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ADSORBED MOLECULES ON SOLVATED LAYER SILICATES: SURFACE MOBILITY AND ORIENTATION FROM ESR STUDIES

M. B. McBride
Department of Agronomy, Cornell University, Ithaca, New York, U.S.A.

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Abstract—The adsorption of nitroxide spin probes on smectites solvated in liquids of greatly different polarity was studied using electron spin resonance (ESR) spectroscopy. Adsorbed probes demonstrate various degrees of restricted rotational motion and alignment at the silicate surfaces, depending upon the properties of the solvating liquid. The results are interpreted in terms of direct surface–molecule interaction modified by solvent competition effects. A fraction of the probe molecules is immobilized in many of the solvated clays because of small spacings between platelets. The data indicate lowered reactivity of surface-adsorbed molecules, especially in the case of hydrated smectites.

INTRODUCTION

Electron spin resonance (ESR) studies utilizing nitroxide spin probes doped into membranes (Keith and Snipes, 1974; Griffith *et al.*, 1971) have produced information about the orientation and mobility of the probes in these systems, thereby revealing fundamental properties of membranes. Recently, this spectroscopic technique has been applied to adsorption studies of a spin probe on layer silicates in an attempt to determine certain principles of the organic–aluminosilicate interaction (McBride, 1976). The probe molecules, which randomly tumble in solution, were found to orient on clay mineral surfaces. Orientation data could be obtained in these studies because of the anisotropic hyperfine splitting constant (A) of the nitroxide probe and the ability of the layer silicates to form well-oriented films.

Although information has been reported regarding the anisotropic motion and orientation of the protonated nitroxide probe (4-amino-2,2,6,6-tetramethylpiperidine N-oxide) adsorbed on ethanol- and water-solvated silicate surfaces (McBride, 1976), a systematic study of the molecule–surface interaction in the presence of numerous solvents is required for a more complete understanding of the processes of adsorption. It is likely that solvents having different chemical properties will modify the interaction between the surface and the organic probe ion, since they have been shown to alter the surface–metallic cation relationship (Berkheiser and Mortland, 1975). Therefore, in this study, solvents of widely varying chemical properties have been used to solvate a smectite doped with the protonated spin probe. In addition, similar experiments were carried out for a vermiculite in order to compare the surface properties of different layer silicates. Measurement of the orientation and mobility of the probe in these systems may permit the mechanisms of adsorption of organic molecules on solvated clay surfaces to be learned.

MATERIALS AND METHODS

A California hectorite ($<2\,\mu$m particle size) with chemical formula and exchange capacity previously reported (McBride *et al.*, 1975) was saturated with Na^+ using excess NaCl solution. The salt was then washed from the clay suspension by repeated centrifuging and discarding the supernatant until a negative $AgNO_3$ test for chloride was obtained. An aqueous solution of the spin probe (4-amino-2,2,6,6-tetramethylpiperidine N-oxide), referred to in this study as TEMPO, was titrated with HCl solution past the equivalence point (determined with a pH meter) to protonate the amine group of the probe. A known quantity of this cationic form of the probe ($TEMPO^+$) was added to the Na^+-saturated hectorite to produce a clay doped near the 10% level of exchange capacity. The clay was then washed free of chloride and excess probe molecules with distilled water. An aqueous suspension of the doped hectorite was dried on a flat surface to produce an oriented, self-supporting film for ESR studies. A $TEMPO^+$-doped Na^+-vermiculite was similarly prepared for ESR studies. The vermiculite, from Llano, Texas, had a chemical formula and exchange capacity as previously reported (McBride *et al.*, 1975).

The clay films were oriented in quartz tubes and ESR spectra of the clays were recorded on a Varian V-4502 spectrometer (X-band). The air-dry clays were equilibrated with various solvents by adding the liquids to the clay films in the quartz tubes and sealing the tubes. The ESR spectra were then recorded with excess solvent present.

A Norelco X-ray diffractometer was used to determine the $d(001)$ spacings of the hectorite films while the films were wetted in the solvents.

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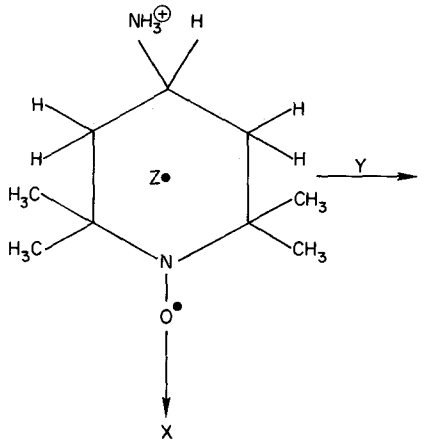


Fig. 1. Diagram of protonated 4-amino-2,2,6,6-tetramethylpiperidine N-oxide (TEMPO$^+$) showing the molecular fixed-axis system.



Fig. 2. ESR spectrum of TEMPO in iso-amyl alcohol at 20°C ($\tau_c = 1 \times 10^{-10}$ sec, $g_0 = 2.0053$, $A_0 = 16.0$ G). The vertical line shown in this and later figures indicates the field position of the free electron ($g = 2.0023$).

RESULTS AND DISCUSSION

The TEMPO$^+$-hectorite system

The TEMPO$^+$ molecule has a structure (Figure 1) that permits the observation of varying alignments with layer silicate surfaces depending upon the state of solvation of the surfaces (McBride, 1976). The N–O bond axis is probably nearly colinear with the C–N bond axis, since it is known that N–O and C=O are colinear in a very similar probe molecule, 2,2,6,6-tetramethyl-4-piperidone N-oxide (Hwang *et al.*, 1975), or TEMPONE. The axis system of the molecule for purposes of ESR is based on the nitroxide group (Figure 1), and the largest hyperfine splitting value (A_{zz}) is observed when the magnetic field (H) is parallel ($\parallel$) to the z-axis of the molecule. Smaller splitting values (A_{xx}, A_{yy}) are recorded by ESR when H is perpendicular ($\perp$) to the z-axis. Splitting of the unpaired electron signal of the N–O π-orbital into three resonances is caused by the nuclear spin of $^{14}N(m_I = 1,0,-1)$.

In most low-viscosity liquids at room temperature, nitroxide spin probes rotate rapidly enough to average the anisotropy of the hyperfine splitting (A) values. A three-line symmetric ESR spectrum is thereby obtained for TEMPO in solution, having a motionally-averaged hyperfine splitting value of $A_0 = \frac{1}{3} A_{xx} + \frac{1}{3} A_{yy} + \frac{1}{3} A_{zz}$. In addition, the anistropic g-tensor is averaged and the ESR spectrum in liquid is centered at $g_0 = \frac{1}{3} g_{xx} + \frac{1}{3} g_{yy} + \frac{1}{3} g_{zz}$. This type of spectrum, demonstrated for TEMPO in amyl alcohol (Figure 2), was observed for TEMPO dissolved in all the solvents used in this study except glycerol. Glycerol has a high enough viscosity at room temperature to prevent motional averaging of A and g (Chignell, 1974). The rotational correlation times (τ_c), which define the time scale of molecular rotation, can be calculated from the peak heights of the ESR spectra by a standard method (Sachs and Latorre, 1974). The τ_c values were found to be in the range of 10^{-10}–10^{-11} sec for TEMPO dissolved in the solvents (except glycerol) used in this study (Table 1). The values of A_0 for nitroxide probes dissolved in various solvents decrease as the solvent polarity decreases (Chignell, 1974). This relationship was found for the solvents used in the study (Figure 3), demonstrating that A_0 increases with increasing dielectric constant. Data of other worker (Snipes *et al.*, 1974) for TEMPONE dissolved in several solvents

Table 1. Rotational correlation times ($\times 10^9$ sec) and hyperfine splitting values (G) for adsorbed and solution TEMPO$^+$

	Rotational correlation time†			Hyperfine splitting value‡		
		Adsorbed			Adsorbed	
Solvent*	Solution	τ_c ($\perp$)	τ_c ($\parallel$)	Soln. (A_0)	$A_\perp$	$A_\parallel$
H_2O	0.053	2.63	1.48	17.0	19.2	15.5
ME	0.012	0.25	0.24	16.0	15.7	15.8
ET	0.023	0.44	0.55	16.0	15.5	15.6
PR	0.061	0.38	0.55	16.0	15.3	15.5
BU	0.087	0.60	0.47	16.0	15.2	15.4
AM	0.103	immobile		16.0	33.6	15.9
BZ	0.036	immobile		15.3	31.2	13.9
CT	0.011	immobile		15.0	31.2	12.8

* Solvents are listed in order of decreasing dielectric constant.

† Values of τ_c were calculated by the method described by Sachs and Latorre. τ_c of the mobile adsorbed probe was determined for both $\perp$ and $\parallel$ orientations of the silicate, although anisotropic motion is not accurately described by the method.

‡ Splitting values were determined for the predominant form of adsorbed TEMPO$^+$.

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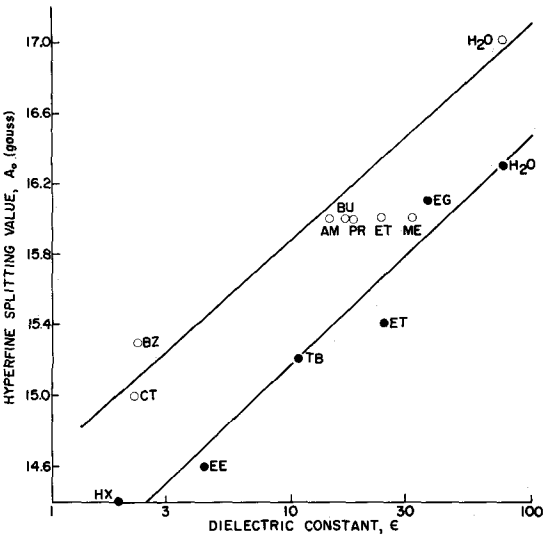


Fig. 3. Relationship of hyperfine splitting values (A_0) of the spin probe in solution (20°C) to the dielectric constant (ϵ) of the solvent. Open circles (○) represent present work while solid circles (●) represent data of Snipes *et al.* for TEMPONE. Symbols for solvents not described in the discussion are: EG (ethylene glycol), TB (*t*-butanol), EE (ethyl ether), HX (*n*-hexane).

are plotted (Figure 3) to substantiate the relationship. From these data, it is apparent that the low-viscosity solvents of this study can be separated into three groups: (a) low polarity benzene (BZ) and carbon tetrachloride (CT), (b) medium polarity iso-amyl (AM), *n*-butyl (BU), isopropyl (PR), ethyl (ET), and methyl (ME) alcohols, (c) high polarity water (H_2O).

When $TEMPO^+$-doped Na^+-hectorite films are solvated in the liquids listed above, the ESR spectra of the probe vary greatly (Figures 4, 5 and 6). These spectra can be described by the values of $A\|$, $A\perp$, and ΔA (Jost *et al.*, 1971), where $A\|$ and $A\perp$ are the field separations in gauss between the low-field and middle resonances of the ESR spectrum for $\|$ and $\perp$ orientation of the *ab* plane of the layer silicate relative to H. The difference between these two splitting parameters, denoted as $\Delta A = A\perp - A\|$, represents the degree of orientation of the probe molecule on the silicate. A value of $\Delta A = 0$ would indicate random orientations of the probe relative to the clay surface, while the maximum value of $\Delta A \cong A_{zz} - A_{xx} \cong 24$ G (Jost *et al.*, 1971) would describe strong alignment of the probe on the surface. The correlation times (τ_c) of $TEMPO^+$ in these systems are calculated from the equations (Sachs and Latorre, 1974):

$$\tau_c = 0.65\, W_0(R_+ - 2)$$

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

where W_0 is the line-width (G) of the central line of the spectrum, and the symbols h_{+1}, h_0, h_{-1} represent the peak height of the low, middle, and high field lines of the spectrum, respectively. This equation is intended for calculation of random-motion τ_c values in the fast-motion region ($\tau_c < 10^{-8}$ sec), and is therefore not totally accurate for the non-random motion observed in this study. However, calculation of τ_c values for the $\|$ and $\perp$ orientations of the silicate relative to H allows general comparisons with τ_c values in solution. The anisotropy of motion on surfaces often results in different τ_c values with different orientations of the sample relative to H. The values of τ_c for $\|$ and $\perp$ orientations, as well as the values of $A_\|$ and $A_\perp$, are presented in Table 1 for $TEMPO^+$ adsorbed on solvated Na^+-hectorite.

The $TEMPO^+$ spectrum in excess H_2O exhibits considerable anisotropy as well as a 20–50 times increased τ_c value (Figure 4a, Table 1). There is little evidence of immobilized $TEMPO^+$ in the interlamellar regions of the hectorite, although spectra previously obtained on the same system below 100% relative humidity have shown the broad, "rigid-glass" spectrum (McBride, 1976), probably caused by probe molecules trapped in partly collapsed interlayers. The

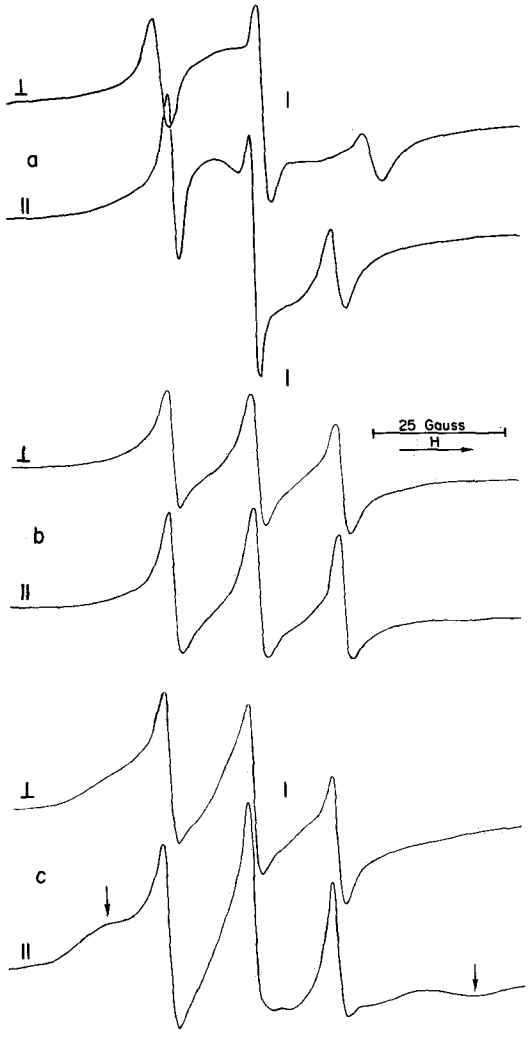


Fig. 4. ESR spectra of $TEMPO^+$-doped Na^+-hectorite films solvated in excess (a) H_2O, (b) methanol, (c) ethanol. Films are oriented perpendicular ($\perp$) and parallel ($\|$) to the magnetic field, H, for each solvent.

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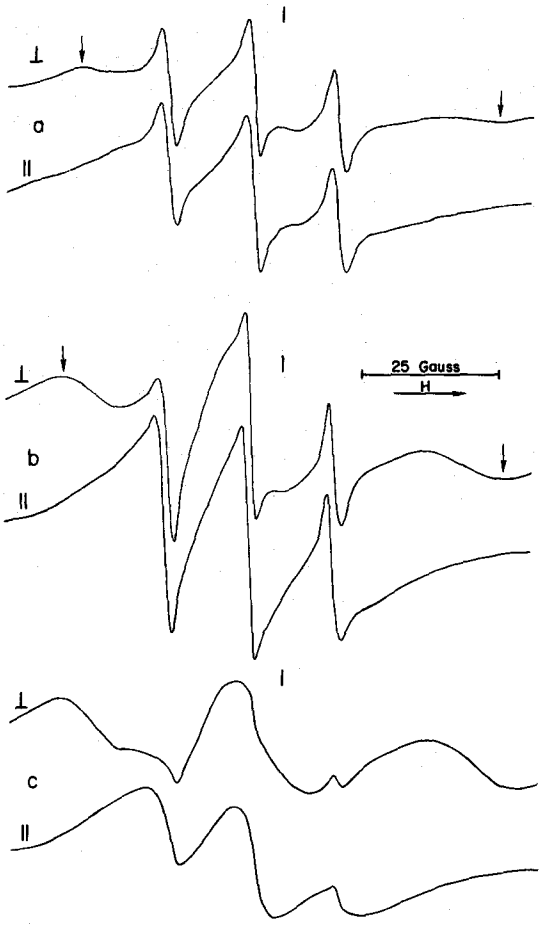


Fig. 5. ESR spectra of $TEMPO^+$-doped Na^+-hectorite films solvated in excess (a) isopropyl alcohol, (b) *n*-butanol, (c) iso-amyl alcohol.

basal spacing of the wet hectorite is near 18 Å (Table 2), apparently large enough to permit considerable interlamellar tumbling of the probe. However, the anisotropy of the spectrum is evidence that the probe is tending to align with the surface as diagrammed in Figure 7a. This orientation is considered to be a consequence of the attraction between the hydrophobic portion of the molecule and the layer silicate surface (McBride, 1976). Infrared spectroscopy has shown that the surface oxygens of smectites have only limited attraction for polar molecules such as H_2O (Farmer and Russell, 1971).

The three-line, nearly isotropic ESR spectra of $TEMPO^+$ in ET- and ME-solvated Na^+-hectorite (Figure 4b, 4c) are evidence of considerable motional freedom of the adsorbed ion in these systems, despite the observed basal spacings of 17 Å (Table 2). The values of ΔA for these spectra are near zero, while τ_c is estimated at about 20 times that for $TEMPO^+$ in solution (Table 1). This mobility suggests a reduced probe-surface interaction as a result of the less polar nature of the solvents in comparison with H_2O. The ET and ME molecules may effectively compete with the probe for surface adsorption sites or may interact more strongly with the probe, preventing its alignment with the silicate surface. Although the spectra in ME show little evidence of immobilized $TEMPO^+$, the ET spectra demonstrate a broad signal partially obscured by the sharper three-line spectrum of solution-like $TEMPO^+$ (Figure 4b, 4c). Since the largest splitting value of this signal occurs when the hectorite films are oriented $\parallel$ to H (see arrows, Figure 4c), the immobilized probe must be oriented with the N–O bond axis $\perp$ to the *ab* plane of the layer silicate. This alignment is depicted in Figure 7b, suggesting that the probe molecule "bridges" across the ≈ 7.5 Å wide distance between layer silicate plates. Such an orientation would allow the charged end of the molecule to approach the surface charge sites while the hydrophobic methyl groups of the probe interact with ET molecules of the interlayer or silicate oxygens on the opposite surface. The broad spectrum of Figure 4c represents probes with reduced molecular motion ($\tau_c \gg 10^{-8}$ sec), a probable result of motional hindrance and surface interactions in the interlayer which has a width similar to the diameter of the probe (≈ 7 Å). It is quite possible that the more mobile probes in these systems are present on external surfaces, or at least, interlayers separated by a

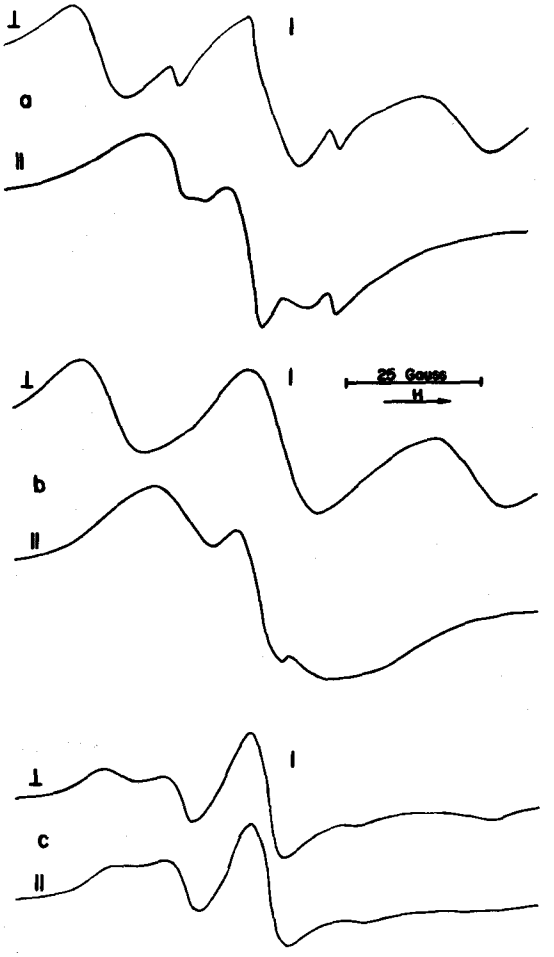


Fig. 6. ESR spectra of $TEMPO^+$-doped Na^+-hectorite films solvated in excess (a) benzene, (b) carbon tetrachloride, (c) glycerol.

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distance greater than 7 Å. The basal spacings determined by X-ray diffraction represent "collapsed" clay platelets; a sizeable fraction of the platelets may remain separated by larger, variable distances that are not detected by diffraction.

The higher molecular weight alcohols with lower dielectric constants than ET and ME, when used to solvate $TEMPO^+$-doped Na^+-hectorite, demonstrate spectra with higher proportions of immobilized probe relative to the more freely rotating probe (Fig. 5) in comparison to the spectra of the probe in ET- and ME-solvated hectorite. The spectra of the PR-solvated system have a relatively narrow, nearly isotropic, three-line signal (Figure 5a) produced by near random tumbling of adsorbed $TEMPO^+$ at a rate about six times slower than in solution (Table 1). The weak, broad spectrum of immobilized $TEMPO^+$ (Figure 5a) is orientation-dependent, with the largest value of A when the hectorite film is $\perp$ to H (see arrows). This dependence of A is indicative of immobilized $TEMPO^+$ aligned with the N–O axis $\parallel$ to the *ab* plane of the silicate, as shown in Figure 7c. The basal spacing of Na^+-hectorite solvated in PR (Table 2) is only large enough to permit the $TEMPO^+$ molecules in interlamellar regions to lie "flat", thereby explaining the immobilized probes. The more mobile $TEMPO^+$ must be considered to occupy external surfaces of the solvated hectorite or interlamellar regions expanded to spacings greater than the dimensions of the probe molecule.

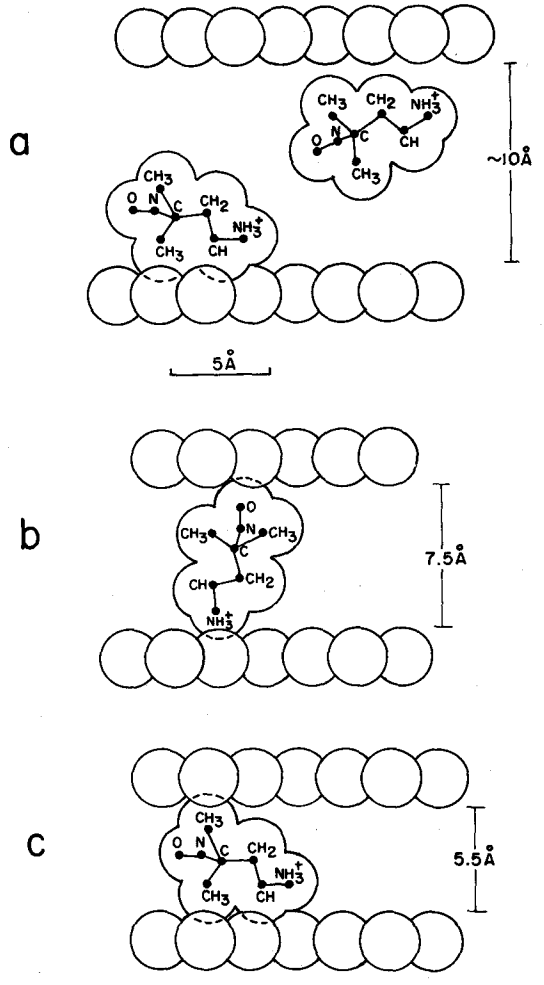


Fig. 7. Diagram of $TEMPO^+$ molecules adsorbed in interlamellar regions between the surface oxygen atoms of hectorite plates. The situations depicted are: (a) partially oriented $TEMPO^+$ in expanded interlayers of hydrated hectorite; (b) "immobilized" $TEMPO^+$ in interlayers of ethanol- and methanol-solvated hectorite; (c) "immobilized" $TEMPO^+$ in interlayers of hectorite solvated in liquids of low polarity.

Table 2. Basal (d_{001}) spacings of Na^+-hectorite in solvents with different dielectric constants (ϵ)

Solvent	ϵ	Basal Spacing (Å) Na^+-hectorite	Basal Spacing (Å) $TEMPO^+$-doped hectorite
H_2O	78.5	$\gg 25$	≈ 18*
ME	32.6	17.0	17.0
ET	24.3	17.0	16.9
PR	18.3	14.2	14.7
BU	17.1	13.6*	14.6
AM	14.7	14.5*	14.8
BZ	2.3	≈ 14*	14.2
CT	2.2	≈ 13.0*	13.8

* Broad diffraction peaks indicating randomly interstratified spacings of hectorite interlayers.

The spectra of BU-solvated hectorite (Figure 5b) are again composed of signals from two distinct probe environments—the more mobile probe undergoing near-random tumbling at a rate reduced nearly six times relative to solution, and the immobilized probe (denoted by arrows) aligned in interlamellar regions. The low basal spacing traps probes in interlamellar sites, and the relative intensity of the signal due to immobile probe appears greater for BU than PR (Figure 5b). In comparison, the spectra of AM-solvated hectorite (Figure 5c) demonstrate essentially no mobile $TEMPO^+$, while the strongly oriented, immobilized $TEMPO^+$ is dominant because of the small interlamellar spacing.

The ESR spectra of $TEMPO^+$ in Na^+-hectorite solvated with the least polar solvents, BZ and CT, are produced by well-oriented, immobilized probes (Figure 6a, 6b, Table 1). The basal spacings of the layer silicate (Table 2) indicate the limited expansion of the interlamellar regions in these solvents, thereby allowing almost all of the probe molecules to be trapped and strongly aligned as depicted in Figure 7c.

It should be pointed out that addition of the probe to the Na^+-hectorite at the $\approx 10\%$ level of exchange somewhat alters the properties of the system. Table 2 demonstrates that the probe tends to increase the basal spacing of the hectorite in solvents which normally produce < 15 Å spacings for Na^+-hectorite. Conversely, the addition of probe decreases the average basal spacings in solvents which produce > 15 Å

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spacings for pure Na^+-hectorite. As previously shown (McBride, 1976), $TEMPO^+$ holds the hectorite plates apart, preventing collapse of interlamellar regions. However, the hydrophobic nature of the probe tends to reduce the swelling of the hectorite in water and other polar solvents. This fact, coupled with the possible demixing of Na^+ and $TEMPO^+$ ions in the interlayers similar to alkylammonium–metal ion segregation (McBride and Mortland, 1975; Barrer and Brummer, 1963) could produce $TEMPO^+$-enriched, non-expanded interlayers that might account for some probe immobilization.

In summary, the spectra produced in the various solvents show some consistent trends. The lower the polarity of the solvent, the less the interlayers of hectorite are able to expand, and the greater the proportion of $TEMPO^+$ that is immobilized by interlamellar adsorption. Thus, hectorite fully solvated in H_2O or ME contains little or no immobile probe, while ET-, PR-, BU-, and AM-solvated hectorites contain increasing proportions of the trapped probe, in that order. The solvents of very low polarity (BZ, CT) allow $TEMPO^+$ molecules to be almost completely restricted in interlayers. The results support the concept that solvent adsorption and interlamellar expansion is largely a result of cation–dipole interactions (Theng, 1974), since polar molecules are capable of solvating the interlamellar Na^+ ions, while non-polar molecules have little attraction for metallic cations and probably interact more strongly with the silicate surface. It is likely that the Na^+ ions in the hectorites solvated with BZ or CT are non-solvated and localized in hexagonal holes of the silicate surface (Berkheiser and Mortland, 1975).

Although the apparent basal spacings for ET- and ME-solvated hectorites are essentially the same, as are the spacings of PR-, BU-, and AM-solvated systems (Table 2), the relative proportions of immobilized probe vary (Figure 4, 5). This suggests that collapse of silicate interlayers is more complete in solvents of lower dielectric constant, assuming that the more mobile probes are adsorbed on external surfaces or in partially expanded interlayers that permit molecular rotation. For example, the lack of mobile $TEMPO^+$ in the AM, BZ, and CT systems suggests that virtually all layer silicate platelets collapse together to a 14–15 Å spacing, leaving very few $TEMPO^+$ molecules on external surfaces.

In general, the degree of restriction of the more mobile fraction of adsorbed $TEMPO^+$ varies with the polarity of the solvent. The adsorbed probe in H_2O-solvated Na^+-hectorite has a rotational correlation time about 50 times that of the probe in aqueous solution (Table 1). In ET- and ME-solvated systems the adsorbed probe is considerably more mobile, with a 20-fold increase in τ_c relative to free solution. In the PR- and BU-solvated systems, τ_c for the mobile probe is only increased about six times. The data suggest that the interaction of $TEMPO^+$ with the silicate surface is controlled by the polarity of the solvent. Highly polar solvents permit strong probe–surface interactions because of the lack of attraction between polar molecules (e.g. H_2O) and the silicate oxygens as well as the weak interaction of polar molecules with the hydrophobic groups of $TEMPO^+$. This strong surface attraction of $TEMPO^+$ in aqueous systems might be compared to the strong adsorption of alkylammonium ions on smectites to form non-expanding, hydrophobic clay systems (McBride and Mortland, 1973).

Although the glycerol-solvated hectorite produces a "rigid-glass" type of spectrum as expected for solvents of very high viscosity (Figure 6c), there is some alignment of $TEMPO^+$ in the ≈ 8 Å wide interlayer as inferred from the orientation-dependent spectrum. The alignment of the N–O axis is imperfect, but appears to be along the *ab* plane of the silicate. Therefore the probe molecule tends to lie "flat" as it did in the hydrated systems. The spectra (Figure 6c) are similar to those reported previously for Mg^{2+}-hectorite equilibrated at 100% relative humidity and cooled to 0°C (McBride, 1976). The relatively high dielectric constant of glycerol ($\epsilon = 42.5$) probably accounts for the similarity in orientation of $TEMPO^+$ in the glycerol and H_2O systems. However, the high viscosity of glycerol lowers the interlamellar mobility of $TEMPO^+$.

The $TEMPO^+$–vermiculite system

As a basis for comparison with the hectorite, $TEMPO^+$-doped Na^+-vermiculite was oriented in films and equilibrated at 100% relative humidity. The spectra of the probe (Figure 8) are composed mainly of the isotropic, solution-like signal with $A_\perp \cong A_\parallel \cong 16.5$ gauss. Some evidence of a broad background signal (immobile probe) seems to present. Apparently, because the Na^+-vermiculite does not expand beyond a basal spacing of ≈ 14.7 Å in water, essentially all of the surface area exposed to the probe molecule can be considered to be external. A part of the $TEMPO^+$ may actually penetrate the narrow interlayers with some difficulty, producing the broad background signal. However, the external surfaces of the vermiculite behave much differently from the "external" surfaces of H_2O-expanded hectorite, permitting very rapid, solution-like, random motion of $TEMPO^+$. The vermiculite surfaces appear to interact weakly with the probe, despite the electrostatic attraction between $TEMPO^+$ and the surface. It is likely that the relatively strong hydration of oxygen atoms on the vermiculite surface (Farmer and Russell, 1971) prevents direct probe–surface contact and preferred alignment of the probe.

Very similar spectra to that obtained for the hydrated Na^+-vermiculite were produced for ET-, BU-, and BZ-solvated vermiculite with $A_\perp \cong A_\parallel \cong 15.3$, 15.0 and 14.5 G, respectively for the surface-adsorbed $TEMPO^+$. The polarity of the solvent influences the splitting value as expected from Figure 3, but has little influence on the strength of the probe-surface

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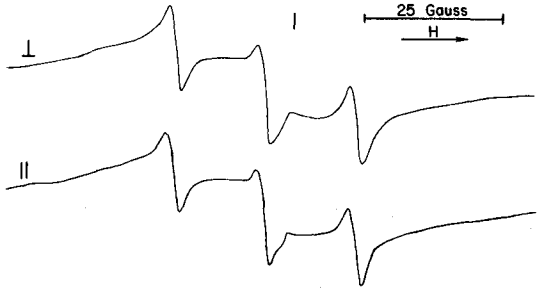


Fig. 8. ESR spectra of $TEMPO^+$-doped Na^+-vermiculite films equilibrated over H_2O (100% relative humidity) and oriented ⊥ and ∥ to *H*.

interaction. It is concluded that the vermiculite surface has less attraction for $TEMPO^+$ in polar solvents because of the affinity of polar molecules for the surface. In non-polar solvents, the organophilic probe is attracted to the solution phase and does not orient on the vermiculite surface. Similar solution-like isotropic spectra of $TEMPO^+$ have been obtained on finely-ground micas equilibrated at 100% relative humidity. The position of negative charges of vermiculite and mica in the tetrahedral layer, as well as the greater charge density and reduced swelling of these minerals compared to smectites, accounts for their similar behavior.

The TEMPONE-hectorite system

Although studies of the cationic probe, $TEMPO^+$, have been shown to provide useful information on the mechanisms of adsorption, use of a neutral probe molecule permits the attractive forces between the molecule and surface to be evaluated in the absence of electrostatic interactions. For this reason, 2,2,6,6-tetramethyl-4-piperidone N-oxide (TEMPONE) was dissolved in various solvents and equilibrated with Na^+-hectorite.

The ESR spectra of aqueous TEMPONE ($\approx 10^{-4}$ M) added to oriented Na^+-hectorite films (Figure 9) consist of an isotropic three-line spectrum due to TEMPONE in free solution as well as a superimposed spectrum of adsorbed TEMPONE (dotted line) with an orientation dependence similar to that of adsorbed $TEMPO^+$ on hydrated hectorite (Figure 4a). Evidently, the lack of charge on the probe molecule does not influence the surface–molecule interaction when adsorption occurs, but does allow many of the probes to remain in solution. The TEMPONE dissolved in ET ($\approx 10^{-4}$ M) appears to be adsorbed by Na^+-hectorite, since the spectrum demonstrates a nearly isotropic signal ($A_\perp = 14.8$ G, $A_\parallel = 15.3$ G) with values of τ_c similar to those for ET-solvated $TEMPO^+$-doped hectorite (0.3–0.5 × 10^{-9} sec). This 20 times reduction in mobility compared to solution may be due to adsorption on external surfaces, or occupation of interlamellar sites that permit considerable freedom of rotation. In addition, a small fraction of the probe is immobilized with N–O axis oriented ⊥ to the *ab* plane of the silicate, as indicated by the weak broad signal (Figure 10a) similar to the spectrum of immobilized $TEMPO^+$ present in ET-solvated hectorite. The adsorption characteristics of $TEMPO^+$ and TEMPONE on the ET-solvated system are similar, again suggesting that the similar chemical nature of the two probes determines the

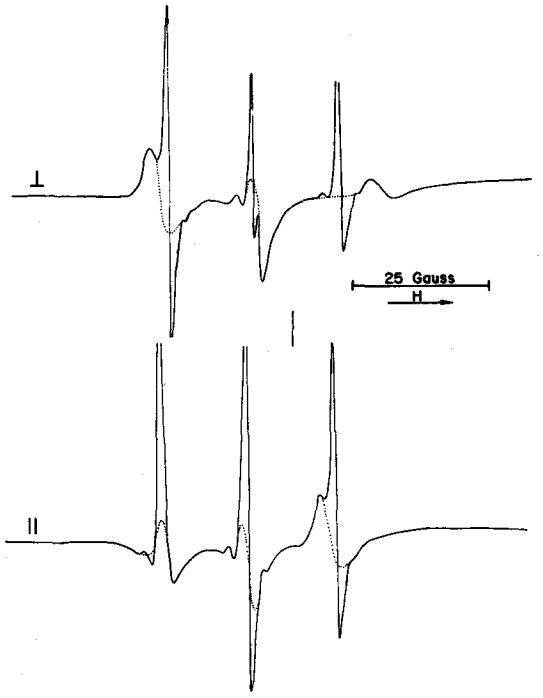


Fig. 9. ESR spectra of Na^+-hectorite films equilibrated with a dilute ($\sim 10^{-4}$ M) solution of TEMPONE and oriented ⊥ and ∥ to *H*. The dotted line outlines the spectrum of adsorbed TEMPONE.

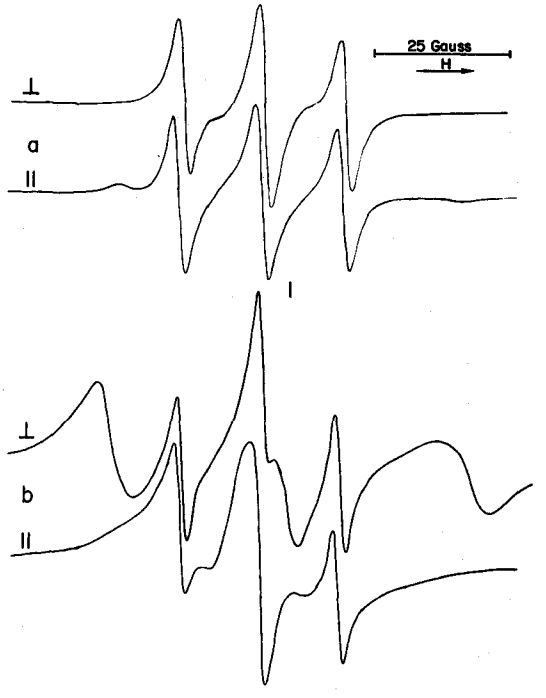


Fig. 10. ESR spectra of Na^+-hectorite films equilibrated with dilute ($\sim 10^{-4}$ M) solutions of TEMPONE in (a) ethanol, (b) benzene and oriented ⊥ and ∥ to *H*.

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mechanisms of surface interaction, while the charge of $TEMPO^+$ simply insures that it is not free to enter the solution phase. The spectrum of TEMPONE dissolved in BZ ($\approx 10^{-4}$ M) and added to dry Na^+-hectorite (Figure 10b) further demonstrates this principle. The spectrum consists of a broad, orientation-dependent signal due to TEMPONE aligned in interlamellar regions that are partially collapsed in BZ. This signal is very similar to that of $TEMPO^+$ in BZ-solvated hectorite (Figure 6a). However, an isotropic three-line spectrum of solution-like TEMPONE is superimposed on the broad signal, probably representing weakly adsorbed or solution TEMPONE in equilibrium with the immobile interlamellar probe.

CONCLUSIONS

The use of nitroxide spin probes for adsorption studies on surfaces is a relatively new technique that promises to provide fundamental information on molecular adsorption processes. This study has shown that the surface–molecule interaction is modified by the solvent present and the nature of the surface. The adsorbed molecule has two features which distinguish it from the solution probe—an increased rotational correlation time (i.e. reduced diffusion constant) and non-random tumbling at the liquid–surface interface. The increased correlation time implies a reduced reactivity of the molecules at the surface. Non-random tumbling is a result of direct molecule–surface contact. Such contact occurs on hydrated smectite surfaces because of the weak attraction of these surfaces for water molecules. However, on the more highly charged vermiculite surfaces, the probe molecules do not adsorb directly, probably because of the solvation of surface oxygens by water. Future studies on various types of surfaces using spin probes with different chemical characteristics are likely to produce further understanding of the processes of physical and chemical adsorption.

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