

Inherent Acidity of Aqua Metal Ions in Solids: An Assay in Layered Aluminosilicates

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Structural information on 2:1 layered silicates has been obtained from ^1H magic angle spinning nuclear magnetic resonance measurements, the acidity of aqua metal ions in the interlayer space being determined. Representative end-members of the smectite group and a set of cations covering wide ranges of $\text{p}K_{\text{a}}$, absolute hardness, ionic radius, and formal charge values were carefully chosen. ^1H spectra were recorded by using conventional single-pulse MAS NMR, and their qualities were similar to those currently obtained by using multiple pulse sequences. The proton spectra of these samples were composed of two different signals, which were attributed to the structural hydroxyl groups located in the silicate lattice and the water molecules residing in the interlayer space. The position and line shape of the hydroxyl contribution was determined by the octahedral nature of the smectite and modulated by its chemical composition. The chemical shift from the water contribution gives valuable information about the acidic strength of the interlayer cation, correlations between the shielding of the protons belonging to the interlayer water molecules, and the $\text{p}K_{\text{a}}$ and absolute hardness values for each cation being observed.

1. Introduction

A wide set of inorganic solids, such as silica–alumina gels, zeolites, layered aluminophosphates, smectites, and mesoporous silicates, constitutes an attractive group of materials due to their acidic properties and are progressively substituting the environmentally undesired liquid acids.¹ To evaluate the activity of these materials, experimental methods are being demanded which give information on the number and distribution of the acid sites as well as on the nature of these sites, including not only the concept of acid strength but also the concept of hard and soft acidity and basicity (HSAB) as introduced by Pearson.² Numerous techniques, including ultraviolet–visible, infrared, and nuclear magnetic resonance studies from adsorbed species, base titration, and chemical methods for the determination of OH groups, have been employed with this aim, although most of them only provide indirect evidence on the acidity of these materials.³ A promising technique that should give direct information on the ability to lend protons is high-resolution ^1H solid-state magic angle spinning nuclear magnetic resonance (MAS NMR).⁴ However, these measurements have been hampered by their relatively poor spectral resolution, due to homo- and heteronuclear dipolar interactions and, to a lesser extent, chemical shift anisotropy.⁵

Very recently, we have shown that the combined use of magnetic fields of 9.39 T and spinning speeds of 12 kHz affords single-pulse ^1H MAS NMR spectra of smectites, recorded with very short acquisition times and a simple instrumental setup, of a similar quality to those currently obtained by using more sophisticated pulse sequences.⁶ On that preliminary account, ^1H MAS NMR spectra provide information on very important structural aspects of these materials, such as the mineralogical composition of the clay framework and the nature of the interlayer cation. At the same time, they resulted in being a

promising technique to examine the acidity of these solids because the position of the ^1H signals, i.e., their chemical shift values, is a function of the shielding of these nuclei and, in consequence, should be a measurement of the ability that the material can lend to these species.

In this full paper, we have studied the ^1H MAS NMR spectra of smectites, by using an adequate collection of minerals and interlayer cations, with a 2-fold purpose. On one hand, we report the refinement of the ^1H chemical shift data and their correlation with short-range order parameters in aluminosilicates, with the two different proton environments in smectites, the structural hydroxyl and interlayer water, being examined separately. The use of numerous samples representative of the smectite group and a wide variety of interlayer cations have allowed us to analyze the relationship between the ^1H MAS NMR spectra and the structural properties of the samples, such as the mineralogical composition of the clay framework and the nature of the interlayer cation. Members of the smectite group, including specimens of the dioctahedral and trioctahedral series with a different tetrahedral Si/Al ratio, and very different interlayer cations have been used to fulfill this purpose. This information should be useful for many researchers in different branches of chemistry who may be interested in these materials from many chemical points of view.

On the other hand, we discuss the ^1H MAS NMR spectra in relation to the acidity of each solid. For this second purpose, we selected a collection of interlayer cations in accordance with their absolute hardness values η and the HSAB principle.⁷ Thus, the selection covers not only a variation in the formal charge of the cations, which ranges from monovalent to trivalent states, and in the ionic radius of these, from 0.51 to 1.06 Å, but also includes a considerable variation for the absolute hardness values of the cations, from 7.93 to 45.77 eV. For this discussion, the ^1H MAS NMR measurements are used to interpret the proton shielding as a consequence of the stability of the adduct bond, in terms of both the HSAB theory and the ECW model,⁸ and

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TABLE 1: Structural Formulas of the Selected Smectites

short name	[4]Si ⁴⁺	[4]Al ³⁺	[6]Al ³⁺	[6]Fe ³⁺	[6]Mg ²⁺	[6]Li ⁺	[6]Ti ⁴⁺	M ⁺
talc	8.00				6.00			
SHCa-1 ^a	7.96	0.04	0.04		5.30	0.66		0.66
SapCa-1 ^b	7.20	0.80		0.14	5.79			0.80
pyrophyllite	8.00		4.00					
Trancos ^c	7.64	0.36	3.09	0.28	0.69			0.87
SAz-1 ^c	7.97	0.03	2.71	0.14	1.13		0.02	1.14

^a Hectorite. ^b Saponite. ^c Montmorillonite.

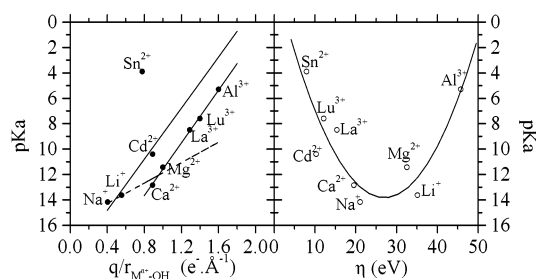


Figure 1. pK_a values for metal-ion M^{n+} hydrolysis (left) as a function of the Coulombic attraction of the metal ion for electrons at the distance of a hydrate-water oxygen nucleus and (right) as a function of the absolute hardness value for each cation.

an estimation of the Brönsted acidity of each sample. A new general method to determine the acidic strength of inorganic solids is proposed. These measurements should be used as a basis to develop a general method to determine the acidic strength of inorganic solids.

2. Materials and Methods

Natural samples of representative smectites with mineralogical compositions close to the ideal ones were selected. Trioctahedral minerals included a saponite, a hectorite, and talc. The dioctahedral minerals selected were two different montmorillonites and a pyrophyllite. Structural formulas and the names of the samples studied in this report are summarized in Table 1 and characterized in more detail elsewhere.⁹

The samples were homoionized by ion exchange methods with different interlayer cations, carefully chosen in order to sweep a wide range of Brönsted acidity and absolute hardness. The acid strength of the metal ions depends mostly on how strongly the charged atom is bonded to the hydrate-water oxygen atoms. The stronger this attraction, the more readily the protons are transferred to surrounding water molecules:



The correlation between acidity values for the cations herewith analyzed pK_a ¹⁰ and the Coulombic attraction of the metal ion for electrons at the distance of a hydrate-water oxygen nucleus $q/r_{M^{n+}-OH_2}$ is included in Figure 1 (left).¹¹ Straight solid lines have been drawn to connect acids, in accordance with Porterfield,¹¹ of quite different strengths and comparable hardnesses, and an additional straight dashed line has been included to connect, as reported by Shriver et al.,¹² what they call hard ions with low charges (i.e., Na^+ , Li^+ , Ca^{2+} , and Mg^{2+}). From any of these correlations, it is clearly observed that the acidity of the cations is not only a simple function of the electrostatic attraction between the water molecules and the cationic species, the ability to form covalent bonds also being an involved parameter. To clarify this aspect, Figure 1 (right) displays the above-mentioned pK_a values against the absolute hardness values for each cation, taken from Pearson.¹³ Since the chemical bonds

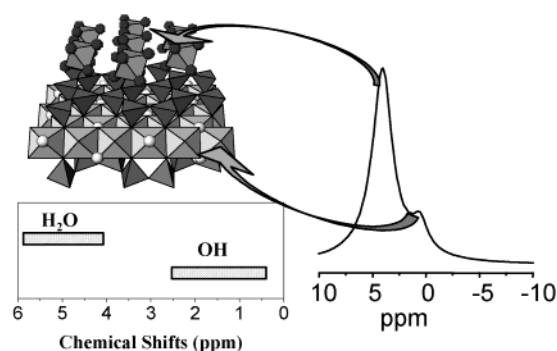


Figure 2. Schematic representation of a 2:1 trioctahedral-layered silicate accompanied by a typical 1H MAS NMR spectrum and a box displaying the chemical shift ranges at which proton signals from structural hydroxyl species and interlayer water molecules appear.

between water molecules and cations have independent covalent (soft or frontier controlled) and electrostatic (charged or charge controlled) contributions, fundamental problems arise when predictions are made from single-parameter considerations. Thus, the cations with the lowest and the highest hardness values show the higher acidities, both contributions, soft and hard, being observed. We have used both considerations to interpret the 1H MAS NMR spectra reported here in relation to the acidity of the solids.

High-resolution 1H MAS NMR spectra were recorded at room temperature for the smectites equilibrated in air (hydrated samples) and after ex situ heating to ensure the complete removal of interlayer water (dehydrated samples) in order to separate the contributions of structural hydroxyl and water. To choose the dehydration temperature, different temperature values between 100 and 400 °C were tested. The temperature of 150 °C was the minimum temperature value employed at which a complete disappearance of the proton signal attributed to interlayer water was achieved, similar results being obtained for the interlayer water signal under more drastic dehydration treatments. In consequence, dehydration treatments were carried out by ex situ heating at 150 °C for longer periods than 24 h. Dehydrated samples were transferred under controlled dry atmospheres into the rotors and precautions were taken to exclude water during the NMR measurements. Spectra were obtained at 9.39 T on a Bruker DRX-400 spectrometer, equipped with a 4 mm probe. The rotation frequency of the rotor was 12 kHz. Pulse spaces of 5 s were used and the radio frequency field for protons was 60 kHz. The chemical shift was referenced to tetramethylsilane.

3. Results and Discussion

Figure 2 includes a structural drawing of a trioctahedral smectite along with its typical 1H MAS NMR spectrum. From this structural drawing, it is observed that smectites are layered aluminosilicates composed of units, depicted at the bottom of the drawing, made up of two silica tetrahedral sheets, which

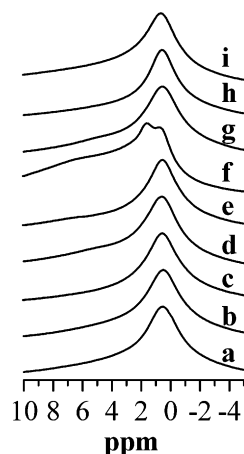


Figure 3. ^1H MAS NMR spectra of saponite saturated with (a) Na^+ , (b) Li^+ , (c) Ca^{2+} , (d) Mg^{2+} , (e) Cd^{2+} , (f) Sn^{2+} , (g) La^{3+} , (h) Lu^{3+} , and (i) Al^{3+} ions, and dehydrated at 150°C .

embed a central octahedral one. If all the octahedral positions of the central sheet are occupied (by magnesium or isomorphous substitutions), the smectite belongs to the trioctahedral series (specimen shown in Figure 2), and if only two-thirds of these positions are occupied (by aluminum or isomorphous substitutions), the smectite belongs to the dioctahedral series. In both cases, the vertices of the octahedra consist of closely packed oxygen and hydroxyl species, these latter being represented by light gray spheres. Isomorphous substitutions in the octahedral or tetrahedral sheets originate a charge deficit, which is compensated for hydrated cations located between the layers: the interlayer space. These hydrated cations have been depicted at the top of Figure 2 as coordination polyhedra, the water molecules being shown as black spheres. Hydrogen atoms, therefore, may be present in smectites in two different structural forms: structural hydroxyl species of the layers—light gray spheres—and water molecules of the interlayer space—black spheres—which are responsible for the two ^1H signals observed in the spectrum included in the figure. These signals can appear at chemical shift values comprised in the two well-differentiated ranges displayed in the figure. However, while some separation between both signals is observed for the ^1H MAS NMR spectra from trioctahedral smectites (Figure 2), a less-separated situation, a single broader band, is observed for the ^1H MAS NMR spectra from dioctahedral smectites (right part of Figure 6). Both contributions will be described for each kind of smectite in this paper, with the chemical shift δ and full width at half-height (fwhh) values being analyzed separately.

Structural Hydroxyl Groups. ^1H MAS NMR spectra were recorded from the smectites studied, intercalated with each cation, and after dehydration at 150°C . Representative ^1H MAS NMR spectra from a dehydrated saponite intercalated with different cations are shown in Figure 3. All the spectra, except that obtained from Sn—saponite, as described below, show a single component, exhibiting constant δ and fwhh values, corresponding to structural hydroxyl groups. Spectra obtained for the rest of the samples behaved similarly, with different δ and fwhh values being observed for each smectite. In consequence, both the line shape and position of the hydroxyl group band were only determined by the nature of the smectite and not by the nature of the interlayer cation. This observation is in agreement with infrared spectroscopic data from adsorbed molecules on these materials, such as water, alcohol, or ammonia, which conclude that interlayer cations do not interact with the lattice hydroxyl groups.¹⁴

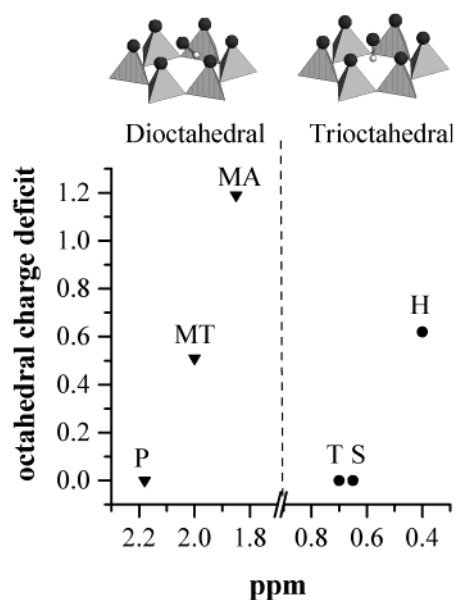


Figure 4. Bottom: Chemical shift values of the ^1H MAS NMR signals corresponding to the structural hydroxyl species as a function of the octahedral charge deficit of each sample (P for pyrophyllite, MT for Tranco's montmorillonite, MA for Arizona montmorillonite, T for talc, S for saponite, and H for hectorite). Top: Schematic representation of the pseudo-hexagonal cavity of the tetrahedral sheet containing the structural hydroxyl group of a (left) dioctahedral and a (right) trioctahedral smectite.

Figure 4 (bottom) shows the hydroxyl proton chemical shift values vs the octahedral charge deficit for each sample, from which a detailed analysis of the relationship between the mineralogical composition of the samples and the position of the signal was carried out. The chemical shift values are, in the first place, divided into two groups, which are in accordance with the octahedral nature of the smectite: the hydroxyl NMR peak shows a value of ca. 0.5 ppm for the trioctahedral samples and of ca. 2.0 ppm for the dioctahedral ones. This difference would be a consequence of the disposition of the hydroxyl group with respect to the layer. Figure 4 (top) includes a structural drawing of the pseudo-hexagonal cavities of the two series of smectites and shows the different OH bond orientation with respect to the *ab* plane. In trioctahedral minerals, the OH bond axes are perpendicular to the layers and point toward the hexagonal cavities, while they are almost parallel to the layers in dioctahedral ones.^{15–17} In consequence, the proton position in dioctahedral smectites allows a hydrogen bond to be formed between these OH groups and the apical oxygen atoms of the tetrahedral sheets, which causes a deshielding of the proton and, hence, a displacement of their resonance to lower fields.

Within each series—dioctahedral and trioctahedral smectites—the chemical shift values are related, in the second place, to the octahedral layer charge: as the octahedral charge deficit increases, the peak position shifts to a higher field. This fact can be explained on the basis of the charge deficit location created by the isomorphous substitutions in smectites, in agreement with former results.¹⁸ If the charge deficit originates in the octahedral sheet, the excess negative charge tends to be delocalized around the whole sheet and the proton shielding of the structural hydroxyls increases as the octahedral charge is elevated. However, if the charge deficit occurs in the tetrahedral sheet, the excess negative charge tends to be localized on single oxygen atoms and the effect on the hydroxyl proton shielding is negligible.¹⁸

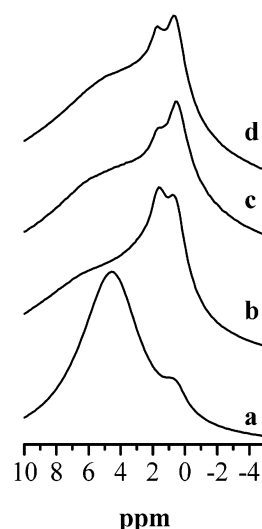
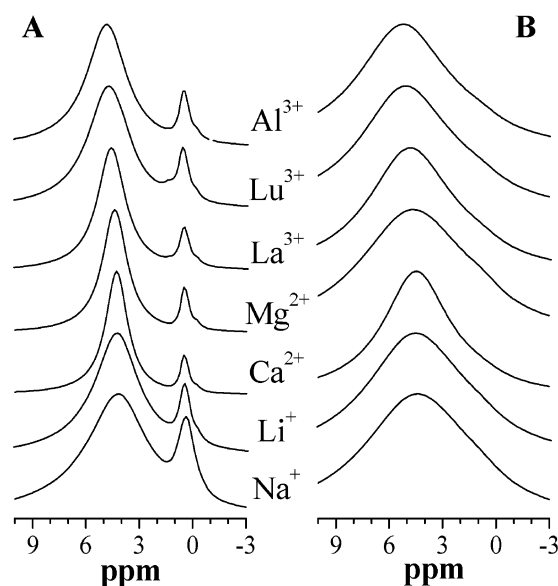
TABLE 2: Aluminum and Iron Content per Unit Cell and Full Widths at Half-Height (fwhh) of Structural OH Signal for the Selected Smectites

samples	aluminum content	iron content	fwhh (ppm)
trioctahedral			
talc			1.2
SapCa-1	0.80	0.14	4.3
SHCa-1	0.08		1.2
dioctahedral			
pyrophyllite	4.00		2.8
Trancos	3.45	0.28	7.9
SAz-1	2.74	0.14	7.3

Table 2 summarizes the fwhh values of these proton signals, which are influenced by both structural and compositional parameters. First, a considerable difference in the line-width value, due to the octahedral occupancy, can be observed, the trioctahedral signals being narrower than the dioctahedral ones. In trioctahedral minerals, the hydroxyl groups are perpendicular to the layer and they point toward the middle of the hexagonal cavity, whereas in dioctahedral minerals, the hydroxyls are tilted and point toward one of the tetrahedra of the hexagonal array, a librational motion being allowed (see top of Figure 4). In consequence, the trioctahedral minerals show a more ordered hydroxyl chemical environment, exhibiting narrower ^1H MAS NMR signals, and the dioctahedral minerals show an average of different hydroxyl orientations, exhibiting wider bands.

Second, the observed fwhh values are related to both the amount of paramagnetic impurity in the sample and the dipolar interactions between proton and other spins, which caused an increase in the bandwidth. Since a combination of all of these factors is ultimately responsible for the line broadening, it is very difficult to determine a straight relationship between the fwhh values and any structural parameter. There is, however, a marked influence of the aluminum content on the line width, with the only exception of pyrophyllite, for two reasons: the absence of both paramagnetic impurities and the isomorphic substitutions in that sample.

As regards the Sn-exchanged smectites, anomalous behavior was found. Spectra obtained after dehydration at 150 °C showed a bump centered at the chemical shift value corresponding to the water molecules, at 4.75 ppm, and a splitting of the hydroxyl group band, a doublet being visible at around 0.60 ppm (see Figure 3 for the particular case of Sn-saponite). These results indicate that heating at 150 °C does not fully dehydrate the sample and subsequent dehydration treatments, at higher temperatures, were carried out. Figure 5 shows ^1H MAS NMR spectra from a Sn-saponite sample before and after heating at different temperatures. After the heating process, a reduction of the band corresponding to water molecules is observed, but even in the case of the sample heated at 500 °C (Figure 5d), the ^1H signal from the residual water molecules and the doublet signal remain, stronger water-cation bonds being inferred. Both signals may be explained on the basis of the high acidity of the Sn^{2+} cations and the formation of stable hydroxycompounds: water and hydroxyl ligands of these species are responsible for the signals, respectively. It is interesting to note that the other studied cations do not have shown this dehydration behavior, not even those cations with similar acidity strengths, i.e., Al^{3+} (see Figure 1). The much smaller ionic radius of the aluminum cation, 0.51 vs 0.93 Å of the Sn^{2+} , can account for this fact, as these ions are accommodated in a different structural location, such as the pseudohexagonal cavities of the tetrahedral sheets, in accordance with the general literature.¹⁹ However, the proton chemical shift values of the hydroxyl shown in this paper do

**Figure 5.** ^1H MAS NMR spectra of Sn-saturated saponite (a) before and after dehydration treatments at (b) 150 °C, (c) 250 °C, and (d) 500 °C.**Figure 6.** ^1H MAS NMR spectra of hydrated (A) hectorite and (B) Arizona montmorillonite saturated with the above-indicated cations.

not seem to be sensitive to this process. Likewise, Madejová et al.¹⁷ observed, from IR measurements, that OH stretching region of some heated montmorillonite is not affected by small cations located in the pseudohexagonal cavity. Further investigations are needed in order to elucidate the actual location of these cations.

Water Contribution. Figure 6 shows the ^1H MAS NMR spectra of two different smectites equilibrated in air: a hectorite as a representative member of the trioctahedral series and an Arizona montmorillonite as a representative member of the dioctahedral one, both of them homoionized with different cations. As reported in the latter section, the structural hydroxyl NMR peaks are broader and appear at lower fields in dioctahedral smectites than in trioctahedral ones. For this reason, structural hydroxyl and water signals appear as a unique NMR contribution in the spectra of dioctahedral samples. To isolate the proton signal corresponding to the interlayer water, spectra from dehydrated samples (with proton signals only corresponding to structural hydroxyl) were subtracted from the hydrated sample spectra (with proton signals from both interlayer water

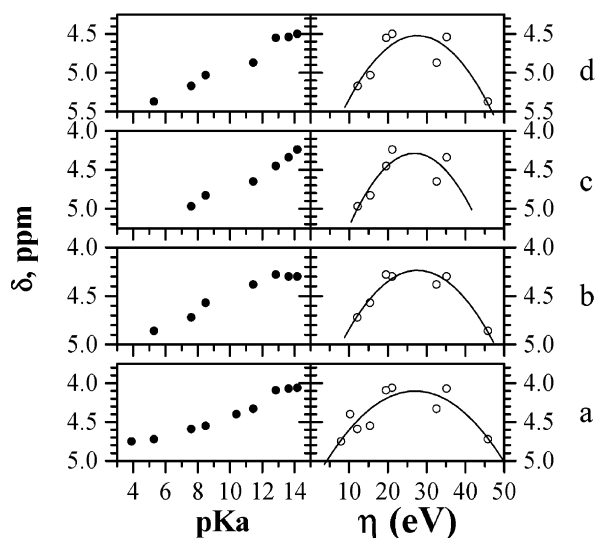


Figure 7. Chemical shift values of the ^1H MAS NMR signals corresponding to the interlayer water molecules (a) saponite, (b) hectorite, (c) Tranco's montmorillonite, and (d) Arizona montmorillonite, as a function of the pK_a values for metal-ion M^{n+} (left) hydrolysis and (right) as a function of the absolute hardness value for each cation.

and structural hydroxyl). The resultant curves, in which the proton signal corresponding to interlayer water was isolated, were fitted to Lorentzian functions.⁶

Figure 7 illustrates the relationship between the computed ^1H chemical shift values from water molecules and the pK_a values obtained for each hydrated cation, extrapolated at infinite dilution¹⁰ (left column), and the absolute hardness values for each cation¹³ (right column). Regarding the first one, δ vs pK_a , there is an almost linear dependence between the chemical shift value found for each cation and its pK_a value. However, both the slope and the intersection in the origin for these straight lines are particular for each smectite. Two important considerations should be taken into account in order to interpret this fact. First, the pK_a values used here were obtained from potentiometric measurements, by extrapolating them to infinite dilution, the water concentration being considered as constant.²⁰ However, in the solid systems being analyzed, the water concentration is far from being constant and the pK_a values are not necessarily constant. Thus, they should be considered only from a qualitative point of view. Second, the interlayer charge for each system is different, see Table 1, and the cation concentration will accordingly be different for each solid. This concentration would also affect the acidity of the solid and to its ability to lend protons in each system. Therefore, these measurements are clearly related to the parameter analyzed first pK_a , but they are related, in a direct way, only to the proton shielding in each particular system.

As regards the second relationship δ vs η , the lowest and highest absolute hardness values are connected with low-field chemical shifts, i.e., highly unshielded protons, and intermediate absolute hardness values are connected with chemical shifts at higher fields. This fact is in agreement with the general HSAB theory. Thus, for water-ion adducts formed through interactions with either highly covalent, low absolute hardness values, or highly ionic, high absolute hardness values, the contributions are strongly bonded, the protons being highly unshielded in both situations. Volcano-shaped curves can be drawn for each solid, the optimized parameters again being different for each smectite. It should be noted that the absolute hardness values used here were obtained from bare cations, and they were different from those expected for the actual situation of the interlayer cations,

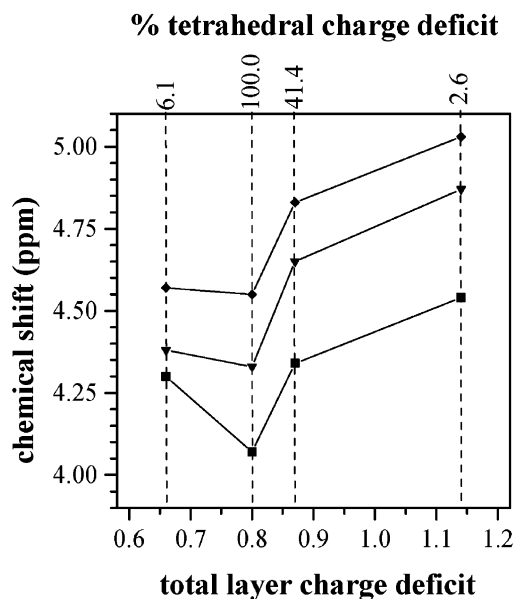


Figure 8. Chemical shift values of the ^1H MAS NMR signals corresponding to the interlayer water molecules for the four smectites saturated with (squares) Li^+ , (triangles) Mg^{2+} , and (diamonds) La^{3+} ions, as a function of the layer charge deficit for each sample. Tetrahedral charge deficit values for each sample, expressed in percentage, are included at the top x-axis.

surrounded by various ligands. In consequence, they should be used only in qualitative terms.¹³ However, the good agreement found between them should be emphasized, taking into account that in polar solvents, like the interlayer water molecules, and in reactions involving solid phases, like the silicate layers, energy contributions from solvation and lattice energies can even dominate the chemistry.²¹ The reasonable relationship obtained between the ^1H MAS NMR measurements and either pK_a or η parameters, modulated for each solid system, indicate, independently of any theoretical consideration, the real importance of these measurements: that is, the reading of the chemical shift value from water molecules in smectites provides direct information on the ability of the solid to lend protons.

A final argument for the influence of the silicate surface on the acidity of the solids is included. Figure 8 displays the chemical shift values attributed to interlayer water molecules from the four smectites saturated with three selected cations against the layer charge for each mineral, the rest of the interlayer cations exhibiting similar behavior. It is observed that (a) all the smectites display the same rank ordering as they change the interlayer cation, which has already been discussed and (b) that the chemical shift values for each cation are shifted to lower fields as the silicate layer charge is increased, saponite being the sole exception. In the water content corresponding to these samples, less than three monolayers in the interlamellar space in all the cases, it is proven that the spatial arrangement of the water molecules derives mainly from the solvation of exchangeable cations.¹⁸ Therefore, it is reasonable that the larger the layer silicate charge, the larger the amount of interlayer cations and, consequently, the higher the acidity values. However, despite the great significance of the exchangeable cations for the structure of interlayer water on smectites, the role of the silicate surface cannot be neglected, as the nature of the interaction between the silicate surface and interlayer species—water molecules and interlayer cations—is dependent on the degree of localization of charge deficits created by isomorphous substitutions in the smectite.¹⁸ Thus, if the deficit occurs in the tetrahedral sheet, as in the case of the saponite

sample, the excess negative charge tends to be localized on single oxygen atoms and simultaneous interactions of interlayer cations with both interlayer water molecules and oxygen atoms belonging to the silicate layers are present. Interactions between the cations and the basal negative-charged oxygen of the silicate, observed from ^{23}Na , ^{133}Cs , and ^{111}Cd MAS NMR measurements,²² reduce the positive electrical charge on the cations and, consequently, their acidity. In short, the total layer charge deficit of the smectites causes an increase in the amount of interlayer cations, and an increase in the aqua metal ion acidity, and the tetrahedral localization of the charge deficit cause an opposite effect because it reduces the cation charge and, therefore, its acidity.

4. Conclusions

This paper shows, for the first time, that the combined use of high magnetic fields and spinning speeds affords single-pulse ^1H MAS NMR spectra of smectites of a similar quality to those currently obtained by using multiple-pulse sequences. The good quality of the spectra permits the examination of the two proton environments in smectites—structural hydroxyl and interlayer water—separately.

^1H MAS NMR signals corresponding to the structural hydroxyl groups are only determined by the nature of the smectite and not by the nature of the interlayer cation. Chemical shift values obtained from these hydroxyl groups are related to the octahedral occupancy (the structural hydroxyl groups are more deshielded in dioctahedral smectites) and to the octahedral charge (peak position shifts to a higher field as the octahedral charge deficit increases). Their bandwidth values are influenced by octahedral occupancy (the trioctahedral signal being narrower than dioctahedral one), paramagnetic impurity, and dipolar interactions between proton and other spins.

The water contribution to the ^1H MAS NMR is affected not only by the nature of the interlayer cation but also by the nature of the smectite and informs directly on the ability to lend protons in this material. There is a clear relationship between the ^1H MAS NMR signals from each cation-exchanged smectite and different parameters associated with the acidity of these ions, such as the $\text{p}K_{\text{a}}$ values for these ions in solution and the absolute hardness values for these bare ions. However, the ^1H MAS NMR signals are not constant for each cation in different solids, these signals being dependent on the actual acidity exhibited for the cations in each solid.

Regarding the nature of the smectite, the chemical shift value from the interlayer water molecules is affected by both the total layer charge deficit and the distribution of this value between the tetrahedral and octahedral sheets. As the total charge deficit increases the proton shielding decreases, the acidity being enhanced, and as the charge deficit is caused by tetrahedral substitutions, the cation electrical charge is reduced, with a composite effect being observed. In any case, the reading of the chemical shift value from interlayer water molecules informs directly on the acidity of the solid.

This paper provides a new, direct method to estimate the acidity of hydrated interlayer cations inserted in the interlayer space of layered aluminosilicates and a new tool with which to study the water coordination of cations entrapped in porous solids by ^1H MAS NMR. New measurements should be made in order to evaluate the application of these in different acid solids, which should allow the development of a new general method to determine the inherent acidity.

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