Soviet-era science, translated into English

Reports of the Academy of Sciences of the USSR

Yu. I. Tarasevich, Academician of the Academy of Sciences of the Ukrainian SSR F. D. Ovcharenko,

1964

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196401.41331

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 156, No. 4

PHYSICAL CHEMISTRY

Yu. I. Tarasevich, Academician of the Academy of Sciences of the Ukrainian SSR F. D. Ovcharenko,
I. V. Matyash, V. V. Mank, A. I. Toryanik

NUCLEAR MAGNETIC RESONANCE OF PROTONS OF WATER ADSORBED ON MONTMORILLONITE

To clarify the state of water adsorbed on clays, in addition to measuring heats of wetting and differential heats of adsorption, it is necessary to apply physical methods of investigation. As studies of the protons of adsorbed water in zeolites ([1,2]), on silica gel ([3,4]), and on calcium hydrosilicate ([5]) have shown, the method of nuclear magnetic resonance (NMR) is very promising in this respect.

In the present work we studied the dependence of the width of the magnetic-resonance line on the amount of water adsorbed on montmorillonite and the influence of exchange ions on the processes of magnetic relaxation of its protons. Ca-, Li-, and K-forms of montmorillonite were selected as the objects of study. Dosing of water vapor into ampoules with cation-substituted montmorillonite was carried out by keeping the samples for 45 days over sulfuric acid of various concentrations at a temperature of 20°. The weighed portions of the samples in the ampoules were 1–1.2 g. Figure 1 presents the obtained isotherms of water-vapor adsorption.

To measure the line width of the protons of adsorbed water, an NMR spectrograph with crossed coils was used. A magnetic field with an intensity of 5000 Oe was produced by a permanent magnet with pole pieces 220 mm in diameter and a gap between them of 37 mm. The rate of change of the magnetic field during signal recording was 0.26 and 0.84 Oe/min, and the modulation amplitude was 60 Hz. The field inhomogeneity in the volume of the sample was less than 0.05 Oe.

Figure 2 gives, as an example, a recording of the derivative of the absorption signal of Ca-montmorillonite with an adsorbed-water content of 0.34 mmol/g. Since the line width is a measure of the mobility of the nuclei, it is clear that the broader line* in the spectrum ($\simeq 4$ Oe) refers to protons belonging to the

SovietRxiv

Fig. 1

Figure 1: Fig. 1

hydroxyl groups of the mineral. Relaxation times were studied by the spin-echo method on the apparatus described earlier ([6]).

Figure 3 presents plots of the dependences of the line width of the protons of water adsorbed on cation-substituted montmorillonite on the degree of saturation of the samples with water. It is known that the absorption-line width ΔH is inversely proportional to the spin-spin relaxation time T_2, and therefore the dependence of T_2 on the degree of saturation of Ca-montmorillonite (Fig. 4) is direct confirmation of the dependence of ΔH on the amount of adsorbed water. The low values of the line width of the protons of adsorbed water (Fig. 3), in comparison with the width of the resonance absorption line of ice protons, which at 0° is equal to $\simeq 7.5$ Oe ([7]), are incompatible with the static, ice-like model of the adsorption layer of water on the surface of clay minerals proposed by some authors ([8,9]). In reality, we are evidently dealing with a dynamic adsorption phase, in which there occurs a constant disruption and renewal of structure and, thus, the ordering of the interlayer water is of a purely statistical nature. In this case the discussion may concern both the motion of water molecules as a whole and the motion of their constituent parts.

Ducreux and Duplan ([10]) assumed that the comparatively narrow (0.3 oersted) singlet NMR lines of the protons of water adsorbed on clays, obtained with a high-resolution spectrometer, can be explained on the basis of ideas about rapid, approximately 10^6 times/sec, exchange of protons between neighboring molecules.

It should be noted that in recent years the catalytic properties of various aluminosilicates in cracking, alkylation, polymerization, etc., reactions have also been associated with the existence on the surface of aluminosilicates of mobile protons capable of splitting off with addition to other substances ([11,12]). These assumptions are reasonable, since recently, as a result of the spectral detection of the presence of the hydroxonium ion in vermiculite ([13]) and the formation of the ammonium ion during the interaction of ammonia with water adsorbed on the surface of montmorillonite ([14]), the reality of the existence of protons on the surface of clays was established experimentally.

Fig. 1. Initial portions of the adsorption isotherms of water vapor on cation-substituted montmorillonite. 1 –Ca; 2 –Li; 3 –K-montmorillonite

Proceeding from modern ideas about the low polarity of the O–H bond in iso-

---

* The line width was determined as the distance between the maxima of the derivative of the absorption signal.

SovietRxiv

Fig. 2

Figure 2: Fig. 2

Fig. 3. Dependence of the line width (ΔH) on the amount of water adsorbed on cation-substituted montmorillonite. 1 –Li; 2 –Ca; 3 –K-montmorillonite.

Figure 3: Fig. 3. Dependence of the line width (ΔH) on the amount of water adsorbed on cation-substituted montmorillonite. 1 –Li; 2 –Ca; 3 –K-montmorillonite.

lated water molecules (15) and its polarization in groupings $Me^{n+} \dots H_2O \dots A$, where A is an anion or water molecules of the more distant hydration environment (16,17), it is clear that the presence of mobile protons on the surface of montmorillonite can be explained by the strong polarization of the O–H bonds of adsorbed water molecules in oppositely charged fields of the oxygen surface of the mineral and of the exchange ions.

Fig. 2. Shape of the derivative of the proton absorption signal of Ca-montmorillonite

However, the rate of proton exchange between neighboring water molecules, at least at low degrees of filling, will evidently depend on the translational motion of the molecules on the surface of clay minerals, which, in turn, must affect the width of the proton resonance line. Therefore, in explaining the results obtained it is necessary to take into account the influence of the two above-mentioned factors simultaneously. The magnitude of the translational motion (self-diffusion) of water molecules adsorbed on montmorillonite, in addition to structural fluctuations of the adsorption energy on the surface of the mineral, is evidently also determined by the intensity of the energy field of the corresponding exchange ions, which, as is known, depends on the size of the ion and its charge. Then it becomes understandable that the proton line width of adsorbed water at the same amount of it is, in the case of Li-montmorillonite, somewhat greater than for Ca-montmorillonite and substantially greater than for K-montmorillonite. This is consistent with the dependence of the line width on the type of exchange complex in zeolites (2) and with the ratios of the average residence times of water molecules near the corresponding ion in solution to the average residence time of water molecules in an equilibrium position in pure

water (⌒18). Comparison of the results shown in Fig. 3 with other data (⌒1, ⌒2, ⌒19) shows that the self-diffusion coefficient for molecules of water adsorbed on montmorillonite at low degrees of filling has a value of the order of 10^{-7} $\text{cm}^2 \cdot \text{sec}^{-1}$ and increases with saturation.

Fig. 3. Dependence of the line width (ΔH) on the amount of water adsorbed on cation-substituted montmorillonite. 1 –Li; 2 –Ca; 3 –K-montmorillonite.

SovietRxiv

Fig. 4. Dependence of T_1 and T_2 for adsorbed water on the degree of saturation of its Ca-montmorillonite.

Figure 4: Fig. 4. Dependence of T_1 and T_2 for adsorbed water on the degree of saturation of its Ca-montmorillonite.

Fig. 4. Dependence of T_1 and T_2 for adsorbed water on the degree of saturation of its Ca-montmorillonite.

Thus, on the basis of consideration of all the experimental data obtained in the present work, it may be concluded that water adsorbed on montmorillonite must be regarded as a dynamic phase, the constant disruption and re-formation of whose structure is determined both by rapid proton exchange between neighboring water molecules and by self-diffusion of the water molecules as a whole.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Physicotechnical Institute of Low Temperatures
Academy of Sciences of the USSR

Received
14 II 1964

REFERENCES CITED

^1 I. V. Matyash, M. A. Piontkovskaya et al., *Zhurn. strukturn. khim.*, **3**, 2, 214 (1962).
^2 I. V. Matyash, M. A. Piontkovskaya et al., *Zhurn. strukturn. khim.*, **4**, 1, 106 (1963).
^3 J. R. Zimmerman, B. G. Holmes, J. A. Lasater, *J. Phys. Chem.*, **60**, 9, 1157 (1956).
^4 V. I. Kvlividze, N. M. Kievskaya et al., *Kinetika i kataliz*, **3**, 1, 91 (1962).
^5 V. I. Kvlividze, K. G. Krasilnikov, *DAN*, **145**, No. 6, 1305 (1962).
^6 A. A. Galkin, I. V. Matyash, *Zhurn. eksp. i teor. fiz.*, **38**, 4, 1332 (1960).
^7 K. Kumme, *J. Phys. Soc. Japan*, **15**, 1493 (1960).
^8 S. B. Hendricks, M. E. Jefferson, *Am. Min.*, **23**, 863 (1938).
^9 H. N. Macey, *Trans. Ceram. Soc.*, **41**, 73 (1942).
^10 P. Ducros, M. Dupont, *C. R.*, **254**, 8, 1409 (1962).
^11 R. Houard, Collection *Catalysis. Catalysts for Organic Reactions*, IIL, 1955, p. 5.
^12 V. K. Skarchenko, *Aluminosilicate Catalysts*, 1963.
^13 G. B. Bokii, D. K. Arkhipenko, *Zhurn. strukturn. khim.*, **3**, 6, 697 (1962).
^14 M. M. Mortland, J. J. Fripiat et al., *J. Phys. Chem.*, **67**, 2, 248 (1963).
^15 L. Burnell, C. A. Coulson, *Trans. Farad. Soc.*, **53**, 403 (1957).
^16 I. V. Aleksandrov, N. D. Sokolov, *DAN*, **124**, No. 1, 115 (1959).
^17 S. N. Andreev, T. G. Blincheva, *DAN*, **148**, No. 1, 86 (1963).

^18 O. D. Samoilov, *Structure of Aqueous Electrolyte Solutions and Hydration of Ions*, Publishing House of the Academy of Sciences of the USSR, 1957.
^19 D. P. Timofeev, I. T. Erashko, *Izv. AN SSSR, OKhN*, **7**, 11, 1192 (1961).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.