

MOBILITY OF SMALL MOLECULES IN INTERLAYERS OF HECTORITE GELS: ESR STUDY WITH AN UNCHARGED SPIN PROBE

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Abstract—Electron spin resonance (ESR) spectroscopy was used to measure the rotational mobility of an uncharged nitroxide spin probe (4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy) in hectorite gels of variable water content. Physical adsorption segregated the probe molecules into two populations: probes in the solution or a solution-like phase, and motionally restricted probes in the adsorbed phase. Although the spectra of these two populations were discrete, indicating that exchange between them was slow on the time scale relevant to ESR, their overlap prevented a straightforward determination of mobility of the adsorbed probes. Even though adsorption was weak, effects of the adsorbed population on the spectral lineshape were detectable for suspensions containing as little as 20 grams clay per liter of water. Orientation of the adsorbed probes on the fully hydrated hectorite surfaces was similar to that of a positively charged nitroxide probe, suggesting that steric factors rather than electrostatic forces control short-range organic molecule interaction with the silicate. The possibility of reaching false conclusions about probe mobility and interlamellar water viscosity when using a weakly adsorbing probe is discussed.

Key Words—ESR, Hectorite, Molecular mobility.

INTRODUCTION

A multitude of studies have been devoted to the properties of water adsorbed on clay surfaces using various approaches ranging from measurements of macroscopic thermodynamic properties to spectroscopic investigations that provide information at scales of time and space sensitive to molecular vibration, rotation, and translation. Nevertheless, the extent of influence of silicate clay surfaces on the organization and structure of interfacial water remains a topic of some controversy. The review by Sposito and Prost (1982) has dealt with the topic in some detail, stressing that different methods of study may produce ostensibly contradictory views of surface water because each experimental method has a characteristic time scale, and can only detect those features of water structure that exist during that time scale. For example, measurement of forces between hydrated mica sheets by Israelachvili and co-workers (Israelachvili and Adams, 1978; Pashley and Israelachvili, 1984) has revealed oscillatory forces that extend to about 15 Å from the surfaces in 10^{-3} M KCl solution. The results have been interpreted as arising from ordered monolayers of H_2O molecules, but these measurements are made on a time scale that is very long compared to the vibrational (10^{-13} s), rotational (10^{-11} – 10^{-12}) and translational ($> 10^{-11}$ s) motion of water molecules. Consequently, the order apparent in the time-averaged positions of these H_2O monolayers, separated by about 2.5 Å, may be blurred at much shorter time scales of observation afforded by spectroscopic techniques such as nuclear magnetic resonance (NMR) and electron spin resonance (ESR).

The structure which averages the effects of vibra-

tional, rotational, and translational motion of water molecules is termed the diffusionally averaged structure (D structure). The water structure “seen” by NMR and ESR is averaged only by vibrational motion, and is termed the vibrationally averaged structure (V structure). It has been shown by NMR studies of smectite gels (Fripiat *et al.*, 1982), that the surface influences water behavior (V structure) only to a distance of about 10 Å (roughly 3 monolayers of water) from the surface, with the surface water having about a 100 times reduction in rotational mobility. ESR studies of hydrated paramagnetic cations such as Mn^{2+} and VO^{2+} adsorbed on fully wetted smectites have revealed rotational mobility of the hydrated cations that is only 30–50% reduced relative to the mobility of these cations in solution (McBride, 1979; McBride *et al.*, 1975). Because these smectites were saturated with divalent exchange cations, the interlayer spacing was limited to about 11 Å. Assuming that the divalent cations are positioned in the center of this interlayer, and that the rotational correlation time, τ_R , of the hydrated cations is correlated to the microviscosity, η , of the immediate environment of the cations according to the Debye model of rotation:

$$\tau_R = \frac{4}{3} \pi r^3 \frac{\eta}{k_B T} \quad (1)$$

(where r is the radius of the rotating ion or molecule), then the microviscosity at a distance of 2 water monolayers (~ 5 Å) from the surface is only 30–50% higher than the viscosity of free water. When it is considered that most of the rigidity in surface water appears to be associated with the first one or two monolayers (Fripiat

et al., 1982; Israelachvili *et al.*, 1988), the ESR results seem to be in reasonable agreement with the NMR results. Measures of H₂O self-diffusion in smectite interlayers (Kemper *et al.*, 1964) have also provided evidence that the effect of the clay surface on mobility decreases exponentially with distance, so that most of the reduction in mobility was assigned to the first two molecular layers of water. It must be stressed that viscosity measured as a microdynamic property of water in clays can be orders of magnitude higher than the macroviscosity of the clay gel (Fripiat *et al.*, 1982).

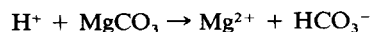
Based on the results to date, it is reasonable to suggest that any water added to smectite beyond the third monolayer would be little different from bulk water as measured by dynamic properties such as rotational and translational mobility. Paramagnetic cations seem a natural choice to probe, using ESR, the silicate clay-water interface at distances beyond the first few layers of water. However, because there are no monovalent inorganic cations with useful ESR spectra at room temperature, none of the ESR studies conducted to date have probed the interlayers of freely-swelling clays such as Na⁺-smectites. Nitroxide spin probes, which are low molecular weight stable organic radicals whose ESR spectra are particularly sensitive to changes in rotational mobility on the time scale of molecular rotation in free and interfacial water (10⁻⁹–10⁻¹¹ s), are available as positively charged, negatively charged, and uncharged molecules. Earlier ESR studies of Na⁺-smectites doped with the cation spin probe, TEMPAMINE⁺, at about 1% of the CEC (McBride, 1986) indicated that even in fully swelled clays, the organic cations remained near the surfaces and maintained a much-reduced mobility and partial orientation. The value of τ_R for TEMPAMINE⁺ in free water and on fully-wetted Na⁺-hectorite was 0.05 and 1.7 nanoseconds (ns), respectively. This difference in τ_R compares favorably to the estimate from NMR that τ_R for surface water is about 100 times longer than that of free water (Fripiat *et al.*, 1982). The fact that the organic cation had a preferred orientation at the hectorite surface, combined with evidence that the cation was less restricted ($\tau_R \approx 0.4$ ns) and less oriented on a fully wetted Na⁺-beidellite, indicated that the motional restriction may have been determined more by adsorption (surface contact) than by the viscosity of the interfacial water. Beidellite, with its tetrahedral layer charge and tendency to hydrogen-bond water more strongly than hectorite, inhibits direct contact of the probe molecule with silicate oxygen atoms. Octahedrally-charged smectites such as hectorite are, for this reason, more organophilic than tetrahedrally-charged smectites.

In summary, these early spin probe studies probably revealed more about the nature of organic-smectite interactions than about the microdynamic properties of interfacial water. It was decided to conduct experiments using neutral and anionic nitroxide probe mol-

ecules in hectorite gels. Because they do not adsorb electrostatically, these probes occupy both the solution phase and the near-surface region of smectite gels. By varying the water content of the gels, it is then possible to measure dynamic properties of different thicknesses of near-surface water by ESR.

MATERIALS AND METHODS

Because a low iron content is necessary to avoid spectral line-broadening by paramagnetic relaxation, hectorite (NL Industries) was used to prepare probe-doped clay gels. This clay had a d-spacing of 12.9 Å in the air-dry state, with no evidence of mineral impurities revealed by X-ray diffraction. However, this material is known to contain carbonate impurities, and the IR spectrum of the hectorite did in fact reveal absorbance bands at 1439 cm⁻¹ and 885 cm⁻¹, bands which were not evident after chemical treatment of the hectorite with citrate-dithionite-bicarbonate (CDB), a method designed to remove oxide impurities from silicate clays (McBride, 1979). Since the absorbance bands are consistent with the presence of magnesite (MgCO₃) in the hectorite (van der Marel and Beutelspacher, 1976), the CDB treatment evidently dissolves this carbonate. Titration of a suspension of hectorite in 0.1 M NaCl (initial pH = 9.6) with HNO₃ revealed the pH to decrease sharply with acid addition until about 60 mmoles of H⁺ had been added per kg of hectorite (pH \approx 7.5). Additions of acid beyond this level decreased the pH more gradually. These data are interpreted to mean that the hectorite contained about 60 mmoles MgCO₃ per kilogram, assuming the neutralization reaction:



Buffering below pH 7.5 may be associated with decomposition of the hectorite structure, which is unstable in acid media. As the CEC of this hectorite is reported to be 710 millimoles per kg (McBride, 1979), the MgCO₃ impurity was considered to be a tolerable contaminant. In fact, a comparison of the mobility of the uncharged spin probe used in this study between a Na⁺-saturated, CDB-treated (carbonate-free) hectorite and an untreated hectorite at several water contents revealed relatively small differences. Consequently the chemically untreated hectorite was used for most of the spin probe experiments.

The spin probe, 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (hydroxy-TEMPO) was obtained from Aldrich Chemical Co. and used without further purification. Aqueous 10⁻³ M and 10⁻⁴ M solutions of the probe were added in appropriate volumes to weighed quantities of air-dry (spray-dried) hectorite powder in glass weighing bottles, producing water/clay weight ratios (M_w/M_c) ranging from 200 to 0.1. This created materials ranging from liquids to stiff gels to tacky powders. The bottles were closed with glass stoppers

and further sealed with Parafilm. Even distribution of the added probe solutions was a particular problem at the lower water/clay ratios. Thorough mixing with a spatula and lengthy equilibration times were employed in order to be reasonably confident that water was distributed as evenly as possible over all clay surfaces. Even so, the longest equilibration time used (1 to 2 weeks) generally showed a significant drift toward higher probe mobility for water contents in excess of $m_w/m_c = 5$.

After a chosen equilibrium time, the bottles were opened and the tip of a capillary tube immediately filled with a sample by pressing into the clay-water mixture. The tube was promptly sealed with plasticine, and placed in a glass ESR tube. Room temperature (20°C) ESR spectra were run at 9.4 GHz (X-band) using a Varian E-104 spectrometer, with modulation and power settings of 1.0 Gauss and 1.0 milliwatt, minimizing signal distortion and saturation effects.

The spin probe spectra were interpreted according to the Debye diffusion model, where the correlation time, τ_R , for rotational diffusion of the probe molecule is interpreted as the length of time over which the molecule maintains a particular orientation before random Brownian motion reorients it. According to Eq. (1), this correlation time depends on the viscosity, η , of the immediate environment as well as the radius, r , of the probe molecule. The rotational diffusion constant, D_R , is related to τ_R by the equation:

$$\tau_R = \frac{1}{6D_R} \quad (2)$$

The 3-line spin probe spectra are used to obtain τ_R according to the equation (Sachs and Latorre, 1974):

$$\tau_R = 0.65W_0(R_+ - 2) \quad (3)$$

where:

$$R_+ = \left(\frac{h_0}{h_{+1}}\right)^{1/2} + \left(\frac{h_0}{h_{-1}}\right)^{1/2} \quad (4)$$

and h_{+1} , h_0 , and h_{-1} are the measured heights of the low, middle and high-field lines, respectively, while W_0 is the width of the middle line (Gauss units). This analysis can only be applied to spectra which are generated from a single population of spin probes undergoing rapid self-exchange: otherwise, the observed "spectrum" is actually a composite of overlapping spectra and the line-shape analysis based upon peak heights is invalid. Eqs. (3) and (4) rely on the assumption that the ratios of linewidths, W_0/W_{+1} and W_0/W_{-1} , can be approximated to $(h_0/h_{+1})^{1/2}$ and $(h_0/h_{-1})^{1/2}$, respectively. This is a good approximation for Lorentzian line shapes unless spectral lines from two or more probe populations are superimposed. The theory of spectral line broadening of nitroxides, from which Eq. (3) is derived, is summarized by Nordio (1976).

To measure partitioning coefficients for the adsorption of hydroxy-TEMPO by hectorite, different volumes of 10^{-4} M aqueous probe solutions (6, 10, 15, 25 ml) were added to 0.50 g samples of dry hectorite, producing suspensions having a range of water/clay weight ratios (m_w/m_c) from 12 to 50. These were stirred and equilibrated overnight. ESR spectra were then obtained of the whole suspension, as well as of the supernatant and clay gel after separation by centrifuging. The hydroxy-TEMPO concentrations in the supernatants were determined quantitatively by measuring ESR peak heights of these supernatants relative to peak heights of standard hydroxy-TEMPO solutions. These estimates of probe concentration were found to be reproducible by repeating the experiment.

RESULTS

Initial interpretation of ESR spectra

The uncharged hydroxy-TEMPO probe, when dissolved in water, had a nearly symmetrical 3-line ESR spectrum at 20°C (Figure 1a), which, when analyzed using Eq. (3), gave $\tau_R = 0.037$ nanoseconds (ns). Rotational mobilities of this order ($\tau_R = 10^{-10}$ – 10^{-11} s) are expected from the Debye model (Eq. (1)) applied to small molecules in water. On the other hand, hydroxy-TEMPO in hectorite suspensions and gels appeared to have much longer τ_R values, evident from broadening of the low-field and high-field lines of the ESR spectrum (Figures 1b–1d). This broadening is a result of the fact that the rate of molecular tumbling is not fast enough to completely average the anisotropy of the hyperfine interaction and g-value. However, closer analysis of the spectra in Figure 1 shows that, for water/clay weight ratios (m_w/m_c) of 5 and higher, the measured peak-to-peak *linewidth* of the central ($m_I = 0$) and high-field ($m_I = -1$) lines are not significantly different. But, broadening due to incomplete motional averaging of the hyperfine anisotropy would necessarily result in the $m_I = -1$ line having a greater peak-to-peak linewidth than the $m_I = 0$ line, and consequently a smaller peak height. Since the greater peak height of the central line was *not* due to a smaller peak-to-peak linewidth, the only possible conclusion is that the spectrum is actually composed of two individual spectra, the dominant one being that of the mobile (solution) probe (see Figure 1a), while an underlying spectrum has notably broadened low-field and high-field lines. This latter spectrum must arise from the adsorbed probe, whose tumbling motion is restricted either by higher viscosity of the surface layer of water or by hindrance to motion caused by the solid surface.

The probe on oriented hectorite films

The nature of the spectrum of the adsorbed probe was more clearly seen in ESR experiments with oriented Na^+ -hectorite films, to which small quantities of

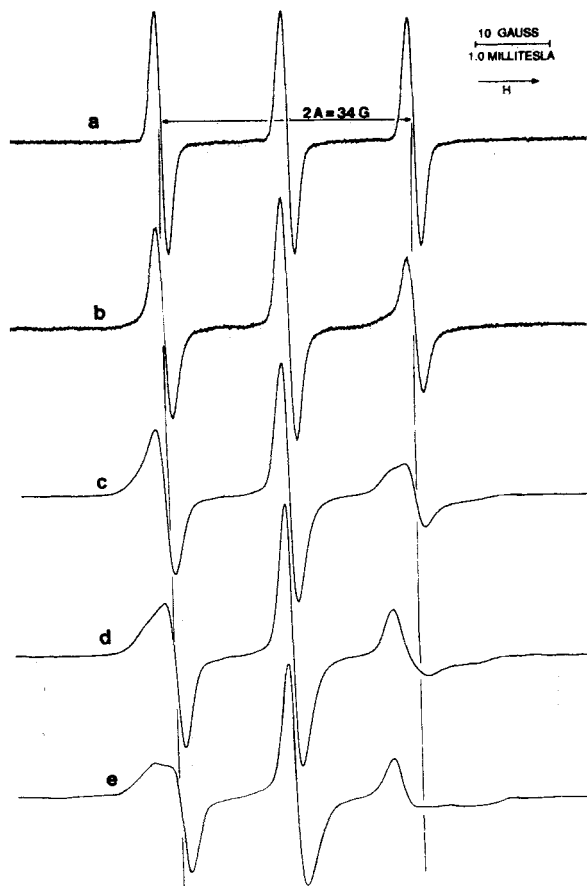


Figure 1. Room temperature ESR spectra of OH-TEMPO in 10^{-4} M aqueous solution (a) and in hectorite gels with $m_w/m_c = 5$ (b), $m_w/m_c = 2$ (c), $m_w/m_c = 1$ (d), $m_w/m_c = 0.5$ (e), after 1 week equilibration. Magnetic field direction and scale are noted.

10^{-3} M hydroxy-TEMPO aqueous solution had been added. The experiments clearly showed a tendency of the probe molecules to orient on the wet surfaces (Figure 2). Furthermore, the hyperfine splittings for the perpendicular (21.3 G) and parallel (15.4 G) orientation of the clay film relative to the applied magnetic field of the ESR spectrometer are nearly identical to those of the TEMPAMINE⁺ spin probe cation on hectorite films under similar conditions (McBride, 1986), where the z-axis of the nitroxide was found to tilt toward the normal to the planar clay surfaces. This suggests that the alignment and mobility of these chemically related probe molecules is determined by physical rather than electrostatic forces, perhaps driven by "hydrophobic attraction" between methyl groups and the siloxane surface. The charge of the cation probe merely restrained it at exchange sites near the surface, while OH-TEMPO is free to diffuse into solution as evidenced by the immediate appearance of the symmetrical three-line spectrum of solution OH-TEMPO when

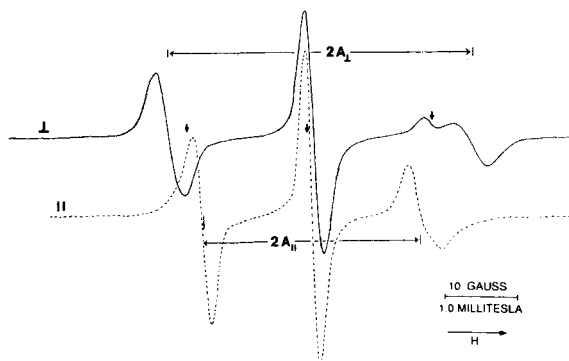


Figure 2. Room temperature ESR spectra of oriented Na⁺-hectorite films after applying sufficient 10^{-3} TEMPO-OH to wet the films. Vertical arrows indicate position of resonances for the solution-phase (free) probe. The \perp and \parallel symbols denote the film orientation at 90° (\perp) and 0° (\parallel) relative to the applied field. Magnetic field direction and scale are noted.

excess water is added to the oriented clay film. This solution spectrum is barely evident in Figure 2 (at position of arrows), but gains in intensity relative to the signal of the oriented probe upon addition of pure water (spectra not shown). Evidently, additional water induces adsorbed probes to diffuse away from the surfaces. The existence of two distinct ESR spectra in the same system is evidence that exchange between the two phases (solution, adsorbed) is slow on the time scale of the ESR method.

Analysis of composite spectra

All of the above observations suggest that physical adsorption of hydroxy-TEMPO occurs on hectorite, thereby partitioning the probe molecules into two populations separated sufficiently in space to prevent exchange across the surface-solution interface from completely averaging the spectra. As shown in Figure 2, the central peak height of the spectrum of adsorbed probe is greater than that of the high-field peak, so that if a spectrum of adsorbed probe underlies the spectrum of a mobile (solution-like) probe, it increases the relative height of the central peak even though the peak-to-peak linewidth, due to the more intense superimposed signal of mobile probe, may remain narrow and consistent with that of a solution-like environment. This is what was observed in hectorite suspensions with water contents ranging from $m_w/m_c = 5$ to 200. Over this range, the solution-like signal determined the peak-to-peak linewidth, yet an underlying signal of adsorbed probe increased the central peak height (h_0) relative to that of the low-field (h_{+1}) and high-field (h_{-1}) peaks (see Figures 1b–1e). The measured height of the central relative to the high-field peak, expressed as a ratio, is plotted in Figure 3 and shows the sensitivity of this ratio to clay water content. Since h_0/h_{-1} is a function of the relative intensity of the underlying broad spec-

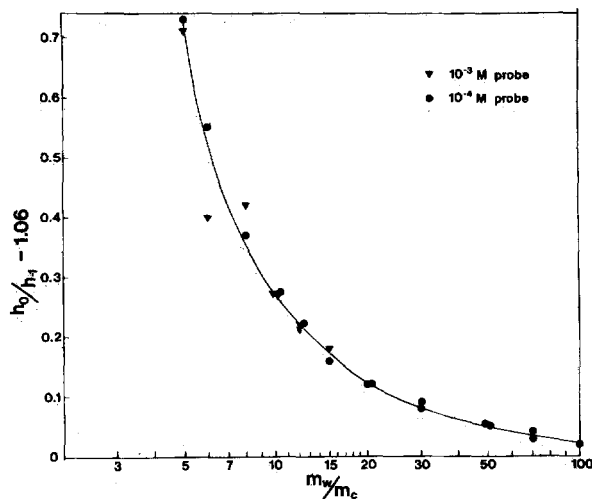


Figure 3. Dependence of the adjusted peak height ratio of the TEMPO-OH spectrum ($h_0/h_{-1} - 1.06$) on the water content of hectorite.

trum attributed to adsorbed OH-TEMPO, the magnitude of h_0/h_{-1} , corrected for the fact that free (unadsorbed) OH-TEMPO has $h_0/h_{-1} = 1.06$, should be approximately proportional to the fraction of probes in the adsorbed state. The dependence of $(h_0/h_{-1} - 1.06)$ on m_w/m_c shown in Figure 3 then reveals virtually no evidence of adsorbed probe at $m_w/m_c \geq 70$, with adsorbed probe contributing most of the signal intensity at $m_w/m_c \leq 5$. The height ratio is not, however, sensitive to the concentration of OH-TEMPO present in the suspension (in the 10^{-3} to 10^{-4} M range tested). The insensitivity of h_0/h_{-1} to probe concentration suggests a constant-partitioning adsorption process, not unexpected because the surface density of adsorbed probe molecules is quite low. It was also found that equilibration times ranging from one day to one week had rather small effects on h_0/h_{-1} , but longer times generally decreased h_0/h_{-1} .

Measurement of adsorption of OH-TEMPO

Measurements of spin probe concentrations in the solution phase after equilibration with hectorite confirmed that significant adsorption of the neutral OH-TEMPO probe was occurring according to constant partitioning. If the amount adsorbed, q , is linearly dependent on the concentration of the probe in solution, C , then the adsorption equation is:

$$q = K_p C \quad (5)$$

Four separate estimates of the partitioning coefficient, K_p , based on the measured adsorption at $m_w/m_c = 12, 20, 30,$ and 50 were 2.0, 2.2, 1.3, and 1.8 liters/kg, respectively. There was no indication of a systematic change in K_p as a function of m_w/m_c .

Because adsorption was detectable, the equilibrium

Table 1. Measured fractions of OH-TEMPO in the solution phase, f_{sol} , and adsorbed phase, f_{ads} , as a function of the water/clay ratio, m_w/m_c .

m_w/m_c	f_{sol}	f_{ads}
12	0.86	0.14
20*	0.90	0.10
	0.87	0.13
30*	0.96	0.04
	0.92	0.08
50*	0.96	0.04
	0.98	0.02

* Results of duplicated experiments, where the variability is attributed to errors in estimating solution probe concentration from ESR signal amplitude.

concentration of probes in the near-surface volume was obviously higher than in the solution phase. Assuming that all probe molecules contribute to the ESR spectrum of the system, the overall spectrum then presents a biased view of water behavior because it "oversamples" the near-surface volume. The extent of this bias cannot be estimated without knowing the thickness of the water layer adjacent to the clay surface that is enriched in probe molecules. However, because adsorption of OH-TEMPO appears to be driven by weak physical forces, it is reasonable to infer that only direct contact of the probe molecules with silicate oxygens is sufficient to generate enough bonding energy to produce a detectable excess of these molecules at the surface. As OH-TEMPO has a diameter of 6–8 Å, then the adsorbed excess of probe may be assumed to reside in a volume estimated from the theoretical surface area of the hectorite ($750 \text{ m}^2/\text{g}$) multiplied by 8 Å. To account for the observed adsorption, the concentration of spin probes in this 8 Å thick layer would then have to be about 3×10^{-4} M, over 3 times the solution concentration. Although the hectorite adsorbed about $0.20 \mu\text{moles OH-TEMPO/g}$, most of the probe molecules remained in the solution phase. This fact is illustrated in Table 1, where the measured fraction of probes in solution, f_{sol} , relative to the fraction adsorbed, f_{ads} , is high, but becomes less as the water content of the hectorite decreases. This trend is responsible for the shape of the function plotted in Figure 3. It is concluded that, while most probes were in the solution phase at m_w/m_c ratios of 12 and higher, the probe was still weakly concentrated at the surface, sampling the near-surface volume disproportionately.

Analysis of spectra at low m_w/m_c values

The partially obscured spectrum of the less mobile (adsorbed) probes was visually detectable at m_w/m_c values of 12 and lower (most conspicuous feature is a shoulder to the low-field side of the high-field line, as shown in Figures 1b, 1c). This spectrum was presumably present at higher m_w/m_c values as well, but too

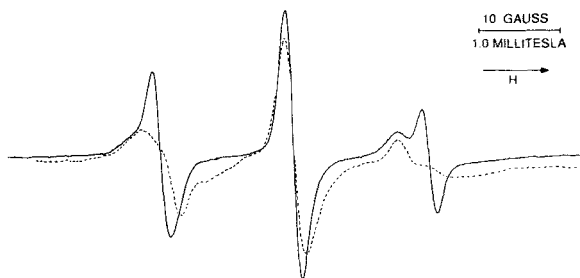


Figure 4. Room temperature ESR spectrum of OH-TEMPO in Ca^{2+} -hectorite at a water content of $m_w/m_c = 1$ (solid line) and $m_w/m_c = 0.2$ (broken line). Magnetic field direction and scale are noted.

weak to be visually detected. The data of Figure 3 suggest that it was present even at m_w/m_c values above 50. Conversely, once the m_w/m_c value was reduced to 0.5 or less, little evidence of the mobile probe remained (Figure 1e). Analysis of these spectra of hectorites with low water contents using Eq. (3) provided estimates of $\tau_R \approx 1$ –2 nanoseconds. These estimates of rotational mobility agree with those obtained previously using the TEMPAMINE⁺ cation probe on the same hectorite in a wet state (McBride, 1986). Since $m_w/m_c = 0.5$ corresponds roughly to a 15 Å interlayer spacing, and the spectrum of a mobile phase of OH-TEMPO is detected at water contents higher than this (Figure 1), it is concluded that a solution-like aqueous phase exists for all clay pastes with interlamellar spacings > 15 Å. Consequently, the rigidity of near-surface water must not extend more than about 3 molecular H_2O layers away from each silicate surface.

Particle arrangement effects on mobility of probe

The microviscosity sensed by the spin probe has no relation to the viscosity of the clay suspensions as a whole. For example, the addition of NaCl or NaOH to hectorite suspensions of low viscosity caused them to become visibly viscous, but no significant effect on the mobility of the incorporated spin probes was detected by ESR. This indicates that gel viscosity is controlled by particle-particle interaction, with most of the interparticle water retaining its liquid nature. Re-arrangement of hectorite platelets into quasicrystals, however, does have some effect on the probe spectra, as demonstrated in the case of fully wetted Ca^{2+} -hectorite ($m_w/m_c = 1$) shown in Figure 4. For Ca^{2+} -hectorite, the partially obscured spectrum of the motionally restricted probe is better resolved than in the case of Na^+ -hectorite (compare to Figure 1d) and becomes even more evident at $m_w/m_c < 1$, as the dotted line in Figure 4 represents the Ca^{2+} -hectorite at $m_w/m_c = 0.2$. Since little evidence of mobile probes is detected at $m_w/m_c = 0.2$, it is concluded that no solution or solution-like phase exists at this water content. The Ca^{2+} -hectorite d-spacing (air-dry) is 15.4 Å (McBride, 1986),

and the added probe solution for $m_w/m_c = 0.2$ would bring this spacing up to about 20 Å, which is near the stable average spacing of wetted Ca^{2+} -hectorite.

Two populations of probe molecules are very clearly resolved in Ca^{2+} -hectorite—those in solution and those in interlayer regions. Exchange between these populations is evidently slow on the time scale; otherwise, a single time-averaged spectrum would be detected. The fact that the two overlapping spectra are better resolved in the Ca^{2+} -hectorite than in Na^+ -hectorite suggests that some degree of time-averaging of spectra occurs in the latter clay, where virtually all surfaces of the dispersed clay are exposed to solution.

DISCUSSION

It is important to note that a superficial analysis of ESR spectra such as those shown in Figure 1, using Eq. (3) to estimate τ_R , could lead to false conclusions about water viscosity in clay gels. In Figure 1, the problem arose from interpreting peak heights of superimposed spectra. In other examples, erroneous conclusions from NMR and ESR spectroscopy—that most of the water in cells of organisms had a viscosity much higher than that of normal water—may have arisen from fast exchange between solution-like and rigid phases (Finch and Harmon, 1974). In the case of the clay pastes, to determine whether the spectral line shape could possibly represent an averaged environment “seen” by the unpaired electron of the probe, it is necessary to calculate a feasible rate of probe exchange between the solution and surface. Line shape averaging will occur if the exchange rate is fast relative to the spectral anisotropy that is being averaged by rotational motion. For nitroxide spin probes such as OH-TEMPO, the hyperfine anisotropy, represented as $A_{zz} - \frac{1}{2}(A_{xx} + A_{yy})$ is about 25 Gauss (Nordio, 1976). Here, A_{xx} , A_{yy} and A_{zz} are the principal values of the hyperfine tensor along the x, y and z-axis of the nitroxide. As 25 Gauss corresponds to a frequency of 70 MHz, the time interval associated with the hyperfine anisotropy of nitroxide probes is 1.4×10^{-8} seconds. Eqs. (1) and (2) can be used to estimate the rotational diffusion coefficient for OH-TEMPO in water. However, rotational and translational motion are related by the fact that Brownian motion drives them both. The equation relating the translational diffusion coefficient at room temperature, D , to τ_R is (Snipes and Keith, 1974):

$$D = 0.22 \frac{r^2}{\tau_R} \quad (6)$$

For the OH-TEMPO molecule, $r \approx 4$ Å, so that in water:

$$D = 0.22 \frac{(4 \times 10^{-8} \text{ cm})^2}{4 \times 10^{-11} \text{ s}} = 4 \times 10^{-5} \text{ cm}^2/\text{s} \quad (7)$$

Mean translation of the molecule along a particular

direction, \bar{x} , is given by the Brownian displacement equation:

$$\bar{x} = (2Dt)^{1/2} \quad (8)$$

For the time period relevant to ESR spectra of nitroxide probes (1.4×10^{-8} s), Eq. (8) gives the mean translation distance of:

$$\begin{aligned} \bar{x} &= (2 \times 4 \times 10^{-5} \text{ cm}^2/\text{s} \times 1.4 \times 10^{-8} \text{ s})^{1/2} \\ &= 1.5 \times 10^{-6} \text{ cm} \\ &= 150 \text{ \AA} \end{aligned}$$

Since average interlayer spacings exceed this distance even for m_w/m_c ratios of 10 or less, it is evident that probe molecules could not diffuse rapidly enough from all the aqueous solution to the interface to completely time-average the spectra, except perhaps at the lowest water contents studied. Furthermore, when considering diffusion *out of* the adsorbed phase, where τ_R is estimated to be much longer (≈ 1 ns), then by a similar analysis, $D = 1.8 \times 10^{-7} \text{ cm}^2/\text{s}$ and $\bar{x} = 7 \text{ \AA}$ in the relevant time interval. Escape from the surface to solution may not be fast enough to allow complete line shape averaging, although exchange between adsorbed and near-surface (non-adsorbed) molecules may do some partial averaging of the spectra.

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