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Abstract

Full Text

PHYSICAL CHEMISTRY

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DIFFUSION OF WATER MOLECULES IN NATROLITE

(Presented by Academician V. N. Kondrat' ev, 18 V 1962)

Natrolite, $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, is a natural aluminosilicate of the zeolite family. Its structure (^{1,2}) is formed by the bonding of $[Al, Si]O_4$ tetrahedra, running in parallel columns, between which there are "channels" penetrating the crystal structure along the c axis. The channels contain Na atoms and H_2O molecules. The most interesting property of natrolite (as of other zeolites) is its ability to lose water on heating to 350°C (^{3}) without destruction of the structure. The diffusion processes that accompany the loss or absorption of water by zeolites have until now been studied macroscopically by weighing (^{4}). It is of interest to apply the method of nuclear magnetic resonance (NMR) to the study of these processes, since the NMR method is very sensitive to all kinds of mobility in the lattice (^{5}) and can provide more detailed information on the processes of diffusion and self-diffusion.

The present work gives the results of an investigation of the diffusion of water molecules in natrolite by the proton NMR method. A colorless natural single crystal of natrolite (Khibiny) measuring $17 \times 10 \times 9$ mm^3 was studied. The proton NMR spectra in natrolite at room temperature are characteristic of crystalline hydrates with a "fixed" arrangement of water molecules. The distances between protons are (1.59 ± 0.015) Å. There are altogether four different proton-proton directions, lying in pairs in the planes $\{110\}$ and $\{1\bar{1}0\}$ at an angle of $\pm 35°$ to the $\{001\}$ plane. For the temperature studies an orientation was chosen in which the field H_0 passed along the [110] direction. With this orientation of the crystal relative to the magnetic field, two proton-proton vectors are situated at an angle of 90° to the direction H_0, and the other two at an angle of 35° to this direction, so that only one doublet is observed, with a splitting of 10.5 Oe. Figure 1, *a* shows the spectrum obtained for this orientation from a single crystal of natrolite at room temperature. When the temperature was raised to 130°, the spectrum did not change. At a temperature of about 135° a central peak begins to appear (Fig. 1, *b*), the intensity of which increases rapidly with increasing temperature at the expense of the intensity of the doublet (Fig. 1, *c*, *d*). At a temperature of 180° the doublet disappears completely and the spectrum consists of a single line located at the center of gravity of the doublet (Fig. 1, *e*). This spectrum is characteristic rather of liquids than of solids, and

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Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

its small width (less than 0.1 Oe) indicates the most general type of motion of the water molecules, implying that they possess not only rotational but also translational degrees of freedom, i.e., that there is molecular diffusion through the crystal lattice.

It should be noted that the spectra contain no peaks corresponding to pure reorientation of the water molecules. Usually, molecules in a solid, as the temperature is raised, first acquire rotational degrees of freedom and then translational ones ([6]). In NMR spectra this is manifested in such a way that, at first, against the background of the spectrum corresponding to a "rigid" re-

lattice, a narrower spectrum appears, with a width of several oersteds. With a further increase in temperature, if diffusion takes place, an even narrower peak appears, characteristic of liquids. In natrolite, however, there is a transition directly from a spectrum characteristic of a "rigid" lattice to a spectrum characteristic of liquids; this means that in the natrolite lattice the H_2O molecules can either be fixed "rigidly" or must diffuse

Fig. 1. Derivative NMR spectra of natrolite at various temperatures. The field H_0 is parallel to 110.

Fig. 2. Scheme of the displacement of water molecules along a channel of the natrolite structure. Projection of part of the structure onto the 110 plane. The numbers in the figure are the vertical coordinates of the atoms in angstroms.

(at high temperatures), but cannot rotate while remaining at fixed sites of the lattice. This means that the potential barrier for diffusion of H_2O molecules in natrolite is lower than the potential barrier for reorientation, so that the excess energy of the water molecules is realized in translational degrees of freedom.

Consideration of the natrolite structure ([1]) makes it possible to understand this feature to some extent. In natrolite, the nearest neighbors of the water molecules are two oxygen atoms of the $[Al, Si]O_4$ groups and two sodium atoms, arranged in the form of a distorted tetrahedron. According to the Bernal-Fowler concept ([7]), the H_2O molecule has four tetrahedral "valencies" of approximately equal strength (~ 0.5 uni-

···of which two "valences" are positive and two are negative. It is natural to assume that in natrolite the water molecules are oriented so that the positive valences are "closed" on electronegative oxygen atoms (hydrogen bonds O–H···O are formed), while the negative ones are connected with electropositive sodium atoms. The Na atoms and the H_2O molecules are arranged alternately along the channels of the structure, so that not only does each water molecule have two Na atoms as its nearest neighbors, but each Na atom also has two water molecules as its nearest neighbors. Figure 2 gives a projection of a portion of the natrolite structure onto the 110 plane, showing the arrangement of H_2O molecules and Na atoms in the zeolite channel.

Let us now consider the possible motions of a water molecule. Among rotational motions, the simplest is rotation of the H_2O molecule about its own second-order axis, since only in such rotations does a rotation through an angle of 180° lead to the initial configuration. This rotation, as is easy to see, must be accompanied by rupture of all four bonds of the water molecule with its environment. As for translational motions, the most natural assumption is that they occur to neighboring vacant sites along the channel of the structure. Since one Na atom is always common to two neighboring positions of the water molecule, one can imagine that the transition of a water molecule between two such positions occurs without breaking the bond of the H_2O molecule with this Na atom. In Fig. 2 such transitions are marked by an arrow. It is seen from the figure that the transition of a water molecule to a neighboring vacant site along the channel of the structure must also be accompanied by the corresponding rotation; the molecule, as it were, "rolls" from one sodium atom to another, remaining all the time bound to one of these atoms. Thus, during translational motions of water molecules in natrolite only three of the four bonds will be broken, whereas during rotational motions all four must be broken. From this point of view it becomes clear that the acquisition of a translational degree of freedom (accompanied by rotations) may prove more favorable than simple rotation.

Translational motions of water molecules reduce practically to zero the intermolecular part of the magnetic dipole-dipole interaction, and rotational motions reduce the intramolecular part. Since the broadening of the NMR line is composed only of these two factors (^{5}), their joint action during the "rolling" of a water molecule from one position to another reduces the line width practically to zero, which is also in agreement with our observations.

The temperature dependence of the NMR spectrum makes it possible to estimate the height of the potential barrier for diffusion. Following Zaitsev (^{8}), the rate of jumping to adjacent vacant sites may be written as

$$\nu_k = \nu_0 \exp(V_0/kT), \tag{1}$$

where ν_0 is the frequency of vibrations of the molecules in the lattice, V_0 is the potential barrier for self-diffusion, k is Boltzmann' s constant, and T is the absolute temperature. The rate ν_k can be determined from our data if one takes into account that, as Das (^{9}) showed, the NMR line width expressed in hertz coincides with the self-diffusion rate ν_k at the temperature of the midpoint of the transition between the spectrum characteristic of a rigid structure and the spectrum characteristic of a liquid. This temperature, according to our estimates, is approximately 155°. The line width at this temperature is equal to $2 \cdot 10^4$ Hz. The value of ν_k, apparently, is of the order of 10^{12} Hz, although even a large error in this quantity will not affect the result in any substantial way. Starting from these values and using formula (1), we find

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$$V_0 = kT(\ln \nu_0 - \ln \nu_k) =\sim 15 \text{ kcal/mol}.$$

This value is very large; however, it correlates with the fact that water loss by natrolite occurs only at temperatures of about 350°. As to the nature of this barrier, one can only suggest that it is due, to a substantial degree, not only to the hydrogen bonds of the water molecule O—H···O, but also to the bond between the oxygen of the water molecule and the sodium atom.

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