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MOBILITY AND REACTIONS OF VO^{2+} ON HYDRATED SMECTITE SURFACES[1]

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Abstract—The electron spin resonance (ESR) spectra of varying quantities of vanadyl ion (VO^{2+}) adsorbed on hydrated hectorite indicated that hydrolysis of VO^{2+} was promoted at low levels of adsorption. The hydrolyzed product was adsorbed on the clay surfaces, with a ligand environment that was partially aqueous and partially hydroxide in nature. Greater amounts of VO^{2+} adsorbed on wetted hectorite obscured the ESR spectrum of the strongly adsorbed hydrolysis product with a solutionlike spectrum. An approximately 50% reduction in rotational mobility of VO^{2+} relative to solution was indicated by the linewidth of this spectrum. Loss in mobility occurred with reduction of the interlamellar spacing until, under strongly dehydrating conditions, the $VO(H_2O)_5^{2+}$ ions became aligned with the $V{=}O$ bond axis normal to the plane of the clay platelets.

Key Words—Adsorption, ESR, Smectite, Vanadium.

INTRODUCTION

The measurement of mobility of adsorbed metal cations on hydrated clay surfaces is of interest for several reasons. Chemical reactivity and availability for catalysis may be related to translational and rotational freedom of adsorbed metals. In addition, information regarding the nature of the surface-adsorbed water may be obtained from the motion of exchange cations. Evidence for the mechanisms by which metals are retained in exchangeable (or nonexchangeable) form may also be derived from the degree of surface mobility. Recent investigations of organic cation rotation at clay surfaces by electron spin resonance (ESR) spectroscopy (McBride, 1976a; McBride, 1977) have demonstrated that motion-dependent ESR spectra of adsorbed paramagnetic cations can provide useful information about adsorption processes. Spectra of the vanadyl ion, VO^{2+}, are particularly well suited to estimation of rates of rotational motion because of the strong dependence of spectral lineshape upon rotational correlation time, τ_R, where τ_R represents the time required for VO^{2+} to reorient in solution by random thermal tumbling. Thus, measured ESR spectral parameters of VO^{2+} in solutions can be functionally related to macroscopic viscosity of these solutions (Chasteen and Hanna, 1972). The purpose of the present study is to describe the motion of VO^{2+} adsorbed on a smectite under different experimental conditions in order to evaluate the factors which influence metal ion retention and mobility at aluminosilicate surfaces.

MATERIALS AND METHODS

The smectite used in the study was a hectorite obtained from the Baroid Division of NL Industries, with a CEC of 71 meq/100 g as determined by the Ba^{2+} conductometric titration method (Mortland and Mellor, 1954). Although the hectorite has a very low Fe content, iron oxides were removed from a portion of the clay by the standard citrate-dithionite extraction procedure in order to evaluate the possible influence of Fe impurities on the ESR spectra. The hectorites were then washed repeatedly with $MgCl_2$–$VOSO_4$ solutions having different mole ratios in order to produce VO^{2+}/Mg^{2+} hectorites with approximately 5, 20, 30, and 50% VO^{2+} on exchange sites. Initial experiments showed that 100% VO^{2+} hectorites had VO^{2+} ESR spectra considerably broadened by dipolar interaction. Excess VO^{2+} was removed from the clays by repeated washing with 10^{-3} M HCl. The acid was expected to minimize hydrolysis of VO^{2+} upon washing; however, water washing was used in a few instances as it caused no apparent change in the results as indicated by the ESR spectra. The VO^{2+}/Mg^{2+} hectorite suspensions prepared in this way were then dried on polyethylene sheets or on a flat quartz ESR tissue cell to form well-oriented clay films.

ESR spectra of the hectorite were obtained on a Varian E-104 spectrometer with the clay films oriented on a flat tissue cell or in quartz tubes either perpendicular ($\perp$) or parallel ($\parallel$) to the magnetic field of the spectrometer.

Long equilibration times required the exclusion of O_2 from the Mg^{2+}/VO^{2+} hectorites in order to prevent oxidation of VO^{2+}, which was indicated by conversion of the clay to a bright yellow color. This color conversion has been observed by other investigators upon exposure of VO^{2+}-hectorite to atmospheric moisture (Pinnavaia et al., 1974), and is probably an indication of the formation of VO_2^+ or an hydrolysis product of VO_2^+. The ESR spectrum of VO^{2+} became much weaker after several days exposure of the clay to air. The conversion of vanadium from the +4 to +5 oxidation state was prevented by exclusion of O_2, with 100% relative humidity maintained at the clay film with flowing N_2 gas bubbled through water.

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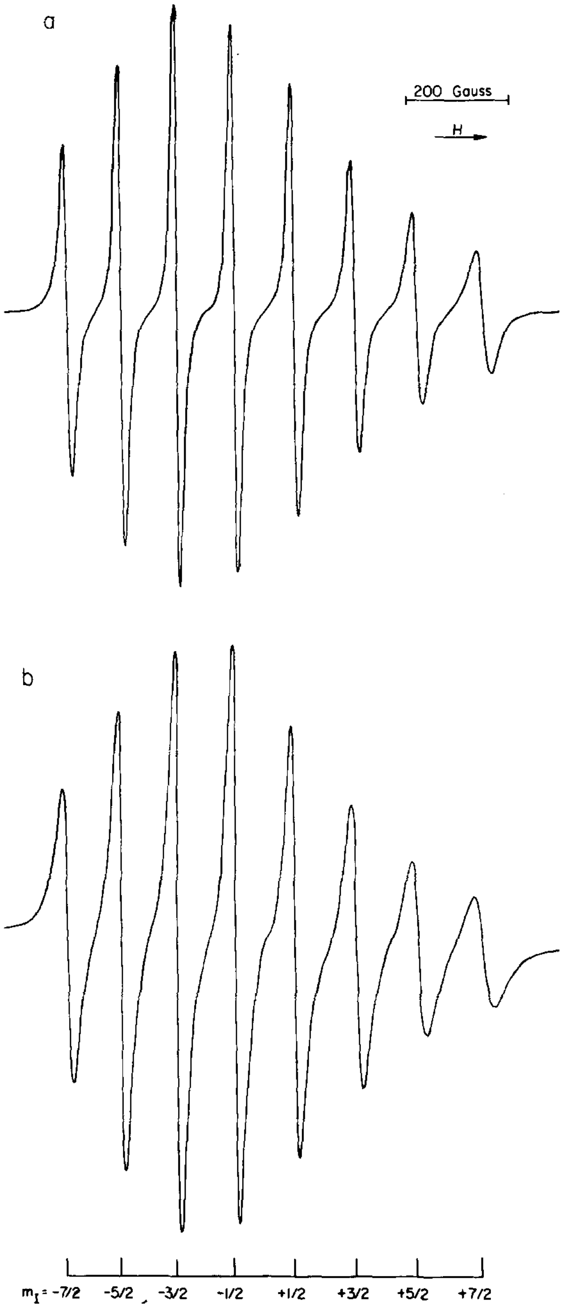

Figure 1. ESR spectra of VO^{2+} at ambient temperature (a) in aqueous solution (2×10^{-2} M $VOSO_4$, pH = 1.5), (b) adsorbed on a fully wetted Mg^{2+}-hectorite film (50% mole ratio of VO^{2+}).

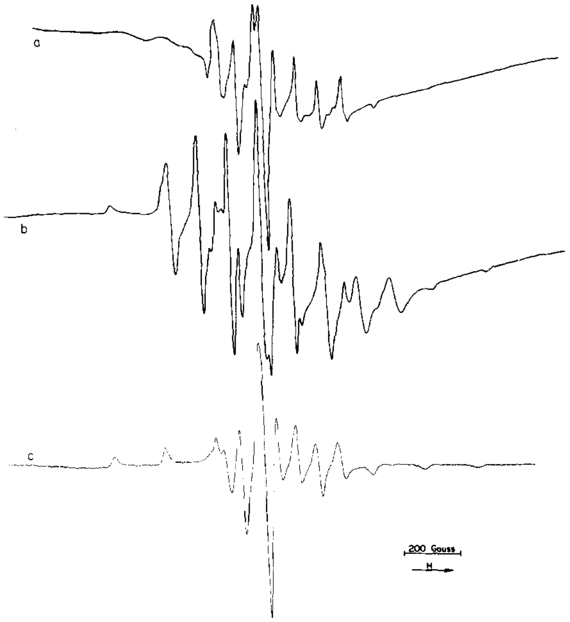

Figure 2. ESR spectra of VO^{2+} at ambient temperature (a) adsorbed on fully wetted Mg^{2+}-hectorite films (∥ orientation) at the ~5% level of exchange (b) adsorbed on fully wetted Mg^{2+}-hectorite films (∥ orientation) at the ≈20% level, (c) coprecipitated in alumina gel (undried) at the 1% level.

RESULTS AND DISCUSSION

The ESR spectrum of vanadium in oxidation state +4 results from a single unpaired electron in the 3d orbital. The ^{51}V nucleus has a nuclear spin (I) of 7/2, so that eight hyperfine lines appear in the aqueous solution spectrum of VO^{2+} (Figure 1a). At the 50% level (approximately) on exchange sites, the spectrum of VO^{2+} on fully wetted hectorite (Figure 1b) is very similar to that in solution. However, at low levels of adsorption (5%), the weak ESR signal observed is indicative of the rigid-limit VO^{2+} spectrum (Figure 2a), probably a result of hydrolysis to $VO(OH)_2 \cdot xH_2O$, which has a solubility product near 10^{-22} (Baes and Mesmer, 1976). The surfaces of smectites are known to promote hydrolysis of metals such as Cu^{2+} (Farrah and Pickering, 1976) and Al^{3+} (Turner and Brydon, 1965; Bloom et al., 1977), apparently by the preferential adsorption of hydrolysis products. Since VO^{2+} forms a less soluble hydroxide than Cu^{2+} (Baes and Mesmer, 1976), the formation of $VO(OH)_2$ in the presence of the clay is expected. The appearance of a grey color in the hectorite suspensions immediately after addition of VO^{2+}, and the grey-brown color of the VO^{2+}/Mg^{2+} hectorite films after drying may be evidence of this hydrolysis product of VO^{2+}. It is likely that the tan-colored form of VO^{2+}-hectorite observed by Pinnavaia et al. (1974) upon air-drying or freeze-drying is also a result of hydrolysis. The ESR spectrum (Figure 2a) supports this interpretation, being very similar to that of immobilized VO^{2+} that has been coprecipitated at a low doping level in $Al(OH)_3$ (Figure 2c). Changing the clay film orientation from ⊥ to ∥ in the magnetic field had little effect on the observed rigid-limit spectrum. These results suggest that initially added VO^{2+} is mainly hydrolyzed and adsorbed on clay mineral surfaces in much the same way that initially adsorbed Al^{3+} on smectite may essentially all form

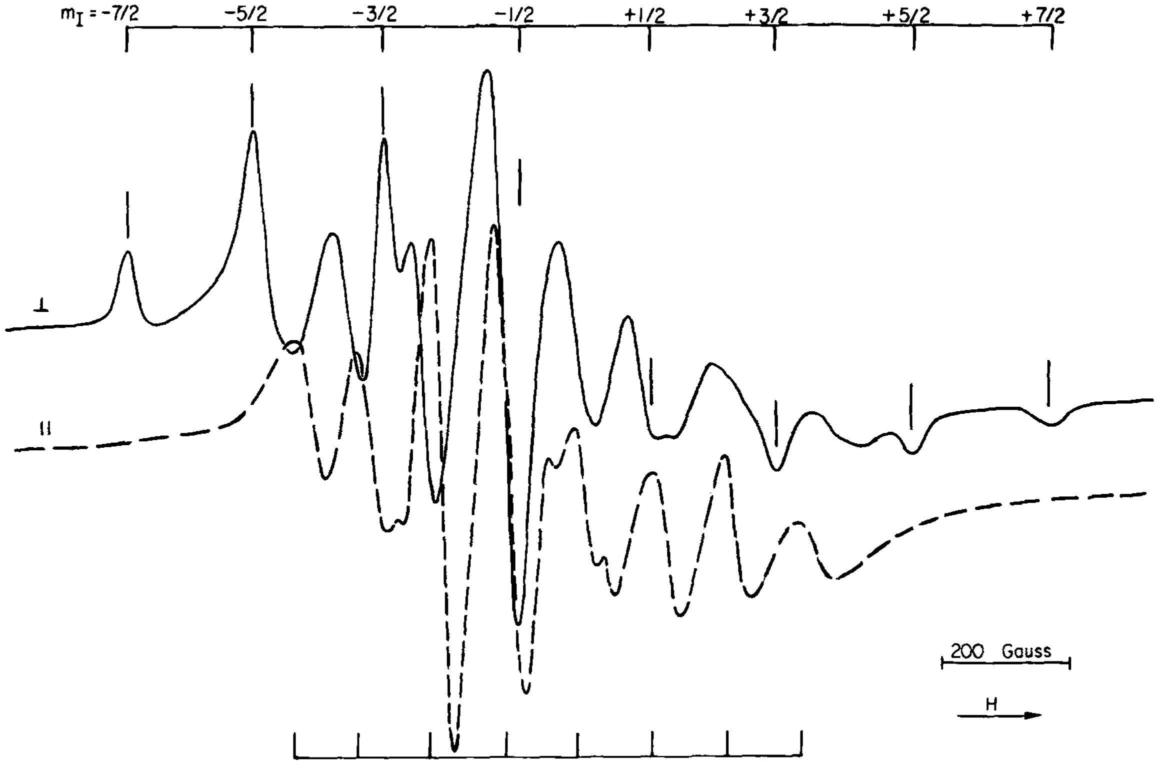

Figure 3. ESR spectra of an air-dry VO^{2+}-saturated hectorite film oriented perpendicular (⊥) and parallel (∥) to H. The hyperfine resonance positions for the ⊥ and ∥ orientations are indicated by the eight markers at the top and bottom of the figure, respectively.

$Al(OH)_3$ because of the higher pH at low Al^{3+} concentrations (Bloom et al., 1977). Thus, the lower pH values maintained by the clays with greater VO^{2+} content may inhibit further hydrolysis of VO^{2+}, thereby allowing the spectrum of hydrated VO^{2+} to dominate, as shown by the increase in the eight line solution spectrum relative to the rigid-limit spectrum on hectorite with 20% VO^{2+} (Figure 2b). When the VO^{2+} occupation of exchange sites reaches 30%, little evidence of the rigid-limit spectrum remains, and it is totally absent (or obscured) at 50% saturation (Figure 1b).

Table 1. ESR linewidths of the $M_I = +7/2$ resonance of VO^{2+} adsorbed on hectorite[1] and in solution.

Sample	Linewidth (gauss)
Aqueous $VOSO_4$ (10^{-3} M, acidified)	23
Fully wetted VO^{2+}/Mg^{2+} hectorite	43
Fully wetted VO^{2+}/Mg^{2+} hectorite with Fe removed	35
VO^{2+}/Mg^{2+} hectorite equilibrated at 100% R.H. (5 hr)	51
VO^{2+}/Mg^{2+} hectorite equilibrated at 100% R.H. (24 hr)	49

[1] Hectorites were 50% saturated with VO^{2+}, washed free of excess VO^{2+} with water.

The ESR spectra indicate *adsorption* rather than *precipitation* of $VO(OH)_2$, since spin-spin interaction of vanadium ions in a precipitate would have produced a very broad nondistinctive spectrum. The lack of orientation-dependence of the rigid-limit spectrum does not eliminate the possibility of alignment of $VO(OH)_2$ on clay surfaces, since an octahedral $VO(OH)_2(H_2O)_3$ species may align with the V=O bond axis at a 45° angle to the plane of the clay particle. This orientation would allow maximized hydrogen bonding between the hydrolyzed species and surface oxygens. The hyperfine splitting constants for the spectrum of the rigid-limit VO^{2+} (Figure 2a) are $A_\parallel = 194$ G and $A_\perp = 71$ G. A comparison with the constants for immobilized VO $(H_2O)_5{}^{2+}$ on hydrated hectorite at liquid N_2 temperature ($A_\parallel = 204$ G, $A_\perp = 81$ G) and coprecipitated $VO(OH)_2$ in $Al(OH)_3$ ($A_\parallel = 187$ G, $A_\perp = 67$ G) indicates that the ligand field of vanadium adsorbed at low levels is intermediate between the H_2O and OH^- ligand fields, supporting the hypothesis that a species such as $VO(OH)_2(H_2O)_3$ was nucleated on the clay mineral surface.

The aid-dired VO^{2+}/Mg^{2+} hectorite has an orientation-dependent ESR spectrum with a smaller hyperfine splitting when the clay platelets are aligned parallel to the magnetic field, H, than when they are perpendicular to H (Figure 3). At liquid N_2 temperature, a rigid-limit

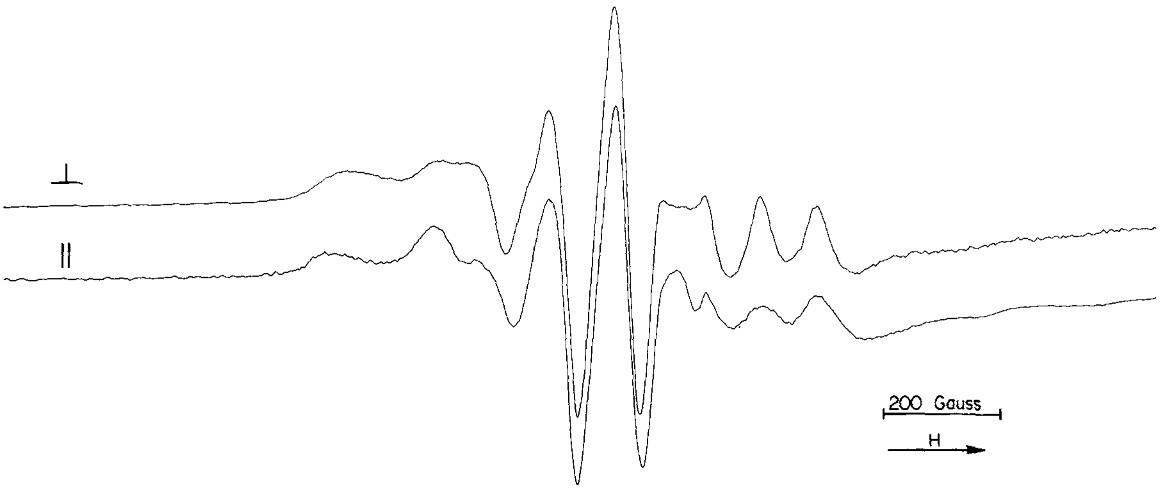

Figure 4. ESR spectra of a Mg^{2+}-hectorite film ≈50% saturated with VO^{2+}, solvated in excess methanol and oriented ⊥ and ∥ to H.

spectrum of VO^{2+} on hectorite is obtained (not shown) with an even more strongly orientation-dependent hyperfine splitting ($A_{\parallel} \approx 204$ G, $A_{\perp} = 81$ G). Evidently, $VO(H_2O)_5^{2+}$ is capable of very limited motion in the interlayers of dry hectorite at room temperature, producing partial averaging of the anisotropic hyperfine splitting. However, the lowered temperature quenches this motion because of reduced thermal energy or further collapse of the clay platelets. At temperatures below 0°C, water is withdrawn from interlayer positions to freeze externally (McBride, 1976a), thereby lowering the spacing between clay platelets and increasing the order of hydrated exchange cations. Since the anisotropy of hyperfine splitting, $|A_{\parallel} - A_{\perp}|$ (where $A_{\parallel}$ and $A_{\perp}$ are the hyperfine splitting constants for the ∥ and ⊥ clay orientations expressed in s^{-1}), is in the range of 10^9 s^{-1}, slow motional spectra of VO^{2+} appear when the tumbling frequency is too slow to average the anisotropy; that is, when τ_R is 10^{-9} s or longer (Campbell and Hanna, 1976). Since anisotropy has not been averaged for the air-dry clay at room temperature, but motion has not been fully quenched, the spectral lineshape indicates that τ_R is probably on the order of 10^{-8} s.

The solutionlike eight-line orientation-independent spectrum of VO^{2+}/Mg^{2+} hectorite films in excess water or an atmosphere at 100% relative humidity demonstrates that motional tumbling of adsorbed $VO(H_2O)_5^{2+}$ is rapid enough to average the anisotropy of hyperfine splittings (Figure 1b). The isotropic hyperfine splitting constant, A_0, for adsorbed $VO(H_2O)_5^{2+}$ was 114.5 G, compared to 115.1 G for $VO(H_2O)_5^{2+}$ in aqueous solution. However, broadening of the spectrum of adsorbed VO^{2+} occurs, as shown by the peak to peak linewidths of the $M_I = +7/2$ lines of a number of spectra (Table 1). Since line broadening can result from a number of phenomena, it was necessary to test the relative importance of each of these. Preliminary work demonstrated that the 50% VO^{2+} clays were not significantly broadened by dipolar interactions between surface-adsorbed VO^{2+} ions. However, a small quantity of adsorbed iron oxides may have broadened the spectra, since the preliminary removal of Fe by citrate-dithionite treatment reduced the linewidth (Table 1). The most pronounced influence on linewidth resulted from variation of the water content of the hectorite. Thus hectorites equilibrated over free water had considerably broader spectra than those wetted in excess water (Table 1). This effect may be the result of somewhat different d-spacings of the clays under these different conditions. After attempts to eliminate possible mechanisms of broadening, the narrowest +7/2 linewidth obtained on fully wetted hectorite was 35 G. It is likely that most of this broadening results from motional restriction in an approximately 10 Å wide interlayer. Since the linewidth of VO^{2+} in dilute solution was 23 G, and since the +7/2 line width is essentially proportional to the rotational correlation time in the range of rapid motion as shown by the data of Chasteen and Hanna (1972), the value of τ_R for adsorbed VO^{2+} is approximately 1.5 times that for solution VO^{2+} at room temperature. The value of τ_R for solution VO^{2+} is about 5×10^{-11} s (Chasteen and Hanna, 1972) and therefore must be near $7.5 = 10^{-11}$ s for adsorbed VO^{2+} on fully wetted hectorite. In comparison, a similar increase in τ_R (30–50%) has been measured for VO^{2+} attached as a counter-ion to decyl sulfate micelles (Stilbs and Lindman, 1974). However, VO^{2+} bound to micelles having carboxylate groups had τ_R values more than 100 times longer than solution (Campbell and Hanna, 1976). Apparently, the VO^{2+} ion is restricted to about the same extent by electrostatic attraction to strong acid sulfate groups as by adsorption on hectorite, a result expected from the strong-acid nature of smectite surfaces. Attraction to weak acid groups (e.g., carboxylate) appears to be strong enough to strip away hydration water, producing an inner-sphere complex where the VO^{2+} is highly restricted. This immobilization occurs when VO^{2+} is adsorbed by soil organic matter (Lakatos et al., 1977; McBride, in press).

The line broadening results indicate that VO^{2+} (and other divalent exchange cations) has rotational mobility only slightly hindered by electrostatic attraction or steric effects, in agreement with the conclusions based on ESR spectra of exchangeable Mn^{2+} (McBride et al., 1975). Since the $VO(H_2O)_5{}^{2+}$ ion has an outer coordination sphere of roughly eight water molecules (Chasteen and Hanna, 1972), the effective diameter of the hydrated ion may be almost as large as the interlamellar space, and some restriction to rotational motion might be expected. The effect of steric restriction is shown by the spectra of VO^{2+}/Mg^{2+} hectorite wetted with methanol (Figure 4). The interlamellar spacing of the solvated clay is about 7 Å, and the spectra demonstrate greatly reduced rotational motion since the anisotropy of hyperfine splitting constants is not averaged (i.e., $\tau_R > 10^{-9}$ sec). However, the 7 Å interlayer does not produce pronounced orientation of VO^{2+}, as indicated by the relative lack of orientation-dependence of the spectra. Spacings on the order of the size of the $VO(H_2O)_5{}^{2+}$ ion are apparently required to impose orientation relative to the clay platelets, and this can be achieved by air-drying the clay.

The lack of restriction of surface-adsorbed divalent metal ions is also evident for kaolinite. Fully wetted kaolinite (CEC $\simeq$ 1.0 meq/100 g) that had been saturated with VO^{2+} and washed free of excess VO^{2+} with 10^{-3} M HCl had a VO^{2+} ESR spectrum with the 7/2 linewidth equal to 44 G. Some of the line broadening was probably due to dipolar interactions between VO^{2+} ions, since exchange sites on kaolinite surfaces are about the same distance apart as on smectites (McBride, 1976b). Therefore, the rotational mobility of VO^{2+} on kaolinite is probably about the same as on smectite surfaces, a conclusion supported by the ESR spectra of absorbed Cu^{2+} and Mn^{2+} (McBride, 1976b).

The solutionlike nature of absorbed VO^{2+} indicated that highly structured (i.e., high viscosity) water near clay mineral surfaces is unlikely. Also implied is the concept that the strong preference of clays for divalent relative to monovalent ions is *not* a result of stronger electrostatic interaction between divalent ions and surfaces, since the cations do not appear to be localized at adsorption sites. The fact that exchange of monovalent ions by divalent ions on smectites is generally endothermic and accompanied by an increase in entropy (Laudelout et al., 1968) supports the idea of relatively weak electrostatic attraction of divalent ions. Their high hydration energies generally allow divalent ions to maintain an outer hydration sphere at smectite surfaces. The spontaneous exchange of monovalent ions by divalent ions must then be promoted by the greater surface disorder relative to the more weakly hydrated, site-localized monovalent cations and by the increase in entropy of solution water as divalent ions in solution are replaced by monovalent ions.

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Резюме—Электронный спинный резонансный (ЭСР) спектр различных количеств ионов ванадила (VO^{2+}), адсорбированного гидратным гекторитом, указывал, что гидролиз VO^{2+} ускорялся на низких уровнях адсорбции. Гидролнзный продукт адсорбировался на поверхностях глины в среде лиганда, который частично был водным, и частично гидроокисным по природе. Большие количества VO^{2+}, адсорбированные на влажном гекторите, затемняли ЭСР спектр сильно адсорбированного гидролизного продукта с растворо-подобмным спектром. Приблизительно 50% уменьшение в ротационной мобильности VO^{2+} по отношению к раствору определялось линейной шириной этого спектра. Потеря мобильности происходила с уменьшением межслойных промежутков до тех пор пока в условиях сильной дегидратации ионы $VO(H_2O)_5{}^{2+}$ выравнивались с осями связи V=O, нормальными к плоскости пластинок глины.

Resümee—Die ESR Spektren verschiedener Mengen von Vanadylion (VO^{2+}), adsorbiert auf hydriertem Hektorit, deutet an, daß Hydrolyse von VO^{2+} bei niedrigen Adsorptionsstufen angeregt wird. Das hydrolisierte Produkt war an der Tonoberfläche adsorbiert, mit einer Ligandenumgebung, die zum Teil wässrig und zum Teil hydroxydhaltig war. Größere Mengen von VO^{2+}, welche auf angenäßtem Hektorit adsorbiert waren, verunklaren das ESR Spektrum des stark adsorbiertem Hydrolyseprodukts mit einem lösungsähnlichen Spektrum. Die Signalweite dieses Spektrums deutete eine etwa 50% Verminderung der rotationalen Beweglichkeit des VO^{2+} im Verhältnis zu lösungen an. Der Verlust in Beweglichkeit ereignete sich während der Reduktion der interlamellaren Abstände bis unter stark dehydrierenden Bedingungen die $VO(H_2O)_5{}^{2+}$ Ionen nach der V=O Bindungsachse ausgerichtet wurden, senkrecht zur Ebene der Tonplättchen.

Résumé—Les spectres de spin d'électrons (ESR) de quantités variés d'ions de vanadyl (VO^{2+}) adsorbée sur de l'hectorite hydratée ont indiqué que l'hydrolyse de VO^{2+} était promue à des niveaux d'adsorption peu élevés. Le produit hydrolysé était adsorbé sur les surfaces argileuses, avec un environment liant qui était de nature partiellement hydroxide et partiellement aqueux. De plus grandes quantités de VO^{2+} adsorbées sur de l'hectorite mouillée ont obscurci le spectre ESR du produit d'hydrolyse fortement adsorbé par un spectre semblable à celui d'une solution. La largeur de la ligne de ce spectre a indiqué une réduction d'approximativement 50% de la mobilité de rotation de VO^{2+} relative à une solution. La perte de mobilité a été de pair avec une réduction de l'espacement interlamellaire jusqu'à ce que, sous des conditions fortement déshydratantes, les ions $VO(H_2O)_5{}^{2+}$ s'alignent avec l'axe de liaison V=O, normal au plan des plaquettes argileuses.