Two types of adsorbed water in natural montmorillonites at low temperatures by dielectric spectroscopy

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Abstract. Dielectric spectroscopy was applied to natural clay mineral - montmorillonite with the exchangeable K⁺ and Ni²⁺ cations where the effect of water adsorption in the samples on the dielectric response was examined in the temperature from -115°C to -75°C and frequency from 1 Hz to 1 MHz ranges. Two relaxation processes (1 and 2) were revealed. The process 1 was related to the adsorbed ordered water structures formed on the interior surface of interlayer channels while the relaxation process 2 was attributed to the disordered water structures built between two surface water monolayers.

1. Introduction
Montmorillonites are widely used in industrial processes in making wine, beer, oils, molding sand, ore pelletization, petroleum, pesticides, catalysts, adsorbents, cosmetics, ceramics, paintings, etc.

Broadband dielectric spectroscopy is certainly one of the most useful tools for investigating the molecular dynamics, the degree of intermolecular hydrogen bond interaction, cooperativity between guest and host molecules [1].

There are many studies on the dielectric properties of montmorillonite [2-9] but so far there are still many open questions in the problem of the interaction of water molecules and ions with the surface of the minerals.

The objectives of this study were to use dielectric spectroscopy in the temperature from -115°C to -75°C and frequency from 1 Hz to 1 MHz ranges at high resolutions to examine the effects of two various types of cations on the existence and properties of bound water in montmorillonite mineral.

2. Samples
Oglandinsky montmorillonite (Turkmenistan) with the exchangeable cations K⁺ and Ni²⁺ were considered in this study. All the samples were prepared in the laboratory of disperse systems of Institute of Colloid and Water Chemistry (Ukraine, Kiev) according to the procedure described previously [10]. All the samples were stored in ambient air humidity, thus one can assume that water molecules were absorbed from the air into the pores.

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3. Experimental

Dielectric measurements in the frequency range of 1 Hz - 1 MHz were performed by BDS 80 based on an Alpha Impedance Analyzer (NOVOCONTROL) with automatic temperature control by QUATRO Cryosystem with a precision of 0.5°C. The accuracy of the complex dielectric permittivity was estimated to be better than 3%. The measurements were carried out in the following way: each of the samples was placed into the sample cell with a parallel plate capacitor configuration at room temperature and the measurements were then performed by cooling the samples from 20°C to -100°C. Then the samples were measured at intervals of 3°C upon heating them from -115°C to -75°C and then heating up to +300°C. The relative water content to the dry sample was determined 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, 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.

At low temperatures from -115°C to -75°C the spectra of montmorillonites consist of two relaxation processes marked 1 and 2 correspondingly. After annealing the samples at 300°C for 3 hours the relaxation processes are disappeared. This fact confirms our assertion that only water is the source of the dielectric relaxation of these materials.

For comparison we also measured the kaolinite samples with different exchangeable cations with the same protocol and did not find the low temperature process at all. We assume that the low temperature relaxation processes in montmorillonites can be associated with the interlayer water molecule relaxations because such water is absent in kaolinites [11-14].

For a quantitative analysis of the isothermal dielectric spectra at low temperatures a superposition of two Cole-Cole functions [15] in the form

$$
\varepsilon^*(\omega, T) = \varepsilon_\infty + \frac{\varepsilon_1 - \varepsilon_\infty}{1 + (i\omega \tau)^{-\alpha}}
$$
and Jonscher’s empirical term, $B(i\omega)^{n-1}$ [16], has been fitted to the complex dielectric permittivity, 
\[ \varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{2} \frac{\Delta \varepsilon_j}{1 + (i\omega \tau_j)^{\alpha_j}} \] (1)

and Jonscher’s empirical term, $B(i\omega)^{n-1}$ [16], has been fitted to the complex dielectric permittivity, 
\[ \varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega). \]
Here $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real and loss parts of the complex permittivity, respectively; $i$ is the imaginary unit and $\omega$ is the cyclic frequency, $\varepsilon_\infty$ is the high frequency limit of the complex dielectric permittivity, $\Delta \varepsilon_j$ is the dielectric strength of the relaxation process, $\tau_j$ is a characteristic time scale and the exponent $\alpha_j$ is referred to as a measure of symmetrical broadening in the dielectric losses relaxation peak ($0<\alpha_j \leq 1$), $n$ is a Jonscher parameter for the high frequency part of the respective relaxation process.

The temperature dependencies of relaxation times for the observed low temperature processes demonstrate Arrhenius behavior (figure 2). The calculated values of the activation energies of the relaxation processes are presented in table 1.

![Figure 2](image)

**Figure 2.** The temperature dependences of the relaxation times of the low temperature processes for montmorillonites. Solid symbols correspond to the 1 process; open symbols are related to the 2 process.

**Table 1.** The calculated values of the relative humidity ($h$) and activation energies of the relaxation processes ($E_a$ and $E_\infty$) and the experimental values of the Gibbs free energy hydration ($\Delta_{\text{hyd}} G^\circ$) of the $\text{K}^+$ and $\text{Ni}^{2+}$ ions [17].

|          | $h$, % | $E_a$, kJ/mol | $E_\infty$, kJ/mol | $\Delta_{\text{hyd}} G^\circ$, kJ/mol |
|----------|--------|---------------|--------------------|--------------------------------------|
| Montmorillonite K | 13.7   | 42            | 18                 | -295                                 |
| Montmorillonite Ni | 14.7   | 55            | 34                 | -1980                                |

The activation energy values for the 1 process are in the same range that had been reported earlier for water absorption in porous silica glasses [18, 19]. In montmorillonites the water molecules responsible for the low temperature relaxations are located near the inner hydrophilic centers of interlayer channels (siloxane bonds and cations trapped in hexagonal rings) and around the interlayer cations [20]. Indeed during the hydration the water molecules interact with the exchangeable cations resulting in removing part of them from the surface with following joint motion as aqua complexes [13, 14, 21]. The slower relaxation process 1 coincides with the low temperature relaxation behavior in glass materials. Most probably, it corresponds to the adsorbed ordered water (ice-like) structures formed on the interior surface of interlayer channels while the faster relaxation process 2 reflects the
disordered water structures built between two surface water monolayers. This explanation is in accordance with the Frank-Wen structural model of solvated ions [22]. According to this model a structural disordered aria of solvent (B) exists between first solvation sphere of ion (A) and bulk solution (C). In the water dielectric relaxation disordering effect of the B zone is manifested in the 2 process. Note that the presence of two layers of mobile water over the first layer of strongly adsorbed water was found by DS method for the water adsorption on α-Fe₂O₃ [23]. Disordered (weakly bound) water was revealed also in many porous materials and its content increases with decreasing the pore sizes [24].

In both processes (1 and 2) the activation energy depends on the type of interlayer cations presented in the structure of the clay and water content (see table 1). Influence of ions nature on the $E_{a1}$ and $E_{a2}$ values (table 1) can be explained by considering ion hydration. The $E_{a1}$ and $E_{a2}$ values change in the row of ions $K^+ < Ni^{2+}$ correlate with changing experimental values of the Gibbs free energy hydration ($\Delta_{hyd} G^o$) for this ions [17] (see table 1). It should be added that $K^+$ is the ion with “negative hydration” (life time of water molecules is less in immediate surrounding of $K^+$ than in bulk solution) [25, 26] and has the higher mobility in comparison with $Ni^{2+}$.

The detailed dielectric investigation of the hydrated clusters formation and their structures as a function of the exchangeable cations and water content in the montmorillonites is an open question for the continuation of the research.

5. Conclusions
Montmorillonites with the exchangeable $K^+$ and $Ni^{2+}$ cations were examined by means of the dielectric spectroscopy in the temperature from -115°C to -75°C and frequency from 1 Hz to 1 MHz ranges. At the low temperature interval the two dielectric relaxation processes (1 and 2) were observed only for montmorillonites but not for kaolinites. The slower process 1 corresponds to the adsorbed ordered water (ice-like) structures formed on the interior surface of interlayer channels while the faster relaxation process 2 corresponds to the disordered water structures built between two surface water monolayers. The parameters of activation of the dielectric relaxation processes 1 and 2 correlate with values of the Gibbs free energy hydration of the exchangeable ions.

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