of highest molcular weight, PB7-10, the semicrystalline polymer melts to a smectic phase. Hence, for the PB7 polymers the stability of the nematic phase decreases, and that of the smectic phase increases, as the polymer molecular weight is increased.

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Registry No. $HO_2C(CH_2)_5CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-23-9; $HO_2C(CH_2)_5CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-60-6; $HO_2C(CH_2)_6CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-24-0; $HO_2C(CH_2)_6CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-61-7; $HO_2C(CH_2)_7CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-25-1; $HO_2C(CH_2)_7CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-19-3; $HO_2C(CH_2)_8CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 70788-15-7; $HO_2C(CH_2)_8CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 70800-12-3; $HO_2C(CH_2)_9CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-26-2; $HO_2C(CH_2)_9CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-20-6; $HO_2C(CH_2)_{10}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-27-3; $HO_2C(CH_2)_{10}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-21-7; $HO_2C(CH_2)_{11}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-28-4; $HO_2C(CH_2)_{11}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 86129-22-8; $HO_2C(CH_2)_{12}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 copolymer, 86129-29-5; $HO_2C(CH_2)_{12}CO_2H$-4-$HOC_6H_4C_6H_4OH$-4 (SRU), 74790-62-8; TBBA, 85628-40-6.

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Proton Tunneling within the Hydration Structure of OH^--Containing Perfluorosulfonate Ionomer Membranes

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ABSTRACT: Structural and dynamic aspects of the ionic-hydrate associations within Nafion (du Pont) sulfonate films that were equilibrated in alkali hydroxide solutions were studied by noting infrared spectral behavior mainly in the region of the O–H stretching vibration. It was seen that a continuous absorption that begins in this region and extends to lower wavenumbers is a characteristic function of the external caustic strength. This phenomenon is attributed to the tunneling of protons across hydrogen bonds. The state of hydrogen bonding, as suggested by the infrared spectra, may be reasonably interpreted within the framework of the accepted cluster morphology.

Introduction

Past infrared and nuclear magnetic resonance spectroscopic investigations of Nafion[1] perfluorosulfonate membranes, in the monovalent cationic salt forms, have yielded much useful information regarding side-chain–counterion interactions and the nature of hydration as a function of water content.[2–4] A knowledge of the nature of molecular interactions within the ionic clusters of membranes containing co-ions, in this case, OH^- (e.g., separators in chlor-alkali cells), is necessary for a rational understanding of OH^- conductivity in this medium.

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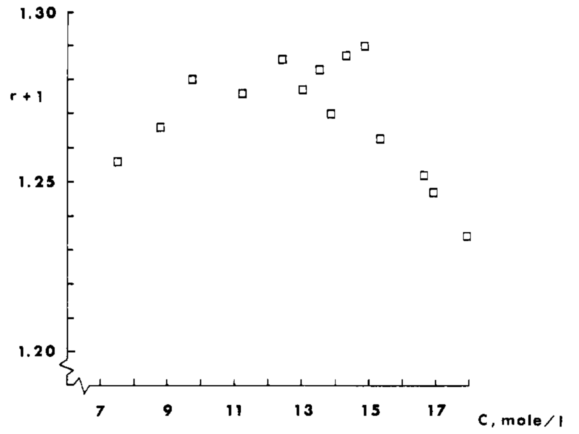


Figure 1. Total number of Na^+ ions ($r + 1$) per side chain in Nafion sulfonate films equilibrated in NaOH solutions of indicated molarities (C) at room temperature.[4b]

For a given external driving force, the flux of OH^- ions through hydrated membranes will, in general, depend on (1) their *internal concentration*, or steady-state distribution across the membrane/caustic interface, and (2) their intrinsic *mobility* within the membrane structure. It will be demonstrated how an analysis of the O-H stretching region of the infrared spectra of Nafion membranes that were equilibrated in caustic solutions can provide unambiguous information relating to cation–H_2O, anion–H_2O, and H_2O–H_2O interactions and the manner in which these interactions shift with varying external caustic strength.

Discussion

NaOH Uptake Studies. Before proceeding with the detailed spectral analysis and interpretation, it is useful to have a knowledge of the internal concentration and amount of sorbed caustic per amount of polymer as a function of external caustic concentration. Films 5×10^{-3} in. thick having an equiv wt of 1100 were equilibrated, at room temperature, in NaOH solutions up to the caustic solubility limit, the samples being initially in the dry Na^+ salt form. r, the average number of internal OH^- ions per SO_3^- site, and t, the average number of internal H_2O molecules per SO_3^- site, were derived from the initial dry weight, equivalent weight, net weight increase, and titration for OH^- content. r and t, of course, are merely numbers relative to a single ion-exchange site and do not imply interactions or associations with SO_3^- groups.

It is noted (see Figure 1) that the electrolyte invasion is characterized by an $NaOH/SO_3Na$ molar ratio that is relatively *invariant*, being ~0.27, over the external concentration range $7.5 \leq M \leq 17.9$. Therefore, the progressive concentration of internal NaOH with increasing external solution molarity seems to be essentially a dehydration process. A plot of t vs. C, the external solution molarity, illustrates this dehydration effect (see figure 2). The constancy of r can be rationalized within the framework of the Donnan equilibrium theory if the volume concentration of SO_3^- groups would somehow increase at the same rate as the internal concentration of Na^+ ions, with increasing C. In other words, the accompanying dehydration would deswell the polymer matrix causing an increase in the ion exchange density, thereby resisting further OH^- uptake through enhanced Donnan exclusion.

On the basis of both ^{23}Na NMR[5] and ultrasonic[6] studies of simple NaOH solutions, the primary hydration number for an NaOH ion pair is about 10, while that of the SO_3Na grouping in Nafion membranes is about 4, as determined by IR and NMR spectroscopies.[2,3] Although there may be controversy over the exactness of these numbers, as well as the overall concept of hydration itself, such values are at least roughly indicative of the average number of adjacent water molecules that will tend to interact more strongly with the ions than other water molecules in a dilute solution.

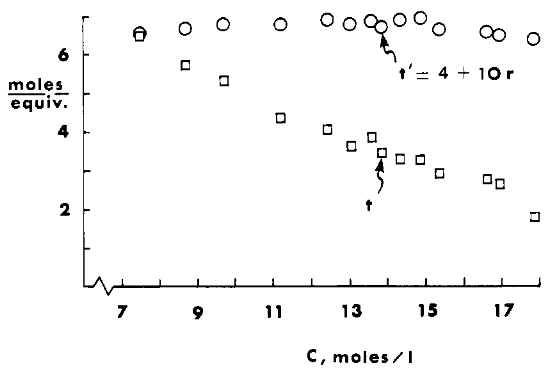


Figure 2. Same as Figure 1 but for total number of H_2O molecules per side chain, t, and the hypothetical quantity t' for "bound H_2O".[4b]

It is instructive to perform the following "imaginary" calculation using these hydration numbers. If, for a given r, there existed *just enough* water to fully hydrate (i.e., form complete primary solvation shells) all the ions within the membrane, then t', the hypothetical number of H_2O molecules per SO_3^- group, would have to be $4 + 10r$. This number, generated with known r values over the range of C, is also displayed in Figure 2. Since $t < t'$ everywhere, it is suggested that most of the water is in intimate contact with ions. For example, at 17 M there would be about eight H_2O molecules available for distribution among 10 ions overall, i.e., four SO_3^-'s, five Na^+'s, and one OH^-, on an average relative basis. Therefore the relative population of internal contact ion pairs, or perhaps higher order multipoles, must be considerable and steadily increasing with increasing C. In a sense, this reasoning assumes the accepted model of the water and ionic components in Nafion as encapsulated as a "microsolution" within clusters[7a] rather than dispersed uniformly throughout the polymer matrix.

Infrared Studies. In a parallel infrared investigation, 2×10^{-3} in. thick, 1500 equiv wt sulfonic acid films were equilibrated, as before, in very concentrated caustic solutions at room temperature. All spectra of surface-blotted dry films were then obtained in transmission with a Nicolet 7199 Fourier transform infrared spectrometer and stored for subsequent digital processing.

It should be remembered that for a given external caustic strength these 1500 equiv wt films will have even lower water contents than the 1100 equiv wt samples used in the previously described NaOH uptake studies.

Shown in Figures 3 and 4 are FT-IR spectra, in the 2600–4000-cm^{-1} region, of films equilibrated in solutions of the various indicated external molarities of NaOH and KOH, respectively. The salient features of these spectra are as follows: (1) There exists a shoulder, or *minor peak*, on the high wavenumber side of the main peak, whose intensity relative to the main peak increases with increasing caustic strength. (2) A *continuous absorption* is seen as a superposition on the spectra, extending from the main peak maxima down to lower wavenumbers.

If clusters can be reasonably thought of as *microsolutions*, i.e., encapsulations of small quantities of electrolyte components, with fixed ion exchange groups, it is then appropriate to initiate a molecular basis of understanding the structural and dynamic aspects within this phase by a scrutiny of earlier established knowledge from spectro-

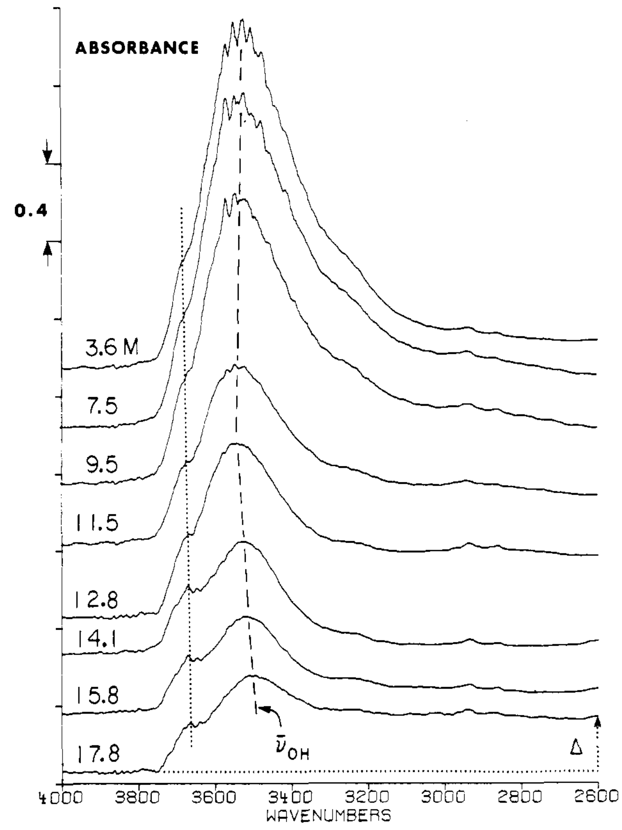


Figure 3. FT-IR absorption spectra in the region of the O–H stretching vibration of Nafion sulfonate films equilibrated in NaOH solutions of indicated molarities at room temperature.

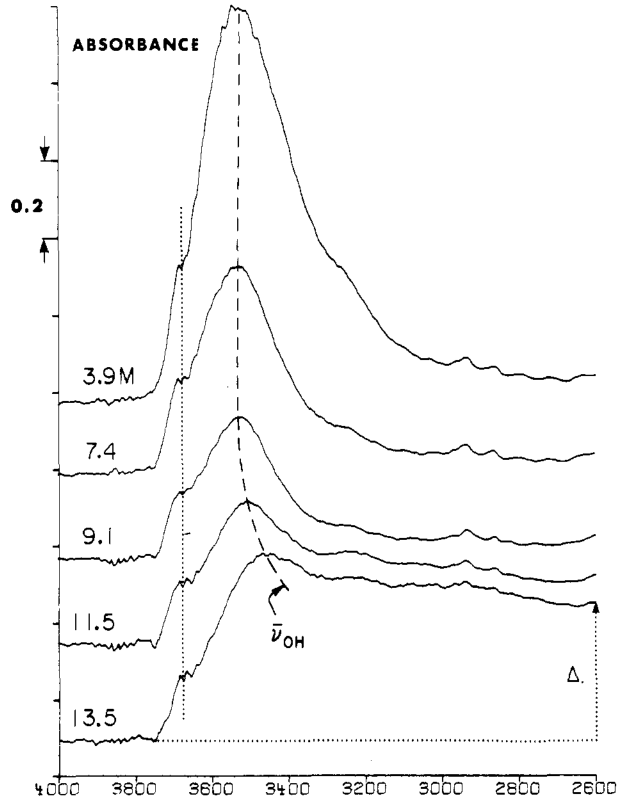


Figure 4. Same as Figure 3 but for KOH solutions.

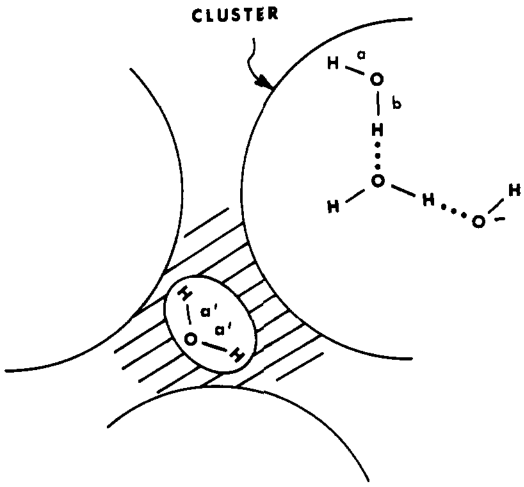


Figure 5. Simplified illustration of three possible modes of incorporation of H_2O molecules within the phase-separated morphology of Nafion membranes, as suggested by IR spectroscopy. *a*, *b*, and *a′* designate three OH groups, each in distinct molecular environments.

scopic studies of simple acidic and basic electrolytes. In particular, fundamental questions of the detection, lifetime, and molecular interactions of OH^- ions in aqueous solutions are quite relevant. Since the necessary volume of such a discussion would detract from the continuity of the present discussion, an enumeration of the most salient points is contained in the enclosed Appendix.

H-Bonded vs. Non-H-Bonded Water. The digitized spectra in this region were curve resolved into a linear superposition of two Gaussian components, each being characterized by a maximum, wavenumber at maximum, and line width. It should be stated that, owing to the inability to model the continuous absorption component that contributes strongly on the low wavenumber side of the main peak (by means of the standard Gaussian or Lorentzian curve forms), only spectral data on the high wavenumber side of the main peak was used in the computerized fitting algorithm.

Whereas the broad main peak at around 3500 cm^{-1} is attributed to O–H groups in hydrogen bonds, the minor peak on its high wavenumber side has been assigned to the stretching vibration of O–H groups that do not participate in hydrogen bonding. As an interpretive reference point, consider the fact that the simple pure caustic solutions are not observed to exhibit this O–H bond differentiation at any concentration. The implication is that the water molecules are somehow distributed throughout the polymer matrix such that most O–H groups participate in hydrogen bonding, but a significant fraction do not. Combined with the knowledge of a clusterlike morphology for Nafion, this evidence suggests the presence of H_2O molecules that reside at the hydrophobic/hydrophilic interface and, therefore, have restricted opportunities for hydrogen bonding. This physical situation is depicted in Figure 5 wherein b and a are OH groups that respectively are and are not in hydrogen bonds. The suggestion of "free" O–H bonds that contact the fluorocarbon environment in the hydrated sodium salt form of Nafion was made earlier by Falk, on the basis of infrared studies.[7b]

Given the knowledge of absorptivities in this spectral region, it should be possible, in theory, to estimate the ratio of the number of interfacial H_2O molecules to total number of H_2O molecules from the areas beneath the curve-resolved component peaks. Nonetheless, in rough description, it is observed that the ratio of a-peak area to total a + b peak area increases with increasing caustic strength and that this ratio is greater for KOH-imbibed membranes than for those equilibrated in NaOH solutions of equal molarity. These results are consistent with the observed progressive membrane dehydration that occurs with increasing caustic strength and also the fact that K^+-con-

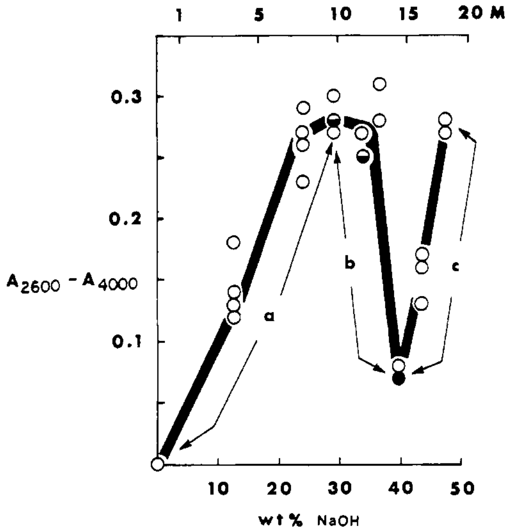


Figure 6. IR continuous absorption vs. concentration profile for Nafion sulfonate films equilibrated in NaOH solutions at room temperature. The empty, half-filled, and solid points represent one, two, and three experiments at the given concentration yielding the same ordinate, respectively.

taining membranes swell to a lesser degree than Na^+-containing membranes.

Infrared Continuous Absorption. As opposed to the familiar discrete peaks observed on an infrared spectrum, arising from local molecular group vibrations, continuous absorption, in general, refers to a diffuse backgroundlike superposition that originates at the peak position of a group that is mechanistically involved in this process and extends to lower frequencies. In this case, these groups are proton donors and the proton can transfer to an adjacent acceptor site in a hydrogen-bond configuration: O–H···O. This transfer reaction, of course, is very fast because of the (1) high force constants, (2) short O–O distances, and (3) small H^+ mass.

The continuous absorption was quantified by measuring the difference between the absorbances at 2600 cm^{-1} (sufficiently removed from the influence of the main O–H stretch peak) and 4000 cm^{-1} (the base line, at which there is no continuous absorption). This arbitrary definition, although reasonable, involves absorbances at two discrete frequencies. However, since this phenomenon is characterized by a continuum, a definition involving *integrated* absorbance should be used, in a strict sense.

Consider now the infrared continuous absorption vs. concentration profiles, shown in Figures 6 and 7, for membranes equilibratred in NaOH and KOH solutions, respectively.

The NaOH system profile is characterized by an initial rise and maximum, and then a minimum, with progressively higher caustic strength. By comparison, the KOH system results also indicate a rise, however, followed by a plateau, or shallow minimum, ending with a precipitous rise. Within the region before the final upsurge at the highest concentrations, the continuous absorption is noticeably greater and more concentration sensitive for the NaOH membranes than the KOH membranes. In essence, nonetheless, it might be argued that the curves are qualitatively similar.

IR Spectra of Pure NaOH and KOH Aqueous Solutions. It was just stated that Nafion sulfonate membranes containing OH^- ions, as a result of equilibration in caustic solutions, exhibit a strong infrared continuous absorption. On the other hand, the same membranes in cationic salt forms that were equilibrated in pure water do not. Therefore, one must conclude that OH^- ions (strong H^+ acceptors) are the primary cause of the continuous absorption phenomenon and that polymer structure, although influential, is not responsible for the primary event.

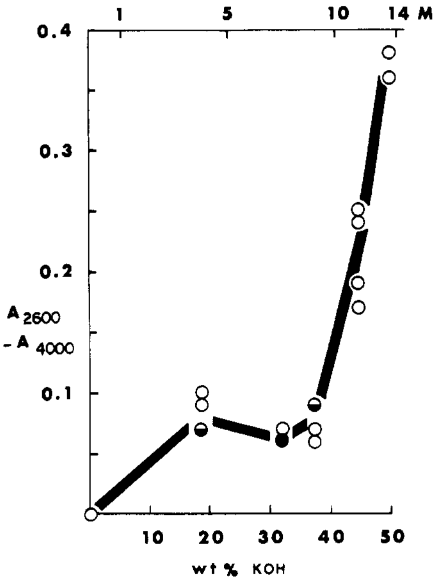


Figure 7. Same as Figure 6 but for KOH.

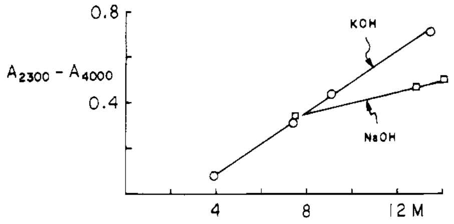


Figure 8. Concentration dependence of the IR continuous absorption of pure NaOH and KOH aqueous solutions at room temperature.

Infrared investigations of simple aqueous NaOH and KOH solutions, performed in this laboratory to provide a base line comparison with the caustic component in the membranes, indicate a very strong continuous absorption at high concentrations. This result, of course, reinforces the logic of the previous paragraph. Furthermore, with reference to Figure 8, it is seen that the continuous absorption of these simple solutions (now quantified by the absorbance at 2300 rather than 2600 cm^{-1} owing to an intrinsically broader peak) monotonically increases with increasing molarity and is cation dependent.

In context, it should be noted that an infrared continuous absorption was reported as early as 1933 for acidic and basic aqueous solutions[8] as well as in later studies of alkali hydroxide solutions[9] and acidic and basic polyelectrolyte systems.[10,11]

By comparison, the concentration profiles for caustic in the membranes are more complex than those of the corresponding free solutions reflecting polymer interactive effects.

Origin of Infrared Continuous Absorption. The molecular event that gives rise to this phenomenon in the spectra of aqueous hydroxide or aqueous hydroxide-containing structures is the same mechanism accounting for the anomalously large conductivity of these solutions.[12,13] This process, historically referred to as the Grotthus mechanism, consists of proton transfer throughout the dynamic hydrogen-bonded network.

At low alkali hydroxide concentrations, the cation and OH^- ion are, on the average, separated by a considerable

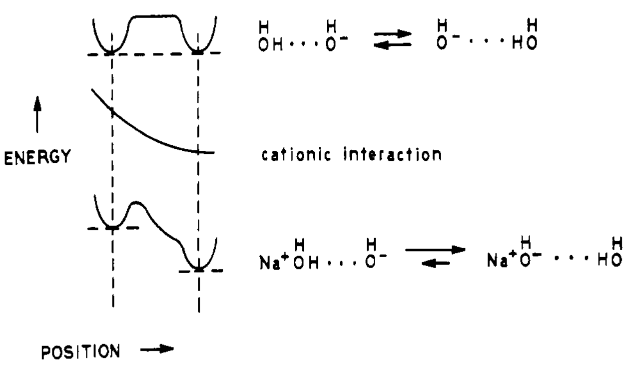


Figure 9. The symmetric double energy well corresponding to proton transfer in $H_3O_2^-$ molecules and its antisymmetrization by the electric field of adjacent cations.

number of H_2O molecules. In this case, one can visualize the proton as executing motion within a *symmetric* double energy well, as depicted in Figure 9 (top). Throughout this protonic motion there must exist a continuum of O–H bonds ranging from being strong and well-defined in the classical sense to being deformed and softer and finally onto the other extreme resembling dissociation. The proton, however, being a light particle, can tunnel, in the quantum mechanical sense, through the activation barrier between the boundary oxygens. Therefore, apart from dynamic rotational or translational motion within the $H_3O_2^-$ group, or external perturbations, the fundamental molecular event (H^+ tunneling in hydrogen bonds) must be independent of temperature. In other words, although the particular characteristics of the energy profile will determine the nature and degree of tunneling, the mechanism is not temperature activated as in familiar rate processes.[14]

Aside from a rigorous and necessarily difficult quantum mechanical treatment, it is, in qualitative description, physically reasonable to expect a net continuity or smearing of "softer" O–H modes to be consistent with the dynamic variance in adjacent O–O distances and structural orientations within the $H_3O_2^-$ grouping, in the liquid state, during H^+ transfer from donor to acceptor. This distribution of geometrical configurations within the $H_3O_2^-$ grouping, in turn, largely results from the fluctuating external perturbations from the electric fields of local cations and water dipoles. While the electrons within this grouping can immediately follow the proton fluctuations in these hydrogen bonds, the more sluggish motion of adjacent ions and water dipoles cannot. What is observed spectroscopically is the time-averaged effect or ensemble average over this heterogeneity of local environment.

Concentration Dependence of Continuous Absorption. In passing from dilute to high alkali hydroxide concentrations (either in simple solutions or within a membrane structure) the symmetry of the double energy wells is increasingly disrupted by the increasing relative population of Na^+–OH^- ion pairs separated by a single molecule, that is, $H_3O_2^-$ groupings having adjacent cations. Within the O–H bond of the H_2O molecule, the proton experiences a repulsion toward the OH^- ion as well as electron withdrawal from its vicinity due to the strong cationic electric field. Energetically, the position at the well furthest from the cation becomes more favorable, the proton becomes more localized, and the infrared continuous absorption becomes suppressed as the hydrogen bond is rendered less polarizable (see Figure 9, bottom). Furthermore, since the contact electric field strength decreases with increasing monovalent cationic radius, the rate of change of continuous absorption with change in concentration should decrease more rapidly in NaOH than KOH solutions. This logic can be used to rationalize the greater sensitivity of the continuous absorption of NaOH membranes than KOH membranes to concentration changes.

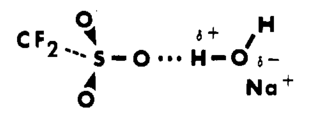


Figure 10. Perturbation of side-chain–water hydrogen bonding by an adjacent cation, at low internal water contents.

Sections a and b (see Figure 6) of the continuous absorption vs. concentration profile can now be reasonably understood on a molecular level. First, the initial rise from low caustic strength is simply attributed to a progressively greater internal concentration of $H_3O_2^-$ groupings, i.e., more H^+ tunneling events. The subsequent decrease in rate of continuous absorption enhancement followed by its decline is attributed to an increase in the relative population of $X^+{\cdot}H_2O{\cdot}OH^-$ groupings wherein the H^+ tunneling process is increasingly inhibited by the antisymmetrizing Coulombic field effect of the adjacent cations.

Hydration Structure at the Highest Caustic Strengths. The final problem, of course, concerns the final upswing on the continuous absorption vs, concentration profile as the external caustic solubility limit is approached. It is very relevant, considering the scarce internal water levels that accompany the highest external caustic concentrations, to investigate the degree and nature of hydrogen bonding as exists.

At high membrane water contents, the prevalent hydrogen bonding is between H_2O molecular dimers (total coordination unknown) or within $H_3O_2^-$ groupings. However, at the lower membrane hydration levels that correspond to the highest ranges of external alkali hydroxide concentrations, the formation of hydrogen bonds between H_2O molecules and SO_3^- groups is expected to be increasingly important.

Past IR studies of the salts of cross-linked polystyrene sulfonate membranes indicate that, *at low degrees of hydration*, the water molecules are interposed between the cations and anion sites in a hydrogen bond configuration similar to that depicted in Figure 10.[10,11] Now, at high degrees of hydration, the cations are removed from the anions by more than one H_2O molecule, and there should be essentially no tunneling of protons across the hydrogen bond of the $SO_3^-{\cdots}H_2O$ grouping because the oxygen on the sulfonate group is a weak proton acceptor. However, as the H_2O/cation ratio decreases and, subsequently, the relative population of Figure 10 type groupings increases, a larger relative population of O–H bonds of the H_2O molecules undergoes an overall stretching deformation due to local cationic fields. As the donor strength of the H_2O molecules thus increases, the asymmetric $SO_3^-{\cdots}H_2O$ hydrogen bonds become more symmetrical and, therefore, stronger. Spectroscopically, this situation would be reflected in an infrared continuous absorption (as observed) with an O–H stretching vibration shifted to lower wavenumbers. It is suggested that this mechanism may also be operational in Nafion sulfonate membranes that, of course, have very low H_2O/Na^+ molar ratios at the highest external caustic strengths.

In fact, it is observed, for both NaOH- and KOH-equilibrated Nafion films, that the main O–H stretching peak shifts to lower wavenumbers, as seen in Figures 3, 4, and 11. The suggestion, partly motivated by the interpretation of the polystyrenesulfonate salt spectral data, is that a tunneling or proton transfer occurs across asymmetric hydrogen bridges between the double energy min-

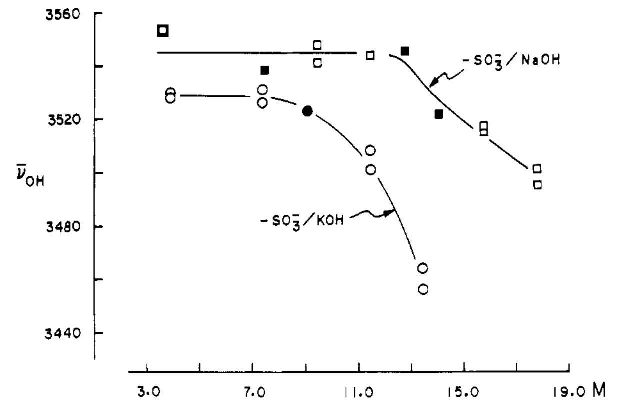


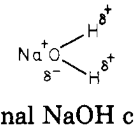
Figure 11. Variation of $\bar{\nu}_{OH}$ (main peak) with external solution molarity for sulfonate membranes in NaOH and KOH at room temperature. Unfilled points represent a single experiment; solid points represent two experimental determinations at the same concentration yielding the same ordinate.

ima that become nearly equal in depth with decreasing water content.

It is seen in Figure 11 that the frequency shift occurs at a lower molar concentration for the KOH membrane. This is reasonable owing to its lower state of hydration than the NaOH membrane at the same external molarity. At any given molarity, the frequency of the KOH film is lower than that of the NaOH film. Presently, the cause of this order is not understood since it would seem that the stronger contact electric field of the Na^+ ion should promote greater H_2O dissociation than that of the larger K^+ ions, for a given ion exchange functionality.

Last, the behavior of the absorbance of the H_2O scissor vibrational mode ($\sim$1630 cm^{-1}) was noted with respect to external caustic strength variance. The area under this peak, with proper correction for variable film thickness, is proportional to the degree of membrane hydration. It will simply be mentioned that this quantity steadily decreases with increasing caustic strength, the KOH curves lying below those for NaOH, as expected.

The behavior of $\Delta\bar{\nu}_2$, the width of this absorption peak at half height, begins to decrease with increasing caustic strength beyond a certain molarity before which it was constant. This quantity, being a measure of the distribution about the absorption maximum, can be interpreted in the following way. One must consider the water within the membrane as an ensemble of molecules wherein a heterogeneity of local environment exists. In other words, some water molecules will be totally surrounded by other water molecules, others will have an adjacent cation, or anion, and so forth. For example, the scissor mode of the H_2O molecule is sensitive to cationic interactions, causing a shift to lower frequencies for molecules in the ensemble having the following juxtaposition:



Therefore, as the external NaOH concentration increases and the internal concentration of water correspondingly decreases, the H_2O environmental distribution necessarily becomes more narrow as the population of "free" water diminishes and the ion-bound, i.e., hydrated, fraction dominates, thus causing $\Delta\bar{\nu}_2$ to decrease.

Consider the actual behavior of the NaOH membranes, seen in Figure 12. Here, with increasing external solution molarity, the onset of a gradual development of relatively more "structural" water can be imagined to occur after about 10 M. Before this value, the distribution of H_2O molecular environment is constant.

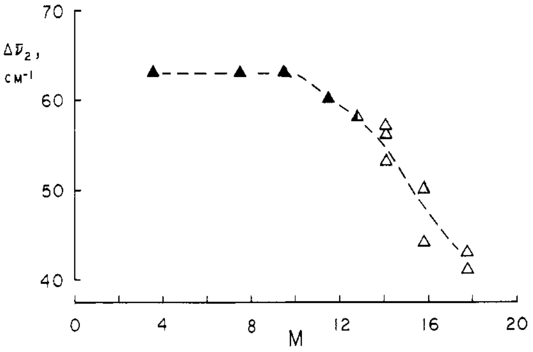
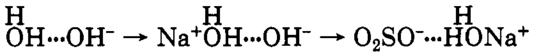


Figure 12. $\Delta\bar{\nu}_2$ vs. external solution molarity for sulfonate membranes in NaOH at room temperature. Unfilled, half-filled, and solid points represent one, two, and three experiments at the given concentration yielding the same ordinate, respectively.

Proceeding beyond this hydration structural onset, the considerable O-H bond deformation, seen in Figure 11, appears at about 13 M (37 wt %), indicating the (postulated) H^+ tunneling between SO_3^- groups and their waters of hydration. To bring the concept full circle, it will be remembered that the minimum in the continuous absorption vs. NaOH concentration profile occurs at 37 wt %.

Conclusions

An interesting absorption continuum has been identified in the infrared spectra of Nafion sulfonate ion exchange membranes that were equilibrated in aqueous alkali hydroxide solutions. The fundamental molecular event giving rise to this phenomenon is believed to be the tunneling of protons across hydrogen bonds within the hydration microstructure of the membrane. The fact that the degree of H^+ tunneling is sensitive to external caustic strength is evidenced by the distinctive structure of the continuous absorption vs. concentration profiles that, in turn, depend on cation type. Furthermore, it seems reasonable to consider a simple progression of significant hydrogen-bond configurations within the membrane structure that generate the continuous absorption response over the range of concentrations. They are, in order of increasing caustic strength:



$$\overset{H}{O}H\cdots OH^- \rightarrow Na^+\overset{H}{O}H\cdots OH^- \rightarrow O_2SO^-\cdots H\overset{H}{O}Na^+$$

The existence of a significant non-hydrogen bonded population of water molecules is very consistent with the hydrophilic/hydrophobic phase separation within these materials. If, in the future, a knowledge of the number density of water molecules at the surface and within the volume of a cluster will be known, the actual ratio of the surface area to volume might be accessible. In other words, cluster *sizes* may ultimately be determined by careful infrared spectroscopic analysis. This concept may be of importance insofar as the water molecules at the hydrophilic/hydrophobic interface are less capable of participating in the proton tunneling mechanism.

Although the above-described experimental conditions, as well as those molecular events discussed in the theoretical rationalization of the results, clearly fall into the realm of *equilibrium* states, there is, however, little difficulty required in transferring these concepts to the task of understanding *steady-state* processes involving, for example, Fickian diffusion, ionic conductivity, or, say a combination of both (e.g., as in Donnan dialysis applications, water electrolyzers, and chlor-alkali cells). The external driving forces will merely serve to *bias* the under-lying, originally isotropic, molecular processes in the direction of chemical or electrical potential gradients, at least for excursions from equilibrium that are not severe.

As mentioned earlier, membrane conductivity depends, first, upon the number density of free charge carriers within the polymer. A Donnan-like equilibrium model would seem to be adequate for this system provided that the effects of swelling/deswelling, on the ion exchange group number density, are appropriately accounted for over the range of external electrolyte strengths.

Second, as amply discussed in the Appendix, the main rate-limiting factor for the Grotthus-like mechanism of proton transfer in OH^- ion conductance is H_2O molecular rotation, and its overall contribution to the OH^- ion mobility must not be neglected. Since the experiment described herein was of an equilibrium, rather than kinetic, situation, however, consideration of this factor in a mechanistic rationale is not critical.

Last, due to the multitude of additional interactive parameters that must be superimposed on this simple system for simulation of the above-mentioned electrochemical processes, the direct extrapolation of these elementary molecular concepts for the purpose of designing membrane systems for optimal efficiency must be approached with caution.

To be sure, a more profound understanding, as exists today, of the dynamic hydrogen-bonded structure within Nafion and similar membrane systems and the strong dependence of this structure on intimate ionic and polymer interactive effects is needed to advance our understanding of the function of these unique separators in extremely concentrated aqueous hydroxide solutions.

These studies have, at the very least, demonstrated that the conventional macroscopic or material continuum approaches to modeling the equilibrium or transport properties of these membrane systems would be completely devoid of these subtle molecular events.

Appendix

The Nature of OH^- Ions in Aqueous Systems. There has been an accumulation of fundamental molecular knowledge, in the area of simple acidic and basic aqueous solutions, that must be reviewed before the question of how these electrolytes will interact with the inner structures of polymeric ion exchange membranes can be resolved.

For the present case, the discussion will begin with "isolated" OH^- ions. The infrared spectrum of solid anhydrous crystalline NaOH consists of a single sharp absorption at around 3637 cm^{-1} at room temperature.[15] There also exists a single sharp Raman line at around 3630 cm^{-1}.[16] A similar infrared spectrum is observed for LiOH, the band having shifted to 3678 cm^{-1}.[17] The spectroscopic information, coupled with X-ray structural results, indicates that there is no hydrogen bonding in these crystals and that little interaction exists between the OH stretching vibrations. In other words, this might be considered as a reference model for a reasonably unperturbed OH^- ion.

In passing to the monohydrate, $LiOH{\cdot}H_2O$, the very sharp absorption band of unhydrated LiOH is seen to remain single, decrease by 104 cm^{-1}, and broaden somewhat, the broadening being due to the formation of hydrogen bonds.[17]

In aqueous systems, OH^- ions are known to combine readily, with no structure-breaking effect, with H_2O molecules by strong hydrogen-bond formation.

Certainly, the O–H stretching region in the vibrational spectra of simple aqueous solutions has long been thought to consist of a superposition of at least two separate contributions, although their mechanistic origins have sometimes been debated. Clearly, the results presented for the system at hand are a fingerprint of even more structural ambiguity. It is tempting, nonetheless, to propose an interpretation of the minor peak on the high-wavenumber side of the main O–H stretching peak on the strength of current notions of the polymer microstructure that is thought to encapsulate the internal electrolyte in small diameter (ca. 20–40 Å) clusters.

The following discussion is a synthesis of mechanistic investigations that are pertinent to OH^- ion behavior in the aqueous environment. It is the view of the authors that the basic concepts can be maintained, though appropriately modified, in the formation of models for alkali hydroxide interactions in perfluorinated ion exchange membranes.

The rate constant, k', of the exchange reaction $H_2O + OH^- \rightarrow OH^- + H_2O$ has been measured by ^1H NMR as $k' \approx 4 \times 10^9$ L mol^{-1} s^{-1} (25 °C).[18] The average time a proton is bonded to a given oxygen atom, τ, is given by $\tau^{-1} = k'[OH^-]$. At, say, $[OH^-] = 1$ M, $\tau \approx 2.5 \times 10^{-10}$ s. It should be noted that τ is an average over all oxygens, many of which, at 1 M, belong to water dimers, between which a slower transfer takes place; therefore, the actual time scale of the exchange from H_2O to OH^- is shorter than 10^{-10} s. Furthermore, although the exact value of k' may need to be adjusted for higher concentrations, it is nonetheless clear that the lifetime of a hydrogen-bonded hydroxyl ion will be shorter yet, perhaps as low as 10^{-12} s.

In fact, 10^{-12} s is what is obtained following an argument similar to that as presented by Eigen and DeMaeyer concerning the lifetime of H_3O^+ ions.[19] Therein, the lifetime is roughly equated to the time of H^+ transit between oxygens, spaced δ angstroms apart, that are members of an H_2O molecule and adjacent OH^- ion. As a random walk process overall, the transit time becomes $\delta^2/6D$, where the diffusion coefficient, D, can be derived from the OH^- mobility, μ, by the familiar equation of Nernst: $\mu = (e/kT)D$. Of course, care must be taken to subtract from the total μ the mobility arising from the translation of the OH^- unit (i.e., hydrodynamic mobility) to obtain the pure anomalous (proton transfer) mobility. By this simple model, the lifetime is about 10^{-12} s.

On the other hand, studies of protonic mobility in ice indicated a transfer time, across the hydrogen bridges, of 10^{-14}–10^{-13} s, which is of the order of the time scale of the infrared motions themselves.[20] This rate, however, is strictly indicative of proton motion within fixed hydrogen bonds within a crystalline structure.

Although the proton jumps, in themselves, can quickly take place, the effective rate of migration and, therefore, lifetime of the OH^- ion is controlled by the rotational time scale of the interval between those molecular orientations favorable for hydrogen-bond formation. The average orientational time for this occurrence can be related to relaxation times from the dielectric dispersion studies of water.[21,22] In general, these studies indicate (a) a slowest relaxation at around 10^{-11} s having an activation energy of 4.5 kcal/mol (the strength of a single hydrogen bond) and (b) at least one more relaxation mode $<10^{-12}$ s involving the breaking of weaker "bonds". The order of magnitude of this dielectric relaxational time scale is quite consistent with the previously-mentioned time for H^+ transit between the oxygens of H_3O^+ and H_2O[19] and H_2O to OH^- migration, as well, also on the basis of the anomalous H^+ mobility, by the authors' calculation. Last, the ^1H NMR kinetic experiment of Meiboom,[18] along with the implications cited earlier in this Appendix, seem to be in harmony with the dielectric evidence. In short, it can be said that protons involved in hydrogen bonds between OH^- ions and adjacent H_2O molecules, although in rapid transference, do spend more time localized at the oxygens than in migration.

The important studies mentioned above, which have addressed questions relating to the detection, lifetime, and molecular interactions of OH^- ions within aqueous solutions, suggest that they are transitory and largely do not have an isolated, or discrete, chemical identity of their own, being intimately incorporated within the hydration microstructure through strong hydrogen-bond interactions. The situation within hydrated ion exchange membranes equilibrated in very concentrated electrolytes must be even more complex. Similar to Ackermann's comments in relation of H_3O^+, the problem is not to look for spectral features of OH^- ions per se but those of dynamic hydration structures of which this ion is essentially a subgroup; discrete identification bands are hardly to be detected.[9]

In the interpretation of spectra for the system at hand, the following observations are viewed as pertinent. First, the very *distinct* shoulder, or minor peak, on the high-wavenumber side of the main O–H stretching peak, for Nafion sulfonate membranes containing aqueous NaOH or KOH, is not seen in the spectra for the very concentrated pure solutions in this laboratory as well as by Ackermann.[9] On the other hand, Falk in infrared studies of hydrated Nafion sulfonate membranes in theNa$^+$ form does discuss a band at around 3668 cm^{-1} that was reasonably proposed as corresponding to the vibration of OH groups of H_2O molecules that are at the aqueous-cluster–fluorocarbon matrix interface.[7b] For thermodynamic reasons, few, if any, H_2O molecules, isolated (see Figure 5) or otherwise, would be expected to reside within the hydrophobic fluorocarbon phase. Because of the close coincidence of the high-wavenumber band presented in this work for Na$^+$ sulfonate Nafion membranes containing an excess of aqueous caustic with that cited by Falk for essentially the same membrane system, but not containing OH^- ions, plus the balance of the concepts enumerated above, it is currently believed that this spectral feature does indeed provide a fingerprint of water molecules at the peripheral "surface" of the clusters.

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Registry No. NaOH, 1310-73-2; KOH, 1310-58-3; Nafion, 39464-59-0; proton, 12408-02-5.

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