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Simple Model for Clustering and Ionic Transport in Ionomer Membranes

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ABSTRACT: Cluster formation of the ionic side groups in an ionomer membrane of the Nafion type has been modeled and its relationship to ionic transport examined. Computer simulations show that the effect of electrostatic and elastic forces on the pendant ionic groups and their neutralizing counterions is such as to form a dipole layer at the surface of an ionic cluster. A model for selective transport is proposed based on the electrostatic potential created by the dipole layer. Qualitative agreement with experiment is obtained for the cluster size and current efficiency as a function of the equivalent weight of the membrane.

I. Introduction

Ion-containing polymer membranes exhibit a sizable difference in permeability between oppositely charged ionic species. Although the origin of this phenomenon is not well understood, it is generally believed that permselectivity arises as a consequence of the electrostatic interaction at the ion exchange sites in the membrane.[1] The ionic groups of the ionomer phase separate into clusters, forming a hydrophilic ionic phase in a hydrophobic polymer matrix.

In this paper we report the results of a modeling of cluster formation in an ionomer membrane and its relation to ionic transport through the membrane. In particular, we consider a system of the Nafion type and describe computer simulations of the spatial organization of ion dipoles within a cluster and have examined the relationship of this structure to ionic transport. The ionomer model that we have considered is highly simplified, containing only the most important ingredients in the problem, namely, the electrostatic and the elastic contributions to the energy. Our calculation is similar, in principle, to that of Eisenberg,[2] with the important difference that we do not assume any particular orientation for any dipole but rather treat these orientations as parameters that must be allowed to vary as the system minimizes its free energy and seeks its most favorable configuration. Perhaps the most interesting result to emerge from our simulations is that under the influence of electrostatic forces alone the ionic dipoles orient themselves to lie in the surface of the spherical clusters. There is thus no effective dipole layer at the cluster surface and the boundary is symmetric to the flow of cations and anions. However, as one will see in section III, the process of cluster formation gives rise to an elastic energy that breaks this symmetry and leads to selective transport.

II. Definition of the Model

While it is clear from experimental observation that clustering of the pendant-side-chain ionic groups does occur, the precise form of these clusters has not been determined. Some evidence exists[3] to suggest that the clusters may deviate from spherical form, possibly even being tubular in nature. In the present work we will make the simpler assumption that the dipolar ionic groups are distributed over the surface of a spherical cluster. We will thus base our calculations on a geometry very similar to that of the inverted-micelle model proposed by Gierke.[4] In choosing this model we are not denying the possibility that the dipoles may form a volume distribution within the cluster; we are rather taking as our first model the more plausible case in which the surface distribution of dipoles is not penetrated by segments of inert chain backbone, with the attendant energy cost. We further assume that the ionic groups, which are taken to be neutralized by counterions and exist in the form of ion pairs or dipoles, form a close-packed arrangement on the surface of the cluster, the nearest-neighbor distance being determined by the molecular pair potential. As mentioned in the Introduction, we consider only elastic and electrostatic effects. The driving force for clustering results from the fact that the electrostatic energy is lowered when dipoles

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aggregate. However, this stabilization is opposed by an increase in elastic energy on clustering that results from the conformational deformation of the polymer chains to which the fixed ions are attached. The equilibrium size of the cluster is determined by the balance of these opposing forces.

We compute the electrostatic energy of the cluster by considering the dipole–dipole interaction between ion pairs. The electrostatic energy E_{es} per dipole is

$$E_{\mathrm{es}} = \frac{1}{N(4\pi\kappa\epsilon_0)} \times \sum_{i>j}^{N}\sum_{j=1}^{N}\left(\frac{\vec{p}_i\cdot\vec{p}_j}{|\vec{r}_i-\vec{r}_j|^3} - \frac{3(\vec{p}_i\cdot(\vec{r}_i-\vec{r}_j))(\vec{p}_j\cdot(\vec{r}_i-\vec{r}_j))}{|\vec{r}_i-\vec{r}_j|^5}\right) \quad (2.1)$$

where $\vec{p}_i$ is the dipole moment of the ith dipole located at $\vec{r}_i$ on the surface of a sphere of radius r, ϵ_0 is the permittivity of space, κ is the dielectric constant, and N is the number of dipoles in the cluster. In our calculations we assume $\kappa = 4$, i.e., the value for bulk poly(tetrafluoroethylene), which constitutes the polymer matrix in Nafion. The implications of this assumption are discussed in section V.

We assume that the ionic dipoles are distributed uniformly over the surface of the spherical cluster. This uniform distribution is only exactly realizable for certain numbers of dipoles, a fact related to the limited number of regular polyhedra. Thus all dipoles are equivalent when located on a spherical surface at points corresponding to the vertices, centers of the faces, or the midpoints of the edges of a tetrahedron, cube, octahedron, dodecahedron, or icosahedron. This allows one to place 4, 6, 8, 12, 20, or 30 points on the spherical surface. Arrays of nearly equivalent points may be constructed by repeated centering of the faces of the various polyhedra, and in this way approximately uniform distributions of 42, 80, 120, and 162 points were constructed.

Computer simulations were performed on clusters of dipoles to determine which orientations of the dipoles minimize the electrostatic energy. Initially a completely random distribution of orientations was constructed, and the dipoles allowed to relax into a self-consistently stable arrangement. This ground state is highly degenerate as a consequence of the symmetry of the array, and so different random initial conditions led to various final orientations. However, the fact that a unique final energy value was always attained showed that no false subsidiary minima were encountered and that the final orientations were all related to each other by simple rotations or reflections. In our simulations the effect of an external, applied field such as exists under membrane operating conditions is not included, because typically the applied field is several orders of magnitude smaller than the local dipole fields.

To obtain an estimate of the elastic energy, we assume that the conformational deformation of the polymer chains connecting successive pendant ionic groups takes place in the following manner: Roughly half of the chains starting from the pendant ions terminate on the same cluster while the remaining chains terminate on a nearest-neighbor cluster (see Figure 1). The average end-to-end separation for half of the chains is then simply the nearest-neighbor distance between dipoles on the spherical cluster, which we define to be d_0, and the average end-to-end separation (Δd) of the remaining chains is

$$\Delta d = 2(R - r) \quad (2.2)$$

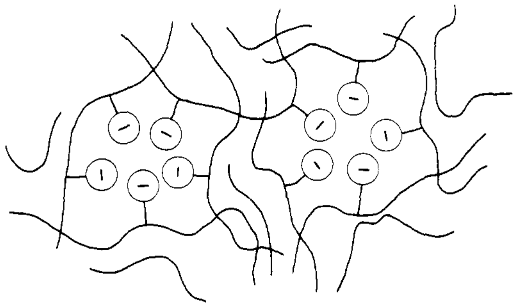

Figure 1. Schematic illustration of the deformation of polymer chains due to clustering of the pendant ions.

where r is the radius of the cluster and R is the edge of the cubic volume occupied by the N ions before clustering. Specifically

$$R^3 = NW_{\mathrm{E}}/\rho N_{\mathrm{A}} \quad (2.3)$$

where ρ is the density of the membrane, N_{A} is Avogadro's number, and W_{E} stands for the equivalent weight of the membrane (defined as the weight of acid polymer that will neutralize 1 equiv of base; i.e., W_{E} roughly equals the monomer molecular weight).

Using the simplest model of rubber elasticity[5] and ignoring effects such as crystallinity in the sample, we find the elastic energy per dipole to be

$$E_{\mathrm{elastic}} = \frac{1}{2}\left[\frac{3k_{\mathrm{B}}Td_0^{\,2}}{2\langle h^2\rangle} + \frac{3k_{\mathrm{B}}T(\Delta d)^2}{2\langle h^2\rangle}\right] \quad (2.4)$$

where $\langle h^2\rangle$ is the mean square end-to-end chain length, T is the temperature, and k_{B} is Boltzmann's constant. Since $d_0 \ll \Delta d$, the first term on the right-hand side of eq 2.4 can be neglected.

Equation 2.4 is strictly valid only for a Gaussian chain and appears to be a gross simplification for an ionomeric system where the chain extension is not small compared with the root-mean-square end-to-end chain length. However, on using non-Gaussian statistics[6] and retaining the next higher order term in an inverse Langevin expansion, we find that our results are not significantly altered. We therefore continue to work with (2.4) for the sake of simplicity. A slightly different formulation of the elastic energy contribution has been given by Forsman.[7] That calculation however does not contain any qualitatively different ingredient and is based essentially on the same approximations that have been outlined above.

The mean square end-to-end distance $\langle h^2\rangle$ appearing in (2.4) can be rewritten as

$$\langle h^2\rangle = \frac{\langle h^2\rangle}{\langle h^2\rangle_{\mathrm{f\text{-}r}}}l^2\frac{W_{\mathrm{E}}}{M_0} \quad (2.5)$$

where $\langle h^2\rangle_{\mathrm{f\text{-}r}} = l^2W_{\mathrm{E}}/M_0$ is the mean square end-to-end distance for a freely rotating chain, l is the C–C bond length, and W_{E}/M_0 roughly equals the number of links in a chain between ionic groups.

III. Results

(a) Orientation of Dipoles Subject to Electrostatic Forces Alone. As described in section II we have carried out computer simulations on clusters of N = 4, 6, 8, 12, 20, 30, 42, 120, and 162 dipoles to determine the equilibrium dipole orientation subject to electrostatic forces alone. Our computer simulations show that in every case the stable configuration is one in which each dipole lies in the surface of the spherical cluster and has no component normal to the surface. Figures 2 and 3 show the dipole orientations corresponding to clusters of 12 and 30 dipoles, respectively.

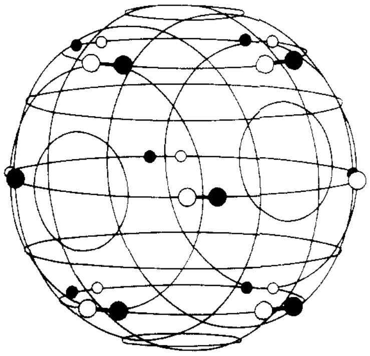

Figure 2. Dipole orientations corresponding to a cluster of 12 dipoles. Open circles indicate anions and closed circles cations.

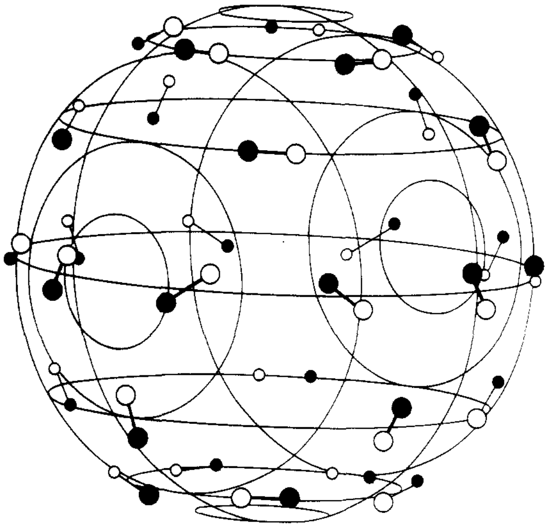

Figure 3. Dipole orientations corresponding to a cluster of 30 dipoles.

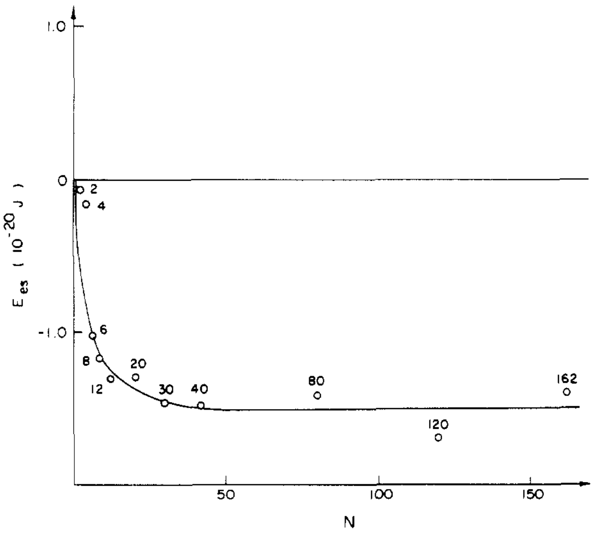

Figure 4. Plot of E_{es} as a function of N. The solid line is drawn to guide the eye.

(b) Electrostatic Energy. Figure 4 is a plot of E_{es} as a function of N, the number of dipoles in a cluster. Here E_{es} is the electrostatic energy per dipole corresponding to the stable configurations obtained in (a) above by assuming that the dielectric constant $\kappa = 4$. We see that E_{es} initially falls as $-N^{0.5}$ with increasing N and reaches a constant value for $N \gtrsim 30$.

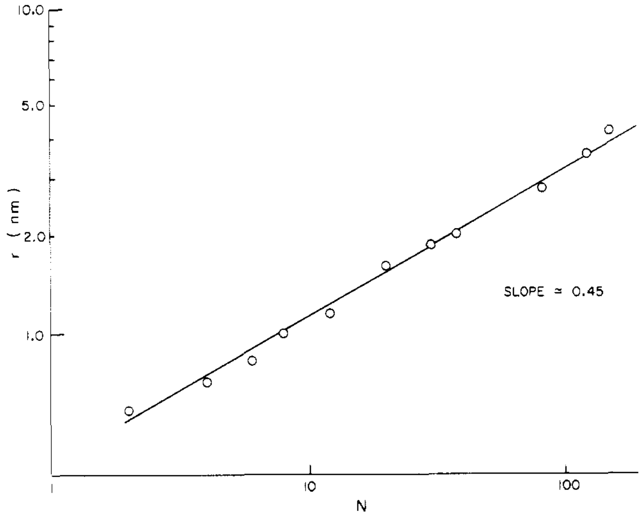

Figure 5. Log–log plot of the cluster radius r as a function of N, when the nearest-neighbor distance between dipoles is kept constant and equal to 1 nm.

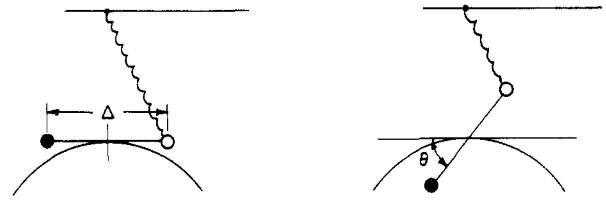

Figure 6.

Figure 5 is a log–log plot of the cluster radius r as a function of N, when the nearest-neighbor distance between dipoles is kept constant and equal to 1 nm. This constraint determines r as a function of N, and we find

$$r = a_0 N^{0.45} \tag{3.1}$$

where $a_0 = 0.35$ nm. The assumption that the dipoles form a close-packed arrangement on the surface of the sphere is a simplifying feature of our model; in reality some element of randomness is to be expected, and we intend to incorporate this feature in future calculations.

(c) Cluster Size and Dipole Orientation Subject to Electrostatic and Elastic Forces. The equilibrium size of the ionic clusters as well as the dipole orientations are determined by balancing the electrostatic and elastic forces. When elastic effects are included, the equilibrium dipole orientation no longer lies in the surface of the spherical cluster, and the result obtained in section IIIa is thus modified. This occurs as a result of the tension in the polymer chain, which acts on the dipole in an asymmetric manner. In the case of Nafion, for example, the tension acts on the negatively charged end of the dipole, and the distribution is thereby distorted in such a way as to increase the radius of the distribution of negative charge relative to that of the positive charge. An effective dipole layer is then formed at the surface of the cluster, as illustrated in Figure 6. The average angle θ by which the dipoles tilt out of the surface is determined by a minimization of the total electrostatic and elastic energies.

Figures 7 and 8 are plots of the total energy as a function of sin θ for different values of N, corresponding to equivalent weight 1100 and 1800, respectively. These plots were made by using typical values corresponding to Nafion for the constants that enter the elastic energy expression, i.e., $\rho = 2$ g/mL and $M_0 = 50$. The C–C bond length l is taken to be 0.15 nm. The energy minimum locates the number of dipoles per cluster and the tilt angle θ for a given W_E. We see that when elastic forces are taken into account the dipoles tilt out of the surface of the sphere by $\theta \simeq 25°$; also

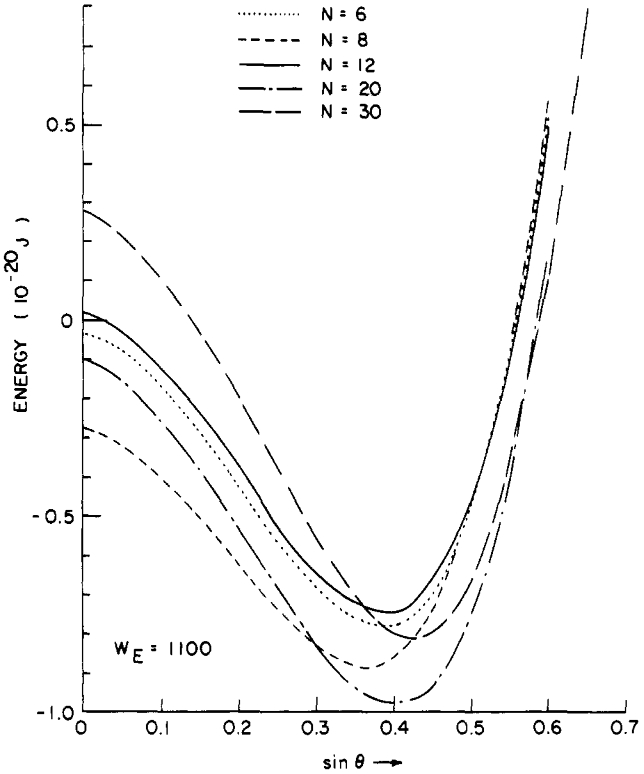

Figure 7. Total energy vs. sin θ for different N (W_E = 1100).

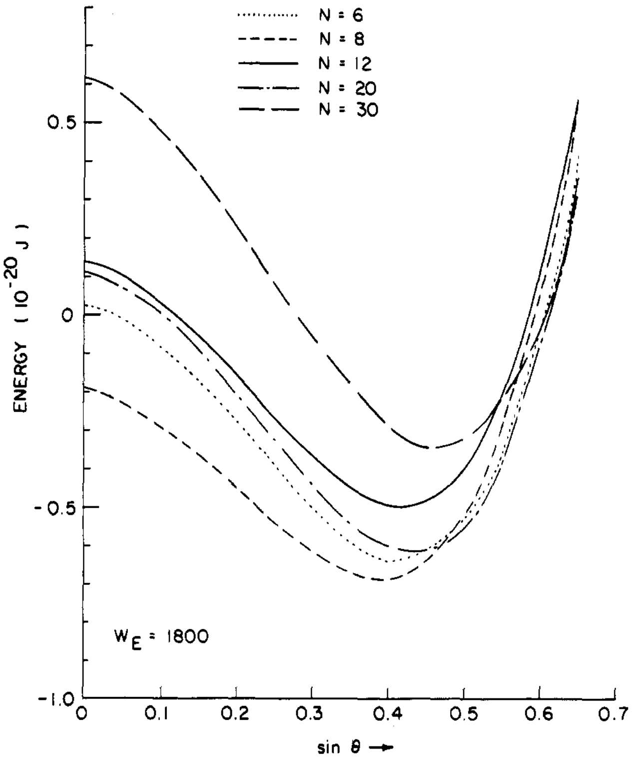

Figure 8. Total energy vs. sin θ for different N (W_E = 1800).

the number of dipoles per cluster increases as W_E decreases, from $N \simeq 8$ at $W_E = 1800$ to $N \simeq 20$ at $W_E = 1100$. This decrease of N with W_E agrees qualitatively with experimental results.[4]

IV. Transport

The dipole layer at the surface of a spherical cluster creates an electrostatic potential that, we believe, may be responsible for selective ionic transport. The model that we propose for transport differs qualitatively from the cluster–network model of Gierke and co-workers,[4] where the electrostatic potential in the channels connecting clusters is responsible for selective transport. The mechanism that we propose is as follows. Ions travel through the membrane by "hopping" between ionic clusters. When an ion moves from the interior of a cluster into the polymer matrix, it must overcome a potential barrier. This barrier is enhanced in the case of anions and reduced in the case of cations by the dipole potential layer, for the case where the ionomer is a polyanion. This leads to preferred transport of cations. The details of the model are elaborated below. We point out that the mechanism for selective transport operates even when the ion pairs or dipoles are dissociated due to hydration. This is so because the free ions still have a higher concentration near the fixed ions, leading to an electrostatic double layer at the surface of the clusters.

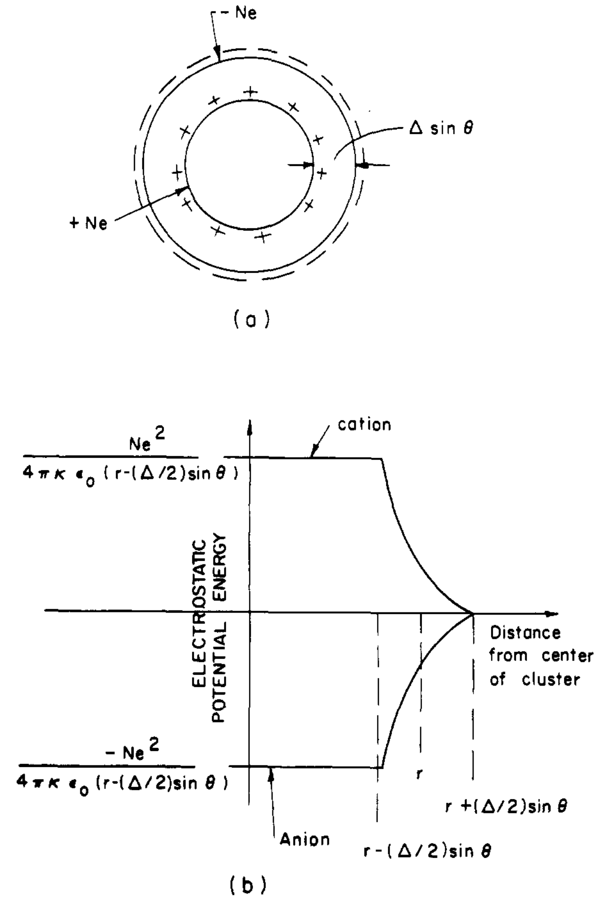

Figure 9.

We have computed the electrostatic potential due to the dipole layer as follows (see Figure 9a). We replace the dipole layer by two concentric uniform spherical shells of charge $\pm Ne$ respectively, separated by a distance $\Delta \sin \theta$, where N is the number of ion pairs per cluster, e is the electronic charge, Δ is the dipole length, and θ is the dipole tilt angle. The electrostatic potential energy of a cation (anion) inside a cluster is shown in Figure 9b. Figure 10 is a schematic illustration of the potential energy of an ion as it moves from the interior of a cluster into the polymer matrix. The potential barrier ΔE_+ (ΔE_-) which a cation (anion) has to overcome to "hop" into the polymer matrix is shown. We define the difference, ΔU, between these barrier heights as follows:

$$\Delta U = \Delta E_- - \Delta E_+ = \frac{Ne^2}{4\pi\kappa\epsilon_0 r}\left(\frac{\Delta \sin\theta}{r}\right) \qquad (4.1)$$

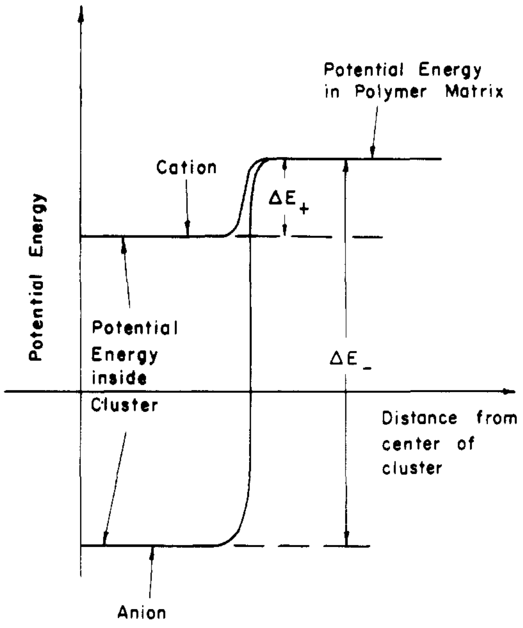

Figure 10.

This term is of purely electrostatic origin, and we will refer to ΔU as the dipole-layer potential difference.

The current through the membrane can be computed by using site percolation theory,[8] in which each cluster is treated as a lattice site. Assuming that the clusters are identical and distributed randomly on a regular three-dimensional lattice, we find the conductivity to be[9]

$$\sigma = \sigma_0 G \tag{4.2}$$

where σ_0 depends on the microscopic details of the system while G depends only on the connectivity of occupied lattice sites and is the same for cations and anions. In particular

$$\begin{aligned} \sigma_0 &\propto e^{-\Delta E_+/k_B T} && \text{for cations} \\ &\propto e^{-\Delta E_-/k_B T} && \text{for anions} \end{aligned} \tag{4.3}$$

where $\Delta E_\pm$ are the potential barriers defined in Figure 9, k_B is Boltzmann's constant, and T is the temperature of the system. This leads to the following expression for the percent current efficiency, E_c, of the membrane.

$$E_c = \frac{\text{cationic current}}{\text{total current}} \times 100 = \frac{100}{1 + ce^{-(\Delta E_- - \Delta E_+)/k_B T}} = \frac{100}{1 + ce^{-\Delta U/k_B T}} \tag{4.4}$$

where c is a constant that depends on the relative mobilities of the two ionic species.

Figure 11 is a plot of the current efficiency as a function of the dipole-layer potential difference, ΔU, for the case where $c = 1$. Of the various terms that enter ΔU (see eq 4.1), we find that N/r^2 and $\sin \theta$ do not vary significantly with W_E and remain nearly constant; however, the dielectric constant κ, which we have held fixed, is likely to decrease as W_E increases, owing to lower water absorption. This would cause the potential barrier to increase with W_E, leading to the higher E_c. This is in agreement with the experimental trend[4] of the variation of E_c with W_E; however, we cannot make quantitative comparison with experiment at this point since we do not know the functional dependence of κ on W_E.

We might note here that our model allows us to predict the effect on the current efficiency of varying the ionic functionality of the fixed ions in the membrane. For example, if the sulfonate ions in a Nafion membrane are replaced by carboxylate groups, the dipole length Δ decreases, and our model predicts that the current efficiency increases, as is experimentally observed.[10] This can be seen quite simply from a dimensional argument. The cluster radius r is proportional to Δ as a consequence of the close-packing constraint described in section II. As is seen from eq 4.1, this implies that the potential barrier ΔU is inversely proportional to Δ, and hence the current efficiency increases as the dipole length Δ decreases.

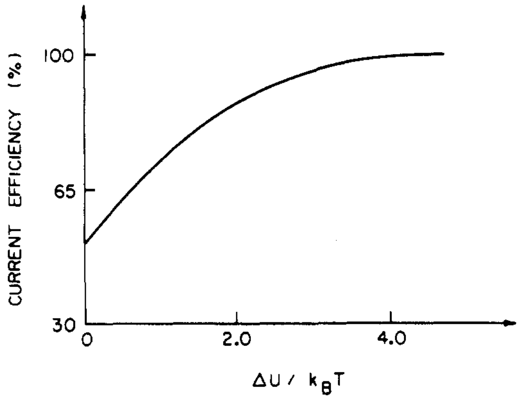

Figure 11. Current efficiency as a function of dipole layer potential difference for the case where $c = 1$.

V. Discussion

We have presented a model for clustering and transport in ionomer membranes by considering the opposing tendencies of electrostatic and elastic forces. The mechanism that we propose for selective transport is qualitatively different from that proposed by Gierke and coworkers.[4]

Despite the severity of the approximations made, our model yields qualitative agreement with experiment with respect to the variation of cluster size with W_E and predicts the experimental trend of variation of E_c with W_E. The most serious assumption of the model lies in the treatment of the system as a uniform dielectric in which the effects of hydration inside the clusters and the variation of κ with W_E are ignored. It is our intention to refine these calculations in the near future and to consider in more detail the effects of temperature, dielectric constant, and conformational deformations in an attempt to apply more stringent tests to the model we have presented.

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