

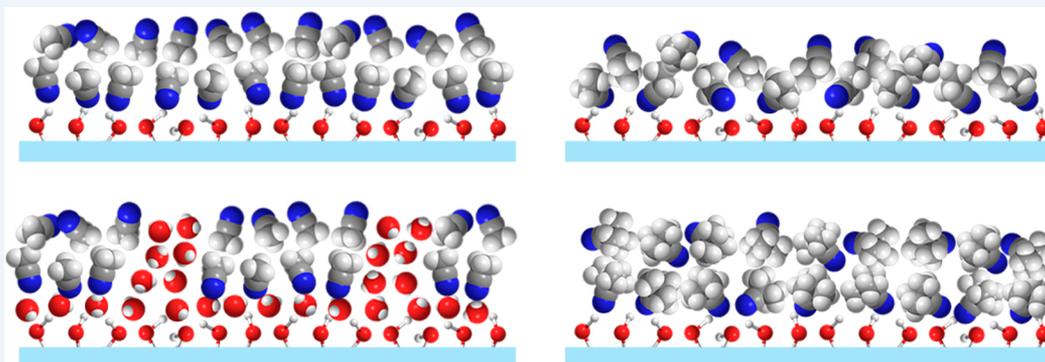
Nitriles at Silica Interfaces Resemble Supported Lipid Bilayers

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CONSPECTUS: Nitriles are important solvents not just for bulk reactions but also for interfacial processes such as separations, heterogeneous catalysis, and electrochemistry. Although nitriles have a polar end and a lipophilic end, the cyano group is not hydrophilic enough for these substances to be thought of as prototypical amphiphiles. This picture is now changing, as research is revealing that at a silica surface nitriles can organize into structures that, in many ways, resemble lipid bilayers. This unexpected organization may be a key component of unique interfacial behavior of nitriles that make them the solvents of choice for so many applications.

The first hints of this lipid-bilayer-like (LBL) organization of nitriles at silica interfaces came from optical Kerr effect (OKE) experiments on liquid acetonitrile confined in the pores of sol–gel glasses. The orientational dynamics revealed by OKE spectroscopy suggested that the confined liquid is composed of a relatively immobile sublayer of molecules that accept hydrogen bonds from the surface silanol groups and an interdigitated, antiparallel layer that is capable of exchanging into the centers of the pores.

This picture of acetonitrile has been borne out by molecular dynamics simulations and vibrational sum-frequency generation (VSFG) experiments. Remarkably, these simulations further indicate that the LBL organization is repeated with increasing disorder at least 20 Å into the liquid from a flat silica surface. Simulations and VSFG and OKE experiments indicate that extending the alkyl chain to an ethyl group leads to the formation of even more tightly packed LBL organization featuring entangled alkyl tails. When the alkyl portion of the molecule is a bulky *t*-butyl group, packing constraints prevent well-ordered LBL organization of the liquid. In each case, the surface-induced organization of the liquid is reflected in its interfacial dynamics. Acetonitrile/water mixtures are favored solvent systems for separations technologies such as hydrophilic interaction chromatography. Simulations had suggested that although a monolayer of water partitions to the silica surface in such mixtures, acetonitrile tends to associate with this monolayer. VSFG experiments reveal that, even at high water mole fractions, patches of well-ordered acetonitrile bilayers remain at the silica surface. Due to its ability to donate and accept hydrogen bonds, methanol also partitions to a silica surface in acetonitrile/methanol mixtures and can serve to take the place of acetonitrile in the sublayer closest to the surface.

These studies reveal that liquid nitriles can exhibit an unexpected wealth of new organizational and dynamic behaviors at silica surfaces, and presumably at the surfaces of other chemically important materials as well. This behavior cannot be predicted from the bulk organization of these liquids. Our new understanding of the interfacial behavior of these liquids will have important implications for optimizing a wide range of chemical processes in nitrile solvents.

■ INTRODUCTION

Nitriles are some of the most widely used solvents in chemistry.^{1–3} The nature of nitriles gives these liquids the ability to solvate a broad range of species, and the interplay between polar/polar and nonpolar/nonpolar interactions leads

to interesting intermolecular ordering.^{4–6} Although the ordering in liquid acetonitrile can be described largely in terms of

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repulsive interactions,⁷ there is also a propensity for dipole pairing.^{4,5} In longer-chain nitriles, the increasing importance of nonpolar/nonpolar interactions with decreasing temperature leads to changes in ordering⁴ that are reflected in dynamics.⁶

The balance of interactions in nitriles can be disrupted by a cosolvent. For instance, acetonitrile is completely miscible in water. However, acetonitrile/water mixtures are structurally inhomogeneous, featuring water-rich regions and acetonitrile-rich regions.^{8,9} This unusual organization is partially responsible for the exceptional performance of this mixture in separation technologies such as hydrophilic interaction liquid chromatography (HILIC).¹⁰

Research performed by our groups and others has led to the discovery that proximity to a polar solid interface can exert a profound influence on the organization of liquid nitriles. Indeed, at silica surfaces these liquids can form structures that, in many regards, are reminiscent of supported lipid bilayers. Remarkably, a nonpolar moiety as small as a methyl group is sufficient to lead to this type of organization. This lipid-bilayer-like (LBL) structure can repeat for 20 Å or more into the bulk liquid, with increasing disorder as the distance from the interface increases.

In this Account, we discuss recent progress in understanding the organization and dynamics of nitriles at silica interfaces. We begin by discussing the experiments and simulations that led to the discovery of LBL organization of nitriles at silica surfaces, and the relationship of this organization to dynamics. We then consider how interfacial organization and dynamics are influenced by changing the alkyl tail or by a cosolvent. Finally, we discuss the implications that the surprising organization of nitriles at silica interfaces has for interfacial chemical processes.

■ PREVIOUS WORK

Jonas and co-workers' NMR experiments probing the orientational relaxation of acetonitrile confined in silica sol-gel glasses¹¹ were the inspiration for the research described here. Sol-gel glasses can be prepared synthetically and feature tortuous, roughly cylindrical pores occupying approximately half of the volume of the amorphous silica.¹² The average pore diameter can be controlled, ranging from ~25 to hundreds of angstroms, and the pore size distribution is typically relatively monodisperse ($\pm 10\%$).¹² Silanization chemistry^{13,14} can be used to change the chemical nature of the pore surfaces throughout the material.

Jonas' experiments probed the influence of orientational relaxation of confined acetonitrile- d_3 on the spin-lattice relaxation of deuterium and ^{14}N .¹¹ Spin-lattice relaxation occurs on a much longer time scale than does orientational relaxation and so effectively averages over the orientational dynamics of the confined liquid. Spin-lattice relaxation is faster in confinement, with pores of smaller diameters exhibiting faster relaxation.¹¹ These results were interpreted in terms of a two-state model, in which molecules in the pore centers exhibit bulk-like orientational dynamics and molecules at the pore surfaces have inhibited dynamics.¹¹ By assuming a surface-layer thickness of one molecular length, the surface orientational relaxation time at room temperature was estimated to be ~10 ps (compared with ~1.0 ps in the bulk). The activation energy for orientational relaxation in the inhibited surface layer was found to be somewhat larger than that in the bulk liquid.¹¹

With these results in mind, in 1998 Fourkas and co-workers used optical Kerr effect (OKE) spectroscopy to study orientational relaxation of acetonitrile in sol-gel monoliths.¹⁵

In OKE spectroscopy,^{16–18} a linearly polarized pump pulse induces an orientational anisotropy in a liquid, creating a transient birefringence that is measured by a probe pulse. This birefringence decays via collective reorientation. The birefringence decay is mapped out by scanning the delay time between the pulses.

OKE spectroscopy measures the orientational correlation function of the liquid¹⁹ and therefore provides a more detailed picture of the liquid dynamics than does NMR. Although the orientational correlation function of bulk acetonitrile decays exponentially, OKE decays in confinement fit well to the sum of three exponentials.^{15,20} At a given temperature, the same three exponential decay components are found in all pore sizes, albeit with different amplitudes. The fastest component has a correlation time matching that of the bulk liquid. The second component has a correlation time that is ~2–4 times longer than the first (depending on temperature), whereas the final component has a correlation time that is ~15 times longer than the first.

The simplest interpretation of these correlation functions is that there are three independently relaxing populations. To test this idea, OKE decays were measured in different pore sizes over the entire liquid range of acetonitrile. According to the Debye–Stokes–Einstein relation,²¹ the orientational correlation time scales with viscosity divided by temperature. The viscosity of a bulk simple liquid is therefore expected to be proportional to the product of the orientational correlation time and the temperature. Accordingly, we can define an effective viscosity that corresponds to each of the longest two orientational correlation times. In simple liquids, viscosity generally follows Arrhenius behavior,²² as is observed for the bulk viscosity and the two effective viscosities (Figure 1A).^{15,20} The bulk viscosity and the effective viscosity corresponding to the slowest relaxation component have nearly the same activation energy, as has been observed for other confined liquids.²³ The activation energy corresponding to the effective viscosity for the intermediate relaxation component is considerably smaller than the other two, indicating that this system cannot be understood based on three dynamic populations that remain distinct throughout the course of relaxation.

An alternative model was developed in which the confined liquid is divided into a bulk-like population in the pore centers and an interfacial population with inhibited dynamics.^{15,20} We assumed that the slowest exponential arises from orientational relaxation of this interfacial population, in which some or all of the acetonitrile molecules accept hydrogen bonds from silanol groups (which typically have a surface density between 3/nm² and 6/nm² on silica, depending the substrate's thermal history²⁴). We also assumed that some of the interfacial population could exchange into the bulk-like population on a time scale faster than that of interfacial reorientation, providing a new channel for orientational relaxation of interfacial molecules. A kinetic scheme based upon this model yields decays that are essentially triexponential, with the lower activation energy for the intermediate exponential being related to the fact that this exponential largely reflects translational rather than orientational diffusion.^{15,20}

Based on this model, it is possible to use the amplitudes of the three exponentials to determine the fractional populations of nonexchangeable and exchangeable interfacial molecules and thereby the thickness of these populations (assuming that the nonexchangeable population is the closest to the surface).²⁰

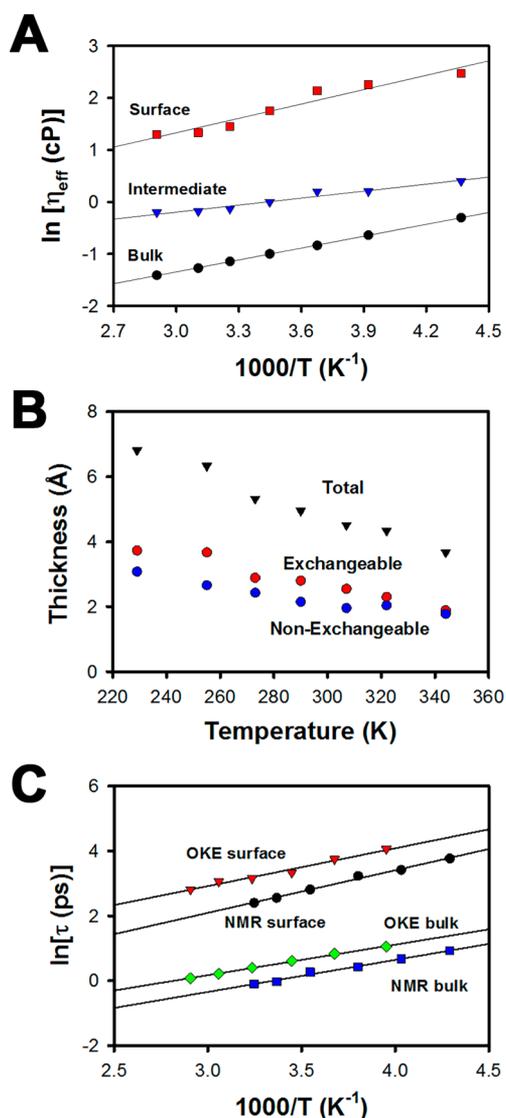


Figure 1. Temperature dependence of (A) the effective viscosity corresponding to the three exponentials in the OKE decays and (B) the estimated thickness of the surface sublayers for acetonitrile confined in silica sol-gel glasses. (C) Bulk and surface orientational correlation times of acetonitrile- d_3 from NMR and OKE experiments. Adapted with permission from ref 20. Copyright 1999 American Institute of Physics.

The estimated thicknesses, shown as a function of temperature in Figure 1B, are identical to within experimental uncertainty and increase with decreasing temperature.

That the NMR single-molecule orientational correlation time and the OKE collective orientational correlation time differ by a multiplicative factor reflects the degree of parallel ordering in the liquid.²⁵ In bulk acetonitrile- d_3 , this constant is essentially independent of temperature (Figure 1C). The surface-layer thickness derived from OKE data can be used to determine the surface relaxation time from Jonas' NMR data.¹¹ Arrhenius plots for the OKE and NMR surface relaxation times are virtually parallel, but are separated by a larger constant than those for the bulk liquid (Figure 1C).²⁰ These results support the exchange model and indicate that there is a stronger propensity for parallel ordering at the pore surfaces than in the bulk.²⁰

Other experiments give important clues as to the nature of the surface populations. First, exchange of the silanol hydrogens with deuterium does not affect the OKE decays, indicating that hydrogen bonds to acetonitrile are not broken in the observed relaxation.²⁰ Second, when the pore surfaces are rendered hydrophobic through silanization, the relaxation becomes biexponential,²⁰ resembling that of confined liquids without specific interactions with the pore surfaces.²³ These pieces of evidence led to the proposal that the nonexchangeable population is composed of molecules that accept hydrogen bonds from surface silanol groups and are oriented roughly along the surface normal, whereas the exchangeable population is composed of molecules that are interdigitated among the tethered molecules, and, although less ordered, tend to point in the opposite direction.

Kittaka et al. used infrared absorption to study adsorption of acetonitrile vapor in MCM-41, porous amorphous silica glasses.²⁶ Their results are in general agreement with the above picture. At low vapor pressures, the only $\text{C}\equiv\text{N}$ stretching peak observed corresponds to cyano groups that accept hydrogen bonds. As the vapor pressure increases, this peak saturates and one corresponding to non-hydrogen-bonded cyano groups appears. These observations likely reflect increasing LBL organization during the capillary condensation process.

Morales and Thompson performed molecular dynamics (MD) simulations that largely support the LBL picture of acetonitrile confined in cylindrical amorphous silica pores.²⁷ They observed interfacial structuring into two distinct orientational sublayers, much as had been predicted from OKE data. The first sublayer, in which molecules accept hydrogen bonds from the silica surface, is highly ordered, whereas the second sublayer is less so due its molecules having fewer orientational constraints. They further demonstrated that this ordering does not require hydrogen bond donation from the surface, so long as the surface charge attracts the nitrile groups.²⁷

These results paint a picture in which the organization of acetonitrile at silica surfaces bears a substantial resemblance to that of a supported lipid bilayer, with a nonpolar alkyl layer sandwiched between two polar layers of cyano groups. The ability to form a LBL structure with methyl groups as the alkyl portion is surprising and leads to many interesting questions. Is the ability to form LBL organization related to confinement, or does it extend to flat or even convex surfaces? How is this organization affected by the nature of the alkyl tail? How is this organization reflected in orientational dynamics? Does this organization persist in the presence of a cosolvent? What role might this organization play in chemical processes? Such questions motivated us to study nitriles at silica interfaces using a combination of ultrafast spectroscopy and MD simulations.

■ ORGANIZATION AND DYNAMICS OF ACETONITRILE AT SILICA INTERFACES

To test the dynamic model described above, Cheng, Morrone, and Berne performed MD simulations of acetonitrile confined in cylindrical amorphous silica pores with 22 and 44 Å diameters.²⁸ They observed the same type of LBL structure reported by Morales and Thompson.²⁷ Cheng, Morrone, and Berne further explored the dynamics of the confined liquid, finding that the overall orientational correlation function, $C(t)$, can be approximated²⁸ using

$$C_{\text{app}}(t) = \chi_s S(t) C_s(t) + \chi_b C_b(t) + \chi_s (1 - S(t)) C_b(t) \quad (1)$$

Here, χ_s and χ_b are the fractions of surface and bulk-like molecules, respectively, $C_s(t)$ and $C_b(t)$ are the corresponding orientational correlation functions, and $S(t)$ is the probability that a molecule at the surface at time 0 is still there time t later. As shown in Figure 2A, $C_{\text{app}}(t)$ provides a good description of

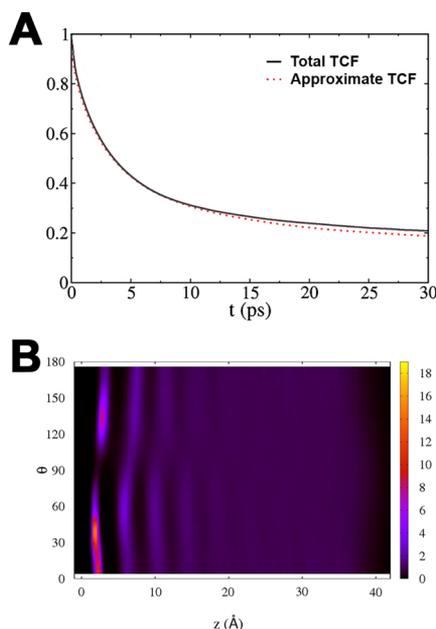


Figure 2. (A) Simulated orientational correlation function for acetonitrile in a 24 Å pore computed directly (black) and estimated from eq 1 (red). Adapted with permission from ref 28. Copyright 2012 American Chemical Society. (B) Joint center-of-mass density and orientation distribution for acetonitrile at a flat silica surface located at $z = 0$. Angles $<90^\circ$ indicate cyano groups that point toward the surface. The sigmoidal contours are indicative of LBL organization. Adapted with permission from ref 31. Copyright 2010, American Chemical Society.

$C(t)$, supporting the exchange model. Norton and Thompson also performed simulations that support the exchange model²⁹ but demonstrated that this model works essentially equally well over a substantial range of assumed thicknesses of the dynamically inhibited surface layer. Thus, the surface-layer thickness may not be able to be determined uniquely by fitting experimental data to such a model.

Hu and Weeks performed MD simulations that revealed the same LBL structure for acetonitrile at flat, idealized, fully hydrated silica surfaces.³⁰ Remarkably, this layering repeats itself, becoming more disordered with each repetition (Figure 2B). Remnants of the LBL structure persist for over 20 Å into the bulk liquid. As in the second sublayer of the surface LBL structure, subsequent layers have full conformational freedom, which leads to the eventual dissipation of the alternating polar and nonpolar layers.³¹ These results show clearly that the layering observed in simulations in silica pores is not related to the pore curvature, but rather to silica itself. The same phenomenon likely occurs for acetonitrile at a wide variety of polar solid surfaces.

Ding et al. performed complementary vibrational sum-frequency generation (VSG) experiments on liquid acetonitrile at an amorphous quartz interface.³¹ VSG^{32,33} is a second-

order nonlinear optical spectroscopy in which an infrared beam and a near-infrared or visible probe beam impinge on a surface, generating a signal at $\omega_{\text{sig}} = \omega_{\text{IR}} + \omega_{\text{probe}}$. Within the electric dipole approximation, VSG is not allowed in an isotropic medium, and so the signal arises entirely from the interfacial region, where centrosymmetry is broken. Signal is generated when the IR frequency is resonant with a vibrational mode that is both IR and Raman active.

Shown in Figure 3A are VSG data for acetonitrile at the silica/liquid (SL) interface in the C–H stretching region of the

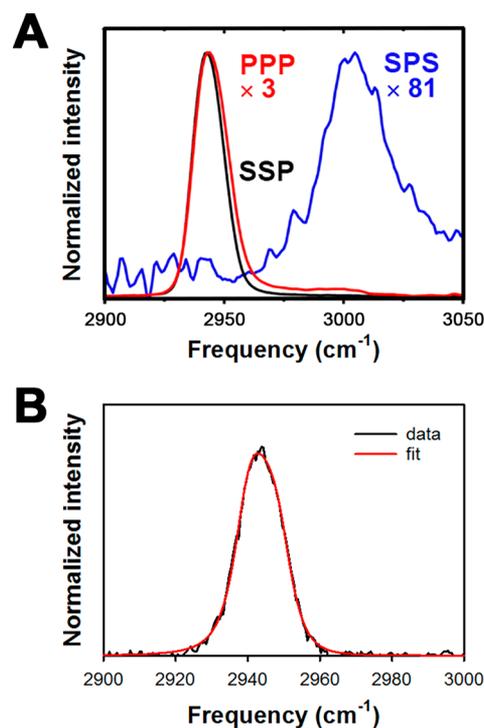


Figure 3. (A) VSG data for acetonitrile at the SL interface under SSP (black), PPP (red) and SPS (blue) polarization conditions. Adapted with permission from ref 34. Copyright 2013 American Chemical Society. (B) Fit of the SSP data to the magnitude squared of two oppositely phased Lorentzians with different center frequencies.

spectrum.³⁴ Under SSP polarization conditions (polarizations are listed in the order signal, probe, IR), which emphasize molecules with IR transition dipoles that have a projection along the surface normal,^{32,33} a strong peak is observed for the symmetric methyl stretch (r^+).³¹ The corresponding absence of the asymmetric stretch (r^-) in the SSP spectrum suggests that the molecules are oriented roughly perpendicular to the interface.

A free lipid bilayer is roughly centrosymmetric, which would suggest that the LBL organization of acetonitrile would not lead to a strong VSG signal. A supported bilayer can exhibit greater asymmetry, and indeed our simulations show that the second sublayer of the surface bilayer of acetonitrile is more disordered than the first.³¹ However, this difference in organization alone is not sufficient to explain a strong VSG signal. The asymmetry of the r^+ peak suggests that the frequency of this mode is slightly different for the two sublayers,³¹ and hydrogen bonding to the cyano group is known to cause a slight shift in this mode.³⁵ The r^+ peak can be fit well to the square of a sum of two Lorentzian features of opposite sign and shifted center

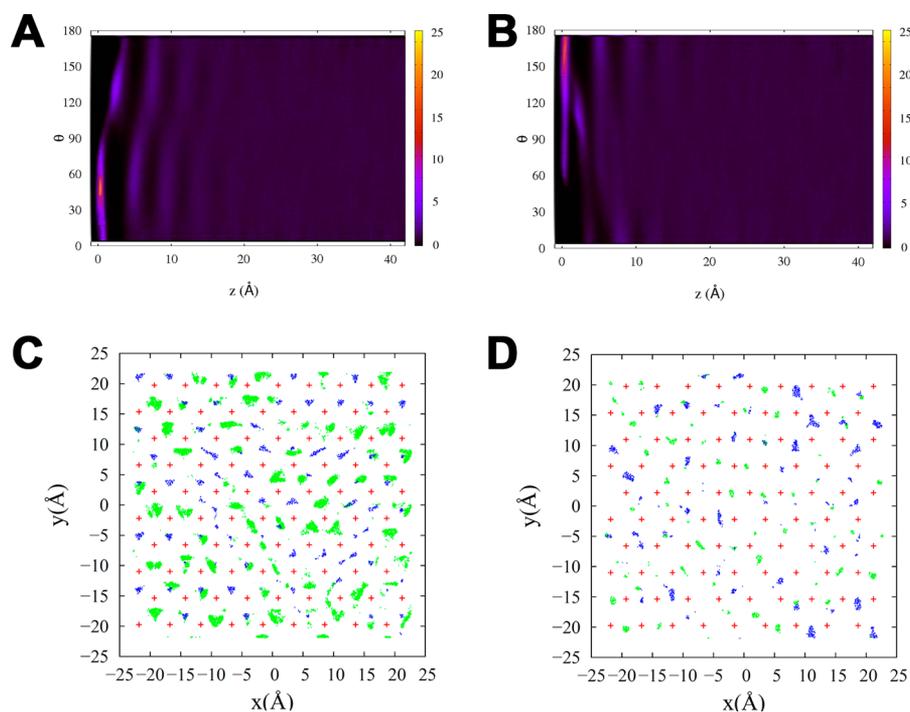


Figure 4. Joint distribution of the cyano group density and the orientation of the (A) cyano and (B) methyl groups of propionitrile at a flat silica surface located at $z = 0$. Angles $<90^\circ$ indicate functional groups that point toward the surface. Spatial probability distribution for the carbon atom bonded to the cyano group in (C) acetonitrile and (D) propionitrile at a flat silica surface. Green and blue represent carbon atoms in the first and second sublayers, respectively. Red crosses denote the sites of surface oxygen atoms. Adapted with permission from ref 39. Copyright 2012 American Chemical Society.

frequencies (Figure 3B), supporting the model of independent spectral contributions from the two sublayers.³¹

The VSG signal is weak under SPS polarization conditions, which emphasize molecules that have an IR transition dipole along the interface.^{32,33} The strong r^+ signal under SSP polarization conditions coupled with the absence of an SPS signal for this mode indicates that the r^+ transition dipoles have a large projection along the interface normal.³⁶ The r^- transition dipole should therefore have an equally large projection along the interface, yet this mode is nearly absent from the SPS spectra. This result highlights the fact that VSG spectroscopy is sensitive to both orientation and orientational dynamics.^{33,37} Reorientation has a stronger effect on SPS spectra than on SSP spectra, and asymmetric modes are especially prone to being washed out by reorientation.^{33,37} Liu and Fourkas have performed simulations that confirm that the spinning motion of acetonitrile is rapid at the SL interface and leads to an extremely weak r^- SPS signal.³⁸

■ NITRILES WITH LARGER ALKYL GROUPS

Given that acetonitrile forms repeating LBL structures at silica interfaces, what can be expected to happen when the hydrocarbon tail is longer or more complex? To address this question, simulations³⁹ and experiments⁴⁰ were performed on liquid propionitrile (ethyl cyanide) at the interface with amorphous quartz. The bent propionitrile might foster substantially different interfacial organization than the linear acetonitrile.

Liu et al. performed MD simulations of liquid propionitrile at an idealized fully hydrated silica interface.³⁹ As shown in Figure 4A, propionitrile also adopts a repeating LBL organization at this interface. The ordering of the CN groups of propionitrile is

even stronger than that in acetonitrile, as is evidenced by the localization of the peak closest to the interface. Only a tiny fraction of the propionitrile cyano groups in the first sublayer ($z < 2.5$ Å) are roughly parallel to the interface, and none have a substantial projection away from the interface.³⁹

In acetonitrile, the methyl and cyano group orientations are necessarily completely correlated, but in propionitrile this correlation is only partial. In Figure 4B, we show the propionitrile methyl orientation as a function of the CN position. In the first sublayer, the methyl groups tend to point away from the interface, although a substantial number are also roughly parallel to the interface.³⁹ In the second sublayer, however, the majority of the methyl groups lie roughly parallel to the interface, and none point away from the interface.³⁹

Together, these data indicate that propionitrile forms a compact, interfacial LBL structure in which the alkyl groups are entangled. Indeed, even though propionitrile is considerably larger than acetonitrile, the 4.9 Å thickness of the surface LBL layer in propionitrile is only slightly larger than the 4.5 Å thickness in acetonitrile. These differences in organization should be reflected in differences in conformational freedom. To gain insight into this issue, in Figure 4C,D we compare the positional spread of the carbon atoms bonded to the cyano groups of acetonitrile and propionitrile, respectively. The red crosses indicate the positions of surface silanol groups, and the green and blue regions denote the most likely positions of these carbon atoms in the first and second sublayers of molecules, respectively, over 300 ps of simulation time. Although the liquids are similar in the first sublayer, there is strikingly less conformational freedom in the second sublayer of propionitrile. Alkyl-group entanglement leads to the formation of a substantially more rigid surface LBL structure in propionitrile than in acetonitrile.³⁹

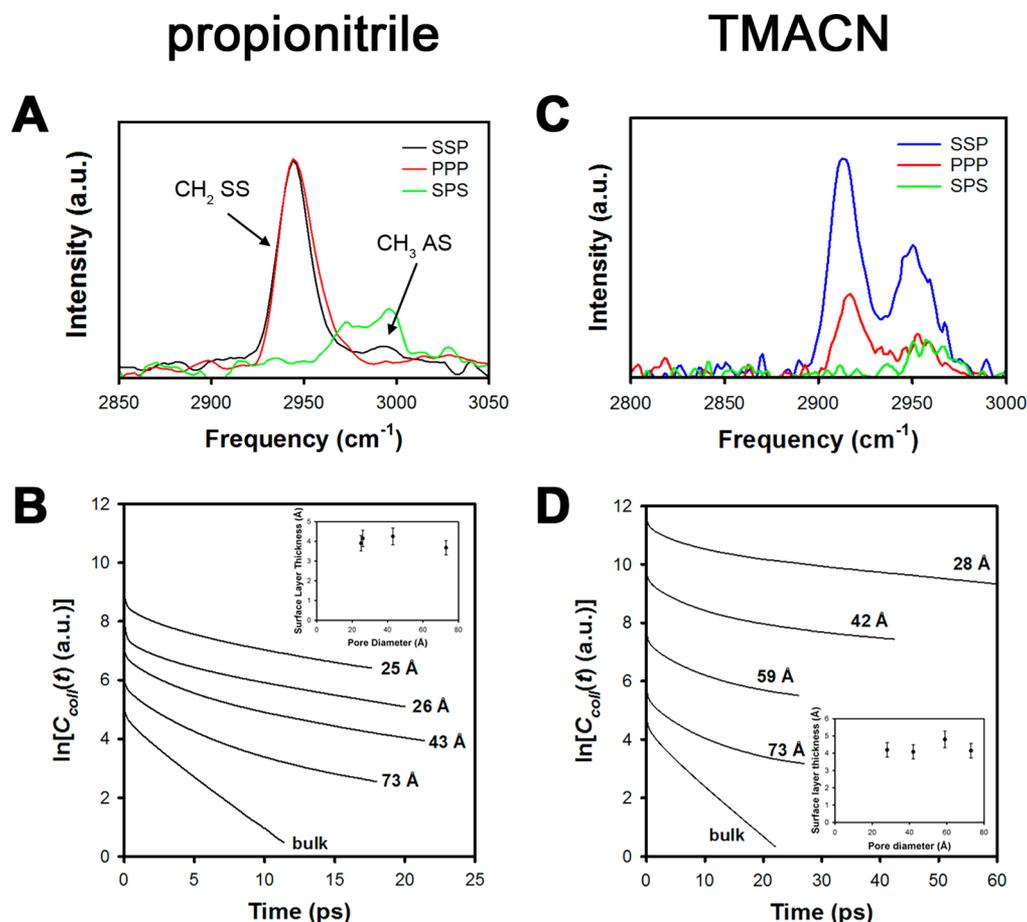


Figure 5. VSGF spectra at the SL interface (A and C) and OKE decays in sol–gel pores of different diameters (B and D) for propionitrile (A and B) and TMACN (C and D). Insets in panels B and D are estimated thicknesses of the dynamically inhibited surface layers for each liquid. Propionitrile plots adapted with permission from ref 40. Copyright 2012 American Chemical Society. TMACN plots adapted with permission from ref 42. Copyright 2012 American Chemical Society.

Ding et al. complemented these studies with VSGF and OKE experiments on propionitrile at amorphous quartz interfaces.⁴⁰ The VSGF spectrum of propionitrile at the SL interface is remarkably simple, being dominated by the methylene symmetric stretch (d^+) peak (Figure 5A). The absence of a strong r^+ peak indicates that the distribution of methyl group orientations is broad, in general agreement with simulation.³⁹ Fitting shows that the d^+ peak arises from two oppositely phased Lorentzians with a small frequency shift between them.⁴⁰ As in the case of the r^+ mode of acetonitrile at the SL interface, these two Lorentzian features presumably arise from the hydrogen-bonded molecules in the first sublayer and the non-hydrogen-bonded molecules in the second sublayer. Overall, the VSGF data agree well with simulation results.

OKE data for propionitrile confined in sol–gel glasses decay biexponentially at room temperature, with one time constant matching the 2.98 ps collective orientational correlation time of the bulk liquid and the other being 13.3 ps (Figure 5B).⁴⁰ The amplitudes of these decays indicate that the thickness of the dynamically inhibited surface layer is ~ 4 Å (Figure 5B, inset), in good agreement with simulation. It is possible that the 13.3 ps collective orientational decay time corresponds to the second sublayer at the surface and that there is an additional exponential corresponding to the first sublayer that is too slow to observe in these experiments. However, simulations suggest that even in the second sublayer, the majority of the

orientational dynamics involves the methyl end of the molecule.⁴¹ The fact that the relaxation in the second sublayer is more than four times slower than that in the bulk (compared with somewhat more than twice as slow as the bulk relaxation in the case of confined acetonitrile) is consistent with the compact, entangled LBL organization in propionitrile leading to considerably slower dynamics than in acetonitrile and inhibiting exchange into the bulk-like population.

Due to steric constraints, nitriles with bulky alkyl groups should not be able to form well-ordered LBL structures. Ding et al. undertook spectroscopic studies of trimethyl acetonitrile (*t*-butyl cyanide, TMACN).⁴² VSGF spectra of this liquid at the amorphous quartz interface are complex but largely in line with the expectation that this liquid cannot form an organized LBL structure (Figure 5C). OKE decays of TMACN confined in silica pores once again are biexponential (Figure 5D), in this case with one time constant matching that of the bulk liquid and the other being approximately an order of magnitude longer. The surface layer thickness is approximately 4.3 Å (Figure 5D, inset). These results suggest that the slower exponential arises from a single layer of molecules that are hydrogen bonded to the surface silanol groups of the pores.

MIXTURES OF NITRILES AND OTHER SOLVENTS

As mentioned above, acetonitrile/water mixtures are important solvents for hydrophilic interaction liquid chromatography.¹⁰ In

an attempt to gain a deeper understanding into HILIC, the properties of this solvent mixture at silica surfaces have been the subject of a number of recent simulation studies.^{43,44} If present, water tends to form a monolayer at the silica surface. Remarkably, these studies indicate that acetonitrile can form LBL structures on top of this monolayer of water, even when the acetonitrile mole fraction is low. It is difficult to simulate a surface that is large enough to delve into the structure of these LBL structures along the interface, but VSGF is well suited to this task.

Rivera et al. investigated acetonitrile/water mixtures at the amorphous quartz interface.³⁴ The width of the r^+ peak of acetonitrile remains essentially constant from the neat liquid down to the lowest acetonitrile mole fraction studied, 0.1 (Figure 6A). Because this peak arises from two oppositely

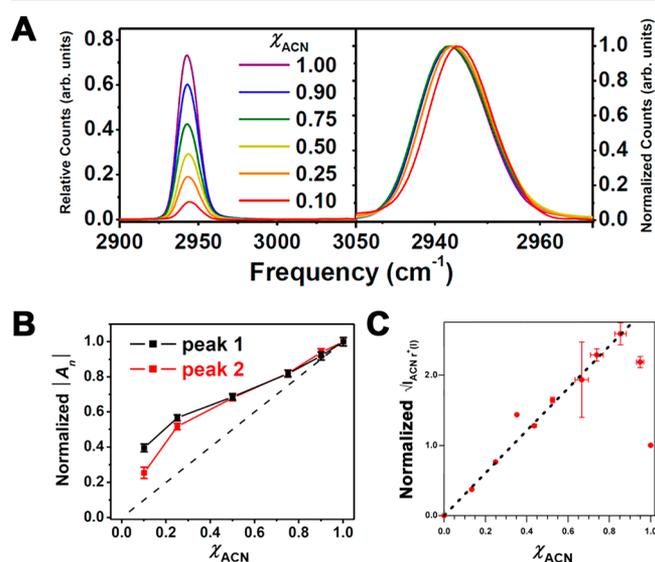


Figure 6. (A) VSGF spectra in the methyl stretching region for acetonitrile/water mixtures at a silica surface. (B) Amplitudes of the two Lorentzian components of the fits to the spectra. (C) Square root of the VSGF intensity for acetonitrile/methanol mixtures at a silica surface. The dashed lines in panels B and C indicate the expected results if the surface and bulk compositions are identical. Panels A and B adapted with permission from ref 34. Copyright 2013 American Chemical Society. Panel C adapted with permission from ref 45. Copyright 2014 American Chemical Society.

phased Lorentzian features,³⁴ LBL structures appear to persist even at high water mole fractions. This peak blue shifts with increasing water mole fraction, suggesting that acetonitrile molecules are becoming increasingly associated with water.³⁴ The intensity of the VSGF signal is proportional to the square of the number of molecules being probed,^{32,33} and so the square root of the signal would be expected to be linear in the acetonitrile mole fraction if the surface composition mirrors the bulk composition. However, the signal is greater than expected at low acetonitrile mole fractions, indicating that acetonitrile partitions to the surface (Figure 6B).

In conjunction with additional evidence from line shape analysis of VSGF spectra,³⁴ these results indicate that acetonitrile bilayers persist at the SL interface even in the presence of a large excess of water. The spectroscopic data suggest that the LBL structures exist as patches rather than as continuous structures that are infiltrated with water.

A different story emerges from VSGF studies of acetonitrile/methanol mixtures at the amorphous quartz interface.⁴⁵ At low methanol mole fractions, the signal from acetonitrile increases substantially, before decreasing again at methanol mole fractions on the order of 0.15 (Figure 6C). These results suggest that methanol molecules partition to the silica surface. Although acetonitrile can hydrogen bond to a monolayer of water on silica, the methyl group of methanol may largely prevent such hydrogen bonding. Instead, the methyl groups of methanol molecules can substitute for those of acetonitrile in the first sublayer of the surface LBL structure. The reduction in destructive interference between acetonitrile methyl groups in the two sublayers leads to an overall increase in the signal from acetonitrile until the methanol mole fraction is large enough that the surface is saturated with methanol or until methanol begins to replace acetonitrile in the second sublayer.

CONCLUSIONS

The studies described here paint the first pieces of a new picture of liquid nitriles at silica surfaces. Much of the canvas remains blank and filling it in will be fascinating. Different alkyl groups or mixtures of alkyl groups offer the possibility of engineering the properties of the hydrophobic portion of the surface LBL structure, for instance. Additional control of LBL properties may be achieved using polyfunctional nitriles or a range of other cosolvents. Other classes of small molecules that are not typically considered to be amphiphiles may exhibit similar behavior.

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Notes

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John D. Weeks received a B.A. in physics at Harvard in 1965, and a Ph.D. in chemical physics at the University of Chicago under the supervision of Stuart Rice. He had postdoctoral positions at UCSD with Kurt Shuler and at Cambridge University with Philip Anderson. He was a Member of Technical Staff at AT&T Bell Laboratories from 1971 to 1990 and moved to the University of Maryland in 1991, where he is Distinguished University Professor in the Department of Chemistry and Biochemistry and the Institute for Physical Science and Technology. His research focuses on the statistical mechanics of nonuniform polar and charged liquids and theories of surface phase transitions and crystal growth.

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