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HYDRATION STATE OF Cu^{2+} IN MIXED Cu^{2+}-HEXADECYLPYRIDINIUM MONTMORILLONITE BY ELECTRON SPIN RESONANCE

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Abstract—Electron spin resonance (ESR) spectra of Cu^{2+}-hexadecylpyridinium (HDP) montmorillonites were investigated as a function of HDP^+ content and the hydration state of Cu^{2+} at relative humidities of $p/p_0 = 0.52$–8×10^{-7} at 298°K. The symmetry of the Cu^{2+} ESR spectra and the intensity of the ESR signal increased upon dehydration of the complex. The HDP^+ cation caused an increase in the hydration state of Cu^{2+} at a given p/p_0 and an increase in the covalency of the Cu–O bond.

Key Words—Cation exchange, Copper, Electron spin resonance, Hexadecylpyridinium, Hydration, Montmorillonite.

INTRODUCTION

Montmorillonite containing both Cu^{2+} and hexadecylpyridinium (HDP^+) cations in the exchange positions adsorbs less water than Cu-montmorillonite (Kłapyta and Żyła, 1977). The large size of the organic cation also increases the basal spacing of the clay. The influence of interlayer HDP^+ on the symmetry and mobility of inorganic cations in the exchange positions of samples having different degrees of hydration may be investigated by electron spin resonance (ESR). Cu^{2+} ions are useful probes in such investigations because their ESR spectra are sensitive to both the changes in the degree of hydration and the symmetry of the environment. Numerous studies have been reported on the mobility of Cu^{2+} and the symmetry of the sites at which it is localized in aluminosilicates (Nicula *et al.*, 1965; Mikheikin *et al.*, 1970; Turkevich *et al.*, 1972; Clementz *et al.*, 1974; McBride and Mortland, 1974; McBride *et al.*, 1975b; McBride, 1976; Neira *et al.*, 1977; Mank and Ovcharenko, 1978; Conesa and Soria, 1978, 1979). On the other hand, only few ESR studies have tackled the problem of mixed organic and inorganic cations in montmorillonites (McBride *et al.*, 1975c, 1975a; McBride and Mortland, 1975; McBride, 1977, 1979).

Some points deserve attention when investigating the influence of organic cations on the hydration degree of inorganic cations in mixed systems: (1) Our preliminary experiments showed significant sensitivity of the Cu^{2+} ESR signal to the changes in humidity of ambient air. Thus, the commonly used expression "air dry" has no specific meaning and corresponds to different degrees of hydration of metal ion. (2) The data on the total sorption of water, which are widely used to characterize the hydration state of the exchange cations, give only the upper limit for the number of water molecules coordinated by exchange cations. Because these cations compete with other centers of water adsorption in the framework of the aluminosilicate, conclusions concerning the hydration of Cu^{2+} may be drawn only from the adsorption data obtained at a lower water pressure than that corresponding to a saturated aqueous solution of KNO_3 ($p/p_0 = 0.52$ at 298°K), i.e., when only solvation water is present. (3) Using vacuum thermal-dehydration techniques in grease-sealed apparatus, Cu may be reduced and produce spurious changes in the ESR spectra (Naccache and Ben-Taarit, 1971; Jacobs *et al.*, 1976; Conesa and Soria, 1978).

In the present work the influence of the large organic cations on the hydration state and localization of copper in the exchange positions of the Cu^{2+}-HDP^+-montmorillonites was studied by ESR spectroscopy. Both the method of dehydration and the relative humidity were chosen in such a way as to avoid these problems.

MATERIALS AND METHODS

The <2-μm fraction of montmorillonite from Chmielnik, Poland, with the chemical formula $Ca_{0.21}(Na,K)_{0.01}(Al_{1.47}Fe^{3+}_{0.05}Mg_{0.50})(Si_4)O_{10}(OH)_2$ was transformed into the Na^+ form and then saturated with Cu^{2+} by several washes with aqueous $CuCl_2$. Excess salt was removed by washing with distilled water until the solution centrifuged from suspension gave no reaction for chloride with $AgNO_3$. To obtain mixed ionic systems an aqueous solution of 1-hexadecylpyridinium chloride was added to a Cu^{2+}-montmorillonite suspension in various ratios and equilibrated by stirring for 16 hr. The reaction product was centrifuged and washed with distilled water until a $AgNO_3$ test for Cl^- was negative. The samples were dried at 323°K in air.

The Cu^{2+} content was determined by atomic absorption spectroscopy after digesting the clay in 0.1 M HCl. The cation-exchange capacity of the Cu^{2+}-montmoril-

Table 1. Hexadecylpyridinium content and basal spacing of Cu^{2+}-HDP^+-montmorillonites.

HDP^+ on exchange sites (%)	Basal spacing (Å)
0	12.6
8.4	13.0[1]
14.4	13.7[1]
37.7	15.5[1]
58.4	17.8

[1] Nonrational basal spacing.

Table 2. Substances used as hygrostats.

Hygrostat	p/p_0 (298°K)[1]
KNO_3 (aq. sat.)	0.52
NaBr (aq. sat.)	0.26
$MgSO_4$	0.043
$CaCl_2$	0.006–0.011
$Mg(ClO_4)_2$	4×10^{-6}
P_2O_5	8×10^{-7}

[1] Tables of Chemical Constants, Polish Technical Editions, Warsaw, 1954; Physicochemical Constants, Polish Technical Editions, Warsaw, 1974.

lonite was found to be 92.2 meq/100 g. The percentage of the total cationic exchange sites occupied by HDP^+ ranged from 0 to 58.4% (Table 1). The error resulting from possible hydrolysis of Cu^{2+} in the course of the washing procedure amounted to about 8%.

X-ray powder diffraction patterns of oriented clay films dried in air at 323°K on glass slides and equilibrated at $p/p_0 = 0.3$ (298°K) were recorded using a TUR M-62 diffractometer and filtered CuKα radiation. Four orders of 001 reflections were observed (Table 1).

ESR spectra were recorded at room and liquid nitrogen temperatures by using an ESR spectrometer operating in the X band with a modulation frequency of 100 kHz. Mn^{2+} in MgO and DPPH ($g = 2.0036$) were used as g-factor standards. The relative changes in the spin concentration were determined by comparing the intensity of the ESR spectra registered under the same conditions, calculated per Cu^{2+} ion.

Before ESR investigations the samples were equilibrated under a constant water pressure for several weeks. The sample placed in an ESR tube remained in contact with an ampul containing one of the substances listed in Table 2. No thermal treatment was applied to these samples.

The amount of water adsorbed on the samples with various HDP^+ contents at a given p/p_0 value was calculated from the BET sorption isotherms (Kłapyta and Żyła, 1977). The samples were dried in vacuo (10^{-3} Pa) at 383°K for 15 hr before adsorption. The error of these estimations was equal to ±10% (Figure 2).

RESULTS AND DISCUSSION

The samples equilibrated over a saturated aqueous solution of KNO_3 gave at 298°K a symmetrical ESR signal of $g = 2.165 \pm 0.005$ and a peak-to-peak line width $\Delta B_{pp} = 12 \pm 0.2$ mT (Figure 1, Table 3). At 77°K a signal with axial symmetry ($g_\perp = 2.054$, $g_\parallel = 2.340$) and a hyperfine splitting around $g_\parallel$ ($A_\parallel = 131 \pm 2 \times 10^{-4}$ cm^{-1}) was observed. The symmetrical line of the isotropic g factor may be attributed to the tumbling $[Cu(H_2O)_6]^{2+}$ ions. At low temperatures the tumbling is hindered and the signal becomes anisotropic revealing distortion of the $[Cu(H_2O)_6]^{2+}$ octahedron. The values of the g factor: $g_\parallel > g_\perp$ indicate elongation of the octahedron along the "z" axis due to the Jahn-Teller effect. Similar changes of the ESR signal symmetry with temperature were observed for Cu^{2+} in hydrated aluminosilicates (McBride and Mortland, 1974; McBride *et al.*, 1975b; Conesa and Soria, 1979) and for aquocomplexes of Cu^{2+} adsorbed on porous supports (Bassetti *et al.*, 1979). The above interpretation is consistent with the results of the quantitative determination of the sorption of water by Cu^{2+}- and Cu^{2+}-HDP^+-exchanged montmorillonites reported previously (Kłapyta and Żyła, 1977). Figure 2 is a plot of the number of adsorbed water molecules per Cu^{2+} ion as calculated from adsorption isotherms at the pressure corresponding to the equilibrium water pressure over saturated aqueous solutions of KNO_3, NaBr, and anhydrous $MgSO_4$ at 298°K vs. the concentration of HDP^+. The amount of water adsorbed at a p/p_0 corresponding to the equilibrium water pressure over a saturated aqueous solution of KNO_3 ($p/p_0 = 0.52$) exceeds 10 molecules per Cu^{2+} ion in all samples and is sufficient to form fully hydrated Cu^{2+} complexes. The HDP^+ cation did not affect the shape of the ESR signal, i.e., the structure of the CU^{2+} complex, or its mobility.

The HDP^+ affected the ESR spectra of the samples equilibrated over a saturated aqueous solution of NaBr. The ESR signals of 37.7 and 58.4% exchanged HDP^+-montmorillonites are symmetrical at room temperature and axial at 77°K, with g factors similar to those described above, indicating the presence of the freely tumbling hexaaquocomplex of Cu^{2+}. In the ESR spectra of Cu^{2+}-montmorillonite and samples containing 8.4 and 14.4% of HDP^+ recorded at room temperature two signals were observed: the isotropic line of $g = 2.16$ and a signal of the $g_\perp$ factor equal to 2.05. At 77°K only one signal of axial symmetry of $g_\perp = 2.045$ and $g_\parallel = 2.313$ was noted in the ESR spectrum.

The appearance of two signals at room temperature in the ESR spectrum of samples equilibrated over saturated NaBr solution may be explained by the formation of various hydrates, e.g., freely tumbling $[Cu(H_2O)_6]^{2+}$ and $[Cu(H_2O)_5]^{2+}$ or $[Cu(H_2O)_4]^{2+}$ that are limited in their mobility by interaction with oxygen atoms of the surface of the interlayer (Velghe *et al.*, 1977). The latter species could give ESR signals of axial symmetry at room temperature. At 77°K only one set of g values was observed in the ESR spectrum. A similar

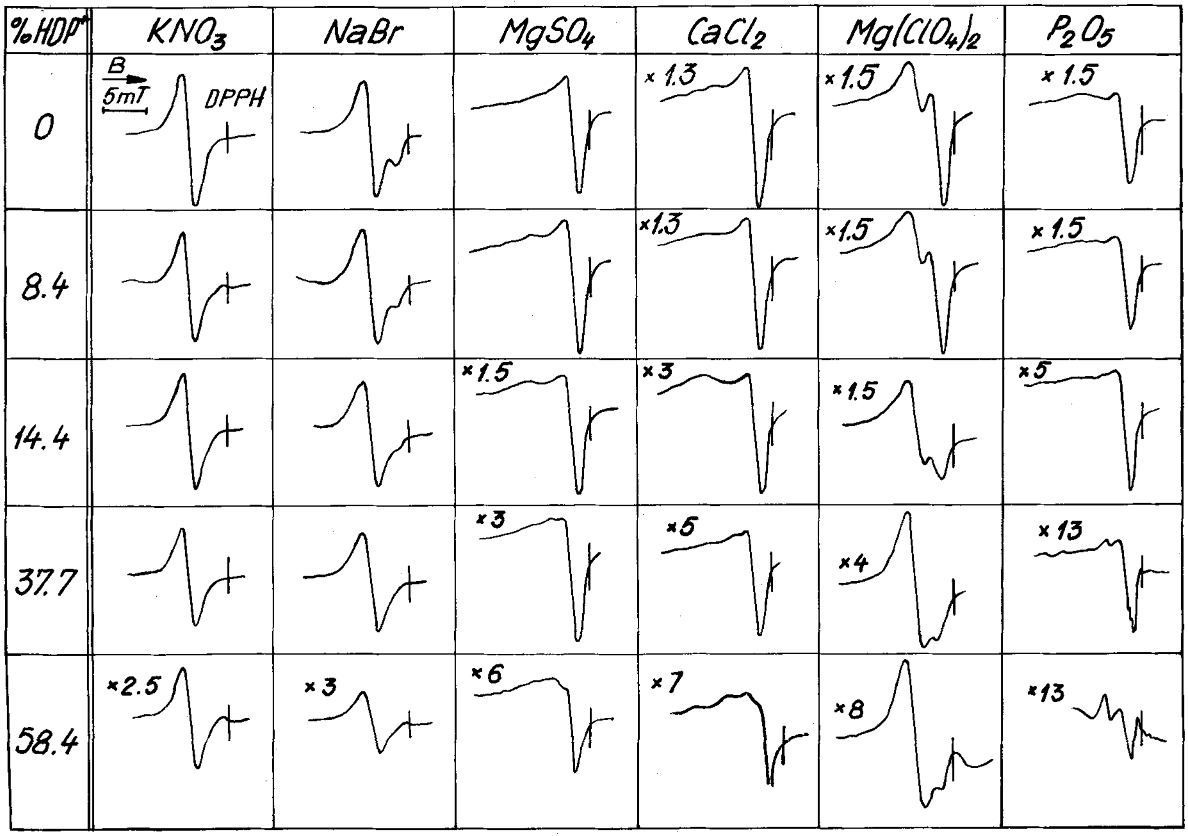

Figure 1. Electron spin resonance spectra of Cu^{2+} in Cu^{2+}- HDP^+-montmorillonites taken at 298°K.

effect was reported by Turkevich *et al.* (1972) and Conesa and Soria (1979) for zeolites.

The above interpretation is consistent with the data presented in Figure 2 which indicate that the total amount of water adsorbed at a pressure corresponding to the equilibrium pressure over a saturated NaBr solution at 298°K ($p/p_0 = 0.26$) is equal to about 6 water molecules per Cu^{2+} ion. Taking into account the fact that the total amount of adsorbed water is distributed among various adsorption centers this value must represent the upper limit of water molecules coordinated by Cu^{2+}. Indeed, the water molecules penetrating the interlayer space of a Cu^{2+}-montmorillonite may be coordinated by Cu^{2+} as well as by other centers of the aluminosilicate framework. The organic cation present in Cu^{2+}-HDP^+-exchanged samples may eliminate some centers of water adsorption due to a screening effect.

The formation of fully hydrated $[Cu(H_2O)_6]^{2+}$ species, which would give rise to only one symmetrical signal in the room-temperature ESR spectrum of 37.7 and 58.4% exchanged Cu^{2+}-HDP^+-montmorillonites, indicates an increase in the degree of hydration of Cu^{2+} in the presence of HDP^+. Thus, this effect may be related to the increase in the basal spacing, which may favor for steric reasons the formation of Cu-complexes coordinating more water molecules than those formed at the same relative humidity in the clays which do not contain HDP^+.

The data concerning the adsorption of water at the pressure corresponding to equlibrium pressure over $MgSO_4$ ($p/p_0 = 0.043$) (Figure 2) indicate that aquo-complexes are mainly formed with coordination numbers less than 6. The asymmetrical signal in the room temperature ESR spectra of samples equilibrated over $MgSO_4$ may be attributed to $[Cu(H_2O)_5]^{2+}$ or $[Cu(H_2O)_4]^{2+}$ complexes.

All Cu^{2+} signals of the samples equilibrated over $MgSO_4$ show a hyperfine structure around $g_\parallel$. The hyperfine splitting decreases with increasing HDP^+ content indicating an increase in the covalent character of the Cu–O bond. From the formulae proposed by Abragam and Pryce (1951):

$$A_\parallel = [(g_\parallel - 2) + 3/7(g_\perp - 2) - 4/7 - k]P \qquad (1)$$

and

$$A_\perp = [(g_\perp - 2) - 3/14(g_\perp - 2) + 2/7 - k]P, \qquad (2)$$

the parameter k, which represents the isotropic s-orbital contribution to the A value, can be calculated. The

Table 3. Electron spin resonance parameters for Cu^{2+}-HDP^+-montmorillonites at 298°K.

	Substances used as hygrostats:					
	KNO_3	NaBr	$MgSO_4$	$CaCl_2$	$Mg(ClO_4)_2$	P_2O_5
	Cu^{2+} montmorillonite					
$g_\parallel$[1]	—	—	2.278	2.295	2.270	2.303
$g_\perp$[1]	—	2.048	2.040	2.043	2.043	2.046
g_{iso}[1]	2.165	2.163	—	—	2.163	—
$A_\parallel$[2]	—	—	165	166	170	140
	Cu^{2+}-HDP^+-montmorillonite (8.4% HDP)					
$g_\parallel$	—	—	2.286	2.280	2.280	2.300
$g_\perp$	—	2.045	2.045	2.045	2.046	2.046
g_{iso}	2.170	2.163	—	—	2.160	—
$A_\parallel$	—	—	149	160	154	145
	Cu^{2+}-HDP^+-montmorillonite (14.4% HDP)					
$g_\parallel$	—	—	2.290	2.290	—	2.303
$g_\perp$	—	2.050	2.050	2.048	2.050	2.050
g_{iso}	2.166	2.165	—	—	2.160	—
$A_\parallel$	—	—	150	150	—	150
	Cu^{2+}-HDP^+-montmorillonite (37.7% HDP)					
$g_\parallel$	—	—	2.300	2.300	—	2.300
$g_\perp$	—	—	2.050	2.050	2.050	2.040
g_{iso}	2.166	2.163	—	—	2.160	2.150
$A_\parallel$	—	—	145	145	—	—
$A_\perp$	—	—	—	—	—	14
	Cu^{2+}-HDP^+-montmorillonite (58.4% HDP)					
$g_\parallel$	—	—	2.290	2.300	—	—
$g_\perp$	—	—	2.050	2.050	2.050	2.040
g_{iso}	2.170	2.163	—	—	2.160	2.150
$A_\parallel$	—	—	144	145	—	—
$A_\perp$	—	—	—	—	—	14

[1] ±0.005.

[2] ±2 × 10^{-4} cm^{-1}.

parameter k is proportional to the unpaired electron density on Cu nuclei, and (1 − k) is a measure of the covalency of the Cu–O bond. If P is a constant equal to 0.032 cm^{-1} and $A_\parallel$ has a negative value, the following values of k can be calculated, in order of increasing HDP^+ content: 0.24, 0.20, 0.21, 0.20, and 0.19. The observed decrease of k indicates an increasing covalency of the Cu–O bond. This effect can be correlated with the increasing degree of hydration of Cu^{2+}, as indicated by the ESR data discussed above, which are in agreement with the findings of other authors (e.g., Nicula *et al.*, 1965).

We propose the following explanation of the HDP^+ influence on the covalency of the Cu–O bond. In the interlayer space several types of hydrogen bonds may be formed between negatively charged surface oxygens of the framework and the water molecules coordinated by Cu^{2+} (Farmer and Russell, 1971). The introduction of the large HDP^+ cations causes an increase in the interlayer spacing (Table 1) and a screening of the interlayer surface from the Cu^{2+}-aquocomplexes. It may be supposed, that these effects make difficult the formation of the hydrogen bonds between water molecules coordinated by Cu^{2+} and surface oxygens, leading to an increase in the covalent character of the Cu–O bond. Another plausible explanation of the observed effect may be related to the increase in the basal spacing in the presence of HDP^+. The Cu^{2+}-aquocomplexes of different coordination number and different k values may be formed at the same RH in the clays of different HDP^+ content due to the steric reasons.

The samples dried over $CaCl_2$ show similar ESR spectra and a similar dependence of k on HDP^+ content. The k values are: 0.26, 0.23, 0.21, 0.20, and 0.20 for the samples containing 0, 8.4, 14.4, 37.7, and 58.4% of HDP^+, respectively, indicating that the organic cation controls the covalency of the Cu–O bond.

The samples dried over $Mg(ClO_4)_2$ gave a complex ESR spectrum which consists of two overlapping signals: an isotropic line of Lorenzian shape and g = 2.16

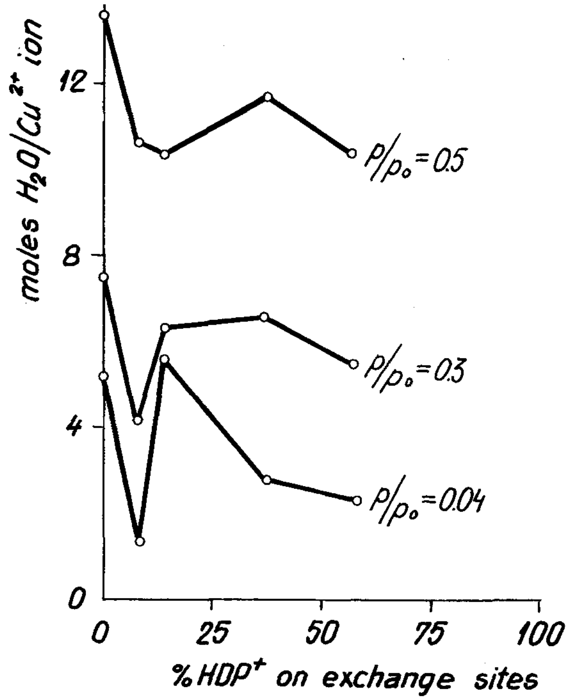

Figure 2. Relationship between HDP^+ content and H_2O/Cu^{2+} ratio calculated from adsorption isotherms (Kłapyta and Żyła, 1977). (Error of the estimation = ±10%).

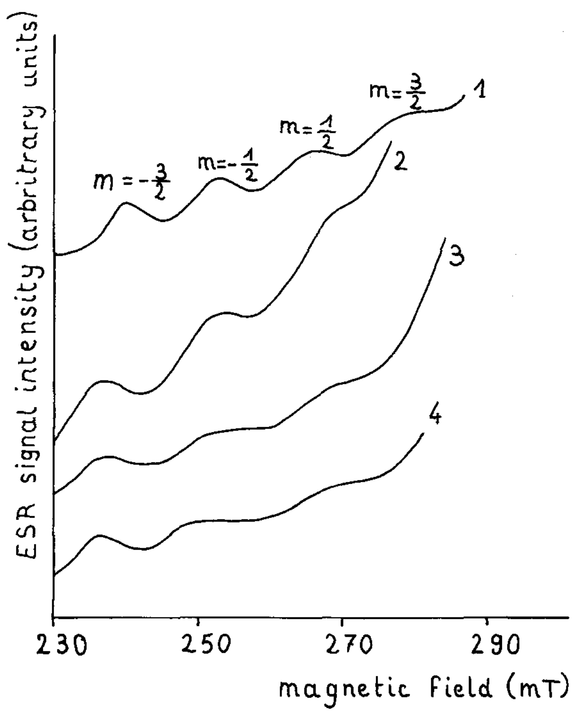

Figure 3. Variation of the width of hyperfine structure components with magnetic field for the samples of different HDP^+ content: (1) Cu^{2+}-montmorillonite equilibrated over KNO_3; (2) Cu^{2+}-montmorillonite equilibrated over $CaCl_2$; (3) Cu^{2+}-HDP^+-montmorillonite (14.4% HDP^+) equilibrated over $CaCl_2$; (4) Cu^{2+}-HDP^+-montmorillonite (37.7% HDP^+) equilibrated over $CaCl_2$. The electron spin resonance spectra taken at 77°K. m = quantum number responsible for a given transition.

and an anisotropic line with $g_\perp \sim 2.05$. The width of the symmetrical signal decreased with increasing content of Cu^{2+}. The total intensity of the ESR spectrum of the samples equilibrated over $Mg(ClO_4)_2$, calculated per Cu^{2+}, is lower than for other drying agents, with the exception of P_2O_5, the effect being most pronounced in samples richest in HDP^+.

The symmetrical line can not be attributed to the freely tumbling $[Cu(H_2O)_6]^{2+}$ complex because the water pressure over $Mg(ClO_4)_2$ is five orders of magnitude lower than that required for full hydration of copper. The simultaneous appearance of two signals, symmetrical and asymmetrical, accompanied by the diminishing of the total intensity of the ESR spectrum, was observed in dehydrated zeolites (Conesa and Soria, 1979). According to their interpretation, the symmetric line can be attributed to Cu^{2+}–O–Cu^{2+} pairs bridged by oxygen from water molecules, and the asymmetrical signal to Cu^{2+} coordinating two water molecules and three oxygen atoms in hexagonal holes of the tetrahedral layers.

The intensity of the ESR spectrum of samples dried over P_2O_5 further decreased indicating that most of the Cu^{2+} ions were involved in the formation of species not detectable by ESR. One of the available sites for Cu^{2+} in highly dehydrated samples is a site of C_{3v} symmetry inside a tetrahedron formed by one water molecule and three oxygen atoms of the framework. The Cu^{2+} ions in such positions closely approach the center of a hexagonal ring formed by SiO_4 tetrahedra; the retained water molecule keeps the Cu^{2+} ion near the trigonal axis minimizing the Jahn-Teller distortion. The resulting splitting of the energy levels is rather small and gives rise to a low-lying excited state. The ESR signal of Cu^{2+} ions in such configuration is below the limit of detection because of the short relaxation time and broadening of the resonance line. With more complete dehydration Cu^{2+} ions lose their residual water and undergo further distortion, approaching two of the coordinated oxygen atoms of the framework. The lowering of the symmetry of Cu^{2+} ions is favored because of the energy gain due to the Jahn-Teller effect. A larger departure from C_{3v} symmetry causes a larger splitting of the energy levels and thus a longer relaxation time which enables observation of the ESR signal of fully dehydrated Cu^{2+} ions at room temperature. We attribute the low intensity asymmetrical signal observed in the ESR spectra of the samples equilibrated over P_2O_5 to such ions. The increase in intensity of this signal with increasing Cu content may be correlated with lowering of the degree of hydration, as stated above on the basis of the ESR spectra of the samples equilibrated over NaBr and $MgSO_4$. The appearance of a small maximum in the low-field range of these spectra suggests the existence of a small concentration of Cu^{2+} ions bridged by oxygen.

Most of the investigated samples revealed hyperfine splitting of the ESR signal around $g_{\parallel}$, which is best resolved at 77°K. As shown in Figure 3 the width of the components of the hyperfine structure increases with increasing quantum number m responsible for a given transition. Hasono *et al.* (1979) attributed such broadening of the hyperfine lines in copper-containing glasses to the inhomogeneity of the crystal field in the structure of glass. In the ESR spectrum of Cu^{2+}-montomorillonite equilibrated over KNO_3, four components were resolved, whereas for the same sample equilibrated over $CaCl_2$ only three much broader lines appeared (Figure 3). Evidently some inhomogeneity of the crystal field exists in the dehydrated Cu^{2+}-montmorillonite which is masked in the presence of water. Replacing Cu^{2+} ions by HDP^+ should diminish the width of the hyperfine structure components by diminishing dipolar broadening, however, the opposite effect was observed. Hence, the additional broadening of the spectra 3 and 4 in Figure 3 is probably due to the presence of HDP^+ ions. It is likely that because of their large size organic cations entering the interlayer space cause fluctuations of the interlayer spacing which contribute to the inhomogeneity of the crystal field and give rise to the additional broadening of the ESR spectra.

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Резюме—Спектры Cu^{2+}-гексадецилпиридиновых (ГДП) монтмориллонитов, полученные методом электронного спинового резонанса (ЭСР), исследовались как функции содержания $ГДП^{+}$ и состояния гидратации Cu^{2+} при относительной влажности $p/p_0 = 0{,}52–8 \times 10^{-7}$ и при температуре 298°K. Симметрия ЭСР лектров Cu^{2+} и интенсивность ЭСР сигнала увеличивались с дегидратацией комплекса. Катион $ГДП^{+}$ вызывал увеличение состояния гидратации *Cu^{2+} при данной величине* p/p_0 и увеличение ковалентности связи Cu–O. [E.G.]

Resümee—Die Elektronenspinresonanz (ESR)-Spektren von Cu^{2+}-hexadecylpyridinium (HDP)-Montmorilloniten wurden in Abhängigkeit vom HDP^{+}-Gehalt und dem Hydratationszustand des Cu^{2+} bei relativen Feuchtigkeiten von $p/p_0 = 0{,}52–8 \times 10^{-7}$ und einer Temperatur von 298°K untersucht. Die Symmetrie der ESR-Spektren von Cu^{2+} und die Intensität des ESR-Signals nahm mit der Dehydration des Komplexes zu. Das HDP^{+}-Kation verursachte eine Zunahme des Hydratationszustandes von Cu^{2+} bei gegebenem p/p_0 und eine Zunahme bei der Kovalenz der Cu–O-Bindung. [U.W.]

Résumé—Les spectres de résonance à spin d'électrons (ESR) de montmorillonites hexadécylpyridinium-Cu^{2+} (HDP) ont été investigués en fonction du contenu en HDP^{+} et de l'état d'hydration de Cu^{2+} à des humidités relatives de $p/p_0 = 0{,}52–8 \times 10^{-7}$ à 298°K. La symmétrie des spectres ESR du Cu^{2+} et l'intensité du signal ESR ont augmenté lors de la déshydration du complex. Le cation HDP^{+} a causé une augmentation de l'état d'hydration du Cu^{2+} à un p/p_0 donné et une augmentation de la covalence du lien Cu–O. [D.J.]