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Molecular Dynamics Simulation of Water–Acetonitrile Mixtures in a Silica Slit

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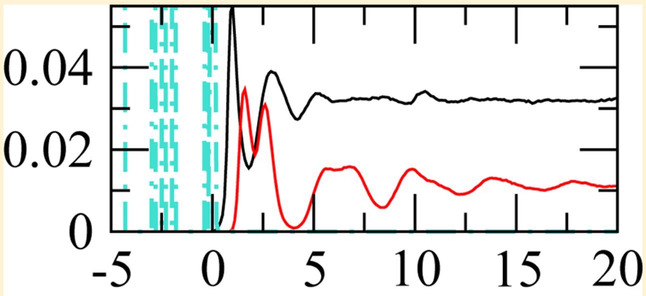
ABSTRACT: Molecular dynamics simulations of aqueous acetonitrile confined in a planar silica slit are presented. It is found, in agreement with experimental observations, that a thin layer of water that excludes acetonitrile is in contact with the hydrophilic silica surface. The organization of the fluid–silica interfacial region is described for fluids with the fraction of water molecules in the system varying from 0 to 1 at 298 K. The width of the slit is set so that the density of the fluid in the central region of the slit is close to the density of the liquid for the temperature and composition of the mixture.



Interfacial structure of water and acetonitrile at a silica interface.

I. INTRODUCTION

This article describes molecular dynamics simulations of water, acetontrile, and their mixtures confined in a planar, hydrophilic silica slit. This configuration is a simple form of the structures employed in hydrophilic interaction chromatography where the mobile phase is exposed directly to a hydrophilic surface such as hydroxylated silica.[1−3] This differs from reversed-phase liquid chromatography where the silica surface is screened by hydrocarbon molecules bonded to the silica surface.[4] There have been several simulation studies of these fluids under confined conditions using a number of model interactions. Confined water has received wide attention.[5−12] Recent studies have addressed confined acetonitrile[13−16] and confined aqueous acetonitrile.[17−19]

There are four types of sytems that are used in the simulation of the confined fluids. Here we consider only the results of those studies that have fully hydroxylated silica surfaces. Some of the studies also considered surfaces with varying degrees of hydrophilicity/hydrophobicity.

The first type of system has a layer of fluid on a silica substrate so that there is both a solid–liquid interface and a liquid–vapor interface. For water[7,9] the nonuniform density profile extends 6–8 Å from the silica surface, while for acetonitrile it extends 15–20 Å from the surface.[15]

In the case of acetonitrile, the layer of molecules next to the surface can be separated into two sublayers with different orientations. The sublayer closer to the surface has dipole moments primarily oriented away from the surface, while the molecules in the other sublayer have dipole moments oriented primarily toward the surface. The observation of this structure leads to the suggestion that a bilayer is formed.[15]

The initial suggestion of this sort of structure was based on an experimental study of acetonitrile in a sol–gel glass with cylindrical pores[20] and was subsequently observed in a simulation.[13] The combined simulation and experimental study of a liquid acetontrile layer on a hydrophilic silica substrate showed that the surface interaction is responsible for the presence of the bilayer rather than confinement in a pore.[16]

The second type of system consists of water confined in a planar slit pore[5] or in a cylindrical pore.[12] In both cases, the pore dimensions are such that the density fluid density in the central part of the pore is that of bulk water. Also, the nonuniform density profile extends only about 6–8 Å from the surface of the pore.

The third type of system consists of a planar slit with the confined fluid in equilibrium with an external bulk liquid. Equilibrium is maintained either by having the slit embedded in a liquid reservoir or by use of Grand Canonical Ensemble Monte Carlo (GCMC) with the chemical potential and temperature set to values for the bulk liquid.

The GCMC method applied to water in a slit of width 13 Å found water at the bulk density in a narrow, 4 Å wide region in the central part of the slit.[8] With narrower slits, the nonuniform density profile next to the surfaces extends from one surface to the other. The GCMC method has also been used to study the filling of a slit as a function of the reservoir pressure of water.[10]

The case of an equimolar water–acetonitrile mixture with a slit embedded in the liquid[17] was examined for slit widths of 15 Å or less. The composition of the mixture in the slit, excluding a tightly bound layer of water that preferentially coats the surfaces, was acetonitrile rich relative to the reservoir composition by a factor of 2 or more.

The fourth type of system consists of a cylindrical pore with the fluid in the pore in equilibrium with a bulk liquid.

The GCMC method has been used to examine water in pores with 20–40 Å diameters.[11] The water in the central

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region of the pore is at the bulk density. A similar study of acetonitrile in the same range of pore diameters found bulk density of the central part of the pore only for the 40 Å diameter pore.[14]

There are two studies of water−acetonitrile mixtures in 30 Å diameter pores that are open to external reservoirs.

The first of these studies had an equimolar mixture in the reservoir.[18] The nonuniform density profiles for both water and acetonitrile extend about 10 Å from the rough surface of the pore. The fluid density approaches the bulk value in the central part of the pore. There is enhanced water and suppressed acetonitrile density near the surface of the pore.

The second study examined three reservoir mole fraction compositions (water/acetonitrile) of 1/3, 1/1, and 3/1.[19] In each case the overall composition of the liquid in the pore is water enhanced and acetonitrile depleted relative to the reservoir composition. There is a water-rich acetonitrile-poor region next to the rough cylindrical surface of the pore. The fluid in the central portion of the pore approaches bulk behavior. Note that the enhancement/depletion measure used in this study is different from the one used in the equimolar slit pore mentioned above.[17] For this reason there is not necessarily a contradiction in the conclusions of the two studies. The surface silanol density for the cylindrical slit is about 20% higher than for the planar slit.

The results from the simulations of type three and type four indicate that when the dimensions of the pore are sufficiently large, the fluid in the central region of the pore has the properties of the reservoir fluid. In practice, sufficiently large dimensions are such that the nonuniform density profiles adjacent to the walls do not extend throughout the pore.

The simulations described here provide an extension of earlier work on systems of the second type and are primarily concerned with the density and orientation profiles of confined aqueous acetonitrile. In each of the simulations, the width of the slit is large enough that the fluid in the central region has the density of a bulk liquid. The composition plus the number density of fluid in the central part of the slit indicates the composition and density of an effective reservoir fluid. The neat fluid cases are included so that the changes in the density and orientation profiles that occur as the composition changes can be compared with the structure of the neat fluids. The description of the solid−liquid interfacial organization of the mixtures as a function of the composition of an effective reservoir fluid is a major outcome of these simulations.

It has been conjectured that the presence of a water-rich layer next to the surface is an important part of the retention mechanism in hydrophilic interaction chromatography where the composition of the water acetonitrile mixture has the mole fraction of water in the 0.15−0.6 range.[2] The simulation results reported here will show how this layer changes with composition of the mobile phase. This should aid in the understanding of the partition of fluids in hydrophilic interaction chromatography.

The models and simulation methods are described in sections II and III. The organization of the density and orientational profiles are presented in section IV. Section V contains a summary of the results obtained. The Appendix contains simulation results for the density of the bulk mixture that is needed when determining the appropriate separation of the silica layers as discussed in section III.

II. MODELS

The slit consists of two parallel slabs with the (1.1.1) face of β-cristobalite arranged so that the density of silanol groups in contact with the confined fluid has a density of 4.53/nm^2. This is the low density case described elsewhere.[7] Each slab contains two Si-layers, three O-layers, and one H-layer. The sequence of the layers, starting with the H-layer in contact with the confined fluid, is H−O−Si−O−Si−O. The three layers closest to the fluid (H−O−Si) are charged, and the other three are uncharged.[5,6] The Coulomb and Lennard-Jones potential parameters for the nonbonded interactions are listed in Table 1. This set of silica parameters has worked well in other simulations of water in silica slits.[5,6,8] The silicon and oxygen sites in the slabs are fixed in space, while the hydrogen sites are bonded to the oxygen sites by harmonic stretch and bend interactions. The bond length is 1 Å, and the harmonic stretch coefficient is 8000 kJ/mol/Å^2. The bond angle is 109.27°, and the harmonic bend coefficient is 835 kJ/mol/rad^2. The hydrogens can move in a circular region but not translate. Each slab is composed of 320 atoms. The x- and y-dimensions of the slabs are 43.85 and 20.143 Å, respectively. The hydrogen layers of the silica slit layers are separated by a distance varying from 33 to 90 Å depending on the composition of the confined fluid. The spacing is adjusted so that the density of the fluid in the middle of the slit is close to the bulk fluid density.[21,22] There are 40 silanol groups on each silica surface in contact with the fluid.

Table 1. Lennard-Jones Parameters and Charges for Water,[23] Acetonitrile (MeCN),[24] and Silica[6a]

		Water	
O	0.65	3.1657	−0.8476
H	0.0		0.4238
		MeCN	
M	0.8167	3.75	0.2690
C	0.50	3.55	0.1290
N	0.50	2.95	−0.3980
		Silica	
Si	0.5336	3.795	0.31
O	0.6487	3.154	−0.71
H	0.0		0.40

[a] The charges on the Si and O sites of silica are only on layers nearest the H sites.

The confined fluid contains a total of 900 molecules. In addition to neat acetonitrile and neat water, five mixtures with varying water content are simulated. The water molecules are modeled using the SPC/E model.[23] The acetonitrile molecules are modeled using the three-site TraPPE-UA model[24] that has been shown to have hydrogen bonding levels with SPC/E water that are in agreement with experiment.[25] As shown in the Appendix, this set of water plus acetonitrile potentials produces the liquid mixture density in close agreement with experimental values. The methyl group in acetonitrile is treated as a united atom. Both the water and acetonitrile molecules are assumed to be rigid. All sites of the fluid molecules and the slab atoms interact with a combination of Lennard-Jones and Coulomb interactions. The potential parameters for like sites are listed in Table 1. The unlike Lennard-Jones parameters are obtained using the Lorentz−Berthelot combining rules[26] as was done in the other simulations discusssed in section I. The Lennard-Jones interactions were truncated, but not shifted, at 10.072 Å.

III. METHODS

The simulation cell has the x- and y-dimensions of the slab and extends for 200 Å in the z-direction so that a variant of the three-dimensional Ewald summation method[27] can be used with periodic boundary conditions in the x- and y-dimensions only to account for the long range Coulomb interactions. As noted above, the long range part of the Lennard-Jones interactions is neglected. The equations of motion of the molecules are integrated using a velocity-Verlet algorithm adapted to use quaternions[28] to describe the orientational degrees of freedom of the rigid molecules.[29] The time step is 1 fs, and the temperature of the fluid was maintained at 298 K by separate Nosé−Hoover thermostats for the translational and rotational degrees of freedom.[30] The time constant for each of the thermostats is 0.5 ps as this provides good temperature stability and control.

A total of seven overall compositions were examined with water/acetonitrile compositions (number of water molecules/number of acetontitrile molecules) of (0/900), (900/0), (90/810), (225/675), (450/450), (675/225), and (810/90). The several mixture cases were generated using a process where the identity of molecules was exchanged. First, a 900 molecule system of acetonitrile was stabilized with the spacing between the hydrogen layers equal to 90 Å. A series of water−acetonitrile mixtures were generated by systematically changing the identity of acetonitrile molecules to water molecules. Once a desired number of water molecules was obtained, the spacing of the slabs was adjusted so that the number density at the center of the slit was close to the bulk density of the model mixture as determined in the Appendix. These simulations are labeled set A. If the width of the slit is so large that the number density of the fluid in the central part of the slit would be significantly less than the bulk density, a cavity will spontaneously form in the interior of the slit while maintaining liquid density in the other parts of the central region.

Next a stabilization run of at least 100 ps was made. Finally a 1 ns run was made to obtain density and orientation measures. This process was used to generate five different mixture compositions.

As a check on the sensitivity of the results to how the systems were prepared, a second set of simulations for the mixtures were developed by starting with an all water system and systematically changing the identity of water molecules to acetonitrile molecules until the desired number of acetonitrile molecules to match the conditions of the first set was obtained. These simulations are labeled set B. The spacing between the slits was adjusted to have the same value as the first set, and the same series of stabilization runs used for set A were made. The results for the stabilized density and orientation measures described below are close to those from the first set and are included when describing average behavoir.

In addition to determining the time averaged center-of-mass density profile, $n(z)$, a center-of-mass orientation profile measure was obtained in terms of the angle, ϕ, between the z-axis of the simulation cell and the dipole moment of the individual molecules. The orientation measure is the time averaged value of $\cos(\phi)$ at position z in the slit. An additional center-of-mass measure, $\cos^2(\phi)$, was also generated. This provides an indication of how uniform the time averaged orientation of the dipole moments is in the central portion of the slit. When $\cos^2(\phi) \approx 1/3$ and $\cos(\phi) \approx 0$, the dipoles are, on average, uniformly distributed. The profiles are generated with a thickness in z of 0.1 Å. In the following figures, $n(z)$ is approximately symmetric about the center of the slit and $\cos(\phi)$ is antisymmetric so that only a part of the full z-dependent profiles is shown. Also it was found that $\cos^2(\phi)$ goes to 1/3 when $\cos(\phi)$ goes to zero. For this reason, the $\cos^2(\phi)$ profiles are not shown.

The volume of the layers used to generate the various profiles is 88.33 Å^3. The bulk acetonitrile number density is 0.0114 Å^{-3} as shown in the Appendix. A layer with that density contains on average one molecule. The bulk water number density is 0.0334 Å^{-3}. A layer at that density contains on average 2.95 molecules. The small z-thickness of the layers makes it possible to resolve small scale features of the profiles that would be lost if thicker layers were used. It does however require long simulation times to obtain stable profiles. A stable profile is one that does not change when the averaging time increases. Several runs with various time durations were made, and it was found that 1 ns was sufficient to obtain stable profiles. Profiles averaged over shorter time intervals are not independent of the averaging time. Profiles for sequential runs of 1 ns duration overlap indicating that the fluctuations in the profiles are small.

The discussion of the profiles makes use of the results for both silica surfaces. Numerical values are averages for the two interfaces; if a feature is said to contain 20 molecules, that number is the average of the content of the feature associated with the two silica surfaces. The two sets of simulations generated from acetonitrile to water (set A) and from water to acetonitrile (set B) are reported separately.

For each of the cases examined, the number density in the central portion of the slit where the density is uniform, n_C, is obtained by counting the number of molecules of each species in that region and then dividing the total number by the volume of that region. The fraction of water molecules in the central region, x_W, is also obtained.

In addition to the spatial extent of the nonuniform density and orientation profiles close to the silica surfaces, the number of acetonitrile molecules in each component of the split peak or bilayer feature observed earlier in a layer of acetonitrile on a silica surface[13,15] is reported. Also, the number of water molecules in a water-rich layer in contact with the silica surface is determined. This layer is a general feature found for all compositions of water−acetonitrile mixtures in contact with silica surfaces and is thought to be an important feature for retention in hydrophilic interaction chromatography.[2,3,31]

IV. RESULTS

In each of Figures 1−7 the position of the hydrogen layer at the left side of the figure is $z = 0$, $n(z)$ is the time averaged number density at position z, and $\cos(\phi)$ is the time averaged cosine of the angle between the molecule dipole moments and the z-axis at positon z. The profiles for $\cos^2(\phi)$ are not displayed as they differ from 1/3 only where $\cos(\phi)$ differs from zero. First we examine the neat acetonitrile, (0/900), and neat water, (900/0), cases.

The results for neat acetonitrile obtained over a 1 ns duration simulation are displayed in Figure 1. The oscillations in $n(z)$ and $\cos(\phi)$ extend about 20 Å from the silica surface. The molecules in the layer closest to the surface have the dipole moment oriented away from the surface, while there is a set of molecules in that layer slightly farther out from the surface with the dipoles oriented toward the surface. The $n(z)$ peak next to the surface is split by about 1 Å and matches the oscillation in $\cos(\phi)$. These features are suggestive of a loose, bilayer

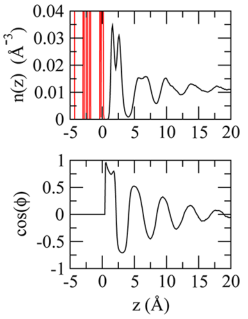

Figure 1. Density and orientation profiles for acetonitrile at 298 K. The vertical lines denote the position of the various layers in the silica with the hydrogen layer centered at $z = 0$. The density in the central region of the slit is 0.0112 molecules/Å^3. The spacing between the hydrogen layers is 90.1 Å.

structure and were observed in other simulations of liquid acetonitrile in contact with a hydrophilic surface using different model interactions.[13,15,16] The value of $\cos^2(\phi)$ in the central portion of the slit is close to 1/3 suggesting that the orientation of the molecules there is uniformly distributed.

As a basis for comparing mixture results, the part of each of the split $n(z)$ peaks that are closer to the silica surface contains 22 molecules and the other part contains 24 molecules. These numbers will change as the overall composition of the confined fluid is varied, and the changes will aid in understanding the corresponding changes in the structure of the bilayer.

The results for neat water are shown in Figure 2. The deviations from the bulk liquid density extend only about 6 Å from the silica surfaces. The orientation of the water molecules deviate from being uniformly distributed, that is, $\cos^2(\phi) \neq 1/3$, only in the same region. The density profile shown here is similar to the one found earlier for water between silica surfaces.[5] Each of the peaks closest the silica surface contains on average 38 water molecules, so the area density is 4.30/nm^2.

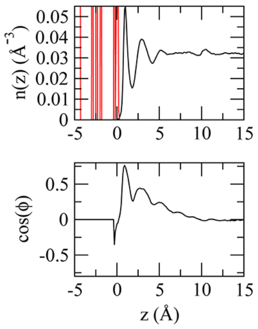

Figure 2. Density and orientation profiles for water. The hydrogen layers are separated by 33.1 Å. The density in the central region of the slit is 0.0314 molecules/Å^3. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at $z = 0$.

Next we examine the density and orientation measure profiles for several compositions of water−acetonitrile mixtures. There are some features of the profiles to consider as the overall composition of the confined fluid changes. There are two aspects of the nonuniform density and orientation profiles of the confined fluid. One is the extent of the nonuniform region away from the silica surface. This is illustrated in the following figures where the profiles for set A are displayed. The differences in the profiles for set B from those for set A are barely visible on the scale of the figures. The second aspect of the profiles is the differences in the number of molecules, N_{Acn}, in the acetonitrile bilayer feature, the number of water molecules, N_{W}, in contact with the silica layer, and the central region density, n_{C}, as a function of the fraction of water molecules, x_{W}, in that region.

These quantities will be introduced in the following paragraphs and will be summarized at the end of this section. The coverage of the silica layer is related to N_{W}, the number of water molecules in the layer, by $(4.53N_{\mathrm{W}}/40)/\mathrm{nm}^2$.

The density and orientation profiles for the (90/810) case are displayed in Figure 3. The spatial order of acetonitrile for this system is less sharp than for the neat acetonitrile case but still extends nearly 20 Å from the silica surfaces. Also, the indication of a bilayer next to the silica surface is clear. Water molecules are fairly uniformly distributed across the slit except for a 1.5 Å region with water in contact with the hydrogen layers. There are 14 molecules in each of these regions for set A and 11 molecules for set B, so nearly 1/3 of the water molecules in the fluid are in close contact with the silica surfaces. The coverage is 1.42/nm^2. Unlike the acetonitrile molecules, there are a few water molecules embedded in the silica surface and have the dipole moment oriented away from the surface. Those molecules slightly further away from the surface have the dipole moment oriented toward the surface. The structure of this water layer has been found to consist of a two-dimensional array of molecules lying at the interstices of the silanol layer.[17]

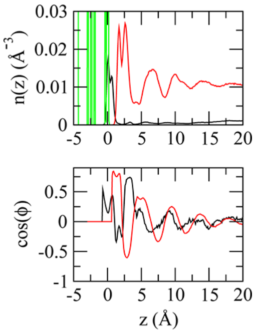

Figure 3. Density and orientation measures for aqueous acetonitrile for the case (90/810). The spacing between the hydrogen layers is 86.1 Å. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at $z = 0$. The black lines are for water, and the red lines are for acetonitrile.

The split peaks for the acetonitrile profile contain 14 molecules for the part closer to the silica surface and 26 for the other part for set A. The corresponding numbers for set B are 18 and 24. The composition distribution of this acetonitrile feature has changed from that of the neat acetonitrile case. There is very little overlap between the water and acetonitrile features. The number density and fraction of water molecules in the central region are, for set A, 0.0115/Å^3 and 0.08. For set B, they are 0.0117/Å^3 and 0.10.

The profiles for the (225/675) case are shown in Figure 4. The spatial order of acetonitrile molecules extends about 15 Å from the silica surface, and the split peak in $n(z)$ suggestion of a bilayer is still present. The nonuniform density of water also extends about 15 Å from the silica surface. Water molecules are broadly distributed across the slit with a substantial but narrow, 1.5 Å wide, region with water molecules next to the hydrogen

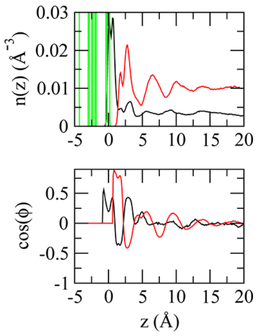

Figure 4. Density and orientation profiles for aqueous acetonitrile for the case (225/675). The hydrogen layers are separated by 76.1 Å. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at *z* = 0. The black lines are for water, and the red lines are for acetonitrile.

layer. That region contains 27 molecules for set A and 28 for set B so the coverage is 3.06/nm^2. The acetonitrile feature contains 9 molecules in the part closer to the silica and 26 molecules in the other part for set A. The corresponding amounts for set B are 9 and 29. The number density and fraction of water molecules in the central region are, for set A, 0.0128/Å^3 and 0.21. For set B, they are 0.0124/Å^3 and 0.17. The correlation measure, cos(ϕ), indicates that the water molecules in the region of the bilayer have dipole moments oppositely oriented to the acetonitrile dipole moments. There is a considerable amount of water in the bilayer region.

The profiles for the (450/450) case are shown in Figure 5. The spatial order for acetonitrile molecules and for the water molecules extends about 10 Å from the surface. The trends noted for the lower water fraction systems are continuing. There are 31 molecules in the water peak next to the silica surface for both set A and set B, and the coverage is 3.51/nm^2. There are 8 acetonitrile molecules in the closer part of the split feature and 20 in the other part for set A. The corresponding numbers for set B are 8 and 25. The number density and fraction of water molecules in the central region are, for set A, 0.0156/Å^3 and 0.43. For set B they are 0.0161/Å^3 and 0.47.

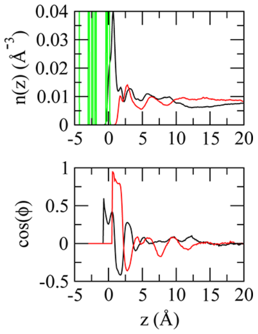

Figure 5. Density and orientation profiles for aqueous acetonitrile for the case (450/450). The hydrogen layers are separated by 60.2 Å. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at *z* = 0. The black lines are for water, and the red lines are for acetonitrile.

The profiles for the (675/225) case are shown in Figure 6. The extent of spatial order of acetonitrile molecules and for water molecules is about 10 Å. The region with water next to the surface is slightly broader than found in lower water concentration cases. The water feature contains 35 molecules for set A and 38 molecules for set B, so the coverage is 4.25/nm^2. The acetonitrile feature has 7 molecules in the closer part and 13 in the other part for set A. The corresponding amounts for set B are 6 and 15. The number density and fraction of water molecules in the central region are, for set A, 0.0237/Å^3 and 0.74. For set B, they are 0.0232/Å^3 and 0.71.

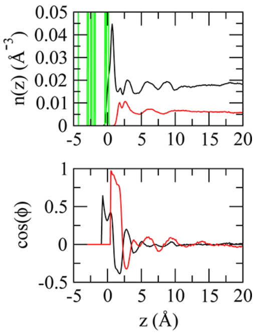

Figure 6. Density and orientation profiles for aqueous acetonitrile for the case (675/225). The hydrogen layers are separated by 42.1 Å. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at *z* = 0. The black lines are for water, and the red lines are for acetonitrile.

The profiles for the (810/90) case are shown in Figure 7. The spatial distribution of acetonitrile molecules is fairly uniform across the slit except for the region next to the silica surface occupied by the water layer. There are 36 molecules in the water region next to the silica surface for set A and 39 molecules for set B, so the coverage is 4.25/nm^2. The water molecules next to, but not overlapping with, the hydrogen layer tend to have dipole moments broadly oriented somewhere between parallel to and toward the surface. In contrast, the water molecules that overlap the hydrogen layer have dipole moments oriented away from the surface. The acetonitrile feature contains 5 molecules in the closer part and 7 molecules in the other part for set A, and the corresponding numbers for set B are 4 and 8. The nonuniform region for acetonitrile extends about 6 Å. The number density and fraction of water molecules in the central region are, for set A, 0.0270/Å^3 and 0.91. For set B, they are 0.0274/Å^3 and 0.89. There are some unusual structures in the water profile that extend about 10 Å from the surface, while the range for the orientation profile is smaller. This is present in the profiles for both set A and set B.

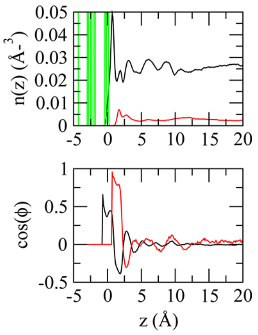

Figure 7. Density and orientation profiles for aqueous acetonitrile for the case (810/90). The hydrogen layers are separated by 36.1 Å. The vertical lines indicate the positions of the silica layers with the hydrogen layer centered at *z* = 0. The black lines are for water, and the red lines are for acetonitrile.

Next we review what has been observed in the simulations. The spatial range of the nonuniform region for neat acetonitrile is about 20 Å from the surface. As water replaces actonitrile, the spatial extent decreases to about 10 Å for the (450/450) case and to about 6 Å for the (810/90) case. For water, the range is about the same as for acetonitrile except for the (810/90) case. The molecules in the water layer next to the surface and in the acetonitrile bilayer have definite orientations relative to the surface. The average orientation of molecules farther away for the silica surface is nearly isotropic.

Figure 8 displays the variation of the density in the center of the slit, n_C, the number of acetonitrile molecules, N_{Acn}, in each part of the bilayer feature, and the number of water molecules, N_W, next to the silica surface. These quantities are plotted as functions of the fraction of water molecules, x_W, in the central region of the slit. The trends for N_W are consistent with limited experimental results.[31]

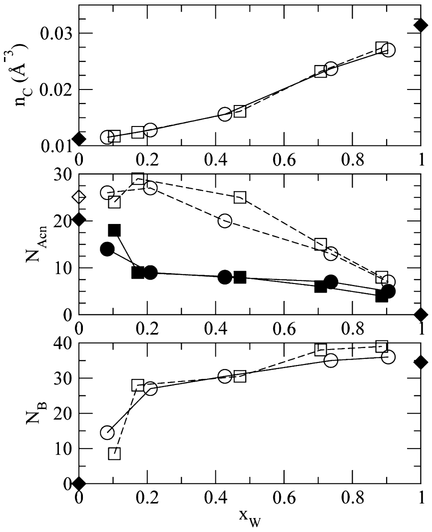

Figure 8. (Upper) Density of the liquid, n_C, in the central part of the slit displayed as a function of the fraction of water molecules, x_W, in that region. In each of the three figures, the diamonds are for the neat fluids, the circles are for set A, and the squares are for set B. Starting from the left, the symbols are for the cases (0/900), (90/810), (225/625), (450/450), (675/225), (810/90), and (900/0). The number of acetonitrile molecules in the bilayer feature, N_{Acn}, is shown in the middle figure. The filled symbols are for the part closer to the silica, and the open symbols are for the other component. The number of water molecules, N_W, in the feature next to the silica surface is shown in the bottom figure.

It is important to note that the symbols for set A and set B for a given set of molecules and property, while close in Figure 8, do not overlap. This indicates that while the set A and set B profiles are stable on the 1 ns time scale, there is some dependence on how the configurations were generated.

These simulations used the low density face of silica with silanol density of 4.53/nm^2. There is an alternative face with a three times higher silanol density of 13.6/nm^2, the high density case.[7] With the much higher charge density on the high density surface, one would expect that the short range ordering of a water acetonitrile mixture would be modified. That has been found for a layer of water in contact with the high density face. Instead of a single peak next to the surface as shown in Figure 2, a well-defined split peak occurs.[7,9] For a mixture one might expect to find modification of the structure of the bilayer.

V. SUMMARY

The fluid mixture−silica interface has a complex structure that has two features of interest. The first is a narrow, 1.5 Å wide, region next to and overlapping with the hydrogen layer that contains only water molecules. The overlap of this water feature with the hydrogen layer is quite small for neat water. The presence of even a small amount of acetonitrile in the mixture increases the amount of overlap. The amount of water in this feature increases with increasing overall water content of the mixture, but the width of the region is independent of the mixture composition for compositions through case (675/225). The water molecules not in this narrow region are more or less uniformly distributed across the slit.

Adjacent to, but not overlapping with, the water feature is a region with a width of 4 Å containing acetonitrile molecules that exhibit a split peak structure. The narrow water feature next to the hydrogen has effectively no overlap with the acetonitrile feature. However, as the water content increases, there is a growing amount of water in same region as the acetonitrile split peak feature.

Also of interest is the range of spatial and orientation structure near the silica surfaces. For acetonitrile the ranges of orientational structure, $\cos^2(\phi) \neq 0$, and of the density are about the same. For case (90/810) it is about 20 Å from the surface. It decreases with increasing water content and is reduced to about 6 Å for the case (810/90).

For water the density profile, $n(z)$, departs from the value in the central part of the slit over about the same range as for acetonitrile from the silica surface for all mixture compositions except for the (810/90) case. The extent of orientational order for water extends through the region of the split peak acetonitrile feature for all mixture compositions. For larger distances from the silica surface, there is no preferred orientation.

A conjectured retention mechanism for hydrophilic interaction chromatography involves the partition of solute molecules into the region containing the water-rich layer next to the silica surface but not into the water feature so that the solutes are in direct interaction with the silanol groups.[1−3] The simulation results examined here show that the number of molecules in the water feature next to the silica surface increases with an increasing amount of water in the mixture. Recall that there are 40 silanol sites on the surface and there are 40 interstices to accommodate water molecules. The density of these sites is 4.53/nm^2. For the (90/810) case there are about 12 water molecules in the feature which amounts to 1.36/nm^2 or about 1/3 of the surface. This leaves 2/3 of the surface available for interaction with solute molecules. For $x_W < 0.5$ the fraction of the surface occupied by water molecules is 2/3 or less. For larger values of x_W, more of the surface is covered by water molecules reducing the area where solute molecules can interact directly with the surface. The use of simulations to investigate the conjecture would be a topic for future studies as called for in a large review of hydrophilic interaction chromatography.[2]

■ APPENDIX: BULK DENSITY DETERMINATION

A series of bulk simulations of the mixtures were made to determine the bulk density of the mixtures at 298 K and 0.1 MPa. In these simulations, 500 molecules were placed in a cubic simulation cell, and the equations of motion for the NPT ensemble with Nosé−Hoover chain dynamics for the thermostats[32,33] were solved using a 1 fs time step and a velocity-Verlet algorithm.[29] The same procedure was used previously to evaluate the hydrogen bonding for water−acetonitrile models.[25] The coupling time for the thermostats is 0.1 ps, and the coupling time for the barostat is 1.1 ps. The thermostat chain for the barostat has a coupling time of 0.11 ps. These values provide good temperature and pressure control. Once the pressure and temperature were stabilized using a 100 ps duration run, a production run of 2 ns duration was made so that the uncertainty in the density of the mixture would be small. The results of these simulations are displayed in Figure 9.

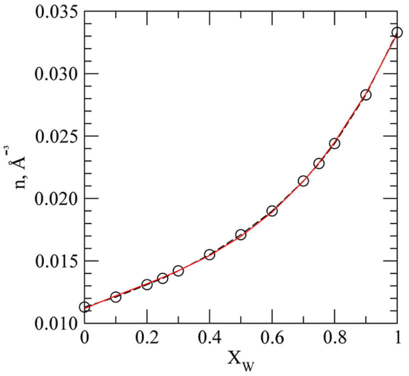

Figure 9. Density, *n*, of the model water−acetonitrile mixtures at 298 K and 0.1 MPa shown as a function of X_W, the mole fraction of water. The circles are the simulation results, and the red curve is a cubic fit.

The uncertainty in the density is less than ±1%. When compared with the experimentally determined densities,[21,22] the simulation results underestimate the density by less than 1%. The red curve in Figure 9 can be represented by the cubic form $n = 0.011\,19 + 0.010\,738X_W - 0.008\,035X_W^2 + 0.019\,289X_W^3$, where X_W is the mole fraction of water in the bulk mixture.

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Notes

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