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Abstract

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STUDY OF THE STATE OF WATER IN PHOSPHOMOLYBDIC ACID BY THE METHOD OF NUCLEAR MAGNETIC RESONANCE

According to the widely accepted Miolati-Rosenheim theory ([1]), heteropoly compounds are derivatives of hypothetical acids H_7PO_6, H_8SiO_6, etc., in which oxygen atoms are replaced by radicals Mo_2O_7, W_2O_7, etc. Therefore, heteropoly acids should be polybasic: $H_7P(Mo_2O_7)_6 \cdot xH_2O$, $H_8Si(Mo_2O_7)_6 \cdot xH_2O$, etc. X-ray structural analysis data lead to a different structure of the heteropolyanion, and chemical studies indicate the low basicity of heteropoly acids ([2]). Of considerable interest is the study of the state of hydrogen atoms directly in the original solid substance. For this purpose we have applied the method of nuclear magnetic resonance (N.M.R.).

Table 1

Number of H_2O molecules per 1 PMA molecule	Second moment (gauss^2) 77° K	Line width (gauss) 293° K	Correlation time (sec) 293° K
30	35	$\sim 10^{-3}$	$\sim 10^{-9}$
15	32	–	–
10	27	–	–
7	25	$3 \cdot 10^{-1}$	$\sim 10^{-6}$
4	25	–	–
Pure water		$\sim 10^{-5}$	$\sim 10^{-12}$

As the object of study we took phosphomolybdic acid (PMA) $H_3PMo_{12}O_{40} \cdot xH_2O$ as a typical representative of heteropoly acids, having great scientific and practical significance. Phosphomolybdic acid was purified by ether extraction according to Drechsel' s method ([3]), followed by recrystallization; the resulting preparation had the composition $P_2O_5 \cdot 23.8\,MoO_3 \cdot 59H_2O$. PMA preparations with different water contents were obtained by dehydrating the original 30-water hydrate in air, over H_2SO_4, and over P_2O_5. The derivatives of the hydrogen absorption lines were recorded on the N.M.R. spectrometer of the Institute of Physical Chemistry, Academy of Sciences of the USSR ([4]), at temperatures of 77-293° K.

Figure 1 shows the derivatives of the PMA absorption lines with different water contents, recorded at 77° K. Table 1 gives the values of the second moments ($\overline{\Delta H^2}$) calculated from the corresponding lines. From the data of Table 1 it is evident that, on going from 30-water PMA to 7-water PMA, ΔH^2 decreases from 35 to 25 gauss^2, approaching the value usual for crystalline hydrates. The character of the spectrum for 10-water PMA and below corresponds to a structure consisting of water molecules and hydroxyl groups. Figure 2 gives the dependence of the value $\overline{\Delta H^2}$ at 77° K for PMA with different water contents. From Fig. 2 it is evident that dehydration substantially changes the proton structure on going from 15- to 7-water PMA. Further dehydration increases the relative content of hydroxyls at the expense of water molecules, without substantially changing $\overline{\Delta H^2}$ and, consequently, the basic structure. (The contribution to the total $\overline{\Delta H^2}$ from hydroxyl protons does not exceed, in our case, 1 gauss^2.) The derivative for 4-water PMA shows a sharp increase in the narrow line from hydroxyls and a decrease in the broad line from protons in water molecules.

Apparently, dehydration leads to a decrease in the possibility of proton migration in the aqueous structure of PMA, owing to an increase in the distance between charged centers, where the protons are fixed as hydroxyls and water molecules.

For a more detailed clarification of the nature of the bound water, the absorption line was calculated for 7-water PMA under the assumption that it contains water molecules H_2O and hydroxyls OH. The normalized form of the absorption line for a polycrystalline sample may be written as follows ([5]):

$$F(h') = w_1 F_1(h') + (1 - w_1) F_2(h'),$$

where w_1 is the fraction of protons in water molecules; $F_1(h')$ is the line-shape function for water molecules; $F_2(h')$ is the same for protons in OH groups.

According to Pake ([6]),

$$F_1(h') = (2\pi)^{1/2} \beta_1^{-1} \int_{h=-3\mu r_1^{-3}}^{+3\mu r_1^{-3}} g_1(h) \times$$

$$\times \exp\left[-(h' - h)(2\beta_1^2)^{-1}\right] dh;$$

an analogous expression is obtained also for $F_2(h')$, but with different indices.

Fig. 1. Experimental derivative absorption lines of protons in PMA with different water contents: 1 –30 mol H_2O/mol PMA; 2 –10; 3 –7; 4 –4 mol H_2O/mol PMA

Fig. 2. Dependence of the second moment on the water content in PMA

In these equations

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$$g_1(h) = \left(6\sqrt{3}\,\mu r_1^{-3}\right)^{-1} \left(1 \pm \frac{h}{\frac{3}{2}\mu r_1^{-3}}\right)^{-1/2}$$

with the + signs for

$$-\frac{3}{2}\mu r_1^{-3} < h < 3\mu r_1^{-3},$$

and with the − signs for

$$-3\mu r_1^{-3} < h < \frac{3}{2}\mu r_1^{-3};$$

$g(h)dh$ gives the probability that the component of the fine structure of the line, characterizing an isolated pair of proton nuclear dipoles, lies between h and $h+dh$ from the center of the absorption line. r_1 is the distance between protons in a water molecule (1.53 Å $\leq r_1 \leq$ 1.65 Å), r_2 is the distance between protons in hydroxyl groups (2.2 Å $\leq r_2 \leq$ 2.7 Å); β is the broadening parameter describing the action of protons of neighboring molecules in the broadened function $g(h)$

$$(\beta \simeq \tfrac{3}{2}\mu x^{-3});$$

x_1 and x_2 are the smallest distance between neighboring proton pairs (2.2 Å $\leq x \leq$ 2.7 Å); μ is the magnetic moment of the proton; w_1, r_1, r_2, β_1, β_2 of the system under study are found by comparing a family of calculated curves with the experimental line. We obtained the following expression for the absorption line of 7-water PMA:

$$F(h') = 0.80F_1(h') + 0.20F_2(h')$$

Fig. 3. Calculated and experimental absorption line (1) and its derivative (2) of 7-water PMA: a –calculated, b –experimental

Figure 3: Fig. 3. Calculated and experimental absorption line (1) and its derivative (2) of 7-water PMA: a –calculated, b –experimental

Fig. 4. Dependence of the second moment on temperature: 1 –30-water PMA; 2 –7-water PMA

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and our principal parameters for the protons in the H_2O molecules and in the OH groups are: $r_1 = 1.63$ Å; $\beta_1 = 1.99$ gauss; $x_1 = 2.2$ Å; $r_2 = 3.10$ Å; $\beta_2 = 0.71$ gauss; $x_2 = 3.10$ Å. For these parameters the calculated absorption line and the experimental line agree well (Fig. 3). The ratio of the number of protons in hydroxyl groups to the number of protons in water molecules is $1 : 4$. This ratio corresponds to the PMA formula $H_3PMo_{12}O_{40} \cdot 6H_2O$. Consequently, the PMA formula $H_7P(Mo_2O_7)_6 \cdot 4H_2O$, adopted according to the Miolati–Rosenheim theory, according to which the ratio of hydroxyl protons to water protons should be $1 : 1.1$, does not correspond to reality.

Fig. 3. Calculated and experimental absorption line (1) and its derivative (2) of 7-water PMA: *a* –calculated, *b* –experimental

Fig. 4. Dependence of the second moment on temperature: 1 –30-water PMA; 2 –7-water PMA

For 30- and 7-water PMA, the dependence of $\overline{\Delta H^2}$ on temperature was obtained in the range 77–293° K (Fig. 4). From Fig. 4 it is seen that the second moment decreases rapidly in a comparatively narrow temperature interval. The spectrum of 30-water PMA at 230° K changes into a narrow line. The line width of 30-water PMA at a temperature of 250–260° K is less than 0.1 gauss and is apparently due not only to reorientation of H_2O molecules but also to their diffusion in the lattice. At a temperature of 293° K the line width of 30-water PMA, estimated from the time T_2 of spin–spin relaxation, proved to be equal to $7 \cdot 10^{-4}$ gauss (T_2 was measured by the spin–echo method and is equal to $60 \cdot 10^{-3}$ sec). The line width of 7-water PMA at the same temperature is $3 \cdot 10^{-1}$ gauss. A comparison of the line widths for 30- and 7-water PMA at 293° K (Table 1) indicates a change in the proton structure of PMA caused by dehydration. Using the dependence of $\overline{\Delta H^2}$ on temperature (Fig. 4), we estimated the correlation frequencies responsible for the observed changes

line shape (7). According to the Gutowsky–Pake equation,

$$\overline{\Delta H^2} = \overline{\Delta H_{\text{v}}^2} + \left(\overline{\Delta H_{\text{n}}^2} - \overline{\Delta H_{\text{v}}^2}\right) \frac{2}{\pi} \operatorname{arctg} \left[\frac{\gamma \left(\overline{\Delta H^2}\right)^{1/2}}{2\pi\nu_c} \right],$$

where $\overline{\Delta H_{\text{v}}^2}$ is the second moment for high temperature; $\overline{\Delta H_{\text{n}}^2}$ is the second moment for low temperature; γ is the gyromagnetic ratio of the proton; ν_c is the correlation frequency of molecular motion.

From the temperature dependence of the correlation frequency ($\nu_c = \nu_0 \exp(-E/RT)$), the activation energy for reorientation of protons in the PMA lattice was calculated; for 30- and 7-water PMA the activation energy is 3.64 and 4.84 kcal/mole, respectively. A decrease in water content increases the potential barrier to reorientation of H_2O molecules, which, apparently, is due chiefly to the interaction of H_2O with the framework of the heteropoly acid.

Thus, the data obtained indicate a change in the nature of bound water in PMA of different water contents. Low-water forms of PMA contain hydrogen in the form of water molecules and hydroxyl groups, and the relative content of the latter increases as dehydration proceeds. 7-water PMA contains 20% hydroxyls, which corresponds to the formula $H_3PMo_{12}O_{12} \cdot 6H_2O$, and not $H_7P(Mo_2O_7)_6 \cdot 4H_2O$.

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