_f / \underline{l}(H^+)_s \qquad (4)$$

imply that all the processes leading up to diffusion of NO_3^- away from the stripping interface actually are in equilibrium. Rather, it is a fortuitous accident that the steady state result can be arrived at in this way.

The hydrodynamic processes in the feed and the strip are governed by $\underline{k}_1$ and $\underline{k}_5$, respectively. Diffusion across the membrane is governed by $\underline{k}_3$. The interfacial processes at the feed and the strip faces are governed by $\underline{k}_2$ and $\underline{k}_4$, respectively. In similar experiments with picrate, the anion concentration was monitored in both the feed and the strip solutions. The sum of these concentrations accounted for at least 98% of the initial picrate. Since NO_3^- is much more hydrophilic than picrate, eq. 3 should be valid.

The thickness of the aqueous Nernst layers is the same on the stripping side and the feed side, because the apparatus and the pumping rate are symmetrical (12). Since $\underline{l}$ is governed by the pumping rate, which is the same on the loading side and the stripping side, it and $\underline{D}$, are the same in the two aqueous solutions. Thus, $\underline{k}_5$ differs from $\underline{k}_1$ only by the factor, $(H^+)_f$ / $(H^+)_s$, which is much greater than unity, so that $\underline{k}_5$ is much larger than $\underline{k}_1$.

Figure 1 shows the variation of $\underline{k}$ for NO_3^- transfer with the pumping rate, under fairly typical conditions, using polyethylene gaskets. All the values are much smaller than those for hydrodynamically limited rates, given by eq. 5 (12), in which $\underline{r}$ is the

$$\underline{k}_1 = (2.5 \times 10^{-3})\underline{r}^{1/2} + (1.9 \times 10^{-3})\underline{r} \qquad (5)$$

pumping rate, in $cm^3\ s^{-1}$. However, if the plateau value of $\underline{k}$ is used to obtain $(1/\underline{k}_2 + 1/\underline{k}_3 + 1/\underline{k}_4)$, $1/\underline{k}_5$ is neglected, and eq. 5 is used for $\underline{k}_1$, eq. 3 gives a reasonably good account of the results, as shown in fig. 1. The rest of the work reported in this paper was done with a pumping rate of 2.55 $cm^3\ s^{-1}$. At this pumping rate eq. 5 gives a value of $\underline{k}_1$ at least an order of magnitude larger than any value of $\underline{k}$ we have observed. Typical values of $\underline{k}$ are nearly two orders of magnitude smaller than $\underline{k}_1$. Therefore, $1/\underline{k}_1$ makes small, and $1/\underline{k}_5$ totally negligible, contributions to $1/\underline{k}$.

The lack of a mass action expression made it impossible for us to quantitatively separate $1/\underline{k}_2$ from $1/\underline{k}_3$, however both of these are expected to remain approximately constant if the composition of the feed solution is constant; neither should be substantially altered by changes in the composition of the strip because the process is substantially irreversible under present conditions. However, as shown in figs. 2 and 3, $\underline{k}$ was increased by making the strip solution more basic and decreased by adding NO_3^- to the strip. These experiments were performed with a five dm^3 reservoir of stripping solution, to preclude any significant change in concentration during the experiment, and concentrations were monitored in the loading solution. This indicates that the stripping interfacial resistance is significant relative to $(1/k_2 + 1/k_3)$.

The effect on $\underline{k}$ of the variation of the pH of the feed, the NO_3^- concentration of the feed, and the reagent concentration in the membrane are shown in figs. 4-6. Figure 5 shows that k does not have the strong dependence on the pH of the loading solution that might have been expected, and, indeed appears to have a constant value of around 4×10^{-4} cm s^{-1} for pH values between 6 and 9. For practical purposes it is very noteworthy that NO_3^- is transferred from unbuffered $NaNO_3$

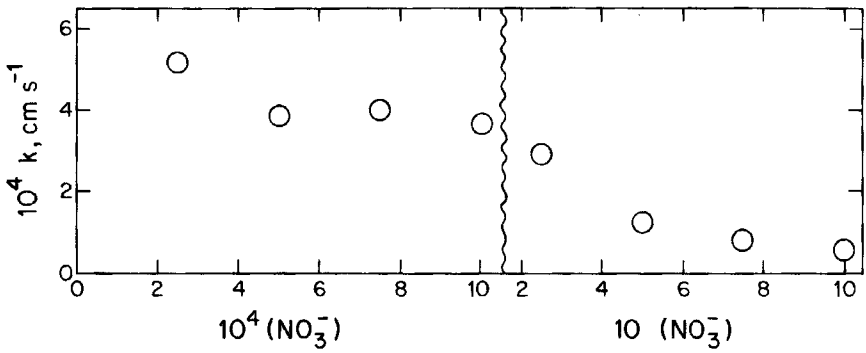


Figure 4. The response of $\underline{k}$ to the variation of the NO_3^- concentration of the feed. The pH of the feed was 7.3, maintained with a phosphate buffer. The membrane contained 0.8 $\underline{M}$ quaternary ammonium N-benzyl-4-methyl-benzenesulfonamidate in TOP. The stripping solution was 1 dm^3 of 0.5 $\underline{M}$ NaOH. Note the scale change.

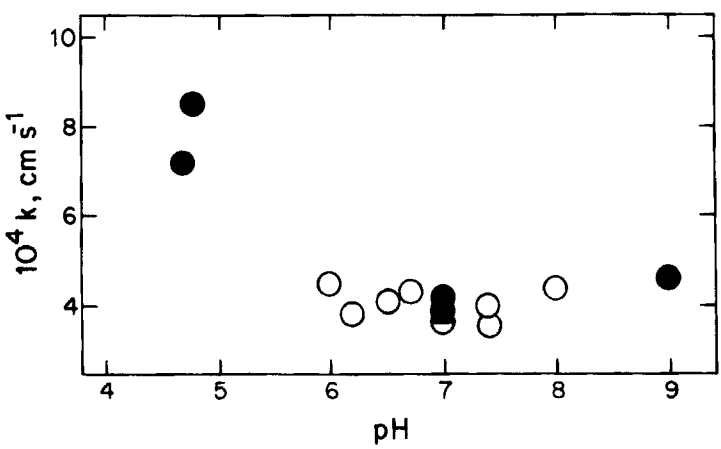


Figure 5. The response of $\underline{k}$ to variation of the pH of the feed. The NO_3^- concentration of the feed was 1 x 10^{-3} $\underline{M}$ throughout. The feed for the experiments represented by open points was buffered with phosphate buffers. It was unbuffered; adjusted with nitric acid; for the closed points. Otherwise the conditions were the same as those for fig. 4.

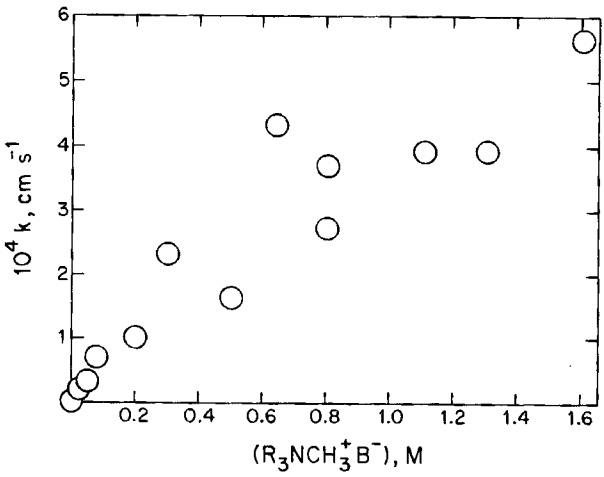


Figure 6. The response of $\underline{k}$ to the membrane reagent concentration. The feed initially contained 1 x 10^{-3} $\underline{M}$ NO_3^-, and was buffered to a pH of 7.3 with a phosphate buffer. Otherwise the conditions are the same as those for fig. 4.

solutions (pH ~9) at the same rate as from solutions buffered to a pH around 7. Figure 4 shows that $\underline{k}$ is not very dependent on (NO_3^-) in the range of concentrations typically found in domestic water, ~10^{-3} M. At higher concentrations some sort of saturation phenomenon seems to appear, and $\underline{k}$ is seriously diminished.

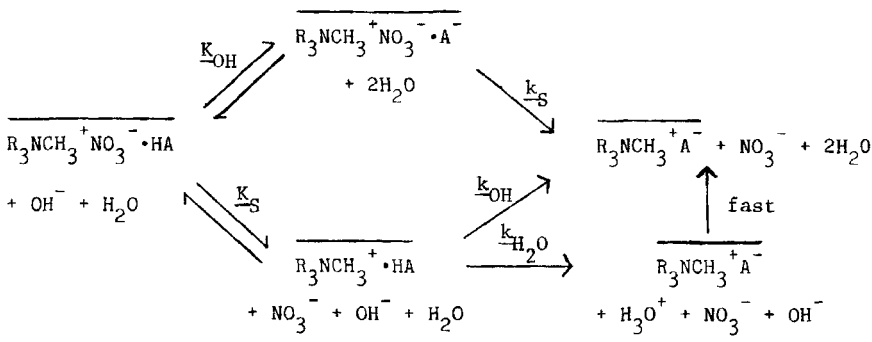
DISCUSSION

The variation of $\underline{k}$ with the composition of the stripping solution is rationalized by the stripping mechanism shown in Scheme I. All the species represented are regarded as localized at the stripping interface. Those marked with an overbar are mainly imbeded in the organic phase; those without, in the aqueous phase. Scheme I leads to eq. 6 for $\underline{j}_4$, the flux per unit area across the stripping interface,

$$\underline{j}_4 = \underline{k}_S\underline{K}_{OH}\underline{I}(OH^-) + \underline{k}_{OH}\underline{K}_S\underline{I}(OH^-)/(NO_3^-) + \underline{k}_{H_2O}\underline{K}_S\underline{I}/(NO_3^-) \qquad (6)$$

in terms of $\underline{I}$, the interfacial concentration of the postulated carrier species, $R_3\overline{NCH_3}^+NO_3^-\cdot HA$. The other concentrations are those of the stripping solution, which is assumed to be homogenous. If the value of $\underline{I}$ which would be in equilibrium with the feed is given by $\underline{C}_1(\overline{NO_3^-})_f$, where $(NO_3^-)_f$ is the nitrate concentration of the feed and $\underline{C}_1$ is constant as long as the loading conditions and membrane composition are constant, then eq. 7 gives $\underline{k}_4$. Under these conditions

Scheme I



$$\underline{k}_4 = \underline{C}_1\left\{\underline{k}_S\underline{K}_{OH}(OH^-) + \underline{k}_{OH}\underline{K}_S(OH^-)/(NO_3^-) + \underline{k}_{H_2O}\underline{K}_S/(NO_3^-)\right\} \qquad (7)$$

the first three resistances to the right of the equality in eq. 3 are constant. Setting their sum equal to $\underline{C}_2$, eq. 8 is obtained.

$$\frac{1}{\underline{k}} = \underline{C}_2 + \frac{1}{\underline{C}_1\left\{\underline{k}_S\underline{K}_{OH}(OH^-) + \underline{k}_{OH}\underline{K}_S(OH^-)/(NO_3^-) + \underline{k}_{H_2O}\underline{K}_S/(NO_3^-)\right\}} \qquad (8)$$

Equation 8 requires that a constant value of $\underline{k}$ and $1/\underline{C}_2$, should be approached asymptotically at high (OH^-) or low (NO_3^-), and figs. 2 and 3 show that this is the case. The selected asymptotic value was 2.7×10^{-4} cm s^{-1}. The other three parameters of eq. 8 were selected as follows to fit the data of figs. 2 and 3: $\underline{C}_1\underline{k}_S\underline{K}_{OH} = 4 \times 10^{-4}$; $\underline{C}_1\underline{k}_{OH}\underline{K}_S = 2 \times 10^{-6}$; $\underline{C}_1\underline{k}_{H_2O}\underline{K}_S = 1 \times 10^{-7}$. With these parameters, figs. 2 and 3 show the fit of eq. 8 to our results. The average discrepancy between observed and calculated values of $\underline{k}$ is 10%; about the experimental uncertainty. Equation 8 also correctly reproduces the trends shown in figs. 2 and 3; $\underline{k}$ is foreseen to diminish at lower base concentrations or higher nitrate concentrations in the strip. In a situation of this complexity it is not possible to definitely prove a mechanism. There are undoubtedly a number of alternative mechanisms that would fit the present results. However, that shown in Scheme I is intuitively satisfying and fits the results. If it is correct, it suggests that the underlying physical origin of interfacial barriers, in systems like this, is the need to pass through energetically unfavorable, charge separated intermediates in assembling and disassembling the ion carrier at the interface.

Figures 4-6 show that $\underline{k}$ values ~4×10^{-4} cm s^{-1} are readily obtained under a variety of conditions. This is an order of magnitude

larger than the k values which were previously obtained, using a secondary amine as carrier (7). This suggests that an analogous device with a membrane area of ~1 m^2 would remove 75% of the nitrate from 100 dm^3 of water per day — enough to provide ample water for a family kitchen. Using hollow fiber membrane technology (19) such a device could be modest in size and cost. A U.S. patent along these lines has been applied for (20).

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