

⁷Li Double Quantum Filtered NMR and Multinuclear Relaxation Rates of Clay Suspensions: The Effect of Clay Concentration and Nonionic Surfactants

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⁷Li double quantum NMR spectra were used to investigate ordering process of synthetic Li⁺-saponites dispersed in water. Synthetic clays suspended in aqueous solutions of poly(ethylene glycol) monoalkyl ethers were also studied by ⁷Li, ²³Na, and ¹³C NMR techniques. The strongest surfactant–Li⁺-saponite interaction occurs with the lowest charged clay. Laponite interacts more strongly with organic molecules than does a similarly charged saponite. The number of oxyethylene units rather than the chain length seems to govern the solid–surfactant interaction. © 1999

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For the past few years, multiple quantum filtering NMR techniques have been used to study local anisotropies in biological systems (1–5), and quite recently to probe a solid surface (6). These NMR methods could be applied to any heterogeneous systems. As a part of our investigations on synthetic clay suspensions (7–9), we have also performed such experiments on ⁷Li cations that counterbalance the negative charges brought by clay platelets. ⁷Li double quantum filtered NMR spectra of clay suspensions have shown residual static quadrupolar interaction. This observation supports a recent model to explain ²³Na nuclear quadrupolar relaxation in aqueous clay dispersions (10).

Studies on the interaction between clays and nonionic surfactants or closely related oligomers have also been published recently (9, 11–13), and we describe here new results with saponite and laponite clays to complement our recent data (9).

The lamellar structure of clays, also named phyllosilicates, consists of layers formed by condensation of sheets of linked Si(O,OH)₄ tetrahedra with those of linked M_{2–3}(OH)₆ octahedra, where M is either a divalent or a trivalent cation. Three-sheet clays result from 2:1 condensation, the octahedral sheet being sandwiched between two sheets of inward-pointing tetrahedra. Saponite and laponite are trioctahedral clays with all three of their octahedral sites occupied by Mg(II). Clay plate-

lets are negatively charged, as a result of cation isomorphous substitution either in the octahedral layer (Li(I) for Mg(II) in laponite) or in the tetrahedral layer (Al(III) for Si(IV) in saponite). Cation isomorphous substitution thus induces negative charges on the clay platelets, and exchangeable cations such as sodium occupy the interlamellar space in order to preserve electroneutrality.

In this paper, we have considered the dependence of the counterion type (Li⁺ or Na⁺), the clay structure (laponite or saponite), and the length of the surfactant oxyethylene chain on the clay–amphiphile interaction. Quadrupolar splittings determined from ⁷Li double quantum filtered NMR spectra appear to be a quite sensitive probe to study the state of lithium counterions as a function of the nonionic surfactant or of the clay content. Particularly, the resulting quadrupolar splittings can be measured even when they are not resolved in the usual single quantum NMR spectrum.

RESULTS

Clay–Nonionic Surfactant Interaction

In order to compare with previous data obtained with Na⁺-saponite suspensions (9), lithiated clays were prepared by the usual exchange process (7). A typical ⁷Li NMR spectrum of a lithium-exchanged saponite suspension is shown in Fig. 1, together with the double quantum filtered spectrum (asymmetric doublet) obtained with the pulse sequence 90°–τ–180°–τ–54.7°–t–54.7° (ACQ) (1).

Similar splitting values are deduced from both spectra. But the double quantum filtering technique remains useful when smaller splittings (≤100 Hz) are not resolved in the usual ⁷Li NMR spectra.

To study clay–nonionic surfactant interaction, solids were suspended as previously (9) in solutions of poly(ethylene glycol) monoalkyl ethers (C_nE_m, *n*: number of carbons in the terminal alkyl chain carbons; *m*: number of OCH₂CH₂ units). C₈E_{4–5} forms micelles in aqueous solutions (14), whereas the monomethyl ethers do not aggregate in such liquid phases.

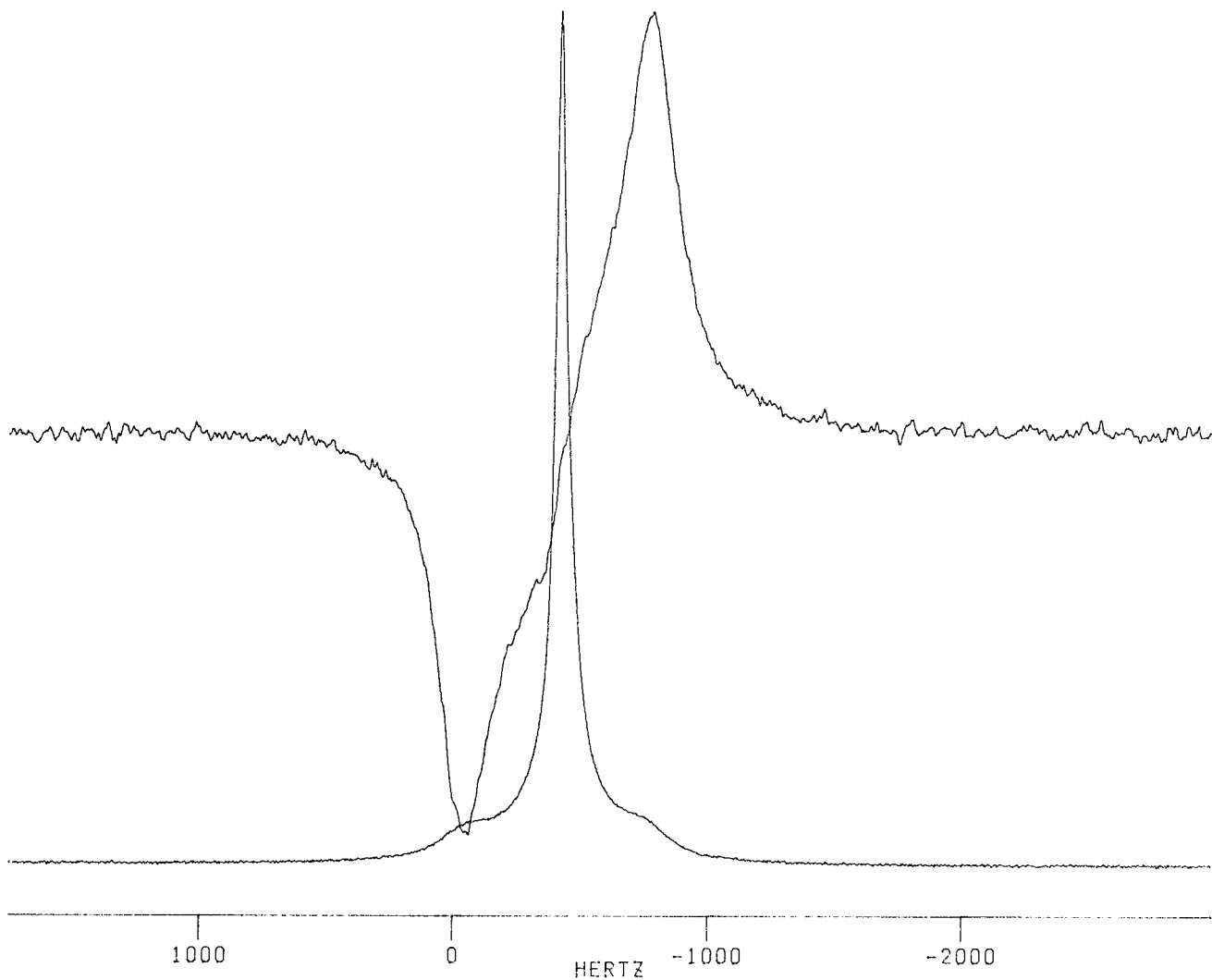


FIG. 1. ^7Li NMR spectrum (lower trace) and ^7Li double quantum NMR spectrum (Bruker AM 300WB spectrometer, $\tau = 20 \mu\text{s}$, $t = 200 \mu\text{s}$, 90° pulse $25 \mu\text{s}$, acquisition time 0.819 s; relaxation delay 0.6 s; number of scans = 12,800) of SA75 clay suspension (212 mg/10 ml).

Several NMR parameters are relevant to characterize the clay–nonionic surfactant interaction (9). As all these results converge to the same conclusion (9), we only report ^7Li and ^{13}C NMR results on suspensions of lithium-exchanged saponites with 0.35 and 0.75 layer charge per half-unit cell (SA35LI and SA75LI, respectively). The ^7Li NMR longitudinal relaxation rates and quadrupolar splittings estimated from the double quantum spectra are summarized in Table 1. To complement these data, the ^{13}C longitudinal relaxation rates of the organic molecules are also given (Table 2).

The influence of the clay structure on its interaction with poly(ethylene glycol) derivatives has been envisaged with suspensions of Na^+ -laponite and Na^+ -saponite. Isomorphous cation substitution occurs in the octahedral and tetrahedral layer for laponite and saponite, respectively. As laponite bears 0.28 charge per half-unit cell (LAP28NA), saponite with the most closely related charged (0.30) (SA30NA) was used for com-

parison purpose. The ^{23}Na counterion relaxation parameters and the ^{13}C longitudinal relaxation rates of amphiphile molecules are shown in Tables 3 and 4, respectively.

TABLE 1
 ^7Li NMR Quadrupolar Splittings Δ and Longitudinal Relaxation Rates R_1 of Lithiated Saponites Suspended in Water or in Polyether Solutions^a

Clay charge	In water		In $\text{C}_{12}\text{E}_{6-8}$		In $\text{C}_{8}\text{E}_{4-5}$	
	Δ (Hz)	R_1 (s^{-1})	Δ (Hz)	R_1 (s^{-1})	Δ (Hz)	R_1 (s^{-1})
0.35	225	4.33	<20	5.16	± 0	5.16
0.75	360	10.36	330	10.16	340	10.30

^a Li^+ : $7.78 \cdot 10^{-4}$ mol/g; $\text{C}_{12}\text{E}_{6-8}$: 51 mg/l H_2O ; $\text{C}_{8}\text{E}_{4-5}$: 43.1 mg/l H_2O ; $T = 300$ K.

TABLE 2
 ^{13}C NMR Relaxation Rates R_1 (s^{-1}) of C_1E_{6-8} or C_8E_{4-5}
 in Water and in Lithiated Saponite Suspensions^a

	C_1E_{6-8} main -OCH ₂ signal	C_8E_{4-5}	
		Main -OCH ₂ signal	Main -CCH ₂ signal
Water	0.804	1.58	1.24
SA35LI	1.91	3.28	1.66
SA75LI	0.808	1.61	1.18

^a Li^+ : $7.78 \cdot 10^{-4}$ mol/g; C_1E_{6-8} : 51.2 g/L; C_8E_{4-5} : 43.1 g/L; $T = 300$ K; clay charge per half-unit cell is 0.35 (SA35LI) and 0.75 (SA75LI).

Effect of Saponite Content

The amount of saponite (SA75LI) dispersed in water influences the quadrupolar splittings measured from ^7Li double quantum filtered NMR spectra (Table 5). Conversely, spin lattice relaxation times are weakly affected ($100 \text{ ms} \pm 10\%$) and they are not considered further.

DISCUSSION

Clay–Nonionic Surfactant Interaction

The ^7Li NMR quadrupolar splitting observed in lithiated saponite suspensions indicates nonzero averaging of the electric field gradient tensor at the alkali nucleus. Such a residual quadrupolar interaction is also expected for other alkali ions such as Na^+ that interact more tightly with the clay surface. This supports a recent model to explain relaxation data of $^{23}\text{Na}^+$ clay counterions. Indeed, the authors have considered a static residual splitting to analyze these relaxation data (10).

In contrast, the ^7Li NMR spectra of lithiated-laponite dispersions do not show such a splitting (7). Adsorbed counterions can form inner and outer sphere complexes (contact and solvent separated ion pairs, respectively), and the relative amounts of each type of complex depend upon the hydration energy of the cation (15–17) and the location of isomorphous cation substitution in clay platelets (18, 19). In saponites, cat-

TABLE 3
 ^{23}Na NMR Relaxation Rates R_1 (s^{-1}) of Na^+ -Clay Suspended
 in Water or in Polyether Solutions^a

Clay	In water R_1	In C_1E_{6-8} R_1	In C_1E_{40} R_1	In C_8E_{4-5} R_1
LAP28NA	61.8	182	334	951
SA30NA	42.6	203	453	935

^a Na^+ : $7.78 \cdot 10^{-4}$ mol/g; C_1E_{6-8} : 51.2 g/L; C_1E_{40} : 51.3 g/L; C_8E_{4-5} : 43.1 g/L; $T = 300$ K; clay charge per half-unit cell is 0.28 for laponite (LAP28NA) and 0.30 for saponite (SA30NA).

TABLE 4
 ^{13}C NMR Relaxation Rates R_1 (s^{-1}) of Polyethers in Water
 and in Clay Suspensions^a

	C_1E_{6-8} main -OCH ₂ signal	C_1E_{40} main -OCH ₂ signal	C_8E_{4-5}	
			Main -OCH ₂ signal	Main -CCH ₂ signal
Water	0.804	1.04	1.58	1.24
LAP28NA	1.30	1.84	2.75	1.53
SA30NA	0.963	1.37	2.08	1.33

^a Na^+ : $7.78 \cdot 10^{-4}$ mol/g; C_1E_{6-8} : 51.2 g/L; C_1E_{40} : 51.3 g/L; C_8E_{4-5} : 43.1 g/L; $T = 300$ K; clay charge per half-unit cell is 0.28 for laponite (LAP28NA) and 0.30 for saponite (SA30NA).

ion replacement occurs in the tetrahedral layer. A negative charge associated with such a cation substitution can be distributed over just the three surface oxygens of one tetrahedron. This localized charge leads to a stronger interaction with counterions than that of the more diffuse charge resulting from the octahedrally substituted laponite. On the other hand, an increase of the layer charge gives rise to a stronger clay–counterion interaction. It induces a reduced mobility of the cation surroundings and a larger electric field gradient at the counterion nucleus. Both effects contribute to the larger quadrupolar splitting of SA75LI (Table 1). Similarly, at the same lithium content, the highest ^7Li longitudinal relaxation rate is observed with SA75LI (Table 1). The extreme narrowing condition ($\omega\tau_c \ll 1$) does not prevail here, as with Li^+ -laponite (7) and Na^+ -saponites (9). Thus, the increase of the relaxation rate with the clay charge stems from a larger electric field gradient at the nucleus rather than from an unrealistic increase of the mobility of the counterion environment.

Addition of C_1E_{6-8} or C_8E_{4-5} to the lowest charged clay suspensions results in a sharp decrease of the ^7Li quadrupolar splitting (Table 1). Higher symmetry and/or higher mobility of the counterion surroundings can explain this behavior. The

TABLE 5
 Variation of ^7Li Quadrupolar Splitting Δ versus Clay (SA75LI)
 Content, $T = 300$ K

Clay content (mg/10ml)	Δ (Hz) ^a
116.8	390
202.0	365
290.0	326
370.0	230 ^b
448.0	129 ^b
598.4	108 ^b
678.3	120 ^b
755.3	113 ^b

^a Determined from double quantum filtered spectra.

^b Unresolved in the single quantum NMR spectrum.

enhancement of the ${}^7\text{Li}$ longitudinal relaxation rates also reflects the ion interaction with polyether oxygens (Table 1). As a decrease in the electric field gradient should lead to lower ${}^7\text{Li}$ relaxation rates, a mobility increase of the cation environment is the dominant factor to account for these data. Clay–surfactant interaction is also expected to decrease the average mobility of amphiphile molecules. Indeed, an increase in the relaxation rates of the polyether carbons (the extreme narrowing condition is valid here) consistent with a reduced molecular mobility occurs with SA35LI suspensions (Table 2).

Conversely, no significant change of these NMR parameters is found with SA75LI (Tables 1 and 2). As a result of their higher hydration power, lithium ions are known to interact more weakly than sodium cations with the clay surface. Nevertheless, the behavior of the investigated poly(ethylene glycols) is similar in Na^+ - (9) and Li^+ -saponite suspensions: A significant interaction occurs only with the least charged clays, and both polyethers (C_1E_{6-8} and C_8E_{4-5}) interact similarly with this clay.

In contrast to the ${}^7\text{Li}$ NMR signal, which is totally NMR-visible (7), the ${}^{23}\text{Na}$ NMR spectra of laponite (7) and saponite (8) suspensions only show the central narrower line ($m = \frac{1}{2} \rightarrow -\frac{1}{2}$ transition). A stronger interaction of sodium cations with the solid surface and a higher quadrupolar moment explain this observation. Outside the extreme narrowing condition, the higher ${}^{23}\text{Na}$ relaxation rates of laponite compared to saponite (Table 3) are consonant with a higher mobility of the ion environment, as expected for a weaker attraction by the octahedrally substituted solid. ${}^{23}\text{Na}$ and ${}^{13}\text{C}$ NMR relaxation rates have been measured to characterize the interaction of poly(ethylene glycols) with the two clays bearing similar charges. As saponite is tetrahedrally substituted, sodium cations are more tightly fixed by the solid surface. A smaller increase of ${}^{13}\text{C}$ relaxation rates (extreme narrowing condition) indicates unambiguously a weaker interaction of amphiphile molecules with SA30NA than with LAP28NA (Table 4). On the other hand, at a constant number of oxyethylene units, the relative increase of the relaxation rates brought by both clays remains similar for C_1E_{6-8} and C_1E_{40} (Table 4). Accordingly, the total number of oxyethylene units rather than the chain length seems to govern the clay–polyether interaction. ${}^{23}\text{Na}$ NMR data analysis is less straightforward since both an increase of the electric field gradient and the cation environment mobility account for the relaxation rate enhancement (Table 3). However, the ${}^{23}\text{Na}$ relaxation rate increases with the particle mass (isolated molecules for C_1E_{6-8} and C_1E_{40} and micelles for C_8E_{4-5}). This observation is in agreement with less symmetric cation surroundings leading to a higher electric field gradients.

Effect of Saponite Content

Except for the lowest SA75LI contents, ${}^7\text{Li}$ quadrupolar splitting remains unresolved in the single quantum NMR spectra. Using double quantum filtering techniques, this parameter

can be directly measured, at least until values of ~ 100 Hz (Table 5). The quadrupolar moment (eQ_{zz}) of lithium nucleus interacts with the electric field gradient (eq_{zz}) generated at the nucleus site. The observed splitting indicates a nonzero averaging of the electric field gradient at the alkali nucleus. For an oriented sample, the ${}^7\text{Li}$ ($I = \frac{3}{2}$) quadrupolar splitting Δ is given by

$$\Delta = |(3 \cos^2 \theta_{\text{LD}} - 1) \sum_i p_i (\chi_i / 4) S_i|$$

with θ_{LD} the mean azimuthal angle between the principal axes of the coordinates systems associated with the laboratory (L) and the director (D). This angle is assumed to be constant at the NMR time scale, i.e., no change in the clay platelet orientation occurs within this period. The value of Δ is a weighted average of the values at the different sites i , due to rapid exchange. The order parameter S_i ($= \frac{1}{2} \langle (3 \cos^2 \theta_{\text{DF}} - 1) \rangle$) describes the (axially symmetric) electric field gradient orientation (F) of the ion fraction p at site i with respect to the director (D), and χ ($= e^2 q_{zz} Q_{zz} / h$) is the quadrupolar coupling constant.

As viscosity increases with the amount of dispersed clay, we could argue that the clay platelet orientation within the magnetic field has not reached equilibrium for the highest concentrated suspensions (20). This partial ordering could reduce the residual static quadrupolar interaction. The constancy of the splitting values for a residence time of ~ 24 h in the magnet rules out this possibility. Similarly, a decrease of the ordering process with the clay content could also account for these observations. The opposite is true. Water deuteron and oxygen-17 NMR spectra show only single Lorentzian lines in dilute suspensions. By contrast, ${}^2\text{H}$ doublets and ${}^{17}\text{O}$ quintets are observed in the NMR spectra of samples with higher amounts of saponite dispersed in water, and alignment is improved. As known from literature, clay aggregation increases with the mineral content. Accordingly, this should lead to a better ordering and an increase of the ${}^7\text{Li}$ NMR splitting. With a highly charged saponite such as SA75LI, lithium counterions are close to each other, and aggregation of the clay platelets may generate repulsion between them. This may change their average position, giving rise to a smaller (more symmetric) electric field gradient and/or an angle θ_{DF} closer to the magic angle. For the highest clay contents, the ordering process seems to be completed. Indeed, quadrupolar splittings do not change with the clay amount or with the residence time in the magnet (Table 5). To substantiate this explanation, similar experiments were performed with a less-charged clay, SA35LI. Here, the mean distance between two neighboring counterions is larger by $\sim 50\%$. As previously with SA75LI, water deuteron and oxygen-17 splittings show a similar ordering process for higher clay contents. In contrast with the results of SA75LI, the expected behavior is found with SA35LI: The ${}^7\text{Li}$ NMR splitting increases progressively with the clay content.

CONCLUSION

A static residual quadrupolar interaction is shown for ^7Li counterion nuclei of lithiated saponite suspensions, and the resulting line splitting can be determined by double quantum filtration techniques, even when one single line is observed in the usual single quantum NMR spectrum. Enhancement of ordering in suspensions is observed with increasing amounts of clay, although the ^7Li quadrupolar splittings evolve differently with the two investigated saponites. ^7Li NMR splittings together with ^7Li , ^{23}Na , and ^{13}C relaxation parameters have been used to study clay interaction with poly(ethylene glycol) monoalkyl ethers. The strongest interaction is observed for the lowest charged clay with isomorphous cation substitution in the octahedral layer. The length of the oxyethylene chain does not significantly affect this interaction, which seems to be governed by the number of such units.

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