Thermodynamics of Nafion™–vapor interactions. I. Water vapor

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Abstract

Interaction between water vapor and Nafion™ perfluorosulfonate ionomer has been investigated via combined flow microcalorimetry and isothermal sorption over a wide range of water relative pressure. The molar enthalpy of sorption was determined for the untreated polymer, the residual polymer after extraction by aqueous propanol, and the extracted fraction. The extract appears to be low molecular weight Nafion™ but with an equivalent weight more than double that of the unextracted polymer. The equivalent weight of the residual polymer is slightly lower than that of the original Nafion™, apparently due to partial alkylation. Molar enthalpy for formation of the sulfonic acid monohydrate is about the same for the residual and unextracted polymers, but much greater for the extracted fraction. For untreated Nafion™, the magnitude and concentration dependence of the molar enthalpy indicates that sorption of water exhibits a clear progression from hydronium ion formation (≤ 1 H_2O/SO_3H) through growth of isolated hydrated clusters (≤ 6 H_2O/SO_3H) to a continuous internal water phase. A more complicated process occurs for the extract and residual polymer fractions in that an endotherm associated with elastic compression of the polymer matrix surrounding isolated water clusters is superimposed on the hydration exotherm over the concentration range of cluster growth. There is only a minor indication of this endotherm for unextracted Nafion™ because of more facile relaxation of the polymer structure due to plasticization by the low molecular weight fraction. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Nafion™, is a proton conductor which exhibits high water permeability, and is a diffusion barrier to nonpolar organic molecules. This branched polymer is composed of a fluorocarbon backbone substituted with a low molar concentration of a fluorodiether side group terminated with a sulfonic acid residue. Nafion™ is utilized in electrochemical processes, fuel cell membranes, coatings for ion selective electrodes, catalysis and pervaporative separations [1,2]. In our laboratory, it is being investigated as a lightweight, permselective barrier material for protective clothing [3,4]. The large difference in polarity between the pendant ion terminated fluoroether and the nonpolar fluorocarbon main chain in Nafion™ influences the nature and extent of phase segregation [5] and the transport properties. Of the many structural models proposed for this ionomer, most focus on the morphological role and spatial distribution of the sulfonate groups. For example, in the Gierke model, hydrated sulfonic acid groups clustered in spherical domains are treated as inverse micelles, essentially pools of water, interconnected by narrow channels which allow water and ion transport [6,7]. A more disordered model developed by Yeager involves some intermixing of ionic groups in the interphase between the fluoroether ligand and the fluorocarbon matrix [8], whereas, in the Eisenberg multiplet cluster model [9], regions of restricted segmental mobility are induced by interactions between sulfonate and cation moities.

Infrared measurements [10–14] demonstrate that the polar end group is preferentially solvated by water but there is little information regarding hydration energetics. A direct relationship between water uptake and sulfonate content was also found by calorimetry [15,16]. Further, despite extensive studies of the structure of Nafion™, little attention has been given to possible compositional heterogeneity and its effect on properties. In the present work, Nafion™ is fractionated by solubilization in aqueous propanol and the enthalpy of hydration is determined directly by flow microcalorimetry for the low molecular weight polymer extract and the insoluble residue, as well as for unextracted Nafion™. Molar enthalpies of hydration as a function of the concentration of dissolved water are obtained by combining

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integral enthalpies of water sorption at fixed vapor activities with sorption isotherms.

2. Experimental details

2.1. Materials

Nafion™ films (DuPont), of thickness 178 μm, were obtained from CG Processing, Inc. This polymer has an equivalent weight of 1100 g and a molecular weight of several hundred thousand g/mol [15–17]. Pretreatment with aqua regia to remove trace impurities has no detectable effect on sorption and calorimetric measurements. The film was converted to a powder form (N117) by cryogenic grinding for flow microcalorimetry studies.

Cryogenically ground samples were also prepared from the dried polymer that remained after immersing Nafion™ in boiling 1:1 aqueous propanol for 3 h followed by washing with water (N117RES), and from the extract recovered by evaporation from the propanol/water mixture (N117EX). The residual film had lost 23.5% of the preextraction weight, exhibited permanent set, and was much stiffer than the starting material. The recovered solid extract (23.8% of the starting material) was identified as Nafion™ by attenuated total reflectance Fourier Transform infrared spectroscopy [18]. N117EX is a soft, presumably amorphous solid that is inferred to be of low molecular weight by virtue of its physical properties. No volatile components were observed by gas chromatography using either mass spectrometric or electron capture detectors.

All polymer samples were dried to constant weight in flowing nitrogen at temperatures ≤ 368 K before calorimetric or sorption measurements. When applied to Nafion™ film, these drying conditions led to a reproducible and reversible maximum water sorption of 0.21 g/g when immersed in liquid at 30 °C. It is reported, however, that traces of absorbed water are retained by Nafion™ up to ca. 523 K [12].

2.2. Equivalent weight

Acid content was determined by titration of protons displaced from dried polymer during equilibration in aqueous solutions containing >100-fold molar excess of sodium ion [19]. Powder samples (0.05–0.15 g) were dried for 1 h at 110 °C then immersed for 5–16 h in 25 ml of 1 M aqueous sodium chloride and 5 ml ethanol, which was added to improve wetting of the finely divided specimen. The exchanged acid in the slurry was titrated rapidly with 0.02 mM sodium hydroxide (standardized against KHP) to a pH 10.5 endpoint using an Orion Ross combination pH electrode and Fisher Accumet 925 meter. The initial pH of the well-stirred aqueous slurries was 2.88 ± 0.13 for N117 and N117RES, and 5.30 ± 0.05 for N117EX. There was no change in the final pH, due to diffusion of additional protons

from the suspended polymer particles, within 15 m following the completion of the titration.

2.3. Flow microcalorimetry

Enthalpies of sorption were determined using a Microscal flow microcalorimeter which has been described previously [20–23]. The microcalorimeter was placed in a constant temperature chamber maintained at temperatures between 293 and 313 K, controlled to ± 0.1 K with a World Precision Instruments Air-Therm heater controller. A computer operated four-way valve was employed to introduce either a pure nitrogen gas stream or a nitrogen stream containing a known concentration of water vapor into the sample chamber [20,21]. The samples were dried in the nitrogen stream for at least 19 h to establish a thermal baseline before introducing water vapor. Exposure to the water vapor stream (8 ml/min) at a constant vapor pressure produced an exothermic response due to sorption of water in the polymer sample. At sorption equilibrium, the thermal response returned to the baseline. At this point, the sample was exposed again to dry nitrogen whereby desorption of water produced an endothermic peak. For each run, a thermal calibration pulse of known energy content was produced by resistive heating in the sample cell allowing the measured sorption/desorption responses to be expressed in energy units (J). An integral enthalpy of sorption or desorption (in J/g) was then calculated using the known sample mass. Varying the temperature of both the microcalorimeter chamber (sample temperature) and the water vapor saturator from 278 to 293 K allowed water vapor relative pressures (P/P_0) in the range 0.05–0.70 to be investigated. A reproducible enthalpy response was obtained for each P/P_0 value independent of the combination of sample temperature and saturator temperature, indicating that the enthalpy of sorption was relatively insensitive to temperature over the range investigated.

Fig. 1 shows a typical thermal response produced by exposing a N117 sample to water vapor at a relative pressure of 0.65. The smaller response is a calibration peak of
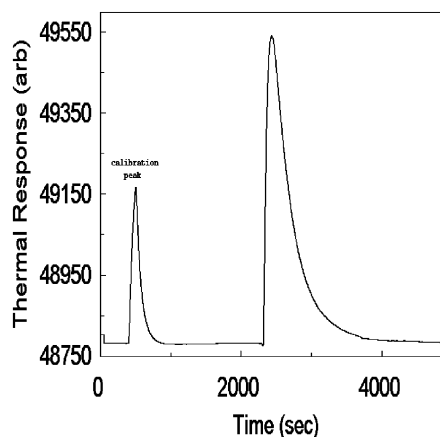

Fig. 1. Thermal response of N117 to water vapor relative pressure of 0.65.

300 mJ. Similar responses were obtained from N117RES and N117EX and were used to compile integral enthalpy of absorption data over the relative pressure range of interest.

2.4. Sorption isotherms

Sorption isotherms were determined with a Cahn 2000D microbalance, which was controlled by a computer interface and software developed by Hiden Analytical. The computer program automatically proceeds through a preset series of vapor concentrations and acquires data for the sample weight, temperature, and gas flow rates as a function of time. Water vapor at the required relative pressures was generated by active control of the mixing ratio between the saturated water vapor stream from the bubbler and the dilution gas stream at a total flow rate of 500 ml/min. The sample was suspended inside a thermostated, water jacketed chamber, maintained at 293 K and the entire assembly was housed in a cabinet for protection from drafts. The samples were dried in a 368 K oven for a preliminary weighing, and then suspended on the balance and dried overnight in a flowing stream of dry nitrogen before starting the run. The amount of water sorption at equilibrium (g/g) was obtained from the sorption isotherm at appropriate relative pressures, and used in conjunction with the experimentally determined integral enthalpy to calculate the molar enthalpy of sorption (kJ/mol).

3. Experimental results and discussion

Titration of acid content resulted in the following values of μeq/g with standard deviation: N117: 908 ± 15, N117RES: 892 ± 25, N117EX: 355 ± 13, which correspond to equivalent weights of 1101, 1121 and 2817, respectively. The much smaller reduction in acid content observed for N117RES could be due to partial conversion of sulfonic acids to propyl sulfonate ester groups during the extraction process, as observed for this sample by qualitative FTIR analysis [18]. A similar analysis was not performed on N117EX. Assuming conservation of composition, if N117 has an acid content of 0.908 mequiv./g and N117EX, which represents 23.7% of the original mass, has 0.355 mequiv./g, then we should find 1.08 mequiv./g for N117RES. Since the measured acid content for N117RES is 0.892 mequiv./g, there is an apparent loss of 17% of the acid sites present in N117.

Water vapor sorption isotherms are shown in Fig. 2 for N117, N117RES and N117EX. The isotherms for N117 and N117RES overlap at most activities but that for N117EX is significantly lower, diverging most clearly at $P/P_0 > 0.3$. The lower sorption level in N117EX is expected as a consequence of its reduced acid content. Integral enthalpies of sorption shown in Fig. 3 for the three polymer samples rise rapidly from the origin and follow individual trends. Enthalpy values for N117 show a relatively smooth increase
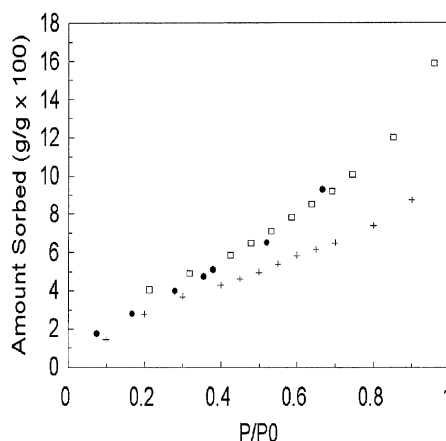
Fig. 2. Water vapor isotherms. (●) N117, (□) N117RES, and (+) N117EX.

with activity. Both N117RES and N117EX exhibit considerable structure in the initial enthalpy increase below an activity of 0.2. At higher activities, N117RES approaches the values for N117, whereas, the integral enthalpy for N117EX is about 30% lower as a result of the reduced sorption for this sample.

Molar enthalpies were calculated from integral enthalpies and a polynomial fit to the isotherm in order to minimize the influence of random experimental variations. These results are shown in Fig. 4, plotted against sorbed water concentration (g/g). Despite some scatter in the data, characteristic trends are well defined. At a water content of 0.016 g/g, which corresponds to one water molecule per sulfonate ($1W_e$) for an equivalent weight of 1100, N117 gives a molar enthalpy of 83 kJ/mol, but N117RES gives a value near 72 kJ/mol, a larger decrease than expected for its slightly higher equivalent weight. For N117EX, the molar enthalpy at a sorbed concentration of 0.0076 g/g ($1W_e = 0.0064$ g/g) is 110 kJ/mol. We have no explanation for this very high enthalpy although it could be due to impurities or hydration of a few high-energy sites. The molar enthalpy obtained for monohydration of Nafion™ is a result of ionization of the sulfonic acid group to SO_3^- and
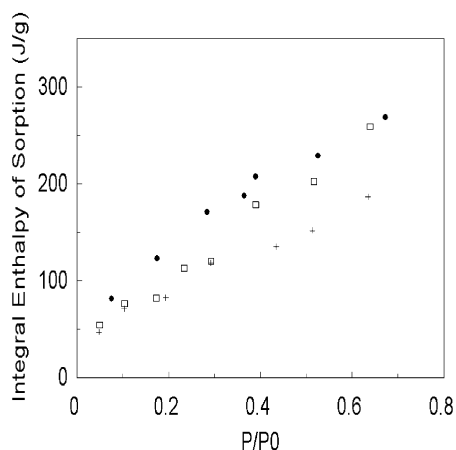
Fig. 3. Integral enthalpy of sorption. (●) N117, (□) N117RES, and (+) N117EX.
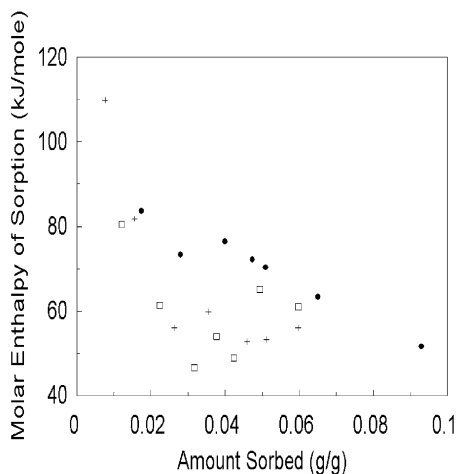
Fig. 4. Molar enthalpy of sorption. (•) N117, (□) N117RES, and (+) N117EX.

H_3O^+ [12,13]. For comparison, the enthalpy of solution of trifluoromethanesulfonic acid in water at 298 K is 79 kJ/mol [24]. The calculated enthalpy for vapor phase monohydration of sulfuric acid is <54 kJ/mol [25,26] which demonstrates the influence of perfluorination on the ionization equilibrium.

There is a nearly linear decrease in the molar enthalpy of water sorption by N117 to a value approaching the enthalpy of vaporization of water (44.7 kJ/mol) at $>6W_e$. Thus sorption at high activity is an equilibrium process in which water molecules transfer from the vapor phase to an unperturbed liquid water phase in the polymer matrix. This behavior is consistent with the three stage hydration process inferred from an infrared study of water sorption in Nafion™ [12]: sulfonic acid hydrolytic dissociation ($\leq 1W_e$), formation of a water cluster around the hydronium ion ($\leq 6W_e$), and then coalescence of clusters to give a continuous water phase ($>6W_e$). The monotonic decrease in molar enthalpy associated with cluster formation indicates that hydration occurs as a statistical process involving ionic centers of equivalent accessibility. Relaxation to accommodate swelling due to water uptake is facilitated in N117 by the plasticizing contribution of the low molecular weight fraction.

In contrast to N117 which shows a small, single concentration minimum near $2W_e$, molar enthalpy for N117RES exhibits a rapid descent above $1W_e$ to a broad minimum which is reasonably well defined in spite of the data scatter around 0.04 g/g, and approaches the values for N117 above $4W_e$. This minimum is attributed to the superposition of an endothermic process on the exothermic hydration, and is associated with loss of the solubilized low molecular weight polymer. Absence of the plasticizing fraction in N117RES results in a relatively high molecular weight material with greater void content and less chain mobility than the original polymer. This provides an increased opportunity for formation of large isolated water clusters at high activity. Evidence for a change in

morphology for N117RES compared to N117 is indicated by a two-fold increase in the immersion uptake of dimethylmethylphosphonate, a nonhydrogen bonding, dipolar aprotic solvent which interacts with less polar regions of the polymer [4]. There is also more than a 20% relative increase in the immersion solubility of water, although there is little difference in sorption at low water activity. The dominant effect of the loss of plasticizing components at low to intermediate activities is an increase in internal stress due to a decrease in chain mobility which results in less relaxation to accommodate swelling. Energetics of this process are described by the Dreyfus model [27], in which growth of the hydration shell around a fixed cation is driven by electrostatic energy and opposed by the elastic compression of the surrounding polymer. Resistance of the matrix to deformation would be observed as an endothermic contribution. Freger [28] presented a refinement of this model in which the expanding water aggregates cause an affine deformation of the surrounding matrix. The modified model predicts the observed linear dependence of elastic pressure on swelling as well as a reduction in elastic pressure upon merging of separated solvent-rich regions. Thus the endotherm increases with elastic pressure until the occurrence of significant stress reduction due to the coalescence of isolated water clusters.

The molar enthalpy for N117EX in Fig. 4 exhibits a minimum between 1 and $6W_e$ which is similar to that for N117RES. However, the low molecular weight and putty-like nature of N117EX indicate that the structural organization is very different from N117 and N117RES, perhaps consisting of a random mixed phase, rather than being phase segregated. As a result, ion-hydrating water clusters in N117EX would be distributed at random throughout the amorphous polymer rather than localized at phase boundaries. Due to the isolated nature of individual water clusters, resistance of the surrounding polymer to swelling represents an elastic compression and endothermal response. This endothermic contribution, which is similar to N117RES but arises from a different morphology, decreases with increasing water uptake when stress is relieved via merging of separated clusters.

4. Conclusions

This work implies that commercial Nafion™ has a distribution of polymer chain lengths, whereby, almost 25 wt% of presumably low molecular weight polymer is readily extracted by boiling in aqueous propanol for several hours. Nafion™ and its post-extraction products differ considerably in equivalent weight as well as physical properties, water sorption isotherms and integral enthalpies. The molar enthalpy of hydration for the unextracted polymer decreases nearly linearly with increasing water concentration after initial ionization of the sulfonic acid. At high water content, the molar enthalpy is similar to the

enthalpy of vaporization of water indicating that an unperturbed liquid–vapor equilibrium is established. From the magnitude and concentration dependence of the molar enthalpy, it is concluded that water sorption proceeds from hydronium solvation ($W_e \le 1$), through hydronium cluster formation ($W_e \le 6$), to a continuous water phase up to the maximum swelling in liquid ($W_e = 13$).

The molar enthalpy for the partially esterified residue (N117RES) is slightly less at $1W_e$ than that for the original polymer (N117). Conversely, the molar enthalpy at $1W_e$ is substantially greater for the extract fraction (N117EX) in spite of its lower total acid content. After removal of a low molecular weight fraction from Nafion™ by extraction with aqueous propanol, the residual and extracted polymers are subject to endothermic elastic deformation of the polymer matrix over the entire concentration range of water cluster formation. The residual higher molecular weight polymer is more prone to formation of liquid inclusions between microphase regions due to lower chain mobility during swelling than is the untreated Nafion™. Molar enthalpies for N117EX and N117RES drop rapidly to a broad minimum with increasing concentration. For N117RES the decrease in enthalpy is associated with the absence of the plasticizing fraction; which leads to enhancement of the elastic compression endotherm due to reduced relaxation, and to condensation in voids within the relatively low mobility matrix. A qualitatively similar minimum is observed for N117EX, although this material consists of short polymer chains, probably randomly oriented within a single phase. Growth of water clusters induces elastic compression in the surrounding low polarity matrix. However, preformed voids, which facilitate water condensation at high activity, are not present.

References

[1] Robertson MAF, Yeager HL. In: Tant MT, Mauritz KA, Wilkes GL, editors. Ionomers, synthesis, structure, properties and applications. London: Blackie; 1997. Chapter 7.

[2] Heitner-Wirguin C. J Membr Sci 1996;120:1–33.

[3] Rivin D, Kendrick CE, Gibson PW, Schneider NS. Polymer 2001;42: 623–35.

[4] Rivin D, Schneider NS, Kendrick CE, Gibson PW. Proceedings of the 22nd Army Science Conference; 2000.

[5] Mauritz KA. In: Tant MT, Mauritz KA, Wilkes GL, editors. Ionomers, synthesis, structure, properties and applications. London: Blackie; 1997. Chapter 3.

[6] Hsu WY, Gierke TD. Macromolecules 1982;15:101–5.

[7] Gierke TD, Munn GE, Wilson FC. J Polym Sci, Polym Phys Ed 1981; 19:1687–704.

[8] Yeager HL. In: Eisenberg A, Yeager HL, editors. Perfluorinated ionomer membranes. ACS Symposium Series 180, Washington, DC: American Chemical Society; 1982. Chapter 4.

[9] Eisenberg A, Hird B, Moore RB. Macromolecules 1990;23: 4098–107.

[10] Lowry SR, Mauritz KA. J Am Chem Soc 1980;102:4665–7.

[11] Falk M. Can J Chem 1980;58:1495–501.

[12] Laporta M, Pegoraro M, Zanderighi L. Phys Chem, Chem Phys 1999; 1:4619–28.

[13] Ludvigsson M, Lindgren J, Tegenfeldt J. Electrochim Acta 2000;45: 2267–71.

[14] Blanchard RM, Nuzzo RG. J Polym Sci, Part B: Polym Phys 2000;38: 1512–20.

[15] Escoubes M, Pineri M. In: Eisenberg A, Yeager HL, editors. Perfluorinated ionomer membranes. ACS Symposium Series 180, Washington, DC: American Chemical Society; 1982. Chapter 2.

[16] Escoubes M, Pineri M, Robens E. Thermochim Acta 1984;82: 149–60.

[17] DuPont Fluoroproducts Technical Data.

[18] Analysis by Dr J. Carlson, Natick Soldier Center.

[19] Chen TY, Leddy J. Langmuir 2000;16:2866–71.

[20] Reucroft PJ, Rivin D. Carbon 1997;35:1067–71.

[21] Reucroft PJ, Rivin D. Thermochim Acta 1999;328:19–24.

[22] Groszek AJ. Proc R Soc 1970;A314:473–8.

[23] Groszek AJ. Carbon 1989;27:33–8.

[24] Benoit RL, Figeys D. Can J Chem 1991;69:1985–8.

[25] Noppel M. J Geophys Res 2000;105D:19779–85.

[26] Mirabel P, Ponche JL. Chem Phys Lett 1991;183:21–4.

[27] Dreyfus B. J Polym Sci, Polym Phys 1983;21:2337–47.

[28] Freger V. Polymer 2002;43:71–6.