Multinuclear Magnetic Resonance Study of Saponite Hydration and of Acetonitrile–Water Competition

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Abstract: Saponite is a trioctahedral 2:1 clay with strongly held water layers in between the platelets. Homoionic Li-saponite is suspended in mixtures of acetonitrile-d_3 and heavy water. Reporter quadrupolar nuclei monitor the occurrence of local order. They are ^2H and ^{17}O for water; ^2H and ^{14}N for acetonitrile; and ^7Li for the counterions. The residual quadrupolar splittings in the resonances for these nuclei are internally consistent within the molecules. As the acetonitrile content of the binary solvent mixtures is raised, more and more lithium ions are extracted from the Stern into the Gouy–Chapman diffuse layer. Stacks of saponite flakes segregate layers of CD_3CN and D_2O molecules from one another. At low acetonitrile content (<20%), some CD_3CN molecules order themselves together with the lithium ions at the clay interface. They follow the outside migration of the lithium ions. They orient themselves, on the average, at the magic angle with respect to the clay surface, at 20 vol % CD_3CN. Up to 50%, the average orientation of interfacial acetonitrile molecules changes continuously with composition of the binary solvent mixture. In the entire 0–50% acetonitrile concentration range, water orientation at the clay surface remains conversely invariant.

Introduction

The diversity of natural clay minerals is mind-boggling. Few well-defined synthetic clays have been made. Accordingly, the state of knowledge lags far behind the numerous practical uses of these minerals for such diverse applications as drilling for oil, paper coatings, cosmetics, foodstuffs, paints, etc. Among the natural clays, saponite is one of the best defined. A hydrous silicate of aluminum and magnesium, this mineral occurs in soft, soapy, amorphous masses, filling veins in serpentine and cavities in traprock. This aspect caused the German mineralogist Svanberg to give it its name in 1841 from the German *seifenstein*, i.e. soapstone.[1] Soapstone is the massive form of talc: while this word evokes cosmetics (8%), other uses include ceramics (32%), paints (22%), plastics (13%), paper (7%), rubber (6%), and numerous other applications. Eskimos and other people have also used soapstone for sculpture.[2]

A member of the smectite, i.e. of the swelling family of clays, it is a 2:1 clay associating one octahedral magnesia layer sandwiched in between two silica layers. It is a trioctahedral clay, in which three octahedral sites out of three are occupied by Mg(II) ions, in contrast to dioctahedral clays, such as montmorillonite, in which two out of three octahedral sites are occupied usually by Al(III). The ideal metallic composition is thus $Mg_6(Al_1Si_7)$. A net negative electrical charge on the layers stems from Al-for-Si substitution in the tetrahedral sites, partially compensated by substitution of trivalent ions into the octahedral sites. Natural saponites have a charge density typical for a smectite, in the range 0.8–1.2 per $O_{20}(OH)_4$. The interlayer cations, needed for maintenance of electroneutrality, are in the range 60–100 mequiv/100 g.[3]

Desmond Bernal, on the strength of his expert knowledge of silicates, presented a vibrant advocacy for the seminal function of clays at the dawn of life on Earth.[4] One of their roles, according to him, was to compartmentalize within their folds (i.e. inside the interlamellar space of swellable clays) the newly-formed organic matter. The present study looks for evidence in support of this belief. The choice of acetonitrile as the organic molecule tested is not altogether innocent: together with hydrogen cyanide and cyanoacetylene, acetonitrile has been detected by radioastronomers in the galaxy (in the atmosphere of Titan, one of the satellites of Saturn) and outside (e.g. Orion nebula).[5,6] It is part and parcel of the primitive nebula and thus of primeval matter.

The electrically-charged plates of a clay can and do order particles in their vicinity. It is so for metallic counterions and for water solvent molecules alike. The latter combine an electrical dipole and their ability at hydrogen bonding. We have shown earlier that indeed water molecules affix themselves to the surface of a clay by hydrogen bonds around which they rotate.[7,8] Other protic solvents such as methanol do likewise. What about highly polar solvents incapable of hydrogen bond donation to the negatively-charged silicate sheet? Would one such solvent, acetonitrile for the reason already stated, undergo preferred orientation at the clay interface, how, and to what extent? How do polar solvent molecules respond to the local forces there, between the orthogonal orientation thrust upon them either by a hydrogen bond donated from a surface silanol group or by an electrostatic bond through an intervening counterion, and the tangential orientation bringing the molecular dipole closest to the electrical charges on the clay sheet?

And what of the competition of a polar solvent such as acetonitrile with a protic solvent, with water in particular? This last is the main question addressed in this study. We were prepared, in gathering the answer to it, to have to disentangle a complex web of interactions, in which acetonitrile and water vied in the restricted space for binding to the same sites on the clay, and where their ordering by the clay interface mutually interfered. To our surprise, such complexity is absent. Acetonitrile and water solvent molecules go to different compartments. And they display largely independent behavior nearly throughout the whole range of binary solvent compositions.

Several pieces of evidence point to strong hydration of the saponite layers. Na-saponite tends to yield a stable single-layer

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water complex, with a basal d_{001} spacing of about 12.5 Å, even at high relative humidities.[9] Single-layer water complexes with interlayer magnesium and calcium cations are stable at 170 °C, yielding a basal spacing of about 11.5 Å. This spacing contracts to 10 Å after heating at 250 °C.[3] While saponite platelets tend to stack in highly ordered arrangements,[10] an author has predicted that "well-defined hydration domains may be expected".[11] We have launched this NMR study to look for such domains.

This paper will report the exceptional structural integrity of these domains and their resistance to encroachment by acetonitrile molecules. NMR has been applied successfully already to determining the structure and microdynamics of species in interfacial regions.[12] It has also been used to study adsorbates. ^{13}C NMR served to elucidate bonding of osmium carbonyls to magnesia[13] and adsorption of methanol onto a zeolite.[14] Information was obtained on model hydrodenitrogenation catalysts.[15] Adsorption of benzene on alumina was revealed to lead to faster reorientation around the 6-fold axis than in liquid benzene itself![16] Encapsulation of organic molecules inside zeolites was scrutinized with the help of ^{129}Xe NMR.[17] ^{2}H quadrupolar splittings reveal minute surface electrostatic changes in latex dispersions.[18] Multinuclear probing[19,20] of adsorbates provides more comprehensive information; each nucleus contributes its type of data and the sum total gives an overview of the interaction with the solid surface. The methodology used here was introduced in several earlier articles, the gist of which we shall now briefly recall.

Quadrupolar Splittings for Oriented Clay Suspensions. Degeneracy of allowed NMR transitions for a quadrupolar nucleus is lifted if it sees a nonvanishing electrical field gradient.[21] In the presence of local order, these no longer degenerate transitions are not time-averaged into a single resonance, and $2I$ lines (I is the spin quantum number, $I \geq 1$) ensue. The pioneering work by Woessner showed as early as 1969 that ^{2}H residual quadrupolar splittings for D_2O molecules in the presence of clay particles are due to preferential orientation of water molecules on clays with low water content, at ambient temperatures.[22] This finding was promptly confirmed.[23] We have observed also such multiplets for both the ^{2}H and the ^{17}O resonances for D_2O in suspensions of a purified bentonite clay in heavy water.[7,8] These splittings are due to the partial orientation of water molecules affixed to the surface of the clay platelets, themselves oriented by the application of the $\mathbf{B}_0$ directing field.[8,24] The observed quadrupolar splitting is determined by the orientation taken by the electric field gradient (efg) tensor with respect to the laboratory referential. The problem has been solved by Halle and Wennerstrøm,[25] and the observed residual quadrupolar splitting (rqs) is given by

$$\mathrm{rqs} = \frac{3e^2qQ}{4I(2I-1)h}(3\cos^2\theta_{\mathrm{LD}} - 1)A$$

where A is the residual quadrupolar anisotropy (with a value between −1 and 1, it is related to the order parameters defined by Halle and Wennerstrøm in their paper), h is Planck's constant, $\chi = (2\pi/h)e^2qQ$ is the quadrupolar coupling constant, and θ_{LD} is the angle between the laboratory referential and the director (which may be an axis normal to the clay platelets). To obtain this expression, the authors performed three successive axes transformations from the electric field gradient to molecular referentials (F–M), from molecular to director referentials (M–D), and from director to laboratory referentials (D–L). The electric field gradient is of intramolecular origin, and reorientation of the director is assumed to be slow on the NMR time scale. The quadrupolar splitting is modulated through residual anisotropy A by molecular reorientation with respect to the director.[25]

In aqueous suspensions of a bentonite clay, only a minute fraction of the water molecules (one in 10 000 is the order-of-magnitude) is in contact with the solid particles. Furthermore, these interfacial water molecules exchange quickly with bulk water molecules at ambient temperatures.[23,25] Only a time-averaged resonance is measured. Accordingly, the residual quadrupolar splitting is also a very small fraction of the quadrupolar coupling constant. The leverage stems from the large values of e^2qQ: taking as an example the deuterons in heavy water, with a quadrupolar coupling constant of ca. 210 kHz, if only one molecule in 10^4 is ordered at the clay surface, the expected rqs is 21 Hz, i.e. the weighted average between the bound and the free sites. The nature of the counterions also affects the magnitude[26] and the sign of the observed rqs.[8,24] For instance, if one changes the relative amounts of sodium and calcium counterions, one is able to reduce the observed rqs, and to make it vanish, just by increasing the proportion of divalent ions. By increasing it further, the rqs reappears but with the opposite sign. We have explained these observations by fast exchange of water molecules between the bulk and two bound sites characterized by residual anisotropies with opposite signs.[8,24]

Materials and Methods

The saponite sample studied was mined in the Ballarat area in California. Its average composition corresponds[27] to the formula $(Ca_{0.19}Na_{0.16}K_{0.02})(Al_{0.15}Fe_{0.06}Mg_{2.61})(Si_{3.77}Al_{0.23})O_{10}(OH)_2$ (iron expressed as ferric ions). Clays were exchanged with various ions as in our previous papers. Measured samples of the resulting homoionic saponites were suspended in D_2O or in D_2O–CD_3CN binary mixtures and stirred overnight. Analysis of exchangeable cations was carried out on a Perkin Elmer 603 atomic absorption spectrometer. NMR spectra were recorded, after equilibration of the samples in the probe so that maximum $\mathbf{B}_0$ ordering was observed, on a Bruker AM 300WB spectrometer ($\mathbf{B}_0$ = 7.05 T) at the Larmor frequencies of 46.073, 116.590, 21.686, and 40.690 MHz appropriate for ^{2}H, ^{7}Li, ^{14}N, and ^{17}O, respectively. The ^{7}Li chemical shifts were measured for $LiBF_4$ (191.5 mg in 10 mL of a solution in H_2O

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(20) Determination of the local structure and of the microdynamics of adsorbates can be approached by monitoring nuclei located at different points in the molecule, each of which providing, as it were, its own viewpoint. The composite picture that emerges gives unique information about the local interactions and their time dependence. Let us provide an analogy: the prowess of multinuclear magnetic resonance at revealing forces responsible for supramolecular structures held only by noncovalent bonds was applied to the important problem of the self-assembly of 5′-GMP (Borzo, M.; Detellier, C.; Laszlo, P.; Paris, A. *J. Am. Chem. Soc.* **1980**, *102*, 1124–1134. Detellier, C.; Laszlo, P. *J. Am. Chem. Soc.* **1980**, *102*, 1135–1141). It occurs via Hoogsten tetramers now known to be responsible for the pairing of chromosomes during meiosis (Sen, D.,; Gilbert, W. *Nature* (*London*) **1988**, *334*, 364–366. Sen, D.; Gilbert, W. *Nature* (*London*) **1990**, *344*, 410–414. Jin, R.; Breslauer, K. J.; Jones, R. A.; Gaffney, B. L. *Science* **1990**, *250*, 543–546).

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or in H_2O–CH_3CN mixtures) with respect to a coaxial tube having LiCl in D_2O as the reference and adjusted for a zero reference value in pure H_2O. The ^7Li longitudinal relaxation time T_1 was measured with the inversion–recovery procedure with waiting times t in the range $0.25T_1 < t < 2.5T_1$, as recommended.[28] The ^7Li T_2 transverse relaxation time was obtained with a Carr–Purcell–Meiboom–Gill sequence. The ^{14}N spectrum was recorded with the help of a spin echo sequence in order to avoid acoustic resonance, which would lead to a sinuous baseline. The rqs was measured after deconvolution of the multiplets into individual lines with an assumed Lorentzian line shape. The resulting error was estimated by summing the errors on the positions of each of the component resonances according to the formula

$$\Delta\delta = \left[\frac{(N/S)}{16x^2d^2} + \frac{1}{12}\right]^{0.5}$$

in which N/S is the noise-to-signal ratio, x is the reciprocal of the line width (at half-height), and d is the distance between two points expressed in hertz.[29] The uncertainties are thus below 1 Hz for ^2H, 5.0 Hz in ^7Li, 3.6 Hz in ^{14}N, and 2.7 Hz in ^{17}O. We checked by an independent procedure the reliability of these values. The double quantum filtering methodology of Furo et al.[30] gave values of the rqs in excellent agreement within the combined experimental uncertainties.

Background

We are studying suspensions of homoionic lithiated saponite in binary mixtures of perdeuterated acetonitrile and water. Accordingly, it is logical to focus at first on the properties of the binary acetonitrile–water mixture and to then determine the preferential solvation of lithium ions in such mixtures.

The acetonitrile–water system has evinced considerable interest. Besides its highly plausible prebiotic relevance, its role in atmospheric chemistry[31] and its frequent use in mechanistic studies of organic reactions[32] have ensured that numerous studies have been devoted to this system. Kovacs and Laaksonen[33] accompany their recent molecular dynamics simulation by no fewer than 26 references to earlier work on the same system. The main molecular interactions of the two partners, according to ab initio calculations,[34] are hydrogen-bonding of the water molecules at nitrogen and the antiparallel side-by-side arrangement of the acetonitrile (3.8 D) and water (1.85 D) electrical dipoles.

To summarize the existing knowledge and the consensus of studies by a variety of thermodynamic and spectroscopic techniques, acetonitrile–water mixtures present three distinct types. At high acetonitrile content, above a mole fraction of 0.75, water molecules disrupt the structure of liquid acetonitrile. The medium range (mole fraction of acetonitrile of 0.2–0.75) is one of microheterogeneity, with disruption of both acetonitrile and water structure, even leading to demixion at 38 mol % acetonitrile (272 K). At low acetonitrile content (mole fraction below 0.2), acetonitrile molecules respect the water structure, perhaps even enhance it slightly, sneaking into the cavities that coexist with the hydrogen-bonded microdomains. The new perspective opened by the recent molecular dynamics results is that addition of acetonitrile to water enhances the radial correlation of water, and that, also at low acetonitrile content, there is an antiparallel close arrangement of the acetonitrile dipoles.[33]

We turn now to the question of preferential solvation of lithium ions in acetonitrile–water binary mixtures. We have investigated it experimentally by way of lithium-7 NMR chemical shifts, in line with our earlier work on preferential solvation of alkali metal cations.[35] The results are depicted in Figure 1. The lithium-7 chemical shifts vary little[36] until a mole fraction in acetonitrile of about 0.6, at which point they dip at first gradually and then abruptly. The straightforward qualitative interpretation is that acetonitrile molecules do not coordinate to lithium ions in the water-rich acetonitrile–water mixtures. Only above a 0.6 mole fraction of acetonitrile do they compete with water molecules for occupation of the first solvation shell. However, it is also evident that acetonitrile molecules occupy the second solvation shell in the range of a 0–0.4 mole fraction, presumably by hydrogen-bonding to water molecules themselves coordinated to lithium ions. While enhancing polarization of the water molecules, this forces the water and acetonitrile dipoles to be opposed, which has to be compensated by the energy of hydrogen-bond formation. These lithium-7 chemical shifts results tell their expected tale: there is pronounced deviation of the system from an ideal solution; preferential solvation occurs, and it favors water over acetonitrile since the lone pairs on the water oxygen are more basic than the lone pair on the nitrogen.

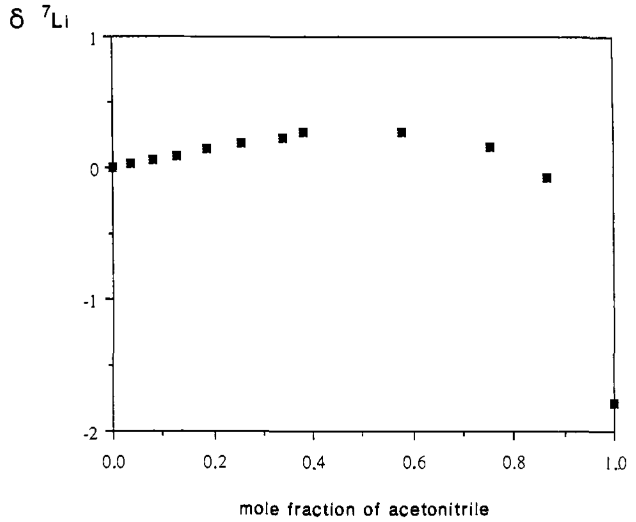

Figure 1. Plot of the ^7Li NMR chemical shift (ppm) for lithium tetrafluoroborate as a function of the mole fraction of acetonitrile in water–acetonitrile binary mixtures, pointing to preferential solvation of the lithium cation by water.

Results and Discussion

The ^2H and ^{14}N rqs's for acetonitrile are directly proportional to one another. Each of these observables can be either positive or negative. Accordingly, when their plot goes through the value zero, this may correspond to one of three cases from a logical standpoint: both rqs's change signs, both rqs's retain the same signs, or only one of the rqs's changes signs. We tested the three possibilities by plotting the linear regression of the ^2H rqs versus that for ^{14}N. The corresponding correlation coefficients are 0.989, 0.994, and 0.879, respectively, for 10 data points. This confirms that the two observables maintain or change signs in unison, as the composition of the binary solvent mixture is changed. Only the ^2H resonances for D_2O display differential line broadening.[37] Hence this criterion could not be used to distinguish between retention or inversion of signs for the ^2H and ^{14}N rqs's. It remains

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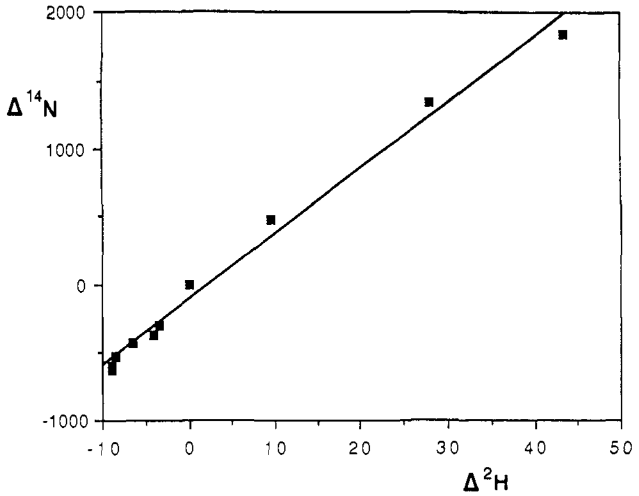

Figure 2. Plot of the residual quadrupolar splittings (Hz) for acetonitrile-d_3 (correlation coefficient = 0.99 for 11 data points).

Table 1. Residual Quadrupole Splittings (Hz) for Various Nuclei in Suspensions of Saponite (27.6 mg/mL) in Binary Mixtures of Heavy Water and Acetonitrile-d_3 as a Function of Solvent Composition

vol % of CD_3CN	Δ^2H (D_2O)	Δ^2H (CD_3CN)	$\Delta^{17}O$	$\Delta^{14}N$	Δ^7Li
0	41.5		214		204
5	38	43.5	192	1850	143
10	38.5	28	197	1350	105
15	38	9.5	193	481	80
20	37	0	198	0	72
23	38	-3.5	204	-308	60
27	37.5	-6.5	190	-428	51
30	38.5	-8.5	203	-528	51
33	40	-9	214	-603	54
50	51	-9	264	-635	57
63	37	-4	241	-369	0

thus to distinguish between going through zero from positive to negative or touching zero as an angular point. The former, intuitively more likely, is also consonant with a change in signs of the residual anisotropy stemming from the θ angle in the 3 $\cos^2 \theta_{DM} - 1$ term going through the magic angle (strictly true for an electric field gradient tensor with 3-fold symmetry). Macroscopic changes accompany these variations in the heavy water and acetonitrile-d_3 rqs's. When the percentages of acetonitrile are smaller than 33 vol %, the suspensions have a low viscosity. In the hours following the stirring, some of the particles settle at the bottom of the tube, which does not affect the observed rqs, only the band widths. The 50 and 63 vol % acetonitrile samples are viscous gels that remain stable for weeks; the clay swells much more under these conditions. The shapes of both the ^2H and ^{17}O water resonances for the latter 63 vol % sample are profoundly perturbed as compared to the other samples: an increase in the intensity of the central region occurs. When the proportion of acetonitrile is 83 vol %, a swollen clay precipitates, and the supernatant is a clear solution. We will not consider at all, in the foregoing, this last heterogeneous sample.

The ^2H and ^{17}O rqs's for D_2O molecules are influenced by the nature of the exchangeable cations, and their ratio follows the decrease observed along the column in the Periodic Table. We have investigated the influence of divalent counterions; it is small.

Interpretation of the data in Tables 2 and 3 is unambiguous as to their predominant feature: there is strong water ordering in the interfacial region; to first approximation, it is little affected by the nature of the counterions. Furthermore, this dependence on the counterion follows a predictable sequence in which the smaller and less polarizable cations (Li^+ and Mg^{2+}) induce a "tighter" ordering of the interfacial layer of water molecules. This observation is consistent with coordination (site binding) of such small counterions at the oxygen of water molecules held by hydrogen bonds to the saponite surface. Larger, more polarizable counterions (Rb^+ and NH_4^+) have a smaller charge dipole net attractive interaction with the water molecules and are likely to be condensed in the electrical double layer rather than entering into site-specific interactions with the interface or with adsorbate molecules.

Table 2. Influence of Alkali and Pseudoalkali Counterions on the rqs for Heavy Water

cation	Δ^2H, Hz	$\Delta^{17}O$, Hz	ratio $\Delta^{17}O/\Delta^2H$
Li^+	55.0	281	5.1
Na^+	49.9	257	5.2
K^+	35.9	162	4.5
Rb^+	28.2	95	3.4
NH_4^+	35.0	167	4.8

Table 3. Influence of Alkaline Earth Cations on the rqs for Heavy Water

cations	Δ^2H, Hz	$\Delta^{17}O$, Hz	ratio $\Delta^{17}O/\Delta^2H$
Ca^{2+}/Na^+			
0.18	56.6	310	5.5
0.71	54.5	266	4.9
Mg^{2+}/Na^+			
0.22	50.8	248	4.9

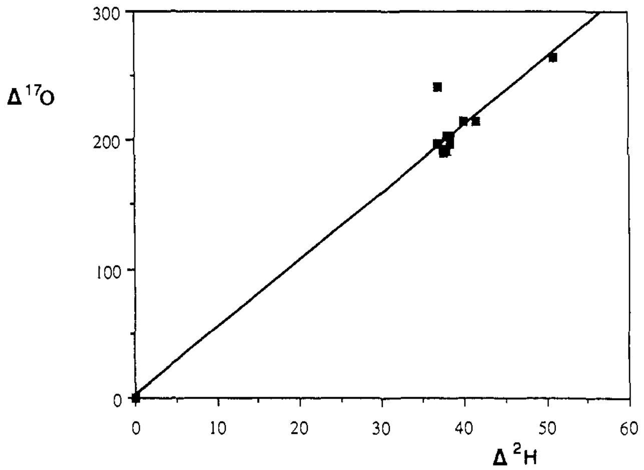

Figure 3. Plot of the residual quadrupolar splittings for D_2O molecules (Hz) (correlation coefficient = 0.97 for 12 data points).

The spectra for the quadrupolar counterions do not display a residual quadrupolar splitting, except for lithium: lithium ions interact more strongly than for example sodium ions with the saponite surface. ^7Li ($I = {}^3/_2$) NMR shows a triplet whose relative intensities (30:40:30) obey theory. One notices however that the high-field component is somewhat broader than that at low field. No significant difference in the rqs (204 Hz at 299 K for a saponite sample, 27.6 mg/mL in D_2O) is observed at the two Larmor frequencies of 116.590 ($\mathbf{B}_0$ = 7.0463 T) and 155.454 MHz ($\mathbf{B}_0$ = 9.3950 T). This can be ascribed to maximum ordering of the sample at the lower applied $\mathbf{B}_0$ already. In the ^6Li (I = 1) NMR, under the conditions just stated, a doublet is indeed observed with a rqs of 11 Hz.

Chemical Exchange Ruled Out. Both the ^2H and ^{17}O quadrupolar interactions are intramolecular in origin. A good regression between ^2H and ^{17}O rqs's for D_2O molecules bears it out (Figure 3). The good regression between the ^2H and the ^{17}O rqs's for D_2O molecules (Figure 3) proves the absence of any significant intermolecular chemical exchange of deuterons. The observed slope is 5.2. It is in order-of-magnitude agreement with the ratio of the quadrupolar coupling constants χ_D = 213.4 kHz[38] and χ_O = 6 525 kHz[39] for the two nuclei, divided by a coefficient representative of the preferred mode of D_2O reorientation of about

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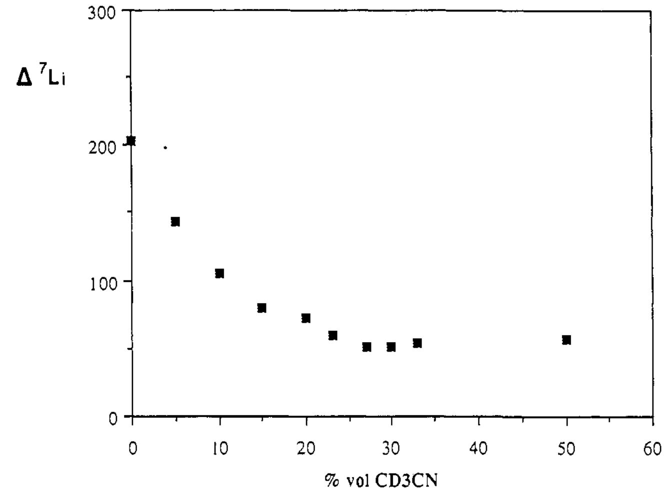

Figure 4. Residual quadrupolar splittings for the lithium ions (Hz). The decrease indicates depletion of the Stern layer in favor of the Gouy–Chapman diffuse layer as the solvent mixture is enriched in acetonitrile-d_3.

5:3.5 about the bisector vs 4.5 for rotation around a hydrogen bond between the heavy water molecule and the charged clay sheet. Accordingly, the observed slope does not provide information on the preferred mode of reorientation of D_2O molecules.[25] Likewise, the ^{2}H and ^{14}N rqs's for acetonitrile-d_3 witness the same ordering (Figure 2). Since these two nuclei share the same quantum number I of unity, the observed slope of 40 is the ratio χ_N/χ_D, in good agreement with the quadrupolar coupling cosntants $\chi_N = 3.47$ MHz[40] and $\chi_D = 156$ kHz[41] for this molecule, together with a ratio of residual anisotropies $A(^{14}N)/A(^2H) \sim 1.8$.

Loss of Lithium Ordering. Let us turn our attention now to the ^{7}Li rqs's and to their *monotonic* decrease as the proportion of acetonitrile in the binary solvent mixture is increased (Figure 4). Firstly, their existence was a surprise. No apparent rqs's were observed with ^{23}Na (and other) counterions, neither in one-quantum transition nor in two-quanta transition experiments.[30] This observation is also at variance with what is obtained with lithiated bentonites for which we did not find any ^{7}Li splitting.[26] The difference can be ascribed to that in structure between saponite and bentonites. In the latter, isomorphous substitution by lower-valent ions occurs mainly in the octahedral layer. Accordingly, since counterions are more distant from this median octahedral as compared to the surface tetrahedral layers, they interact more weakly with the basal oxygens on the tetrahedral layers. The finding of an rqs for lithium counterions implies that some reside in the Stern layer next to the bentonite interface.

These lithium counterions in their vast majority are associated with the surface rather than with the edges of clay platelets. There are two limiting interpretations of the results. The first is deviation from zero of the angle between the director and the main axis for the electrostatic field gradient tensor, as acetonitrile molecules start penetrating the water structure and place themselves in the second coordination shell for the lithium ions. The second interpretation does not invoke a tilting of the *efg* axis away from the director but simply depopulation of the lithium ions in direct interaction with the interface. To resort to an old-fashioned but graphic description, they partition themselves between the Stern[42] and the Gouy–Chapman[43,44] layers. In such a conventional description, the results would appear to imply Li^+ migration from the Stern layer to the Gouy–Chapman diffuse layer as the mixture is gradually enriched in acetonitrile. The extent of this Stern layer depletion is rather small, less than a factor 3 up to 50 vol % of CD_3CN (Figure 4). A more accurate description would compute the distribution of condensed cations from polyelectrolyte theory, which can be done at various levels of sophistication:[45–48] the present results make this distribution tail out until greater average distances from the clay interface, as the mole fraction of acetonitrile increases.

How can this spreading be understood? With a *continuum* picture of the solvent, infusion of acetonitrile into an aqueous solution diminishes the bulk dielectric constant. This ought to enrich tight ion pairs (Stern layer) at the expense of loose ion pairs (Gouy–Chapman layer), contrary to observation. Consideration of image charges, set up in the clay dielectric, symmetrically with respect to the interface, by the lithium ions in the solution, leads to the same counterfactual conclusion. In a *molecular* picture of solvent molecules, Lewis basic sites on acetonitrile (nitrogen lone pair) are less nucleophilic than those on water molecules (oxygen lone pairs), as found experimentally (Figure 1). Accordingly, acetonitrile enrichment affects the competition for lithium ions attachment between the solvent molecules (water or acetonitrile) and the charged basal oxygens on the clay surface: in a totally counterintuitive manner, acetonitrile molecules appear to pull lithium counterions away from the charged wall.

The interpretation just given for the ^{7}Li results is not at conflict with reports of symmetrical hydration of counterions associated with saponite. We are alluding to the X-ray and IR evidence on a hydrated calcium saponite showing that the divalent cation is fully hydrated and that two water molecules are bound to the basal oxygens.[49] For one thing, lithium ions differ in behavior from calcium ions. Furthermore, the tiny fraction of lithium ions in the Stern layer has a disproportionately large influence on the NMR results (through the leverage of a considerable value for their intrinsic rqs), while their small population would not show up significantly in the X-ray nor in the IR. Before leaving the lithium part of the story, one more comment is in order. A German group has reported a doubling of the electrostatic field gradient perceived by ^{6}Li adsorbed on a Si(111) surface as a function of coverage, due to a change in binding geometry of the Li atoms.[50] While we cannot exclude a similar effect for those lithium ions that we postulate as occupying the Stern layer, we note that the decrease in the ^{7}Li rqs (Figure 4) exceeds such by a factor of 2 and must be taken to imply distancing from the interface, and not a local geometrical reorganization, as the percentage of acetonitrile is raised.

This conclusion is bolstered by measurement of the lithium-7 T_1's (Figure 5). Their monotonous decrease with an increase in the proportion of acetonitrile-d_3 translates (since they are outside extreme narrowing as proved by the increase of T_1 with the value of $\mathbf{B}_0$, 44.6 ms at 7.05 T and 59.3 ms at 9.4 T) into a reduction in the reorientational correlation times for lithium cations. A T_2 value of ca. 2 ms confirms this assertion. As more and more acetonitrile molecules come in, lithium ions become more mobile. Furthermore, the two parameters follow similar trends (Figures 4 and 5): the simplest interpretation is that the common cause is indeed migration of the lithium ions away from the charged saponite wall as the binary solvent mixture is enriched in acetonitrile.

Loss of Acetonitrile Ordering. The rqs data for acetonitrile-d_3 (Figure 6) are eloquent, and the story they appear to tell is compelling.[51] That the changes in the order parameters for the

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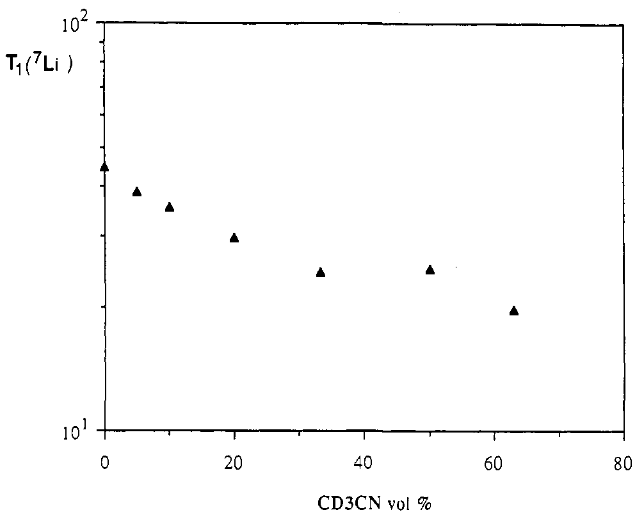

Figure 5. Plot of the longitudinal relaxation times T_1 (ms) ±1% for the lithium cations as a function of solvent composition.

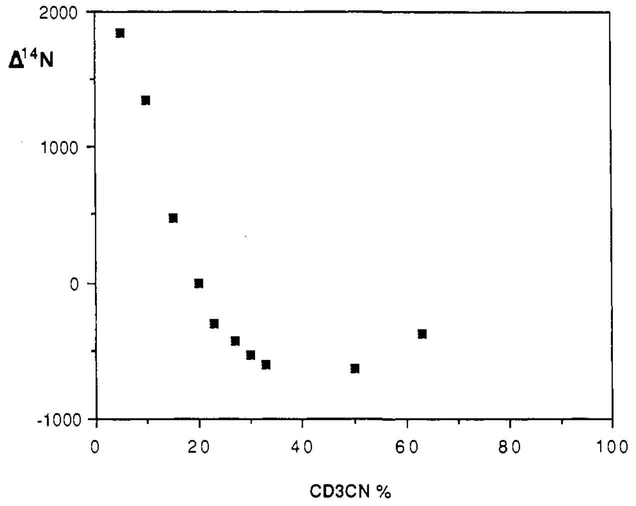

Figure 6. Residual quadrupolar splitting (^{14}N, Hz) for acetonitrile-d_3, molecules as a function of solvent composition.

acetonitrile molecules echo those for the lithium ions (Figure 4, the regression has $\rho = 0.83$ for seven points) between 0 and 20 vol % CD_3CN is indeed nicely consistent with the above description of a tight ($Li^+\cdots NC-CD_3$) association.

The residual quadrupolar anisotropy A (as described in Quadrupolar Splitting for Oriented Clay Suspensions) is proportional to the $3\cos^2\theta_{DM} - 1$ term, whether the ^2H or the ^{14}N nuclei of CD_3CN are being monitored. The angle θ is that between the molecular referential, the C_{3v} axis of the molecule, and the director, specifying the orientation of the clay platelet. The decrease in magnitude, followed by the vanishing and by the change in signs of the ^2H and ^{14}N rqs's with increasing acetonitrile content, is best explained by a change in the average value $\langle 3\cos^2\theta_{DM} - 1\rangle$ of this angular term. Let us now spell out a description consistent with the data.

In the absence of an organic solvent, most lithium counterions are fully hydrated and congregate next to the clay interface (ionic condensation). Some lithium counterions interact more strongly at specific sites on the clay surface (site binding). The latter appear unaffected by the presence of the organic solvent in the binary mixtures. At low acetonitrile levels, the average θ_{DM} angle is close to zero. As pictured in Figure 7, the acetonitrile molecules coordinate lithium cations with the negatively-charged nitrogen and align themselves, on the whole, perpendicular to the interface. As the amount of acetonitrile is increased, this induces greater coordination of lithium ions by the organic molecules. With more than one acetonitrile molecule in the lithium coordination sphere, this sets up a distribution of orientations and on the average an increase of the θ_{DM} angle. Thus the residual anisotropy A, following the $\langle 3\cos^2\theta_{DM} - 1\rangle$ term, decreases, and likewise for the rqs. When the average value $\langle\theta_{DM}\rangle$ becomes the magic 54.4° angle, the rqs vanishes. At still greater $\langle\theta_{DM}\rangle$ values, the splitting reappears but with the opposite sign. Since at these relatively higher acetonitrile compositions yet more acetonitrile molecules have entered the coordination shell for each lithium ion, one can expect a spread of orientations θ_{DM} around the lithium ions, which does lead to a further distancing of the lithium ions from the interface, as shown by the ^7Li results. Such a description implicitly assumes a fixed p_B fraction of interfacial acetonitrile molecules, which of course is not the case. This description is relevant only to adsorbate interfacial molecules, which do not mirror bulk properties such as microheterogeneity of the acetonitrile–water mixture[52] in a range of solvent compositions.

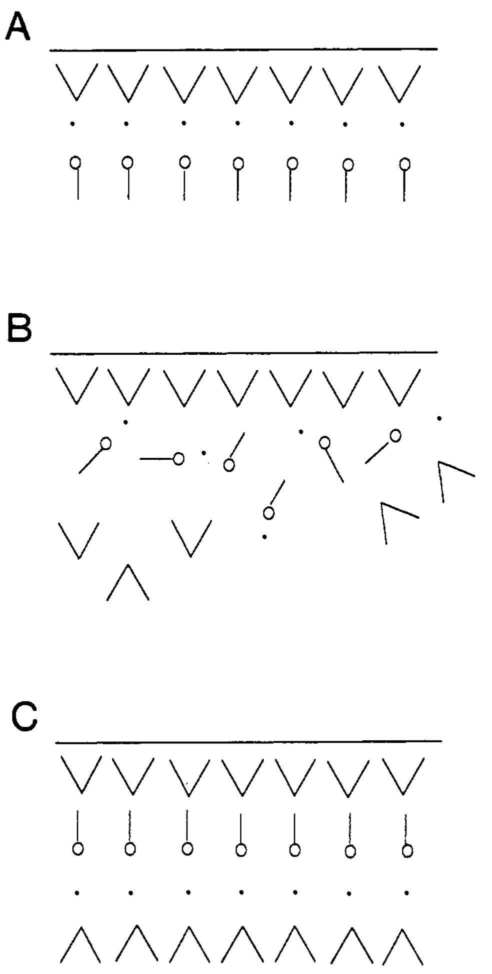

Figure 7. Schematic depiction of various orientations for acetonitrile-d_3 molecules (A) at low acetonitrile content, (B) in the range of 20–50% acetonitrile, and (C) at an idealized limiting situation, of full dipole reversal by the acetonitrile molecules. While it does not describe the system at any of the investigated compositions, the system appears to change gradually in that direction.

Compartmentalization of Acetonitrile and Water at the Interface. We turn now to the water results summed up in Figure 8. Throughout most of the range of compositions for the binary solvent mixtures, the water deuteron and oxygen-17 rqs's remain

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(51) Both the ^{14}N and ^2H quadrupolar splittings for acetonitrile-d_3 change signs above 20 vol % of CD_3CN in the binary mixtures. This is indicated by a better correlation coefficient in the regression of Figure 2: 0.993 instead of 0.986 for 11 points, assuming a sign reversal. A much stronger argument is that the plot of Figure 6 would display an angular point (two distinct tangents) with a sign change, leading to an unrealistic geometry variation.

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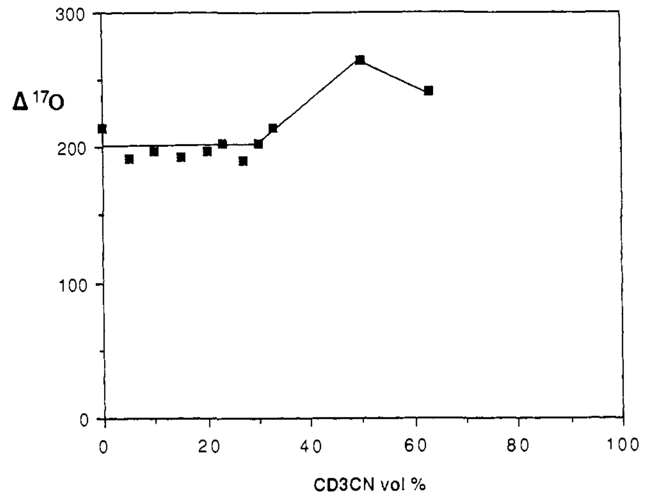

Figure 8. Residual quadrupolar splittings (^{17}O, Hz) for D_2O molecules as a function of solvent composition.

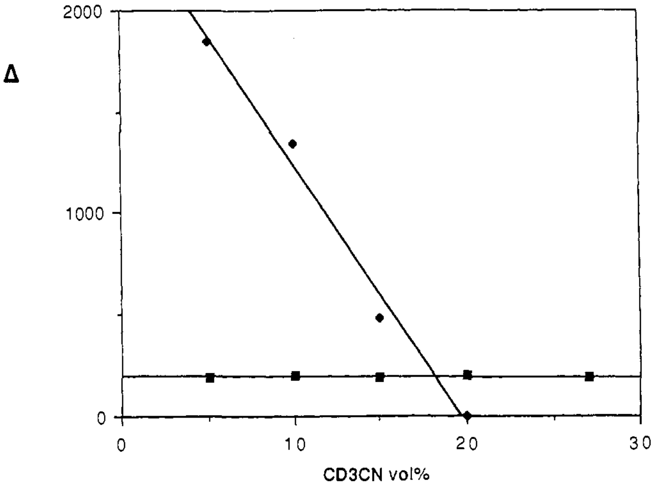

Figure 9. Contrast between the invariance of the D_2O (squares) rqs and the pronounced variation of the CD_3CN (diamonds) rqs (Hz) in the 0–27 vol % range of compositions for the binary solvent mixture.

invariant. Thus interfacial water orientation is essentially unaffected. There is no comparison with either lithium ions or acetonitrile molecules (Figure 9): D_2O molecules occupy different and separate compartments. Indeed they interact strongly with the charged oxygens on the clay surface. The oxygens in the ditrigonal cavities are more basic, harder too in saponite than they are in a montmorillonite. This occurs because delocalization of the negative charge stemming from isomorphous substitution in the octahedral layer is greater than if isomorphous substitution occurs *in* the tetrahedral layer.[53-55] Hence, the picture that imposes itself is that of highly structured aqueous domains. Since our NMR method is blind to water molecules trapped *inside* the saponite stacks and thus unable to exchange rapidly with bulk water,[56] these are domains that are both *outside* the aggregates of platelets and yet separated both from the bulk solvent and from the layer populated predominantly with acetonitrile molecules. This description points to a layer of water molecules, strongly hydrogen-bonded with one another.

The compartmentalization of water and acetonitrile, *in* the water-rich range of compositions, is consistent of course with the representation of the binary mixture (in the absence of the clay) consisting of a hydrogen-bonded network of water molecules, with acetonitrile molecules occupying cavities within that network.[33]

Compartmentalization of acetonitrile and water domains has been depicted here as a stratification (Figure 7). The solid surface organizes homogeneous solvent layers parallel to it. An alternate picture is that of islanding, with separate microdomains of the demixed solvents hugging the interface. The results considered as whole give better support to the former interpretation. Islanding would imply extraction of the lithium ions out of the acetonitrile and into the water microdomains. The pronounced correlation between the lithium structural (Figure 4) and microdynamic (Figure 5) parameters, on one hand, and the acetonitrile structural parameters (Figure 6), on the other, appears to rule out islanding.

An experiment confirms these findings. A nondehydrated saponite is stirred overnight in acetonitrile. The IR spectrum of the clay thus treated, after drying at 20 °C, does not show any absorption for the nitrile group, even after spectral accumulation for 50 scans. Thus, even at concentrations overwhelming the residual humidity, acetonitrile does not displace adsorbed water. Only with the clay dried at 100 °C—prior to mixing with acetonitrile—can one observe two CN absorptions in a similar experiment.

As increasing mole fractions of acetonitrile leach out the lithium counterions from the Stern layer, the *outer* interface charges up electrically. The water molecules in the highly structured layer next to the *inner* interface for the very same saponite platelet restabilize the attendant negative charge by hydrogen-bonding onto it. This restructuration is passed along to the water molecules that serve as our probes, if indeed there is a continuity enforced by hydrogen-bonding between inner and outer ordered water adsorbates. This compensatory effect may contribute to the observed increased order parameter for heavy water in the range 30–50 vol % of CD_3CN.

The increased order of D_2O molecules in the range 30–50 vol % of CD_3CN (Figure 8) is reminiscent of the effect of acetonitrile on preferential solvation by water in the water-rich range for the binary mixtures (Figure 1); the increased polarization of water molecules by hydrogen-bonded acetonitrile molecules is another likely cause for the slight increase found for the rqs.

The state of adsorbed water appears highly sensitive to the precise nature of the lamellar mineral it is associated with. In general, the interlayer cations are fully hydrated. Sometimes, the coordinated water molecules interact strongly with the mineral surface; sometimes they interact weakly and the hydrated counterions tumble freely in the interlayer space. In our earlier work on an homoionic Na-montmorillonite, we found predominant reorientation of the water adsorbates around a hydrogen bond between the water molecule and a negatively-charged basal oxygen. Divalent Ca^{2+}-, and Mg^{2+}-exchanged montmorillonites displayed a change of the orientational axis to the stronger metal–oxygen bonds. The results were consistent with the concept of atmospheric condensation of the fully hydrated divalent ions next to the charged interface.[8] For Cu^{2+}-exchanged montmorillonites, the divalent ions are also hexahydrates, but they appear to reorient freely in the interlamellar space.[57,58] In a manner not unlike that reported for Na-montmorillonite, Skipper found in the two-layer hydrate of Ni-vermiculite that the Ni^{2+} ions are hexahydrates with the water ligands donating hydrogen bonds to basal surface oxygens.[59] Slade reported for two-layer hydrates of Na- and Ca-vermiculites octahedral coordination of Na^+ ions to water molecules, located between the triads forming the bases of tetrahedra bordering the interlamellar space. Six-fold coordinated Ca^{2+} ions were located between the bases of adjacent tetrahedra.

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Slade had evidence too for 8-fold coordinated Ca^{2+} ions between the pseudohexagonal cavities.[60] One aspect of our present results is thus conspicuous: the water molecules are rather insensitive to the nature of the counterions, as manifested by their order parameters (Tables 2 and 3).

The Composite Picture and a Possible Solution to the Paradox. The picture that can thus be pieced together is that represented by Figure 7. Let us emphasize that one deals exclusively with adsorbate species, both neutrals (D_2O and CD_3CN) and ions (Li^+), since the rqs's constitute the means for observation. The observed neutrals are but a minute fraction of the total population of solvent molecules. Accordingly, the strong ordering of these very few solvent molecules at and by the saponite interface does not violate the second principle. It is consistent, conversely, with irreversible thermodynamics. A considerable concentration (activity) gradient for each of the chemical species is set up near the interface. Structuring can be expected in the presence of such a gradient. Indeed, the boundary layer nearby the plane of a phyllosilicate with its natural concentration gradients is an ideal location for observation of nonequilibrium chemical patterns. Moreover, as the boundary layer of atoms is nearly motionless, hydrodynamic convection would not be expected to disturb significantly the pattern formation.

The second point for discussion is the unexpected finding of an increase in mobility of the lithium ions, together with a plausible increase of their distance from the interface, with the acetonitrile content in the water-rich solvent mixtures (Figures 4 and 5). Because of the strong correlation with the decrease in the rqs of the acetonitrile molecules themselves (Figure 6), we have described the common cause for both types of results as a pulling of the lithium ions away from the interface by the acetonitrile molecules. This is the one extremely paradoxical result in this study, since water and not acetonitrile molecules are expected to coordinate more strongly with lithium ions. A first possible explanation is in similar terms to those in the previous paragraph: a peculiar structuring due, locally, to nonequilibrium thermodynamics. Another and more likely explanation, as depicted graphically in Figure 7, is that very simply the interfacial region structurewise is not representative of the bulk. Even at relatively low acetonitrile mole fractions, the interfacial region should see some penetration by acetonitrile molecules: since lithium ions congregate near the interface, they set up image charges in the saponite dielectric slab. The electrostatic attraction between the lithium point charges and the image charges created symmetrically with respect to the interface is proportional to the reciprocal of the effective dielectric constant in the intervening medium. Since acetonitrile is a lower dielectric liquid than water, the system can locally lower its energy by pulling a few acetonitrile molecules in between the charged silicate layer and the lithium counterions. While the attendant picture (Figure 7C) is blatantly unrealistic even at the highest acetonitrile contents, there appears to be a move in that direction of a collective gradual flip of the acetonitrile molecules. If indeed the ^{14}N rqs is dominated by the $\langle 3 \cos^2 \theta_{DM} - 1 \rangle$ term, then the average θ angle appears to increase (Figure 6) past 90° in the range 50–80 vol % of acetonitrile. An alternative and mutually inconsistent explanation—we believe both to be complementary—is for acetonitrile molecules to enter the lithium coordination sphere (Figure 7B) under various orientations relative to the interface, at thermodynamic equilibrium, so as to minimize the Gibbs free energy: entropywise, with the broadest angular distribution, and enthalpywise, to strike the best compromise in the coordination sphere between the attractive ion–dipole interaction and the mutually repelling dipoles of the water and acetonitrile molecules with their steric constraints too and, outside of the coordination sphere, so that the greatest fraction of these dipoles be ordered by the local electrostatic fields originating at the charged interface and at the lithium counterions.

From the vantage viewpoint of lithium-7 NMR, the binary acetonitrile–water mixtures, in the absence of suspended clay particles, show composition-dependent structures mostly above an acetonitrile mole fraction of 0.7. Below this value, the ^7Li chemical shift varies but little with composition. In water-rich mixtures, acetonitrile molecules can fit inside cavities within the water structure. For saponite suspensions, this picture endures; in water-rich mixtures, indeed acetonitrile molecules fail to perturb the strong structuring of the water layer(s) at the interface. Since the rqs observables provide information only for the interfacial region, one cannot generalize this assertion to the bulk solution.

Conclusion

A comparison of the evolutions with the solvent composition of the residual quadrupolar splittings for heavy water and for acetonitrile-d_3 has shown how much they differ: water sticks to the saponite surface, whereas acetonitrile forms another parallel layer at a distance from the interface. This distance is fixed by that of the lithium counterions. Water molecules are glued to the saponite wall by a combination of hydrogen bonding and of coordination to the lithium ions, themselves attracted by the negatively charged saponite sheet. Whereas the adsorbed water molecules are not significantly affected by the presence of acetonitrile below 60 vol %, the orientation of the organic molecules varies very greatly in that 0–60% range. The decrease, the going through zero, and the change of signs of the rqs's for CD_3CN are consistent with a description in terms of interaction with the lithium ions. This partial coordination onto lithium goes together with an increase of the mean distance of the lithium ions from the interface, as seen by the ^7Li parameters.

In general, physical chemistry of surfaces can utilize the rqs information, easily available from very many nucleides in the Periodic Table, to probe the structure of adsorbates under conditions (liquid phase) very close to those for practical use of such minerals, for instance as heterogeneous catalysts. The only necessary condition is ordering by a magnetic induction field, which very many platelets made of lamellar material (such as clays) will fulfill.

There is a wealth of prebiotic implications as well. Saponite is a natural mineral that is widespread on the surface of the planet; indeed, it exemplifies one of the major types within the smectite family of clays. That the saponite wall creates next to its very strong electrical fields (up to 10^{10} $V \cdot m^{-1}$ [61]) separate aqueous and organic phases, that will selectively dissolve organic monomers and oligomers, in close proximity to incipient catalytic centers, pinpoints a possible role for clay minerals at the origin of life, that has been speculated about[62] but for which hard evidence has been lacking.

Thus multinuclear magnetic resonance[19] provides once again information with the complementary virtues of wealth, coherence, and readability at first sight.

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