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CATIONIC SPIN PROBES ON HECTORITE SURFACES: DEMIXING AND MOBILITY AS A FUNCTION OF ADSORPTION LEVEL[1]

M. B. McBRIDE

Department of Agronomy, Cornell University, Ithaca, New York 14853

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Abstract—The electron spin resonance (ESR) technique has been used to study the motion and segregation of an organic spin probe cation (4-amino-2,2,6,6-tetramethylpiperidine N-oxide) on K^+-hectorite as a function of average surface concentration. The organic cation tends to concentrate in certain interlayers of aqueous hectorite suspensions even when it occupies a small fraction of the cation-exchange sites. This demixing effect is not evident in methanol-solvated hectorite. The average mobility of the probe increases at higher adsorption levels as a result of the shift of the equilibrium in favor of the solution state. Calculated time-averaged orientations of the probe on the clay surfaces are quite different for methanol- and water-solvated systems, emphasizing the importance of the solvent in modifying the surface-cation interaction.

Key Words—Adsorption, Cation Spin Probe, ESR, Hectorite, Organic Cation, TEMPAMINE$^+$

INTRODUCTION

Interactions between various organic cations and clay minerals have been investigated, but most of these studies utilized adsorption isotherms, X-ray powder diffraction, and infrared spectroscopy to elucidate molecular orientations and mechanisms of retention of the organic at the surface (Theng, 1974). Infrared and X-ray techniques have generally required that the clays have high organic cation contents and could not be used to study clay-water systems at equilibrium. However, recent investigations have shown that electron spin resonance (ESR) spectroscopy of clays containing small quantities of adsorbed organic radical cations provides insight into clay–organic interactions in water and various other solvents (McBride, 1976, 1977a, 1977b). The advantages of this approach are (1) a very small fraction of the total exchange sites can be occupied by the organic cation, resulting in little effect of the adsorption upon the hydration and expanding properties of the clay, (2) adsorption can be studied over a wide range of organic cation concentrations because of the sensitivity of the ESR technique, and (3) studies can be made of aqueous suspensions as well as dry powders and films. The radical cation (spin probe) reports its orientation and rate of tumbling at the clay surface through its ESR spectrum. Unfortunately, relatively few molecules exist as stable radicals, so that the choice of molecular species for studies of this type is limited.

The present investigation is designed to observe the effect of molecular cation concentration on the clay surface upon mobility and orientation, since previous results (McBride, 1977b) have shown that the ESR spectrum of the adsorbed cation is dependent upon the level of adsorption. The K^+ ion was chosen as the complementary cation in order to permit free swelling of clay platelets at low probe-adsorption levels, thereby maximizing the possibility of homogeneous clay-water-probe system. Previous work has shown that the type of exchange cation has relatively little influence on the surface mobility of the probe (McBride, 1977b).

MATERIALS AND METHODS

Natural hectorite from Hector, California, obtained from the Baroid Division of NL Industries was used in all studies because of its low structural iron content. API project 49 lists the structural formula of this material as $M^+_{.64}(Mg_{5.42}\,Li_{.68}\,Al_{.02})(Si_8O_{20})(F, OH)_4$ and its cation-exchange capacity (CEC) as 77 meq/100 g. The hectorite, however, is known to contain carbonate impurities. Samples of K^+-saturated hectorite (0.25 g) were placed in centrifuge tubes, and quantities of an acidified 0.0125 M solution (pH = 3.0) of protonated 4-amino-2,2,6,6-tetramethylpiperidine N-oxide (TEMPAMINE $^+$) were added to the samples at levels roughly equivalent to 1, 2, 5, 10, 20, 40, and 100% of the CEC. The total volume was then made up to 20 ml with distilled water, and the clay-water suspensions were mixed and equilibrated for 2 hours. After centrifuging and removal of the supernatants, portions of the hectorite pastes were placed in capillary tubes, and ESR spectra were obtained on a Varian E-104 (x-band) spectrometer at room temperature. The remainder of the clay samples was washed free of excess salt with two distilled water rinses, and oriented films were prepared by drying the suspensions on polyethylene sheets. The films were then oriented in the magnetic field, H, of the ESR spectrometer, and spectra were obtained in the wet and dry state with the films aligned parallel ($\parallel$) and perpendicular ($\perp$) to H. The wet films

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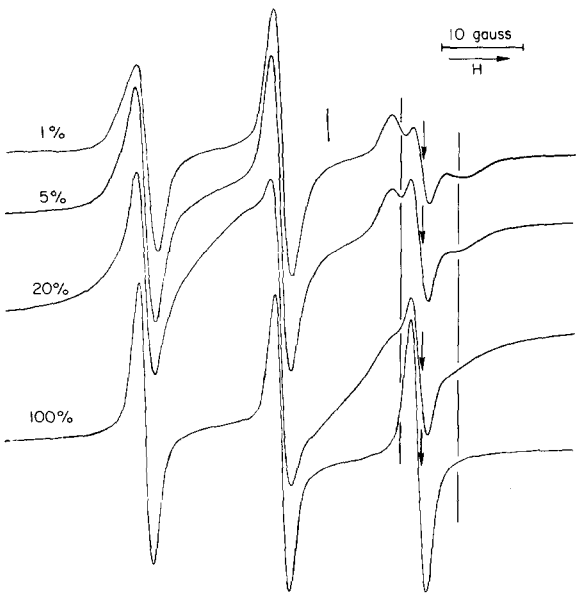


Figure 1. ESR spectra of TEMPAMINE$^+$-doped K$^+$-hectorite gels (nonoriented). The loading levels of TEMPAMINE$^+$ roughly correspond to 1, 5, 20, and 100% of the CEC. The high field components of the solution spectrum are indicated by arrows, while the two positions of the high field resonance of adsorbed probe are marked with vertical lines. A short vertical line in this and following figures denotes the approximate g = 2.002 position.

were prepared by placing dry films on a flat quartz holder and adding a small excess of distilled water. The d(001) spacings of the oriented hectorite films in the wet and dry state were determined on a Norelco X-ray diffractometer.

The clay samples, washed free of excess probe, were analyzed for exchangeable TEMPAMINE$^+$ content by displacing the probe from known quantities of clay with tetramethylammonium ions. Quantitative ESR analysis of those solutions (using TEMPAMINE$^+$ standards) indicated 0.8, 2.2, 6.8, 14.0, 28.3, and 35.7% loading of the 1, 2, 5, 10, 20, and 40% systems, respectively. Evidently, water washing must have removed very little of the probe added initially.

RESULTS AND DISCUSSION

Since the equilibrated clay suspensions were initially not washed free of excess ions, the ESR spectrum of TEMPAMINE$^+$ in the solution phase of the suspension was superimposed on the spectrum of adsorbed ions (see selected spectra, Figure 1). The relative quantity of TEMPAMINE$^+$ in solution clearly increases with increasing additions of the probe to the suspension, despite the fact that the first three suspensions represented in Figure 1 had only enough probe added to occupy 1, 5, and 20% of the exchange sites. Competition by protons contained in the solution of TEMPAMINE$^+$

Table 1. Basal d(001) spacings of TEMPAMINE$^+$-exchanged hectorites.

Equivalent fraction of TEMPAMINE$^+$ added	d(001) spacing (Å)	
	air-dry[1]	wet
0.01	11.8	>30
0.02	11.8	>30
0.05	11.9	14.5
0.10	12.4	14.5
0.20	13.4	14.5
0.40	14.0	14.6
1.00	14.0	14.7

[1] Diffraction peaks were broad, indicating interstratification, and had shoulders toward lower spacings.

(pH = 3) and K$^+$ ions desorbed by exchange must account for the increasing prevalence of the solution probe, until the 100% level produces little evidence of adsorbed TEMPAMINE$^+$ (Figure 1). The presence of two discrete spectra in a homogeneous suspension at equilibrium indicates that the probe ion movement from the adsorbed state to solution is slow on the ESR time scale, with exchange requiring more than 10^{-8} sec.

The nature of the spectrum of the adsorbed probe has been discussed previously (McBride, 1976, 1977a, 1977b) and will not be described in detail here. However, an additional broad resonance centered on the $M_I = 0$ (middle) resonance of the TEMPAMINE$^+$ spectrum is evident at the 10% loading level, increasing in relative intensity to the 40% level, and finally decreasing again at the 100% level. This spectrum has been noted before on clay films at the 10% doping level (McBride, 1977c), and is attributed to spin exchange of adsorbed probes. The linewidth of the spectrum is about 9 gauss (G) compared to approximately 6.5 G for a 0.1 M solution of nitroxide probe radicals (Wertz and Bolton, 1972). A 0.1 M solution corresponds to an *average* probe-probe distance of 25 Å; however, spin exchange may be much less efficient on a clay surface where ionic mobility is restricted by electrostatic interaction and restraints of interlamellar volume. Spectra of adsorbed TEMPAMINE$^+$ attributable to low *and* high (spin-exchanged) concentrations can be observed in the same clay suspension, indicating nonhomogeneous distribution of probes (i.e., demixing of ions) even at low loading levels (e.g., 10–20%). Organic cation segregation from metal ions has been suggested by other studies using X-ray powder diffraction and surface area measurements (McBride and Mortland, 1975; Berkheiser and Mortland, 1977). There has been some question as to whether demixing occurs upon drying the clays or spontaneously in suspension. These results indicate that the latter can occur, and the d(001) spacings of the wetted clay films (Table 1) support this hypothesis, since a 14.5-Å peak begins to appear near the 5% level of adsorbed TEMPAMINE$^+$, becoming more evident with further additions of the probe. Since smec-

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tites saturated with TEMPAMINE$^+$ cannot expand in water (McBride, 1976), the 14.5-Å spacing is evidence that the probes concentrate in certain interlayers until collapse of clay platelets occurs. The collapse appears well below the levels that would be expected if adsorbed K^+ and TEMPAMINE$^+$ were randomly distributed on the exchange sites. Interlamellar collapse is likely caused by the inability of probe ions to hydrate strongly, permitting platelets to approach one another. Hydrated metal ions would then be displaced to "external" surfaces in the partially dispersed clay.

After washing the equilibrated suspensions free of most of the excess salt, an expected large reduction in the intensity of the ESR spectrum of the solution probe relative to adsorbed probe occurs (Figure 2). The orientation dependence of the spectrum of adsorbed TEMPAMINE$^+$ is clearly shown by the different hyperfine splittings ($\bar{A}$) for the $\perp$ and $\parallel$ orientations of the clay films (Table 2). The difference between $\bar{A}\perp$ and $\bar{A}\parallel$, where these values are measured as half the field distance in gauss between the low field and high field peaks of the spectrum for the $\perp$ and $\parallel$ orientations of the clay films, respectively, can be defined as $\Delta\bar{A}$. At low loading levels of the probe on the clay, $\Delta\bar{A} \cong 5$ G, and the order parameter, S (Seelig, 1976) can be given as:

$$S = \frac{(\bar{A}_\perp - \bar{A}_\parallel)}{(A_{zz} - A_{xx})} = \frac{\Delta\bar{A}}{(A_{zz} - A_{xx})} \qquad (1)$$

where A_{zz} and A_{xx} are the rigid-limit hyperfine splitting parameters of the probe molecule for alignment of the magnetic field along the z and x axes of the molecule. These values have been estimated to be $A_{zz} = 31.4$ G and $A_{xx} = 9.7$ G from the rigid-limit ESR spectra of air-dried TEMPAMINE$^+$-treated hectorite films. Thus, at low levels, Eq. (1) is used to calculate an order parameter of 0.23. By defining an external fixed axis system (x', y', z') in addition to the molecular axes (x, y, z), one can then define the angle θ between the z and z' axes:

$$\cos\theta = \vec{z}\cdot\vec{z}'$$

In this experiment, the z' axis has been chosen normal to the plane of the silicate sheets of the clay, and the z axis by convention is along the direction of the nitrogen 2p π-orbital on the N–O portion of the probe molecule. The angle θ fluctuates rapidly with time, but assuming rotational symmetry of molecular motion about z' (as must be expected because of the random orientation of platelets in the x'y' plane of the clay film), the time-averaged system is axially symmetric. The following equations can then be derived for orientations of the magnetic field $\perp$ and $\parallel$ to the z'-axis (Seelig, 1976):

$$A_\perp = \tfrac{1}{2}(1 - \langle\cos^2\theta\rangle)(A_{zz} - A_{xx}) + A_{xx} \qquad (2)$$

$$A_\parallel = \langle\cos^2\theta\rangle(A_{zz} - A_{xx}) + A_{xx} \qquad (3)$$

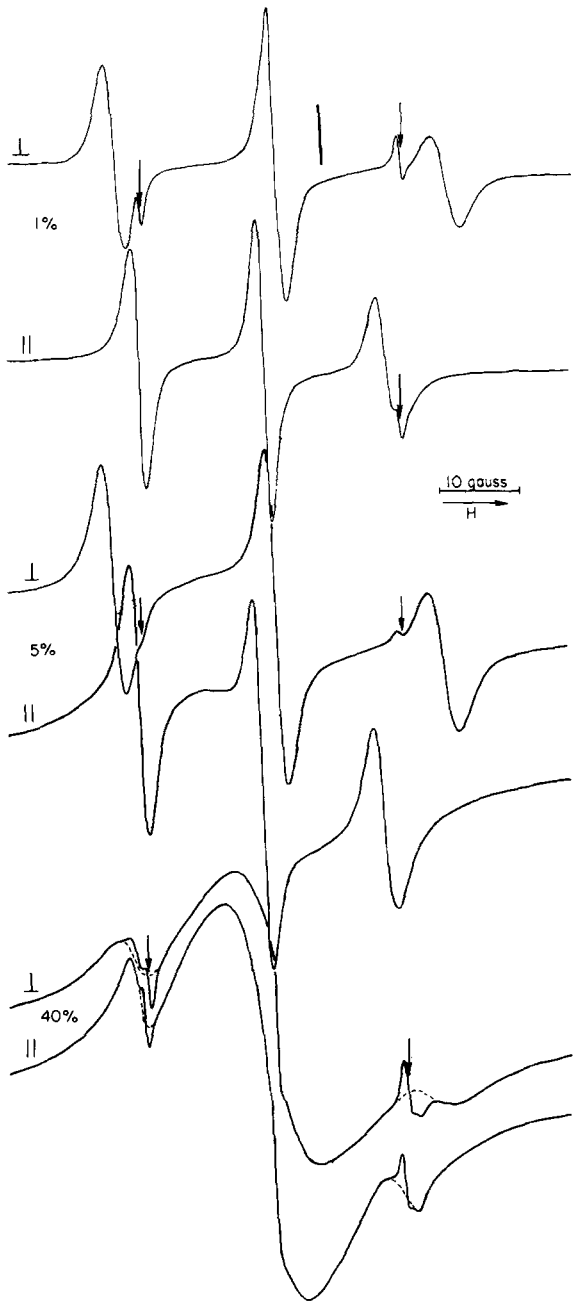


Figure 2. ESR spectra of water-washed TEMPAMINE$^+$-doped K^+-hectorite films wetted in water and oriented $\perp$ and $\parallel$ to H. The loading levels correspond to 1, 5, and 40% of the CEC. The positions of the high and low field resonances of the *solution* phase probe are indicated by arrows. Overlap of solution and adsorbed probe spectra at the 40% level required estimation of the outer line shapes of the spectrum of adsorbed TEMPAMINE$^+$ (broken lines).

where $\langle\cos^2\theta\rangle$ is the time-averaged value of $\cos^2\theta$. It should be noted that when the magnetic field is oriented parallel to the plane of the clay film, it is directed perpendicular to the z'-axis. As a result, $A_\parallel = \bar{A}_\perp$ and

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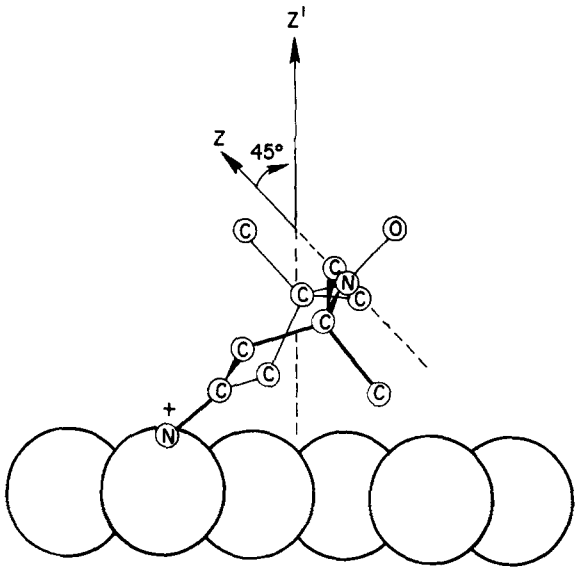


Figure 3. Probable *average* alignment of TEMPAMINE$^+$ on the surface oxygen atoms of wetted hectorite. The framework structure of the molecule is shown with hydrogen atoms omitted.

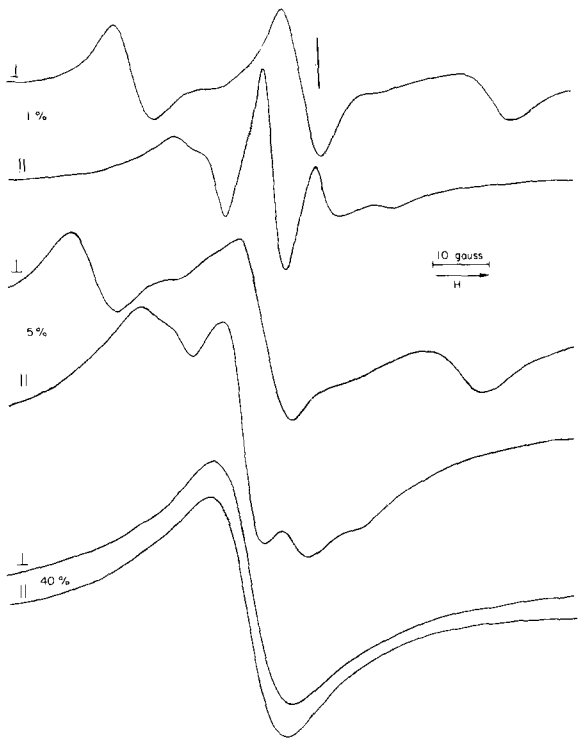


Figure 4. ESR spectra of air-dry K$^+$-hectorite films containing TEMPAMINE$^+$ (loading levels of 1, 5, and 40% of CEC), and oriented ⊥ and ∥ to H.

$A_\perp = \bar{A}_{||}$. Using the values of $A_\perp$ = 15.2 G and $A_{||}$ = 20.2 G (Table 2) in Eq. (2) and (3), apparent *average* θ values of 45.4° and 45.9°, respectively, are obtained.

The results of the above analysis produce some interesting observations regarding interaction of TEMPAMINE$^+$ with hectorite fully wetted in H_2O. Since $S \neq 0$, motion of the adsorbed probe is not totally random. Random tumbling would produce an *apparent* orientation angle of 54.7° (Seelig, 1976). The structures of the probe molecules (2,2,6,6-tetramethylpiperidine N-oxide) are well enough known (Lajzerowicz-Bonneteau, 1976) that a surface alignment can be hypothesized to account for the 45–46° orientation angle (Figure 3). The alignment would permit the charged amine group to contact or "key" into the surface oxygens, and maximize van der Waals interactions between methyl groups and the surface. In this configuration, the molecule might be expected to rotate rather rapidly about the z'-axis (possibly with the amine group at a fixed position in the ESR time scale) but more slowly about any axis perpendicular to z'. The latter "flopping" motion would require a significant activation energy to overcome the van der Waals or electrostatic attractions. Anisotropic motion as described here would produce different values of the apparent rotational correlation time, τ_c, for the ⊥ and ∥ orientations of the clay, and this is verified in Table 1. However, the equations used to estimate τ_c are based on isotropic tumbling motion and become invalid for very anisotropic motion.

As increasing quantities of TEMPAMINE$^+$ are adsorbed by the hectorite, the evidence suggests that orientation of the adsorbed probe becomes less pronounced (i.e., $\Delta\bar{A}$ becomes smaller), especially with 20% or higher loading levels of the probe (Table 2). Unfortunately, these levels also produce more intense

Table 2. Spectral parameters for ESR signals of TEMPAMINE$^+$ adsorbed on hectorite in the wet and dry state.

Equivalent fraction of TEMPAMINE$^+$ added	Wetted hectorite (H_2O)				Air-dried hectorite		
	$\bar{A}_\perp$(G)	$\bar{A}_{||}$(G)	$\frac{1}{3}(\bar{A}_\perp + \bar{A}_{||})$	τ_c(× 10^9 sec)	$\bar{A}_\perp$(G)	$\bar{A}_{||}$(G)	$\frac{1}{3}(\bar{A}_\perp + 2\bar{A}_{||})$
0.01	20.5	15.2	17.0	1.88(⊥), 1.15(∥)	31.4	9.7	16.9
0.02	20.2	15.3	16.9	1.65(⊥), 1.06(∥)	31.6	9.8	17.1
0.05	20.4	15.2	16.9	n.d.[1]	32.3	9.8	17.3
0.10	20.2	15.2	16.9	n.d.	32.3	n.d.	n.d.
0.20	18.9	15.8	16.8	n.d.	n.d.	n.d.	n.d.
0.40	18.6	16.1	16.9	n.d.	n.d.	n.d.	n.d.

[1] n.d. = could not be determined because of overlapping spectra.

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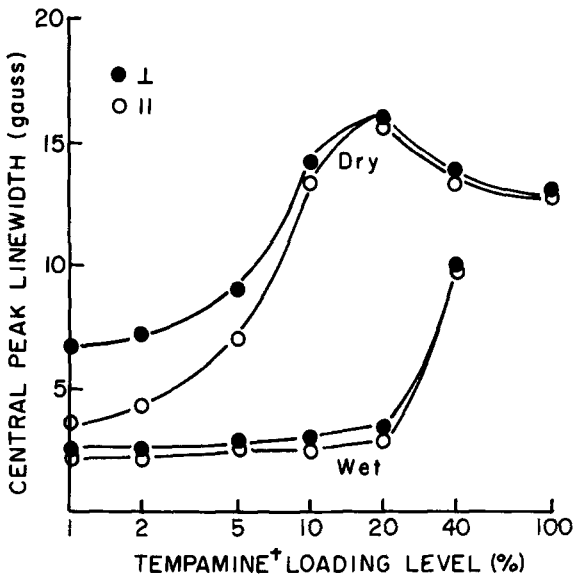


Figure 5. Relationship between quantity of TEMPAMINE$^+$ adsorbed on wet and dry hectorite and linewidth of the dominant midfield resonance. At high levels, this resonance results from spin exchange between TEMPAMINE$^+$ ions.

broad spectra due to spin exchange which partially obscure the spectra of interest (see Figure 2, 40% level) and prevent calculation of apparent τ_c values. An explanation has been suggested for the apparent composition-dependent mobility (McBride, 1977c), based upon the concept that only a fraction of the adsorbed TEMPAMINE$^+$ ions have direct contact with the surface (as in Figure 3) at a given instant in time. The remainder is separated from the surface by at least one layer of solvent molecules. Exchange between the positions is rapid on the ESR time scale, producing an averaged spectrum. However, at high loading levels, equilibrium would favor the less localized probes because of the lower entropy (increased order) associated with surface-localized ions.

Upon drying the clay films, surface alignment becomes much more pronounced, as shown by the strongly orientation-dependent spectra of Figure 4. The collapse of basal spacing associated with air-drying (Table 1) forces the probe ion to align in a more "flat" position in interlayers so that the N–O bond axis is nearly parallel with the plane of the clay platelets. There is also evidence of spectral broadening at much lower levels of adsorbed probe than in the case of fully wetted clays (Figure 5). Even at the 2% adsorption level, significant line broadening occurs, probably resulting from dipolar interactions between probes. The drying process reduces the average probe–probe intermolecular distance by bringing dispersed clay platelets together, and possibly by enhancing demixing of ions as well. At levels of adsorbed TEMPAMINE$^+$ above 5–10%, a broad isotropic resonance appears in the dry films (see Figure 5, 40% level), becoming more narrow at levels greater than 20% (Figure 5). The line-narrowing can be attributed to the phenomenon of exchange-narrowing, where electron spins on adjacent molecules exchange so fast that the time average of the hyperfine field splitting approaches zero (Wertz and Bolton, 1972). The effect can only be observed when the radical molecules are very close together, such as in pure solid free radicals.

Since the average hyperfine splitting constant given by $a = \frac{1}{3}(\tilde{A}_\perp + 2\tilde{A}_{||})$ is sensitive to changes in polarity of the probe's environment (Seelig, 1976), becoming larger for more polar environments, a different "a" value might be expected for the adsorbed TEMPAMINE$^+$ compared to the 16.9-G value found for TEMPAMINE$^+$ in aqueous solution. However, "a" is not significantly changed by adsorption of TEMPAMINE$^+$ on hydrated clay surfaces (Table 2), probably because water molecules still surround the N–O portion of the adsorbed probe.

Previous studies of TEMPAMINE$^+$ adsorbed on smectites solvated in ethanol and methanol have shown spectra attributable to highly oriented as well as nearly randomly tumbling species (McBride, 1976, 1977a, 1977b). The present study reveals that the former species predominates at very low adsorption levels, while the latter solutionlike species becomes more prevalent at higher levels (Figure 6). Using Eq. (1) and the data for the hyperfine splitting of the oriented probe (Table 3), an S value of -0.37 is obtained, indicating greater order and in the opposite sense to that for the aqueous system. In addition, the apparent average θ value is 73.8 and 72.3° using Eq. (2) and (3), respectively. Since the basal spacing of the hectorite in methanol is 17.0 Å (McBride, 1977b), the orientation of the probe suggests an interaction across platelets as a result of van der Waals attraction to surfaces (Figure 7). It is likely that the more strongly oriented, less mobile probe is reporting more aqueous environments that are segregated from the bulk of interlayers solvated by methanol, while the more rapidly tumbling probe exists in methanol solvated interlayers. There is considerable evidence for this hypothesis of solvent demixing on the clay surface. First, the value of $\frac{1}{3}(\tilde{A}_\perp + 2\tilde{A}_{||})$ is near 17.0 G for the strongly oriented probe, but only 16.1–16.3 G for the mobile species (Table 3). A more polar microenvironment is indicated by the higher value, while the lower value is similar to that observed for TEMPAMINE$^+$ dissolved in methanol (McBride, 1977a). However, it is possible that the surface oxygens of hectorite are polar enough that direct probe-surface contact produces a splitting of 17.0 G. This is suggested by the values of $\frac{1}{3}(\tilde{A}_\perp + 2\tilde{A}_{\parallel})$ on air-dried hectorite (Table 2). Additional evidence comes from previous studies which have shown that not all of the adsorbed water in air-dry hectorite is removed by an initial wash with alcohol (McBride, 1977). Repeated washing with

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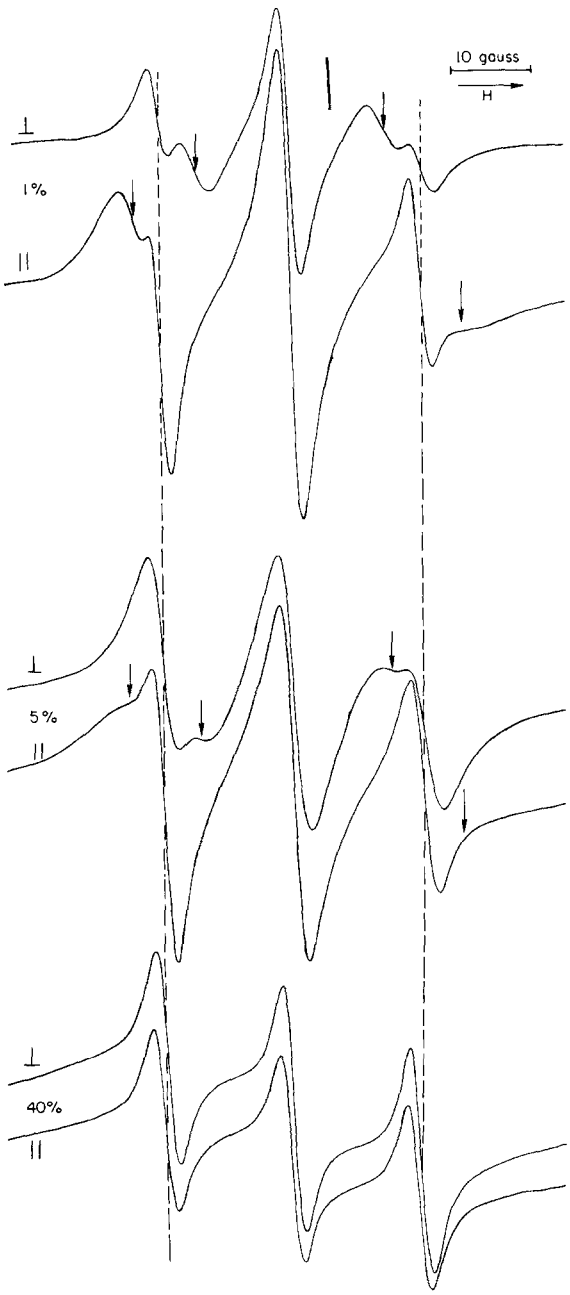


Figure 6. ESR spectra of methanol-solvated, K^+-hectorite films containing TEMPAMINE$^+$ (loading levels of 1, 5, and 40% of CEC), and oriented ⊥ and ∥ to H. The vertical broken lines indicate the positions of the outer resonances of the mobile fraction of the probe, while the arrows locate the outer resonances of the strongly oriented probe.

ethanol, for example, lowers the value of $\frac{1}{3}(\bar{A}_\perp + 2\bar{A}_{||})$ for the mobile probe while reducing the intensity of the ESR signal representing the less mobile probe. Also, only a small quantity of probes (relative to the CEC) appears to occupy sites which produce strong alignment, since the signal of very mobile probes dominates the ESR spectrum at loading levels of 5% or higher (Figure 6). Hydrated interlayers would show a greater affinity for the probe than methanol-solvated surfaces because of the rather hydrophobic nature of smectites. Thus, small amounts of TEMPAMINE$^+$ would tend to concentrate in interlayers containing significant amounts of water. The proposed orientation for these probes (Figure 7) may arise from the partial expansion of air-dry hectorite in methanol, thereby permitting the long axis of the probe to reach across the interlayer and contact opposing surfaces.

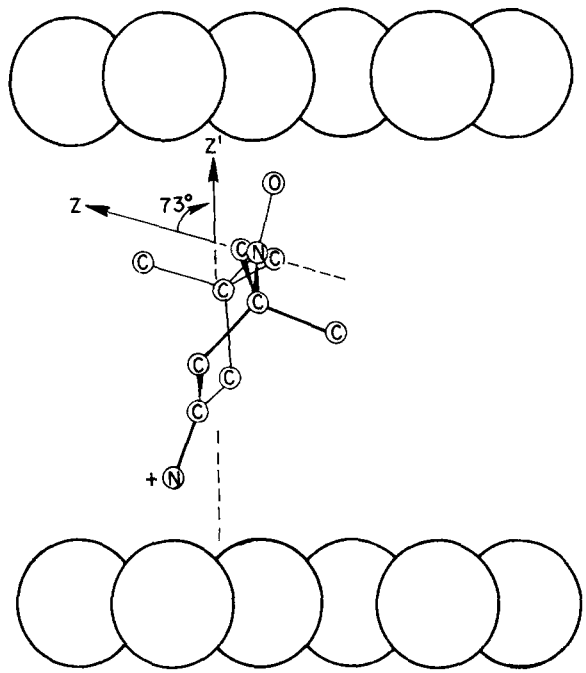


Figure 7. Probable *average* alignment of strongly oriented TEMPAMINE$^+$ in the ~7-Å interlayers of methanol-solvated hectorite.

Most of the probe cations in the methanol-solvated hectorite are weakly attracted to the surfaces as shown by the predominance of the spectrum of weakly oriented TEMPAMINE$^+$ at high loading levels. Although measurement of mobility by calculating rotational correlation times for this spectrum is difficult because of the overlapping spectrum of the less mobile species, some concept of the relative solutionlike nature of the mobile probe can be obtained by measuring the ratio (h_{+1}/h_{-1}), where h_{+1} and h_{-1} are the low field and high field peak heights, respectively. Since h_{+1}/h_{-1} is very nearly 1.0 for TEMPAMINE$^+$ in methanol solution, values larger than 1.0 represent a loss in mobility as a result of adsorption. The relationship between h_{+1}/h_{-1} and quantity of adsorbed probe (Figure 8) demonstrates that the "mobile" probe is more greatly restricted at low adsorption levels. This restriction is more apparent for the ⊥ orientation of the clay films, reflecting less

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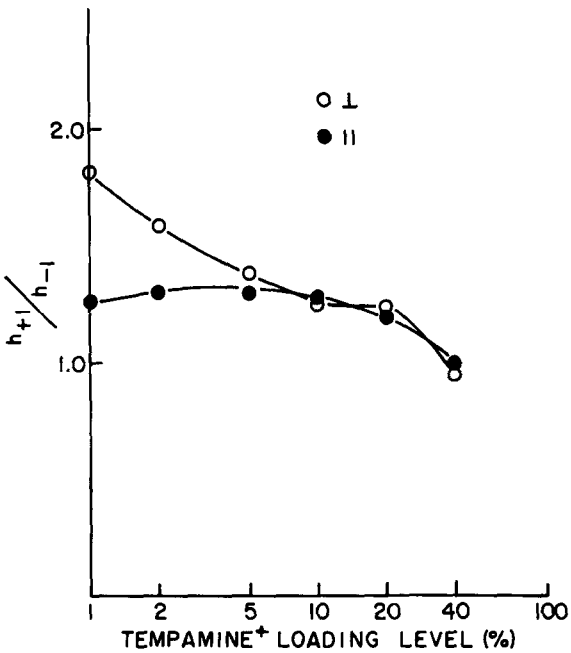


Figure 8. Effect of surface concentration of TEMPAMINE$^+$ upon the observed ESR spectrum of the methanol-solvated hectorite system, where (h_{+1}/h_{-1}) is the ratio of low-field to high-field peak heights. Hectorite films were oriented ⊥ and ∥ to the magnetic field.

isotropic motion. At the 40% adsorption level, the spectrum indicates that most of the probe is in the solution phase, a reflection of the fact that the less polar solvent reduces the ability of the clay to remove TEMPAMINE$^+$ from solution.

The dependence of average mobility upon surface loading level can be explained by entropy considerations, since the probability of desorption of a probe ion is proportional to the fraction of surface sites occupied by the ion. The lack of ion demixing even at high loading levels, as shown by the lack of a broad single resonance due to spin exchange, contrasts with the aqueous clay system. The segregation in aqueous systems is probably driven by the formation of hydrophobic interlayers in which probe–probe and probe–surface interactions are maximized. However, in methanol, the probe–solvent attraction may be at least as strong as these interactions. Thus, the probe has a tendency to maintain a solvation shell, preventing demixing and interlayer collapse in the clay phase, and promoting an equilibrium in which the probe cation is shifted toward the solution phase.

CONCLUSIONS

The main effects of adsorption level upon the ESR spectrum of the spin probe, TEMPAMINE$^+$, result from ion demixing and equilibrium which favor the solution state of the probe at high adsorption levels. Demixing occurs even at low surface concentrations in hydrated clays, and appears to result from the strong attraction of the hydrated clay for the probe combined with weak probe–solvent interaction. In contrast, demixing is not evident in methanol-solvated clays because of the stronger probe–solvent interaction and the inability of the probe to compete with methanol molecules for surface adsorption sites. The orientation of TEMPAMINE$^+$ at clay surfaces is much more pronounced for hydrated than for methanol-solvated systems, but a small quantity of probe is highly oriented in the latter, possibly in interlayers from which water has not been effectively removed.

Segregation of organic cations from metal ions in interlamellar regions of clay suspensions appears to be a general phenomenon that is likely to prevent a simple description of adsorption by ion exchange, and that may explain hysteresis effects often observed in these systems. The demixing process appears to be essentially unaffected by the type of metallic cation, being as evident in Mg^{2+} and Na^+ exchange forms of hectorite as it is in K^+-hectorite.

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Table 3. Spectral parameters of the two species of TEMPAMINE$^+$ adsorbed on methanol-solvated, K^+-hectorite films.

Equivalent fraction of TEMPAMINE$^+$ added	Strongly oriented probe			Nonoriented probe		
	$\bar{A}_\perp$(G)	$\bar{A}_\parallel$(G)	$\frac{1}{3}(\bar{A}_\perp + 2\bar{A}_\parallel)$	$\bar{A}_\perp$(G)	$\bar{A}_\parallel$(G)	$\frac{1}{3}(\bar{A}_\perp + 2\bar{A}_\parallel)$
0.01	11.7	19.7	17.0	16.4	16.1	16.2
0.02	11.7	19.9	17.2	16.3	16.1	16.2
0.05	n.d.[1]	n.d.	n.d.	16.4	16.2	16.3
0.10	n.d.	n.d.	n.d.	16.2	16.1	16.1
0.20	n.d.	n.d.	n.d.	16.5	16.2	16.3
0.40	n.d.	n.d.	n.d.	15.7	15.8	15.8

[1] n.d. = spectrum obscured by the spectrum of the nonoriented probe.

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Резюме—Методика электронного спинного резонанса (ЭСР) использовалась для изучения движения и отделения органического спинного радикального катиона (4-амино-2,2,6,6-тетраметилпайперидин N-окись) в гекторите как функции средней поверзностной концентрацпи. Органический катион стремится концентрироваться в определенных межслоях водной суспензии гекторита даже когда он заннмает небольшую часть катионных обменных участков. Этот эффект разложения не очевиден в гекторите, сольватированном в метаноле. Средняя мобильность радикала возрастает на более высоких уровнях адсорбции как результат сдвига равновесия в сторону растворенного состояния. Вычисленные осредненные во времени ориентации радикала на поверхностях глины значительно отличаются для метанол- и водно-сольватированных систем, что указывает на важную роль сольвента в измененний взаимодеиствия поверхность-катион.

Resümee—Elektronenspinresonanz ist benutzt worden, um die Beweglichkeit und Ausscheidung eines organischen Spinsondenkations (4-Amino-2,2,6,6-tetramethylpiperidin N-oxid) auf Hektorit als Funktion der durchschnittlichen Oberflächenkonzentration zu untersuchen. Das organische Kation zeigt eine Tendenz, sich in bestimmten Zwischenschichten von wässrigen Hektoritsuspensionen zu konzentrieren, auch wenn es einen kleinen Anteil der Kationenaustauschplätze einnimmt. Dieser Entmischungseffekt ist nicht sichtbar in Hektoriten, die durch Methanol solvatisiert sind. Die durchschnittliche Mobilität der Sonde nimmt zu mit höherer Adsorption, als Folge einer Verschiebung des Gleichgewichts zu Gunsten des Lösungszustandes. Durchschnittliche, über verschiedene Zeiten errechnete Orientierungen der Probe auf der Tonoberfläche sind sehr unterschiedlich für Methanol-Wasser solvatisierte Systeme, was auf den Einfluß hindeutet, den das Lösungsmittel auf die Oberflächen-Kationen Einwirkung ausübt.

Résumé—La technique de spin d'électrons a été utilisée pour étudier le mouvement et la ségrégation d'un cation organique de probe de spin (Oxide-N 4-amino-2,2,6,6-tétraméthylpipéridine) sur de l'hectorite en fonction de la concentration moyenne de surface. Le cation organique tend à se concentrer dans certaines couches interfeuillets de suspensions aqueuses d'hectorite même lorsqu'il n'occupe qu'une fraction minime des sites d'échange de cations. Cet effet de "démélange" n'est pas évident dans le cas de l'hectorite dissolue au méthanol. Un déplacement de l'équilibre en faveur d l'état de solution résulte en un accroissement de la mobilité moyenne de la probe à des niveaux d'adsorption plus élevés. Des orientations de probe sur des surfaces argileuses, calculées avec moyenne de temps, sont très différentes pour les systèmes dissolus au méthanol et à l'eau, soulignant l'importance du solvant dans la modification de l'interaction surface-cation.

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