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Adsorption of a Cationic Polyacrylamide onto the Surface of a Nafion Ionomer Membrane

Young-Hoon Kim, Daniel Oblas, and Anastasios P. Angelopoulos*

Department of Chemistry and Center for Advanced Materials, University of Massachusetts Lowell, Lowell, Massachusetts 01854

Stephen A. Fossey

U.S. Army Materials Research Center, Natick, Massachusetts 01760

Luis J. Matienzo

IBM Corporation, Endicott, New York 13760

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ABSTRACT: Time-dependent adsorption of a high-molecular-weight cationic polyacrylamide (acrylamide/β-methacryloxyethyltrimethylammonium methyl sulfate copolymer) from sulfuric acid solution onto a perfluorosulfonate ionomer (Nafion) membrane was characterized using X-ray photoelectron spectroscopy (XPS), ultraviolet/visible spectroscopy (UV/vis), and dynamic contact angle measurements in water. Flourine and nitrogen atomic surface concentrations determined from XPS were well correlated to the adsorbed polymer surface coverage from water contact angle analysis via the Cassie relationship and the adsorbed polymer concentration from UV/vis, respectively. Cationic polyacrylamide surface coverage remained constant at about 60% for all immersion times investigated. On the other hand, the adsorbed polymer concentration increased with immersion time, approaching a plateau after about 9 min. Such behavior was attributed to the transition from an expanded, two-dimensional, adsorbed polymer chain configuration at early times to a three-dimensional configuration composed of either coils or multilayers as immersion time increased.

I. Introduction

Self-assembly of polymers from solution onto surfaces is of rapidly growing interest for photonic and electronic applications.[1−8] Polymer self-assembly combines the flexibility of organic synthesis with enhanced stability over poled or Langmuir−Blodgett films to produce a rich variety of materials with unique electronic and optical properties. Ionic interaction is routinely employed to build stable alternating layers of opto- and electro-active polyanions and polycations onto various substrates.[4−7] Multilayer macromolecular assembly through nonionic interaction between two polymers containing functional groups with complementary bonding character (i.e., hydrogen bonding, dipole−dipole, and dipole−ion interactions) has also recently been demonstrated with polyaniline.[8]

In the present study, the adsorption behavior of a high-molecular-weight acrylamide/β-methacryloxyethyltrimethylammonium copolymer from sulfuric acid solution onto a Nafion ionomer membrane was investigated as a function of immersion time. The cationic polyacrylamide is typically applied onto dielectric materials to enhance the deposition of colloidal metal catalyst particles for the nonelectrolytic, liquid-phase metallization of microelectronic components.[1−3] Insufficient cationic polyacrylamide coverage yields voids in the metallization layer subsequently grown on the substrate. On the other hand, excess polyacrylamide yields adhesive failure of photoresist from the substrate during metallization, causing electrical shorting between circuit lines. Cationic polyacrylamide coverage on various polymeric substrates was previously found to depend on both the pH of the polyacrylamide solution and subtle changes in the acid/base character of the substrate surface.[1−3] Surface coverage was found to be independent of immersion time. However, changes to the configuration of the adsorbed cationic polyacrylamide chains as a function of immersion time were not investigated.

In the present study, Nafion was chosen as the substrate with which to investigate the adsorbed polymer chain configuration of the cationic polyacrylamide. Nafion is a perfluorosulfonate ionomer manufactured by DuPont and is typically employed as a semipermeable coating to enhance the chemical specificity of electrode surfaces.[9] Fluorine is unique to the substrate and screening of fluorine photoelectrons by adsorbed polymer is a measure of the adsorbed polymer surface coverage. Since Nafion does not contain nitrogen, the XPS nitrogen N(1s) signal is an indication of the adsorbed cationic polyacrylamide concentration. Water contact angles and UV/vis spectra provided corroborating evidence for adsorbed polymer surface coverage and concentration, respectively. Comparisons between adsorbed polymer surface coverage and concentration as a function of immersion time in aqueous cationic polyacrylamide solution yielded information as to the adsorbed cationic polyacrylamide chain configuration on Nafion.

The use of Nafion in conjunction with previous work on nonionic substrates such as poly(tetrafluoroethylene) (PTFE)[2] also has permitted a comparison of the effect of electrostatic vs nonelectrostatic interactions on cationic polyacrylamide adsorption behavior.

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* To whom correspondence should be addressed.

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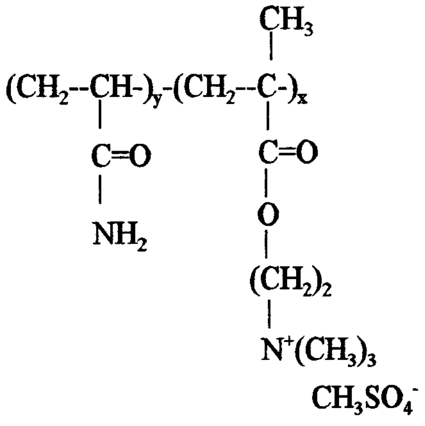

Figure 1. Schematic of cationic polyacrylamide.

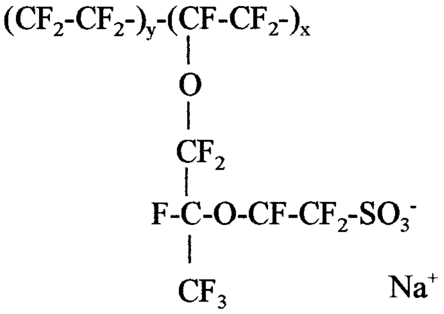

Figure 2. Schematic of Nafion.

II. Experimental Section

II.A. Materials. The acrylamide/β-methacryloxyethyltrimethylammonium copolymer employed as the adsorbate in the present study has been previously characterized using XPS in powder and cast film form as well as potentiometric titration and infrared analysis in aqueous solution.[1] A schematic representation of the polymer structure is given in Figure 1. The atomic concentration of sulfur in the polymer has been previously obtained from the S(2p) XPS signal to be about 1.6% and used to determine that the fraction ($x/(y + x)$) of quaternary amine repeating units along the polymer backbone which is about 0.10. The source of the sulfur in this polymer is the methyl sulfate counterion.

Cationic polyacrylamide adsorption was carried out from aqueous solution with the pH adjusted to a value of 1 with H_2SO_4 (Aldrich) in deionized (DI) water. The polymer concentration in the adsorbate solution was 0.6 g/L. Potentiometric titration of the cationic polyacrylamide in solution combined with infrared analysis (FTIR) has shown that 10% of the repeating units along the polymer backbone consist of hydrolyzed amide groups which ionize at a pH value between 10 and 11.[1] Under acidic conditions, the cationic polyacrylamide thus contains both strong (ionic) and weak (polar) acidic pendant groups of roughly equal proportion, with the remainder of the backbone containing basic amide pendant groups.

The Nafion membrane employed as the substrate in the present study was used, as-received, from the DuPont Corp. The bulk equivalent weight of Nafion expressed in terms of grams of polymer per moles of sulfonate repeating units is given by the manufacturer as 1100 Da. The structure of Nafion polymer is shown in Figure 2. Calculations based on this structure show that the average fraction of sulfonate repeating units along the polymer backbone ($x/(x + y)$) is about 0.13 in the bulk for an equivalent weight of 1100 Da. The Nafion surface was characterized via its wetting behavior in various probe liquids as well as XPS. Molecular dynamics simulations using a CVFF force field as well as semiempirical quantum mechanical calculations using an AM1 basis set were also performed to better visualize the geometry of the sulfonate side chains relative to the Nafion backbone.

Nafion samples were immersed into the cationic polyacrylamide solution for the desired time interval, rinsed in DI water for 2 min, and allowed to air-dry overnight prior to analysis. Water wetting, UV/vis, and XPS data were all obtained ex situ from samples prepared at the same time (i.e., samples used for each analytical technique were cut from the same original piece).

II.B. Methods. Wetting force measurements were obtained with a Sigma 70 wetting balance from KSV Instruments. The retractable stage was moved at a velocity of 0.2 mm/min for all experiments reported here. Work of adhesion for each probe liquid was extracted from a force balance on the sample as previously described.[1]

Semiempirical techniques developed by Fowkes, Good, and van Oss[10] permit representation of solid surface tension, γ, by basic, γ^-, acidic, γ^+, and dispersion, $\gamma^{\,d}$, bonding components according to

$$\gamma = \gamma^{d} + \gamma^{AB} \tag{1}$$

where AB indicates a generalized acid–base interaction such that

$$\gamma^{AB} = 2\sqrt{\gamma^{+}\gamma^{-}} \tag{2}$$

Surface bonding strength was characterized from the work of adhesion of three probe liquids whose fundamental surface tension components are known. The three probe liquids employed in this study were: DI water, ethylene glycol (Aldrich), and diiodomethane (Aldrich). The fundamental surface tension components for these liquids may be found in the literature.[10] DI water was obtained by passing tap water through a series of filters (one Absorbate II and two Research II filters from U.S. Filter Corp.). Water purity was confirmed through contact angle measurement (DI water contact angle exceeded 71.8 dyn/cm in every case reported here vs an upper limit of 72.8 dyn/cm from the literature[10]). The pH of the water used in contact angle measurements was obtained potentiometrically using an Orion model 920A meter equipped with a Ross[7] combination electrode and was found to fall between 6.0 and 6.5 in all cases reported here. Dissolved carbon dioxide is the only likely source of water acidity. The use of buffers was avoided to eliminate possible interaction with the Nafion surface. Negligible variation in Nafion surface wettability (with and without adsorbate) was observed within the range of measured DI water pH values.

Scanning electron microscopy (SEM) using an AMRAY instrument was employed to verify that the Nafion membrane surfaces were sufficiently smooth to eliminate the effects of texture on wetting in the above analysis. Samples were sputter-coated with 300 Å of platinum and imaged with 10 or 15 keV accelerating voltage.

Cationic polyacrylamide surface coverage was determined by monitoring changes to the photoelectron yield from fluorine atoms via XPS. XPS was performed with either a PHI 5500 multiprobe spectrometer using monochromatized Al Kα radiation at IBM Corporation facilities in Endicott, NY, or an ESCALAB MK II spectrometer using Mg Kα radiation at University of Massachusetts facilities in Lowell, MA. High-resolution spectra in the case of the PHI instrument were collected in the region of interest with a pass energy of 11.4 eV. A pass energy of 20 eV was employed at the analyzer for the later instrument. A minimum of five scans were employed for the high-resolution spectra with a scan range of 20 eV. Both instruments are equipped with a constant energy hemispherical analyzer. The Nafion film was mounted as-received or after surface adsorption on a metal pedestal using adhesive backed copper tape, compatible with UHV applications. The sample was large enough so that only the film contributed to the XPS spectrum. There was no indication of damage to the Nafion film or changing signal intensity as a result of X-ray exposure. The sample surface was aligned perpendicular to the axis of the collecting lens. The atomic concentrations of the respective elements utilized the high-resolution peak areas for the respective elements in conjunction with the Scofield sensitivity factors. No other adjustments to the data were carried out. Analyses of pure cationic polyacrylamide and the raw Nafion substrate were performed utilizing both instruments and comparable results for x and y in Figures 1 and 2 were obtained. Binding energy values were corrected to the C(1s) peak, with the adventitious C(1s) taken as 285 eV.

Since fluorine is not present in the cationic polyacrylamide, complete screening of fluorine photoelectrons by adsorbed polymer yields the following expression for the fractional adsorbate surface coverage, f_a^{XPS}:

$$f_a^{XPS} = 1 - \frac{A_{F(1s)}}{A_{F(1s)}^{o}} \tag{3}$$

where $A_{F(1s)}^{o}$ and $A_{F(1s)}$ are the atomic percentages of flourine obtained from the F(1s) photoelectron signal (at ~690 eV) before and after immersion into the polyacrylamide solution, respectively.

The use of eq 3 to determine adsorbed polymer surface area coverage assumes complete attenuation of the fluorine signal by a thick polymer coating only on those areas where adsorption occurs. Incomplete screening of photoelectrons from fluorine atoms covered by adsorbate layers can yield surface coverage values obtained from eq 3 that are too low. Corroborating data for cationic polyacrylamide surface coverage was therefore obtained using water contact angle measurements. As will be shown in a subsequent section, the Nafion substrate is hydrophobic, with a contact angle in water greater than 90°. On the other hand, the cationic polyacrylamide is highly water-soluble and yields zero water contact angle[2] (work of adhesion = 145.6 dyn/cm) on a completely coated surface. Application of the Cassie relationship[2] to the observed water contact angles between these two extremes provided a measure of the Nafion surface fraction covered by adsorbate, f_a^{W}:

$$f_a^{W} = \frac{W - W_s}{W_a - W_s} \tag{4}$$

where W is the observed work of adhesion, W_a is the work of adhesion of the solid polymer adsorbate (145.6 dyn/cm), and W_s is the work of adhesion of the raw substrate.

The Nafion substrate does not contain nitrogen. The intensity of the nitrogen photoelectron signal is thus an indication of the concentration of adsorbed polymer. Adsorbate concentration on Nafion may be expressed relative to that on some reference substrate according to the parameter χ_a^{XPS} defined below:

$$\chi_a^{XPS} = \frac{A_{N(1s)}}{A_{N(1s)}^{o}} \tag{5}$$

where $A_{N(1s)}^{o}$ and $A_{N(1s)}$ are the atomic percentages of nitrogen obtained from the N(1s) photoelectron signal (at ~400 eV) on the reference substrate and on Nafion after immersion into the polyacrylamide solution, respectively. An atomic nitrogen concentration of 10.4% has been previously obtained for reference substrates composed of pure cationic polyacrylamide (in either powder or cast film form).[2]

The parameter χ_a^{XPS} in eq 5 will be comparable to the fractional surface coverage (parameters f_a^{XPS} or f_a^{W}) when the packing density of the adsorbate layer on Nafion is comparable to that on the reference substrate (i.e., pure cationic polyacrylamide powder or cast film). A deposited polymer structure on Nafion more porous than that on the reference substrate will yield a fractional concentration, χ_a^{XPS}, greater than the fractional surface coverage.

Corroborating data for the change in the concentration of adsorbed cationic polyacrylamide with immersion time was obtained utilizing a GBC Scientific UV/vis 916 spectrophotometer. The UV spectrum of concentrated (~30 g/L) cationic polyacrylamide solution at pH 1 exhibited a sharp absorption peak at 207 nm. The Nafion membrane exhibited substantial absorption intensity only below 200 nm. Assuming that the Beer–Lambert law applies over the entire concentration range of interest in the present study, the adsorbate concentration at any time may be expressed relative to that at equilibrium according to χ_a^{UV}:

$$\chi_a^{UV} = \frac{A}{A^{o}} \tag{6}$$

where A is the absorption intensity of the Nafion membrane after a given immersion time in adsorbate solution and A^{o} is the absorption intensity of the Nafion membrane when equilibrium is attained, both measured at 207 nm. UV/vis absorbance measurements are reported with raw Nafion employed as the background in every case.

III. Results

III.A. Nafion. The atomic concentration of sulfur on the surface of Nafion was determined from the S(2p) XPS signal to be about 1.3%. The fraction of sulfonate repeating units on the film surface was therefore calculated to be 0.11, indicating little difference in sulfonate concentration between the bulk and the surface. To better visualize the geometry of the sulfonate side chains relative to the tetrafluoroethylene Nafion backbone, a molecular dynamics simulation was performed using a CVFF force field. A schematic representation of the optimized geometry of a Nafion chain after 1000 steps is shown in Figure 3. If sulfonate groups are assumed to point away from the Nafion surface, then calculations based on sulfonate geometry generated from an AM1 semiempirical calculation indicate that the adsorption cross section for each sulfonate group is roughly 8.75 Å^2. This area is comparable to an adsorption cross section of roughly 7.23 Å^2 per CF$_2$ group based on a phase II triclinic crystal for PTFE (13 CF$_2$ at 16.9 Å × 5.56 Å).[11]

The work of adhesion of Nafion in the various liquids is shown in Table 1 along with the acid, basic, and dispersion fundamental solid surface tension components. The work of adhesion values in this table represent an average of at least three measurements with a standard deviation no greater than 5% from the mean. Only advancing surface tension component data are reported in Table 1 since Nafion was completely wetted by all three probe liquids in the receding mode. Hysteresis between advancing and receding contact angles was highly reproducible when cycling between the advancing and receding wetting modes. In addition, the SEM image shown in Figure 4 reveals that the Nafion surface was smooth at a resolution limit of 50 nm. The surface roughness of Nafion determined via SEM is qualitatively similar to that of Teflon surfaces previously investigated and found to have relatively negligible wetting hysteresis.[2] These observations suggest that chemical heterogeneity is the source of the wetting hysteresis.

Substantial surface basicity was observed in the advancing wetting mode ($\gamma^- = 6$ dyn/cm) which approached that of poly(methyl methacrylate) (PMMA, $\gamma^- \sim 9$ dyn/cm (ref 10)). Such wetting behavior corroborates the fact that sulfonate groups are present at the surface of the film. The dispersion surface tension component had a value of 12.7 dyn/cm and approached the value previously found for poly(tetrafluoroethylene) (PTFE).[2,10] As expected, on the basis of the structure shown in Figure 2, the acidic surface tension component for Nafion was comparatively negligible.

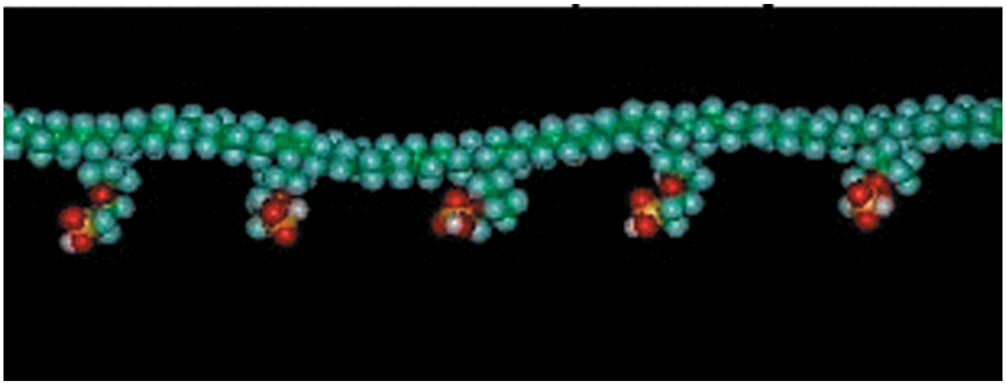

Figure 3. Optimized Nafion geometry using AM1 basis set.

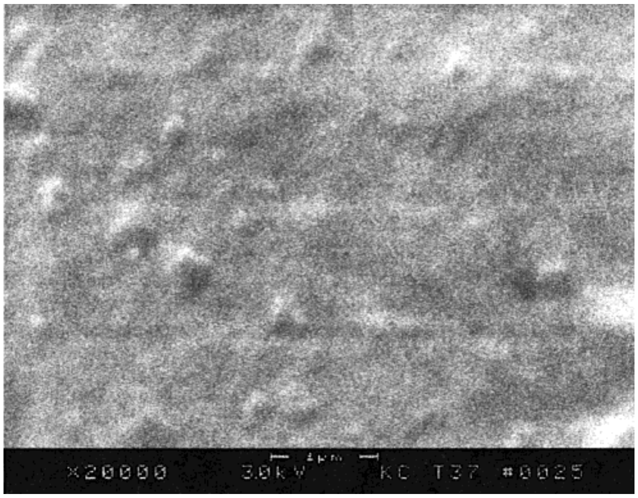

Figure 4. SEM of Nafion surface at 20 000 magnification.

Table 1. Advancing Wetting Data for Nafion with an Equivalent Weight of 1100 Da

work of adhesion (dyn/cm)			fundamental surface tension components (dyn/cm)		
water	ethylene glycol	diiodomethane	γ^d	γ^-	γ^+
60.6	48.6	50.8	12.7	6.0	0.1

III.B. Adsorbed Polymer. The effect of immersion time in cationic polyacrylamide solution on water wetting of the Nafion substrate in the advancing mode is shown in Table 2. Also shown in this table is the corresponding adsorbate surface coverage, f_a^W, obtained using the Cassie relationship (eq 4). The means and standard deviations (denoted by the "±" symbol) in this table were obtained from at least two samples prepared on different days using freshly mixed adsorbate solutions. The fractional adsorbate surface coverage showed a substantial increase from 0 to an average value of 0.58 with an immersion time of 3 min. Surface coverage remained insensitive to subsequent increases in immersion time, within experimental error, out to 15 min. As observed for the raw Nafion substrate in the preceding section, surfaces subsequent to immersion in polyacrylamide solution were completely wetted in the receding mode.

The effect of immersion time on the atomic flourine content (percent of total atomic concentration) is shown in Table 2 as well as the corresponding adsorbate fractional coverage, f_a^{XPS}, obtained utilizing eq 3. Measurements were performed on samples prepared at the same time as those used to obtain wetting measurements. Adsorbate surface coverage obtained using XPS was well correlated to that obtained from water wetting and the Cassie relationship. Fractional surface coverage obtained using both techniques is shown as a function of immersion time in Figure 5 (where the value of zero at an immersion time of zero has been excluded for the sake of clarity). Error bars on either side of each mean in this figure represent one standard deviation. Second-order nonlinear regression was used to fit lines to the experimental data points.

Equation 3 for the fractional surface coverage assumed that flourine photoelectrons are completely screened by the adsorbate. This assumption was consistent both with the previously presented water wetting data as well as the fact that the flourine-to-nitrogen ratio from XPS declined as the photoelectron detection axis was rotated 60° with respect to the surface normal for all immersion times investigated, indicating that the adsorbate sits astride the substrate.

The effect of immersion time on the atomic nitrogen content (percent of total atomic concentration) as well as the corresponding fractional concentration, χ_a^{XPS} (obtained utilizing eq 5), is shown in Table 3 for samples prepared simultaneously to those used to generate the data in Table 2. The fractional concentration after 3 min immersion was found to have a value of 0.57. This value is comparable to the adsorbate surface coverage previously determined from both wetting and F(1s) XPS data. Unlike the surface coverage, however, the adsorbate concentration increased with increasing immersion time, gradually approaching an equilibrium value comparable to that detected on the surface of pure cationic polyacrylamide powder or cast film as the immersion time exceeded 9 min.

Table 3 also shows the average and standard deviation of the UV absorption at 207 nm (relative to the bare Nafion substrate) as a function of immersion time as well as the corresponding fractional adsorbate concentration, χ_a^{UV} (obtained from eq 6), for at least two measurements. A value of 0.106 was employed for A^o in eq 6. This value corresponds to an immersion time of 15 min, where adsorption appears to have reached equilibrium. The change in adsorbate concentration obtained from both XPS and UV/vis is shown in Figure 5. Good agreement was observed between the two analytical techniques, within experimental error.

IV. Discussion

The presence of sulfonate groups on the Nafion surface was confirmed both by XPS measurements in the S(2p) photoelectron binding energy region and by Nafion wetting behavior relative to PTFE. As shown in

Table 2. Adsorbate Fractional Surface Area Coverage as a Function of Immersion Time from Water Wetting and XPS Data

immersion time (min)	advancing water work of adhesion (dyn/cm)	adsorbate fractional surface area coverage from water wetting (f_a^W in text)	atomic % F from XPS	adsorbate fractional surface area coverage from XPS (f_a^{XPS} in text)
0	60.6 ± 1.8	0.00	49.3 ± 2.5	0.00
3	109.5 ± 3.8	0.58 ± 0.05	21.1 ± 2.6	0.57 ± 0.07
6	111.9 ± 6.4	0.60 ± 0.08	19.7 ± 1.6	0.60 ± 0.06
9	110.5 ± 3.5	0.59 ± 0.05	18.9 ± 0.6	0.62 ± 0.04
12	109.5 ± 6.4	0.58 ± 0.08	18.2 ± 1.9	0.63 ± 0.07
15	105.9 ± 4.0	0.53 ± 0.05	17.6 ± 1.1	0.64 ± 0.05

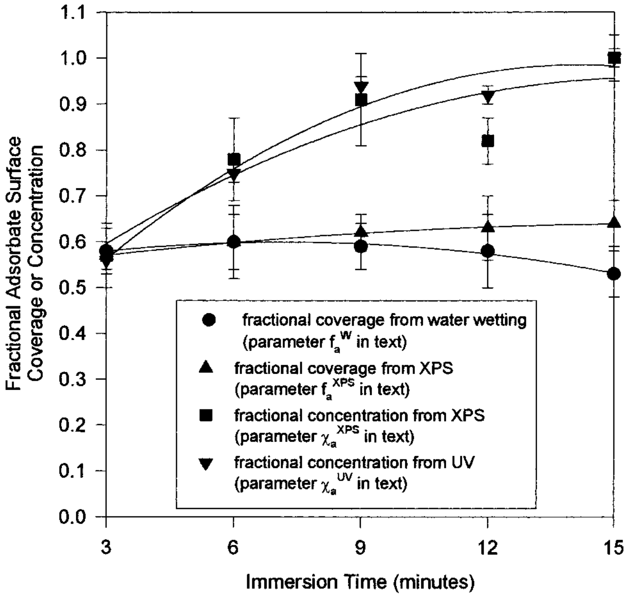

Figure 5. Experimental adsorbate fractional surface coverage and concentration obtained using water contact angle measurement, XPS, and UV/vis, as indicated.

Table 1, Nafion exhibited substantial surface basicity. Attractive electrostatic interactions are thus expected between the cationic quaternary amine groups on the adsorbate and anionic sulfonate groups on the Nafion surface. Weaker attractive dipole-ion interactions may also occur between the weakly acidic hydrolyzed amide groups on the polyelectrolyte and the anionic sulfonate groups on Nafion.[7]

As shown in Table 2 and Figure 5, adsorbate surface coverage from both XPS and wetting analyses reached an average value of 0.58 after 3 min immersion time and remained constant, within experimental error, at longer immersion times. Such behavior is in stark contrast to the negligible cationic polyacrylamide adsorption previously observed in the case of PTFE regardless of immersion time.[2] Negatively charged groups on the Nafion surface appear to substantially promote cationic polyacrylamide adsorption relative to PTFE.

From Figure 5, the average fractional surface coverage (0.58) corresponds to the adsorbate surface concentration (0.57) obtained using XPS and UV/vis at early immersion times. As shown in Table 3 and Figure 5 for the Nafion substrate, the fractional concentration of cationic polyacrylamide gradually increased with immersion time from an average value of 0.57 at 3 min until, at roughly 9 min, the concentration approached an equilibrium value comparable to that detected on pure cationic polyacrylamide powder or cast film. Over the same period of time in Table 2 and Figure 5, the fractional adsorbate surface coverage remained constant. Thus, additional cationic polyacrylamide was accommodated on the Nafion surface as immersion time increased beyond 3 min without altering the adsorbed polymer surface coverage.

As previously discussed, similarity between f_a^{XPS} and χ_a^{XPS} at early immersion times indicates an adsorbate packing density comparable to that of pure cationic polyacrylamide powder or cast film. On the other hand, the increasing difference between f_a^{XPS} and χ_a^{XPS} as immersion time increased indicates an accompanying decrease in the adsorbate packing density relative to the pure solid.

The adsorbed polymer surface coverage experimentally observed in the present study is consistent with enthalpy-driven interaction between chemically heterogeneous adsorption sites on both Nafion and expanded cationic polyacrylamide chains. Only 11% of the repeating units on the Nafion substrate contain basic (anionic) groups which may interact with acidic groups on the adsorbing polymer (both cationic and weakly acidic) to yield negative (favorable) adsorption enthalpy. Remaining interactions are distinctly repulsive (acrylamide—sulfonate) or neutral at best (quaternary amine—tetrafluoroethylene (TFE), hydrolyzed acrylamide—TFE, and acrylamide—TFE). Total adsorption enthalpy is maximized when every acidic repeat unit on the polyacrylamide (20% of the total) adsorbs onto every available sulfonate repeat unit on Nafion (11% of the total). The surface coverage which maximizes the absolute adsorption enthalpy is readily calculated if one assumes (a) comparable adsorption cross-sectional areas for the various polymer repeat units (i.e., adsorption sites), (b) negligible repulsive lateral interactions between adsorbed chains, and (c) a random distribution of adsorption sites.

Examination of the raw material schematics in Figures 1 and 2 would suggest that assumption "a" in the preceding paragraph is too drastic, especially in the case of sulfonate repeat units vs TFE repeat units. However, results from molecular dynamics simulation of the Nafion structure (Figure 3) as well as the semiempirical quantum mechanical calculations previously discussed suggested otherwise, yielding comparable adsorption cross sections for the two repeat units. Assumption "b" is applicable in the case of cationic polyacrylamide adsorption on Nafion since the fractional adsorbate surface coverage was experimentally determined to be relatively dilute (0.58).

The adsorption model outlined in the previous paragraphs is depicted schematically by the two-dimensional checkerboard shown in Figure 6. The checkerboard has a total of 25 squares (adsorption sites) and is used to represent the Nafion substrate. Black squares (a total of three) represent the approximate proportion of sulfonate repeat units to TFE repeating units on the Nafion surface. The TFE repeat units are represented by the

Table 3. Relative Adsorbate Concentration as a Function of Immersion Time from XPS and UV/vis Data

immersion time (min)	atomic % N from XPS	rel concn from XPS (f_m^{XPS} in text)	UV absorption at 207 nm	rel concn from UV (f_m^{UV} in text)
0	0.00	0.00	0.00	0.00
3	5.9 ± 0.1	0.57 ± 0.01	0.059 ± 0.001	0.56 ± 0.02
6	8.1 ± 1.0	0.78 ± 0.09	0.080 ± 0.001	0.75 ± 0.02
9	9.5 ± 1.0	0.91 ± 0.10	0.100 ± 0.001	0.94 ± 0.02
12	8.5 ± 0.4	0.82 ± 0.05	0.098 ± 0.001	0.92 ± 0.02
15	10.4 ± 0.4	1.00 ± 0.05	0.106 ± 0.001	1.00 ± 0.02

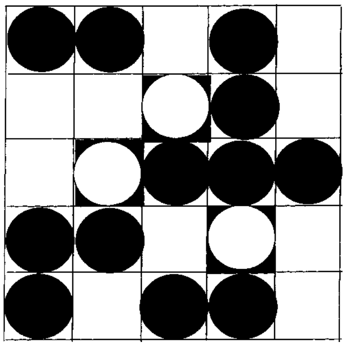

Figure 6. Schematic representation of the two-dimensional enthalpy-driven model for cationic polyacrylamide adsorption on Nafion at early times (as described in text).

remaining 22 white squares. The three white checkers and 12 black checkers represent the rough proportion of acidic (quaternary amine and hydrolyzed acrylamide) to nonacidic (acrylamide) groups on the cationic polyacrylamide. In Figure 6, every white checker rests on every available black square in order to maximize the total absolute adsorption enthalpy. The diameter of every checker is the same and is equal to the width of every square (approximately satisfying assumption “a”, above). The remaining black checkers are distributed randomly over the remaining white squares. From Figure 6, one observes that a total of 15 squares are occupied by checkers, yielding a fractional surface coverage of 0.6 (neglecting the difference in area between squares and checkers). For a checkerboard possessing an infinite number of squares and checkers (a surface of infinite extent), the fractional surface coverage becomes 0.55. This value is in excellent agreement with those obtained experimentally using XPS (0.57) and water wetting (0.58).

The experimentally determined adsorbate surface coverage is thus well represented by enthalpy-driven adsorption of expanded chain molecules onto a random distribution of sulfonate repeat units on the Nafion surface. However, previous X-ray scattering studies of Nafion indicate that sulfonic acid groups associate to form hydrophilic clusters within a hydrophobic PTFE matrix[12] which are not consistent with such a random distribution of repeat units (assumption “c”, above). Unfortunately, direct experimental evidence for the distribution of sulfonate groups on the Nafion surface is not available in the literature and cannot be obtained utilizing the analytical techniques employed in the present study.

When combined with the experimental observation that the adsorbate packing density decreases with time, the results of the adsorption model outlined above suggest that the adsorbed polymer chain configuration transitions from a two-dimensional structure composed of expanded chains at early immersion times to a three-dimensional structure at long immersion times composed of either coils or multilayers. Insufficient experimental evidence is available in present study to determine whether the observed increase in adsorbate concentration with immersion time as the surface coverage remains constant is due to multilayer formation through self-association of complementary adsorption sites on the cationic polyacrylamide or whether adsorbed polymer chains gradually coil in response to the approach of additional chains from solution. Once all sulfonate groups are occupied by quaternary amine groups, the enthalpic driving force for such chain coiling stops and the adsorbate concentration plateaus. On the other hand, equilibrium adsorption behavior in the case of multilayers could result from the increased repulsive interaction between acrylamide groups. Neither mechanism can be discounted at present.

To maximize the adsorption enthalpy of expanded cationic polyacrylamide chains at early times, the adsorption model assumed that ion−dipole interactions between sulfonate and hydrolyzed amide groups are as important as electrostatic interactions between sulfonate and quaternary amine groups. The importance of nonelectrostatic interactions on cationic polyacrylamide adsorption behavior has been previously demonstrated in a study of cationic polyacrylamide adsorption onto various nonionic epoxy resin substrates.[1,2] Surface coverage values obtained in this earlier study were found to be comparable to those obtained for Nafion in the present study.

V. Conclusions

1. Comparable surface and bulk sulfonate concentrations were obtained for “as-received” Nafion ionomer membrane with an equivalent weight of 1100 Da. Sulfonate surface groups were found to influence both the wetting and adsorption behavior of the Nafion surface relative to PTFE. From the standpoint of wetting, an increase in the Good and van Oss fundamental basic surface tension component from 0 to about 6 dyn/cm is observed for Nafion relative to PTFE. In the case of adsorption, cationic polyacrylamide fractional surface coverage is found to increase from 0 to about 0.6 for Nafion relative to PTFE.

2. The fractional cationic polyacrylamide surface coverage on Nafion was found to have a value of about 0.6 through application of the Cassie relationship to water contact angle measurements. This value was consistent with XPS measurements. The adsorbed polymer surface fraction on Nafion was found to be insensitive to immersion time and to be comparable to that previously observed on nonionic epoxy resin substrates.

3. Comparison of the concentration of adsorbed cationic polyacrylamide on Nafion to the surface coverage yielded an adsorbate packing density comparable to that of pure cationic polyacrylamide powder or cast film at early immersion times. The adsorbate concentration gradually increased with immersion time as the packing

density decreased. Equilibrium was attained after about 9 min.

4. Enthalpic consideration of the interactions between randomly distributed complementary sites on the substrate and expanded adsorbate chains (both ionic and nonionic) yielded surface coverage results comparable to experimental data. When combined with the experimental observation that the adsorbate packing density decreases with time, the results of this model suggest that the adsorbed polymer chain configuration transitions from a two-dimensional structure composed of expanded chains at early immersion times to a three-dimensional structure at long immersion times composed of either coils or multilayers.

References and Notes

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