Differences in behaviour of adsorbed water in kaolinites and montmorillonites in temperature range from -90°C to +140°C by dielectric spectroscopy

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Abstract. Two different types of natural layer aluminosilicates (clay minerals), montmorillonite with the exchangeable K⁺ and Ni²⁺ cations and kaolinite with the exchangeable K⁺ and Ba²⁺ cations, were investigated by dielectric spectroscopy. The different effects of water adsorption in montmorillonites and kaolinites on the dielectric response were observed in wide temperature (-90°C ÷ +140°C) and frequency (1 Hz ÷ 1 MHz) ranges. The influence of the nature of the hydration centers on adsorbed water dynamics and influence of ions nature on the activation energy values of the relaxation processes were discussed.

1. Introduction

Kaolinites and montmorillonites are widely applied in many fields such as pharmaceuticals, ecology, hydrogeology, catalysis, and etc., due to their high specific surface area, chemical and mechanical stabilities, variety of surface and structural properties, higher values of cation exchange capacities, etc.

The physical effects related with the interaction of bound water with clay minerals play an important role in numerous technological applications. The useful information about the mechanism of the water molecules interaction with clay-contained substances on the mesoscopic level can be obtained by means of dielectric spectroscopy method. In spite of many studies on the dielectric properties of montmorillonites and kaolinites [1-8] full understanding of the adsorption mechanisms in clay materials was not achieved up to date.

The main aim of this study was to use dielectric measurements in wide temperature (-90°C ÷ +140°C) and frequency (1 Hz ÷ 1 MHz) ranges to examine the effects of the clay structure and various types of cations on the existence and properties of bound water in montmorillonites and kaolinites.

2. Samples

As objects of study two types of natural layer aluminosilicates (clay minerals), Oglanlinsky montmorillonite (Turkmenistan) with the exchangeable cations K⁺ and Ni²⁺ and Glukhovetsky kaolinite (Ukraine) with the exchangeable cations K⁺ and Ba²⁺, were taken. All the samples of clay

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minerals were prepared in the laboratory of disperse systems of Institute of Colloid and Water Chemistry (Ukraine, Kiev) according to the procedure described previously [9]. The samples were stored in ambient air humidity, thus one can assume that water molecules were absorbed from the air into the pores.

Montmorillonite and kaolinite are layer silicate minerals composed of tetrahedral (T: Si tetrahedra) and octahedral (O: Al octahedra) sheets. Montmorillonite is formed by TOT layers. In this mineral isomorphic substitution (i.e., replacement of ions in the crystals without change of the structure) results in a net negative charge which is balanced through the electrostatic adsorption of cations in the interlayer space and cations on or near the external surfaces. Kaolinite is formed by TO layers and isomorphic substitution is rather small. Depending on their structure, type of interlayer cation, activity of water, and the degree of compaction, clays can be hydrated by a variable amount of water molecules in the interlayer space and on external surfaces. In the case of montmorillonite water is located between particles and in the interlayer space. In kaolinite water and ions are located on the external surfaces (figure 1).

Figure 1. Schematic structure of the montmorillonite (a) [10] and kaolinite (b) [11] clay minerals.

3. Experimental
For investigation broadband dielectric spectrometer BDS 80 based on an Alpha Impedance Analyzer (NOVOCONTROL) was used. Measurements were performed in the frequency range of 1 Hz ÷ 1 MHz with automatic temperature control by QUATRO Cryosystem with a precision of 0.5°C. The measurement protocol: each of the samples was placed into the sample cell with a parallel plate capacitor configuration at room temperature and the measurements were then made by cooling the samples from +20°C to -90°C. Then the samples were measured at intervals of 3°C upon heating them from -90°C to -58°C and at intervals of 6°C from -52°C to +140°C and then heating up to +300°C. The relative water content to the dry sample was obtained by weighing the samples prior to and immediately after heating up to +300°C (see table 1). The inner diameter of the sample cell for dielectric measurements was 16 mm and the minimum spacing between electrodes was 0.5 mm.
4. Results and discussion
A typical view of the 3-D plots of the dielectric losses vs. frequency and temperature is shown in figure 1.

![Figure 1](a)

![Figure 1](b)

![Figure 1](c)

![Figure 1](d)

**Figure 1.** Three-dimensional plots of the frequency and temperature dependence of the dielectric losses for montmorillonite K (a), Ni (b) and kaolinite K (c) and K, Ba (d).

In temperatures from -90°C to +140°C a relaxation process with a specific saddle-like shape and distinctive kink point was observed twice for montmorillonite Ni (processes 1 and 2) at different frequency-temperature intervals while only one relaxation process 1 is observed in the case of kaolinite samples and montmorillonite K. Annealing the samples at 300°C for 3 hours leads to full disappearance of the relaxation processes. It means that the only water is the source of the dielectric relaxation.

Experimental data for the relaxation process 1 in kaolinites K and K, Ba were described by a single Cole-Cole function [12] with additional Jonscher’s [13] empirical terms and conductivity term [14].
the same time the process 1 in montmorillonites K and Ni in the full temperature range can’t be well described by any known functions and we give for it only relaxation times corresponding to the maximum position of the relaxation peak (figure 2). Anomalous broadening of the spectral lines in the process 1 for montmorillonites may be explained by the exchange between several states but such exchange is not a fast enough and therefore described by very complex relations [7] being subject to further investigation.

The quantitative analysis of the measured dielectric spectra was performed based on the model described earlier [15, 16]. It considers the relaxation act as an occurrence of two simultaneous events: (a) the molecule reorientation and (b) presence of a defect site in its vicinity. In the framework of the model the temperature dependence of the relaxation time can be written in the form:

\[
\tau = \tau_0 \exp \left( \frac{H_a}{kT} + C \exp \left( - \frac{H_d}{kT} \right) \right)
\]

where \(H_a\) is the height of the potential barrier of the reorientation of water molecules; \(H_d\) is the energy of the defect formation; \(C\) is inversely proportional to the maximum possible defect concentration. The pre-exponential time constant \(\tau_0\) can vary with temperature.

The increasing temperature leads, on the one hand, to an increase in the probability to attain sufficient energy to break the bonds between the reorienting molecule and its neighbors. On the other hand, it leads to a decrease in the probability of finding a defect in the vicinity of the moving molecule. The interplay of these two terms yields the appearance of the minimum observed in the temperature dependence of the relaxation time.

The experimental data of the relaxation times were fitted to equation (1) by means of a least-squares fit procedure. The fitting curves are presented in figure 2 and the fitting results are listed in table 1.

![Figure 2](image_url)

**Figure 2.** The temperature dependence of the relaxation times for montmorillonite and kaolinite samples (solid lines correspond to the fit by equation (1); two saddle-like processes 1 and 2 are marked by solid and open symbols respectively).
We associate the slower relaxation process 1 with intergranular water which is present both in kaolinites and montmorillonites. Thus the process 1 reflects the dynamics of the adsorbed water molecules at the outer surfaces of the powder particles.

The faster relaxation process 2 in montmorillonite Ni corresponds to the more disordered water. We suppose that the relaxation process 2 reflects mainly dynamics of the water molecules in interlayer space of the montmorillonite structure. Such type of water is absent in kaolinites. The apparent absence of the process 2 for montmorillonite K may be explained by strong disOrdering effect of K⁺ ion on interlayer water that leads to shift of the process 2 in high-frequency range inaccessible for observation in the frequency range of the present experiment. Indeed, K⁺ is characterized by “negative hydration” at which life time of water molecules is less in immediate environment of ion than in bulk solution [17, 18].

Table 1. The calculated values of the relative humidity (h) and the fitting parameters of the relaxation processes 1 and 2 according to equation (1).

|                | h, % | $H_{d1}$, kJ/mol | $H_{d2}$, kJ/mol | $\tau_{0(1)}$, s | $H_{e1}$, kJ/mol | $H_{e2}$, kJ/mol | $\tau_{0(2)}$, s |
|----------------|------|------------------|------------------|-----------------|------------------|------------------|-----------------|
| Montmorillonite K | 13.7 | 43.2             | 36.0             | 2·10⁻¹²         | -                | -                | -               |
| Montmorillonite Ni | 14.7 | 55.6             | 42.5             | 1·10⁻¹⁴         | 53.2             | 27.7             | 3·10⁻¹⁸         |
| Kaolinite K       | 2.3  | 46.6             | 26.3             | 2·10⁻¹⁶         | -                | -                | -               |
| Kaolinite K, Ba   | 5.4  | 50.3             | 31.6             | 6·10⁻¹⁶         | -                | -                | -               |

The values of the activation energies of the process 1 ($H_{d1}$ and $H_{d2}$) for all clays under study are in a rather good agreement with the energies of molecular reorientation and defect formation in ice-like water [19] but depend on the properties of individual ions. Moreover, the values of $H_{d1}$ and $H_{d2}$ for kaolinites and montmorillonites (table 1) correlate with the Gibbs free energy hydration ($\Delta_{\text{hyd}}G^\circ$) of ions (-295, -1250, and -1980 kJ/mol for K⁺, Ba²⁺, and Ni²⁺ respectively [20]).

5. Conclusions
Montmorillonites with the exchangeable K⁺ and Ni²⁺ cations and kaolinites with the exchangeable K⁺ and Ba²⁺ cations were examined by means of the dielectric spectroscopy in wide temperature (-90°C ÷ +140°C) and frequency (1 Hz ÷ 1 MHz) ranges. Two types of relaxation processes (1 and 2) were revealed. The relaxation process 1 observed for montmorillonites K and Ni and kaolinites K and K, Ba was related to water on the outer surface of granules. The relaxation process 2 in montmorillonite Ni has been ascribed to interlayer water molecules. The activation parameters of the dielectric relaxation process 1 are in correlation with values of the Gibbs free energy hydration of the exchangeable ions.

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