STUDY OF THE N.M.R. OF WATER PROTONS IN ZEOLITES AT LOW TEMPERATURES

PHYSICAL CHEMISTRY

1965

SovietRxiv

Abstract

Full Text

UDC 54.183

PHYSICAL CHEMISTRY

V. I. KVLIVIDZE, V. F. KISELEV, V. V. SERPINSKII

STUDY OF THE N.M.R. OF WATER PROTONS IN ZEOLITES AT LOW TEMPERATURES

(Presented by Academician M. M. Dubinin on May 8, 1965)

The study of nuclear magnetic resonance spectra of an adsorbed substance makes it possible to obtain a number of valuable data on the state of the surface phase and on phase transitions in it. Previously we studied ([1],[2]) the n.m.r. of protons of water adsorbed on silica gel. Zeolites, in contrast to such classical adsorbents as silica gels and activated carbons, constitute a very convenient model object for studying the state of the adsorbed phase, since from X-ray data we know the structure and geometrical dimensions of the cavities of the crystalline lattice of the zeolite. This circumstance considerably simplifies the interpretation of the observed phenomena. In works ([3–5]) the n.m.r. spectra of water in synthetic zeolites were studied. However, in works ([3],[4]) the measurements were carried out only at room and higher temperatures, and in work ([5]) the dependence of the spectra on filling was not investigated. The study of n.m.r. spectra at low temperatures considerably broadens the information obtained on the behavior of adsorbed molecules, since thermal motion at room temperatures complicates the interpretation of the observed spectra ([2]).

In the present work the n.m.r. spectra of water protons in zeolite were studied as a function of the amount of adsorbed water in the temperature range from 90° to 230° K. A synthetic zeolite NaX, studied earlier ([6]), was used. The samples were dehydrated in vacuum at 350° C. The amount of adsorbed water was varied from 0.3 to 17.3 mmol/g. To improve heat exchange, ampoules with the zeolite were filled with helium. The n.m.r. spectra were recorded on a spectrometer for broad lines ([1]). The cryostat in which the sample under study was placed made it possible to obtain temperatures from 90° to 273° K with an accuracy of $±$0.5°. From the spectra obtained, the second moment S of the absorption line and the line width (the distance between the maxima of the derivative) were determined. For samples with a water content below 2 mmol/g, accurate calculation of the value of S is difficult because of the small signal-to-noise ratio.

The observed n.m.r. signals are shown in Fig. 1. As is seen from the figure, at 90° K the spectra for samples with a water content $\leqslant 7.15$ mmol/g have the

Fig. 1. Derivatives of the NMR absorption signals of water protons in zeolite at different temperatures: a —water content 17.3, b —7.15, c —2.72 mmol/g

Figure 1: Fig. 1. Derivatives of the NMR absorption signals of water protons in zeolite at different temperatures: a —water content 17.3, b —7.15, c —2.72 mmol/g

form of doublets typical of crystal hydrates ([7]), in which the water molecules are rigidly fixed and are at a comparatively large distance from one another. At fillings $\geqslant$ 11.95 mmol/g, the character of the spectrum changes: the doublet structure disappears and a broad line is observed. The small peak in the center, observed in all spectra, including the spectrum of the initial dehydrated zeolite, is partly due to protons in the glass of the ampoule and, possibly, to a small quantity of protons retained in the zeolite after its calcination. Figure 2 gives the dependence of the second moment on the amount of adsorbed water at a temperature of 90° K. An increase in adsorption leads to an increase of the second moment from 22 to 32 oersted^2.

Studies of the temperature changes of the n.m.r. spectra of samples with different amounts of adsorbed water make it possible to obtain additional information on the character of the bonding of water molecules in the cavity of the zeolite.

As is seen from Fig. 1, when the temperature is raised the shape of the NMR signal line changes, which is associated with the appearance of a narrower component, whose width and intensity vary with temperature. An estimate of the integral intensities showed that the intensity of the narrow component increases with increasing temperature according to an exponential law.

Fig. 1. Derivatives of the NMR absorption signals of water protons in zeolite at different temperatures: *a* —water content 17.3, *b* —7.15, *c* —2.72 mmol/g

The narrow and broad components coexist over a wide temperature interval. Figure 3 gives the dependence of the second moment and the width of the broad component on temperature for samples with different water contents. It follows from Fig. 3 that the width of the broad component changes only slightly up to a temperature of 185°K for samples with loadings from 2.72 to 7.15 mmol/g and up to a temperature of 200°K for the sample with 17.3 mmol/g of water. Above these temperatures the broad component rapidly disappears and the spectrum narrows, acquiring the form characteristic of liquids. Because of the insufficiently high resolution of our spectrometer, we did not investigate narrow lines at these and higher temperatures.

The observed character of the change in the NMR spectrum for samples with different water contents at 90°K, as well as the temperature changes of the spectrum, make it possible to put forward some considerations concerning the mechanism of pore filling. The large cavities of the zeolite have a volume of 881 Å^3 and, when completely filled, accommodate about 30 water molecules ([6]). In a zeolite cavity there are on average 9 Na^+ ions, compensating the negative

Fig. 2 and Fig. 3

Figure 2: Fig. 2 and Fig. 3

charge of the aluminosilicate tetrahedra. Of this number, 4 ions are located near the centers of the large six-membered windows. Thus, there exist at least two types of energetically nonequivalent adsorption centers.

In the initial region of filling of zeolite pores, the water molecules are located far from one another, interacting only with the framework skeleton and not interacting with one another. This is indicated by the small value of the second moment (Fig. 2A). For the sample with loading $a = 2.72$ mmol/g, the value S is 22 oersted^2. Using this value for the second moment of a polycrystalline sample, we calculated, by the Van Vleck formula, the distance between the protons of the water molecule $r =$

$= 1.59$ Å. Such a value of the interproton distance was obtained [8] for natrolite. For a free water molecule $r = 1.54$ Å. In crystalline hydrates, the observed change in the interproton distance from 1.54 to 1.63 Å [9] indicates deformation of the molecule. According to [10], adsorption of water at these loadings occurs with the release of fairly high heats, 20-15 kcal/mole. It is generally accepted that in the initial stage of filling, adsorption is mainly due to ion-dipole interaction. Some authors [11,12], on the basis of investigations of the infrared spectra of the zeolite-water system, point to the possibility of the formation of a hydrogen bond between the water molecule and the oxygen atoms of the lattice. Consideration [13] of bond hybridization in siloxane bridges does not confirm this point of view.

Fig. 2. A –dependence of the second moment and the line width on the water content at a temperature of 90°K.
1 –second moment, **2** –line width.
B –adsorption isotherm of water vapor at room temperature on zeolite NaX

Fig. 3. A –dependence of the second moment; **B** –dependence of the line width of the broad component on temperature for samples with different water contents.
1 –water content 2.72, **2** –7.15, **3** –17.3 mmole/g

Analysis of the NMR spectra measured at different temperatures (Figs. 1 and 2) shows that the temperature at which the narrow component is detected is lower, the smaller the magnitude of water adsorption. The magnitude of the line width of the narrow component at the temperature of its appearance makes it possible to consider that first rotational and then translational mobility of the water molecules arises, with only a small fraction of the adsorbed molecules participating in these motions, which indicates their energetic nonequivalence. For the sample with a loading of 2.72 mmole/g, which corresponds on average to $\sim$ 5 water molecules per large cavity of the zeolite, at a temperature of 180°K approximately 20% of the molecules participate in the motion. In other

words, four molecules are fixed immovably, while one moves from one equilibrium position to another. This fact once again indicates the nonequivalence of the adsorption centers—the Na^+ ions. The activation energy for this sample proved to be $\sim$ 3-4 kcal/mole.

The question of the participation of the small cavities of the zeolite in the adsorption of water molecules cannot at present be considered settled. With respect to the filling of the large cavities, two points of view are possible: either it is assumed that the water molecules are distributed nonuniformly over the pores of the zeolite, so that, alongside filled pores, empty ones may exist, or the water molecules are distributed uniformly over the pores. The form of the NMR spectrum at small loadings and its change with increasing amount of water indicate that the second possibility is realized.

With increasing pore filling, the second moment of the line increases (Fig. 2), which is associated with the appearance of intermolecular interaction between the adsorbed water molecules. For samples with amounts of adsorbed water of 5.65 and 7.15 mmol/g, the second moment at 90° K is equal to 27 oersted^2. The molecules are still situated rather far from one another, since the contribution of protons of neighboring molecules to the second moment does not exceed 20%. A further increase in filling leads to an increase in the second moment to 32 oersted^2; in this case the line shape approaches that observed for ice ([14]). It must be noted, however, that in this case there is a noticeable difference in the magnitudes of the second moments. As is known, for ice at a temperature of 90° K the second moment is equal to 36.7 oersted^2 ([14]). A decrease in the second moment for adsorbed water in comparison with the second moment for ice was also observed by us in the case of adsorption on silica gel ([2]). This is apparently connected, first, with the greater dispersity of the ice formed and, second, with the presence of defects in its structure. Because the positions of the water molecules in the pores of zeolite NaX are not determined, an exact calculation of the second moment is impossible.

With increasing temperature, the mobility of the adsorbed water molecules increases (Fig. 3). For a sample with water content a = 7.15 mmol/g (i.e., approximately 12 molecules per cavity), the number of mobile molecules at a temperature of 180° K is equal to four. This number is close to the number of molecules not bound to localized Na^+ ions. The activation energy for this sample was found to be $\sim$ 4.2—4.9 kcal/mol, which indicates the appearance of interaction between water molecules. For the sample with complete filling, the activation energy is $\sim$ 5.2—5.9 kcal/mol, which is close to the energy of the hydrogen bond. The appearance of mobile water molecules (or protons) at complete filling can be explained by the presence of a large number of defects in the structure of the water frozen in the zeolite pores.

The authors of ([15]), on the basis of small fluctuations in the limiting adsorbed volume for various substances, as well as corresponding deviations in the heat capacities of the adsorbed substance from those of a normal liquid, conclude that "the substance in the zeolite channel is not in a liquid-like state." Although

the term "liquid-like state" itself is not sufficiently definite, it may nevertheless be thought that such facts as the high mobility of water molecules and the sharp narrowing of lines characteristic of phase transitions of the melting type indicate the closeness of the state of the adsorbed phase to the liquid state (at not too low temperatures).

We take this opportunity to express our gratitude to O. A. Vasil' eva for assistance in carrying out this work.

Moscow State University
named after M. V. Lomonosov

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
11 I 1965

REFERENCES

[1] V. I. Kvlividze, N. M. Ievskaya et al., *Kinetics and Catalysis*, **3**, 1191 (1962).
[2] V. I. Kvlividze, *Doklady Akademii Nauk SSSR*, **157**, No. 1, 158 (1964).
[3] P. Ducros, X. Pare, *Acad. Sci. (Geneva)*, **13a**, 383 (1960); P. Averduch, P. Ducros, X. Pare, *C. R.*, **250**, 322 (1960).
[4] I. V. Matyash, M. A. Piontkovskaya et al., *Journal of Structural Chemistry*, **3**, 214 (1962); **4**, 106 (1963).
[5] S. P. Gabuda, G. M. Mikhailov, *Journal of Structural Chemistry*, **4**, 446 (1963).
[6] M. M. Dubinin, S. P. Zhdanov et al., *Izv. AN SSSR, OKhN*, 1962, 1573.
[7] G. E. Pake, *J. Chem. Phys.*, **16**, 327 (1948).
[8] S. P. Gabuda, A. N. Lyubim et al., *Crystallography*, **8** (3), 338 (1963).
[9] F. I. Skripinov, N. M. Aleksandrov, *UFN*, **75**, 585 (1961).
[10] O. M. Dzhigit, A. V. Kiselev et al., *ZhFKh*, **38**, No. 7, 179 (1964).
[11] S. P. Zhdanov, A. V. Kiselev et al., *Doklady Akademii Nauk SSSR*, **150**, No. 3, 584 (1963).
[12] G. V. Tsitsishvili, G. D. Bagrationvili, in: *Synthetic Zeolites*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 38.
[13] R. West, L. S. Whatley, K. J. Lake, *J. Am. Chem. Soc.*, **83**, 761 (1961).
[14] K. Kume, *J. Phys. Soc. Japan*, **15**, 1493 (1960).
[15] A. V. Kiselev, A. A. Lopatkin, *Kinetics and Ca-*

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