# NMR Studies of the Effect of Adsorbed Water on Polyelectrolyte Multilayer Films in the Solid State

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ABSTRACT: Fast-MAS ^{1}H NMR is used to probe the structure and dynamics of the adsorbed water and polymer components in polyelectrolyte multilayer (PEM) films and the bulk polyelectrolyte complex (PEC). The films, ranging in size from a single layer to 5 bilayers, consist of poly(diallyl dimethylammonium chloride), PDADMAC, and poly(sodium-4-styrenesulfonate), PSS, adsorbed onto colloidal silica. Relaxation and line width measurements show that the adsorbed water is less mobile in the films than in the analogous PEC. The environment of the water throughout the film is found to be affected by the nature of the outer layer with the water displaying a higher mobility and chemical shift when PDADMAC forms the outer layer. Relaxation measurements, together with ^{1}H double-quantum (DQ) NMR experiments, reveal that polymer dynamics in the PEMs are strongly influenced by the layer number and water content. 2D spin diffusion and DQ NMR are used to detect polymer−polymer and water−polymer association. The results support the diffuse interpenetrating model of the different layers and a partitioning of the water to the PSS component and to the surface layer.

## 1. Introduction

Polyelectrolyte multilayer films have received considerable attention because of their ease of assembly onto both planar[1] and nonplanar[2] substrates as well as the many potential applications ranging from conductive coatings[3] to polymer-based LEDs[4] to drug delivery.[5] Using techniques such as X-ray and neutron reflectivity, it has been found that binary films of polyelectrolytes resemble polyelectrolyte complexes (PEC), particularly for thick films, as a result of the high amount of interpenetration of the layers.[6−9] While it is widely accepted that adsorbed water could have a large influence on the behavior of the film, neutron reflectivity is unable to observe it directly, although it has been incorporated into models for the data.[6] Thus, only a few studies so far have been able to probe the behavior of water in the films,[10−12] and none have probed it directly in the solid state.

The study of surface-adsorbed systems by NMR has long been hampered by the poor signal-to-noise, compounded by the low sensitivity of ^{13}C or other heteronuclei with broad chemical shift ranges. The high sensitivity of protons makes this a favorable nucleus for surface NMR studies; however, the large line widths, due to strong homonuclear dipolar interactions, combined with a narrow chemical shift range, lead to poorly resolved ^{1}H NMR spectra in the solid state. Solid-state NMR has progressed to the point where high-resolution spectra of strongly dipolar-coupled protons are obtainable, even for thin surface layers.[13,14] Magic-angle spinning (MAS) at rates up to 35 kHz is capable of averaging to zero most of the dipolar couplings that normally broaden ^{1}H NMR spectra beyond usefulness. Additionally, the observation of protons eliminates the reliance on the isotopic enrichment that facilitates the observation of heteronuclei.[15] The improved resolution

### Scheme 1. Polyanion Poly(sodium 4-styrenesulfonate) and Polycation Poly(diallyldimethylammonium chloride)
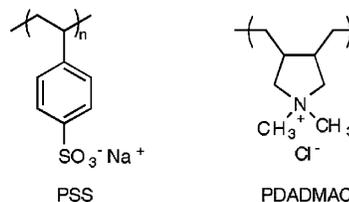


has permitted the development of sophisticated pulse sequences that allow for the extraction of information similar to that found in liquid-state experiments.[16−22]

In this paper, we apply novel solid-state ^{1}H NMR techniques to directly observe the interactions among the two polyelectrolyte components and the water adsorbed in the film. From these NMR experiments, we are able to extract information on the nature of water adsorbed within the film as a function of water content and the last polyelectrolyte layer adsorbed, the effect of water on the dynamics of the polymers as a function of content, and the overall structure and interactions among the components in the film. Comparisons to the analogous polyelectrolyte complex as well as the bulk polymers are made. The results reflect the strong effects that the outer layer has on the nature of the film.

## 2. Experimental Section

**2.1. Materials.** Poly(diallyldimethylammonium chloride) (PDADMAC) is purchased from Sigma (Milwaukee WI) and has a molecular weight of 70 kDa. Poly(sodium 4-styrenesulfonate) is purchased from Aldrich (St. Louis, MO) with a molecular weight of 500 kDa (Scheme 1). The polymers are deposited onto a substrate of Snowtex colloidal silica (70−100 nm) purchased from the Nissian Chemical Co.

**2.2. Assembly.** 500 mL of a 0.02 M PDADMAC, 0.2 M NaCl solution was added to 1 g of silica colloid suspension. The samples were sonicated, and the adsorption solution was left to stand for a minimum time of 30 min. The solution was then

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centrifuged, and the supernatant was removed. 500 mL of water was then added to the sample, and the solution was sonicated and left to stand for a minimum of 30 min. The supernatant was then removed to rinse the unadsorbed polyelectrolyte from the colloids. A total of three 500 mL washings were performed after the adsorption of each polyelectrolyte layer. A small amount of sample was then removed and dried overnight at 70 °C for characterization studies. 500 mL of a 0.02 M PSS, 0.4 M NaCl solution was added to the remaining colloidal solution. Similar adsorption and washing steps were performed until films of five PDADMAC−PSS bilayers had been prepared. The resulting half-integer bilayer films are capped with PDADMAC, while full integer bilayers have PSS as an outer layer.

**2.3. Sample Preparation.** Prior to the NMR experiments, the samples were dried in an oven under vacuum at 100 °C for 12 h and then allowed to equilibrate in the atmosphere. Dried samples are measured immediately following at least 12 h in a vacuum oven at 100 °C. Samples that were saturated with $H_2O$ were prepared by storing the samples in a closed container in the presence of a pool of water, leading to a $H_2O$-saturated atmosphere. $D_2O$-saturated samples were prepared identically after drying for 12 h at 100 °C in a vacuum, but with a $D_2O$ reservoir.

**2.4. NMR.** Proton spectra are collected on Bruker DSX500 or AVANCE700 spectrometers using magnets operating at 11.74 and 16.45 T, respectively, in Bruker 2.5 mm fast-MAS probes at a rotation frequency of 25 kHz. Conventional spin-echo experiments reveal information on the chemical environment of the components of the films through the observed chemical shift as well as their mobility via the line width, which is inversely proportional to the spin−spin relaxation time, $T_2$. Spin−lattice relaxation, $T_1$, measurements, using the inversion−recovery pulse sequence, further clarify the mobility of both the polymer components and adsorbed water by sampling the spectral density function at specific values. Molecular mobility can also be probed by measuring the relative strengths of the homonuclear dipolar couplings among protons in the film, which are strongest for rigid spin pairs separated by less than 0.4 nm and are reduced by molecular motions occurring in the in the 10−100 kHz range.[15] Through-space connectivity of different types of protons can be probed and separated on the strength of the dipolar couplings experienced by the protons. Double-quantum coherences can be generated between rigid, strongly coupled protons by recoupling pulse sequences such as back-to-back (BABA).[16] By varying the length of time the dipolar coherences are allowed to develop, the relative strength of the couplings can be determined, with rigid strongly coupled protons developing coherences in a shorter period of time than those of more weakly coupled protons. The double-quantum coherences can be correlated with the single-quantum chemical shifts of the constituent members of the proton pair using a two-dimensional version of BABA.[21] Finally, three-pulse exchange (NOESY) experiments[19,20,23] are used to examine the dipolar couplings of all interacting spins. In these experiments, cross-relaxation and spin diffusion result in the flow of magnetization among protons. Cross-peaks are generated for even weakly coupled protons. With this suite of ¹H experiments, the structure and dynamics of the film are probed by solid-state NMR.

## 3. Results

**3.1. ¹H Chemical Shifts and Relaxation Measurements.** The NMR spectra of samples rehydrated with water from the atmosphere are dominated by the large water peak (Figure 1). The water resonance associated with the film in layers 0.5 and 1.5 overlaps with the water associated with the substrate at ca. 5 ppm.[24] As plotted in Figure 2, there is a strong alternation of the chemical shift of the water adsorbed in the film depending on whether the polyanion or polycation forms the outer layer. Films capped with PDADMAC (open sym-
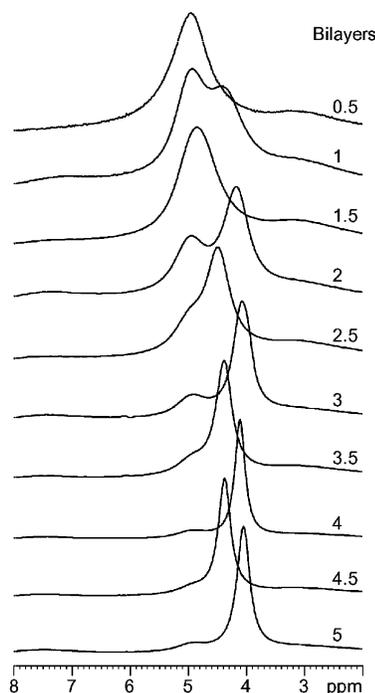


**Figure 1.** ¹H spin-echo NMR spectra of PEM films equilibrated with atmospheric moisture. The peak at about 5 ppm is water associated with the substrate. The shift of the water associated with the film changes depending on which polymer was last adsorbed. Full bilayers have PSS on the surface. Half bilayers have PDADMAC on the surface.
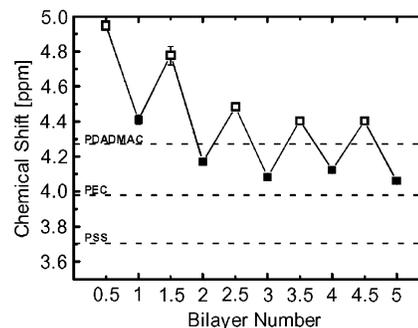


**Figure 2.** Plot of the chemical shifts of the water adsorbed as a function of bilayer number in PEM films equilibrated with atmospheric moisture. Open symbols are samples which have PDADMAC as an outer layer, and filled symbols have PSS as an outer layer. In addition, the shifts of water associated with the bulk polymers and polyelectrolyte complex are indicated with dashed lines.

bols) have a water resonance similar to that of water adsorbed into bulk PDADMAC (4.3 ppm). The water resonance in films with PSS (filled symbols) on the outer surface approaches the value found for water adsorbed into the bulk polyelectrolyte complex (PEC) (4.0 ppm) as opposed to the shift of water associated with bulk PSS (3.7 ppm). Moreover, the line width of the water signal depends on the bilayer composition. The full width at half-height (fwhh) of the water associated with the film is broader than water associated with the analogous PEC and bulk PSS; however, it is narrower than water associated with bulk PDADMAC. These trends hold for the residual $H_2O$ signals in samples rehydrated with $D_2O$, although the residual water peaks in these samples are narrower than $H_2O$ hydrated samples (Figure 3). Line widths for the residual $H_2O$ resonance in $D_2O$-saturated samples are plotted in
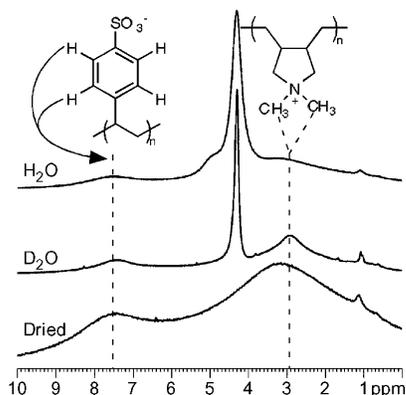
**Figure 3.** Spin-echo spectra of a 3.5-bilayer PEM film after equilibration with atmospheric moisture ($H_2O$), after saturation with $D_2O$, and after drying. Shifts of the aromatic protons of PSS and the methyl protons of PDADMAC are indicated. The residual water peak in the $D_2O$-saturated sample is much narrower than the film water in the atmospheric sample because of a significantly diluted proton dipolar network.
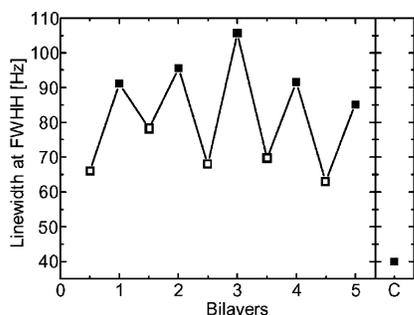


**Figure 4.** Line width in hertz measured as the full width at half-maximum intensity for samples saturated with $D_2O$. Open symbols are samples that have PDADMAC as an outer layer, and filled symbols have PSS as an outer layer. *C* indicates the line width of water associated for an identically treated PEC.
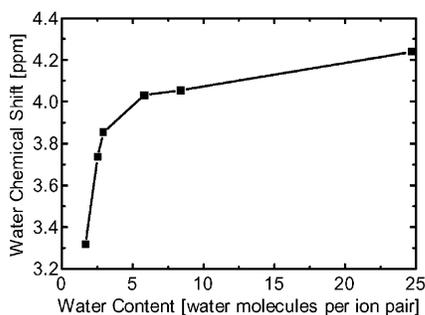


**Figure 5.** Water chemical shift as a function of water content for a 5-bilayer film.

Figure 4. The water resonance is observed to shift to lower ppm values as the amount of water in a given film decreases, as demonstrated in Figure 5 for a 5-bilayer film. Upon drying, the polymer resonances can be distinguished as signals in the aromatic region centered at 7.4 ppm and the aliphatic region at 3.0 ppm.

The deconvolution of the spectra is complicated by the large number of peaks from the components of the film as well as intensity from the substrate. As a result, the water contents extracted for thinner films from this method are approximate at best, and only data for films thicker than 1.5 bilayers are plotted in Figure 6. In samples exposed to the atmosphere, values between 5.5 and 7.5 water molecules per ion pair are found, which
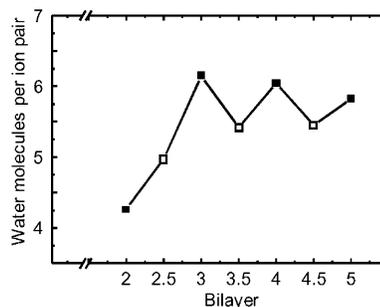


**Figure 6.** Water content as a function of bilayer number for films equilibrated with atmospheric moisture. Open symbols are samples which have PDADMAC as an outer layer, and filled symbols have PSS as an outer layer. Deconvolution for early layers is hampered by the relative intensity and overlap of the water associated with the substrate; therefore, the plot shows only data for films of 2 bilayers and thicker.

agrees fairly well with the IR and thermogravimetric analysis data of Farhat et al.[8] The data demonstrate that for thicker films there is more water adsorbed into the full bilayer films than in PDADMAC-capped films. For samples exposed to $H_2O$-saturated atmospheres, 20−25 water molecules per ion pair are typical. These high numbers may be the result of capillary forces retaining water between the particles. Schmitt et al.[10] have shown that PAH−PSS samples equilibrate with humid environments in less than 2 h; in fact, rehydration of dried samples and dehydration of saturated samples could be observed over time during the acquisition of NMR spectra.

Dried samples show the removal of water from both the polyelectrolyte film and the substrate (Figure 3). Samples rehydrated with $D_2O$ are used to diminish the large water peak, allowing the polymer protons to be more easily resolved. As shown in Figure 7, narrow aliphatic resonances are observed for half-integer layers for films of less than 3 bilayers, i.e., with PDADMAC at the outer surface. However, the narrow peaks still appear above a relatively broad proton background. The aromatic peak also narrows to a lesser extent for the integral layers, especially below 3 bilayers. At higher layer numbers, the resonances of PSS-capped films resemble those of the PEC, while at half-integer bilayers, the aliphatic peak resembles that found in bulk PDADMAC. At elevated temperature, both proton peaks associated with the aromatic PSS protons at 7.5 and 6.6 ppm can be easily resolved and are narrower for films of less than 3 bilayers with PSS on top (Figure 7).

The spin−lattice relaxation times were measured at both 500 and 700 MHz on the samples saturated with $D_2O$. A total of 12−14 data points were taken between 1 ms and 10 s with a recycle delay of 10 s. The intensities fit well to a single-exponential decay. A sawtooth pattern superimposed on a monotonic increase with increasing film thickness is observed for the relaxation times (Figure 8). The field dependence of the $T_{1H}$ values indicates that the motion of the polymers is slow compared to the Larmor frequency. The relaxation times of the bulk polyelectrolyte complex exposed to saturated $D_2O$ environments are very similar to those observed in the 10-layer film (918 ms for PSS and 884 ms for PDADMAC). The $T_{1H}$ values of the dried samples are larger than those for the hydrated films. For thin films, the $D_2O$- and $H_2O$-saturated samples have comparable values; however, for films of more than 3 bilayers, the $T_{1H}$ for hydrated films stays relatively
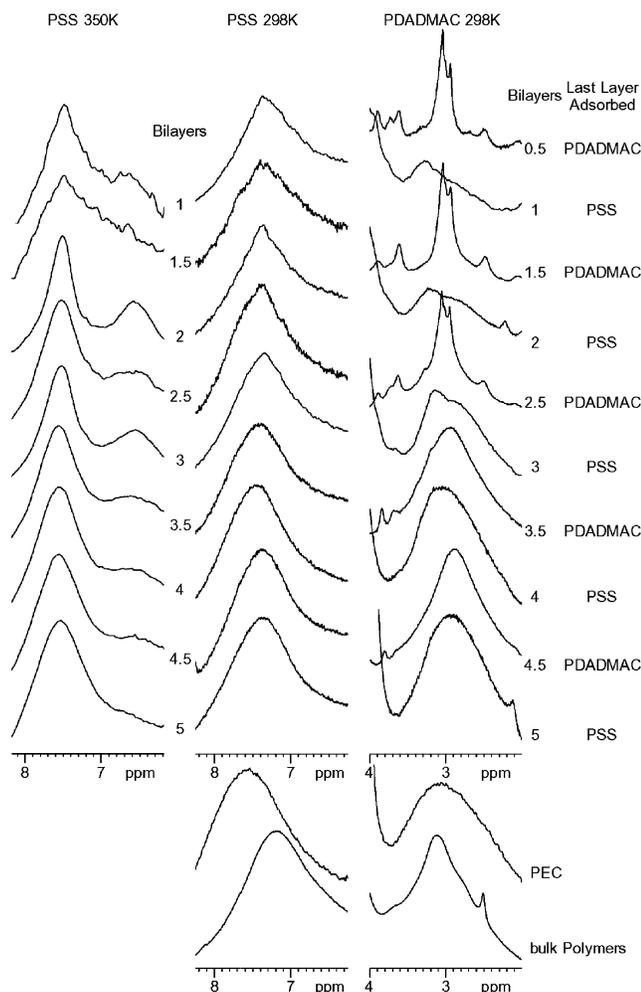
**Figure 7.** Close-up of the PSS and PDADMAC region at 298 K of the spectra of $D_2O$-saturated samples. The narrow lines indicate increased motion for the PDADMAC samples when it is the last layer adsorbed. The narrowing of the PSS is not as pronounced. Also shown are the same regions for the PEC and bulk polymers. On the left is the PSS region for the same samples at 350 K.
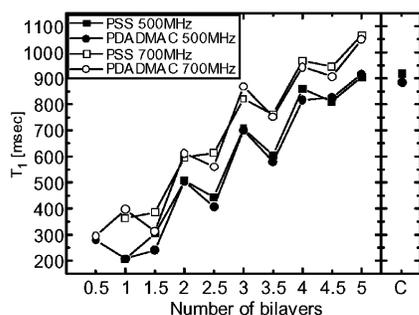


**Figure 8.** Plot of the spin−lattice relaxation times for $D_2O$-saturated PEM films. Squares represent the PSS component, and the circles represent the PDADMAC component. Filled symbols were measured at 500 MHz and open symbols at 700 MHz. The $C$ values are for a $D_2O$-saturated PEC at 500 MHz. Higher values indicate more restricted motion (slow-motion limit).

constant, while that for $D_2O$-saturated films continues to increase. It should be noted that thin films were easier to dry than thicker films. For films of more than 3 bilayers, drying was incomplete, even after 48 h at 100 °C and under vacuum, or the films were partially rehydrating during acquisition of the NMR spectra. In
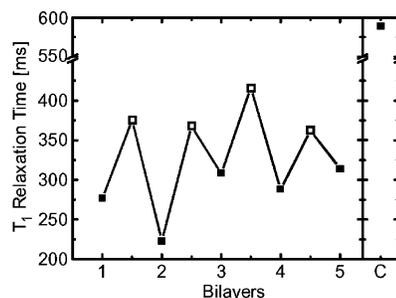


**Figure 9.** $T_1$ relaxation times of water in PEMs rehydrated by exposure to atmospheric moisture. $C$ is the measured value for an identically treated PEC. Higher values indicate more mobility (fast-motion limit). Open symbols are samples that have PDADMAC as an outer layer, and filled symbols have PSS as an outer layer.
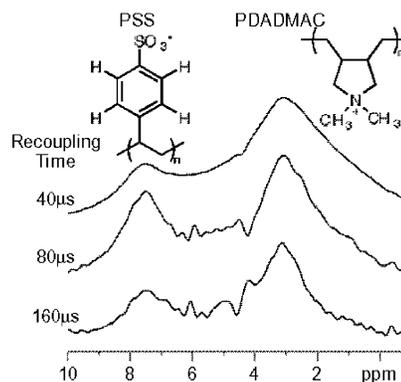


**Figure 10.** Double-quantum-filtered back-to-back spectra of an atmosphere-equilibrated 3.5-bilayer film. Clearly visible are the aromatic PSS protons and the PDADMAC methyl protons.

partially rehydrated samples, the aliphatic peak was seen to shift from 2.9 to 3.3 ppm due to a broad water resonance in proximity to the methyl peak of PDAD-MAC. The $T_1$ of the water associated with the film in hydrated samples displays a sawtooth pattern as a function of the last layer adsorbed (Figure 9). For all samples where the substrate-bound water and the water associated with the film can be distinguished, the film-bound water $T_1$ is shorter than that of the polymer components.

**3.2. $^1H$ Double-Quantum (DQ) MAS NMR.** The back-to-back pulse sequence (BABA)[16] allows for the controlled reintroduction of the dipolar coupling normally removed by MAS. In one-dimensional DQ-filtered spectra (1D DQF BABA), protons with strong dipolar couplings (i.e., static and separated by distances smaller than 0.4 nm) recouple in one or two rotor periods (40−80 $\mu$s). Spins with weaker dipolar couplings require longer recoupling times to evolve signals that will survive the filtering process. Figure 10 shows typical spectra for the back-to-back experiments for an atmosphere-equilibrated film of 3.5 bilayers. The polymer resonances survive the DQ filter, while the water resonance associated with the film is removed. The water resonance associated with the substrate reappears at long recoupling times (>160 $\mu$s), indicating a weak dipolar coupling (spectrum not shown). At these longer recoupling times, the polymer resonances decay as a result of multispin coherences developing from the complex dipolar network or a random motional process where the dipolar coupling is changing on the time scale of the experiment (microseconds).[15] Figure 11 shows the 1D DQF BABA spectra for 40 $\mu$s recoupling times of
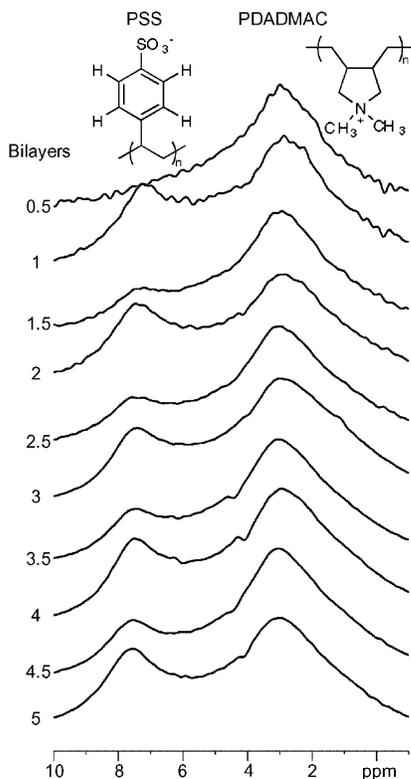
**Figure 11.** 1D double-quantum-filtered back-to-back spectra (1024 transients) at 40 $\mu$s recoupling time. Note the alternation of the relative intensities of the aromatic PSS peak and the PDADMAC methyl peak. Also note the overall increase in signal-to-noise with an increase in film thickness.

samples exposed to the atmosphere. Observed is an alternation of the relative height of the aliphatic and aromatic peaks as a function of the amount of each polymer in the film. In addition, there is an absolute increase of intensity (i.e., better signal-to-noise) as the number of bilayers in the film increases. Experiments were run to examine the variation of the strength of the dipolar couplings with bilayer number and water content. Such measurements provide another probe of the polymer mobility, since the dipolar couplings will be averaged by molecular reorientations occurring on the kilohertz time scale. The ratio of the intensity of the 1D DQF BABA spectra to the intensity of the peaks in a reference spectrum without double-quantum filtration, achieved by changing the phase cycle to select single-quantum coherence pathways, yields information on the amount of sample able to develop double-quantum coherences.[15] By plotting the normalized intensity, a sawtooth pattern again emerges for the hydrated films with PDADMAC on the surface. The dried films and the PSS portion of the hydrated films do not show such a regular pattern (Figure 12).

The two-dimensional double-quantum back-to-back (2D DQ BABA) experiment was used to directly observe the coupling between the aliphatic and aromatic regions (Figure 13). The diagonal and cross-peaks, appearing in the SQ dimension at the location of the resonance and at the double-quantum resonance at the sum of the resonances of the two protons involved in the coupling, are observed for films greater than 0.5 bilayers of thickness, as observed previously for a 2-bilayer film.[13] The relative intensities of the cross-peak and the diagonal peaks did not noticeably change with increasing number of layers.
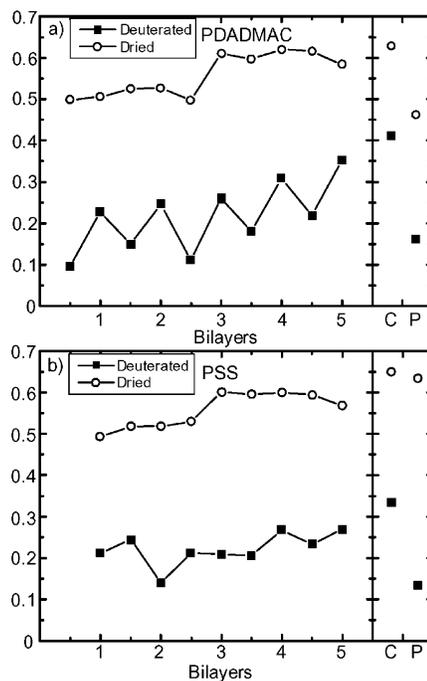


**Figure 12.** Plot of intensities of (a) the PDADMAC methyl and (b) aromatic PSS regions of the DQF BABA spectra relative to the spin echo for 40 $\mu$s recoupling time. The dried samples (open circles) have been shifted up by 0.25 for clarity. The $D_2O$-saturated samples (solid squares) are samples that have been dried and rehydrated with $D_2O$. *C* denotes the values for the PEC, and *P* represents the values for (a) bulk PDADMAC and (b) bulk PSS.
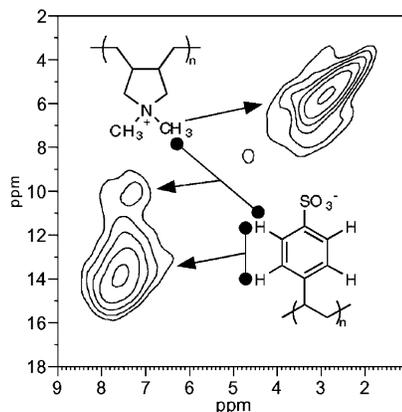


**Figure 13.** 2D double-quantum back-to-back spectrum of a 3-bilayer film. Auto-peaks and cross-peaks are labeled. The PSS aromatic "auto" peak does not lie on the diagonal because of the different resonance frequencies of the two protons involved.

**3.3. $^1$H Spin Diffusion.** Three-pulse exchange experiments (NOESY) measure the spin diffusion within the sample.[20] Spin diffusion is mediated by homonuclear dipolar couplings, giving rise to the spatial migration of magnetization and providing through space connectivities.[19,20,23] A representative spin diffusion (NOESY) spectrum for a film of 3.5 bilayers is shown in Figure 14. The samples are rehydrated with $D_2O$ to reduce the intensity of the water peak. The cross-peak between water in the film and the PDADMAC peak only builds up for films of a half-integer number of layers (Figure 15). The PDADMAC−PSS cross-peak develops very quickly because of the strong dipolar coupling between the two polymers, while the PSS−water cross-peak grows more slowly. The diagonal peaks decay as a result
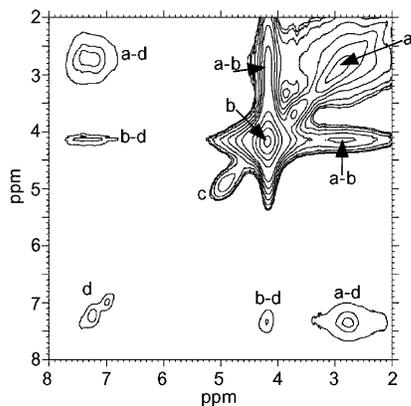
**Figure 14.** Three-pulse exchange spectrum of a 3.5-bilayer film saturated with $D_2O$. Observable are the diagonal peaks for (a) the PDADMAC methyl groups, (b) the water associated with the film, (c) the water associated with the substrate, and (d) the aromatic protons for PSS as well as cross-peaks between the polymer components and each polymer with the water associated with the film.
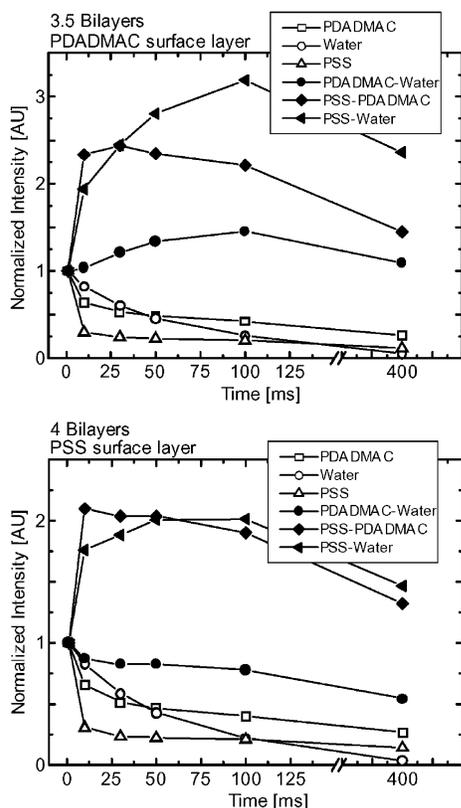




**Figure 15.** Buildup curves from two series of three-pulse exchange experiments as a function of mixing time (a) for a 3.5-bilayer film with PDADMAC on the surface and (b) for a 4-bilayer film with PSS on the surface. Cross-peaks are solid symbols, and open symbols are diagonal peaks. Integrals at $t = 1$ ms are set to a value of 1 for ease of viewing. Note that for complete bilayers the water−PDADMAC peak does not build up but rather decays weakly.

of relaxation and the loss of intensity to the cross-peaks. Where the resolution allows (i.e., for half integer films of less than 3 bilayers), intramolecular cross-peaks are also observable.

## 4. Discussion

The NMR study clearly shows that the behavior of the films, as measured by the chemical shift of the water

resonance, the mobility of the adsorbed water, and the polymer mobility, depends on which polyelectrolyte forms the surface layer. Many techniques probe surface-dependent properties. The contact angle of water obviously depends only on the nature of the surface, but our NMR techniques probe the entirety of the film; although in certain cases, the effect of the outer surface layer may be dominant. In this section, we consider whether the effects observed are a direct result of interactions on the surface or whether the entire film character is changing as a function of the nature of the last layer adsorbed.

**4.1. Behavior of Water in the Film. 4.1.1. Chemical Shifts and Intensities of the Adsorbed Water.** Water has a large effect on the structure and dynamics of the film. The location and width of the water resonance, about 0.7 ppm away from that of bulk water (4.8 ppm, shimmed to a fwhh of 6 Hz), indicate that the water does not exist in macroscopic "pools" but rather is associated with the polyelectrolyte film and the silica surface. The appearance of only one peak associated with the polyelectrolyte film implies that there are not multiple well-separated types of nonexchanging water but, rather, either a single "type" of water in the film or multiple types of water rapidly exchanging (on the NMR time scale) within the film. Interestingly, the water resonance oscillates between values similar to water adsorbed in PDADMAC when PDADMAC is on the surface and that for water adsorbed in a PEC complex when PSS is on the surface. If this were purely a direct measurement of surface water, oscillation between the chemical shift values for water associated with bulk PDADMAC and bulk PSS would be expected. Second, the intensity of a water peak mostly associated with the polyelectrolyte film's outer surface should decrease relative to the polymer intensities, but the adsorbed water peak increases steadily with film thickness. If the water is exchanging rapidly among several reservoirs (e.g., the bulk of the film and the film's surface layer), as the film became thicker, the relative size of the two reservoirs would change, leading to a damping of the oscillations of the water chemical shift. The oscillation, however, is decreasing neither in value nor in magnitude above 2 bilayers, indicating a systemic effect of the last layer adsorbed on the nature of the film.

The water resonance shifts to higher ppm values with adsorption of more water, most likely the result of the adsorption of more mobile water in the film, which is less strongly bound to the polymer. Full bilayer films have higher water contents per ion pair but smaller water chemical shifts than films capped with PDADMAC; therefore, the change in shift with layer number is not simply a result of higher water contents. The monotonic and dramatic increase in the intensity of the film-bound water peak indicates that it is associated with the entirety of the film and not just with the surface layer. We conclude that the nature of the water environment *within* the film depends on whether the outer layer is the polycation or the polyanion.

**4.1.2. Mobility of the Adsorbed Water.** The water associated with the film differs significantly from the narrow peak observed for water associated with the PEC (40 Hz for PEC vs 148 Hz in a 5-bilayer film). The decreased mobility of the water associated with the film as compared to the bulk complex reflects a stronger association with the polymer chains. The line widths

for the films rehydrated with $D_2O$ are much narrower than those rehydrated with $H_2O$ due to a dilution of the proton dipolar network. The line width for $H_2O$ in the PEC also decreases when replaced by $D_2O$, but not as significantly (40 Hz with $H_2O$ vs 32 Hz with $D_2O$). The smaller decrease in line width for the PEC indicates that the proton dipolar couplings are weaker, the result of more mobile water molecules.

The line width data in Figure 4 clearly indicate that the water is more mobile in films with PDADMAC as the surface layer than in films with PSS on the surface. In the fast motion limit, where the correlation time of the water molecule is faster than the inverse of the carrier frequency, longer $T_1$ values indicate more mobility. In Figure 9, we observe longer $T_1$ relaxation times, and hence more mobility, for water when PDADMAC is on the surface. The line width and $T_1$ data have only an oscillation and are not superimposed on a constant gradient, demonstrating that we are not observing two rapidly exchanging reservoirs of different relative populations (rigid and surface), but rather an effect on the water within the film from the type of polyelectrolyte (polyanion vs polycation) forming the outer layer. However, the mechanism by which this variation in the water mobility occurs is unknown at this point.

From $^1H$ NMR solvent relaxation studies of polyelectrolyte multilayers deposited on latex particles, Schwarz and Schönhoff concluded that the electrostatic potential of the last layer determines the water immobilization in the internal layers of PAH/PSS multilayers in contact with solution. The observed alternation of the solvent relaxation times of PAH/PSS multilayers is attributed to a surface potential driven swelling, which occurs when the polycation forms the outer layer.[12] The mechanism was speculated to be due to uncompensated charges within the multilayer assembly or changes of the dissociation equilibrium or ion content within the layers. In their study, higher water contents are observed in PSS-capped multilayers, similar to our results. However, no even/odd alternation of the solvent relaxation times was observed for PDADMAC/PSS multilayers. The absence of swelling/deswelling behavior was attributed to the fact that PDADMAC is a strong polyelectrolyte, whereas PAH is a weak polyelectrolyte with exchangeable protons. It is suggested that the degree of protonation of PAH plays a role in the different behaviors of PAH and PDADMAC. This explanation for a film structural change due to alternation of the surface potential would apply only to PEMs in contact with solvent. In our system, where no bulklike water is detected, no net surface charge is expected to develop.

**4.2. Polymer Dynamics. 4.2.1. Effect of Water Content on Polymer Mobility.** While no mobility changes are observed when $H_2O$ is adsorbed into stoichiometric PECs, water greatly affects the dynamics of the polymers within the multilayers (Figures 7 and 8). Increased resolution of the polymer resonances of the multilayers with added water is the most obvious result. Another effect is the decrease in spin−lattice relaxation times. The field dependence of the $T_{1H}$ relaxation times of the adsorbed polymers indicates that, unlike the water in the film, the polymer dynamics are in the slow-motion regime relative to the Larmor frequencies of 500 and 700 MHz. Therefore, the decrease in the polymer $T_{1H}$ values indicates that the polymer mobility increases with water content. This mobility trend is not unexpected. Experimentally observed voids are believed to

be created by the inability of electrostatically paired polymer chains to rearrange upon drying.[6] Schmitt and Helm have theorized that upon rehydration, by exposure to the environment, these voids adsorb water, which allows for a decrease of strain on the chains or perhaps acts as a lubricant.[10]

**4.2.2. Effect of Number of Layers on Polymer Mobility.** For PDADMAC-capped films, the increase in chain mobility with added water is much more dramatic than for complete bilayers (PSS on the surface). The large increase in mobility that is seen in PDADMAC but not in PSS may be the result of the intrinsic mobility differences between the two bulk polymers. The glass transition temperature of dry PDADMAC ($\sim$70 °C) is much lower than that of bulk PSS (>150 °C). Both polymers are plasticized by the adsorption of water with the $T_g$ of PDADMAC being lowered to below room temperature when the water content exceeds 20%.[25] Whereas water-plasticized PDADMAC shows a well-resolved $^1H$ NMR spectrum under slow MAS at room temperature, PSS with a similar water content must be heated to 100 °C to see the onset of motional narrowing.[26] The polyion that forms the outer layer will be only partially complexed with the lower layers, leaving more mobile segments forming loop and tails, which are charge compensated by small counterions. When PDADMAC forms the outer layer, its noncomplexed segments are more mobile than those of PSS when it forms the outer layer. Another possibility is the difference in molecular weight; although it has been shown that if the molecular weight is such that the contour length of the polymer is greater than the thickness of a layer, there are no effects.[27] The increased mobility is believed to be polymer specific and will not be observed for all polycations or half-integer films, only polymers with sufficient inherent mobility. The order of the adsorption (PSS-capped films being half-integer vs full integer films) is not believed to have an effect. The adsorbing polymer sees only a charged surface and cannot detect whether the film is a integer or half-integer film. The local charge balance of the outer layer is specific to that layer and is charge-balanced by the polymer layer below and small counterions from solution, producing a surface of opposite charge regardless of the number of layers in the film.[28−30]

The overall increase in the polymer $T_{1H}$ values with the number of bilayers reflects a decrease in the polymer chain mobility with increasing film thickness. The decreasing mobility of the polymer with increasing bilayer number contrasts with that of the adsorbed water, which showed *constant* oscillations between a more mobile state (PDADMAC top layer) and less mobile state (PSS top layer). As the assembly progresses, more of the film is trapped in a given conformation by the electrostatic interactions, increasing the size of the strongly bound bulk film reservoir as compared to the loops and tails at the surface. The relaxation times of a 5-bilayer film are very close to those for the PEC complex under similar conditions. $^1H$ spin diffusion, a result of the strong dipolar coupling between the polymer components, leads to the measuring of essentially a single $^1H$ spin−lattice relaxation time for all polymer protons in the sample. Additionally, we see that films with PDADMAC on the surface tend to have slightly shorter $T_{1H}$ values, indicating somewhat more mobile polymer species compared to the full bilayers (e.g., polymers in a 2.5-bilayer film are more mobile than

polymers in a 2-bilayer film). This is most likely a result of the higher innate mobility of the PDADMAC over PSS on the surface. NMR observes the entire ensemble of protons in the film and not just on the surface although the surface protons could be acting as a fast relaxing sink for the film as a result of the spin diffusion. The oscillations seem to be getting smaller with film thickness, indicating perhaps an equilibrium value is being approached. Dried films have longer spin–lattice relaxation times (about 1 s for PDADMAC and 900 ms for PSS), indicating less motion, as expected, and displayed no oscillation, underscoring the effect of adsorbed water on the mobility of the polymers. The $^{13}C$ relaxation studies allow the dynamic behaviors of the polyanion and polycation to be independently monitored since $^{13}C$ spin diffusion is negligible. $^{13}C$ spin–lattice relaxation measurements of the same samples studied here show that the PDADMAC motion becomes restricted as the number of layers increases, but the PSS chain mobility remains constant.[31]

The 1D DQF BABA data also illustrate the variation in polymer mobility with layer number. The intensity of the signal that survives the DQF is higher for PDADMAC when PSS is on the surface. Higher values indicate a more strongly dipolar coupled system (smaller intergroup proton–proton distances or less motion). The alternation is observed in both deuterated and hydrated samples, but not in dried samples. The sawtooth pattern of the dipolar coupling strength is superimposed on a monotonic increase, in complete agreement with the polymer $T_{1H}$ data, indicating an increased mobility of PDADMAC when it is on the surface which seems to be heading for the PEC values for full bilayer films and grows from the value of bulk PDADMAC. These data complement the $^{13}C$ spin–lattice relaxation data,[31] with the PDADMAC becoming less mobile as the number of layers increases and the PSS mobility staying relatively constant. The lack of oscillation of the dried samples highlights the effect of water on the mobility of the polymers within the film. The lack of oscillation of the PSS chain mobility could be accounted for by the innate differences in mobility of the two polymers.

The decrease in line width of the polymers with added water is only noted for films less than 3 bilayers. There is a broad component under the narrow components, but the transition at 3 bilayers is quite sudden. This is interesting when viewed in the context of a study by Dubas and Schlenoff that shows a nonlinear buildup (thin film regime) of the PDADMAC–PSS multilayers on planar surfaces up to 3 bilayers, before the system begins to grow in a linear fashion.[9] Likewise, Arys et al.[32] found that PDADMAC/PSS films less than 3.5 bilayers are too thin relative to the multilayer or substrate roughness to be observed by X-ray reflectometry. In the thin film regime, the surface has not reached its equilibrium roughness.[6,33] Thus, the increased mobility of the polymers in the first layers may be the result of particularly mobile loops and tails that appear as the smooth surface of the substrate transitions to some equilibrium roughness as the number of layers increases. Once a certain roughness is reached, polymer molecules that adsorb perhaps have shorter loops and tails because there are binding sites at different elevations of the polymer landscape. Upon heating to 350K, the PSS mobility is also enhanced for integral films of 3 or fewer bilayers. The fact that the mobility of both components changes at the 3-bilayer

mark is perhaps indicative of the transition from the thin film regime to the equilibrium film regime (the linear growth regime).

**4.3. Nature of the Complexation. 4.3.1. Polycation–Polyanion Complexation.** The 2D DQ BABA spectra show strong autocorrelation and cross-correlation peaks for films of 1 bilayer or greater regardless of water content, the effect of the strong dipolar coupling between the PDADMAC and PSS protons. The cross-peaks indicate intimate mixing between the two polymers supporting a picture of diffuse, interpenetrating layers as concluded from neutron reflectivity.[6] The three-pulse exchange experiments clearly display both polycation–polyanion and water–polyelectrolyte cross-peaks. The cross-peak between the aromatic protons of PSS and the aliphatic amine methyl groups of PDADMAC develops more quickly than the cross-peaks associated with the water. This is a result of the strong dipolar coupling between the polymers, indicative of both close proximity and rigidity. These attributes lead to the observation of the same cross-peaks in the 2D DQ BABA spectra and the measurement of a single $T_{1H}$ value for both polymer components.

**4.3.2. Water–Polyelectrolyte Association.** The water–polyelectrolyte cross-peaks develop more slowly because the mobility of the water partially averages the dipolar coupling. The PDADMAC–water cross-peak builds up for films capped with PDADMAC and for a 1-bilayer film. For the other films capped with PSS, it decays weakly. The PSS–water peak always builds to higher intensities regardless of the number of layers. This stronger association of the water with PSS is not surprising given that bulk PSS is more hygroscopic than bulk PDADMAC. The spin diffusion results indicate that more water sits closer to the PSS protons than to those of PDADMAC within the film. Lösche et al.[6] postulated that twice as much water, volume-wise, is associated with PSS as with PAH in order to fit their neutron reflectivity data. The higher water content in PSS-capped films is further evidence of this phenomenon. Water associates strongly with the last polymer layer adsorbed regardless of species due to the presence of the small counterions required to balance the charge of the noncomplexed polymer segments at the surface.

In the bulk polyelectrolyte complex, the PDADMAC–PSS cross-peak also develops quickly, but the water–polyelectrolyte cross-peaks develop very slowly and have not reached a maximum after 400 ms due to the much weaker coupling between the more mobile adsorbed water and the components of the complex as compared to the films. The larger mobility of water in the complex as compared to that in the films may be explained by the different populations of small inorganic counterions and their associated water molecules. A higher number of small counterions are necessary to enforce electroneutrality in the film that are not necessary in the stoichiometric PEC. It has been observed that when proteins are lyophilized, there is a species of water that is very difficult to remove because it binds to the charged patches of the protein to hydrate the counterions bound to the globule.[34] In the polyelectrolyte multilayers, the stronger water–polymer association due to the presence of small counterions is most likely a surface-based effect. While water is observed throughout the film, as evidenced by the strong PSS–water cross-peak and the observation of the substrate water autopeak, the PDADMAC–water cross-peak observed

only for PDADMAC-capped films could be the result of the large number of the small counterion compensated charges on the surface and their associated water molecules. When PDADMAC forms only inner layers, with few associated small counterions, the water associates significantly only with the PSS. The 1-bilayer anomaly is perhaps the result of incomplete coverage of the extensive loops and tails from the first PDADMAC adsorption step.

## 5. Summary

For clarity, the large amount of information on the dynamics and complexation of the polymers and the associated water from solid-state $^1$H NMR studies is summarized below:

**5.1. Adsorbed Water.** (i) The mobility of adsorbed water is more restricted in the polyelectrolyte multilayer (PEM) films than in the bulk polyelectrolyte complex (PEC). (ii) The water mobility is lower and the water content higher for PSS-capped PEMs as compared to PDADMAC-capped PEMs. (iii) The $^1$H NMR peak intensity of the film-bound water increases in a monotonic fashion with bilayer number, and the chemical shift oscillates in a constant fashion between that of water adsorbed in bulk PEC vs bulk PDADMAC.

**5.2. Polymer Dynamics.** (i) Addition of water increases the polymer mobility in the PEMs but not in the PECs. (ii) Enhanced polymer mobility is observed for hydrated PDADMAC-capped films relative to PSS-capped films. This oscillation in the polymer mobility dampens and is superimposed on a gradient of decreasing mobility with film thickness. (iii) The variations in the polymer mobility with water content and layer number are primarily associated with the PDADMAC component. No changes in polymer mobility with layer number are observed for dry films.

**5.3. Complexation.** (i) Polycation−polyanion complexation of the PEMs is similar to that of the bulk PEC. (ii) Water−polymer association in the PEMs is much stronger than in the PEC. (iii) The water is always associated with the PSS component in the PEMs and is only significantly associated with PDADMAC when it forms the outer layer.

## 6. Conclusions

Significant differences are observed in the NMR parameters of PEM films of PDADMAC and PSS adsorbed onto colloidal silica as a function of the last adsorbed layer and hydration state. The films adsorb water from the atmosphere into a single mobile reservoir that acts to plasticize the polymer components. The water adsorbed by the film is less mobile and interacts more with the polymer components than in the analogous PEC. This behavior can be attributed to the presence of small inorganic counterions required for electroneutrality of the film and the absence of these ions in the stoichiometric PEC.

The differences in the bulk properties of the component polymers are reflected in the mobility of the surface layer and the water partitioning. In the PEM, water associates more strongly with PSS than with PDAD-MAC, reflecting the relative hygroscopicity of the two polymers. Water associates strongly with PDADMAC only when it forms the outer surface of the film where more small counterions are located. More water is adsorbed into the film when PSS is on the surface, but

that water is systemically less mobile. The constant oscillations of the water chemical shift and mobility with layer number appear to originate from changes in the environment of the water throughout the film and cannot be attributed to water only at the surface.

The polymer components in the film can be seen as two reservoirs, a rigid bulk component, which grows with film thickness, and a more mobile surface component. Polymer mobility is enhanced for PDADMAC-capped films, but this oscillatory mobility trend dampens with film thickness as the chain motion becomes increasingly restricted. The changes in the polymer mobility are primarily associated with the PDADMAC component, reflecting the higher intrinsic mobility of this polymer as compared to that of PSS. The polymer components are intimately mixed and strongly dipolar coupled, leading to $^1$H$-^1$H double-quantum peaks and spin diffusion. Changes in the polymer mobility with film growth reflect a change in regime from nonlinear film growth, the thin film regime, to linear film growth at 3 bilayers. The water in the entire film is effected strongly by the nature of the last layer adsorbed, while observed changes in the polymer dynamics are associated only with the surface layer.

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