A Water Sorption Isotherm Model for Ionomer Membranes with Cluster Morphologies

Kenneth A. Mauritz*

Department of Polymer Science, University of Southern Mississippi, Hattiesburg, Mississippi 39406

Charles E. Rogers

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received July 9, 1984*

ABSTRACT: A simple theory attempting to model equilibrium hydration states of clustered ionomer membranes is presented. In the formulation, the driving force for cluster expansion during equilibration with aqueous media is represented as the osmotic pressure of the ionic microsolutions encapsulated within the clusters. This osmotic pressure is derived from a molecular theory of water activity, which, in turn, reflects (a) the hydrative capacities of the ion-exchange group and counterion, as well as the free/bound water ratio, and (b) the counterion dissociation equilibrium. This osmotic tendency is resisted by a polymer contractile pressure that is a function of the Young's modulus and cluster radius extension ratio. Equilibrium is then depicted as a condition where the two pressures become equal and the resultant equations are considered as either vapor pressure or liquid sorption isotherms. In a sample calculation, it was seen that the application of this prototype model to Nafion membranes yields a water uptake that is quite reasonable in consideration of the fact that no arbitrary adjustable parameters have been introduced.

Introduction

Much has been documented, since around 1945, of the swelling, electrolyte sorption, and ion-exchange equilibrium properties of organic cross-linked ion-exchange resins. The compilations of Helfferich,[1] and later of Marinsky,[2] remain authoritative in the listing of rules, contributed by numerous investigators, that relate these resultant properties to general underlying chemical factors such as cross-link density, p*K* and number density of ionogenic groups, nature of counterion, external solution concentration, etc. Also, accompanying the experimental developments in this area have been theoretical models of cross-linked polyelectrolyte gels, the most noteworthy being those of Gregor,[3] Katchalsky et al.,[4] and Harris and Rice.[5]

There also exists a more recent body of knowledge of ion-containing polymers known as *ionomers*[6] which, in contrast to the traditional ion-exchange resins, are rendered insoluble through the presence of crystalline domains, e.g., "polyethylene-like" for the ethylene/methacrylic acid copolymer salts (e.g., commercial Surlyn[7]), or "poly(tetrafluoroethylene)-like" for the perfluorosulfonate membranes (e.g., commercial Nafion[7]) used as separators in electrochemical applications. Likewise, for ionomers, models of the energetics of the separation of the ionic fragments of the macromolecules into cluster domains have been proposed.

The less complex straightforward model of Eisenberg,[8] using no adjustable parameters, gives, for example, average intercluster distances for ethylene–sodium methacrylate copolymers that are slightly better than order-of-magnitude correct as compared with experiment. The inherent simplicity of this pioneering theory, however, limits its effectiveness in the simulation of a broad class of materials. On the other hand, the more elaborate theory of Hopfinger et al.,[9] largely based on the model of Eisenberg, is overburdened with many questionable assumptions, many specific to the Nafion system, as well as many required calibration procedures that limit its flexibility in material design. In any case, it should be stated, within a historical context, that the development of both the Eisenberg and the Hopfinger models preceded the considerable quantity of structural characterization that has been reported since their inceptions.

More recently, Hsu and Gierke[10a] have reported a semiphenomenological elastic theory of clustering, applied to the Nafion system, that produces trends consistent with their small-angle X-ray studies.[10b] Again, the minimization of the system free energy, taken to be resolved into an elastic deformation term, and bulk and surface interaction terms, for a hypothetical single growing cluster, generate equilibrium cluster diameters. Perhaps the greatest significance of this effort lies in the reduction of an intrinsically complex problem to manageable proportions without losing important ingredients. On the other hand, the interactions utilized, although given specific physical significance, are somewhat oversimplified representations possessing no structural detail of the interacting groups. Also, the extension of bulk, or macroscopic formalism to phenomena on a 50-Å scale can be seriously questioned as the molecular granularity renders continuum concepts such as "surface", or "elastic modulus", less meaningful.

Within an ideal statistical mechanical framework, a macroscopic equation of state should be derived from a partition function involving energetics of the entire ensemble of fundamental interactions within both hydrophilic and hydrophobic phases. Differences in the local environment and mobility of water molecules (e.g., hydrogen-bonded vs. non-hydrogen-bonded water, or, water of ionic hydration vs. "bulk" water), as well as differences in the environment/mobility of the ions (e.g., dissociated vs. bound) should clearly be reflected in a realistic modeling effort as being important in controlling the internal osmotic condition. The fact that these molecular distinctions are indeed real has been amply demonstrated spectroscopically by Lowry and Mauritz,[11] Komoroski and Mauritz,[12] and Mauritz and Gray.[13] This paper attempts to factor some of these specific concepts into a simple rational model of water uptake by clustered ionomers.

Less extensive, however, has been specific information regarding the structure and dynamic behavior of the hydrophobic polymer backbone in the intercluster regions. Meaningful information, described later in this work (Starkweather[14]), has just begun to surface and will be of crucial importance in the mathematical representation of polymer matrix elasticity, as well as intercluster ion and water transport.

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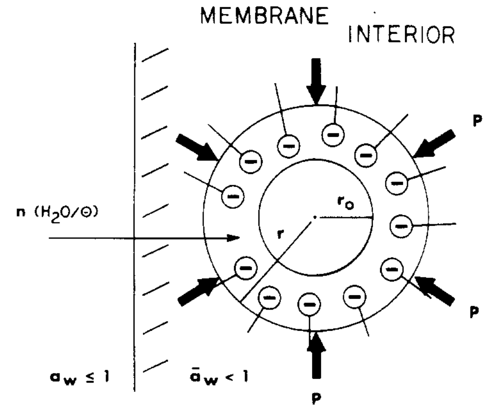


Figure 1. Single spherical ionic cluster illustrating the dry radius (r_0), equilibrium swollen radius (r), and polymer matrix resistive pressure (P) for a membrane in contact with pure water.

The objective of this report is mainly to present the mathematical framework of what is, in essence, a vapor pressure isotherm, or, also, an isotherm for water uptake from the bulk liquid, for clustered ionomers containing no excess electrolyte. Although the model is general within the constraint of a cluster morphology, a specific numerical example that could represent perfluorosulfonate ionomers is carried throughout the abstract mathematical development.

Solvent Sorption Isotherm Model

General Model Formulation. Assume that a polymeric strong acid ion-exchange membrane is in equilibrium with water vapor or pure liquid water. In the general concept, the driving force for membrane swelling is the tendency for the external water to dilute the (assumed originally dry) ion-containing polymer matrix prior to equilibrium. During the progression from the dry to equilibrium swollen state, the internal osmotic pressure (Π) becomes increasingly resisted by a pressure due to the retractive force of the expanding polymer matrix. This concept was briefly discussed in an earlier paper by Mauritz and Hopfinger.[15]

Consider now, a single ionic cluster, assumed, in the usual sense, to be spherical, whose radius before equilibration (dry state) is r_0. It is reasonable to believe that, for all practical purposes, including thermodynamic arguments relating to hydrophobicity/hydrophilicity, all the sorbed water molecules will be incorporated within these clusters. It will also be assumed that all clusters are chemically identical and equal in size. This statement is considered to be merely a working hypothesis which will be loosened in future studies in which chemical and/or size distributions about an "average" cluster will be systematically investigated. At the membrane water content of n molecules per ion exchange site, λ, the extension ratio for the cluster, is r/r_0, where r is the new radius (see Figure 1).

If, *at equilibrium*, the water activities within and external to the membrane are $\bar{a}_w$ and a_w, respectively, then

$$RT \ln a_w = RT \ln \bar{a}_w + \Pi v_w \qquad (1)$$

where R is the universal gas constant, T the absolute temperature, and v_w the partial molar volume of the water.[16] In deriving eq 1 it is assumed that v_w in the membrane does not depend on pressure and is uniform everywhere. It must be remembered that this is, in fact, a thermodynamic equation that does not account for microstructural heterogeneity in itself. For pure liquid water, of course, $a_w = 1$. In equilibration with water vapor, $a_w = x$, where x is the relative humidity. One can also deal with an electrolyte–membrane interface, although the analysis becomes considerably complicated by the transference of mobile ions as well as water between the exterior and interior of the membrane.

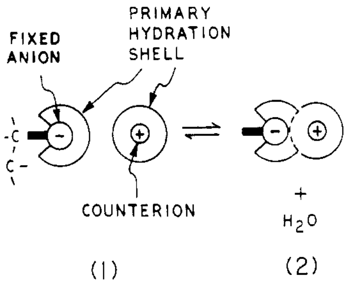


Figure 2. Two-state model of hydration-mediated equilibrium between unbound counterions and counterions bound in an outer sphere complex.

As mentioned, during equilibration, the water, when in the cluster, is under progressively greater pressure than the external liquid due to polymer contractile pressure. This excess pressure, P, will be taken as equal to that required to increase a spherical hole in an "infinite" block of elastic material from radius r_0 to r:[17]

$$P = (E/6)(5 - 4\lambda^{-1} - \lambda^{-4}) \qquad (2)$$

Here E is the Young's modulus of the material which, in derivation, is assumed to be both macroscopic and constant over the range of values of λ. It should be allowed for, in the mathematical description, that E, for ion-containing polymers, is in fact a function of water content and will also vary during the approach to equilibrium.

For external pure liquid water ($x = 1$), or water vapor ($x < 1$), eq 1 can be written as

$$-\ln (\bar{a}_w/x) = v_w P/RT \qquad (3)$$

with $\Pi = P$.

Counterion–Side-Chain Interactions and a Theory of Cluster Water Activity. Consider a microscopic interpretation of $\bar{a}_w$. If the "microsolutions" encapsulated within the clusters were ideal, then $\bar{a}_w$ would simply be the mole fraction of water, that is, $n/(n + 1)$. However, not all of the water molecules are liquid bulklike, that is to say, osmotically active, some being constrained as water of hydration about the internal ions. Furthermore, not all of the counterions can be assumed to be dissociated but some may be strongly bound in ion pairs with the anionic side chains.[11,12] This concept of ion pairing, of course, dates back to much earlier studies of simple electrolytes.[18]

Let us now consider, for the side chain–counterion association, an on–off model that will consist of an equilibrium between (1) a totally dissociated and fully hydrated (+) species plus a fixed and totally hydrated (−) species, and (2) a (+)(−) ion pair that is an outer sphere complex, as depicted in Figure 2, formed at the expense of ejecting water molecules from the hydration shells in between the free ions. A very general off–on model was assumed by Komoroski and Mauritz[12] in the interpretation of the ^{23}Na NMR spectra of hydrated perfluorosulfonate membranes, but, it should also be noted that a more sophisticated four-state statistical mechanical model of the counterion dissociation equilibrium, based on the concept of Eigen,[19] has been reported by Mauritz.[12,15] The primary motivations for using a two-state, rather than four-state, model in these studies are as follows. First, it is desired to see if this simpler mechanism, deleting the states representing the contact ion pair and also that corresponding to the contact of the "surfaces" of the primary hydration shells, could still portray a realistic situation. Second, it is sensible to provide a mechanism that does not exceed the degree of sophistication of the remaining aspects of the sorption-swelling model, as presented herein.

A simple physical rationale for neglecting the contact ion pair consists of the following argument that concludes that this state is energetically unfavorable at high membrane water contents.

It was indeed shown, in the earlier theoretical results of Mauritz,[20] that the population density of the contact ion pair state is essentially zero, the reason being the difficulty in removing the final water molecules interposed between cation and anion. This can be understood on a simpler level in the following way using a semiquantitative argument. The total energy of hydration of, say, a Na^+ ion, has reported experimental values ranging from −73.4 to −114 kcal/mol, by the authors' knowledge,[21a–e] while most investigators would agree upon a primary hydration number of 4,[21a,b] although the number 8 was reported in one instance.[22] In any case, if an energy of hydration of, say, −80 kcal/mol is assumed and there are 4 H_2O molecules in the hydration shell, an *average* energy of interaction between an H_2O molecule and Na^+-like ion would be roughly −20 kcal/mol per H_2O molecule.

In addition, the remaining H_2O molecules to be removed to allow for formation of a contact ion pair from the outer sphere complex would unquestionably interact with the anion as well as cation. Therefore, the "activation" needed for requisite dehydration may be around +40 kcal/mol per H_2O molecule for this particular H_2O molecule. Furthermore, additional H_2O molecules, although perhaps less tightly bound, may need to be displaced. Therefore, one may need to consider an energy expenditure of at least 50 kcal/mol to affect contact ion pair formation. This number, while certainly a rough benchmark, is considerable and not sufficiently compensated for by a lowering of the Coulombic potential energy of interaction between (+) and (−) by bringing them closer together. If r_+ and r_- are the bare ionic radii of cation and anion, respectively, and d_w the size of a water molecule, then the potential energy is lowered by an amount

$$\Delta U = -(332/K)[(r_+ + r_-)^{-1} - (r_+ + r_- + d_w)^{-1}] \quad (4)$$

in kcal/mol if the distances are in Å. In this expression K is, as in the earlier theoretical simulations,[23] an effective "local" dielectric constant that is assumed to depend on n, the average number of internal H_2O molecules available per ion-exchange site. For water contents, n, less than the combined hydration numbers of (+) and (−), i.e., $n_+ + n_-$, K was assumed to increase linearly from 1 to 80 as n proceeded from 0 to $n_+ + n_-$. As this work is concerned with the regime $n > n_+ + n_-$, $K = 80$ is appropriate. It is felt that the electrostatic shielding of the ionic charges, by the highly polar medium, is accounted for in this way.

For $r_+ = 0.95$ Å, $r_- = 2.00$ Å, and $d_w \approx 3.00$ Å, $\Delta U = -0.709$ kcal/mol, which is clearly less than adequate to supply the energy requisite for water molecule displacement. It should also be noted that RT (=0.583 kcal/mol, 20 °C), a measure of the cation's thermal kinetic energy, is also considerably less than the energy required to form a contact ion pair.

For state 1, it will be assumed that the Coulombic energy of attraction between (+) and (−) is small and will thus be neglected. This, of course, would strictly exist if the dielectric screening (through medium polarization) and/or (+)-(−) separation were appreciable.

Furthermore, it will be assumed that, for the membrane water contents considered, the ionic hydration shell structures will be largely the same as they exist in the corresponding free solutions. We will then utilize, within the membrane context, ionic hydration numbers and hydration energies derived from earlier experiments on these free solutions.

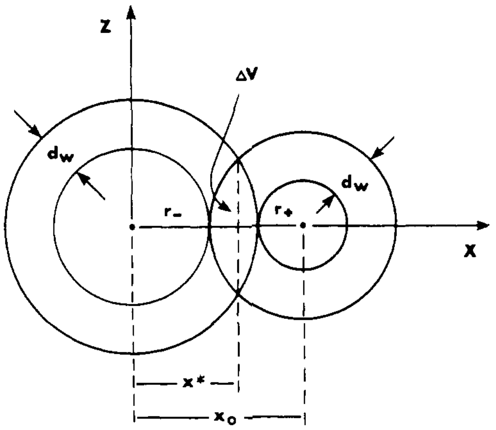


Figure 3. Relative geometry of the overlapping of monomolecular-thick hydration shells of a cation and anion in an outer sphere complex.

Of course, the specific primary hydration structures of single ions, derived from numerous experimental procedures, remain under debate. Further, equating the hydration properties of ions in ionomers with those of the corresponding electrolyte analogues, might well be questioned. Nevertheless, the concept of primary hydration shells, or ionic "co-spheres", as earlier labeled by Gurney,[24] has been quite useful through many years of ionic solution theory and has also received considerable attention in theoretical studies of the conformations of biopolymers.[25]

In any case, the above discussion outlines the general structure of a working hypothesis that will be evaluated on the basis of its capability of producing a reasonable physical model in the end.

Now, consider a specific model for the change in the energetics of ionic hydration in passing from state 1 to state 2. First, attention will be paid to the relative geometry of the overlapping of (+) and (−) primary hydration shells, each assumed to be one H_2O molecule thick, and for the specific situation where the ionic centers are separated by a distance of $r_+ + r_- + d_w$, as shown in Figure 3. The monomolecular-thickness assumption is appropriate for all alkali metal cations, save for perhaps Li^+, for which 5–7 H_2O molecules are strongly bound about an ion of only about 0.6-Å radius—a steric impossibility within a monomolecular constraint.

After the usual straightforward integration procedure and laborious algebra (see Appendix for derivation), the overlap volume, Δv, for the geometry of Figure 3, is

$$\Delta v = (2\pi/3)(R_-^3 + R_+^3) - \pi[R_-^2 x^* + R_+^2(x_0 - x^*)] + (\pi/3)[(x^*)^3 + (x_0 - x^*)^3] \quad (5)$$

In this equation, x^*, the distance from the center of (−) to the plane passing through the circle of intersection is given by

$$x^* = (2x_0)^{-1}(R_-^2 - R_+^2 + x_0^2) \quad (6)$$

where the center-to-center ionic spacing = $x_0 = r_- + d_w + r_+$.

Before the overlap, there were n_- and n_+ molecules in the respective hydration shells having "occupied volumes" of

$$v_- = (4\pi/3)(R_-^3 - r_-^3)$$
$$v_+ = (4\pi/3)(R_+^3 - r_+^3) \quad (7)$$

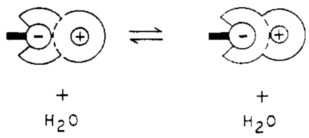


Figure 4. Two boundary modes of hydration shell penetration in outer sphere complex formation.

In eq 5–7, R_- and R_+ are the *hydrated* radii of the respective ions, i.e.

$$R_- = r_- + d_w$$

$$R_+ = r_+ + d_w \tag{8}$$

A major concern is the determination of the relative contribution of (–) vs. (+) to the total number of H_2O molecules ejected on the basis of this requisite steric overlap. The two extreme, or boundary, situations are (1) the persistence of the (+) hydration structure with (–) contributing solely to the water loss, and (2) the reverse of (1) (see Figure 4). The actual situation, of course, is more sensibly visualized as existing somewhere in between these two cases, particularly if the packing numbers and ion–H_2O interactions are comparable so that neither anion nor cation can maintain an undisturbed hydration structure after penetration. It is then quite reasonable to model this state as an energetically weighted average of these two extreme structures.

Let H_- and H_+, both positive, be the energies of complete hydration of (–) and (+) respectively. Then the *average* energies of binding to the respective ions, for *single* H_2O molecules, are

$$-\Delta H_- = -H_-/n_-$$

$$-\Delta H_+ = -H_+/n_+ \tag{9}$$

Although it might not be expected that, for a given ion, the binding energy of, say, the second molecule ejected is exactly equal to that of the first, etc., the use of the average, defined in this way, will at worst provide the correct order of magnitude as well as a semiquantitative energetic comparison between different ions. In refinement, the results of the experiments of Dzidic and Kebarle[21e] offer some insight in understanding this aspect of the problem. In any case, the present level of development assumes that the energy of binding of an H_2O molecule to a given ion is independent of the instantaneous population of the hydration shell during the stripping process.

If now, hypothetically, the (–) hydration shell is penetrated while that of (+) is maintained intact, the hydration energy of (–) is assumed to be reduced by a fraction, f_-, of the original energy where this fraction is taken as the ratio $\Delta v/v_-$. Similarly, for an outer sphere complex formed with the (–) hydration shell intact at the expense of losing some of the (+) waters of hydration, the (+) hydration energy will likewise be considered to decrease by a fraction $f_+ = \Delta v/v_+$. The final total energies of hydration, for the ion pair, for the former and latter boundary cases are

$$\begin{aligned} H_1' &= -(1 - f_-)H_- - H_+ \\ &= -(1 - \Delta v/v_-)H_- - H_+ \end{aligned} \tag{10a}$$

$$\begin{aligned} H_2' &= -H_- - (1 - f_+)H_+ \\ &= -H_- - (1 - \Delta v/v_+)H_+ \end{aligned} \tag{10b}$$

At this point, $\langle H' \rangle$, an average energy of hydration for the outer sphere complex, will be introduced as an admixture by a Boltzmann weighting procedure:

$$\langle H' \rangle = H_1'p_1 + H_2'p_2 \tag{11}$$

where $p_1 = 1/\{1 + \exp[(H_1' - H_2')/RT]\}$ and $p_2 = 1 - p_1$. The Coulombic interionic attractive energy need not be included since it has the same value for both situations within the framework of this simple model.

On the average, then, the total number of H_2O molecules remaining bound in the outer sphere complex is

$$\langle n_+ + n_- \rangle_2 = [n_+ + (1 - f_-)n_-]p_1 + [(1 - f_+)n_+ + n_-]p_2 \tag{12}$$

The total energy of this state is

$$E_2 = \langle H' \rangle - 332/(Kx_0) \tag{13}$$

where K is taken as 80 to account for the dipolar screening by interposed H_2O molecules. Perhaps an effective K of less than 80 may be a better choice as only 1–3 H_2O molecules would separate cation and anion in this state. Furthermore, the average number of H_2O molecules packed between cation and anion in this state would decrease for $n < n_+ + n_-$, that is, there would be insufficient water for complete hydration shell occupancy. K is, in fact, a macroscopic parameter that cannot be adequately represented on this nebulous molecular level. In any case, it will be seen later in this text that the Coulombic term is overwhelmed by the energy of hydration. In short, there is nothing to be gained by refining K for these calculations. In accordance with a previous assumption, the total energy of the state of dissociation will be

$$E_1 = -H_- - H_+ \tag{14}$$

Therefore, the relative populations of states 1 and 2 will be

$$P_1 = 1/\{1 + \exp[(E_1 - E_2)/RT]\}$$

$$P_2 = 1 - P_1 \tag{15}$$

Before proceeding further, let us compute P_1 and P_2 for the case of (+) = Na^+ ($n_+ = 4$, $H_+ = 73.4$ kcal/mol, $r_+ = 0.95$ Å) and a hypothetical fixed anion for which $n_- = 3$, $H_- = 35.0$ kcal/mol, and $r_- = 2.00$ Å. For this exercise, $f_- = 0.112$, $f_+ = 0.217$, $H_1' = -104.5$ kcal/mol, and $H_2' = -92.5$ kcal/mol. At $T = 20$ °C, p_1 is essentially unity. Thus, the admixture shown in Figure 4 overwhelmingly favors the situation on the left, being more energetically favorable than the other boundary structure by 12 kcal/mol. The number of H_2O molecules in this outer sphere complex, from eq 12, is $\langle n_+ + n_- \rangle_2 = 6.66$, or 0.34 H_2O molecule must be displaced to accommodate the formation of the complex. Of course, to preserve the discrete nature of molecules, we must in reality select the greatest integer less than $\langle n_+ + n_- \rangle_2$, which is equivalent to saying that 1 H_2O molecule should be ejected in this case.

Finally, $E_1 = -108.4$ kcal/mol and $E_2 = -105.2$ kcal/mol, using eq 13 and 14. It should be noted that the Coulombic contribution in eq 13 is –0.697 kcal/mol, slightly larger than RT, and contributes little to the overall energetics.

Thus, $P_1 = 0.996$, $P_2 = 0.004$, or, on the average, only about 4 out of every 1000 side chains are binding a cation in the state of equilibrium at high water contents (i.e., $n > 7$ H_2O molecules/(–)(+) pair). At this point, the reader is reminded that there is a 1:1 ratio of (+)/(–) species in the system. A rough comparison can be made with the earlier cited work of Komoroski and Mauritz[12] in which the mole fractions of bound Na^+ ions were determined from the chemical shifts and line widths of the ^{23}Na NMR spectra of Nafion perfluorosulfonate membranes at various water contents at 30 °C. According to this experimental determination, depicted in Figure 5, P_2 is 1/100 for 10% water content (6 $H_2O/SO_3^-Na^+$), 5/1000 for 20% (12 $H_2O/SO_3^-Na^+$), and 4/1000 for 30% (18 $H_2O/SO_3^-Na^+$).

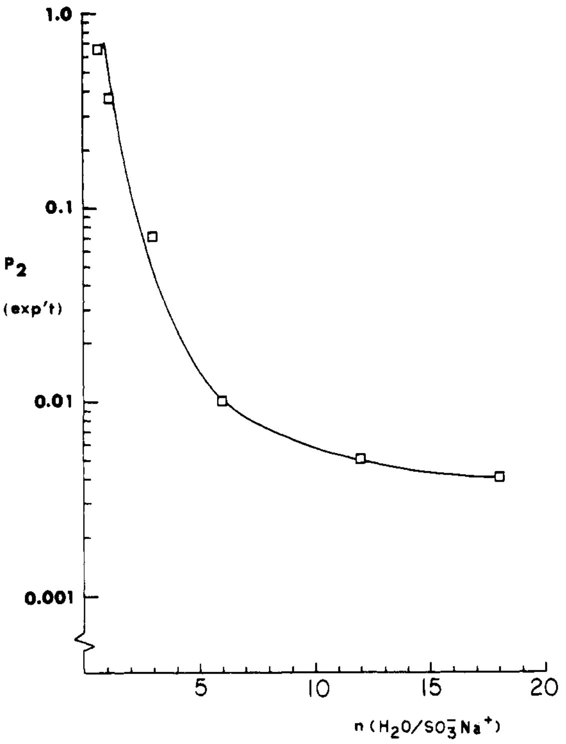


Figure 5. Relative population of bound Na^+ ions (P_2) in 1100 equivalent weight Nafion perfluorosulfonate membranes, at 30 °C, for various water contents, calculated from ^{23}Na NMR spectra. Data of Komoroski and Mauritz.[12]

It is concluded, then, that the theoretical model for the equilibrium between bound and free counterions, although crude, appears to be quite consistent with the experimental evidence for perfluorosulfonate membranes in the Na^+ form at higher water contents.

It was also seen in the earlier calculations using the four-state model that the relative population of outer sphere complexes approach zero as n increased from $n_+ + n_-$.[12,15] For the two-state model presented here, P_2 can be expected to considerably increase from essentially zero as n decreases from $n_+ + n_-$ because the hydration energetics are progressively reduced in magnitude and the electrostatic (+)–(–) interaction becomes less shielded (i.e., K moves from 80 toward 1).

For the present example, P_1, the degree of ionic dissociation, is to all practical purposes unity.

Finally, with the water activity in an "average" cluster now being considered as the ratio of the number of molecules of *free*, i.e., osmotically active, or non-ionically-bound water, per (–)(+) pair, $n - P_1(n_+ + n_-) - P_2\langle n_+ + n_-\rangle_2$, to the sum of this number plus the number of *free* counterions per side chain, P_1, $\bar{a}_w$ can be more realistically represented as

$$\bar{a}_w = \frac{n - P_1(n_+ + n_-) - P_2\langle n_+ + n_-\rangle_2}{n - P_1(n_+ + n_-) - P_2\langle n_+ + n_-\rangle_2 + P_1} \qquad (16)$$

For the earlier-discussed example (Na^+, hypothetical r_- = 2.0 Å anion), eq 16 considerably simplifies because $P_1 \to 1$ and $P_2 \to 0$:

$$\bar{a}_w = \frac{n - n_+ - n_-}{n - n_+ - n_- + 1} \qquad (17)$$

This equation is recognizable as equivalent to a water activity representation that was earlier discussed by Helfferich, based on Gregor's method of division of internal liquid into components.[26] $\bar{a}_w$ from eq 17 and P from eq 2 can be substituted into eq 3 to yield

$$\ln\left[\frac{x(n - n_+ - n_- + 1)}{n - n_+ - n_-}\right] = \frac{v_wE}{6RT}(5 - 4\lambda^{-1} - \lambda^{-4}) \qquad (18)$$

For a given n_+, n_-, x, and E, the solution of this equation consists of finding the equilibrium cluster expansion ratio (λ) and water uptake (n) from the dry state. It should be noted here that the only material properties in this formulation are the primary hydrative capacities of the ions and the elastic modulus of the polymer matrix which itself must necessarily be sensitive to water content.

Water Uptake–Cluster Geometry Relationship and a Water Sorption Isotherm. The immediate problem consists of interrelating n and λ in a reasonable way so as to render eq 18 a function of but one variable, either n or λ, and therefore unambiguously solvable.

In studies of the dependence of the total gel volume vs. degree of hydration of common organic cross-linked sulfonated ion-exchange resins, it is seen that, proceeding from the dry state, no significant volume change occurs initially and that v_w for these low water levels can be considerably smaller than the bulk value of 18.1 mL due to electrostriction.[27] In fact, a gel contraction has been known at times to accompany the incorporation of the first tightly bound molecules of hydration. Last, in principle, the osmotic pressure within clusters, which is the driving force for polymer matrix expansion, should mainly derive from H_2O molecules possessing considerably more kinetic energy than those electrostricted about the ions. Therefore, it is not without good reason to adopt an assumption of no volume expansion to occur for $n \leq n_+ + n_-$ either on the macroscopic level or in the dimensions of clusters.

Let $V_0 = 4\pi r_0^3/3$ be the average cluster volume in the dry state up to $n = n_+ + n_-$, and let $V = 4\pi r^3/3$ be that for water contents $n > n_+ + n_-$. The percent of volume increase can then be written as

$$(V - V_0)/V_0 = \lambda^3 - 1 = (C_n/C_0)[(n - n_+ - n_-)/(n_+ + n_-)] \qquad (19)$$

In this equation, C_0 and C_n are, for the membrane dry state and state having water content n, respectively, the number of ion-exchange groups within an average cluster. The assumption embodied in eq 19 is that the fractional volume increase per cluster is directly proportional to the number of water molecules, per ion-exchange group, added in excess of $n_+ + n_-$, times the number of these groups in the cluster *at n*.

It would be tempting to assign a value of unity to the factor C_n/C_0 in eq 19, i.e., assume the number of side chains incorporated into a cluster is independent of n. Although more critical experiments are needed to illuminate this point, a straightforward analysis by Hsu and Gierke,[10] based on small-angle X-ray studies of Nafion perfluorosulfonate (equivalent weight = 1200) membranes with varying water contents, C_n will almost double as the water content moves from 5 to 20 g of H_2O/100 g of dry polymer. Whether this analysis reflects a real phenomenon, or, if so, is also characteristic of all similar ionomers, is not known as yet. In any case, one must presently assume either a fixed value or function of n for C_n/C_0. Actually, the *theoretical* model of Hsu and Gierke,[10] in fact, assumes a value of unity for purposes of calculation.

This problem can be transformed into another problem in the following way.

If ρ and ρ_0 are the bulk mass densities (g/cm^3) of the ionomer in the wet and dry states, respectively, and M_{eq} the polymer equivalent weight, then the average number of ion-exchange groups per Å^3 can be shown to equal $0.602\rho/M_{eq}$ (wet) and $0.602\rho_0/M_{eq}$ (dry). These volume number densities are, however, representative of a homogeneous distribution of ion-exchange sites and what is required here are the densities of sites as segregated within clusters. Let ϕ and α be the volume fractions of clusters in the wet and dry states, respectively. Then, the "local" (i.e., intracluster) anion densities are appropriately increased to $0.602\rho/(\phi M_{\mathrm{eq}})$ and $0.602\rho_0/(\alpha M_{\mathrm{eq}})$, and the total numbers of anions in the cluster phases are obtained by multiplying by the cluster volumes:

$$C_n = \frac{0.602\rho}{\phi M_{\mathrm{eq}}}(4\pi r^3/3)$$

$$C_0 = \frac{0.602\rho_0}{\alpha M_{\mathrm{eq}}}(4\pi r_0{}^3/3) \tag{20}$$

Finally

$$C_n/C_0 = \rho\alpha\lambda^3/(\rho_0\phi) \tag{21}$$

In this equation, ρ/ρ_0 vs. water content must be known from experiment, the fraction α must be estimated, and ϕ, the morphological parameter, is unknown, being in fact a desired outcome of the theory. If desired, however, ϕ can be eliminated in the following way, contingent on the validity of a following assumption.

In the dry state, let ν_0 be the volume from the total sample volume occupied by the (dry) cluster phase, and ν' the volume occupied by the hydrophobic "matrix" phase. In the wet state, let ν be the volume from the total sample volume occupied by the (wet) cluster phase and *assume that the volume of the hydrophobic phase remains unchanged* at ν'. Then, one can write

$$\alpha = \nu_0/(\nu_0 + \nu')$$

$$\phi = \nu/(\nu + \nu') \tag{22}$$

Aside from resultant mathematical simplification, the assumption of constant ν' is believed to be reasonable for the Nafion-like materials in the light of the model proposed for the structure of the fluorocarbon backbone by Starkweather.[14] The Starkweather model, based on X-ray structural analysis, suggests that there is considerable crystallinity present in the hydrolyzed form that does not seem to be affected by water content. In particular, the backbone appears to crystallize into a hexagonal bilayer structure similar to that of poly(tetrafluoroethylene) at high temperatures. These bilayers, with sulfonate groups presumably extending from either side of the plane of the bilayer into the clusters, have been thought of as possibly forming the faces of polyhedra that surround the clusters. If this is true, then two important implications for the theoretical modeling of these materials must be recognized. (1) On a structural scale of the order of these "fringed micelles" (30–40 Å), the close packing of the polymer chains would necessarily be accompanied by strong interchain interactions that would resist a local structure deformation. This condition fortifies the assumption of constant ν'. (2) Also, the steric restraints of the crystalline environment of a given chain should unquestionably rule out the use of any Gaussian coil representations (as in earlier modeling efforts[8,9]) as the configurational entropy will clearly be altogether too low. If the Starkweather concept is correct, then it would seem that the process of swelling might involve the relative motion of these polyhedra about short-chain segment "hinges" that are perhaps of the approximate length of the chain folds of polymer single crystals.[28] The deformational free energy would then mainly reside in the internal energy needed to appropriately alter the distribution of chain-rotational conformers within these short segments rather than the largely entropic change involving the disturbance of rotational states along the entire molecular chain contour, as viewed within the theory of rubber elasticity.[29]

Equations 22 can be combined to yield

$$\phi = (\nu/\nu_0)[(\nu/\nu_0) + \alpha^{-1} - 1]^{-1} \tag{23}$$

In eq 23, the ν's refer to water as distributed over all clusters, rather than the water-occupied volume of single clusters.

If N and N_0 are the total numbers of clusters in the sample for the wet/dry states, then, as V is the volume of a single wet cluster, and V_0 that for a single dry one, $\nu/\nu_0 = NV/(N_0V_0)$, and

$$\phi = \frac{(N/N_0)\lambda^3}{(N/N_0)\lambda^3 + \alpha^{-1} - 1} \tag{24}$$

The ratio α/ϕ can be determined from this equation, then substituted into eq 21 to yield

$$C_n/C_0 = (\rho/\rho_0)(N_0/N)\{\alpha[(N/N_0)\lambda^3 - 1] + 1\} \tag{25}$$

Of course, without a knowledge of the dependence of N/N_0 and ρ/ρ_0 on n, as well as a reasonable estimate for α, C_n/C_0 still remains undetermined. It may, however, be of advantage to work with the quantities of eq 25 for reasons that are specific to a given system.

n is eliminated from eq 18 using eq 19 to yield

$$\ln\left\{x\left[1 + \frac{C_n/C_0}{(n_+ + n_-)(\lambda^3 - 1)}\right]\right\} = \frac{v_{\mathrm{w}}E}{6RT}(5 - 4\lambda^{-1} - \lambda^{-4}) \tag{26}$$

This equation, subject to the assumptions in its derivation, represents either an *equilibrium vapor pressure isotherm*, or *liquid sorption isotherm* depending on whether $x < 1$ or $x = 1$, respectively. Ideally, then, for a given polymer of cluster morphology, having ion-exchange groups of hydration number n_-, with an equal number of totally dissociated counterions of hydration number n_+, and, given the dependence of C_n/C_0 and E on n, there will be an *equilibrium* λ for a given x at a given system temperature. In practice, one might let $f(\lambda)$ equal the left-hand side of eq 26 and $g(\lambda)$ the right-hand side. The zeros of the function $F(\lambda) = f(\lambda) - g(\lambda)$ will then represent equilibrium extension ratios.

Of course, the zeroes of $F(\lambda) = 0$ can only be extracted for systems for which the dependence of C_n/C_0 and E, on n, can be stated in specific functional forms. At present, this is largely impossible. To be sure, the experiments of Hsu and Gierke,[10] on a particular single system, do offer some insight for understanding the problem of C_n/C_0, but there is no straightforward general theoretical formulation of the manner in which ion-exchange groups reorganize, by intercluster hopping, as the water content changes. In the following analysis, it will be assumed, as done by Gierke and Hsu, that one is dealing with a hypothetical situation for which C_n/C_0 is unity. Of course, one could experiment with such simple relationships as $C_n/C_0 = 1 + Bn$ but there is no a priori theoretical basis and the assignment of B would be arbitrary.

In addition, consider the case of equilibration in pure liquid water ($x = 1$). Define $n_{\mathrm{h}} = n_+ + n_-$, and E_{r}, a "reduced modulus", as $v_{\mathrm{w}}E/(RT)$.

Then, it would be of interest to use eq 26 to see what E, or E_{r}, would have to be under the above-stated conditions in order to cause a balance of the osmotic pressure

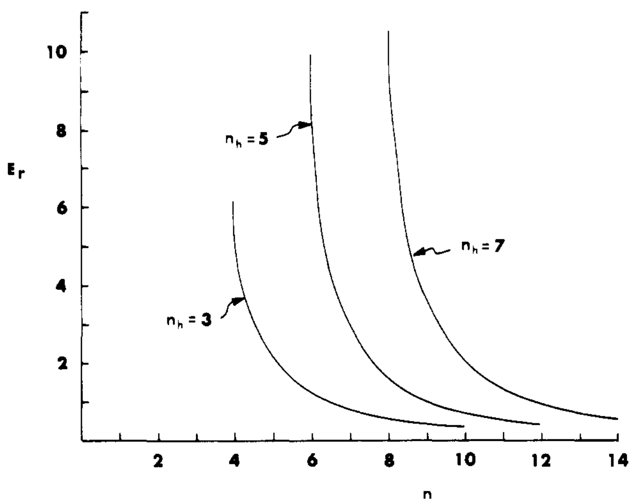


Figure 6. Reduced modulus, E_r, required for equilibrium water uptake of n molecules per ion-exchange group for $n_h = n_+ + n_- = 3, 5, 7$.

within a cluster over a reasonable range of n. Specifically, it is required that

$$E_r = \frac{6 \ln \{1 + [n_h(\lambda^3 - 1)]^{-1}\}}{5 - 4\lambda^{-1} - \lambda^{-4}} \tag{27}$$

where $\lambda = (n/n_h)^{1/3}$.

Shown in Figure 6 are plots of E_r vs. n ($n > n_h$) using eq 27, for n_h = 3, 5, and 7. Overall, it is seen that E must steadily decrease with increasing n. The physical reason for this decrease is that the cluster "solution" is being progressively diluted (and its osmotic pressure correspondingly lowered) and therefore less elastic resistance to swelling is required to produce equilibrium. Also, at a given n, E is greater the greater the n_h. Consider that, for the same n, the amount of *free water* in these hypothetical clusters decreases with increasing n_h. This results in an increasing osmotic pressure, with increasing n_h, that must necessarily be counteracted by a greater E, as is indeed depicted in Figure 6.

To date, perhaps the mechanical investigations most relevant to this discussion were those of Kyu and Eisenberg,[30] who, in an underwater study of the stress relaxation of 1200 equivalent weight Nafion in the Na^+ form, report 10-s tensile moduli over a range of temperatures. At 60 °C, for example, this modulus is 10^8 N/m^2, corresponding to $E_r = 0.662$. The amounts of water in the samples are not reported but most have been rather high. Also, in the dry state, this sample had a modulus of slightly less than 10^9 N/m^2, giving an E_r of about 10. Kyu and Eisenberg propose that, in proceeding from the dry state, increased hydration loosens the counterion from the anion, diminishes the strength of ionic association, and therefore reduces the modulus.

Earlier, empirical formulae used to determine the equilibrium water contents and the tensile moduli at these water contents, as a function of cation type and equivalent weight, for Nafion sulfonate membranes, were reported.[31] It should be stressed that these quantities relate to a prescribed sample pretreatment and that membrane history prior to equilibration indeed can be a significant parameter in comparative studies. In Table I are listed E and n values that were calculated for the Li^+, Na^+, and K^+ forms for an equivalent weight of 1200 at 23 °C. For the Na^+ form, at 23 °C, $E_r = 0.912$, which is seen to be greater than the value derived from the data of Eisenberg and Kyu, although it must be remembered that the latter number reflects a higher temperature.

Table I
Experimental Tensile Moduli (E), in N/m^2, and Membrane Water Contents (n), in Average Number of H_2O Molecules per Side Chain, for Ionic Forms of 1200 Equivalent Weight Nafion Sulfonate Membranes at 23 °C[a]

counterion	n	E
Li^+	22	1.05×10^8
Na^+	18	1.25×10^8
K^+	13	1.54×10^8

[a] These calculations are based on the empirical formulae in ref 32.

Table II
Equilibrium n, λ, and ϕ Values for Experimental E_r

E_r	n	λ	ϕ
0.662	13.3	1.24	0.301
0.912	12.2	1.20	0.280

One must be cautious in comparing moduli that relate to macroscopic deformation with something akin to the "E" of this theory in that the latter has been specially defined as a parameter having significance on but a local microstructural level. It is nonetheless natural to test the degree to which equating the two will predict a value of n that is physically reasonable. The equivalent of locating the zeroes of $F(\lambda) = 0$ is to consider the graphs of Figure 6 as a family of master curves, one curve per selected $n_h = n_+ + n_-$. Once a reasonable n_h has been selected, the experimental E_r value uniquely determines the equilibrium water uptake, n. Perhaps a reasonable n_h for a dissociated SO_3^-–Na^+ ion pair is 7, i.e., $4H_2O/Na^+$ and $3H_2O/SO_3^-$ (one H_2O molecule hydrogen bonded to each sulfonate oxygen).

The resultant n and λ values for E_r = 0.662 and 0.912 are listed in Table II. First, in comparison with the experimental value of n = 18 (see Table I), it is significant that the calculated n's are in the correct proximity, considering the model's simplicity and absence of adjustable parameters. With reference to Table I, the computed n is more in line with an equilibrium-swollen K^+-form membrane. However, it is evident that but a slight lowering of E_r (i.e., via theoretical model refinement) would bring theory in line with experiment.

Having calculated n, the fractional increase in mass, from the dry state, is simply $18n/M_{eq}$.

Lastly, ϕ, the volume fraction of the ionic cluster phase in the equilibrium water-swollen state, remains to be determined. With reference to eq 24, this morphological parameter could be calculated, for a given λ, if N/N_0 and α were known. For reasons discussed earlier, N/N_0 is presently an inaccesible function and will be assumed here, as in the theoretical model of Hsu and Gierke,[10] to be unity. α, the volume fraction of the ionic cluster phase in the dry state, is also not readily obtainable but will be estimated in the following way.

If, in the dry state, it is correct to assume that the polymer chains and their side groups are packed efficient enough so as to produce a reasonably uniform spatial distribution of free volume, then α could be estimated as the ratio of the sum of the space-filling volumes of the atoms in the "ionic (i.e., cluster-associated) fragment" to the sum of the space-filling volumes of all the atoms in the polymer repeat unit (i.e., average side chain-to-side chain structure). If there are n_k atoms of type k and having bonded radius of r_k, and if there are J types of atoms altogether within the repeat unit, then

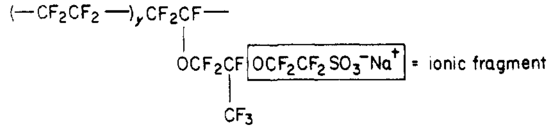
$$\alpha = \left(\sum_{\text{cluster } k\text{'s}} n_k r_k^3\right)\left(\sum_{k=1}^{J} n_k r_k^3\right)^{-1} \tag{28}$$

Table III
Atomic Population and Radii within a Chemical Repeat Unit of 1200 Equivalent Weight Nafion in the Na^+ form

k	n_k	r_k, Å
	Ionic Fragment	
Na^+	1	0.95
O[a]	3	0.96
S	1	1.04
C	2	0.77
F	4	0.96
O[b]	1	1.01
C	5	0.77
F	9	0.96
O[b]	1	1.01
	TFE Fragment	
C	15.12	0.77
F	30.24	0.96

[a] Sulfonate oxygen. [b] Ether oxygen.

In applying this procedure to Nafion, consider the chemical formula for the Na^+-sulfonate form:



$$(\text{—}CF_2CF_2\text{—})_yCF_2CF\text{—}\,|\,OCF_2CF(CF_3)\boxed{OCF_2CF_2SO_3^-Na^+} = \text{ionic fragment}$$

In order to facilitate efficient molecular packing, the ionic fragment should include a segment of the side chain longer than the $SO_3^-Na^+$ grouping. Furthermore, the ether oxygens are hydrophilic. Therefore, the ionic fragment was selected to be $OCF_2CF_2SO_3^-Na^+$, although the choice is somewhat arbitrary.

The quantities relevant to eq 28 are listed in Table III. The r_k values were obtained from Ealing CPK molecular model listings based on representative crystallographic data. Utilized values were actually averages between van der Waals and covalent radii. y, for a given equivalent weight, is given by

$$y = (M_{eq} - 444)/100 \tag{29}$$

For $M_{eq} = 1200$, $y = 7.56$, on the average; the side chains are separated by about 15 backbone carbons. The resultant value of α is 0.184. ϕ, for $N/N_0 = 1$, becomes

$$\phi = \frac{\lambda^3}{\lambda^3 + \alpha^{-1} - 1} \tag{30}$$

which has the numerical values listed in Table II for the λ's listed therein.

Hsu, Barkley, and Meakin,[32] in their theoretical studies of ion percolation in hydrated Nafion sulfonate membranes, considered $\phi = f_V/(1 + f_V)$, where f_V is the fractional increase in membrane volume from the dry state. There seems to be, however, in the literature, considerable variation in measured f_V's for a given M_{eq} and cation form, the differences perhaps being due to varying conditions of membrane pretreatment. The value of $f_V = 0.443$, reported by Gierke et al.,[10b] appears to be the most appropriate for use in the above equation and a value of $\phi = 0.307$ results. The latter number is seen to be in reasonable agreement with the numbers in the last column of Table II.

Conclusions

The formulation of a simple theory to be used for the prediction of the water sorption characteristics of clustered ionomers has been initiated. Specifically, the average number of water molecules per ion-exchange group, cluster radius expansion ratio, and volume fraction of the cluster phase can be determined for membrane equilibration with water vapor of given relative humidity, or pure water.

The central concept is a consideration of the thermodynamic equilibrium of an "average" cluster, although the driving force for cluster expansion, i.e., osmotic pressure, is derived from a molecular theory of cluster water activity. This water activity, in turn, is a function of the energetics of the dissociation equilibrium of a specific fixed anion–monovalent cation combination, as well as of the water content. On the other hand, a molecular-based model of the resistance, to deformation, of the polymer matrix, is not at hand and experimental tensile moduli have been substituted in sample calculations. It is significant that no arbitrary adjustable parameters have been introduced and manipulated to bring theory in line with experiment. With this in mind, it is then somewhat encouraging to see that the simple theory, which is considered to form but the nucleus of a future, more sophisticated model, already produces reasonable results, as demonstrated by the outlined application to the Nafion–sulfonate system.

In addition to calculations applied to situations involving high degrees of hydration, the theory can be applied to systems having incomplete (i.e., P_1 considerably less than unity) cationic dissociation. Consider, for examples, membranes having large, weakly hydrated cations, or, say, the lower state of membrane hydration existing at the lower end of a vapor pressure isotherm.

However, the practicality of the model, as a predictive tool in a program of material design, would be greatly enhanced if one could derive such basic quantities as C_n/C_0 (or N/N_0), E_r and α from a more fundamental procedure such as that of theoretical structure calculations based on macromolecular energetics.[25] Clearly, the mechanical, dielectric, ionic selectivity, and ionic transport properties are related to the structural parameters derivable from this model.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant CPE-8115115.

Appendix

Calculation of the Volume of Overlap of Monomolecular Hydration Shells of a Cation and Anion in an Outer Sphere Complex. With reference to Figure 3, all points on the outer surfaces of the hydration shells of the anion and cation are defined by

$$x^2 + y^2 + z^2 = R_-^2$$

$$(x' - x_0)^2 + (y')^2 + (z')^2 = R_+^2 \tag{A1}$$

respectively, where the y direction is into the paper. The x coordinate of the circle of intersection of these surfaces, x^*, is that for which $y = y' = 0$, $z = z'$ and $R_-^2 - (x^*)^2 = R_+^2 - (x^* - x_0)^2$, or

$$x^* = (2x_0)^{-1}(R_-^2 - R_+^2 + x_0^2) \tag{A2}$$

The differential volume element for integrating from x^* to R_- is $dV = \pi(R_-^2 - x^2)\,dx$, the total overlap volume to the right of x^* being $(2\pi/3)R_-^3 - \pi R_-^2x^* + (\pi/3)(x^*)^3$. Similarly, for the remaining region of overlap to the left of x^*, $dV = \pi[R_+^2 - (x' - x_0)^2]\,d(x' - x_0)$. After a change-of-variable and integration, the total contribution to the left of x^* is $\pi\{R_+^2[2R_+/3 - x_0 + x^*] + (x_0 - x^*)^3/3\}$.

Finally, the *total* volume of overlap, i.e., sum of the two above expressions, is

$$\Delta V = (2\pi/3)(R_-^3 + R_+^3) - \pi[R_-^2x^* + R_+^2(x_0 - x^*)] + (\pi/3)[(x^*)^3 + (x_0 - x^*)^3] \quad (A3)$$

which is eq 5 of the text.

Registry No. H_2O, 7732-18-5; Nafion, 39464-59-0.

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Modeling Phenolic Resins and Their Thermolysis

Ron Ozer, Mary P. Monaco, Francis P. Petrocelli, and Michael T. Klein*[†]

Department of Chemical Engineering and Center for Composite Materials, University of Delaware, Newark, Delaware 19716. *Received August 14, 1984*

ABSTRACT: A simple interpretation of the structure of phenolic resins permitted development of a mathematical model for their thermolysis. The resin was viewed as an ensemble of single-ring aromatics linked into a polymer by diphenylmethane (DPM) bonds. The rate of thermal fission of the polymer's DPM bonds was used to deduce the rate of evolution of single-ring products. Previous pyrolyses of related model compounds provided the reaction pathways and kinetics for the polymer's DPM bond fissions. Simple probability concepts allowed calculation of six individual product identities and yields. Experimental pyrolyses of an actual phenolic resin permitted evaluation of these model predictions.

Introduction

The prediction of a polymer's pyrolysis pathways and rates is of interest in such areas as polymer thermal stability,[2] polymer recycle,[5] and coal liquefaction.[14] Unfortunately, these fundamental pathways and kinetics are usually obscured in the complexity of both the polymer's structure and its pyrolysis product spectra. Predictions and correlations based on observations of actual polymer pyrolysis can thus be difficult. In contrast, the comparatively simple structure and product spectra of model compounds[1,6,11,13] permit resolution of reaction fundamentals. This motivated the present development of a mathematical model of phenolic resin pyrolysis that is based on the pathways, kinetics, and mechanisms of a model compound's pyrolysis.

This paper describes the development, execution, and analysis of the pyrolysis model. We begin with a simple analysis of phenolic resin structure. This is combined with model compound pyrolysis information and elementary probability concepts into the polymer pyrolysis model. A delineation of experimental techniques, model predictions, and experimental results follows. We then compare experimental results and model predictions, and conclude by considering the utility and limitations of the present modeling approach.

Model Development

The analysis of a phenolic resin's thermolysis is complicated by its large and distributed molecular weight and apparently randomly branched structure. We thus con-

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[†] To whom correspondence should be addressed at the Department of Chemical Engineering.

0024-9297/85/2218-0491$01.50/0