EXAMINING THE PROPERTIES OF SORBED WATER BY DIELECTRIC METHODS

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Results are shown of an experimental study concerning the behavior of water molecules sorbed in peat and of dipole functional groups in an external electric field.

Water bonded to various colloidal capillary-porous materials plays an important role in heat and mass transfer processes. Recently nuclear-magnetic-resonance methods [1, 2] and dielectric methods [3, 4] have been used for examining the structure and the mobility of sorbed water molecules. The authors have studied the state of water sorbed in a typical colloidal capillary-porous material, namely in peat.

In order to detect the mechanism of interaction between peat and sorbed water, we analyzed the dependence of the dielectric permittivity ε' and of the dielectric loss tangent $\tan\delta$ on the moisture content W, on the frequency of the external electric field f, and on the specimen temperature T.

The curves in Fig. 1 of dielectric permittivity versus moisture content in the material indicate an appreciable effect of sorbed water molecules on the polarization of a peat specimen. Naturally, the trend of these $\varepsilon'(W)$ characteristics is different for different grades of peat. This could be due to a different degree of bonding between water molecules and the material, it could also be due to accompanying changes which occur in the peat. Foremost here are changes in the mobility of macromolecules in individual polar functional groups in peat which accompany changes in the moisture content. Furthermore, an increase in the moisture content contributes to the formation of a mesh of hydrogen bonds within a specimen. In that case the probability of polarization in the material increases on account of the migration of protons along the hydrogen bonds in the direction of the electric field [5, 6].

The energy of interaction between peat and sorbed water can be evaluated from the relation between the dielectric loss tangent and the temperature. Within the 0.05-10 MHz frequency range and the –60 to 0°C temperature range one observes in these characteristics a maximum of relaxation losses (Fig. 2). Both the absence of such a maximum in the case of perfectly dry peat and the increase in the extremum value of $\tan\delta$ with increasing moisture content support a hypothesis that these maxima are related to the relaxation of sorbed water molecules.

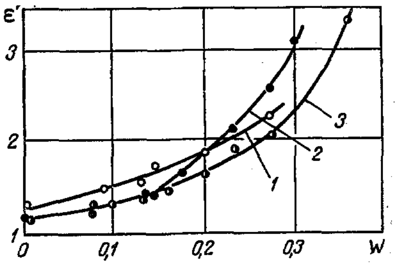

Fig. 1. Dielectric permittivity of peat ε' as a function of its moisture content W (kg/kg): 1) topsoil peat with R_p = 5-7%; 2) topsoil peat with R_p = 25-30%; 3) subsoil with R_p = 20-25%.

The logarithm of the frequency at which a maximum relaxation loss occurs is related to the polarization activation energy and to the temperature as follows [7]:

$$\lg f_{\text{м}} = A - \frac{H}{2.303R} \cdot \frac{1}{T}. \tag{1}$$

This formula yields the value of H which characterizes the potential barrier to be overcome by a water molecule before the latter can align itself with the external electric field. In the case of water sorption in peat the activation energy depends on the moisture content in the material. At moisture contents of 0.34, 0.20, and 0.12 kg/kg in our tests it amounted to 50, 59, and 69 kJ/mole respectively.

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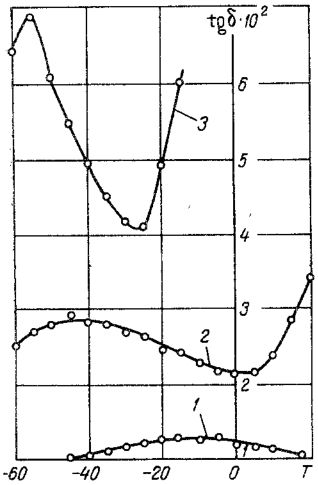

Fig. 2. Dielectric loss tangent tan δ as a function of the temperature T (°C) at f = 6 MHz: 1) W = 0.10; 2) 0.34; 3) 0.70 kg/kg.

The decrease in the polarization activation energy observed during an increase in the moisture content agrees closely with the results of calorimetric tests [1]. The trend of H can, evidently, be explained as follows. When the sorbate content in peat is low, the water molecules are bonded primarily to the most active sorption centers. As the moisture content increases, the sorbate molecules occupy also less active centers and settle in the micropores of peat. At a moisture content above the monosorption level there begins an interaction between sorbate molecules in various active centers and a formation of molecule complexes which eventually merge.

An increase in the bond energy of sorbed water molecules, which occurs when the moisture content decreases, can also be deduced from the temperature characteristics of the dielectric loss tangent at one frequency (Fig. 2). According to the test results, a decrease in the moisture content causes the maximum tan δ to shift toward higher temperatures. This is possible if an inverse relation exists between the activation energy and the moisture content in peat, because the following relation must be satisfied at a constant frequency:

$$f_{\text{M}} = f_0 \exp\left(-\frac{H}{RT}\right), \tag{2}$$

with f_0 = const within the test range of temperatures.

By applying the general theory of dielectrics to peat systems we have also obtained information about the nonuniform energy distribution of sorbed water molecules, based on the distribution of relaxation times. According to the Cole–Cole theory [8], the $\varepsilon'' = f(\varepsilon')$ characteristic within the region of a relaxation maximum for dielectric dipoles with one value of relaxation time is represented by a semicircle with the center on the ε'-axis. In the case of different dipole bond energies this characteristic becomes an arc of a circle with the center at the point:

$$\varepsilon'_{ts} = \varepsilon'_{\infty} + \frac{\varepsilon'_s - \varepsilon'_{\infty}}{2} \text{ and } \varepsilon''_{ts} = \frac{\varepsilon'_s - \varepsilon'_{\infty}}{2} \operatorname{tg} \frac{\alpha\pi}{2}. \tag{3}$$

With the thus obtained value of parameter α one can now plot the relaxation time distribution function. For peat with a moisture content of 0.7 and 0.4 kg/kg Eq. (3) yield the values 0.505 and 0.755 respectively for the parameter α (Fig. 3). The graph of the relaxation time distribution function is more sloped for W = 0.4 kg/kg (Fig. 4) than for W = 0.7 kg/kg, which has to do with the greater energy nonuniformity of sorption centers at lower moisture contents:

$$F = \frac{1}{2\pi} \, \frac{\sin \alpha\pi}{\operatorname{ch}(1-\alpha)\ln \frac{f_{\text{M}}}{f} - \cos\alpha\pi}. \tag{4}$$

At higher moisture contents the sorbate–sorbate interaction predominates and this causes a reduction in the energy spectrum of sorbed water molecules.

The change in the nonuniform energy distribution of sorbed water molecules can be evaluated qualitatively by analyzing the relaxation maxima at various moisture contents in the specimen. It is easy to see (Fig. 2) that, as W decreases, the tan δ maximum becomes flatter. According to Eq. (2), this indicates a wide bond energy spectrum of water molecules interacting with the sorbent and with one another. Of special theoretical interest is determining the dipole moment of a sorbed water molecule, which will also help to reveal both the sorption mechanism and the energy distribution of bonded water molecules. This problem can be solved in two ways: by the theory of dipoles in static fields or by the dielectric increment in an alternating field.

In the first case we have the Froehlich equation [7]:

$$\varepsilon'_s - \varepsilon'_{\infty} = \frac{3\varepsilon'_s}{2\varepsilon'_s + \varepsilon'_{\infty}} \left(\frac{\varepsilon'_{\infty} + 2}{3}\right)^2 \frac{4\pi N_0 \mu^2}{3KT}. \tag{5}$$

The values of ε'_s and ε'_{∞} in Eq. (5) will be more appropriate if taken from the Cole–Cole diagrams than if based on measurements, because test values contain an appreciable conductive component.

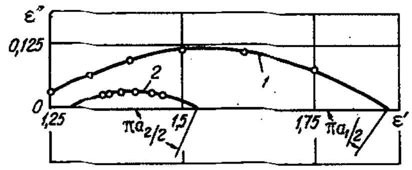

Fig. 3

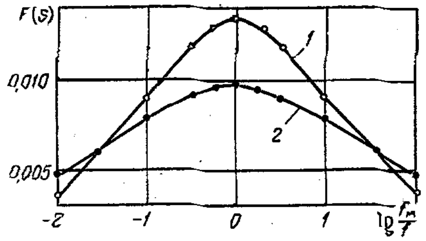

Fig. 4

Fig. 3. Cole–Cole diagram for topsoil peat: 1) W = 0.7; 2) 0.4 kg/kg.

Fig. 4. Relaxation time distribution function: 1) W = 0.7; 2) 0.4 kg/kg.

The number of sorbed water molecules is related to the moisture content in the material as follows:

$$N_0 = \frac{mWN_A}{M_W}. \tag{6}$$

We determine ε'_s and ε'_∞ with the aid of the Cole–Cole diagram for W = 0.4 kg/kg. The density of dry material in this case is 587 kg/m^3. From Eqs. (5) and (6) we find that a molecule of sorbed water should have a dipole moment equal to

$$\mu_{s,w} = 2.65 \cdot 10^{-18} \text{ esu} = 2.65 \text{ D}.$$

In determining the dipole moment on the basis of the dielectric increment, i.e., from the change in the dielectric permittivity of the mixture due to the content level of the component under investigation, we use the equation for an ideal mixture:

$$\varepsilon'_s - \varepsilon'_\infty = \frac{4\pi\mu^2 N_0}{3KT}\left(\frac{\varepsilon'_0 + 2}{3}\right)^2 \tag{7}$$

and the Debye equation for dipolar dielectrics [9]:

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_0}{1 + (\omega\tau)^2}. \tag{8}$$

From Eqs. (6), (7), and (8) we can derive a formula for calculating the dipole moment of a sorbed water molecule (at the temperature T = 293°K):

$$\mu_{s,w} = \left[\frac{0.2085 \cdot 10^{-36}(1 + \omega^2\tau^2)}{m(\varepsilon'_0 + 2)^2}\left(\frac{d\varepsilon'}{dW} - \frac{d\varepsilon'_\infty}{dW}\right)\right]^{1/2}. \tag{9}$$

Within the range of low moisture contents one may, evidently, disregard the contribution of electron polarization in sorbed water molecules to the total polarization of the specimen, i.e., one may let $d\varepsilon'_\infty/dW = 0$. The relaxation range is sorbate molecules at low moisture contents and at frequencies within the 0.1–10 MHz range may extend to T = 293°K, i.e., the magnitude of the quantity $(\omega\tau)^2$ remains within the [1, 0] range. The dipole moment of a sorbed water molecule, calculated by this formula with the density of dry material taken into account, as well as the dielectric permittivity of perfectly dry specimens and the dielectric increment are given here for various grades of peat and for the extreme values of $(\omega\tau)^2$. In composite topsoil peat with R_p = 5%, in the same with R_p = 25–30%, in subsoil reed-sedge peat (R_p = 30%), and in sedge peat (R_p = 20–25%) the molecules of sorbed water have dipole moments within the following ranges respectively: 2.50–1.77D, 2.72–1.93D, 2.26–1.60D, and 2.72–1.93D.

The dipole moment of a sorbed water molecule, calculated by the two methods, is not smaller than the dipole moment of a water vapor molecule (μ = 1.83D). The polarization activation energy of such a molecule corresponds to the energy of 3–4 hydrogen bonds, on the other hand, which means that aligning a water molecule with an electric field requires the breakup of so many bonds. These contradictory conclusions reached on the basis of classical formulas indicate that one may not treat the (peat + sorbed water) system as an ideal mixture, especially when calculating the dipole moment of a sorbate molecule. In calculations with the aid of Cole–Cole diagrams the quantity $(\varepsilon'_s - \varepsilon'_\infty)$ contains a component due to the dispersion of dielectric permittivity in the medium – in the polymer mixture with various size macromolecules and with variously bonded dipolar functional groups. In the second case an appreciable contribution to the dielectric increment is made by additional polarization mechanism which depends on the specific conditions of water sorption in peat.

Along with the quantitative characteristics of the energy distribution (H and α), however, the dipole moment of sorbate molecules, calculated by either one of the two methods shown here, can be considered a qualitative characteristic of the state of sorbed water. Furthermore, from the value of $\mu_{s.w}$ one can assess any changes within the sorbent due to physical or physicochemical effects.

NOTATION

H	is the polarization activation energy;
R	is the gas constant;
ε'_s, ε'_∞	are the dielectric permittivity at the frequency of the external field equal to zero and to infinity respectively;
A	is a constant;
N_0	is the number of water molecules per unit volume;
K	is the Boltzmann constant;
μ	is the dipole moment;
m	is the density of dry material;
W	is the moisture content in the material;
N_A	is the Avogadro's number;
M_W	is the molecular weight of water;
τ	is the relaxation time of dipolar molecules;
$\mu_{s.w}$	is the dipole moment of a sorbed water molecule;
f	is the frequency of the external field;
R_p	is the decomposition level of peat;
ω	is the radian frequency;
ε'_0	is the dielectric permittivity of a weakly polarized medium containing molecules of the component under investigation.

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