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Ionic Permselectivity of Perfluorinated Ionomer Membranes

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Ionomer membranes, with ionizable groups attached to organic polymer backbones, exhibit a large difference in permeability between oppositely charged ionic species. This permselectivity is believed to result from the electrostatic interactions at the ion exchange sites. There is mounting evidence that the ion exchange sites in these membranes phase separate from the fluorocarbon matrix to form clusters.[1-4]

The permselectivity phenomenon is made use of in separation processes where Nafion perfluorinated membranes are used in the operation of chlor-alkali cells. The current efficiency in such cells is a measure of the degree of membrane ionic selectivity. For some Nafion membranes, it has been found[5,6] that the current efficiency, when plotted against the NaOH concentration in the cathode compartment of the chlor-alkali cells, exhibits a minimum as well as a maximum, as shown schematically in Figure 1.

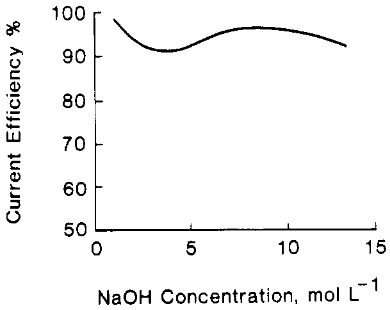

Figure 1. Schematic representation of the current efficiency as a function of NaOH catholyte concentration for Nafion membrane in a chlor-alkali cell.

Recently, Datye et al.[7] have proposed a model to explain the ionic permselectivity of Nafion membranes. In this model, it was argued that there exist dipole layers at the surface of spherical ionic clusters. The transport of ions through membranes was assumed to take place via hopping between clusters. The dipole layer at the cluster surface creates a deeper potential well for a negatively charged ion than for a positive one, thus making cation transport easier because of the lower potential barrier these ions have to overcome in order to diffuse through the membrane.

In this report we show that an extension of that model to include the dependence of the potential barrier on the water content of the membrane can account for the dependence of the current efficiency on NaOH concentration.

It is generally believed[8] that as water diffuses into the membrane, hydration shells will be formed around the negative and positive ions in the membrane clusters. We assume that oppositely charged ions exist in two possible states, either associated or dissociated. This assumption is derived from the model of Mauritz and Hopfinger[8] for the hydration-mediated dissociation equilibrium between unbound and side-chain-associated counterions in Nafion membranes. The fraction α of ion pairs remaining bound to each other will vary with the number n of water molecules present per ion pair.

In the model we consider, the dielectric constant κ will vary linearly with n for small n and will saturate at some value $1 + \kappa_0$ for infinite dilution. To fit these conditions we choose the otherwise arbitrary form

$$\kappa = 1 + \kappa_0 \tanh (n/n_0) \qquad (1)$$

since the precise variation of κ with n is not important in determining the qualitative results of the model. Mauritz and Hopfinger[8] have suggested a similar but piecewise linear variant of this.

The dependence of α on n may be found by arguing that its rate of change, $\mathrm{d}\alpha/\mathrm{d}n$, will be governed by two factors. First, there will be a term proportional to $-\alpha$, since the number of ion pairs dissociating when $n \rightarrow n + \mathrm{d}n$ will be proportional to the number α of bound ion pairs available. Secondly, there will also be a factor of $1 - \alpha$, since the potential barrier to release of a counterion is reduced by the number of already dissociated ions in its immediate vicinity. We thus have

$$\mathrm{d}\alpha/\mathrm{d}n = -c\alpha(1 - \alpha)$$

with c some constant. This has the solution

$$\alpha(n) = [1 + \exp(c(n - n_1))]^{-1} \qquad (2)$$

which is the familiar Fermi–Dirac function. The constant of integration, n_1, like n_0 in eq 1, is expected to be of the order of the hydration number. In the Mauritz–Hopfinger model[8] a similar but piecewise linear form is postulated for $\alpha(n)$.

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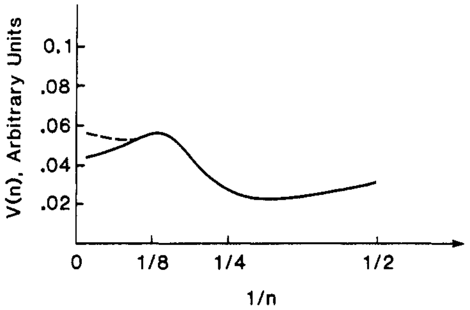

Figure 2. Electrostatic potential V within a cluster is shown in arbitrary units as a function of $1/n$, the reciprocal of the water content.

We assume a geometry in which the negative ions are constrained by their strong bonding to the chain backbone to remain distributed over the surface of a sphere of radius R_1. The bound positive ions, as in the model of ref 7, are then found on the surface of a sphere of smaller radius R_2 and are fewer in number of a factor of α. The dissociated positive ions, the number of which is proportional to $1 - \alpha$, are assumed found on a yet smaller sphere of radius R_3. We take R_1, R_2, and R_3 to be roughly independent of n, although this assumption may not be strictly justified in the regime where hydration is complete.

The potential at the center of the cluster will be proportional to

$$\begin{aligned} V(n) &= \frac{1}{\kappa(n)}\left[-\frac{1}{R_1} + \frac{\alpha(n)}{R_2} + \frac{1-\alpha(n)}{R_3}\right] \\ &= [A - B\alpha(n)]/\kappa \end{aligned} \tag{3}$$

with A and B positive constants and $A > B$. Substitution of eq 1 and 2 in this expression yields a form for V that varies with the choice of constants n_0, n_1, and c. From an initially high value at small n, the potential falls as the dielectric constant increases, but may then rise again if α decreases sufficiently abruptly. It may then pass through a maximum as κ continues to increase and V is again reduced. This behavior is shown as the solid line in Figure 2 for the arbitrary choice of constants $A = 1$, $B = 0.75$, $C = 2$, $n_0 = 6$, $n_1 = 5$, and $\kappa = 79$.

At very large n, it is likely that the assumption of the constancy of R_1 and R_3 will cease to be valid. Even after dissociation is complete, the addition of more water molecules will still tend to separate further the positive and negative ions. The constant A, which is equal to $(1/R_3 - 1/R_1)$ will thus be increased, and the potential V may once again rise. Such behavior is indicated schematically in the dashed line in Figure 2.

Because the current efficiency in the model of ref 7 increases monotonically with V, while the water content varies inversely with concentration of NaOH, the predictions of Figure 2 are qualitatively consistent with the experimental observations shown in Figure 1. The minimum and maximum in $V(n)$ at large and intermediate n (Figure 2) correspond, respectively, to the minimum and maximum in the current efficienty at low and intermediate NaOH concentrations (Figure 1). In contrast with the experimental curve, Figure 2 suggests an increase in the current efficiency for very small n. For such values of n, however, the membrane will be almost dry, and our model will no longer be relevant to describe the passage of ions through membranes since such passage is assumed to take place via hopping between clusters of high water content. The upturn in current efficiency at low caustic concentrations, which is predicted from the dashed line in Figure 2, is also interpretable in terms of the Donnan exclusion mechanism.[9]

In summary, we have presented an extension of the model of Datye et al.[7] for the ionic permselectivity of a membrane. The variation of current efficiency with membrane water content is the resultant of two competing processes. As the water content increases, the ionic association–dissociation equilibrium is shifted in the dissociation direction and the dielectric constant increases. This can give rise to maxima and minima in the current efficiencies. We should note that the mechanism we suggest is an alternative to one based on proton tunneling that was proposed by Mauritz and Gray.[10] We should also note that the model we have presented is far from being complete. In a more detailed study, the assumption of two possible states for ionic pairs should be replaced by an assumption of a continuum of states whose energies depend on the separation between the two oppositely charged ions of a pair. Such a calculation would also give a better picture of the distribution of positive counterions within the cluster. However, we believe our model to contain the essential elements of the problem and that the assumptions made, although imprecise, nevertheless give a reasonably good qualitative description of the experimental situation.

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Registry No. NaOH, 1310-73-2; Nafion, 39464-59-0.

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