VARIABILITY IN EXCHANGE ION POSITION IN SMECTITE: DEPENDENCE ON INTERLAYER SOLVENT*

V. Berkheiser and M. M. Mortland

Department of Crop and Soil Sciences, Michigan State University
East Lansing, Michigan 48824, U.S.A.

Abstract—Full and reduced charge smectite saturated with Na(I), Ca(II), Cu(II), or tetralkylammonium ions were swollen by a series of solvents of various bulk physical properties. In the full charge smectites, swelling occurred in all solvents regardless of the exchange ion or the initial water content. Charge differences did not usually result in differential swelling of the smectite. Little correlation was found between the degree of swelling and the Gutmann donor numbers, bulk dielectric constants, bulk surface tensions, or dipole moments of the solvents. The intensities of the high field Fe(III) resonance ($g = 3.6$) in the esr spectra of full charge smectite swollen in various solvents reflected variability in exchange ion positions and depended upon the Gutmann donor number of the solvent. Considerable variety in the stereochemistry of Cu(II)-solvent complexes was revealed by esr spectra of the swollen systems.

INTRODUCTION

Crystalline swelling of clays has been related to the charge density of the clay surface, to the nature of the exchange ions present on the clay surface and to the dielectric constant of the interlayer medium (Norrish, 1954). Cation movement from the clay surface to positions midway between the clay sheets is generally believed to occur upon swelling as in the case of Mg–vermiculites (Walker, 1961). However, on the basis of conductometric measurements, the fraction of ions remaining at the surface of the clay was shown to be related to the nature of the cations and the kind of interlayer solvent (Shainberg and Kemper, 1966). Barshad (1952) has suggested that for solvents of low coordinating strength, the cations in swollen smectite reside in the surface hexagonal holes.

This paper reports an investigation of the relationship between exchange cation position as indicated by electron spin resonance spectroscopy and the Gutmann donor number of the interlayer solvent. In addition the effect of a number of factors on smectite swelling is reported. These include surface charge density, nature of the interlayer cations, and the bulk dielectric constants, dipole moments and surface tensions of the added solvent. The Gutmann donor number is the negative molar enthalpy of the reaction between a particular solvent and $SbCl_5$ in 1,2-dichloroethane (Gutmann, 1968). Since ion solvation is an important phenomenon in smectite swelling (Norrish, 1954), this parameter might be of use in describing clay solvent interactions. Relationships between crystalline swelling and charge density may be obtained from full and reduced charge smectites swollen in the selected solvents. Application of the methods of Clementz, Pinnavaia and Mortland (1973) to the present systems allow electron spin resonance investigation of the stereochemistry of the Cu(II)-solvent complexes.

EXPERIMENTAL

Preparation of reduced charge smectite

Li(I) saturated Upton, Wyoming montmorillonite (A.P.I. H-25) was heated at 220°C for 24 hr to produce reduced charge smectite, according to the method of Brindley and Ertem (1971). Cation exchange capacities were found to be 27 and 87 m-equiv/100 g, for the reduced and full charge clay respectively, by conductometric titration of Cu(II) according to the method of Clementz et al. (1974).

Cation exchange forms

The high and low charge smectites were washed in a large excess of 0·5 N chloride 95% ethanol solutions of Na(I), Ca(II), Cu(II), and tetramethylammonium (TMA) cations. Excess salts were removed with 95% ethanol until a negative Cl^- test with $AgNO_3$ was obtained after which they were dried at 110°C. Smectite containing about 10 mole % Cu(II) doped into Ca(II) was prepared by washing the clay 5 times with a chloride solution of 10 mole % Cu(II) and 90 mole % Ca(II); excess salts were removed by dialyzing against deionized water until Cl^- free. After evaporation from aqueous suspensions, the clays were stored air-dried until used.

Solvents

Reagent grade solvents were used throughout as they were received from the distributor without

---

Table 1. Solvents used and their properties

Solvent Name	Abbreviation	Gutmann Donor Number*	Dielectric Constant[†]	Dipole Moment[†], Debye
1,2-dichlorethane	DCE	0.0	10.1	1.19
Nitrobenzene	NIB	4.4	34.8	4.27
Acetonitrile	AN	14.1	38.0	3.84
Diethylcarbonate	DC	16.4	89.0	1.10
Methylacetate	MA	16.5	6.7	1.72
Diethylether	DE	19.2	4.3	1.15
N,N-dimethylformamide	DMF	26.6	36.7	3.82
Dimethylsulfoxide	DMSO	29.8	45.0	4.3
Ethanol	EtOH	31.5	24.3	1.69
Water	H_2O	33.	81.0	1.85
Pyridine	PY	33.1	12.3	2.26
N-methylformamide	MF	—	182.4	3.83

* Donor numbers are taken from V. Gutmann (1968) except for water which is taken from Ehrlich et al. (1970).

[†] Dielectric constants and dipole moments are taken from Handbook of Chemistry and Physics.

further purification. Homoionic clays from above were heated for 2 hr at 110°C and then placed into sealed beakers containing each solvent. The clays were in contact with the solvents for 10 days at which time measurements were taken. Selected properties of the solvents used in this study are given in Table 1. Abbreviations for solvent names will be used.

X-ray diffraction measurements

The (001) basal spacings were measured on a Philips X-ray Diffractometer using Ni filtered Cu-K_α radiation. In most samples three orders of reflections were detectable while each clay was kept wet with its respective solvent during the measurement.

Electron spin resonance measurements

A Varian E-4 ESR spectrometer operated at a proximal frequency of 9.47 GHz was used for recording broad-line spectra. Thin films of the clay specimens were oriented in quartz tubes, heated overnight, and then the solvents were added. After 10 days of equilibration, the excess solvent was removed with a syringe and the spectra of the structural Fe(III) resonances at $g = 4.2$ and $g = 3.6$ and of Cu(II) on exchange sites were recorded. McBride et al., 1975 have shown that the intensity of the $g = 3·6$ resonance is sensitive to the distance between the exchange ion charge and the silicate surface.

RESULTS AND DISCUSSION

It is seen from Table 2 that for smectite dehydrated at 110°C, little relationship exists between the degree of swelling and the Gutmann Donor Number of the solvent except for the Cu(II) system which was significantly correlated at the 5% level of confidence. Similar negative results for all systems were obtained when the basal spacings were plotted against bulk dielectric constants and surface tensions of the solvents. When the basal spacings were plotted against dipole moments of the above solvents, those with moments above 2.3 D tended to swell the TMA saturated smectites, whereas solvents with dipole moments of below 2.3 D tended not to swell the TMA-smectite beyond that defined by the organic cation itself (13.8 Å). Swelling of high and low charged smectites saturated with inorganic cations showed little relationship to dipole moment.

In most cases, there is little variation in swelling with charge density differences. This effect could be explained on the basis of balancing of the swelling force and the force of attraction between the negatively charged silicate surfaces and the interlayer cations which results in spacings not greatly different for both the reduced and fully charged systems.

Most interesting is the anomalous behavior of Na(I)-smectites in water. The full charge smectite swelled to such large spacings in water that no diffraction peaks were observed, whereas the reduced charge smectite remains largely unswollen in water in accordance with the results of Brindley and Ertem (1971). In addition to their results, information obtained here indicated that swelling of the reduced charge smectite occurs in a wide range of solvents.

Table 2. d-spacings of smectite saturated with various cations swollen with selected solvents (Å)

Solvent	Reduced charge smectite				Full charge smectite			
	Na(I)	Ca(II)	Cu(II)	TMA[+]	Na(I)	Ca(II)	Cu(II)	TMA[+]
DCE	12.6–13.0*	13.8*	9.8–13.0*	13.8	12.6–13.0*	14.7	13.0	13.8
NIB	14.8*	14.9*	15.1*	21.2	15.0	15.0	14.7	21.0
AN	19.6	19.8	20.0*	20.1	19.6	19.6	20.0*	20.5
DC	13.0*	14.7*	13.0	13.8	13.6	13.2*	13.2	13.8
MA	16.0	15.0	15.0	14.7	15.5	15.5	15.1	14.5
DE	19.4	18.0	16.4*	13.8	15.5	15.8	16.1	13.8
DMF	19.3	19.3	14.5–17.7*	16.7*	19.0	19.1	13.0–16.7*	17.7*
DMSO	19.0	18.8	18.8	15.0*	18.8	18.8	18.4	17.3*
EtOH	17.4*	17.5	17.8	14.0	17.0	17.2	17,0	14.0
H_2O	9.8*	19.2*	21.0*	13.8*	>20	19.4	18.8	14.5
PY	19.6	19.9	18.5*	14.7	19.6	19.6	19.4	14.7
MF	12.8–17.7*	17.0*	12.6–17.0*	13.0*	>20	17.4	17.3	15.5*

* Denotes an interstratified system.

It should be noted that there are varying amounts of water remaining on the smectite, depending upon the cation present and the temperature of dehydration. Van Olphen and Deeds (1962) reported the effects of mixed PY–H_2O systems upon Na–smectite swelling. Thermogravimetric analyses show that at 110°C the clay contains on the average 6–8 water molecules per Cu(II) ion, 3–4 molecules per Ca(II) ion and about 1 molecule per Na(I) ion based upon 225°C heated clay. If water were propping the interlayers open, the effect of this remaining coordinated water would be to facilitate entry of solvent molecules into the interlayer space which induces swelling. However, as shown in Table 3, the initial water content has little effect upon the amount of swelling. These homoionic clays were thermally dehydrated and then placed into three solvents. For each solvent and a given cation, the basal spacing remains almost constant regardless of the degree of dehydration before treatment, which indicates that the added solvent determines the interlayer spacing.

Exchange cation positions

Even though the clays are swollen in each solvent, cations do not necessarily move to positions midway between the clay sheets. This effect was observed by recording the esr spectra of the structural iron in Upton montmorillonite after the same treatment as in Table 3. McBride *et al.* (1975), by using powder samples, have shown that the intensity of the high field Fe resonance ($g = 3.6$), increases as the distance between the exchange cation and the Fe(III) associated with Mg(II) in the octahedral layer increases.

When observed in oriented thin films, this high field Fe(III) resonance at $g = 3.6$, is strongly anisotropic as is shown by a Ca(II) montmorillonite solvated in
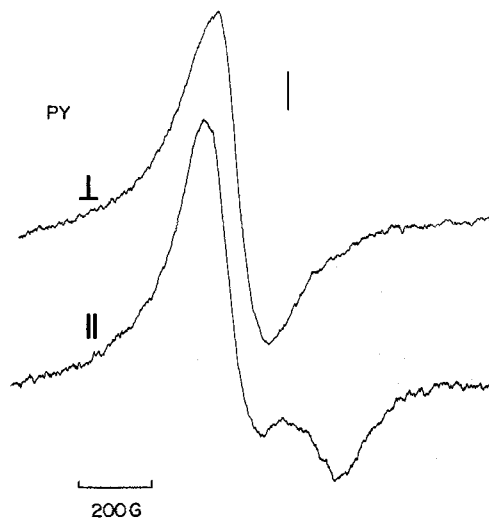

Fig. 1. Orientation dependence in esr spectra of structural Fe(III) in a film of Ca(II) smectite solvated with pyridine. The vertical bar indicates $g = 3.88$.

PY in Fig. 1. This anisotropy suggests that the $g = 3.6$ resonance originates from Fe(III) whose magnetic axes lie in different planes than those of the Fe(III) which gives the strong $g = 4.2$ resonance. Absence of the $g = 3.6$ resonance in the fully reduced charge smectite suggests this site becomes magnetically similar to the $g = 4.2$ site upon entry of Li into the octahedral layer. Since the $g = 3.6$ signal intensity is maximized when the clay sheets are parallel to the magnetic field, this orientation was used throughout the study. When decreases in intensity of the $g = 3.6$ resonances are observed, the exchange cations are thought to approach the smectite surface. Figure 2 illustrates this effect for Na(I) full charge smectite. Before adding the solvents and after heating, the ions approach the smectite surface more closely as the degree of dehydration increases resulting in a corresponding decrease in intensities of the high field Fe(III) resonances. At 225°C the Na(I) ions reside in hexagonal holes as the basal spacing is only 9·8 Å. Swelling by solvents of differing Gutmann donor numbers causes a regain of this high field Fe(III) resonance to various degrees depending upon initial water content and the solvent. For DCE the high field Fe(III) resonance intensity decreases as dehydration increases and almost disappears at 110°C [225°C in the case of Ca(II)]. The important point here is that after solvent treatment, the cation position varies with initial water content even though the clay is swollen to equivalent spacings as previously suggested by Barshad (1952). From the difference in signal intensity, it appears that NIB keeps the cations at a greater distance from the clay surface on the average than does DCE since it coordinates a given cation somewhat more strongly than DCE. In PY the high field Fe(III) resonance intensity is even greater, probably due to the combined effects of increased cation solvation and the higher basal spacing.

Table 3. Basal spacings (Å) of full charge Upton montmorillonite in selected solvents after heat treatments

Exchange cation	Solvent added	Heat treatment				
		25°C	110°C	140°C	180°C	225°C
Na(I)	H_2O^Δ	12.3	9.8	--	--	9.8
	DCE	13.0*	12.6–13.0*	--	12.6	12.6*
	NIB	15.0	15.0	15.0	15.0	15.0
	PY	19.6	19.6	19.6	19.6	19.6
Ca(II)	H_2O^Δ	15.2	--	--	--	9.5[†]
	DCE	15.0	14.7	14.7	14.7	14.7
	NIB	15.0	15.0	15.0	15.0	15.0
	PY	20.3	19.6	19.6	19.6	19.6
Cu(II)	H_2O^Δ	12.4	12.0	--	--	--
	DCE	13.2	13.0	13.0	13.0	--
	NIB	15.0	14.7	14.7	14.7	--
	PY	19.4	19.4	19.4	18.6*	--

* Denotes interstratified system.

† Taken from Norrish (1954).

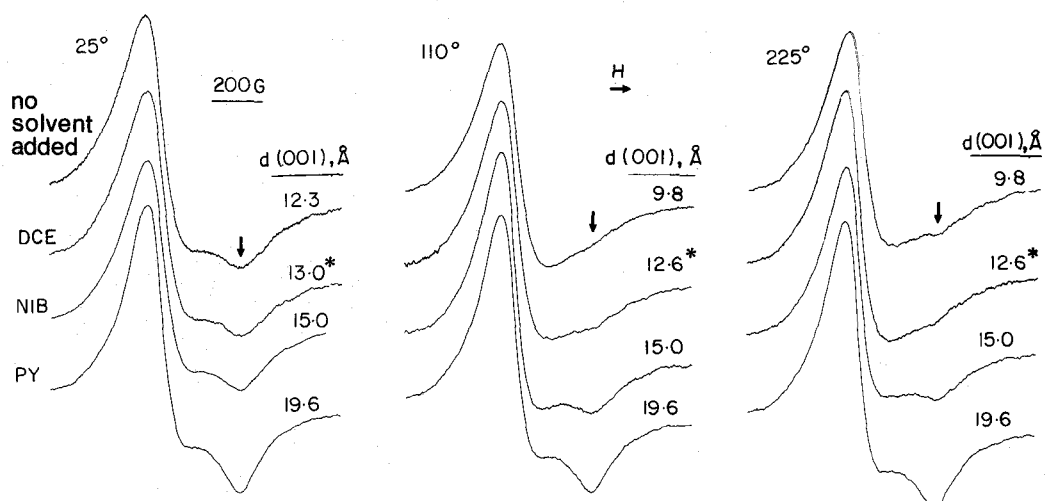Δ Adsorbed from atmosphere after heat treatment.

Fig. 2. Esr spectra of structural iron in oriented films of Na(I) smectite after heat treatment and solvation. The downward arrow indicates $g = 3.6$.

These results qualitatively agree with those of Shainberg and Kemper (1966) who showed that the fraction of relatively immobile ions residing at the clay surface in pastes increased in the series $H_2O <$ methanol $<$ ethanol. In the case of Cu(II) smectite, the minimum temperature of dehydration at which the high field Fe(III) resonance disappears is $\sim 140°C$ for both DCE and NIB whereas for Ca(II) smectite in NIB, the high field resonance Fe signal remains even after the 225°C heat treatment and resolution.

The degree to which the ion is removed from the smectite surface (or hexagonal hole) appears to be related to the Gutmann Donor Number of the solvent and the nature of the exchangeable cation. Figure 3 shows that for Na(I) smectite dehydrated at 110°C and resolvated with the indicated solvents, a Gutmann Donor Number of about 14 is required for complete solvation of Na(I) which results in its removal from the surface. Above this value, the sodium ions appear to be fully solvated as indicated by the high field Fe(III) resonance intensities. However, the same experiment (i.e. dehydration at 110°C) conducted with Ca(II) and Cu(II) saturated montmorillonite indicates that these divalent ions retain some coordination water which keeps the ion away from the surface, since the high field Fe(III) resonance was clearly visible even in DCE and NIB and supported by i.r. spectra indicating the presence of water. Since exchange of a low donor number solvent molecule (DCE or NIB) for a coordinated water molecule on the cation is unlikely, the size of the cation–water complex precludes penetration of the ion into the hexagonal hole in the silicate surface in contrast with the case of unsolvated Na(I) ion. Consequently, the Fe(III) in the $g = 3.6$ site is not perturbed by Ca(II)– and Cu(II)–water complexes as much as by dehydrated Na(I).
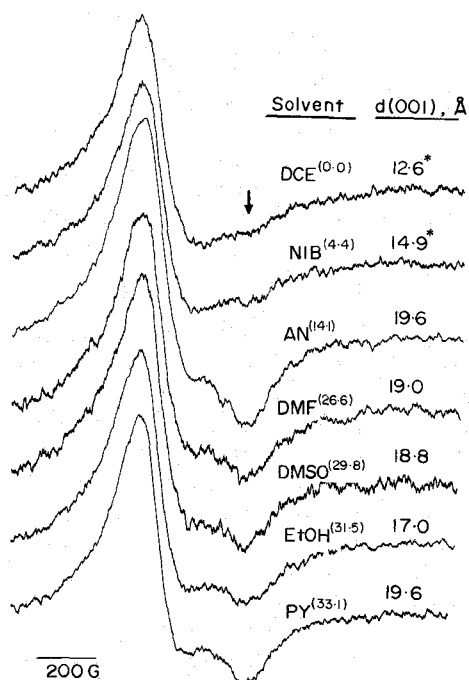

Fig. 3. Esr spectra of structural iron in oriented films of Na(I) smectite swollen by various solvents. Numbers in parentheses are Gutmann Donor Numbers, while the other numbers are the (001) spacings. The downward arrow indicates $g = 3.6$. Asterisks denote interstratified systems.

Table 4. Electron spin resonance data for Cu(II) in smectite treated with various solvents*

Exchange ion	Added solvent	$g_\parallel$	$g_\perp$	g_{iso}	$A_\parallel$, cm^{-1}
Cu(II)	DCE	2.30	2.10	--	0.0132
	NIB	--	--	2.14	--
	AN	2.27	2.07	--	0.0140
	DMF	2.29	2.09	--	0.0142
	DMSO	--	--	2.14	--
	EtOH	--	--	2.16	--
	PY	2.24	2.06	--	0.0139
Ca(II)·Cu(II) (9:1 mole ratio)	DCE	No observable spectrum			
	NIB	No observable spectrum			
	AN	2.27	2.06	--	0.0140
	DMF	--	--	2.11	--
	DMSO	--	--	2.11	--
	EtOH	--	--	2.11	--
	PY	2.24	2.05	--	0.0154

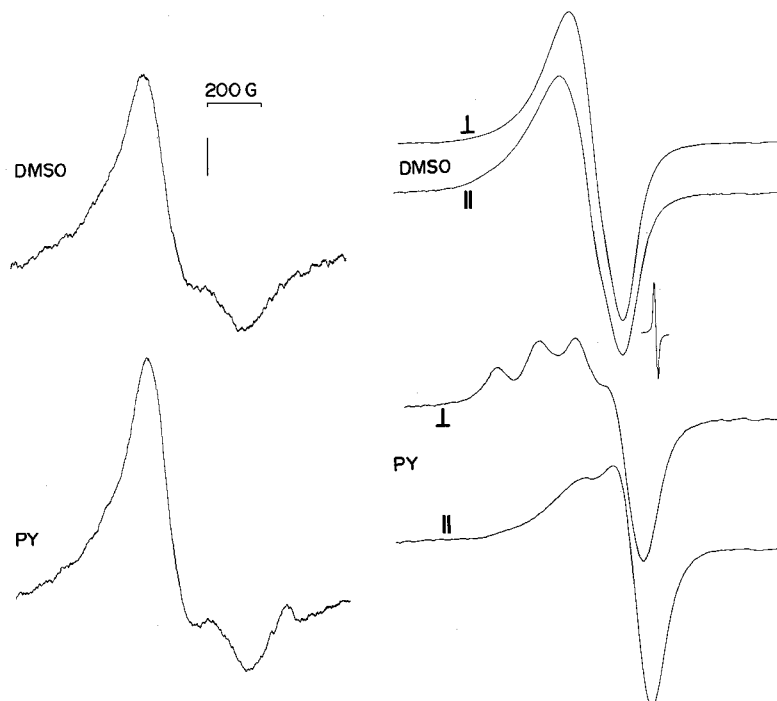* Smectite was heated at 110°C before solvents were added.

Fig. 4. Esr spectra of structural iron (left) and exchangeable Cu(II) (right) in oriented films of Cu(II) smectite solvated in DMSO and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g = 3.88$; the free electron signal indicates $g = 2.0028$.

Stereochemistry of Cu(II)–solvent complexes

Results from esr spectra of Cu(II) smectite in the solvents shown in Table 4 and X-ray diffractograms indicate that the stereochemistry of the Cu(II)–solvent complexes depends largely upon the nature of the interlayer solvent. The esr data in Table 4 illustrate the variation in types of spectra obtained. Spectra from Cu(II) saturated montmorillonite heated to 110°C and solvated with DMSO and PY are shown in Fig. 4 as examples of the shapes of Cu(II) spectra obtained. Spectra of the high field Fe(III) resonance accompany the Cu(II) spectra to illustrate the positions of the Cu(II) ions and the basal spacings are given in Table 2. As mentioned previously, these high field Fe(III) resonances indicate that the Cu(II) ions are solvated and are located away from the surface.

Spectra similar to that for DMSO were also obtained for EtOH, and together with the basal spacings, the spectra indicate that the Cu(II)–solvent complexes are rapidly tumbling in the interlayer either by rotation of the Cu(II)–solvent complex or by rapid Jahn–Teller dynamics which averages the anisotropic components of the g-tensor to give g_{iso} near 2.15. Similar isotropic spectra were previously observed in fully water solvated Cu(II) smectites (Clementz et al., 1973). In the case of PY, the esr spectra showed the presence of tetragonally distorted octahedral complexes of Cu(II) as indicated by the orientation dependence of the $g_\perp$ and $g_\parallel$ components of the g-tensor. Similar spectra were obtained for AN. The lower values for $g_\parallel$ in PY and AN probably indicate the

increased covalent nature of the Cu–nitrogen bond over the Cu–oxygen bond in those solvents with oxygen donor atoms (Kivelson and Neiman, 1961). The basal spacing of these two systems would allow space for four PY or AN molecules in equatorial positions and two water molecules in axial positions in each complex with the H_2O–Cu–H_2O axis oriented perpendicular to the silicate sheets. These observations do not preclude the existance of a Cu(II) complex in which some of the PY in equatorial positions is linked to the Cu(II) ion through water molecules as suggested by Farmer and Mortland (1966).

The spectra of the DMF system indicate a mixture of tetragonally distorted octahedral complexes whose z-axes are not perpendicular to the clay sheets and square planar complexes which lie parallel to the smectite sheets. Clementz et al. (1973) noted similarly oriented octahedral complexes in hydrated Cu(II)–vermiculite in which both $g_\parallel$ and $g_\perp$ components of the g-tensor were resolved when the clay sheets were oriented either perpendicular or parallel to the magnetic field. This interpretation is consistent with the 13·0–16·7Å basal spacing when the presence of mixed Cu(II)–H_2O–DMF is taken into account in which distorted octahedral complexes occupy the more swollen interlayers and the square planar complexes occupy less expanded interlayers.

Esr spectra of Ca(II)–montmorillonite doped with 10 mole % Cu(II), heated to 110°C and treated with solvents were recorded for both Cu(II) and the high field Fe(III) resonance which are exemplified by spectra shown in Fig. 5. The high field Fe(III) resonances
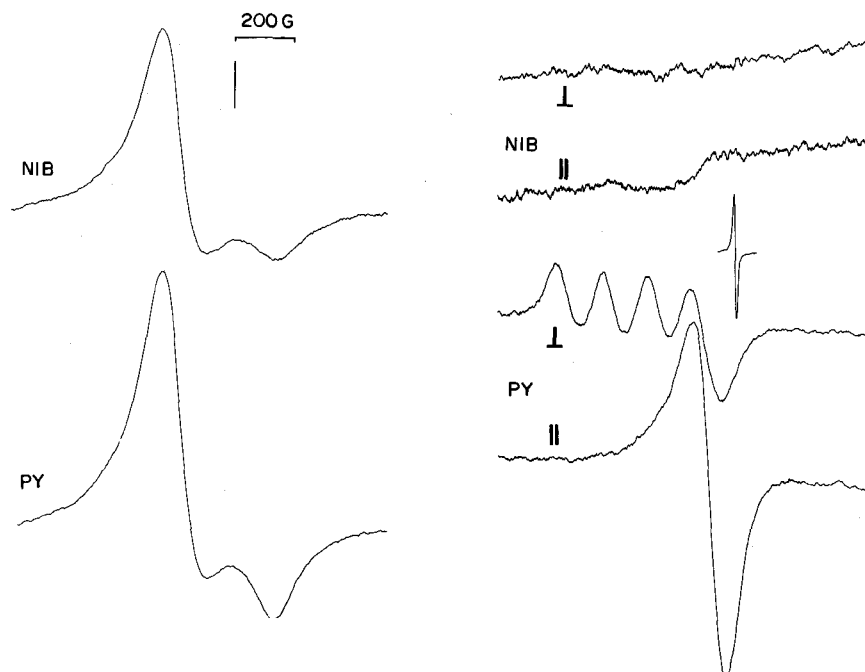
Fig. 5. Esr spectra of structural iron and exchangeable Cu(II) in oriented films of Cu(II)-doped Ca(II) smectite solvated in NIB and PY. Cu(II) spectra are shown for two orientations of the films with respect to the magnetic field. The vertical bar indicates $g = 3.88$; the free electron signal indicates $g = 2.0028$.

indicate that in all cases most, if not all, of the inter-layer ions are away from the surface of the silicate. Spectra of Cu(II) in this doped smectite solvated with AN, DMSO, EtOH, and PY were similar to the corresponding Cu(II) spectra in the fully Cu(II) saturated smectite as Table 4 indicates. The spectrum of Cu(II) in the doped smectite solvated with DMF was isotropic in shape which indicated averaging of the $g_{\parallel}$ and $g_{\perp}$ components. This spectrum was not orientation dependent as was that of the fully saturated Cu(II)–smectite solvated in DMF, probably because of the higher basal spacing in the doped smectite (19.1 Å vs 16.7 Å interstratified in the Cu(II)–smectite).

With DCE and NIB as the added solvents, spectra of Cu(II) in fully saturated Cu(II)–smectite and Cu(II)–doped Ca(II)–smectite dehydrated at 110°C before solvent treatments, reveal differences in the rigidities of Cu(II)–solvent complexes in the interlayer space. The spectra of Cu(II) in fully saturated Cu(II)–smectite solvated with DCE are similar to those in Fig. 4 for PY, thus indicating that the Cu(II)–solvent complex in DCE is tetragonally distorted with its z-axis perpendicular to the clay sheets. These observations are consistent with the basal spacing of 13·2 Å in which there is a square planar complex of hydrated Cu(II) ions. In NIB, the fully saturated Cu(II)–smectite swells to 14.7 Å which allows the Cu(II)–H_2O complex to tumble in the interlayer. This greater degree of tumbling averages the $g_{\perp}$ and $g_{\parallel}$ components of the g-tensor to give an isotropic spectrum similar to that in Fig. 4 for DMSO.

In the case of the Cu(II)–doped–Ca(II)–smectite, dehydrated at 110°C and treated with DCE and NIB, no Cu(II) spectrum is observed. Since the spectra reappear at 77°K, rapid spin relaxation mechanisms are apparently operating which broaden the Cu(II) signal beyond recognition at room temperature. Since the Cu(II) is hydrated even in the presence of excess NIB or DCE because of the low Gutmann donor number of DCE and NIB, the Cu(II)–water complex could be spinning rapidly in the solvent and relaxed through anisotropic g-tensor and spin-rotational relaxation mechanisms (Wilson and Kivelson, 1966; Atkins and Kivelson, 1966). The differences between the spectra of Cu(II) in the fully Cu(II) saturated clay and the Cu(II)–doped–Ca(II) clay (both solvated by DCE and NIB) may be explained on the basis of different dehydration levels of the two clays. The lack of an observable Cu(II) spectrum in the Cu(II)–doped–smectite indicates that water associated with a given Cu(II) ion in the Cu(II)–doped–Ca(II) interlayer (where there are 3–4 water molecules per ion) apparently interacts less with another cation–water complex than does a given Cu(II)–water complex in the fully Cu(II) saturated clay (where there are 6–8 water molecules per ion). Since this interionic–complex interaction may be less in the Cu(II)–doped clay, the complex is freer to tumble or rotate, and the electron spin is thus relaxed to a greater degree. Water structure is apparently better developed in the fully Cu(II) saturated clay; hence, the complexes are more rigid and unable to cause extreme broadening of the esr signal. Similar observations were made in other

Cu(II)–doped smectites (McBride *et al.*, 1975 to be published).

CONCLUSIONS

(1) Little relationship is found between the crystalline swelling of smectite and various *bulk* properties of the interlayer solvent. These properties include dielectric constant, dipole moment, surface tension, and Gutmann donor number.

(2) Crystalline swelling is not necessarily accompanied by cation movement to positions midway between the silicate sheets. The removal of Na(I) ions from hexagonal holes in the silicate surface requires a solvent with a Gutmann donor number of about 14 or greater.

(3) No relationship between crystalline swelling and charge density is found except in the case of water as the solvent. Anomalous behavior occurred in the reduced charge Na(I) saturated smectite systems in that water was the only solvent in which the smectite did not swell.

(4) Esr data indicate considerable variety in the stereochemistry of Cu(II) ions in the interlayers in concurrence with Olejnik, Posner and Quirk (1974). Factors influencing this stereochemistry include: (a) the nature of the added solvent, (b) the initial water content of the interlayer and its strength of interaction with the added solvent, (c) the basal spacing. Where complex formation is non-homogenous, mixed spectra are obtained. The results from X-ray diffraction and esr spectroscopy reported here illustrate the complexity of smectite swelling.

REFERENCES

Atkins, P. W. and Kivelson, D. (1966) Esr linewidths in solution—II. Analysis of spin-rotational relaxation data: *J. Chem. Phys.* **44**, 169–174.

Barshad, I. (1952) Factors affecting the interlayer expansion of vermiculite and montmorillonite with organic substances: *Soil Sci. Soc. Am. Proc.* **16**, 176–182.
Brindley, G. W. and Ertem, G. (1971) Preparation and solvation properties of some variable charge montmorillonites: *Clays and Clay Minerals* **19**, 399–404.
Clementz, D. M., Mortland, M. M. and Pinnavaia, T. J. (1974) Properties of reduced charge montmorillonites: Hydrated Cu(II) ions as a spectroscopic probe: *Clays and Clay Minerals* **22**, 49–57.
Clementz, D. M., Pinnavaia, T. J. and Mortland, M. M. (1973) Stereochemistry of hydrated copper (II) ions on the interlamellar surfaces of layer silicates. An electron spin resonance study: *J. Phys. Chem.* **77**, 196–200.
Ehrlich, R. H., Roach, E. and Popov, A. I. (1970) Solvation studies of sodium and lithium ions by sodium-23 and lithium-7 nuclear magnetic resonance: *J. Am. Chem. Soc.* **92**, 4989–4990.
Farmer, V. C. and Mortland, M. M. (1966) An i.r. study of the coordination of pyridine and water to exchangeable cations in montmorillonite and saponite: *J. Chem. Soc.* (A) 344–351.
Gutmann, V. (1968) *Coordination Chemistry in Non-Aqueous Solvents*, p. 19. Springer, Berlin.
Kivelson, D. and Nieman, R. (1961) ESR studies on the bonding in copper complexes: *J. Chem. Phys.* **35**, 149–155.
McBride, M. B., Pinnavaia, T. J. and Mortland, M. M. (1975) Perturbation of structural Fe^{3+} in smectites by exchange ions: *Clays and Clay Minerals* **23**, 103–107.
Norrish, K. (1954) The swelling of montmorillonite: *Trans. Farad. Soc. Lond.* **18**, 120–134.
Olejnik, S., Posner, A. M. and Quirk, J. P. (1974) Swelling of montmorillonite in polar organic liquids: *Clays and Clay Minerals* **22**, 361–365.
Shainberg, I. and Kemper, W. D. (1966) Conductance of adsorbed alkali cations in aqueous and alcoholic bentonite pastes: *Soil Sci. Soc. Am. Proc.* **30**, 700–706.
van Olphen, H. and Deeds, C. T. (1962) Stepwise hydration of clay–organic complexes: *Nature, Lond.* **194**, 176–177.
Walker, G. F. (1961) Vermiculite minerals: In *The X-ray Identification and Crystal structures of Clay Minerals*, (Edited by Brown, G.) Mineralogical Society, London, pp. 297–324.
Wilson, R. and Kivelson, D. (1966) Esr linewidths in solution—I. Experiments on anisotropic and spin-rotational effects: *J. Chem. Phys.* **44**, 154–168.