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Publisher’s version / Version de l'éditeur:
https://doi.org/10.1149/1.2123797
Journal of The Electrochemical Society, 129, 1, pp. 85-89, 1982-03-06

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Transport Properties of Nafion^R Membranes in Concentrated Solution Environments

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ABSTRACT

The transport properties of perfluorinated cation exchange membranes in chlor-alkali cell solution environments have been studied using a newly designed membrane test cell. A radiotracer-weight method was used to measure sodium ion and water transport numbers for two Nafion® perfluorosulfonate membranes. A homogeneous film shows rapidly decreasing sodium ion transport numbers with increasing NaOH catholyte concentration, reaching a value of 0.56 mol F^{-1} with 12.5M solution at 80°C. A fabric-backed material with a sulfonamide exchange site layer yields considerably higher values with a more complicated concentration dependence. Water transport numbers for the latter membrane are also higher; a value of about 3 mol F^{-1} is found for typical experiments in which the anolyte solution is 5M NaCl. Results are discussed in terms of the mechanism of ionic membrane transport in relation to polymer water and electrolyte sorption.

Recently we have reported self-diffusion coefficients for sodium ion in several Nafion^R perfluorosulfonate ion exchange membranes in concentrated sodium hydroxide solutions at elevated temperatures (1). The determination of membrane diffusion coefficients is part of an experimental program to provide parameters for a multicomponent transport model of membrane chlor-alkali cells (2-4). In addition to measurements of ionic diffusion and membrane water and electrolyte contents (1), it is also necessary to determine the dynamic properties of the membrane under conditions typical of an operating cell. These conditions include concentrated solution environments, elevated temperatures, and high current densities. Here we report a new cell design for measurement of the sodium ion and water transport numbers in ion exchange membranes under these conditions.

A rather extensive literature exists on the determination of ionic and water transport numbers in ion exchange membranes. The majority of this work has been reviewed by Lakshminarayanaiah (5, 6). Two methods for ionic transport measurements are Hittorf-type electrolysis experiments and indirect emf methods. In similar fashion, membrane water transport numbers can be measured by electrolysis techniques or by streaming potential measurements. Aside from the systematic discrepancies which have been observed between emf and the true electrolysis results (5), the former techniques are inappropriate for this work because we wish to measure membrane properties under conditions of high current density. Electrolysis methods based on measuring changes in either solution volume or weight can be employed. Volume methods are generally more convenient, but are susceptible to errors due to membrane movement and are difficult to use at elevated temperatures. Sinha and Bennion (7) have determined potassium ion transport numbers for a cation exchange membrane in 2-10M potassium hydroxide solutions at room temperature. Low current densities, 12 A m^{-2} or less, were used and results were determined by measurement of solution volume changes and titrimetric analysis. The average relative standard deviation obtained for the potassium ion transport number was 6% even for these carefully performed measurements. The need to create a measurable concentration change during electrolysis with this approach presents a particular problem for ionic transport number measurements in concentrated solution environments. If concentration changes are kept small it is difficult to obtain sufficient accuracy in solution analysis to obtain a reliable result. If larger concentration changes are produced, such membrane properties as water and electrolyte content are altered. In the latter case interpretation of results becomes difficult. Meares and Sutton (8) have described an elaborate method for measuring membrane ionic transport numbers at constant chemical composition using radiotracers. Although this apparatus is not readily adaptable to the experimental conditions of interest here, it demonstrates that the use of radiotracers can be effective in largely removing the problem of concentration changes in the measurement of membrane transport parameters. Thus the experiments which are described here are based on the radiotracer determination of sodium ion transport numbers, combined with a weight method for the measurement of water transport numbers. Results are discussed in terms of the factors which influence the overall transport characteristics of an ion exchange membrane in a chlor-alkali cell.

Experimental

Apparatus.—A diagram of the membrane transport test cell is shown in Fig. 1 and 2. The cylindrical cell is constructed entirely of Teflon, with an outside diameter of 15 cm. The Teflon stirring assembly in each half-cell is held in place using a press-fit bearing the threaded end cap. Teflon-coated magnetic

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* Electrochemical Society Active Member.

Key words: current efficiency, ion exchange, electrolysis.

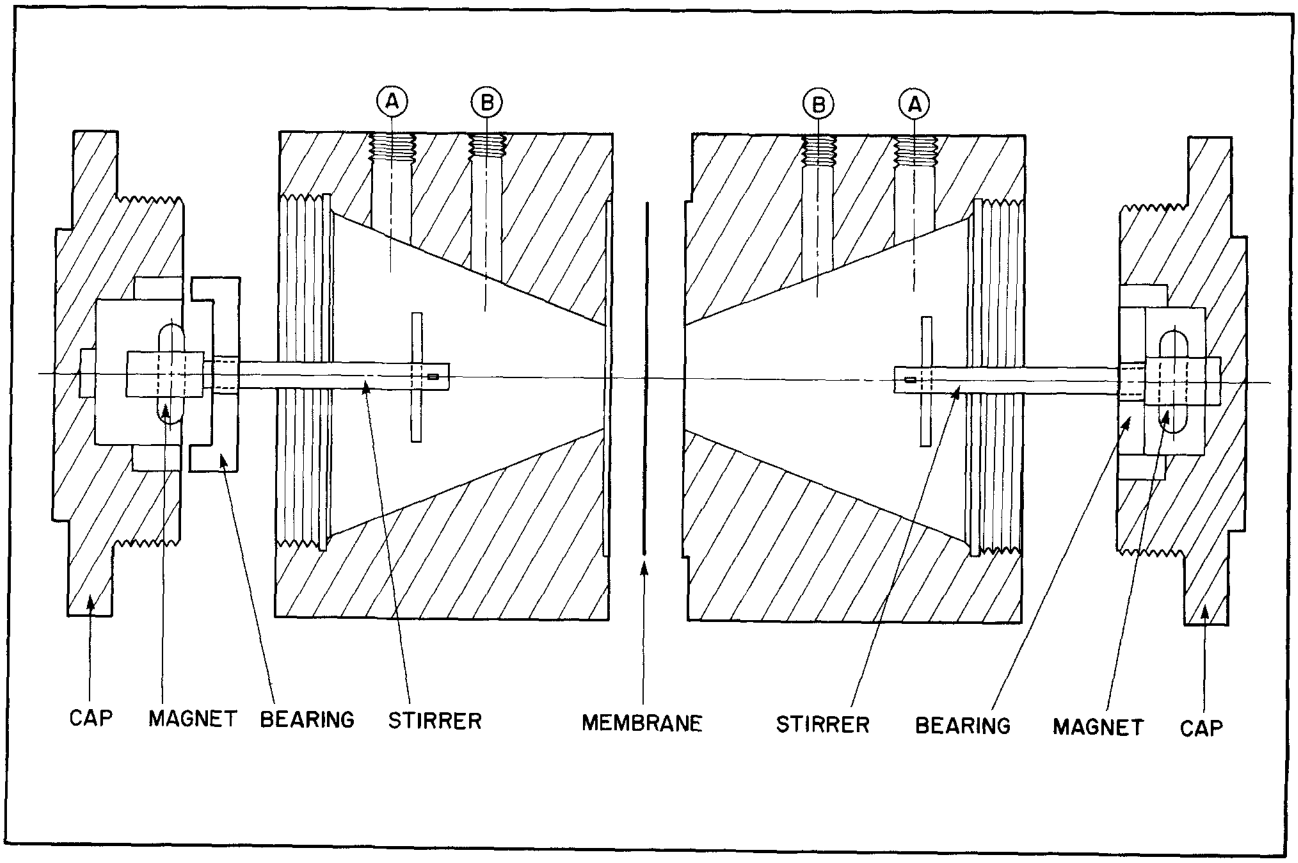


Fig. 1. Ion exchange membrane transport cell

stirring bars provide coupling to externally placed magnets which are attached to constant speed motors. Solutions are stirred at speeds of 600 rpm to avoid concentration polarization at membrane surfaces and to hasten temperature equilibration. The ion exchange membrane is placed between the half-cells using silicone rubber gaskets, and the cell assembly is then clamped together with brass end plates and threaded bolts (not shown). The interior compartment of each half-cell is conical in shape; this design allows for even distribution of current lines of flux through the membrane, optimum drainage for solution recovery, and gas bubble disengagement space above the solution level.

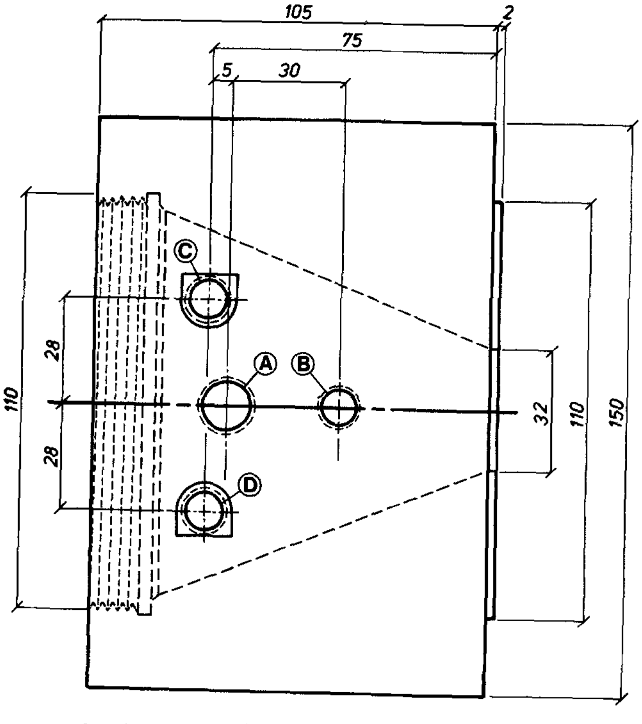


Fig. 2. Top view of a half-cell, with dimensions in mm

Circular platinum mesh electrodes of 6 cm diam are used in the cell; platinum wire leads are fitted through threaded Teflon fittings in openings B. The electrodes have center holes to accommodate the stirrer shafts. Openings A are used for solution delivery and sample withdrawal. Weighed drying tubes filled with molecular sieves are fitted here during the experiment so that water lost by evaporation can be determined. Solutions are heated with 80W cartridge heaters (Watlow Electric Manufacturing Company) placed in each half-cell; temperature control (±1°C) is achieved using a platinum temperature sensor and proportional temperature controller (Cole-Parmer Instrument Company). The heaters and temperature sensor are inserted into titanium tubular holders which are fitted into openings C and D (Fig. 2).

Procedure.—The membrane is equilibrated with appropriate solutions at elevated temperature in the cell for up to 24 hr. These solutions are then carefully removed by syphoning and replaced with weighed portions of identical solutions, about 330 ml for each half-cell. After temperature equilibration is achieved, the anode compartment is doped with sodium-22 radiotracer, an initial weighed sample of anode solution is removed, and constant current (±0.1%) is initiated. The exposed membrane area is 8 cm^2; a current of 1.6A is used in all experiments to yield a current density of 2 kA m^{-2}. Electrolysis is continued for 1-2 hr until solution concentrations have changed by about 1%. Finally, anode and cathode solutions are syphoned and weighed, and samples of cathode solution are analyzed for radioactivity and composition by titration. Typically 0.5% of the original radioactive sodium-22 is transferred during an experiment.

Experiments were conducted in which solutions were initially weighed into a dry cell, and the cell was disassembled to determine last traces (<1g) of solution left after syphoning. Both procedures yield identical results, confirming the accuracy of the simpler approach.

The sodium ion transport number, t_{Na^+}, is calculated from the weight concentration and radioactivity of the anode solution and the total amount of transferred radioactivity. The true sodium ion transport number describes the net amount of sodium ion transported from the anode to the cathode compartment; back-diffusion of sodium ion generates an error when using radiochemical methods, particularly at low current densities (8). Experiments were therefore performed where the cathode solution was doped with radiotracer and its appearance in the anode solution was monitored. Corrections to t_{Na^+} were less than 0.5%, as would be expected at a current density of 2 kA m^{-2}.

To calculate the transport number of water, t_{H_2O} (mol F^{-1}), the weight of water in the cathode solution before and after electrolysis is determined from solution weight concentrations and weights. The transport number is then given by

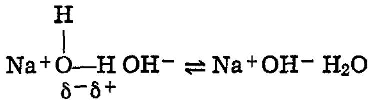
$$t_{H_2O} = \frac{(\Delta wt_{H_2O})F}{18.01\,(i,A)\,(t,\mathrm{sec})} + 1 \qquad [1]$$

The second term in Eq. [1] corrects for the consumption of water in the cathode reaction. Estimated standard deviation for t_{Na^+} and t_{H_2O} are 0.015 and 0.5 mol F^{-1}, respectively.

Materials.—Two Nafion membranes were studied: 1150 equivalent weight unbacked film and Nafion 295. The latter material is an 1150 EW membrane which is backed with an open weave Teflon fabric (70% open area), and the cathode surface of the membrane has been treated with ethylenediamine to produce weakly acidic sulfonamide exchange sites. Various properties of these membranes in concentrated sodium hydroxide solution have been reported previously (1).

Results and Discussion

Sodium ion and water transport numbers for 1150 EW are listed in Tables I and II. The values in Table I are those of experiments in which identical NaOH solutions were used in anode and cathode compartments. In Table II all experiments utilized 5M NaCl as the anode solution while cathode solutions were either 5M NaCl or various concentrations of NaOH. As seen in the tables and Fig. 3, t_{Na^+} decreases smoothly with increasing NaOH concentration for 1150 EW. This would be expected due to increasing electrolyte sorption into the membrane phase. However, it has been observed that although electrolyte invasion does occur for Nafion membranes in concentrated NaOH solutions, the amount of sorbed electrolyte remains relatively constant over the concentration ranges used in this work (1, 9). Membrane water contents for 1100 EW (9) and Nafion 295 (1) are seen to be greatly affected though, and so the only major change in membrane composition is the reduction in water content with increasing electrolyte concentration. (This is reflected in Table I by the generally lower t_{H_2O} values for 1150 EW as NaOH concentration increases.) Mauritz and co-workers suggest that a tunneling process of the form



$$\mathrm{Na^+}\underset{\delta^-\,\delta^+}{\overset{\mathrm{H}\atop|}{\mathrm{O}}\text{—}\mathrm{H}}\ \mathrm{OH^-} \rightleftharpoons \mathrm{Na^+OH^-\ H_2O}$$

would enhance hydroxide ion transport in environments of decreasing water content due to increased polarization of the O—H bond (9). This explanation appears reasonable in light of the measured transport numbers and the rather unusual electrolyte sorption characteristics of these membranes.

An interesting aspect of the t_{Na^+} values for 1150 EW in concentrated solution is their relatively large magnitude. In general the low concentration of exchange sites (about 1.0 × 10^{-3} mol/g swollen polymer) in 1150 EW would not be expected to cause sufficient Donnan exclusion of electrolyte to allow t_{Na^+} to rise much above 0.5. In comparison, Kressman and co-workers measured t_{Na^+} for a heterogeneous sulfonate ion exchange membrane with much larger ion exchange capacity and found that in concentrated NaOH solution at 25°C, t_{Na^+} falls below 0.5 for solution concentrations larger than 4M (10). We would attribute the difference to the ion clustered morphology of Nafion. The ion clusters generate centers of high exchange site concentration rather than a more even distribution throughout the membrane phase as for conventional materials (11). The ion clustering phenomenon has been shown to produce a variety of un-

Table I. Sodium ion and water transport numbers for 1150 EW Nafion, sodium hydroxide solution

Temperature (°C)	Solution concentration (mol l^{-1})	t_{Na^+} (mol F^{-1})	t_{H_2O} (mol F^{-1})
80	5.0*	0.78	2.4
	9.8	0.64	0.5
	10.9	0.62	1.2
	11.2	0.61	0.6
	12.8	0.56	0.5
90	5.0	0.76	3.0
	9.8	0.64	0.4
	13.0	0.60	0.9

* Molar concentrations were determined at room temperature.

Table II. Sodium ion and water transport numbers for 1150 EW Nafion, sodium chloride and sodium hydroxide solutions

Temperature (°C)	Anode solution (mol l^{-1})	Cathode solution (mol l^{-1})	t_{Na^+} (mol F^{-1})	t_{H_2O} (mol F^{-1})
70	NaCl, 5.0	NaCl, 5.0	0.99	3.6
80	5.0	5.0	0.99	2.8
90	5.0	5.0	1.00	2.3
80	NaCl, 5.0	NaOH, 5.0	0.80	2.1
80	5.0	9.5	0.69	1.9
80	5.0	11.0	0.62	1.9
80	5.0	12.4	0.58	1.7

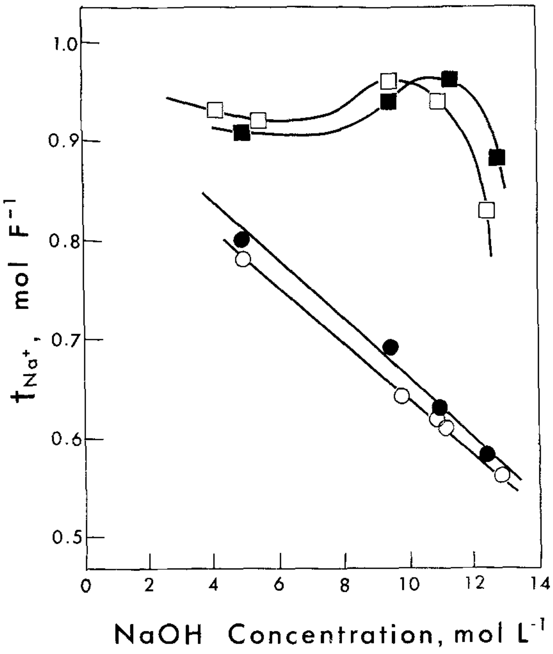


Fig. 3. Sodium ion transport number vs. NaOH catholyte concentration. ○, ●: 1150 EW membrane; □, ■: Nafion 295. Anolyte solution is NaOH for light symbols and 5M NaCl for dark symbols.

usual thermodynamic and transport properties for Nafion membranes in dilute solution environments (12-15). The t_{Na^+} values of near unity in NaCl/NaCl systems in Table II are particularly noteworthy. The membrane concentrations of sodium ion and chloride ion in 1150 EW equilibrated with 5M NaCl solution at 80°C are 1.9×10^{-3} and 0.4×10^{-3} mol cm^{-3}, respectively (16), indicating that while there is breakdown of Donnan exclusion and subsequent electrolyte sorption, chloride does not participate in conduction of current at a high current density.

The transport numbers in Table I for NaOH/NaOH systems are seen to have little temperature dependence. A similar result was obtained for the temperature dependence of self-diffusion of sodium ion in 1150 EW for 9.5M NaOH solution, where the activation energy of diffusion from 60° to 90°C was only 2.5 kcal mol^{-1} (1).

Transport numbers for Nafion 295 are presented in Table III for experiments using identical NaOH solutions and for those in which the anode solution was fixed at 5M NaCl. These results may be compared to other measurements of the transport properties of Nafion 295. Hora and Maloney report an average caustic current efficiency of 88% for this membrane when used in a chlor-alkali cell (17). Maloney also reports a current efficiency of 93% at 5M NaCl, 10M NaOH concentrations and 2 kA m^{-2} current density (18) Berzins measured a water transport number of 3.2 mol F^{-1} for 9M NaOH caustic strength with a membrane of the 295 composition but without fabric backing (19). In a recent report, Dotson and co-workers (20, 21) measured t_{Na^+} and t_{H_2O} for Nafion 295 at 85° and 1-3 kA m^{-2} current density. For experiments where identical NaOH concentrations are used as anolyte and catholyte, they report t_{H_2O} values from 4.0 to 1.5 over the concentration range studied in Table III, in excellent agreement with our results. However, their t_{Na^+} values are all about 0.1 mol F^{-1} lower than ours, although they observe a peak in t_{Na^+} at about 11M NaOH as seen in Fig. 3. No explanation can be offered here for this discrepancy. These workers have observed that the transport properties of Nafion 295 are independent of current density in the 1-3 kA m^{-2} range (18, 20, 21). Thus we have not varied current density here but have focused instead on the influence of other parameters.

As seen in Table III and Fig. 3, the dependence of t_{Na^+} on NaOH concentration has change dramatically with the introduction of the sulfonamide layer on the cathode surface of the membrane. At intermediate concentrations t_{Na^+} actually increases with increasing concentration followed by a rapid decrease as the NaOH cathode solution concentration is raised about 12M. The sulfonamide layer is characterized by both reduced water content and sorbed electrolyte and thus serves as a barrier to hydroxide transport (1, 17). As discussed by Mauritz *et al.*, in environments of extremely low water levels, as would be present in the sulfonamide layer, ion pairing would reduce the effect of a proton tunneling mechanism of hydroxide transport (9). Similar but less pronounced improvements in current efficiency are seen even with Nafion composite membranes where the cathode surface of the membrane is simply a higher equivalent weight sulfonate form, yielding fewer exchange sites (19).

Table III. Sodium ion and water transport numbers, Nafion 295, 80°C

Anode solution (mol l^{-1})	Cathode solution (mol l^{-1})	t_{Na^+} (mol F^{-1})	t_{H_2O} (mol F^{-1})
NaOH, 4.2	NaOH, 4.2	0.93	4.1
5.5	5.5	0.92	3.1
9.5	9.5	0.96	1.8
11.0	11.0	0.94	1.4
12.5	12.5	0.83	1.4
5.8	5.8	0.80*	2.2*
NaCl, 5.0	NaOH, 5.0	0.91	3.9
5.0	9.5	0.94	2.9
5.0	11.4	0.96	3.0
5.0	12.8	0.88	2.9

* Treated membrane surface facing anode solution.

The presence of a minimum in the t_{Na^+} plots for Nafion 295 can be related to the effects of electroosmosis. In general t_{H_2O} is a function of t_{Na^+} and other membrane parameters, but also strongly depends on anolyte concentration for cation exchange membranes (5, 21). Sodium ion, as the major current carrier, transports net positive amounts of water across the membrane. The frictional interaction between this water and hydroxide serves to increase t_{Na^+}. Kressman and Tye provide a general discussion of the effects of electroosmosis on cation transport number for cation exchange membranes in concentrated solution environments (22). They predict a minimum can be obtained in the concentration dependence of t_{Na^+} for a sufficiently large electroosmotic effect, even if anode and cathode solutions are of the same concentration. With fixed NaCl concentration and increasing NaOH concentrations in the cathode compartment, an osmotic component to water transport might also be expected. This would serve to increase water-hydroxide frictional interaction. As seen in Fig. 3, the result for Nafion 295 is to shift the t_{Na^+} curve to higher concentrations of NaOH for the mixed electrolyte experiments. For the 1150 EW membrane, where t_{H_2O} values are smaller, much smaller differences in t_{Na^+} are seen between the two types of experiment.

Although water transport provides a positive contribution to t_{Na^+}, the presence of large amounts of water in a membrane serves to favor hydroxide migration relative to that of sodium ion. These opposing effects lead to current efficiencies generally lower than 90% for homogeneous Nafion materials in highly concentrated NaOH solution environments. Berzins measured current efficiencies and water transport numbers for three Nafion membranes in NaCl/NaOH systems at 80°C and 3 kA m^{-2} current density: 0.1 mm thick 1100 EW, 0.05 mm 1500 EW, and a composite membrane composed of the two homogeneous films (19). The 1100 EW membrane shows current efficiencies of 55%, 40%, and 70% at NaOH concentrations of 6M, 10M, and 14M, respectively. For the 1500 EW membrane, current efficiency steadily declines from 85% to 55% over this concentration range. The water transport number increases for 1100 EW from 2 to 3.5 mol F^{-1} while for 1500 EW it decreases from 3 to 2 mol F^{-1} with increasing NaOH concentration. The performance of the composite film is very similar to that of the 1500 EW membrane, with the exception of slightly increased water transport. As predicted by Kressman and Tye, a minimum in current efficiency is seen for the membrane with larger water content and, probably due to an osmotic contribution, the 1100 EW membrane actually has a superior current efficiency at highest NaOH concentrations. Thus the overall performance of a homogeneous membrane is the net result of complicated interactions among cation transport, electroosmosis, osmosis, and the effect of membrane water content on the hydroxide transport mechanism. We would attribute the higher current efficiency of Nafion 295 over the 1100 EW/1500 EW composite membrane to the lower acidity of sulfonamide exchange sites, which would reduce water content, enhance ion pairing, and thus discourage hydroxide ion transport.

The water transport number for Nafion 295 in NaCl/NaOH experiments is seen to remain at about 3, independent of NaOH concentration. This value is similar to that of 1150 EW in 5M NaCl solution. It is interesting to note that the sulfonamide layer does not appear to restrict water transport. An increase in water concentration in the 1150 EW portion of the 295 membrane due to electroosmosis might be responsible for this behavior, perhaps resulting in intramembrane pressure gradients (2).

Krishtalik discusses the performance of a hypothetical two layer cation exchange membrane in chlor-alkali electrolysis (23). One layer would be highly conducting, but have low selectivity for transport of cations over anions, and the second layer (such as the sulfonamide layer in Nafion 295) would have opposite properties. His treatment yields the result that when the selective layer faces the hydroxide solution, the current efficiency of the composite membrane would be the same or slightly higher than that of the layer when used alone as a homogeneous film. If the placement of the composite membrane is reversed in the cell, the current efficiency should be somewhat better than using the nonselective film alone, but much lower than that of the composite membrane in the opposite placement. One experiment was performed here for Nafion 295 in NaOH solutions, in which the sulfonamide layer faced the anode compartment. As predicted, the t_{Na^+} value of 0.80 is marginally higher than the 0.78 result for 1150 EW, but much smaller than the value of 0.92 when the membrane is used in the opposite configuration.

In conclusion, the current efficiency of a chlor-alkali membrane cell is seen to be a complicated function of several membrane and solution parameters. These interactions become more complex in composite membranes. General features which lead to high current efficiencies are large ion exchange capacity to enhance cation diffusion and reject electrolyte sorption, low water content to prevent hydroxide migration by a tunneling effect, and osmotic or electroosmotic water transport to increase the frictional interaction between water and hydroxide ion. The optimization of membrane performance therefore depends on the difficult task of simultaneously improving each of these properties.

Acknowledgments

Dr. R. L. Dotson of Olin Chemicals provided valuable design assistance and Mr. Fred Jarvis supervised construction of the membrane transport cell. N. Tyrer and B. Kipling performed some experimental portions of this work. The authors thank E. I. du Pont de Nemours and Company for providing membrane samples. Financial support for this research was provided by the Olin Corporation, Chemicals Division, Southeast Process Technology, Electrochemical Technology Group.

Manuscript submitted March 6, 1981; revised manuscript received *ca.* July 1, 1981. This was Paper 394 presented at the St. Louis, Missouri, Meeting of the Society, May 11-16, 1980.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1982 JOURNAL. All discussions for the December 1982 Discussion Section should be submitted by Aug. 1, 1982.

Publication costs of this article were assisted by The University of Calgary.

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