

EXCHANGEABLE CATION AND SOLVENT EFFECTS UPON THE INTERLAMELLAR ENVIRONMENT OF SMECTITES: ESR SPIN PROBE STUDIES

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Abstract—The ESR spin probe, TEMPAMINE⁺, was used to study the interlamellar behavior of adsorbed organic cations on hectorites solvated with water, ethanol, and water–ethanol mixtures, and saturated with several monovalent and divalent metallic cations. The mobility and orientation of the probe was affected greatly by the solvent, and to a lesser extent by the predominant exchangeable cation on the silicate surface. Most of the effects could be interpreted in terms of the basal spacings of the hectorite. In all instances, the adsorbed probe was much less mobile than in solution despite the different interlamellar volumes available for molecular motion.

INTRODUCTION

Recent studies of the interaction between organic cations and layer silicate surfaces using ESR spin probes have described the influence of the solvent, temperature, and type of mineral upon the interaction (McBride, 1976a; McBride, 1976b). In addition, the level of doping of the probe molecule, TEMPAMINE⁺ (protonated 4-amino-2,2,6,6-tetramethylpiperidine *N*-oxide) has been shown to influence the apparent rotational correlation time, τ_c , of the adsorbed probe, as well as have an effect upon demixing of the surface cations (McBride, in press). The present investigation has the purpose of resolving the effect of the exchangeable metallic cation upon the surface environment as reflected in the behavior of the adsorbed probe. The much different swelling properties of monovalent-saturated (M^+) smectites compared to divalent-saturated (M^{2+}) smectites might be expected to influence surface adsorption, and some evidence of cation effects was observed previously (McBride, 1976a). In addition, the water “structure” at surfaces might be expected to be controlled in large part by the hydration energy of the adsorbed metal ions, and this effect could possibly be measured by the “viscosity” reported by the adsorbed spin probe. The doping level of the probe in the present study was kept very low to minimize influence of the hydrophobic probe upon swelling behavior as well as prevent ion demixing accompanied by spin exchange. In addition, the effect of the solvents water and ethanol, and mixtures of these solvents, upon orientation and mobility of adsorbed TEMPAMINE⁺ is investigated in detail.

MATERIALS AND METHODS

A California hectorite (<2 μ m particle size) with chemical formula and exchange capacity previously reported (McBride *et al.*, 1975) was saturated with

Li⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺, and Ba²⁺ exchange ions using excess quantities of chloride salt solutions. Excess salt was removed from the suspensions by centrifuging and discarding the supernatant until a negative AgNO₃ test for Cl[−] was obtained. An aqueous solution of TEMPAMINE⁺ was prepared by titrating a solution of the neutral probe with HCl past the equivalence point. Known quantities of this cationic form of the probe were added to each of the exchange forms of hectorite in order to produce a maximum doping level of 2% of the CEC. The clays were then washed several times in distilled water to remove excess Cl[−] and probe molecules. Aqueous suspensions of the doped hectorites were dried on polyethylene sheets to produce oriented, self-supporting films for electron spin resonance (ESR) and X-ray powder diffraction studies.

The ESR spectra were obtained for oriented films of hectorite in quartz tubes using a Varian V-4502 spectrometer (X-band). Air-dry clay films were equilibrated with ethanol, water, or ethanol–water mixtures by adding excess liquid to the films in the tubes and sealing the tubes. The spectra were recorded for the fully-solvated samples, although dielectric absorption in the ESR cavity prevented the use of large excesses of water in the hydrated clay systems.

The *d*(001) spacings of the hectorite films wetted in ethanol, water, and ethanol–water mixtures were recorded using a Norelco X-ray diffractometer. Several washes of the films were required to produce unchanging *d*-spacings in the solvents containing high ethanol.

RESULTS AND DISCUSSION

The spin probe, TEMPAMINE⁺, tumbles rapidly enough in aqueous solution ($\tau_c \approx 5 \times 10^{-11}$ sec) to average the anisotropy of the hyperfine splitting (*A*) and *g* tensors (McBride, 1976a). However, as demonstrated by the non-symmetrical ESR spectrum of

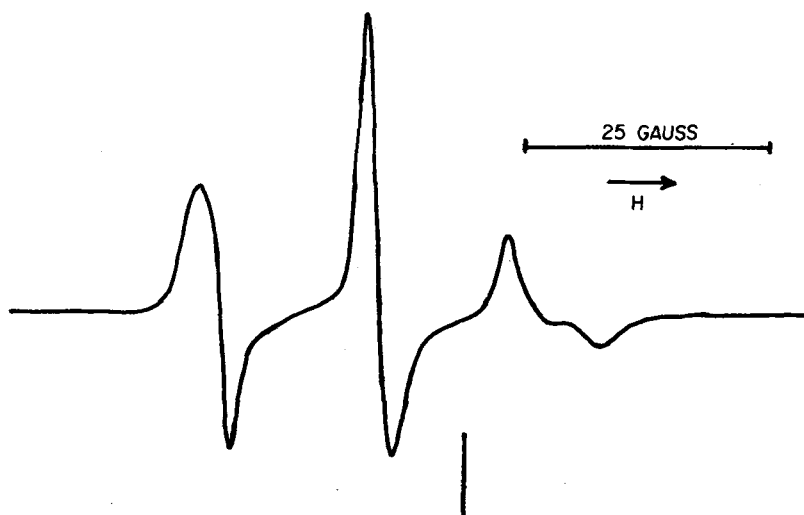


Figure 1. ESR spectrum of TEMPAMINE⁺ adsorbed on fully hydrated, randomly oriented K⁺-hectorite (paste). The vertical line indicates the field position corresponding to $g = 2.0023$.

TEMPAMINE⁺-doped, non-oriented K⁺-hectorite in excess water (Figure 1), the adsorbed probe is not solution-like. This type of spectrum can be shown to contain two directional components with different hyperfine splitting values, one observed with the ab plane of the hectorite platelets oriented parallel (\parallel) to the magnetic field, H , and one observed with the ab plane perpendicular (\perp) to H (Figure 2). The difference of the value of A for the two orientations, $\Delta A = A_{\perp} - A_{\parallel}$, is a measure of the degree of anisotropic tumbling or ordering of the probe molecule on the silicate. Random tumbling of the probe relative to the crystal axis system of the hectorite would produce a ΔA value of zero. However, adsorbed probe

molecules in aqueous clay systems do not rotate randomly, and ΔA values have been reported in the range of 3–5 gauss (McBride, 1976a) as compared to the theoretical maximum of 25–30 gauss for perfectly aligned, immobile probes. The data of Table 1 indicate that this general degree of alignment occurs for all metal ion exchange forms of fully hydrated hectorite. Thus, the N–O bond axis and the length of the molecule tend to align along the plane of the silicate surface, possibly in order to maximize methyl group contact with surface oxygens (McBride, 1976b). However, the ΔA values for the M²⁺-saturated hectorites are less than those for the M⁺-hectorites, suggesting an effect of the interlamellar basal spacings or hyd-

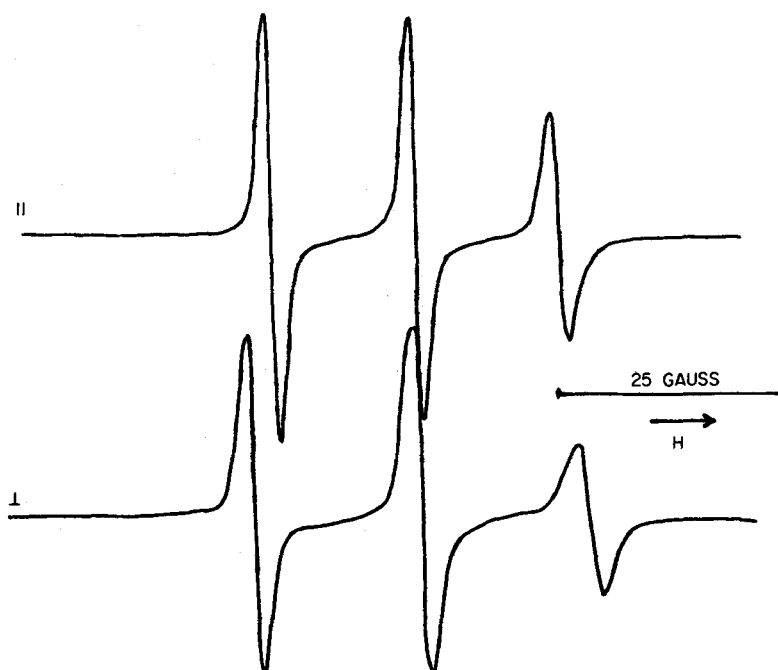


Figure 2. ESR spectra of TEMPAMINE⁺ adsorbed on fully hydrated, oriented Li⁺-hectorite films for the perpendicular (\perp) and (\parallel) orientations of the films relative to the magnetic field, H .

Table 1. The hyperfine splitting parameters (A_{\perp} , A_{\parallel} , ΔA) and apparent rotational correlation times (τ_{\perp} , τ_{\parallel}) for the \parallel and \perp orientations of water-solvated M^{2+} - and M^{+} -hectorite films doped at the 1–2% level with TEMPAMINE⁺

Exchange Ion	A values (gauss)			τ values ($\times 10^9$ sec)	
	A_{\perp}	A_{\parallel}	ΔA	τ_{\perp}	τ_{\parallel}
Li ⁺	18.5	15.7	+2.8	0.93	0.45
Na ⁺	19.2	15.1	+4.1	1.1	0.62
K ⁺	19.1	15.4	+3.7	1.7	0.96
Mg ²⁺	17.2	16.1	+1.1	3.0	1.2
Ca ²⁺	17.0	15.2	+1.8	3.3	1.4
Ba ²⁺	17.1	15.9	+1.2	3.6	1.4

ration energy of cations upon molecular orientation. The monovalent clays expand in water to a greater extent than the divalent clays (Table 2), so that greater interlamellar volume is expected to be available for molecular tumbling in the M^{+} -hectorites. However, the stronger surface alignment in the monovalent systems may indicate that the TEMPAMINE⁺ cation interacts more strongly with silicate surfaces occupied by weakly hydrating, loosely adsorbed monovalent metal ions. Divalent ions, with their strong surface attraction and high hydration energy, may inhibit probe-surface contact by competition for surface positions. Within the monovalent and the divalent systems, the observed trend of ΔA does not seem consistent with hydration energy (Table 1), but this effect may be a result of the strong surface attraction for K⁺ relative to Na⁺ and Li⁺, and Ba²⁺ relative to Ca²⁺ and Mg²⁺.

Further evidence for the exchange cation effect upon adsorbed molecular cations is found in the apparent rotational correlation times (τ_c) for adsorbed TEMPAMINE⁺ (Table 1). These values are calculated from the ESR spectra by the method described by Sachs and Latorre (1974), which is only useful in the fast motion region ($\tau_c < 10^{-8}$ sec) for random tumbling. The A and τ values determined for the \parallel and \perp orientations for the hydrated systems (Table 1) are indicative that the probe is tumbling more rapidly about one molecular axis than about others. In isotropic media, asymmetry in tumbling is expected because of the axially symmetric ellipsoid shape of the probe (Hwang *et al.*, 1975); however,

Table 2. Basal [$d(001)$] spacings of M^{2+} - and M^{+} -hectorite films solvated in excess ethanol, 50/50 ethanol/water (by volume), and water

Solvent	Basal spacing of hectorite (Å)					
	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺
ethanol	16.4	16.1	16.1	16.7	16.5	16.1
50/50 ethanol-water	24†	24†	24†	21.5*	21.0*	20.5*
water	>25	>25	~22†	20.4	20.3	19.5

* Broad X-ray diffraction peak representing random interstratification.

† Very broad diffraction peak indicating extreme interstratification.

the silicate surfaces impose an asymmetric potential and an external axis system upon the probe, magnifying and directing the asymmetry of rotational motion and diffusion. Because of the non-random tumbling, the τ_{\perp} and τ_{\parallel} values cannot be considered good estimates of rotational correlation times for the two orientations, but are useful in comparisons between hectorite systems. The τ values for adsorbed TEMPAMINE⁺ on hydrated hectorites are in the range of $1-3 \times 10^{-9}$ sec (Table 1), indicating a 20–60 times reduction in the rate of molecular rotation resulting from adsorption from solution. However, the calculated τ values are greater for the divalent than the monovalent systems, a possible result of the lower basal spacings in the M^{2+} -hectorites or the more highly structured aqueous interlayer produced by the strongly hydrating divalent metal ions. Since the correlation time appears to increase with decreasing hydration energy of the exchange cation within the monovalent and divalent systems (Table 1), the explanation involving basal spacing is the most likely. There is some evidence from X-ray powder diffraction data (Table 2) that the more weakly hydrating exchange cations permit smaller interlamellar spacings, thereby reducing the volume available for molecular rotation. The effective rotational diameter of the spin probe is about 6.5 Å (Hwang *et al.*, 1975), so that tumbling in a ~ 10 Å wide interlayer might be expected to be somewhat restricted.

In contrast to the aqueous systems, the ESR spectra of the hectorites solvated in 50/50 ethanol-water (by volume) showed no significant ordering of the probe relative to the silicate axes (i.e. $\Delta A = 0$), and little difference between the τ_{\perp} and τ_{\parallel} values (Table 3, Figure 3). Since the cations are likely to remain largely hydrated in the mixed solvent, the similarity between the monovalent and divalent systems could be attributed to the similar swelling behavior of the hectorites in ethanol-water (Table 2) rather than a solvation effect of the cations. The lack of probe alignment is probably a result of large basal spacings combined with a competition for surface adsorption sites by ethanol molecules as well as solvation of TEMPAMINE⁺ by ethanol. Although the correlation times of TEMPAMINE⁺ are shorter in the ethanol-water systems than in pure water (Table 3), they are in the range of 25–50 times longer than τ_c for the probe in pure ethanol, and 10–20 times longer than the τ_c value in water. Therefore, despite the near-random motion of the adsorbed probe, a very significant reduction in rotational motion results.

In ethanol-water solvated systems, the M^{2+} -hectorites demonstrate a longer correlation time than the M^{+} -hectorites. The divalent systems appear to have, on the average, somewhat smaller basal spacings than the monovalent systems (Table 2), which may explain the difference in τ_c . More aqueous interlayers in the M^{2+} -hectorites resulting from the large hydration energies of the divalent ions might also produce longer τ_c values.

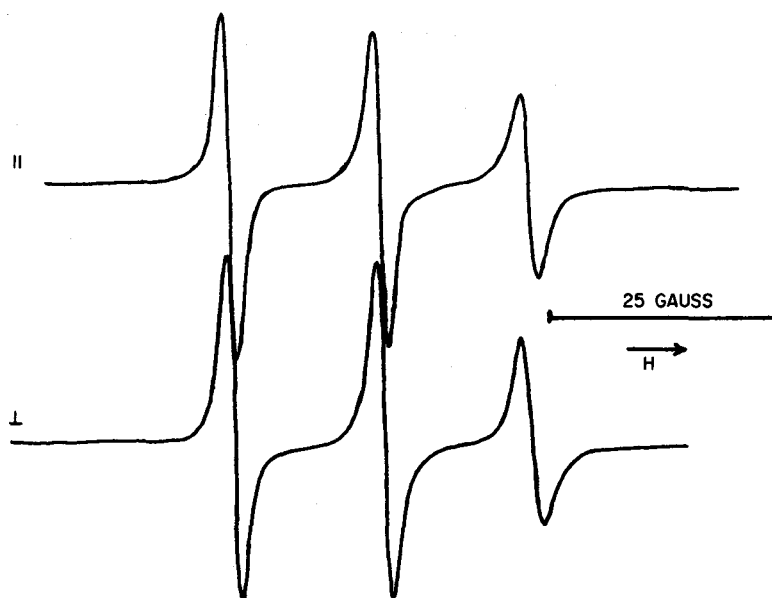


Figure 3. ESR spectra of TEMPAMINE⁺ adsorbed on oriented Li⁺-hectorite films solvated in 50/50 ethanol-water

The ethanol-solvated Na⁺-hectorite has been shown to produce a different alignment of the probe ion from that obtained in the aqueous clay systems (McBride, 1976a). This orientation is shown to be a general result for all metal ion forms of the hectorite (Table 4). The value of ΔA is negative, indicating a tendency for non-random tumbling in which the orientation of the N-O axis normal to the silicate surfaces is preferred. However, orientation becomes more pronounced when the ethanol-solvated hectorite is degassed and resolvated in ethanol, as indicated by the increase in ΔA (Table 4). The change in ΔA is most pronounced for the hectorites saturated with the most strongly hydrating cations, indicating that the first ethanol wash of air-dry hectorites does not readily remove the water of hydration of ions such as Li⁺ and Mg²⁺ and the probe ion is influenced by a partially aqueous interlamellar environment. Evidently, ethanol is competing with water for coordination positions on exchange ions as has been demonstrated previously by infrared spectroscopy (Dowdy and Mortland, 1967). The large preference

of exchange cations for water molecules relative to ethanol is apparent from the observation that air-dry hectorites initially equilibrated with 100% ethanol (or ethanol-water mixtures high in ethanol) had large basal spacings, but continued washing with the solvent reduced the spacing to 16–17 Å.

The ordering factor, ΔA , in the ethanol-solvated hectorites is in the same range for the monovalent as for the divalent systems (Table 4) a probable result of the similar basal spacings for the M⁺- and M²⁺-hectorites in ethanol (Table 2). The non-random motion may be the result of TEMPAMINE⁺ ions preferring an alignment which bridges across interlayers, since the interlamellar spacing is about the same as the longest dimension of the probe. The apparent increase in the magnitude of ΔA with increasing hydration energy of the exchange cation (Table 4) may be a result of slightly higher basal spacings in the more strongly solvating systems (Table 2), which permit stronger alignment across platelets than along surfaces. Thus, there are subtle effects of exchangeable cations upon the interlamellar environment of the probe, but the most significant result is the lack of orientation of the probe along surfaces as ethanol molecules appear to disrupt the probe-surface interaction. The correlation times of the probe in the ethanol-solvated hectorites are higher than those in either the hydrated or mixed-solvent systems (Table 4), most likely as a result of the motional restrictions in a relatively narrow interlayer. The molecular rotational rates, as a result, are slowed by about two orders of magnitude relative to the free solution probe. The effect of hydration energy of cations upon τ_c is not very noticeable, especially after the degassing and resolvation process, most likely because the cation-dipole bond is much weaker for the ethanol than for the water systems (Theng, 1974).

Table 3. The hyperfine splitting parameters (A_{\perp} , A_{\parallel} , ΔA) and apparent rotational correlation times (τ_{\perp} , τ_{\parallel}) for the \parallel and \perp orientations of 50/50 ethanol-water solvated M²⁺- and M⁺-hectorite films doped at the 1–2% level with TEMPAMINE⁺

Exchange Ion	A values (gauss)			τ values ($\times 10^9$ sec)	
	A_{\perp}	A_{\parallel}	ΔA	τ_{\perp}	τ_{\parallel}
Li ⁺	16.7	16.7	0.0	0.48	0.40
Na ⁺	16.4	16.5	-0.1	0.49	0.45
K ⁺	16.4	16.4	0.0	0.71	0.54
Mg ²⁺	16.4	16.4	0.0	0.88	0.70
Ca ²⁺	16.4	16.5	-0.1	0.85	0.76
Ba ²⁺	16.4	16.5	-0.1	0.89	0.78

Table 4. The hyperfine splitting parameters (A_{\perp} , A_{\parallel} , ΔA) and apparent rotational correlation times (τ_{\perp} , τ_{\parallel}) for the \parallel and \perp orientations of ethanol-solvated M^{2+} - and M^{+} -hectorite films doped at the 1–2% level with TEMPAMINE⁺

Exchange Ion	A values (gauss)			τ values ($\times 10^9$ sec)	
	A_{\perp}	A_{\parallel}	ΔA	τ_{\perp}	τ_{\parallel}
Li ⁺	15.3 (14.2)*	17.0 (17.0)	-1.7 (-2.8)	3.7 (3.2)	1.1 (1.8)
Na ⁺	15.2 (14.6)	16.8 (17.0)	-1.6 (-2.4)	3.8 (3.2)	1.2 (1.7)
K ⁺	15.5 (15.2)	16.3 (16.3)	-0.8 (-1.1)	4.9 (3.3)	1.7 (1.8)
Mg ²⁺	15.9 (14.7)	16.8 (17.3)	-0.9 (-2.6)	3.4 (4.4)	1.5 (2.4)
Ca ²⁺	15.8 (15.2)	16.8 (17.2)	-1.0 (-2.0)	3.4 (3.7)	1.5 (1.8)
Ba ²⁺	16.1 (15.3)	16.8 (16.7)	-0.7 (-1.4)	3.6 (5.5)	2.0 (2.7)

* Values in parentheses represent parameters of TEMPAMINE⁺ spectrum after degassing and resolving the hectorite films in ethanol.

Therefore, the major influence upon τ_c becomes the restricting interlamellar volume.

The ethanol-solvated hectorites were the only clay systems studied to demonstrate a spectrum of immobilized TEMPAMINE⁺ (see arrows, Figure 4). This spectrum is superimposed upon the three line spectrum of more mobile TEMPAMINE⁺, and represents strongly oriented probe molecules trapped in interlamellar regions (McBride, 1976b). The alignment is with the N–O bond axis perpendicular to the ab plane of the silicate, suggesting that the lower basal spacings of the ethanol-solvated hectorite produce this phenomenon as some probes electrostatically attach to one surface and physically interact with the adjacent surface of the interlayer. The mobile ($\tau_c < 10^{-8}$ sec) and immobile ($\tau_c > 10^{-8}$ sec) probes may be in dynamic equilibrium with one another if the mean lifetime of the probe in each environment is long on the time scale of ESR (i.e. $> 10^{-10}$ sec). Investigation of the relative intensity of the spectrum of immobilized TEMPAMINE⁺ indicates that the K⁺-hectorite contains the highest proportion of im-

mobile probes, a possible result of weak ion–dipole forces that would allow interlamellar collapse.

The influence of the ethanol/water ratio in solution upon the adsorption of TEMPAMINE⁺ by solvated Na⁺-hectorite is demonstrated by the relationship between A_{\parallel} , A_{\perp} and the % ethanol (by volume) initially in bulk solution (Figure 5). In addition to A_{\parallel} and A_{\perp} , the separation between the low and high field lines of the spectra for the two orientations, $2\bar{A}_{\parallel}$ and $2\bar{A}_{\perp}$, are plotted in Figure 5 because of the larger differences observed between the latter hyperfine splitting values. Evidently, increasing ethanol content of the interlayer reduces the alignment of probes on surfaces until near-random orientation occurs (i.e. $A_{\parallel} = A_{\perp}$) at an external ethanol/water ratio of one (Figure 5). However, the interlamellar ethanol/water ratio would be expected to be much lower than one as a result of weak cation–dipole interaction energy in the case of ethanol (Theng, 1974). As the ethanol/water ratio increases beyond one, some collapse of basal spacing occurs (Table 5), and non-random tumbling of TEMPAMINE⁺ occurs in the opposite sense

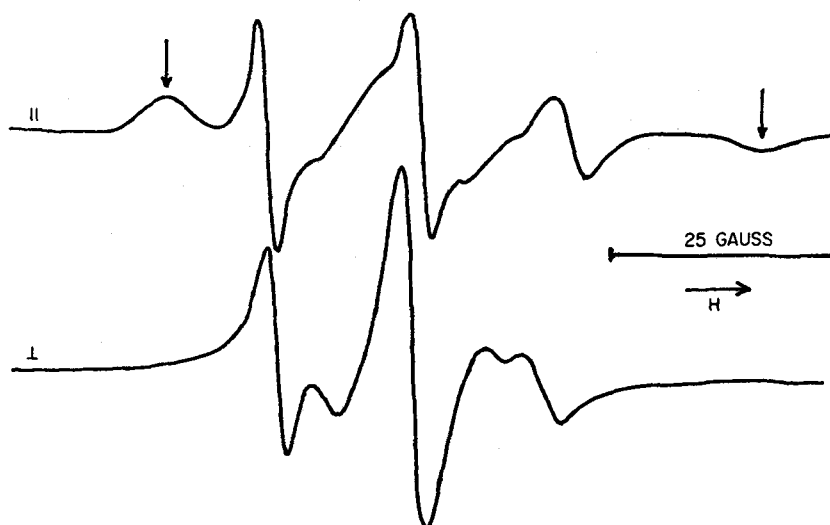


Figure 4. ESR spectra of TEMPAMINE⁺ adsorbed on oriented Li⁺-hectorite films solvated in ethanol (without degassing). The separated spectral features of the immobilized TEMPAMINE⁺ are indicated by arrows.

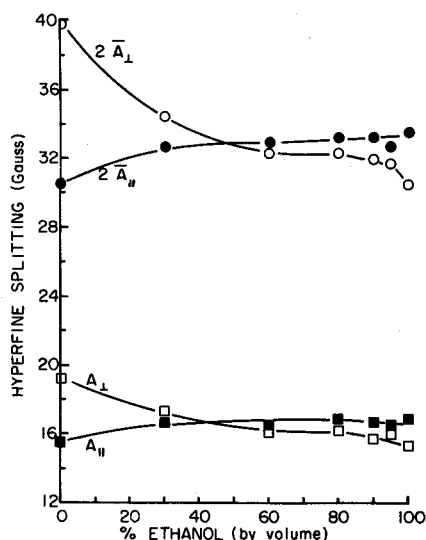


Figure 5. Relationship between % ethanol in mixed ethanol-water solvents and the hyperfine splitting parameters of adsorbed TEMPAMINE⁺ on solvated Na⁺-hectorite.

to that observed for the aqueous system since the value of ΔA becomes negative. In addition, some probes become "immobilized" as the basal spacing decreases, so that even hectorite solvated in 60% ethanol contains "rigid" probes (i.e. $\tau_c > 10^{-8}$ sec).

CONCLUSIONS

The ESR spin probe is found to be affected by the exchangeable metallic ions largely occupying the exchange sites of hectorite, but much of this effect is a result of different swelling properties of the clays exchanged with different ions. Small perturbations of the rotational mobility and orientation of the adsorbed probe occur as the exchange cation is varied while the basal spacing and solvent are unchanged. The direct influence of the complementary cation is apparently relatively minor compared to the influence of the solvent or the basal spacing upon molecular adsorption or mobility. In all the M⁺- and M²⁺-hectorites studied, fully hydrated surfaces tend to adsorb TEMPAMINE⁺ in a manner that produces align-

Table 5. Basal spacings of wet Na⁺-hectorite films washed several times with ethanol-water mixtures

% H ₂ O (by volume)	Basal spacing (Å)†
100	> 25
70	> 25
40	22*
20	19*
5	16.8
0	16.8

* Broad diffraction peaks indicating random interstratification.

† For high ethanol/water ratios, initial spacings were higher than those reported, but repeated washing with the same solvent lowered the spacings to constant values.

ment of the N-O bond axis with the surface, probably maximizing methyl group interaction with surface oxygen atoms. This orientation, along with a marked reduction in mobility relative to solution, occurs whether or not the spacings between silicate platelets are large and undetermined, as in M⁺-hectorites, or are relatively small and fairly well defined, as in M²⁺-hectorites.

The hectorites solvated in 50/50 ethanol-water allow the adsorbed TEMPAMINE⁺ to have considerable freedom of motion, as indicated by relatively short rotational correlation times (0.4–0.9 nsec) and little alignment at surfaces. This result is probably a combination of the large basal spacings observed for the system and the reduced attraction of TEMPAMINE⁺ for the surface in the presence of less polar ethanol molecules. However, the adsorbed probe is less mobile than the probe in solution despite the apparent lack of direct probe-surface contact.

The ethanol-solvated hectorites produce both immobilized and mobile probes as the basal spacing is reduced by the weak cation-dipole interaction energy. Orientation of both types of probes tends to be such that the N-O bond axis is normal to the *ab* plane of the silicate platelets. The basal spacing may determine this orientation by trapping some TEMPAMINE⁺ molecules, while permitting others to tumble fairly slowly in a non-random manner. The effect of the metal cation on the surfaces has only minor effects on the probe since the basal spacing is largely determined by forces other than ion-dipole interactions between ethanol and the exchange ion.

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